

APPLICATION OF SIMULTANEOUS ADSORPTION AND TRANSESTERIFICATION PROCESS IN BIODIESEL PRODUCTION FROM USED COOKING OIL

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Abstract

In this work, the process of production of biodiesel from used cooking oil with a high-water content using simultaneous water adsorption onto bentonite and transesterification reactions was studied. The results showed that the process parameters studied, i.e., the water content of the used cooking oil, the amount of bentonite added and stirring speed, affect the yield of biodiesel. Simultaneous water adsorption and transesterification produced a higher yield than the conventional process (without bentonite addition). The highest biodiesel yield of 96.8% was obtained with the addition of 3 wt.% bentonite, a moisture content of 0.8 wt.%, and a stirring speed of 600 rpm. Scanning electron microscopy images showed that after the transesterification process, the bentonite surface was covered by absorbed materials. The Fourier transform infrared spectra confirmed the presence of various functional groups in the biodiesel, while gas chromatography-mass spectrometry analysis showed that the main component obtained in biodiesel is methyl palmitate. The properties of biodiesel showed that density, kinematic viscosity, and acid numbers met the Indonesian National Standard No. 7182:2015.

Keywords: Adsorption, Simultaneous, Transesterification, Used cooking oil.

1. Introduction

In recent times, there has been a greater awareness among researchers and policymakers of the use of biodiesel due to depleting sources of petroleum fuels, environmental concerns and the continuous growth of energy consumption. The competitive advantages of biodiesel are renewability, biodegradability, and clean burning which produce fewer greenhouse gases and toxic pollutants than petroleum [1].

The main shortcoming in biodiesel production is the high cost of raw materials. Raw materials consume 70-75% of the total cost of biodiesel production [2]. Biodiesel is mainly produced from refined oils such as palm, castor, hazelnut, and soybean, which are relatively expensive. The use of refined oil as raw materials is not economically feasible in producing biodiesel, so efforts need to be made to reduce total production costs by using cheap and low-quality raw materials. These kinds of raw materials usually contain high contents of free fatty acid and water. In order to lower the raw material cost and to give a solution for the food-fuel controversy, many researchers have investigated the use of used cooking oils, non-edible vegetable oils, and algae. These kinds of raw materials have potential for biodiesel production because they have the hydrocarbon chain characteristics of petroleum diesel but do not raise the food-fuel controversy. Some studies have reported the potency of used cooking oil as a raw material for the production of biodiesel [3, 4]. Al-Sakkari et al. [3] reported that the measured properties of biodiesel produced from used cooking oil were indicated it to be comparable to the diesel fuel. Mohamed et al. [4] also reported that the physicochemical properties of the biodiesel produced from used cooking oil were close to the commercial diesel and the ASTM standards biodiesel D6751. Used cooking oil has the potential to be further developed because of its worldwide generation and abundance in availability.

In addition to raw materials, effective and efficient use of processes is also a consideration in reducing the total production cost of biodiesel. Many researchers have attempted to use low-cost raw material for biodiesel production using various processes, such as catalytic hydroprocessing, catalytic cracking, thermal cracking, and catalytic hydrocracking [5-8]. However, some issues have not been addressed, such as miscibility limitations, heavy carbon residues during combustion, and unstable fuel properties [9].

Transesterification with homogeneous catalysts is widely applied in commercial biodiesel production [10, 11], but this reaction is susceptible to water [10]. The presence of water significantly inhibits the transesterification reaction since it competes with the reactant alcohol to hydrolyse the oil (triglycerides), leading to the formation of free fatty acids. Further, the free fatty acids react with alkaline catalysts, which then triggers saponification and emulsion formation which will decrease the yield of biodiesel and increase the acidity of the biodiesel which is produced. In general, the presence of water decreases the performance of the transesterification reaction [12]. Many studies suggested that the water content of raw materials must be lower than 0.06 wt.% for successful homogeneous base-catalysed transesterification [10, 13]. The raw material may be submitted to pre-treatments, which allow the oil to attain properties that meet specifications established for biodiesel production.

The dehydration of raw materials as a pre-treatment step has been widely used in biodiesel production. Adsorption is a technique that is often used to absorb water in the pre-treatment of raw materials for making biodiesel [14]. This causes an increase in energy consumption and raises the total cost of biodiesel production. Also, adsorption alone is not efficient because it requires an extended processing time. Khan and El Dessouky [15] stated that as raw material, the oil used should be free from moisture; thus, they recommended the use of silica gel for moisture removal. Meanwhile, Lucena et al. [16] have used a novel reaction system consisting of an esterification reactor combined with an adsorption column to pre-process raw materials. An adsorption column filled with zeolite 3A was used to remove the water produced during the esterification reaction in order to shift the reaction equilibrium towards biodiesel production. This reaction system produced a biodiesel yield of 99.7%.

Bentonite clay has been widely used in many applications, such as drilling mud, adsorbent, binder (such as iron ore pelletizer and foundry-sand bond) and as a groundwater barrier. It is mostly composed of montmorillonite. It has a large specific surface area, small particle size, and strong water adsorption capacity [17]. The catalytic activity of bentonite in the transesterification of oil into biodiesel has been studied by many investigators [1, 18, 19].

Recently, Wu et al. [13] proposed a new reaction system in which bentonite was introduced as a water adsorbent in a base-catalysed transesterification system for biodiesel production from refined soybean oil. The addition of bentonite was proven to enhance the transesterification reaction and significantly inhibit hydrolysis and saponification, the primary side reactions. They found that the yield of biodiesel was increased when a suitable amount of bentonite was added.

In a similar study, Wu et al. [20] found that the biodiesel production achieved an optimum yield of biodiesel (98.56%) at the following conditions: 7.47:1 methanol to oil molar ratio; 0.77 wt.% catalyst NaOH concentration; 57.8 °C reaction temperature; 1.76 wt.% bentonite. The simultaneous adsorption and transesterification process eliminates the requirement of two separate processes of water adsorption and transesterification, which reduces the time and cost of required processing. However, there is little report about application of the simultaneous adsorption and transesterification process for biodiesel production from low-cost raw material with high water content.

The present study is a continuation of our previous work [21], in which a further examine the potential of simultaneous water adsorption and transesterification for biodiesel production from used cooking oil with high water content was conducted. In addition, the performance of the simultaneous water adsorption and transesterification process will be compared with the conventional process.

2. Material and Methods

2.1. Reagents and materials

The samples used in this study were used cooking oil obtained from domestic dwellings around Banda Aceh, Indonesia. Natural bentonite originating from North Aceh, Indonesia, was used as the adsorbent. The technical grade of methanol was used throughout this study. NaOH of 99.9% purity was purchased from a local distributor, and other ingredients used included phenolphthalein and KOH

indicators. Meanwhile, the distilled water used in this study had a conductivity of less than 1 $\mu\text{S}/\text{cm}$.

2.2. Experimental methods

The experiment was conducted by the following steps, i.e., adsorbent preparation, used cooking oil preparation as well as biodiesel production and purification.

2.2.1. Adsorbent bentonite preparation

The bentonite was dried to remove the water content, then activated by the physical method. The process of activation was carried out using a furnace at 400°C for 6 h. After the activation process, bentonite was crushed to a size of <1 mm, weighed and dried in the oven at 76°C repeatedly until a constant weight was recorded. Following this, the dried product was cooled, triturated by mechanical milling, and sieved until it was $125\text{--}149$ μm in size. Figure 1 shows samples of the bentonite before and after physical activation. The specific surface area of bentonite after physical activation process was 16.5 m^2/g determined by Brunauer, Emmett and Teller (BET) method.



Fig. 1. Samples of the adsorbent: (a) Natural bentonite before the activation process; and (b) Bentonite after the activation process.

2.2.2. Used cooking oil preparation

Used cooking oils from a variety of sources were filtered by vacuum pump using Whatman filter paper number 41 to remove impurities, such as mud and particles. The oils were then mixed and homogenized at a temperature of 60°C . The characteristics of the used cooking oil used are shown in Table 1. Raw materials with water contents of 0.8, 1, 2, 3, and 5 wt.% were prepared by addition of distilled water to the raw used cooking oil. The conditioning of the water content of the oil was done to quantitatively investigate the effect of the water content on the process performance.

Table 1. Characteristics of used cooking oil.

Parameter	Unit	Value
Density	kg/m^3	910
Viscosity	cSt	6.9
Acid number	mg KOH/g	0.56
Water content	wt.%	0.25

2.2.3. Biodiesel production

Figure 2 illustrates the apparatus for biodiesel production. The used cooking oil was placed in a 1000 mL round bottom flask reactor equipped with a mechanical stirrer, condenser, and sampling outlet. The reactor was placed in a thermostatic water bath to maintain a constant temperature during the process. The oil was heated 45 °C. In a separate flask, an amount of the NaOH catalyst equal to 1 wt.% of the oil was dissolved in a specified amount of methanol. After the desired temperature was reached, a molar ratio of 1:6 oil to methanol was transferred to the reactor. Bentonite was also added into the reactor so that the transesterification reaction and adsorption processes could take place simultaneously. The process was carried out at 60 °C for 90 minutes of processing time. After the reaction had proceeded for the desired processing time, the reaction mixture was immediately cooled to room temperature. Once cooled, the reaction mixture was filtered to separate the solid residue of adsorbent from the liquid using a filter paper. To recover any product that had adhered to the adsorbent, the solid residue was washed repeatedly with methanol. The liquid product was poured into a separating funnel and left overnight until two layers were formed. The bottom layer contained the glycerol phase, while the upper layer contained the ester phase. The upper layer was washed several times with warm water (40-50 °C) for removing the excess methanol and catalyst in biodiesel product. Finally, the biodiesel produced was weighed and stored for further analysis.

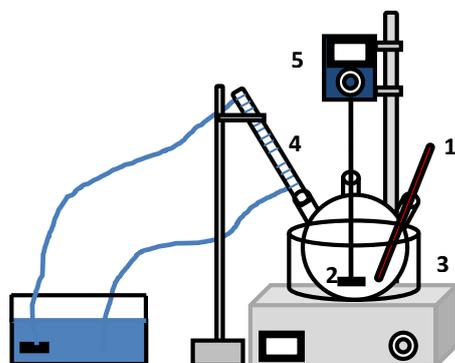


Fig. 2. Schematic apparatus for biodiesel production:

(1) Thermometer; (2) Reaction mixture (used cooking oil, methanol, catalyst and bentonite); (3) Water bath; (4) Condenser; (5) Agitation motor.

In the first set of experiments, the effect of the initial water content of used cooking oil (0.8, 1 and 2 wt.%) and amount of bentonite added (0, 2, 3 and 4 wt.%) on the yield of biodiesel was investigated with a constant stirring speed of 600 rpm. In the second set of experiments, the effect of the water content of used cooking oil (0.8, 1 and 2 wt.%) and the stirring speed (200, 400, 600 and 700 rpm) on the yield of biodiesel was investigated with a constant amount of bentonite added (based on the highest biodiesel yield of the first experiments). Then, based on the first and second sets of experiments, the best condition for simultaneous adsorption and transesterification was obtained. This best process condition was used in the subsequent experimental studies, i.e., comparison with conventional process and product analysis.

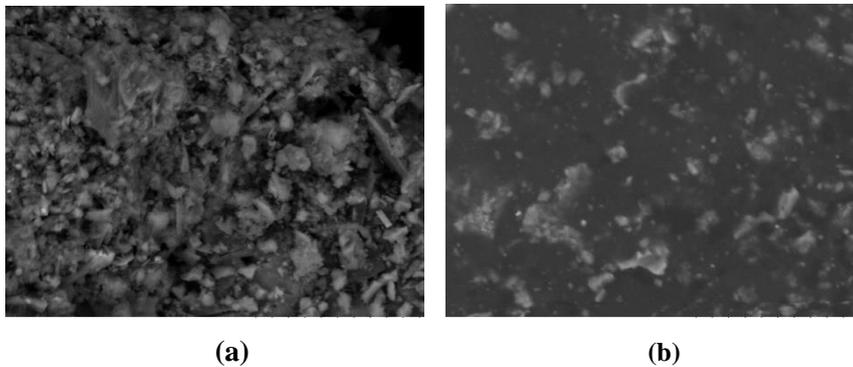
The biodiesel production using a conventional process without adsorbent with a stirring speed of 600 rpm was carried out for comparison. The process was

conducted in a similar operating condition with the simultaneous adsorption and transesterification process.

2.3. Analytical methods

2.3.1. Scanning electron microscope (SEM) analysis of bentonite

The morphological structure of the bentonite was provided by a scanning electron microscope (SEM) TM 3000 (Hitachi, Japan) at an accelerating voltage of 15 kV 1 phase, 50/60 Hz. SEM analysis was utilized to observe and evaluate the morphological surface of the bentonite before and after the process of transesterification to confirm the role of bentonite as the adsorbent in the process. As presented in Fig. 3(a), before transesterification, the surface of bentonite exhibited porous properties with some chasms, indicating a high specific surface area. The bentonite had a narrow range of pore sizes. However, significant disparities in the structure of the bentonite surface after the transesterification process were observed. After the transesterification process, the bentonite surface was covered by some materials, which were assumed to be water and other adsorbed materials Fig. 3(b) [13]. Besides having a good water adsorption capacity, bentonite also had a good adsorption capacity for soap, glycerine, and methanol [20].



**Fig. 3. SEM images of the bentonite (2500×):
(a) Before transesterification and (b) After transesterification.**

2.3.2. Product analysis

The results were presented in terms of biodiesel yield determined by Eq. (1). The water content of the used cooking oil was determined using the Karl Fischer method. The acid-base titration method was utilized to determine the acid number of the used cooking oil and the biodiesel product. The density and viscosity of the biodiesel were measured according to the Indonesian National Standard No. 7182:2015.

$$\text{Biodiesel yield} = \frac{\text{Weight of biodiesel}}{\text{Weight of used cooking oil}} \times 100\% \quad (1)$$

Following this, an analysis of the main functional groups was conducted using Fourier Transform Infrared (FTIR) Spectroscopy on a Shimadzu IR-Prestige 21 spectrometer. The spectra collected in the range of wavenumber from 4000–400

cm^{-1} at a resolution of 2 cm^{-1} . The fatty acid components of the biodiesel were determined by gas chromatography-mass spectrometry (GC-MS) (Model QP 2010 Plus; Shimadzu, Japan), with a capillary column Rtx-5MS column (30 m, 0.25 mm, $0.25 \mu\text{m}$). Helium was used as a carrier gas. The components of the product were determined by matching mass spectra to those from the library database (Wiley and National Institute of Standards and Technology libraries).

Duplicate measurements were conducted for all the variables of operation studied, and the average values for the measured data were taken into detailed consideration. The data deviation was found to be less than 5% of the mean value for the entire experiments, which displayed a satisfactory reproducibility of data.

3. Results and Discussions

3.1. Effect of process parameters

The effect of the amount of bentonite added on biodiesel yield with variation in water content is presented in Fig. 4. It can be seen that the water content and amount of bentonite have a significant influence on biodiesel yield. Increasing the water content decreased the yield of biodiesel. During the transesterification process, excess water is known to inhibit the transesterification reaction because the water will hydrolyse triglycerides, which triggers a saponification reaction [22]. As a result, the efficiency of the catalyst was decreased so that the yield of biodiesel obtained has decreased.

In the absence of bentonite, the biodiesel yield produced was between 89.5-91.7%. As expected, the presence of bentonite led to a higher biodiesel yield, as increasing the added bentonite to 3 wt.% produced an increase of 5.1-5.8% of biodiesel yield. These results are similar to the results previously reported by Wu et al. [13] over the same range of bentonite addition. This improvement in yield occurs because bentonite can quickly absorb both water contained in raw materials and water produced from the reaction between free fatty acids and NaOH. The introduction of bentonite inhibits the side reaction of saponification and increases the activity of the NaOH catalyst such that the reaction proceeds in the right direction, which ultimately increases the biodiesel yield [13, 20]. The water tolerance of the transesterification reaction system increased when a suitable amount of bentonite was added. This could explain why the yield of biodiesel increased with the increase of the amount of bentonite added in the range of 0 to 3 wt.%.

Further increasing the amount of bentonite added from 3 to 4% significantly decreased the yield of biodiesel because the excess bentonite interfered with the reaction via methanol absorption. This excessive amount of bentonite also complicated the separation at the end of the process as a result of the formation of gelatinous substances when soap and glycerol were absorbed by bentonite [13]. The excess bentonite also had adverse effects on the reaction due to the adsorption of methanol, reducing the molar ratio of oil to methanol. On the other hand, the content of soap in the alcohol and oil phase could be reduced with the presence of bentonite, which is useful for the refining of the biodiesel products. Also, the adsorption of glycerine was advantageous to make the transesterification reaction go in the right direction. However, the absorbance of glycerine was small and had little effect on the equilibrium of the reaction [20]. As reported by Wu et al. [13], this effect was proven by the difference of biodiesel loss between the amount of refined and crude biodiesel

during the refining stage. It is also possible that the bentonite still contained a small amount of biodiesel in the gelatinous substance [20].

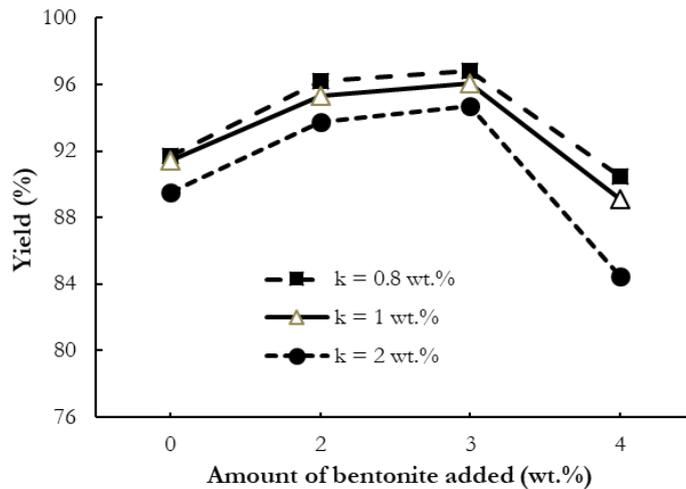


Fig. 4. The effect of the amount of bentonite added on biodiesel yield with variation in water content (k) at a stirring speed of 600 rpm.

Since the highest yield of biodiesel was obtained with 3 wt.% bentonite added, this condition was used in subsequent experimental studies. To determine the effect of stirring speed effect on the yield of biodiesel, the stirring speed was varied between 200 and 700 rpm. Due to their immiscibility, the reactants of oil and methanol formed a two-phase liquid system in the initial stage of the process. Stirring should produce a more homogeneous mixture, leading to a faster reaction rate, and the formation of the biodiesel products will also improve the solubility of reactants. As can be seen in Fig. 5, the increase of stirring speed also caused an increase of biodiesel yield in the range of 200 to 600 rpm. This could have occurred due to the formation of a more homogeneous reaction to improve the collisions between the molecules of reactants as the stirring speed increased. However, at a stirring speed of 700 rpm, the biodiesel yield decreased significantly. Al-Sakkari et al. [3] and Ajala et al. [23] previously reported that an increase in turbulence within the reaction medium at high agitation speeds has the high potential to produce a saponification reaction, which would then reduce the number of desired products. Abukhadra et al. [19] also reported that further increase in the stirring speed above 900 rpm will decrease biodiesel yield. This result might be related to the role of the high stirring speed in increasing the turbidity between the reactants which reduces the homogenous mixing between reaction mixture and reduces the transesterification efficiency. Thus, a proper stirring speed must be determined to achieve an efficient process with good performance.

In the range of experimental conditions studied, the best conditions for the formation of biodiesel were: 3 wt.% bentonite, 0.8 wt.% water content and a stirring speed of 600 rpm. The yield of biodiesel obtained under these conditions was 96.8%. The biodiesel produced at the best conditions was used in subsequent experimental and analysis studies.

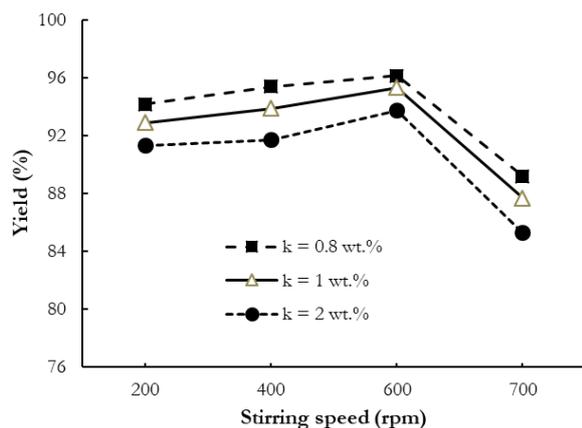


Fig. 5. The effect of stirring speed on biodiesel yield with variation in water content (k) at 3 wt.% bentonite added.

The comparison of the biodiesel yield of the simultaneous process of adsorption and transesterification and the conventional process at different initial water contents (0.8, 1, 2, 3, and 5 wt.%) is presented in Fig. 6. The process comparison was conducted at the best condition of the simultaneous process of adsorption and transesterification, whereas the conventional process was conducted without bentonite addition. It can be seen that the biodiesel yields of the simultaneous process of adsorption and transesterification were higher than the conventional process in the range of the water content of used cooking oil studied. The biodiesel yield of the simultaneous process of adsorption and transesterification was 2.7 to 7.2 times higher than the conventional process. Further, this indicates that the reaction system is less water-tolerant. As presented in Fig. 6, the yield of biodiesel decreased with an increase in water content of used cooking oil. The presence of water promotes a saponification reaction to produce soap. An excess of the catalyst used also caused a similar result [24]. In addition, water competes with the methanol, thereby leading to the formation of free fatty acids and promotion of the ester hydrolysis reaction [25]. The same trend was also observed by Wu et al. [20] for biodiesel production from refined soybean oil.

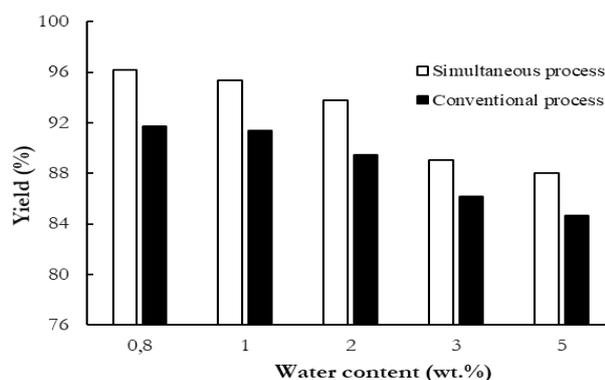


Fig. 6. Comparison of biodiesel yields of simultaneous adsorption and transesterification versus the conventional process.

3.2. Properties of biodiesel

The appearance of the biodiesel produced was a clear yellow liquid. The identification of the biodiesel functional groups was carried out using FTIR. The FTIR spectrum is displayed in Fig. 7, and the results of identification of the functional groups can be seen in Table 2. The formation of ester compounds can be identified from changes in wavenumbers in the common absorption areas of the C-O and C=O groups. A slight shift of wavenumbers to lower wavenumbers shows the occurrence of changes in compounds in the material [26]. Figure 7 shows the absorbance peak at 1438.90 cm^{-1} , which is a typical absorption area of the methyl ester group. The shift of absorption area C=O from wavenumber 1743.65 cm^{-1} to 1741.72 cm^{-1} shows the conversion of oil (triglycerides) to methyl ester (biodiesel). This is reinforced by a shift in the CO ester absorption peak from the 1159.22 cm^{-1} to 1195.87 and 1168.86 cm^{-1} . A similar result was previously reported by Mohamed et al. [4] and Elkady et al. [27].

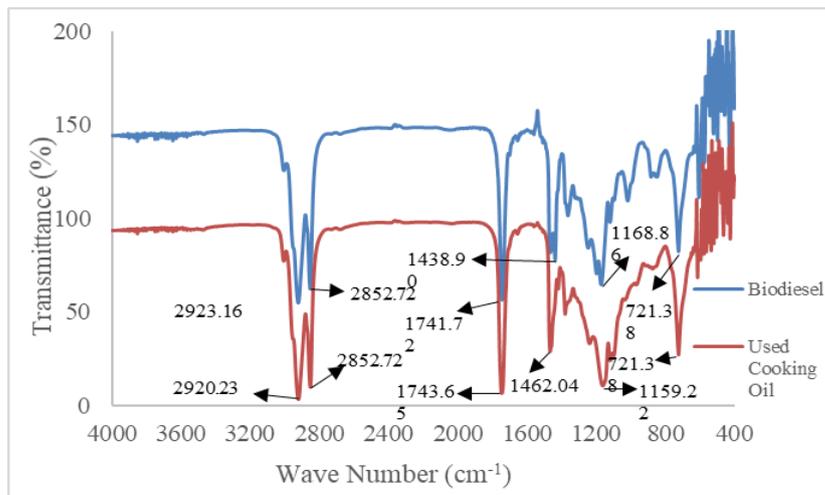


Fig. 7. FTIR Spectra of used cooking oil and biodiesel product.

Table 2. Functional group identification.

Functional groups	Wavenumber (cm^{-1})	
	Used cooking oil	Biodiesel
-CH ₂ rocking	721.38	721.38
Bending vibrations of CH ₂ group	1375.25	1359.82
C=O ester stretch	1743.65	1741.72
Split C-O stretching	-	1195.87
Split C-O stretching	1159.22	1168.86
-O-CH ₂ -C	1114.86	1116.78
Methyl ester group (CO-O-CH ₃)	1462.04	1438.90
-CH ₂ stretching	2920.23	2922.16

A summary of the GC-MS results of the biodiesel samples is presented in Table 3. The main component obtained is methyl palmitate, where palmitic acid is the dominant fatty acid in palm oil. Methyl palmitate is known to be the component of biodiesel that provides the highest cetane response [28]. The fatty acid composition of the biodiesel is very similar to the composition of palm oil [29].

Table 4 presents the properties of the biodiesel. The specified properties of biodiesel produced using both simultaneous and conventional process meet the criteria for biodiesel according to the Indonesian National Standards No. 7182:2015.

Table 3. Biodiesel composition.

Compound	Composition (%)
Methyl Myristate (C14:0)	1.46
Methyl Palmitate (C16:0)	60.47
Methyl Stearate (C18:0)	4.75
Methyl Oleate (C18:1)	27.57
Methyl Linoleate (C18:2)	4.56

Table 4. Properties of biodiesel.

Property	Simultaneous Process	Conventional Process	SNI 7182:2015
Density, 15 °C (kg/m ³)	864	879	850-890
Kinematic viscosity, 40 °C (cSt)	3.5	5.7	2.3-6
Acid number (mg KOH/g)	0.25	0.38	≤0.5
Ester content (%-mass)	97.9	97	≥96.5

4. Conclusions

Our results show that the use of simultaneous water adsorption and transesterification has benefits superior to the conventional process for production of biodiesel from used cooking oil with high water content. The biodiesel yields obtained by the simultaneous process were approximately 2.7 to 7.2 times higher than those obtained by the conventional process. The highest yield of biodiesel from the simultaneous water adsorption and transesterification process was 96.8%. It was obtained at 3 wt.% bentonite added, 0.8 wt.% water content, and a stirring speed of 600 rpm. SEM images showed that the surface of the bentonite before and after the process of transesterification differed. It was observed that the bentonite surface was covered by absorbed materials after the transesterification process. FTIR result confirmed the presence of various functional groups in biodiesel. Meanwhile, GC-MS results showed that biodiesel was formed in the reaction product. The main component obtained in biodiesel is methyl palmitate. The present results proved the ability of the simultaneous process of adsorption and transesterification to produce biodiesel from used cooking oil which complies with Indonesian National Standards No. 7182:2015 for density, kinematic viscosity, and acid number.

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