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SYNTHESIS OF BIODIESEL AVOCADO SEED OIL THROUGH THE TRANSESTERIFICATION PROCESS USING BEEF BONE CATALYST

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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. The solvents used are n-hexane and methanol, with a ratio of 1:5. The characteristics of the biodiesel tested were in the form of Free Fatty Acid (FFA) analysis, density, viscosity, and acid number. Biodiesel with n-hexane solvent 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℃ obtained an FFA of 1.50% to 0.468%. The research showed that all biodiesel quality tests met SNI 04-7182-2015 standards except for the quality density test. The FTIR results of biodiesel are: wave number 2585-2956 cm^{-1} C-H (alkanes) asymmetrical stretching shows free fatty acid chain bonds, 1749.88 cm^{-1} Carbonyl ester group C=O, peak-C-H group wavelength 1459 cm^{-1}, The position of the carbonyl ester is strengthened by the presence of the C-O ester position at a wavelength of 1378 cm^{-1}, the C=H group (alkene) with a length of 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 are 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 is 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). At this time, the process of making biodiesel is being Development is a one-step process (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). The application of the two-stage process is because oil containing more than 1% Free Fatty Acid will form a soap emulsion which makes it difficult to separate biodiesel (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 if used 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**.

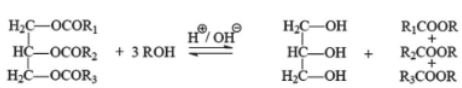

Figure 1. Transesterification Reaction Mechanism (Thanh et Al, 2012)

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 uses a cow bone catalyst to process avocado seeds into an environmentally friendly biodiesel alternative fuel.

Research methods

Time and Implementation of Research Research variable

This research began on February 2 2023 until March 18 2023 at the Integrated Science and Technology Laboratory of UIN Walisongo Semarang.

Tools and materials

Laboratory equipment and materials used in this study include: Stative, Clamps, Measuring flask (100mL, 500mL), Erlenmeyer flask (250 mL), Thermometer, Beaker glass (50mL, 100mL, 250mL), Measuring Cup (10mL, 50mL, 100mL), Boiling stone, Heating Plate, Hot Plate, A set of Soxhlet Tools, Furnace, Digital Analytical Balance, Porcelain Cup, Oven, Spatula, Stir Bar, Separatory Funnel, Ostwald Viscometer, Burette, Magnetic Stirrer, Mortar Pestle and Rotary Evaporator Dlab Re100-Pro brand at the Chemistry Laboratory of UIN Walisongo Semarang.

The materials used in this study included: beef bones, avocado seeds taken from fruit workers, 99% technical methanol, n-hexane, aquadest, 1% phenolphthalein (PP) indicator, aquadest, and anhydrous Na_2SO_4.

The instrument used for measuring and characterizing biodiesel samples is the *Fourier Transform Infrared* (FTIR) 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.

Avocado Seed Oil Extraction

Avocado seeds that have gone through the process of drying and refining the texture into powder will proceed to the extraction process to get the extract in the form of unrefined oil. The extraction was done through the soxhletation stage using 2 variations of methanol and n-hexane solvents. The extraction results are then put into the evaporation stage using a *Rotary evaporator vacuum* aimed at separating the alcohol solvent from avocado seed oil marked by the sample being thick.

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. After drying from the water content, the beef bones are ground to a powdery texture and then sent to the furnace stage for 2 hours at a temperature of 900°C until it becomes white ash and then pulverized using an 80 mesh sieve until smooth.

Free Fatty Acid Analysis

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

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

Transesterification Process

Total of 30 mL of avocado seed oil samples was made in a 1:5 ratio with methanol solvent. Then mix the methanol with 0.5% beef bone catalyst from the sample weight. Heated using reflux at 60°C for 1 hour. After that, put it into a 200 mL separatory funnel and let it stand for one day until 2 layers are formed, namely methyl ester and glycerol (remains of catalyst, methanol, and impurities). After that, separate the glycerol (bottom) and biodiesel (top). Then, washed using warm distilled water at 70°C repeatedly until the color of the biodiesel is clear yellow to remove the remaining methanol in the biodiesel, add warm water to change the methanol phase to steam and let it stand for one day, then separate it using a separatory funnel. Add anhydrous Na_2SO_4 crystals aiming to bind the remaining water from biodiesel.

Characterization of Biodiesel Avocado Oil

Density (40°C)

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

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

Viscosity (40°C)

As much as 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

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

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

Results and Discussion

Avocado Seed Preparation

The preparation begins by changing the texture of the 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 pulverized with a mortar pestle and sifted 80 mesh in size to become a powder texture, as can be seen in Figure 2.

Figure 2. Avocado seed powder (left) and fine powder (right)

A total of 132 grams 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. Then in the second 232 gram sample using 800mL n-hexane solvent, a clear yellow extract was obtained with a 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 66mL, yield 28.4%. The identified colors have different clarity levels between the two samples, as seen in **Figures 3a and 3b**.

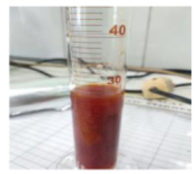

Figure 3a. Methanol Dissolving Avocado Seed Oil

Figure 3b. Avocado Seed Oil n-hexane solvent

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

Table 1. Characteristics of methanol solvent avocado seed oil

No.	Characteristics	Result
1	Density (40°C)	0.9556 g/cm^3
2.	Free Fatty Acid (FFA)	11.86%
3.	Acid Number	1.186 mg/KOH g
4.	Colour	Slightly yellow brown

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

No.	Characteristics	Result
1	Density (40°C)	0.918 g/cm^3
2.	Free Fatty Acid (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 stage because the FFA value is <2%. This also proves that methanol solvent cannot dissolve the methyl ester components contained in avocado seeds. So, n-hexane solvent is the right choice to dissolve the oil components in avocado seeds.

Beef Bone Preparation

As much as 200 grams of beef bones were cut into small pieces measuring 2-3 cm and cleaned of the remaining attached meat and then dried from the water content using an oven with a temperature of 130° for 3 hours, which was then ground again to become powder so that it could continue in the process. Calcination using a 900°C furnace for 2 hours until the white color can be seen in **Figure 4**.

Figure 4. Before (left) and after (right) calcination of beef bones at 900°C.

Table 3. free fatty acids 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

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. Characteristics of Avocado Oil Biodiesel

Table 4. Characteristics of Avocado Oil Biodiesel.

No.	characteristics	Avocado seed oil	Units
1.	Density (40°C)	0,75	g/cm^3
2.	FFA	0,468	%
3.	Acid Number	0,732	mg KOH/g
4.	Viscosity (40°C)	-	cSt
5.	Colour	clear yellow	-
6.	pH	6,5	-
7.	yield	28,8	%
8.	flash point	>130	°C

Based on the results of Table 4. There is a discrepancy in the results of the SNI 04-7182: 2015 standard Biodiesel: Density (40°C) of 0.75 and yield of 28.8%. Meanwhile, the Free Fatty Acid (FFA) yield was 0.468%, the acid number was 0.732 mg KOH/g, the pH value was 6.5, and the flash point was >130°C.

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Characterization of Fourier Transform Infra Red (FTIR) of Biodiesel and Glycerol

Biodiesel

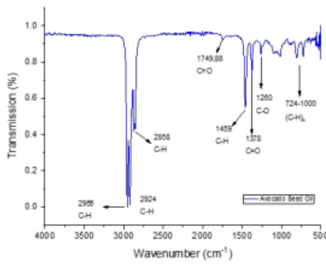

Figure 5. FTIR Result Biodiesel

Based on the FTIR spectrum data in Figure 5. The results of the Fourier Transform Infrared (FT-IR) test show peak wave numbers 2585-2956 cm^{-1} C-H (alkanes) unsymmetrical stretching showing free fatty acid chain bonds, wavelength 1749.88 cm^{-1} shows the carbonyl ester group C=O, the peak of the -C-H group with a wavelength of 1459 cm^{-1}. The position of this carbonyl ester is strengthened by the presence of the C-O ester position at a wavelength of 1378 cm^{-1}, the C=H group (alkene) with a length of 1060 cm^{-1}.

Glycerol

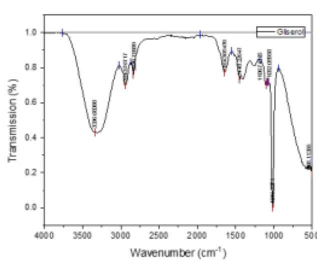

Figure 6. FTIR Glycerol biodiesel by product

Based on the results of the Spectrum data in Figure 6. There is a wide 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 (CH2), showing an absorption area of 1448.22 cm^{-1}. This result has similarities with the results of the glycerol compound library. It's just that the methylene absorption of 1448.22 cm^{-1} is not sharp downward.

Conclusion

Avocado oil Biodiesel Characteristics Test obtained some suitable data, not by SNI 04-7182..2015 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 and a flash point level at a temperature of more than 130°C. Conformity of the data values with the standard is affected by the comparative condition of using CaO catalyst which is too low.

Testing the characteristics with the *Fourier Transform Infrared* (FTIR) instrument was carried out in 2 tests, namely the FTIR of biodiesel avocado oil and the by-product of biodiesel in the form of glycerol. The results of the Fourier Transform Infrared (FT-IR) test show that there is a peak wave number of 2585-2956 cm^{-1} C-H (alkane) asymmetrical stretching indicates free fatty acid chain bonds, a wave length of 1749.88 cm^{-1} indicates the C=O carbonyl ester group, the peak of the -C-H group with a wavelength of 1459 cm^{-1}, then for the second test spectrum results there is a wide 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 (CH2), showing 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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