

Effect of Mesh Size Variations on Glycerin Adsorption by Silica from Rice Husk Ash in Biodiesel Purification

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Abstract. Biodiesel synthesized via transesterification of vegetable oils is traditionally purified by water washing process. This research aims to reduce wastewater produced from purification of biodiesel by using silica from rice husk ash (RHA), particularly focused on the effect of mesh size of extracted silica on glycerin adsorption. The structure and composition of the RHA were studied. The specific surface area and pore diameter of RHA (60-80, 80-100, 100-120, and 120-200 mesh) were found in the range of 38-47 m²/g and 15-30 nm, respectively. Maximum sorption was achieved at room temperature with 5 % (w/w) of 80-100 mesh size of RHA adsorbent and contact time for 20 minutes. The optimal pore diameter for glycerine adsorption is 15.55 nm. Adsorption isotherm of RHA was fit to Langmuir isotherm.

Keywords: Biodiesel purification, Rice husk ash (RHA), Mesh size.

1. Introduction

Biodiesel is clean burning energy, derived from vegetable oils or animal fats. Biodiesel is alternative energy as same as conventional or fossil diesel. The advantage of Biodiesel over fossil fuel is simple to use, biodegradable, non-toxic, carbon neutral and free of sulphur and aromatic [1]. Biodiesel can be synthesized by using transesterification/ esterification reaction. After the completion of reaction, crude biodiesel must be purified to confirm in EN and ASTM standards. The conventional purification of biodiesel is water-washing. However, the water-washing process has several disadvantages for example yields loss in effluent; high soap levels that cause emulsification and high cost of treatment. In addition, water-washing process normally use large amount of water which will generate wastewater that cause environmental problem. To solve these problems, the research to date has tended to focus on using various adsorbents such as CaO, MgO, Mg₂CO₃, magnesium silicate, activated charcoal and bentonite to purify biodiesel instead of water washing process. Thailand is agricultural country which produces a large amount of rice husk. The beneficiation of rice husk has been used in many applications. Burning rice husk as fuel to generate energy resulted in the waste product, rice husk ash (RHA). RHA is contain a large amount of silica (60%) [2,3].

In this study, silica from rice husk ash, an alternative low cost sorbent obtained from the middle region in Thailand, will be used. Furthermore, the effect of mesh size on glycerine adsorption of RHA adsorbent will be studied. The characteristic of RHA was also studied by using XRD, BET, and FTIR.

2. Materials and Methods

2.1. Adsorption Preparation

Rice husk ash from rice mill (in middle region of Thailand) was burnt at 700°C for 6 h. In 250 ml flask,

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Ten grams of RHA samples and 80 ml of 2.5 N NaOH solution were added. Then, the mixture was refluxed with stirring for 3 h. After that, the mixture was filtered and the residual was washed with 20 ml boiling water. The filtrate was allowed to cool down to room temperature. The pH of the filtrate was adjusted to pH 2 by 5N H₂SO₄ solution and adjusted back to pH 8.5 by 30% NH₄OH. The mixture was allowed to stand for 3.5 h. The precipitated was then dried at 120°C for 12 h. Silica from rice husk ash was then ground, screened through 60-80, 80-100, 100-120 and 120-200 mesh sieves and then stored in tightly capped glass bottle for future use [3].

2.2. Biodiesel Production via Base-Catalyzed

400 g of palm oil was added into 1000 mL of round bottom flask equipped with condenser. The solution of sodium hydroxide (4.0g) in methanol (115.85 mL) was slowly added into the reaction and then the mixture was heated to 65°C for 1 h. The reaction mixture was transferred to a separatory funnel, and allowed glycerine to separate. The methyl ester layer was brought to purification process.

2.3. Biodiesel Purification

- Effect of contact time on glycerine adsorption

In a 150 mL of glass bottle, 30 g of crude biodiesel was treated with 3% (w/w) of 80-100 mesh size of RHA adsorbent and various contact times: 10, 20, and 30 minutes at room temperature, with stirring at 150 rpm. Then the RHA adsorbent was removed by filtration. The glycerine content was determined by titration method.

- Effect of amount and mesh size on glycerine adsorption

In a 150 mL of glass bottle, 30 g of crude biodiesel was treated with five amounts of difference mesh size (60-80, 80-100, 100-120, and 120-200 mesh) of RHA adsorbents: 1, 3, 5, 7, and 10 % (w/w) at room temperature, with stirring at 150 rpm and contact time for 20 minutes. Then the RHA adsorbent was removed by filtration. Samples were analysed using titration method and GC method.

2.4. Adsorption Isotherm

The adsorption isotherm was studied to evaluate the adsorption capacity of RHA adsorbent for glycerine removal from biodiesel production. In a 50 mL of glass bottle, 10 g of crude biodiesel was added in to varied concentration of adsorbents (1-10 % (w/w)) with stirring rate at 150 rpm at room temperature and contact time for 20 minutes. The RHA adsorbent was removed by filtration and the glycerine content were analysed by using titration method.

2.5. Characterization of Silica from Rice Husk Ash

- Surface area measurement: Specific surface area and pore size distribution of silica were measured by nitrogen adsorption-desorption isotherm using BET method.
- Phase analysis by X-ray diffraction: X-ray diffraction was used to determine the phase of silica. The scanning rate was 20 min in the 2 θ diffraction angle between 20 $^{\circ}$ and 80 $^{\circ}$
- Functional groups analysis by Fourier Transform Infrared (FTIR): the analysis was performed using FTIR Spectrometer (model attenuated reflectance) in the range of 4000-400 cm⁻¹ with resolution of 4 cm⁻¹ and 100 scans.

2.6. Characterization of Biodiesel

Titration method with hydrochloric acid solution is used to determine the amount of glycerine and unreacted catalyst. Acid number was determined by EN The ester content was determined according to method EN 14103 and free and total glycerine by method EN 14105. Those analytical methods were performed in Gas chromatography GC-FID (Varian).

3. Results and Discussion

3.1. Characterization of RHA

Fig 1 shows the N₂ adsorption-desorption curves of RHA. The RHA shows predominantly adsorption in high P/P₀ value, above 0.7, indicating mainly the presence of large mesopores [4]. The surface area and pore diameter were shown in table 1.

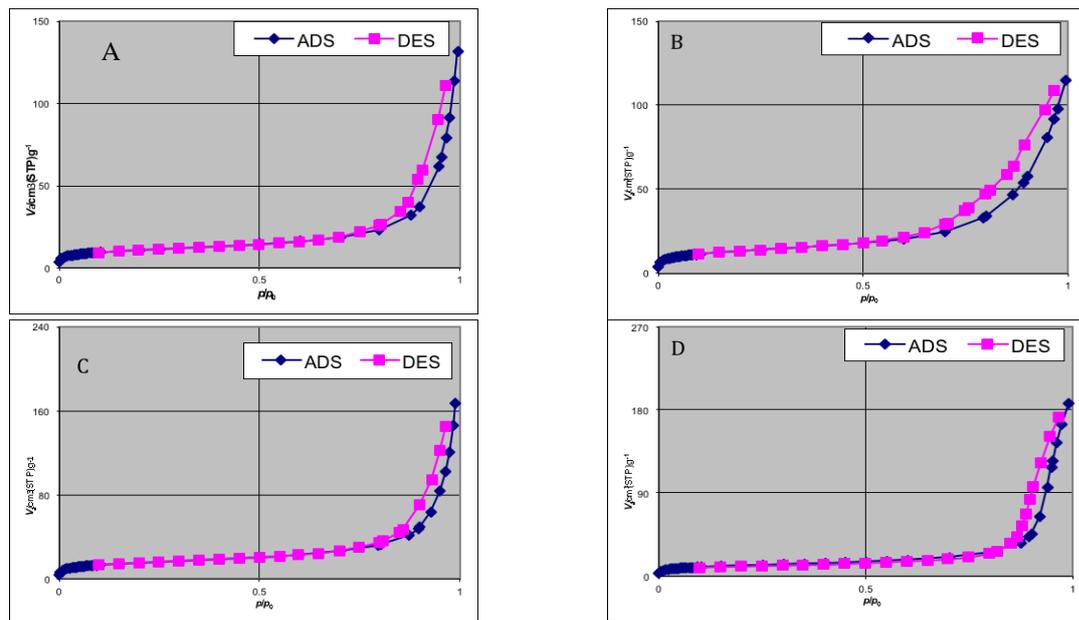


Fig. 1: Adsorption-desorption isotherm of various mesh size of RHA adsorbents: (A) 60-80; (B) 80-100; (C) 100-120; (D) 120-200

Table 1: BET analysis for difference mesh size of RHA adsorbents

Mesh Size (mesh)	60-80	80-100	100-120	120-200
Surface area (m ² g ⁻¹)	38.90	43.82	39.23	47.70
Pore diameter (nm)	19.69	15.55	29.45	28.1

XRD pattern of RHA (Fig. 2) shows sharp phases. These sharp peaks suggested characteristic of crystallization.

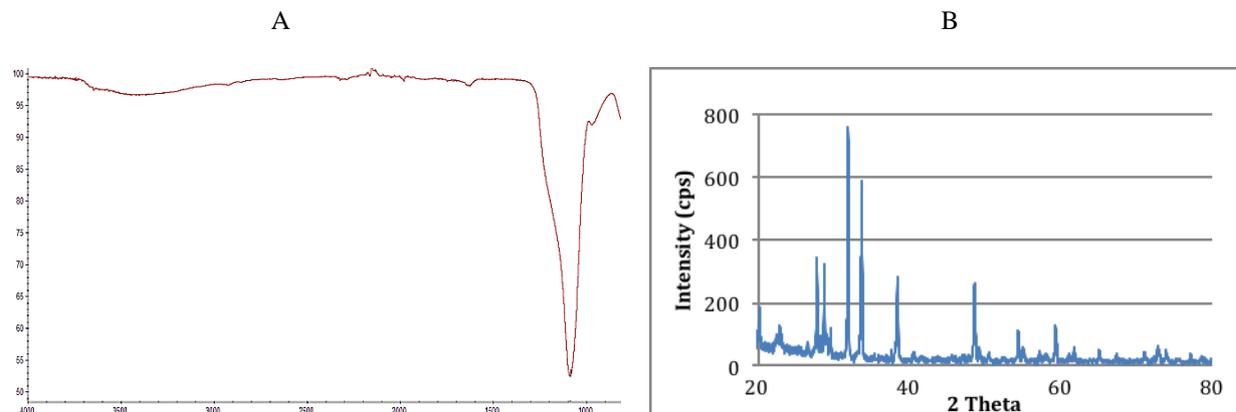


Fig. 2: (A) FTIR spectra of silica produced from RHA; (B) XRD pattern of extracted silica from RHA.

The infrared spectrum of RHA that is shown in Fig. 2 presents typical silica bands [7, 8]. The band with maximum in 1100 cm⁻¹ is due to Si-O stretching vibrational modes, the band at 800 cm⁻¹ is attributed to ring structure of SiO₄ tetrahedral of silica and band at 110 cm⁻¹ is assigned to deformation of Si-O-Si [8,9]. The band present at 3400 cm⁻¹ is due to the O-H stretching of the silanol SiOH groups on the silica surface

[6, 8]. Therefore, the infrared analysis indicates that the RHA adsorbent is a material with high content of SiO₂ and very low content of organic components.

3.2. Characterization of Purified Biodiesel

- Effect of contact time: The effect of contact time on sorption of glycerin was shown in Fig. 4.

It can be observed that glycerine content was decreased from 4724.58 to 672.54 ppm and remain constant by treating with 3 % (w/w) of RHA adsorbent at 20 minutes. So the appropriate contact time could be 20 minutes.

- Effect of amount and mesh size on glycerine adsorption: From Fig. 2 (B) it could be seen that all Mesh size of RHA adsorbent showed the efficiency to remove catalyst and glycerine. However, 1 % (w/w) of 80-100 mesh size RHA adsorbents showed the best result on glycerine removal (Table 2). The glycerine content was dramatically removed from 6145.07 to 113.42 ppm. This can be explained considering that RHA has a strong affinity for polar compounds and its surface is a predominantly mesopore allow getting holds large molecules making the diffusion of species to be adsorbed [8]. Hence, the approximately pore size to remove glycerine molecules could be 15.55 nm of 80-100 mesh size RHA adsorbent (Fig.3 (B)).

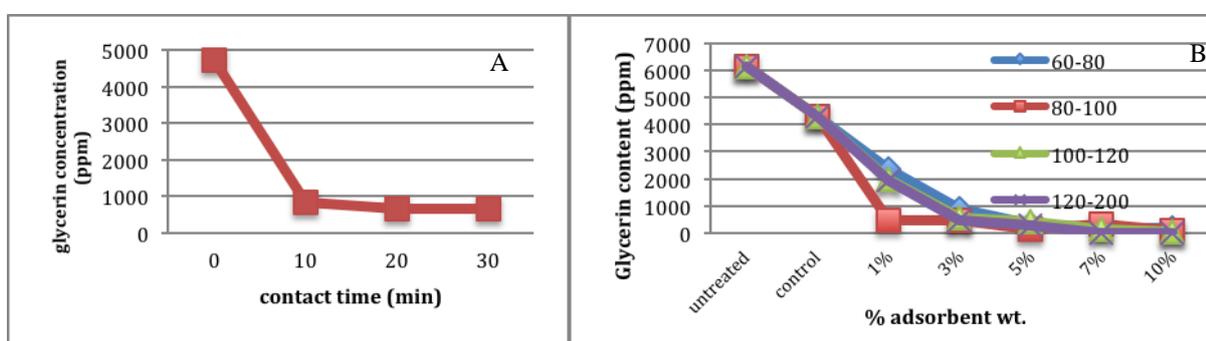


Fig.3: (A) Glycerin content vs. various contact times; (B) Glycerine content vs. various amount of different mesh size of RHA adsorbent

Table 2: Characteristic of purified biodiesel with 5% (w/w) of 80-100 mesh size of RHA adsorbent.

<i>type</i>	<i>Catalyst</i> (ppm)	<i>Glycerine</i> (ppm)	<i>Free glycerol</i> (m/m) (<0.02)	<i>Mono-glyceride</i> (m/m) (<0.80)	<i>Di-glyceride</i> (m/m) (<0.20)	<i>Tri-glyceride</i> (m/m) (<0.20)	<i>Total glyceride</i> (m/m) (<0.25)	<i>Acid number</i> (mgKOH/g) (<0.50)
Crude biodiesel	73.66	61450.07	-	-	-	-	-	0.15
5%(w/w)80-100mesh RHA	0	113.34	1.54×10^{-3}	0.3	0.03	0	0.11	0.15

- Adsorption isotherm: From Fig.4 The adsorption isotherm of silica from rice husk ash was fit to Langmuir equation. It can be explained that the glycerin is strongly attracted to RHA surface. This adsorption involves the attachment of only one layer of glycerin to RHA surface. This Langmuir equation is also describes chemisorption process [4].

4. Conclusions

Extracted silica from rice husk ash obtained from middle region of Thailand could be used as adsorbent for purifying biodiesel as it has a strong affinity to adsorb glycerine, which is polar compound include biodiesel. The structure of RHA is crystalline which predominantly in mesopores. The specific surface area

and pore diameter of RHA (60-80, 80-100, 100-120, and 120-200 mesh) were found in the range of 38-47 m^2/g and 15-30 nm, respectively. The optimal pore diameter for glycerine adsorption is 15.55 nm. By using the optimal condition as follow: 5% (w/w) of 80-100 mesh size of RHA adsorbent and contact time for 20 minutes, the level of glycerine, free and total glycerol is lower than the specification of biodiesel standard. The adsorption isotherm of this RHA is fit to Langmuir equation.

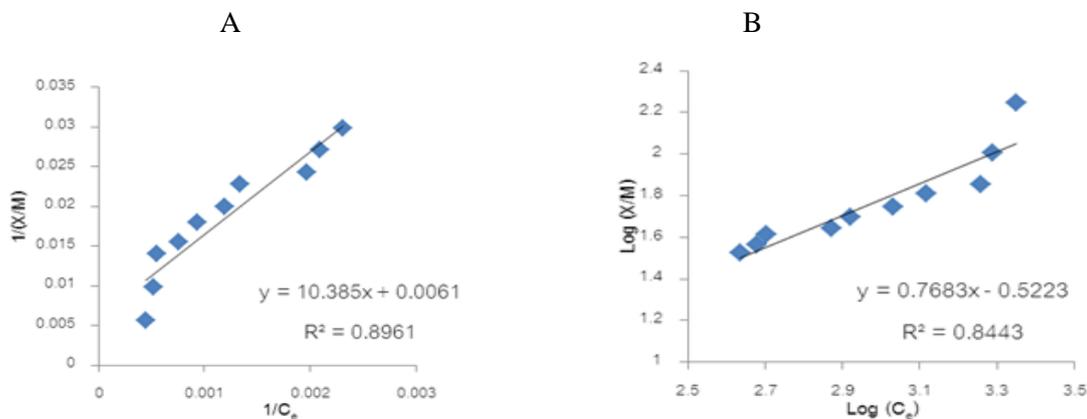


Fig. 4: Adsorption isotherm: (A) Langmuir adsorption isotherm; (B) Freundlich adsorption isotherm.

5. Acknowledgement

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6. References

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