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Purification of Biodiesel from Waste Cooking Oil Using Bentonite as Dry Washing Agent

Nanda Suriaini[1)], Tika Thalia Febriana[2)], Andesta Yulanda[2)], Adisalamun[2)], Yanna Syamsuddin[2)], Muhammad Dani Supardan[2)]*

[1)] Graduate School of Chemical Engineering, Faculty of Engineeering, Universitas Syiah Kuala, Jln. Syech Abdurrauf, Darussalam, Banda Aceh 23111
[2)] Departement of Chemical Engineering, Faculty of Engineeering, Universitas Syiah Kuala, Jln. Syech Abdurrauf, Darussalam, Banda Aceh 23111

*Email: m.dani.supardan@che.unsyiah.ac.id

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Abstract

The process of biodiesel purification is an important step in getting biodiesel products that meet specifications as a substitute for fossil-based fuels. Dry washing method has been developed to achieve an effective purification strategy in order to produce high-quality biodiesel. Bentonite can be used as dry washing agent because it has a good adsorbing properties as well as a large pore and surface area therefore can attract polar substances such as glycerol and methanol. The purpose of this research is to know the capability of activated bentonite as dry washing agent for purification of biodiesel produced from waste cooking oil. The activation process of bentonite was carried out using sulfuric acid with concentration 1.5 M. Characterization of the bentonite was conducted using X-Ray Diffraction (XRD) for minerals content and *Brunauer–Emmett–Teller* (BET) method for surface area. Bentonite was used as dry washing agent for biodiesel purification by varying washing time (10, 20, 30, 40 and 50 minutes) and adsorbent amount (1, 2, 3, 4 and 5%). The experimental results showed that purification of biodiesel by dry washing using activated bentonite resulted in a better yield and quality than wet washing and dry washing using non-activated bentonite, except the acid number. The best operation condition resulted from this research is at 10 minutes washing time and 1% adsorbent with yield of 94.1%; acid number of 0.4208 mg KOH/gram; density of 0.8838 gram/cm^3, viscosity of 3.0617 mm^2/s and water content of 1.17%.

Keywords: bentonite, dry washing agent, biodiesel, waste cooking oil

1. Introduction

The purification process is one of the important steps to produce biodiesel with certain specifications. Water washing is a conventional biodiesel purification method that is widely used both on an experimental and commercial scale. However, this process has many shortcomings. The purification process with the dry washing method is an alternative biodiesel purification method that has been developed. This method uses certain adsorbents to adsorb impurities contained in crude biodiesel as a product of transesterification reaction. An adsorbent material that has a high silica content such as bentonite has the potential to be used in the biodiesel refining process (Stojkovića et al., 2014; Berrios et al., 2011). In general, the advantages of the dry washing method include shortening the biodiesel refining process time, reducing the amount of water used, reducing waste generation, and lower operating costs. In addition, the energy consumption of this method is 23% smaller than the method of washing with water (Alamsyah and Loebis, 2014).

Several studies reported that the purification process of biodiesel with dry washing was a prospective method to be applied. Suppalakpanya et al. (2010) used bleaching earth to purify biodiesel from CPO. Berrios et al. (2011) used magnesium silicate and bentonite to purify biodiesel from used cooking oil. Meanwhile, Faccini et al. (2011) compared the performance of 4 commercial adsorbents namely Magnesol®, silica, Amberlite BD10 DRY®, and Purolite PD 206® for the purification of biodiesel from soybean oil. The results of previous studies show the dry washing method has the same performance even better than conventional purification methods using water. However, the potential of bentonite as a dry washing agent in the process of biodiesel production is still not much studied.

Bentonite has a high silica content so that it is potentially used in the biodiesel refining process (Sohling et al., 2010; Bertram et al., 2005). On the other hand, our country is rich in natural resources including mineral bentonite. The great potential of bentonite in Indonesia needs to be utilized to its full potential to support national energy independence. The community generally utilizes bentonite as pile land for house yards. Several studies have been carried out related to the use of bentonite such as dye adsorbents (Brito et al., 2018), catalyst in the cracking process for biofuel making (Rabie et al., 2018), and sealing material (Akgün and Koçkar, 2018).

Meanwhile, the depletion of petroleum reserves causes the price of petroleum-based fuels to increase. Another aspect that has also become a concern in recent years is pollution caused by the use of fossil fuels. It is one of the causes of an increase in the temperature of the earth known as the issue of global warming (Gashaw and Teshita, 2014). This underlies the need for the development of biofuels such as biodiesel, to replace the use of fossil-based fuels. Some of the advantages of biodiesel compared to fossil-based fuels are biodegradable, renewable, produce less pollution and particulates, and produce less carbon monoxide and other hydrocarbon emissions (Supardan, 2011). Efforts still need to be done in order to find cheap alternative biodiesel raw materials and their usage which cannot compete with basic human needs. Commercialization of biodiesel production from vegetable oils has not been promising in terms of economics because of the high price of biodiesel raw materials used will cause an increase in the price of biodiesel produced (Supardan et al., 2012). The use of used cooking oil as an alternative raw material is very effective in reducing the price of biodiesel production (Gashaw and Teshita, 2014; Hussain et al., 2016).

This research aim is to study the effect of time and amount of bentonite in the process of biodiesel purification using the dry-washing method. The quality of biodiesel produced will be compared with conventional washing methods using water.

2. Materials and Method

2.1. Materials

The materials used are used cooking oil, bentonite, sulfuric acid (H_2SO_4) 98% (Merck, Germany), aquadest, sodium hydroxide (NaOH) (Merck, Germany) and ethanol technical grade. The bentonite used was obtained from the Kuala Dewa area, North Aceh Regency. Used cooking oil was obtained from several restaurants located around the city of Banda Aceh.

2.2. Bentonite Activation Process

Ball mill is used to get the size of certain bentonite particles which will be used in the biodiesel refining process. 50 g of bentonite was dissolved in 300 mL of 1.5 M sulfuric acid and then stirred with a magnetic stirrer for 1 hour at a speed of 80 rpm at 80°C. Then the mixture of the ingredients was filtered with filter paper and washed with warm aquadest. Next, bentonite was crushed and sifted to get the desired size of bentonite. Bentonite with 60-80 mesh sieve size was then dried in an oven at 110 ° C for 24 hours until the weight of the activated bentonite was constant to remove water that was still trapped in the pores. Furthermore, activated bentonite is used as a dry washing agent.

2.3. Biodiesel Production

The main equipment used was a transesterification reaction system consisted of a three-neck flask equipped with a thermometer, electric heater (Yamato Scientific MAG-MIXER Model MH800, Japan), magnetic stirrer and condenser. Used cooking oil was first homogenized using a magnetic stirrer. This process was carried out at 60°C for 10 minutes. The result of the acid-base titration method showed that the free fatty acid (FFA) of used cooking oil was 0.5%. Trans-esterification reaction was carried out by reacting used cooking oil with ethanol 96% (molar ratio of oil to ethanol 1: 6) with the help of NaOH as catalyst (1% mass of oil) to accelerate the reaction. The transesterification process was carried out at 60°C for 90 minutes. The transesterification product was then put into a separating funnel to separate biodiesel and glycerol as a side product.

2.4. Dry Washing Process

The dry washing process of biodiesel produced was carried out in a beaker glass. Biodiesel added with bentonite according to the variation of the bentonite to biodiesel mass ratio (1, 2, 3, 4 and 5%). Stirring was carried out using a magnetic stirrer with a speed of 40 rpm. The duration of the purification process was according to the variation of washing time (10, 20, 30, 40, 50 minutes). Biodiesel with adsorbent solids was then separated using filter paper. Purified biodiesel was then analyzed. The process of biodiesel purification using water was also carried out as a comparison.

2.5. Characterization of Bentonite and Biodiesel Analysis

Characterization of bentonite adsorbents was carried out including mineral compound content with X-Ray Diffraction (XRD) and surface area with N2 Adsorption-Desorption Surface Area Analyzer using the Brunauer-Emmett-Teller (BET) method. While the analysis of biodiesel carried out includes yield, acid number using the titration method, density using a pycnometer, viscosity using the Ostwald viscometer, water content using heating at 105ºC and ethanol content using gas chromatography-mass spectrometry (GC-MS) Shimadzu QP 2010 plus.

3. Results and Discussion

3.1. Characterization of Bentonite

The results of bentonite characterization using XRD are shown in Figure 1. Types of constituent minerals and the level of crystallinity of component structures are indicated by a peak value of 2θ as well as high and low peak intensities. From Figure 1 (a), it is seen that bentonite without activation has a mineral composition consisting of montmorillonite ($Al_{0.86}Fe_{0.1}H Li_{0.08}Mg_{0.14}O_{10}Si_{3.9}$), quartz ($SiO_2$) and corundum ($Al_2O_3$). The montmorillonite mineral has the sharpest intensity at the peak area of 2θ = 22.00 ° (d = 4,0365 Å). Furthermore, the sharpest peak of quartz mineral lies at the peak 2θ = 26.71 ° (d = 3.3354 Å) and corundum minerals are interpreted at the peak 2θ = 35.97 ° (d = 2.4945 Å)..

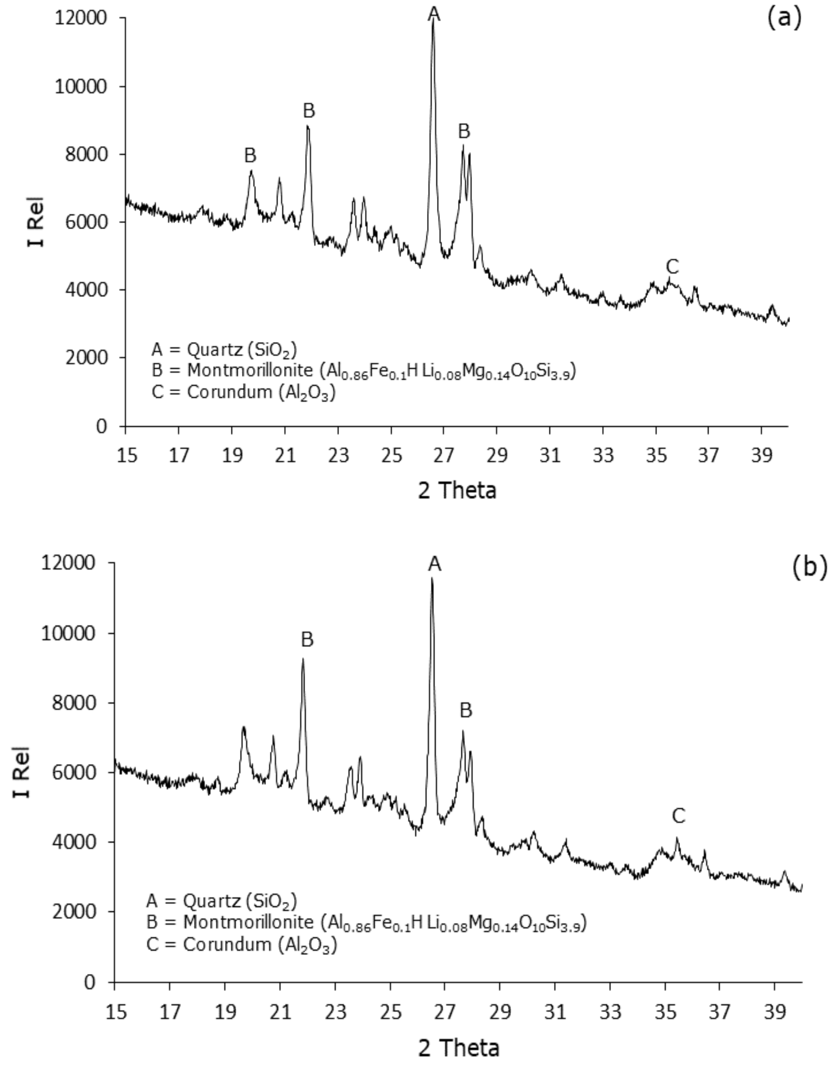

Figure 1. XRD analysis results (a) bentonite without activation and (b) activated bentonite

Meanwhile, the XRD analysis results of activated bentonite as presented in Figure 1 (b), showed that the mineral content was dominated by quartz minerals with the highest peak at 2θ = 26.73 ° (d = 3.3328 Å). The mineral montmorillonite and corundum can also be seen at peaks 2θ = 21.78 ° (d = 4.0767 Å) and 2θ = 35.07 ° (d = 2.5566 Å). In general, the intensity of montmorillonite peaks in bentonite without activation and activated bentonite showed no significant difference. Thus, it can be concluded that the activation process did not change the structure of bentonite (Rabie et al., 2018). Bentonite without activation still contains more diverse ions. However, when bentonite is chemically activated, interactions with activators will release Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+} ions and other impurities present in natural bentonite to make the crystal lattice becomes cleaner (Febriawan et al., 2014).

Meanwhile, the results of bentonite characterization using the BET method showed that activated bentonite had a larger surface area than bentonite without activation. During the activation process, the acid activator will react with components that cover the pores of the adsorbent such as tar, Ca salt and Mg (Tanjaya et al., 2006). This causes the bentonite pores to be cleaner and larger in size. The greater the pores of the adsorbent will have an impact on increasing the surface area and adsorbent absorption ability (Febriawan et al., 2014). Rabie et al. (2018) also reported a similar trend where the activation process using hydrochloric acid could increase the surface area and pore size of bentonite

3.2. Utilization of Bentonite as Dry Washing Agent

Yield of the dry washing process is determined by comparing the mass of biodiesel after purification with the mass of biodiesel before purification. The results of the analysis can be seen in Figure 2. The results showed that the amount of bentonite and washing time had an influence on biodiesel yield. The more bentonite added in the dry washing process, the less yield is obtained. This is due to substances that can be absorbed by more bentonite. Bentonite contains SiO_2 compounds which can absorb alcohol, soap and glycerol that can increase the efficiency of the biodiesel refining process (Wu et al., 2016). It is also shown that the washing time has the same effect. The longer the washing time, it is possible for bentonite to absorb more alcohol, soap and glycerol in crude biodiesel.

The effect of the amount of bentonite and washing time on the acid number of biodiesel can be seen in Figure 3. The mass of bentonite and washing time also have an influence on the acid number of biodiesel products. The more bentonite added in the dry washing process, the higher the acid number tends. The washing time variable also shows the same result trend.

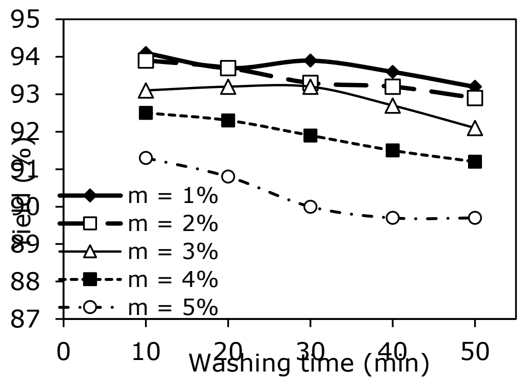

Figure 2. Yield of biodiesel after purification using activated bentonite

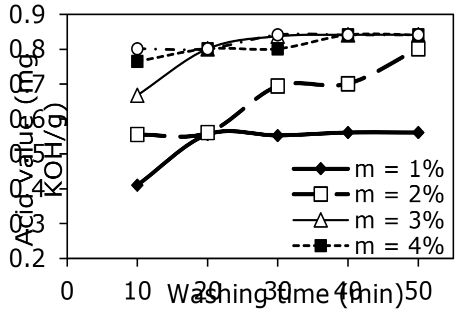

Figure 3. Acid number of biodiesel after purification using activated bentonite

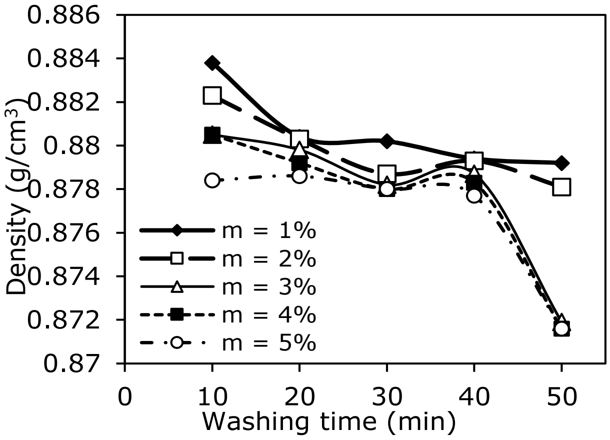

Figure 4. Density of biodiesel after purification using activated bentonite

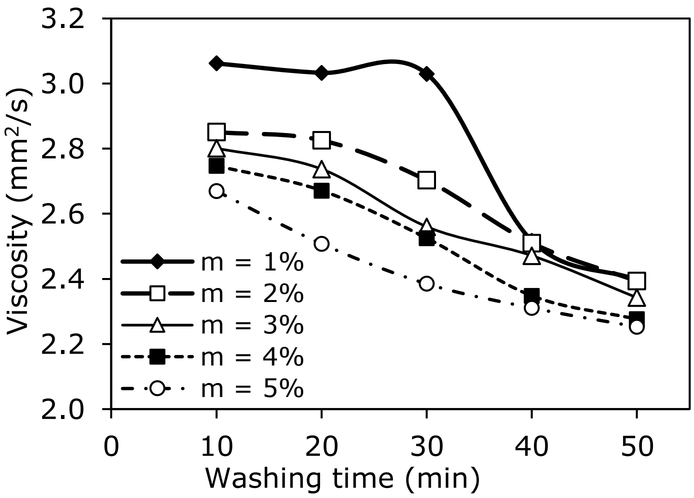

Figure 5. Viscosity of biodiesel using activated bentonite

Table 2. Moisture content of biodiesel using dry washing and wet washing at washing time 10 minutes

	Dry washing using activated bentonite					*Dry washing* using non-activated bentonite	*Wet washing*
	1%	2%	3%	4%	5%		
Water content (%)	1,17	1,14	1,19	1,23	1,3	1,94	2,67

Table 3. Comparison of the quality of biodiesel produced against SNI No. 07-7182-2006

Parameters	*Dry Washing* using bentonite		*Wet Washing*	SNI 2006
	Activated	Non-activated		
Acid value, mg KOH/g	0,42-0,84	0,41	0,41	max. 0,8
Density, g/cm^3	0,87-0,88	0,88	0,88	0,85-0,89
Viscosity, mm^2/s	2,25-3,06	3,28	3,24	2,3-6,0
Water content, % volume	1,17-1,32	1,94	2,58	max. 0,05

The experimental results showed that the bentonite adsorbent used was classified as acid where the bentonite had a pH of around 5 after the activation process. This is due to the washing and neutralization of activated H_2SO_4 bentonite using aquadest with a pH of 5. As a result, the activated bentonite produced is not in a neutral pH condition even though repeated washing has been carried out in the activation process of bentonite. Figure 4 shows the results of the biodiesel density analysis. It can be seen that the density value tends to decrease as the increasing of the amount of bentonite and washing time. Decreasing in density is due to impurities such as water, glycerol, residual ethanol and soap that can be absorbed by bentonite (Wu et al., 2016).

Figure 5 shows the results of the biodiesel viscosity analysis. The experimental results showed that the viscosity value of biodiesel after purification using activated bentonite ranging from 2.253 to 3.062 mm^2/s. The results showed that as the amount of bentonite and washing time increased, the viscosity of biodiesel decreased. Biodiesel with too low viscosity will provide poor lubrication and can result in leakage to the pump. Conversely, very high viscosity can cause dirty smoke, problems in atomization, damages the fuel injector and slow to flow (Prihandana et al., 2006).

Based on the results obtained, it can be seen that the viscosity and biodiesel density values obtained are directly proportional. The smaller the viscosity, the smaller the biodiesel density will be (Aini and Tjahjani, 2013). Meanwhile, Table 2 shows that the water content in biodiesel after dry washing using activated bentonite is lower than the wet washing using water. The moisture content of dry-washing samples using activated bentonite with washing time of 10 minutes and the mass of adsorbent 1%, 2%, 3%, 4% and 5% were 1.17%; 1.15%; 1.20%; 1.25% and 1.32%, respectively. As a comparison, biodiesel after purification using wet washing method has a water content of 2.67%.

These results proved that bentonite can act as a dry washing agent that is able to absorb water in biodiesel produced. The same trend also reported by several other researchers, including Darmawan and Susila (2013) and Wu et al. (2016). Water content is an important quality standard of biodiesel because of the application of biodiesel to the engine. The water content in biodiesel can form paraffin crystals at cold temperatures which can further clog the fuel flow. In addition, the water content can also cause corrosion of the engine (Sundaryono, 2011).

The results of the ethanol content analysis of biodiesel after purification showed that the ethanol content produced by dry washing was lower than the results of the wet washing. This is because bentonite can absorb residual alcohol found in biodiesel products (Wu et al., 2016). The ethanol content of biodiesel purified from the dry washing using activated bentonite and wet washing was 0.15% and 0.33%, respectively. In the process of biodiesel production using a transesterification reaction, excess alcohol is used in order to shift the equilibrium of the reaction to the product.

Furthermore, it is expected that during the product purification process the residual ethanol can be remove to produce pure biodiesel. Ethanol can cause problems when biodiesel is applied as fuel for the engine. The -OH group is chemically aggressive towards non-ferrous metals and chrome alloys. In addition, alcohol in biodiesel can form deposits in the combustion chamber (Prihandana et al., 2006).

3.3. Characteristics of biodiesel

Comparison of the quality of biodiesel produced through the dry washing process (using activated bentonite and without activation) and wet washing with Indonesian National Standard (SNI) No. 04-7182-2006 are shown in Table 3. Biodiesel obtained from the dry washing and wet washing method has fulfilled the SNI requirements for three parameters, namely acid number, density, and viscosity. Meanwhile, the water content of biodiesel of the purification method of dry washing and wet washing does not meet SNI requirements with a maximum moisture content 0.05%.

4. Conclusions

The characterization results showed that bentonite as a dry washing agent was dominated by the minerals Montmorillonite, quartz (SiO2) and Al2O3. The chemical activation process of bentonite using H2SO4 can reduce the impurity content of bentonite thereby increasing the content of SiO2 compounds. Activation of bentonite with H2SO4 also increased the surface area. Based on the analysis of biodiesel products after purification, the highest biodiesel yield 94.1% obtained by dry washing method with activated bentonite at conditions: 1% of bentonite mass and 10 minutes of washing time. The biodiesel produced has acid number 0.4208 mg KOH/g, density 0.8838 g/cm3, viscosity 3.0617 mm2/s and biodiesel moisture content of 1.17%. The acid number, density, and viscosity of biodiesel produced from the dry washing and wet washing method have fulfilled the SNI No. 04-7182-2006.

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