

Purification of Crude Glycerol from Acidification Using Tea Waste

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Abstract. Biodiesel production generates crude glycerol with low purity as a byproduct. It must be purified to increase the economic value of glycerol. Purification can be performed using adsorbent from tea waste. This study aimed to examine the optimum condition of adsorption process, characterize the biosorbent from tea waste and determine the quality of purified glycerol. Crude glycerol was produced by transesterification reaction of used cooking oil with methanol using KOH as a catalyst. The reaction temperature was 60°C which was maintained for 60 minutes. Crude glycerol was separated from biodiesel and added with H₃PO₄ 85% until the pH reached ± 2.5 . Glycerol level after acidification was 77%. After that, adsorption was performed using tea waste which was previously activated by 0.05 M NaOH. Adsorption process was conducted by varying contact time (30, 60, 75, 90 and 120 minutes), adsorption temperature (30, 45, 60 and 75°C), biosorbent concentration (6, 9, 12, 15 and 18 %) and biosorbent particle size (180, 250 and 630 μ m). The highest glycerol level (95.9544%) was achieved by setting the contact time for 90 minutes, adsorption temperature at 60°C, biosorbent concentration at 12% and particle size at 180 μ m. The glycerol obtained from this process meets the quality requirements set by SNI 06-1564-1995 with water content 3%, ash content 0.3% and MONG level 0.7%. In addition, the purified glycerol had density 1.26 g/mL, potassium metal content 107 ppm and had no sugar. There were alterations in functional group and surface morphology of tea waste after the adsorption took place.

Keywords: adsorption, activation, tea waste, biosorbent, crude glycerol.

1. INTRODUCTION

Transesterification reaction of used cooking oil produces glycerol and biodiesel. Every 10 kg of biodiesel produces about 1 kg of glycerol [1]. The yielded glycerol is impure and usually called crude glycerol. This type of glycerol contains 10-30% methanol, 8-20% catalyst, 5-15% soap and $\leq 5\%$ water [2], which makes its purity very low. The quality of this glycerol does not meet the market standard, therefore it needs to be purified.

Impurities like catalyst can be converted to inorganic salts, by adding sulfuric acid into crude glycerol. The addition of this acid is also able to convert the soap content in crude glycerol into insoluble free fatty acids [2]. However, the addition of acid does not remove all impurities. Methanol, ester, oil and water are still present in the crude glycerol. Therefore, it needs further purification step using adsorbent.

Previous study on crude glycerol was conducted by Aziz [3] using acidification by sulfuric acid (H₂SO₄) and adsorption using Lampung natural zeolite. The process generated 88.91% glycerol. In this research, tea waste was used as biosorbent. The tea waste contains 37% cellulose with a hydroxyl functional group which may interact with the adsorbate, hence it can be used as a biosorbent. Furthermore, biosorbent from the tea waste has several advantages of being low cost, high availability, easy to prepare, high efficiency in a dilute solution and easy to regenerate [4]. This research aimed to



obtain the optimum condition of adsorption process and characterize the biosorbent from tea waste using FTIR and SEM. The quality of glycerol after adsorption process was also measured.

2. METHODOLOGY

2.1. Materials

Materials used in this research were used cooking oil from one restaurant in Ciputat-South Tangerang, the tea waste from Poci tea bag, KOH, methanol, aquades, NaOH, NH_4Cl , bromothymol biru, NaIO_4 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$, $\text{C}_2\text{H}_6\text{O}_2$, HCl, and H_3PO_4 . Equipment used were pycnometer, oven, vacuum pump, Scanning Electron Microscope (SEM) Hitachi Su3500, Fourier Transform Infrared Spectrometer (FTIR) Shimadzu IR Pretige 21, UV-VIS spectrophotometer and atomic absorption spectrophotometer (AAS) Shimadzu AA-6800.

2.1.1. Production of Crude Glycerol [5]

Approximately 1.8 gram potassium hydroxide (KOH) was dissolved in 50 mL metanol. Meanwhile, 200 mL used cooking oil was heated until the temperature reached 60°C . Then, the oil was combined with the freshly prepared sodium methoxide solution and gently mixed with magnetic stirrer on a hot plate. Stirring rate was set at 700 rpm. Then the mixture was allowed to stand for 60 minutes, while making the temperature of the solution constant at 60°C . The product was inserted into a separating funnel and allowed to stand for 24 hours until the separation process completed. The upper phase was biodiesel and the lower phase was crude glycerol.

2.1.2. Acidification of Crude Glycerol [6]

Crude glycerol as acidified by 85% H_3PO_4 until the pH reached ± 2.5 . The solution was kept for ± 12 jam to allow the formation of three separate layers. The top layer consisted of free fatty acids, middle layer was glycerol solution, and the bottom layer was composed of inorganic salts. Glycerol solution was separated from the other phases through filtration.

2.1.3. Biosorbent Activation [7]

Powdered tea waste was activated with 0.05 M sodium hydroxide (NaOH) with ratio 1:1000 (100 gram tea waste:1000 mL NaOH) for 4 hours. It was then washed with aquades until reached neutral pH and dried in oven at 60°C for 24 hours. Upon drying, the biosorbent was sieved to a particle size fraction of $630\text{ }\mu\text{m}$. The functional group and surface morphology of activated biosorbent were characterized using FTIR and SEM, subsequently.

2.1.4. The Adsorption Process of Impurities in Crude Glycerol [3]

Approximately 10 gram crude glycerol was weighed and added by 1,2 gram biosorbent from tea waste (12% total weight of crude glycerol). The mixture was stirred at 60°C using varying contact time (30, 45, 60, 75, 90 and 120 minutes), then kept for 24 hours. The filtrate was then filtered to measure glycerol content. After the optimum contact time achieved, other parameters including adsorption temperature, biosorbent concentration, and biosorbent particle size were analyzed to get optimum condition of the adsorption process by varying them as follow: adsorption time (30, 45, 60 and 75°C); biosorbent concentration (3%, 6%, 9%, 12% and 15% total weight of crude glycerol) and biosorbent particle size (180, 250 and $630\text{ }\mu\text{m}$). The light absorbance of the crude and purified glycerol samples were examined using UV-Vis spectrophotometer. The glycerol content, density, water content, ash content, MONG content, sugar content and potassium metal content of purified samples were measured.

3. RESULTS AND DISCUSSION

3.1. Determination of Optimum Operation Parameters for the Adsorption of Crude Glycerol

Effect of Contact Time

The glycerol content in purified glycerol after adsorption process during certain contact times was showed in Figure 1. It can be seen from Figure 1 that the highest glycerol content (93.5%) was produced at 90-minute contact time. This might be because the interaction impurities and between hydroxyl group on cellulose reached equilibrium after 90 minutes. After 120-minute contact time the glycerol content decreased until 85.8%, which was probably attributed to saturated capacity of biosorbent in capturing impurities. In that case, it would lead to the desorption process (the release of adsorbate from biosorbent). Hal ini disebabkan karena gugus fungsi dari biosorben telah jenuh untuk berinteraksi dengan senyawa pengotor, semakin lama waktu kemungkinan akan terjadi proses desorpsi atau pelepasan kembali antara biosorben dan adsorbat.

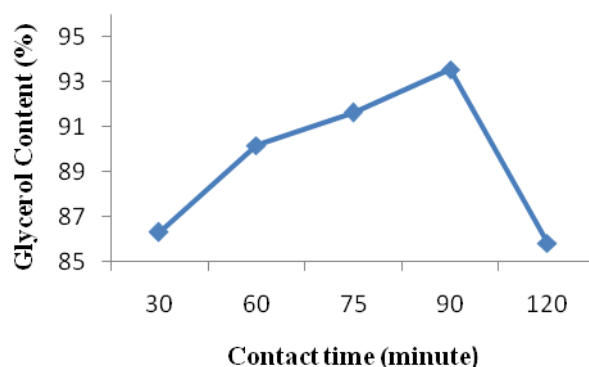


Fig. 1 The effect of contact time on glycerol content

3.2. Effect of Adsorption Temperature

Increasing the reaction temperature from 30°C to 60°C led to an increase in the glycerol yield from 89.7% to 93.5% (Figure 2). The increase in adsorption temperature might increase kinetic energy of impurities in glycerol solution, which allows them to diffuse faster into the biosorbent's pores. A subsequent decreased yield was seen when the temperature reached 75°C. At this point, the rise of temperature might intensify the desorption process. It means the number of adsorbate were released from the pores of biosorbent as the temperature rose [8].

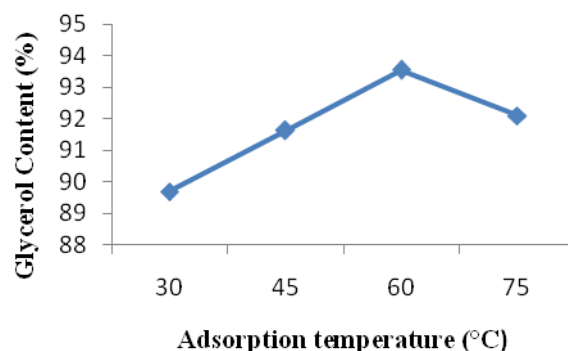


Fig. 2 The effect of adsorption temperature on glycerol content

3.3. Effect of Biosorbent Concentration

Figure 3 showed that glycerol content gradually increased when the biosorbent concentration increased until it reached 12% total weight of crude glycerol. Hidayat [9] suggested that the higher biosorbent concentration, the more adsorbate and biosorbent involved in adsorption process. This might be due to multilayer adsorption of adsorbate on hydroxyl-rich surfaces of cellulose, which could facilitate the adsorption of more impurities. However, the glycerol content decreased when the concentration was higher than 12%. This is probably attributable to the saturation of active groups of the biosorbent, which in turn reduce the number of adsorbed molecules [10]. It showed us that the optimum biosorbent concentration for the adsorption process was 12% of total weight of crude glycerol, which gave us the highest content of glycerol (93.5%).

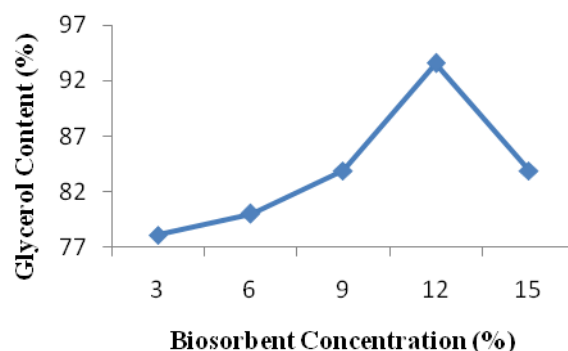


Fig. 3 The effect of biosorbent concentration on glycerol content

3.4. Effect of The Particle Size of Biosorbent

Figure 4 showed that the highest glycerol content was attained when the particle size of biosorbent was 180 μm . The smaller the particle size, the wider the surface area and the better the adsorption force [11].

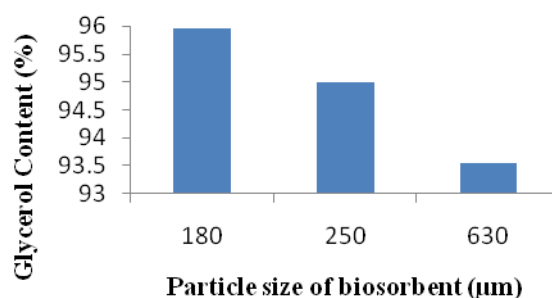


Fig. 4 The effect of the particle size of biosorbent on the adsorption process

3.5. Properties of Glycerol After Adsorption

Table 1 showed the quality of crude glycerol before acidification, after acidification and after adsorption process.

Table1. Properties of crude glycerol on the given conditions

Analysis type	Before acidification	After acidification	After adsorption	National Standard SNI 06-1564-1995 [13]
Glycerol content (%)	67.0	77.0	96.0	Min. 80
Water content (%)	16.2	12.2	3.0	Max. 10
Ash content (%)	11.6	7.9	0.3	Max. 10
MONG content (%)	5.2	2.9	0.7	Max. 2.5
Sugar content	-	-	-	-
Density (g/mL)	1.0	1.2	1.26	1.261[12]
Potassium logam content (ppm)	1204	139	107	Not required

As shown in Table 1, the quality of glycerol after adsorption using tea waste as a biosorbent has been improved and met the quality requirement of crude glycerol based on Indonesian national standard (SNI) 06-1564-1995. The highest glycerol content (96%) was obtained under optimum condition. It demonstrated that the biosorbent from tea waste was effective in reducing impurities in crude glycerol such as free fatty acid, biodiesel, catalyst, water and methanol.

3.6. FTIR Spectra of Tea Waste

FTIR spectral analysis in the frequency range of 400-4000 cm^{-1} was conducted to examine functional groups in the tea waste before activation, after activation and after adsorption. The transmittance spectra of three samples were showed in Figure 5

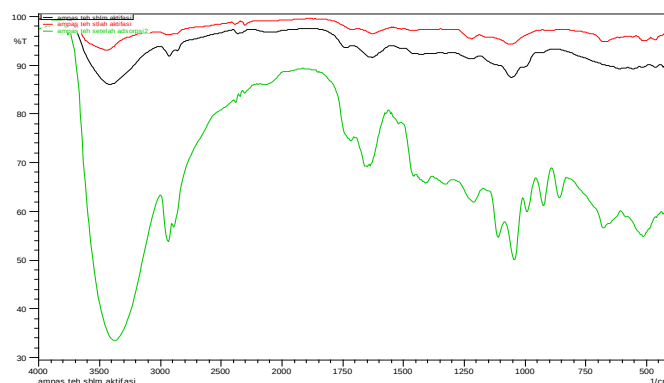


Fig. 5 .Spectra of tea waste sample before activation (black line), afteractivation (red line) andafteradsorption (green).

Table2. The interpretation of FTIR spectraof tea waste samples

Before Activation		After Activatiob		After Adsorption	
Wave number (cm ⁻¹)	Funci onal Group	Wavenu mber (cm ⁻¹)	Funci onal Group	Wavenu mber (cm ⁻¹)	Functional Group
3406.29	hydro xyl (-OH)	3437.15	hydro xyl (-OH)	3375.43	O-H hydroxyl
2922.16	alkyl (C-H)	2862.36	alkyl (C-H)	2931.80	C-H alkane
1735.93	carbon yl (C=O)	1463.97	aryl (C-C)	1406.10	(C-O) (C-O-H bending) from ether
1498.69	aryl (C-C)	1219.01 - 1058.92	ether (C-O)	1320-1210	carbonyl (C=O) from carboxylic acid
1220.94-1055.06	ether (C-O)	600-500	Silica (SiO ₂)	750-650	Hydroxyl-bound vibration (O-H bend)
600-500	Silica (SiO ₂)			900-690	C-H bending

It can be seen from Table 2 that there was a significant alteration on functional groups before and after adsorption. The peak area of the tea waste after adsorption (3375.43 cm⁻¹) became weak and wide which could be attributable to the binding of impurities to hydroxyl groups on the biosorbent surface. Furthermore, the peaks at the fingerprint area of 970-1250 cm⁻¹ showed the vibrations of hydrogen-bonded OH groups indicating the presence of impurities such as free fatty acid and water. The peaks at 1406.10 cm⁻¹ showed ether group (C-O) (C-O-H bending) from ester exhibiting the presence of methyl ester (biodiesel). The peaks at 1320-1210 cm⁻¹ could be assigned to carbonyl (C=O) of carboxylic acid (RCOOH) indicating the presence of free fatty acid. The peak at 750-650 cm⁻¹ showed the hydroxyl-bound vibration (O-H bend) and the peak at 900-690 cm⁻¹ was due to C-H bending suggesting the presence of methanol.

3.7. SEM Analysis

The pore size and surface morphology of tea waste were analyzed by SEM before and after adsorption. Figure 6 showed the micrograph of tea waste at 500x magnification

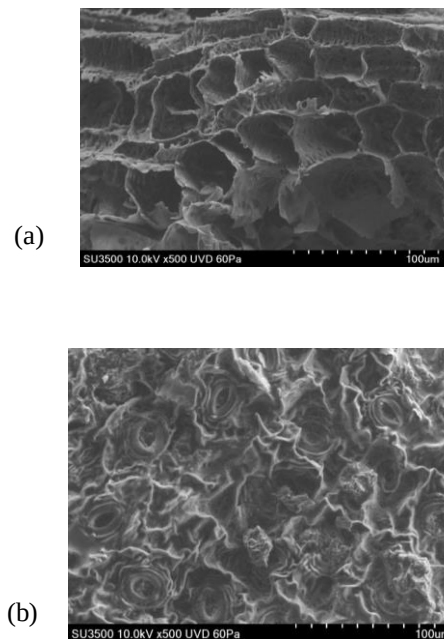


Fig. 6. Surface morphology of tea waste with 500x magnification:
Before adsorption (a) after adsorption (b)

Before adsorption, the tea waste had many pores with open cavity and homogenous. After adsorption, the surface morphology became rougher and the pores became tighter indicating the adsorption of impurities to the tea waste biosorbent. This is in line with the theory stating that there will be a binding in the adsorption of free fatty acid if the compounds were detained at active site or stuck in the pores due to activation process.

4. Conclusion

1. The optimum conditions for the adsorption process using tea waste were as follows: contact time of 90 minutes, temperature 60°C, biosorbent concentration 12% and biosorbent particle size 180 µm, which generated 96% glycerol content.
2. The quality of glycerol after adsorption process on optimum conditions met the quality requirement of SNI 06-1564-1995 with glycerol 96%; water content 3%; content abu 0,3%; content MONG 0,7%. Further more, the density of glycerol after adsorption was 1.26 g/ml, potassium metal content 107 ppm, and has no sugar
3. The functional groups and morphological feature of the biosorbent from tea waste changed after adsorption process.

5. ACKNOWLEDGMENT

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