Refining Process of Used Cooking Oil Using Moringa Seed Powder to Improve Biodiesel Quality

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Abstract

Used cooking oil components can contain various chemical compounds due to uncontrolled heating and repeated frying in various types of food. In making biodiesel, used cooking oil needs to be purified to improve the quality of the results by using moringa seed powder and charcoal and moringa seed powder activated with nitric acid. The purpose of this study was to analyze biodiesel from the results of refining used cooking oil using moringa seeds in the form of powder, charcoal and powder moringa seeds activated with nitric acid. The results of refining used cooking oil using moringa seeds showed a qualitative change in pH so that it is good to use as a biodiesel raw material. The quality of biodiesel from proximate results such as volatile compounds, water content, ash, and fixed carbon is in accordance with SNI. The analysis of volatile compounds was followed by GCMS analysis. The percentage of volatile compounds by proximate increases the acquisition of volatile compounds but the ester compounds formed by GCMS are less than 96% using used cooking oil raw materials refined with Moringa seed powder, this result is best from charcoal and Moringa seed powder activated with nitric acid.

Keywords: biodiesel, charcoal, moringa seed, powder, quality, used cooking oil

1. Introduction

The use of energy sourced from petroleum (petroleum products) in Indonesia continues to increase along with the growth of industry, motor vehicles for transportation activities as the backbone of the economy. The increase in the use of fuel as an energy source causes subsidies to continue to increase every year which causes the state budget to also increase. A large government budget must be balanced by a high per capita income of the community. Based on data from the Department of Energy and Mineral Resources, Indonesia's average petroleum production is 500 million barrels per year and will run out in 18 years due to increased fuel use. To reduce high fuel subsidies and increase people's per capita income, one of the efforts that can be made is to utilize other energy sources.

Biodiesel from publications, made from several oils such as Karanja and jatropha oil whose properties from analytical testing are in accordance with the standard range according to ASTM and it is also said that this oil is a good source for making biodiesel [11]. Moringa seed oil with ethanol solvent has high significance on particle size, temperature, and reaction time, in accordance with the results of bioethanol from rice husk so that this bioethanol can be used as a raw material for making biodiesel [1]. The biodiesel obtained contains methyl esters as performance and emission characteristics in the engine [13]. Biodiesel, diesel, and biogas can be used in diesel engines with a percentage of more than 50% in the mixture without changing its emission performance [9].

In addition to the various oils above, used oil from fried foods known as used cooking oil has been processed into biodiesel, but needs to be improved to obtain quality according to biodiesel requirements. Efforts are made to refine used cooking oil by utilizing natural materials that are widely available in the environment such as Moringa seeds. The main content of biodiesel is esters such as Fatty Acid Ethyl Ester (FAEE) from coconut cooking oil using 99% ethanol (pro analysis degree) and sulfuric acid catalyst, which has been presented at the international conference Chemistry and Applied Science (HKICEAS) in Hong Kong, on December 19-21, 2013. FAEE from used cooking oil with arak reagent obtained density > 8 with pH 6 [2] and gas chromatography mass spectrometry (GC-MS) showed that the peak area of ethyl laurate was higher (about 40%) and ethyl palmitate was lower (10%), this is in accordance with the theory that the highest fatty acid content in coconut oil is lauric acid with several other fatty acids with smaller content [3].

Development and analysis of biodiesel continues to be pursued by replacing sulfuric acid catalysts with phosphoric acid and sodium hydroxide in the ultimate way [4]. Development is also carried out on raw materials (used cooking oil) by refining and homogeneous catalysts are replaced with heterogeneous catalysts such as calcium oxide (CaO) as a substitute for sodium hydroxide [17]. Biodiesel using a combination catalyst of CaO and Moringa seed powder has also been published, the content of volatile compounds is more than 90% using CaO and Moringa seed powder, according to SNI-04-7182-2006 and European EN 14214 [5]. Aisyah et al. (2010) [7] in their publication stated that moringa seed activated charcoal is very effective in reducing free fatty acid (FFA) and peroxide numbers in used cooking oil. Biodiesel has detected ester compounds both in infrared and GC-MS [14,15].

Based on the above results as a development and utilization of existing materials in the environment, used cooking oil needs to be refined using Moringa seed powder, then the esterification and tranesterification processes are carried out according to standard methods that have been carried out in previous studies.

2. Materials and Methods

The materials used were used cooking oil from household food frying, moringa seed powder, CaO, ethanol pro analysis (E. Merck), H_3PO_4, anhydrous $CaCl_2$, distilled water, litmus paper. Equipment included: a set of glassware and reflux, measuring cup, glass jar, measuring cup, pipette, heater, thermometer, two neck flask, bucket, analytical balance, separatory funnel.

Method of making biodiesel: A total of 100 mL of used cooking oil and refined used cooking oil with powder, activated moringa seed charcoal, and nitric acid-activated moringa seed powder, respectively, were heated at 35^oC. 20 mL of ethanol was added and stirred for 5 minutes, and 0.5 mL of phosphoric acid was added. Then it was heated for 2 hours and allowed to stand for 24 hours. After the solution cooled down, 3 mg of CaO heterogeneous catalyst was added and then 20 mL of ethanol was added, after which it was heated for 2.5 hours at 55^oC, put into a separatory funnel and allowed to stand for 1 hour. Next, the top and bottom layers were separated, then the top layer was washed with heated distilled water (nail warm) until the washing water was clear. The solution was collected and added anhydrous $CaCl_2$, then filtered to obtain alternative fuel and then characterized.

3. RESULT AND DISCUSSION

Moringa seeds that are old and dry from the tree, collected and washed and dried for 1 month. The dried moringa seeds were blended and sieved using a sieve to obtain moringa seed powder. Moringa seed powder was then heated in a furnace for 1 hour at 500^oC and other conditions were standardized in the furnace set. Biodiesel made by the standard method, namely used cooking oil, was esterified using ethanol and phosphoric acid catalysts and then continued with the transesterification process using CaO catalysts.

Used cooking oil compared to the refined used cooking oil with Moringa seeds showed a change in pH as a sign that it could be used as raw material. Used cooking oil is also an oil or fat obtainable and available in the local community that can be used as a manufacturing material or alternative energy source for diesel engines [18; 10]. The proximate results of biodiesel are shown in Table 1. Biodiesel (B4) made from used cooking oil with ethanol using phosphoric acid and moringa seed powder, respectively in the esterification and transesterification processes, obtained the results shown in Table 1. The proximate measurement results showed that the volatile compounds and ash percentage in biodiesel using used cooking oil refined with moringa seed powder and the process following the standard procedure of phosphoric acid and calcium oxide as catalyst (B7) were close to B4 and in accordance with ASTM standards [16], but the others (B6, B8, and B9) using used cooking oil refined with $CaCl_2$, moringa seed charcoal, and activated moringa seed powder using nitric acid, respectively, had not reached the volatile compound requirements of SNI. This can be clearly seen in Figure 1 corresponding moisture, ash and volatile compound contents for samples B4 and B7.

Tabel 1. Hasil analisis proximate beberapa biodiesel (B4, B6, B7, B8, dan B9)

Kode Biodiesel	Initial Mass (g)	Moisture	Volatile	Ash	Fixed carbon
B4	1,02	3,79	96,65	-0,29	-0,15
B6	1,03	86,8	11,02	2,47	-0,29
B7	1	6,95	93,12	0,16	-0,23
B8	1,01	96,7	2,26	2,33	-0,29
B9	1,02	95,64	2,65	2,07	-0,35

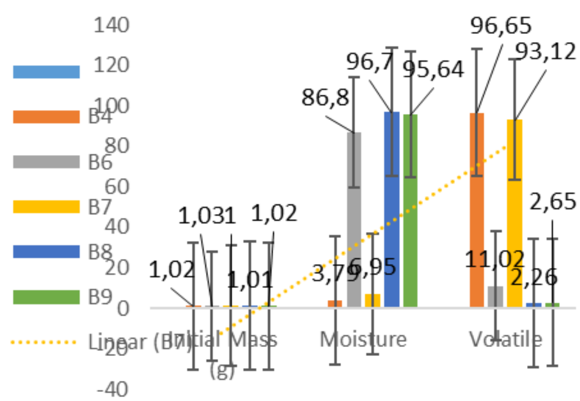

Figure 1. Moisture and volatile compounds in varies biodiesel

The biodiesel obtained was analyzed by gas chromatography-mass spectrometry and 31 chromatogram peaks were detected. The separation results can be improved by refining the used cooking oil before the biodiesel making process. The separation and peaks obtained were reduced from the standard biodiesel. This shows that the purification of used cooking oil with $CaCl_2$ is expected to improve the acquisition of biodiesel, purification of used cooking oil using Moringa seeds either powder, charcoal or powder activated using nitric acid. The peaks as a marker of compounds that appear in biodiesel are different and the amount of content also varies. This indicates that purification can improve the content and amount of compounds in biodiesel, which is important for research development.

GC-MS analysis of biodiesel obtained peaks as markers of compound content with varying percentages of less than 10% dodecanoic acid, less than 9% n-hexadecanoic acid, and other compounds between 0-3% of other acids and esters such as hexanoic acid ethyl ester, octanoic acid ethyl ester, decanoic acid ethyl ester, dodecanoic acid ethyl ester, and octadecanoic acid ethyl ester. Other compounds were lauric anhydrid, ethyl oleate, arachidonic acid 2.36; 0.75; and 0.65% respectively.

Different peak differences with the refining of used cooking oil, various variations of moringa seed powder. The same number of peaks as 17 peaks or 17 compounds using refining used cooking oil with $CaCl_2$ (B6) and activated moringa seed powder nitric acid (biodiesel B9) but different percentages. Biodiesel from refining used cooking oil with $CaCl_2$ obtained a maximum percentage of about 30% as dodecanoic acid ethenyl ester, 23% as 2-dibenzofuranamine, 14.41% as carbamic acid, 13.8% 4-dibenzofuranamine, and 7.67% lauric anhydride and less than 3% each as other acid and ester compounds.

Biodiesel from the refining of used cooking oil using moringa seed powder activated by nitric acid could increase lauric anhydride to 19.15% and detected 4 nitrophenyl laurate about 29%, fumaric acid 22%, and pyrimidine about 12%, and other compounds varied from 0.27 to 4.66%.

Biodiesel B7 and B8, respectively, from used cooking oil refined using moringa seed powder and moringa seed charcoal are expected to support the proximate analysis results. The percentage of volatile compounds in B7 is more than 90%, which is close to the standard biodiesel production method, meaning that the use of moringa seed powder as a catalyst in biodiesel production and as a material to purify used cooking oil is able to retain volatile compounds rather than moringa seed charcoal. This is supported by the results of the analysis using GC-MS, where the peaks obtained were 26 or 26 more compounds using moringa seed charcoal. Although the volatile compounds have been maximized proximate, the esters formed by GC-MS have not reached the standard. This indicates that it is necessary to look for optimization of moringa seed powder catalyst either directly used as a catalyst in biodiesel production or as a catalyst in the refining of used cooking oil as biodiesel material as shown in Figure 2..

Based on the GC-MS separation results, the used cooking oil material from the refining of moringa seed powder is better than charcoal and activation with nitric acid even though with different percentages with compound names as shown in Table 2. This is supported by the research of Agarwal et al., 2015 that the catalyst concentration affects the yield obtained, so optimization is needed. The fatty acid composition of biodiesel from Moringa seed oil varies with cis 9 octadecanoic or oleic about 70% as the highest percentage, hexadecanoic or palmitic less than 8%, octadecanoic or stearic less than 6%, linoleic about 4%, and some other fatty acids less than 3% each (Mofijur et al., 2014). The increase in oleic percentage of about 82% in the publication of Fernandes et al., 2015 that Moringa oil has potential as a source of biodiesel feedstock and antioxidant additive in biodiesel with low oxidation stability

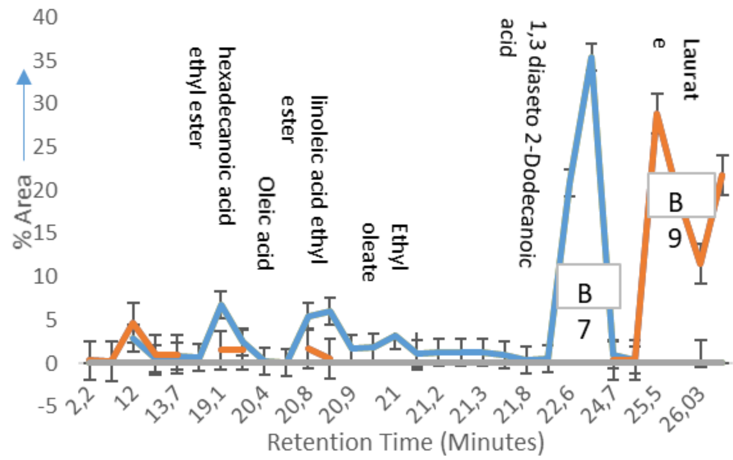

Figure 2. Percentage of varies compounds in biodiesel (B7 and B9)

Table 2. Retention time /tR (minutes), Area (%), and compounds in biodiesel (B7 dan B9)

tR (minutes)	Area (%) B7	B9	Compounds
2,2		0,29	Silanediol
2,5		0,27	Silanediol
12	2,86	4,66	benzenamine 4 methyl N,N, bis 4 methyl phenyl
13,2	0,58	0,89	phenylfosfanol acid
13,7	0,81	1,03	2,3,7-trifenyl
18,7	0,63		Hexadecanoic acid methyl ester
19,1	6,74	1,48	2-hexadecanoic acid
19,4	2,41	1,58	hexadecanoic acid ethyl ester
20,4	0,18		Oleic acid
20,5	0,11		Oleic acid
20,8	5,46	1,66	oleic acid
20,8	6,02	0,54	linoleic acid ethyl ester
20,9	1,64		Octadecanoic acid 2 OH 1,3 propanediy ester
20,9	1,81		Silane
21	3,13		ethyl oleate
21,1	1,06	1,56	ethyl oleate
21,2	1,21		Diethyl ester oleic acid
21,2	1,29		lauric anhydride
21,3	1,24		1,2-cyclohexanedicarboxylic acid
21,8	0,97		dodecanoic acid
21,8	0,43		cyclo octanoic
22,2	0,46		Myristin
22,6	20,9		dodecanoic acid
22,8	35,32		1,3-diaseto 2-dodecanoic acid
24,7	0,91	0,33	Antrazena
25,11	0,39	0,36	benzo quinolone
25,5		28,8	4-nitrophenyl laurate

25,7		19,15	lauric anhydride
26,03	1,08	11,54	Pyrimidine
26,2		21,72	fumaric acid

4. Conclusions

Biodiesel from used cooking oil refined using moringa seed powder with ethanol reagent, phosphoric acid catalyst and calcium oxide contains optimal volatile compounds both proximate and GCMS compared to other refinements, namely moringa seed powder activated with nitric acid and using moringa seed charcoal.

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