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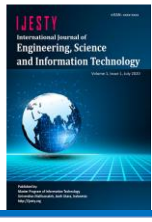

Application of Pisang Awak Bunch-Derived Heterogenous Base Catalyst in Transesterification of Palm Oil into Biodiesel

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Abstract

Biodiesel is an alternative fuel for diesel machine comprosied of alkyl monoesters deriving from vegetable oils or animal fats. Cooking oil is an oil originated from vegetable or animal fat which has been priorly purified, where it appears in liquid form at room temperature and is usually used to fry food ingredients. Heterogenous catalyst is a catalyst present in different phase with the reagent in a reaction it catalyzes. Kalium content in banana in a banana bunch is sufficiently high reaching 94.4%. The aim of this study was to utilize banana bunch which has been priorly ashed using furnace at 700°C for 4 hours, thereafter, applied as a heterogenous catalyst in a the preparation process of biodiesel from cooking oil. Processing variables investigated in this research included the influences of the number of catalyst (3, 4, 5, 6, and 7%) and molar rasio of oil and methanol (1:5, 1:6, 1:7, 1:8, and 1:9) against the properties of produced biodiesel, namely density, viscosity, and water content which later compred with Indonesian standard (SNI). From the study, it was obtained maximum yield of 90.97% with methanol:oil rasio of 1:7 at processing temperature of 60°C with reaction time of 90 minutes and catalyst as much as 3 % w/w. The characteristics of the cooking oil-based biodiesel obtained from the a reaction with oil: methanol rasio of 1:6 and catalyst as much as 3% w/w were density 850 kg/m3 and viscosity 621 mm2/s. This research showed that the obtained biodiesel characteristics had been sufficient according to the SNI, and the use of calcinated banana bunch was very potential in the production of biodiesel acting as solid catalyst person.

Keywords: *Biodiesel, Heterogenous Catalyst, Cooking Oil, Banana Bunch.*

1. Introduction

Based on sustainable development plant, bioenergy is considered as futuristic fuel [1]. The demand for fuel is increasing with time, which cannot be separated from the civilization. This increment keeps on occurring as human population increases along with industrial activities and transportation technologies [2]. The scarcity of fossil fuel and environmental problems (i.e., global warming and air pollution) drive scholar communities in finding alternative renewable energy source as a substitute for fossil fuel, of which is biodiesel.

Biodiesel could be understood as long chain mono alkyl esters deriving from fat compositions of renewable resources (such as vegetable oil and animal fat), aimed for diesel engine. The utilization of biodiesel could attenuate vairous probems, including in anticipating the energi crisis. Moreover, a number of efforts have been put in the development of biodiesel production to explore environmentally friendly alternative fuel[3].

The production of biodiesel from vegetable oil is conducted by converting triglycerides into fatty acid methyl esters using catalyst to allow the transesterification process. This reaction involve the chemical interaction between triglicerides and methanols yielding methyl esters and glycerols. The speed of the process could significantly improved by the addition of catalyst. In this regard, base catalyst is relatively more preferable than acid catalyst or enzymes, because of high methyl esters yield as well as less requiring time [4]. Among many developed base catalysts, of which is ash deriving from banana bunch.

Banana is harvested along with its bunch, where each of it consists of several combs with 6-22 fruits (depending on the variety). Several minerals could be found in the banana bunch through calcination, including K (94.4%), Mg (1.37%), P (1.32%), S (1.31%), NO (1.26%), Na (0.04%), and Ca (0.005%) [5] [6] [7].

Kalium could be obtained from the nature or prepared through chemical synthesis. Naturally kalium content in banana bunch is relatively high [8]. This availability leads to the potential application of banana bunch-based kalium as a solid catalyst for oil and methanol transesterification. With this in mind, the production of biodiesel could be more environmentally, and consequently contributing to the realization of green energy framework. Taken altogether, it leads us to the current work of employing banana bunch-based kalium catalyst for the production of biodiesel from cooking oil [9] [10].

Heterogenous base catalyst, despite its less catalyzing ability in comparison with that of homogenous catalysts, it still considered an alternative in the biodiesel production. It is due to the fact that heterogenous base catalyst offer simple, cheap, safe, and eco-friendly biodiesel production process. Moreover, its utilization could benefits the industry as it can be recovered and recylced, thus less waste is expected from the production process [11].

2. Literature Review

2.1. Cooking Oil

Oil derived from plant or animal fats that are purified and liquid at room temperature are usually used for frying foodstuffs called cooking oil. A mixture of fatty acid esters with glycerol which will form glycerides is oil and fat, these esters are commonly called triglycerides [12]. Triglycerides are triesters of glycerol with fatty acids, namely carboxylic acids with carbon atoms 6 to 30. Triglycerides are mostly contained in oils and fats, and are the largest component of vegetable oils. In addition to triglycerides, there are also monoglycerides and diglycerides[13].

2.2. Biodiesel

Alternative fuels to replace diesel oil produced from vegetable oils or animal fats are called biodiesel. The nature of biodiesel is biodegradable, non-toxic, and free from sulfur and aromatic compounds and has a flashpoint value (flash point) that is higher than petroleum diesel so it is safer to store and use [14]. The advantages are that the price is relatively stable and the production is easily adjusted to the needs, environmentally friendly, does not contain sulfur so that it can reduce environmental damage caused by acid rain [15], combustion efficiency and higher cetane number than diesel fuel derivatives. petroleum, the content of sulfur and aromatic compounds is lower than diesel fuel so that the emission of gas from combustion is lower than the emission of petroleum-derived diesel fuel. In addition, it can also be degraded naturally [16].

The raw material of biodiesel is very environmentally friendly because it comes from renewable sources, with the composition of fatty acid esters from vegetable oils, including: palm oil, coconut oil, jatropha oil, kapok seed oil, and there are more than 30 kinds of plants. Indonesia has the potential to be used as biodiesel [14]

The transesterification reaction is a reaction between triglycerides and methanol to produce methyl esters and glycerol. This reaction can be carried out using an acid or a base catalyst. The use of alkaline catalysts is 4000 times faster than acid catalysts [17]. The transesterification reaction can be seen in Figure 1

Triglycerides Methyl Methyl Esters Glycerol

Fig 1. Transesterification Reaction

3. Method

3.1 Material

Apparatus used in this research were oven, a set of distillation equipment, three neck flask, hot plate, pycnometer, viscometer, volumetric glass, spatula, analytical balance, funnel, Beaker glass, and Erlenmeyer. Meanwhile, materials involved during the research were cooking oil (collected from the local store), ash from the bunch of pisang awak, methanol 96% (Merck).

3.2 Catalyst Preparation

Banana bunch was cut small, cleaned, and then dried at 105°C until constant weight was obtained. Calcination was carried out afterward using furnace (Muffle Furnace Nabertherm Controller P320, Nabertherm, Germany) at 700°C for 4 hours to remove the contained carbon. Characterization was carried out by X-ray diffraction (XRD) analysis employing Shimadzu XRD-700 (Kyoto, Japan) to evaluate the crystallinity of the catalyst produced.

3.3 Transesterification

Cooking oil was added into a reactor (three neck flask) and heated to 60°C. The prepared catalyst was priorly dissolved in methanol 96% and then added into the reactor containing heated cooking oil. The reactor was heated for 60 minutes to allow the transesterification to complete before filtered to remove the catalyst. Two-separated layers were formed, where upper layer consisted of methyl esters and lower layer – glycerol. The methyl esters layer (biodiesel) was separated and characterized for its viscosity, water content, acid number, and yield. Gas Chromatography – Mass Spectroscopy (GC-MS) analysis was carried out in Shimadzu GC-MS QP2000A (Kyoto, Japan) to determine the compounds present in the biodiesel.

4. Results and Discussion

Products yielded from the transesterification of cooking oil and methanol are methyl esters. In this study, variables identified for the prepared biodiesel product were density, viscosity, water content, and acid number relative to catalyst weight. The effect of different molar ratios was also observed against the biodiesel yield. It was found that, when the catalyst was 0%, the product yield was dramatically small due to the unfit operational condition for the free-catalyst transesterification.

4.1Effect of Catalyst Percentage and Oil:Methanol Ratio on Biodiesel Yield

Write text here The effects of molar ratio of oil:methanol and catalyst percentage (w/w) against the biodiesel yield have been presented in Figure 1. The increase in the number of catalysts resulting in decreasing trend of biodiesel yield. According to [18], catalyst addition does not necessarily improve the biodiesel yield, where on contrary, it could result in yield reduction. It is ascribed to the tendency of the reaction to run in reversible manner as more catalyst present in the mixture. Due to the excessive amount of catalyst, the mixutre becomes over-condensed causing difficulties in the mixing and stirring [19].

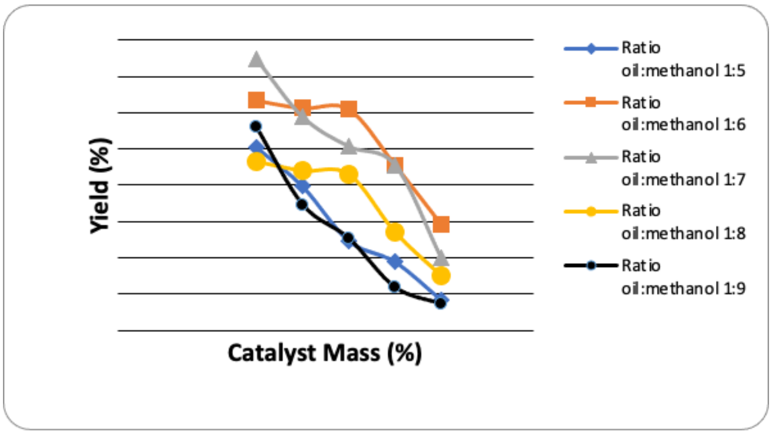

Fig 1. The effects of molar ratio (oil:methanol) and the amount of catalyst on biodiesel yield

In the case of molar ratio variation, excessive methanol may lead the reaction to the shift of the reaction to the equilibrium that consequently contributes to optimum yield of biodiesel. Nonetheless, the increasing methanol to the rasio of 1:8 (oil:methanol) reduced the biodiesel yield, associated with the overproduction of glycerol contributing to the inhibition methanol mobility to reach the reactant and catalyst [20].

4.2. Effect of Catalyst Percentage and Oil:Methanol Ratio on Biodiesel Density

Density shows the comparison of weight per volume unit (w/v). Density is correlated with viscosity. Biodiesel identified with density value exceeding the standard will undergo imperfect combustion. Density characteristics of each biodiesel sample obtained using different catalyst percentages and oil:methanol ratios are exhibited in Figure 2.

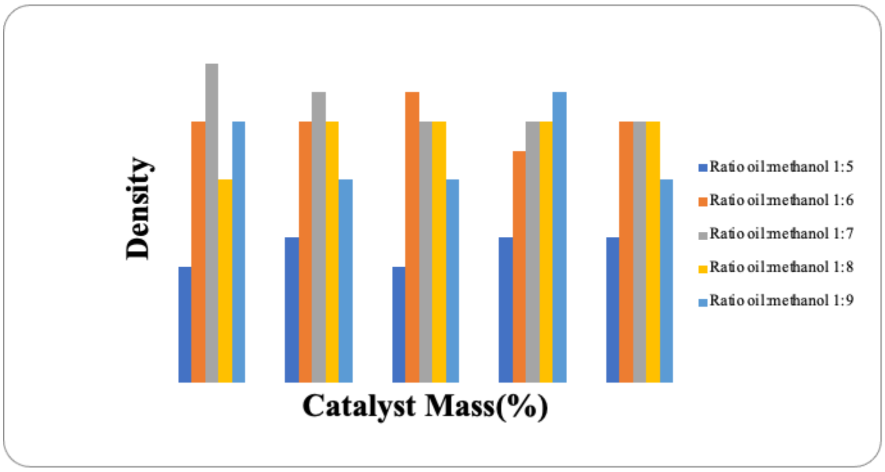

Fig 2. Effect of catalyst percentage and oil:methanol ratio on biodiesel density

In this research, the increases in catalyst number and molar ratio (oil:methanol) were found affecting the density of the produced biodiesel. As can be seen, different values of density were obtained in each sample prepared using different the catalyst percentage. There was no consistent trend observed in the change of density against the variation of catalyst percentage. It is ascribed to the presence of impurities in the sample, including methanol and water. According to [21], poor purification step could cause a variation in the bio-diesel density.

According to [22] the use of base catalyst could induce more saponification. It can lead to the presence of higher impurities from the reaction along with the unreacted fatty acids that eventually contributes to higher density of methyl esters. The use of less base catalyst, may result in methyl esters with lower density.

4.3Effect of Catalyst Percentage and Oil : Methanol Ratio on Biodiesel Viscosity

One of important parameter in the production of biodiesel is viscosity. Vegetable oil in general has high viscosity. Visocity is an intrinsic property of fluid that indicates the fluid resistance against its flow. The friction in the inner part of the mobile fluid could affect the atomization of fuel during its injection to the combustion chamber, resulting in deposition in the engine. Hence, the viscosity of the obtained biodiesel was characterized and presented in Figure 3.

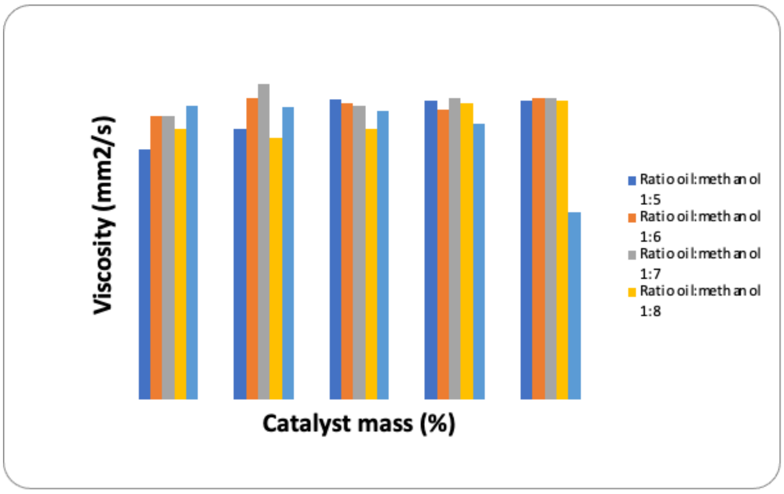

Fig 3. Effect of catalyst percentage and oil:methanol ratio on biodiesel viscosity

Our finding suggest that average viscosity in each variable is within the acceptable range of Indonesian standard (SNI) (2.3 – 6.0 mm^2/s). Hereafter, the catalyst percentage was observed affecting the viscosity of the biodiesel, where the viscosity of each sample did not forma tren. As mentioned earlier, the excessive base catalyst used in the reaction could drive higher saponification resulting more impurities in the end product. The presence of impurities and unreacted materials could contribute to higher viscosity of the biodiesel. Thus, using base catalyst with a less amount could lead to the production of biodiesel possessing lower viscosity. The value of viscosity could be reduced owing to the longer duration and higher temperature involved in the transesterification process

4.4 Hydrocarbon composition in the biodiesel

Methyl esters obtained from the transestifiration of cooking oil and methnaol were analyzed using GC-MS. The analysis was qualitative and quantitative, used to identify the component of fatty acids in the biodiesel along with their respective quantity. The GC-MS chromatogram of the produced biodiesel could be seen in Figure 4.

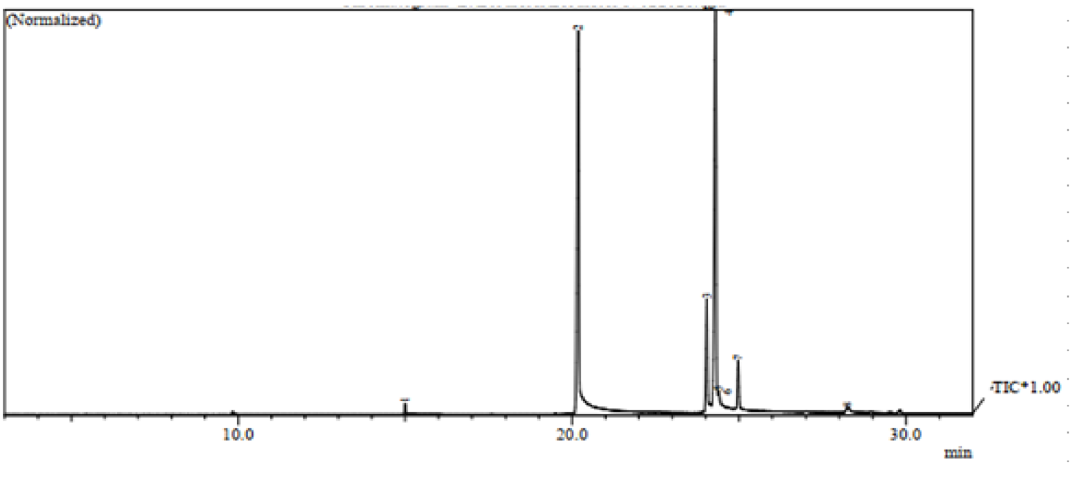

Fig 4. GC-MS chromatogram of produced biodiesel

Based on the GC-MS analysis, we obtained the overall fatty acids composition of the biodiesel which has been presented in Table 1.

Table 1. Composition of produced methyl esters based on GC-MS analysis

Compounds	Retention time	Peak	Area (%)
Methyl myristate	15.000	1	0.64
Methyl palmitate	20.182	2	42.63
Methyl linoleate	24.033	3	8.80
Methyl oleate	24.397	4	32.38
Methyl cis octadec-11-enoate	23.393	5	3.64
Methyl stearate	21.972	7	9.58
Methyl ricinoleate	28.256	8	1.19

Above data suggest the presence of methyl esters that are in line with the composition of fatty acids in the cooking oil. Nonetheless, the content of methyl linoleneat was not observable, despite the fact that linolenic acid is pretty common in the cooking oil. Probably, methyl linoleneat was indeed formed in a small number by the transesterification, but was not observable because of the overwhelming number of methyl palmitate, myristate, oleate, and linoleate so the methyl linoleneate was overshadowed.
Based on the GC-MS analysis, the primary component of fatty acid in the cooking oil sample was indicated in peak 2 and 4 assigned for palmitic acid (42.63%) and oleic acid (32.38%), respecitvely. In the chromatogram, peak 3 and 7 were assigned to the content of linolic acid (8.80%) and stearic acid (9.58%), respectively. Furthermore, the least intense peak 1 suggests the presence of saturated fatty acid – myristic acid with a content occupying only 0.64%.

4.5 Crystallinity of The Prepared Pisang Awak Bunch-Based Catalyst

In this study, XRD analysis was carried out to identify the crystalline phase of the prepared catalyst by determining the parameter of the lattice structure to calculate the size of particle and crystal of a solid material. All materials containing specific crystals could be analyzed in XRD patterns that depicts typical peaks of the tested material as can be seen in Figure 5.

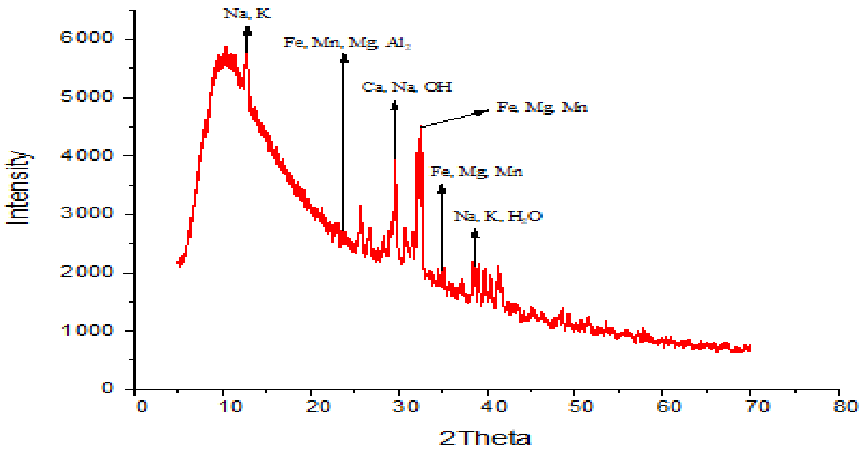

Fig 5. XRD patterns of the prepared pisang awak bunch-based catalyst

The results revealed the presence of several dominant elements in the catalyst namely K, Ca, Na, Mg, Mn, and so on. Those elements are typically common in banana bunch obtained from the activiation process. XRD analysis indicates the success preparation of Kalium/CaO catalyst from the pisang awak bunch which was calcinated at 700°C for 4 hours. The presence of high kalium content in the banana bunch allows its application as a feed ingredient in the catalyst preparation. The catalytic activity of pisang awak bunch-base catalyst in this study had been proven by the conversion of methyl esters from cooking oil as already explained previously

5. Conclusion

Based on the discussion, we could draw a conclusion that pisang awak bunch could be used as a heterogenous catalyst to obtained a high yield biodiesel (90.97%) with catalyst weighed 3% w/w cooking oil. Results from GC-MS proved the end product was methyl esters, with the most dominant fatty acid of the cooking oil was palmitic acid and oleic acid amounting for 45.24 and 37.92% total weight, respectively. The optimum biodiesel was obtained from 1:6 (oil:methanol) and 3% catalyst (w/w cooking oil), where values of its density, viscosity (at 40°C), water content, acid number were 850 kg/m3, 6.21 mm2/s, 0.04%, and 0.33 mg-KOH/g, respectively.

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