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PURIFICATION OF BIODIESEL USING RICE STRAW AND *DIOSCOREA ALATA* STARCH AS NATURAL ADSORBENTS

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Abstract. Janeng starch (*Dioscorea Alata*) and rice straws are developed to be used as adsorbents in dry washing method to purify crude biodiesel. In this study, we evaluate the potential of rice straw and janeng starch as natural adsorbents in the purification of biodiesel that replace the role of water in absorbing contaminants from biodiesel. The SEM characterization results show that the starch adsorbent and rice straw has an open and porous surface and is evenly distributed for janeng starch. Both adsorbents, either the janeng starch or rice straw, can be applied for the purification of biodiesel. The quality of biodiesel is influenced by the amount of adsorbents used in biodiesel purification. The effectiveness of the adsorbent is shown by the decrease in free fatty acids, alkali numbers, soap numbers and turbidity levels in biodiesel. The concentration of free fatty acid oil in crude biodiesel before the purification step was 0.769 mg-KOH/g, then decreased to 0.128 mg-KOH/g after the adsorption. This acid value had been very low and met the Indonesian quality national standard for biodiesel spesically 0.50 mg-KOH/g. Either janeng starch or rice straw adsorbent was able to reduce the soap content of potassium oleate to level 53.33 ppm from the initial content of 106.67 ppm. These two natural adsorbents can be the alternative adsorbents in the purification of biodiesel that employs dry washing method.

Keywords: biodiesel, dry washing, purification, adsorption, rice straw, janeng starch

I. INTRODUCTION

Generally, biodiesel is defined as fuel for diesel engine made of renewable materials, in particular ester alkyl and fatty acid [1]. Biodiesel produced by trans-esterification is obtained by reacting oil (triglycerides) with methanol yielding methyl ester and glycerol. After separated from the glycerol, the methyl ester was then called biodiesel. The crude biodiesel has to be purified from the impurities after the production process to be used as biodiesel. The impurities in biodiesel, some of them are glycerine, water, alkalies, soap residue, fatty acid and the remaining alcohol [2]. Purification of methyl ester to obtain biodiesel is one of important biodiesel production steps. Today, a standard method used in biodiesel purification is water washing, this has some weaknesses including repetitive washing, impure products, and a high amount of wastewater. Another purification method alternative that can be employed in the purification of biodiesel is dry washing method, the purification by utilizing adsorption process to remove the impurities from crude biodiesel. Dry washing technique aims to remove the pollutants in the biodiesel. This is a low-cost method, moreover, it is benefitted from the selective properties of some adsorbents [3]. Studies on dry washing technique has been reported to use some natural adsorbents, such as starches and celluloses, in purification of biodiesel. The starches used were extracted from potato, cassava and corn [2]. Even though there have been many studies on biodiesel purification employing dry washing technique, there has been no report on janeng starch (*Dioscorea Alata*) and rice straw cellulose used as the adsorbents. Rice straw cellulose and janeng starch have some superiority because they are massively available in nature, biodegradable, relatively low cost, biocompatible and high potential to be used as natural adsorbents in the purification of biodiesel [4]. In dry washing method, rice straw and janeng starch serve to replace water in the adsorption of contaminants from the biodiesel. Cellulose and starch are expected to have better performance in adsorbing the methanol, catalyst and soap residue and glycerol from biodiesel [2]. Therefore, in this research, janeng starch and rice straw will be used as adsorbents in biodiesel purification with dry washing method.

II. METHODOLOGY

Equipment used in this research are beaker glass, graduated cylinders, test tubes, volumetric flasks, Erlenmeyer flasks, funnels, petri dish, sieve 100 mesh, spatula, and magnetic stirrer. Materials used in this research are janeng (*Dioscorea Alata*) and rice straw obtained from Lambunot Paya, Kuta Baro District, Aceh Besar Regency, biodiesel (used cooking oil), acetone 98%, KOH, HCl 37%, CH_3OH 98%, Phenolphthalein indicator, bromophenol blue, ethanol, NaOH, $NaHSO_3$, $AgNO_3$ and aquadest.

Isolation of Janeng Starch
Janeng tuber as many as 12 kg were peeled and washed clean with aquadest, then cut into small cubes and blended with the addition of $NaHSO_3$ until the fine janeng pulp obtained. Next, aquadest was poured into the janeng pulp, and then the mixture was squeezed and filtered using muslin fabric. The filtrate was left for precipitation for 24 h. After the precipitate formed, the water on the top layer was removed, the obtained precipitate was dissolved with aquadest and filtered with vacuum filtration (using Büchner flask and funnel). The precipitate was washed repeatedly until the toxic removed and no brown sediment formed from the filtrate when tested with $AgNO_3$. Then the precipitate was dried in an oven at 70^{o}C for 24 h. After that, the dried precipitate was grinded and sieved (100 mesh), the janeng powder then obtained [5].

Preparation of Rice Straw
The straw was weighed for 10 g and cut into 1 cm, then soaked in NaOH 15 wt% for 30 min with the straw and solvent ratio of 1:20 w/w. The mixture was stirred continuously by a magnetic stirrer. The extracted fibre was rinsed with water, then dried and used as adsorbent [6].

Biodiesel Purification
On purification of biodiesel, the method employed was dry washing with two different adsorbents, janeng starch, and rice straw. Crude biodiesel used was made of palm oil. The purification process was conducted by respectively adding 5% (b/v) adsorbents into crude biodiesel, and the mixture was stirred continuously by a magnetic stirrer for 15 min at room temperature. After the purification, the separation was done by filtration. Biodiesel from dry washing was taken then was added into sample bottles and stored for further analysis [2]. In this research, the influence of contact time (15 min) was also evaluated.

Biodiesel Characterization
Characterization of biodiesel was conducted by determining the concentration of free fatty acid, alkalies, and soap and the turbidity (Eq (1) and (2) [7].

$$Acid\ Value = \frac{mL\,KOH \times N\,KOH \times MW}{10(sample)} \quad (1)$$

$$Acid = \frac{mL\,HCL \times N\,KOH \times MW}{10(sample)} \quad (2)$$

Adsorbent Characterization
The characterization of adsorbent functional groups in this research was conducted using infrared spectroscopy (FTIR) at the wavelength between 4000-600 cm^{-1} [2]. Meanwhile, the morphology structure of the adsorbents was examined using SEM (Scanning Electron Microscopy) with a range of 20 kV [6].

Content Determination of Water
As many as 1.00 g adsorbent powders were added to porcelain evaporating dish and put into an oven at 110^{o}C. The obtained product of the procedure was inserted into desiccators and weighed until the constant weight reached.

Content Determination of Ash
As many as 2.00 g adsorbent powders were added to porcelain evaporating dish and put in a furnace at 850^{o}C for 5 h. The obtained product was inserted into a desiccators and weighed until the constant weight reached.

III. Result and Discussion

Isolation of Janeng Starch
The starch powder obtained from the isolation is white in colour and free from cyanide (HCN). The concentration of cyanide in janeng tuber was estimated to be around 700 mg/kg [5]. From 10 kg fresh samples of janeng tuber, the janeng powder obtained is as much as 1 kg. Therefore, the yield percentage is 10% per janeng sample weight used in the procedure. Janeng starch powder obtained can be directly used as the adsorbent to adsorb the impurities from biodiesel

Preparation of Rice Straw
The addition of NaOH was performed to mince the straw; thus some of the impurity components can be removed to activate the adsorbent. NaOH concentration used for this treatment is 15%.

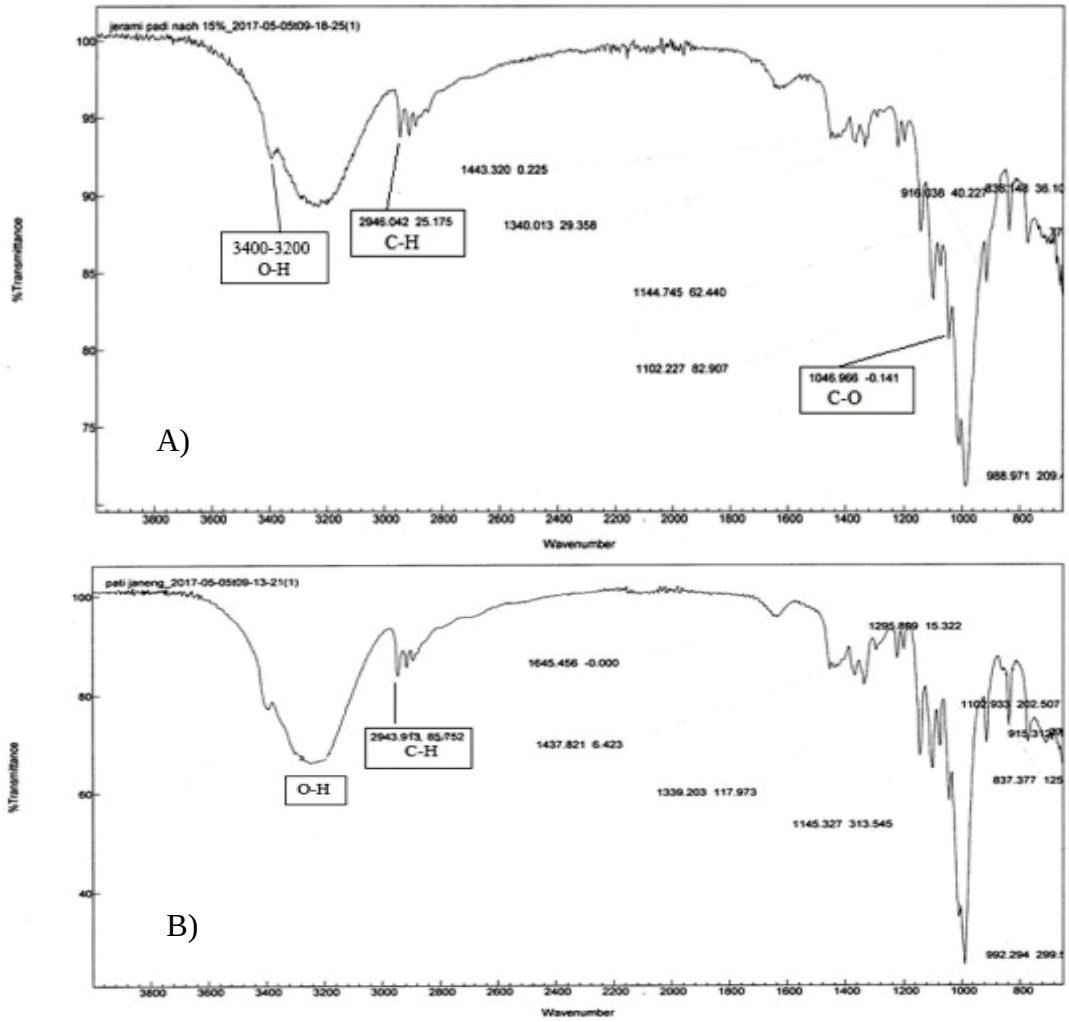

Figure 1. The spectrum of FT-IR analysis of a) rice straw and b) janeng starch adsorbent.

The prepared rice straw can be used directly as the adsorbent to adsorb the contaminants from biodiesel. Characteristics of janeng starch powder and rice straw as adsorbents were determined through functional group analysis using FTIR, ash content, and the surface morphology using SEM.

***Fourier Transform Infra-Red* (FTIR)**

The result of characterization using FTIR shown by Figure 1(a) for rice straw adsorbent and 1(b) for janeng starch adsorbent. Figure 1(a) shows the absorbance at wavenumber 2946.042 cm^{-1} which indicates the presence of C-H groups. The presence of C-O groups can be observed at the wavenumber 1046.966 cm^{-1} and –OH groups at 3400-2400 cm^{-1} [8]. Meanwhile at Figure 1(b) for janeng starch adsorbent, also shows the absorbance at wavenumber 2943.913 cm^{-1} which indicates the presence of C-H groups and at 3400-2400 cm^{-1} indicating the presence of C-O groups. The presence of –OH and C-H groups can be observed at wavenumber 3340-2920 cm^{-1}. Wavelength 1730 shows the presence of C-O stretching. The absorbance at 1320 and 1360 cm^{-1} indicate the presence of C-H and C-O aromatic. Moreover, at wavelength 1060 cm^{-1} the presence of C-O-C can be observed [6]. The result of FTIR analysis of both adsorbents signifies the presence of functional groups within the molecular structure which plays an important role in their use as the adsorbent, especially to remove the contaminants from biodiesel.

Scanning Electron Microscopy (SEM)

The characterization of rice straw and janeng starch adsorbent using SEM instrument *(Scanning Electron Microscopy*) aims to identify the structure morphology structure of the adsorbents. SEM morphology of rice straw can be seen in Figure 2. The SEM characterization result shows that the rice straw adsorbent has an open and porous surface. With the presence of pores, it helps the adsorbent to bind the target compounds onto the surface of the rice straw adsorbent.

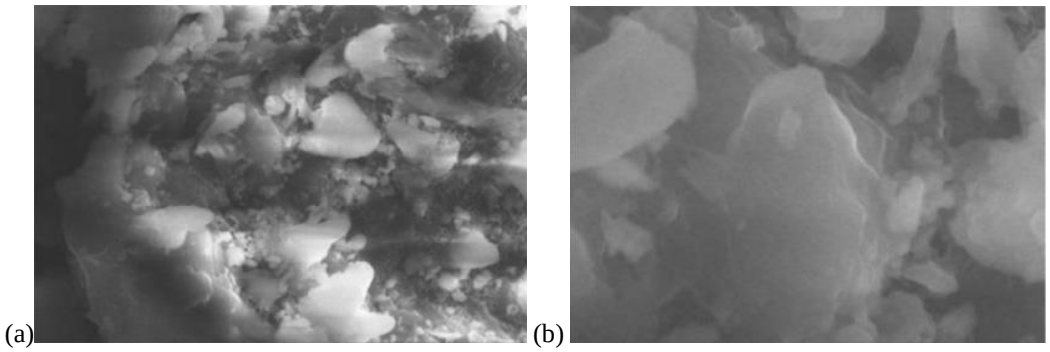

Figure 2 SEM images of rice straw with a) 10.000x and b) 50.000x magnifications

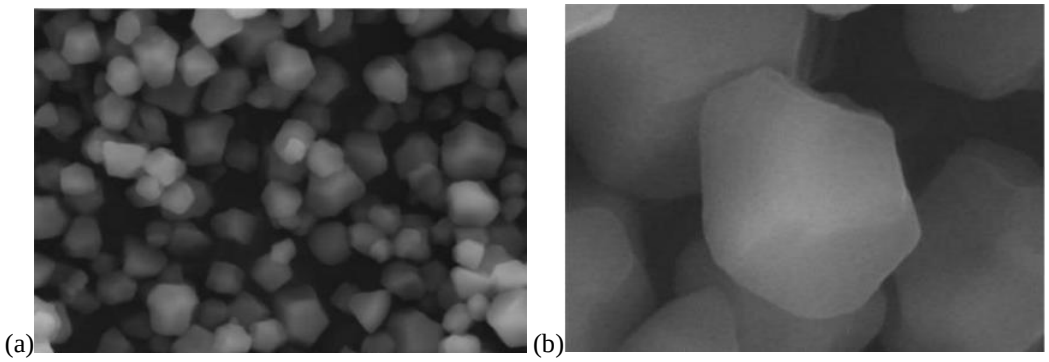

Figure 3 SEM images of of janeng starch with a) 10.000x and b) 50.000x magnifications

Meanwhile, the result of SEM analysis for janeng starch adsorbent can be seen in Figure 3. The SEM characterization result shows that the janeng starch adsorbent also has a homogenous morphology which is porous and evenly distributed. Due to its even distribution, the janeng starch adsorbent was expected to have a better ability to adsorb the impurities of biodiesel.

Content Determination of Water and Ash

The determined ash content is useful to evaluate the amount of mineral residue concentration in janeng starch and rice straw adsorbents. Ash content was determined based on the loss of weight after the combustion at a high temperature of 850^{o}C to remove organic compounds. Based on the result, it can be seen that the ash content in janeng starch is 0.79% and in rice straw is 0.11%. The presence of excessive ash causes the adsorbent pores blockage; thus the surface area is reduced. Meanwhile, the test on water concentration in the janeng starch and rice straw adsorbents shows the low water content. The water content in janeng starch is 0.74%, meanwhile, in rice straw, the water content is 0.17%. Water content affects the quality of adsorbents, based on the result, the water content in both adsorbents are relatively low. The low water content can be caused by the drying and storing process which have been carried very well, and it also can be attributed to the non-hygroscopic properties of the adsorbents.

Dry Washing Treatment

The produced biodiesel cannot be used directly, due to the presence of impurities that can damage the combustion system. Therefore, biodiesel purification was carried out by using Dry Washing method. Dry washing method is a purification process with the help of adsorption to remove the contaminants from biodiesel [2]. Both adsorbents, either the janeng starch or rice straw, were used for the purification of biodiesel. The amount of adsorbents used affected the biodiesel quality obtained. The more adsorbents were added, the more contaminants were removed.

Biodiesel Quality

A concentration of free fatty acid

The fatty acid is the main component of vegetable oils or fat is the material for lipid in living creatures.

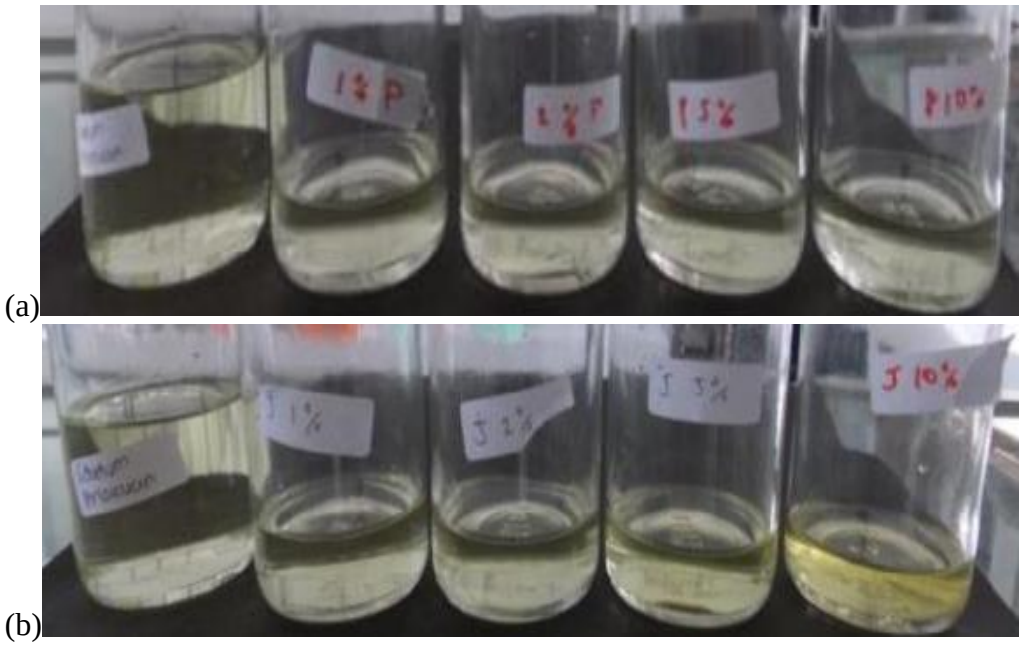

Figure 4 Biodiesel product after dry washed with (a) janeng starch and (b) rice straw.

Based on the results given by janeng starch and rice straw adsorbents, before and after the purification, the concentration of free fatty acid oil decreased. The concentration of free fatty acid oil in biodiesel, before the purification was 0.769 mg-KOH/g, then decreased to 0.1282 mg-KOH/g after the adsorption. This acid value had been very low and met the Indonesian quality national standard for biodiesel (0.5 mg-KOH/g).

Soap content analysis

Based on the obtained results from the above graphs, it can be seen that janeng starch and rice straw adsorbents, before and after the purification, reduced soap content. The lesser the soap content of biodiesel, the better the quality. Both adsorbents had a similar capability to reduce the soap content in biodiesel. Based on the test result, either janeng starch or rice straw adsorbent was able to reduce the soap content of potassium oleate to level 53.33 ppm from the initial content of 106.67 ppm.

Turbidity

Turbidity is a measure which informs the visual aspects of biodiesel which can be correlated to the presence of impurities. The presence of glycerine, water, and some sediment are degraded the biodiesel performance, damages the combustion system and quickens the filter saturation and triggers the damage on the fuel system. Based on Figure 4, it can be seen that the purification process used dry washing with different adsorbents exhibits the effective removal of biodiesel turbidity [2]. Through visual observation, it can be seen that the biodiesel colour dry washed with janeng starch is more transparent as opposed to the one with rice straw which is more yellowish. In general, the increase in adsorbents addition improved the turbidity removal.

CONCLUSIONS

Janeng starch isolated from janeng tuber and rice straw prepared with Natrium hydroxide base can be used as alternative adsorbents for biodiesel purification. Both of these adsorbents are capable of removing the contaminants in crude biodiesel. These two natural adsorbents can be the alternative adsorbent in the purification of biodiesel that employs dry washing method.

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