

Glycerin Removal in Biodiesel Purification Process by Adsorbent from Rice Husk

Saengprachum.N^{1,2}, Poothongkam.J³, Pengprecha.S⁴

¹ International Postgraduate Programs in Environmental Management, Graduate School, Chulalongkorn University, Bangkok, Thailand.

² Center of Excellence for Environmental and Hazardous Waste Management (EHWM), Chulalongkorn University, Bangkok, Thailand.

³ Department of Environmental Science, Chulalongkorn University, Bangkok, Thailand, 10330.

⁴ Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand, 10330.

somchai.pe@chula.ac.th

Abstract—Biodiesel is traditionally purified by water washing process. The possibility of reducing wastewater in biodiesel purification was investigated using adsorbents which was activated carbon and extracted silica from rice husk ash (RHA). Activated carbon was produced by treating rice husk ash with $ZnCl_2$ in the weight ratios of 1:0.25, 1:1 or 1:2 (RHA : $ZnCl_2$), followed by the carbonization at 700 °C. Extracted silica was produced by heating rice husk at 700 °C, followed by the treatment of 2.5 N NaOH. The biodiesel was directly purified by using 5% wt. of adsorbents, 150 rpm of agitation rate, at 50 °C for 10 min. The result showed that glycerin could be removed up to 84.8%. The regenerated silica could be used up to five times with 75-80%. The adsorption isotherm of this process was fit to Langmuir model.

Keywords—Biodiesel purification, Adsorption, Glycerol, rice husk ash

I. 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 [1,2]. The process to produce biodiesel is by transesterification/ esterification reaction. After the completion of reaction, the common ways to purified 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 of wastewater. To solve these problems, the research to

date has trended to focus on using various adsorbents such as CaO, MgO, Mg_2CO_3 , magnesium silicate, activated charcoal and bentonite as well as ion exchange resin [3]. Thailand is agricultural country where 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%) [4,5].

In this study, when separating the glycerol, the crude biodiesel was purified using $ZnCl_2$ -Activated carbon and extracted silica from rice husk ash. Furthermore, the used adsorbents were regenerated and the purification efficiency of these adsorbents compared with original adsorbents. The characteristic of $ZnCl_2$ -Activated carbon and extracted silica from rice husk ash (RHA) were also studied by using iodine value, methylene blue, XRD, BET, and FTIR [6].

II. MATERIALS AND METHODS

A. $ZnCl_2$ Activating

Rice husk from rice mill was reflexed with 1 N NaOH for 4 h. Then, the sample was washed with DI water until the pH was 7. The sample was then dried at 120 °C for 24h. The obtained sample was activated by $ZnCl_2$ in the ratio of RHA to $ZnCl_2$ was 1:0.25, 1:1, and 1:2, respectively. The mixture was immersed

with DI water at 100 °C for 24h. The sample was then calcite at 700 °C for 1h in close system. After that calcite sample was washed with 5% HCl solution at 100 °C for 1h The sample was then washed with DI water until the pH was 7, dried at 110 °C for 24h, ZnCl₂-activated carbon was then ground, screened through 120-200 mesh sieves and then stored in tightly capped glass bottle for future use [7].

B. Silica extraction

Rice husk ash from rice mill (in middle region of Thailand) was burnt at 700°C for 6 h. In 250 ml flask, Ten grams of RHA samples and 80 ml of 2.5 N NaOH solution were added. Then, the mixture was refluxed with stirred 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 5 N 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 120-200 mesh sieves and then stored in tightly capped glass bottle for future use [5].

C. Characterization of adsorbent

Surface area of ZnCl₂-Activated charcoal was determined by their adsorptive capacity of iodine, which is iodine number adsorption number (IAN) according to ASTM (1999). Adsorption capacity for the ZnCl₂-Activated carbon was determined through their adsorption of methylene blue (MB) from its aqueous solution. The surface functional groups of extracted silica were analyzed by a Fourier transform infrared (FTIR) spectroscope (model attenuated reflectance) in the range of 4000-400 cm⁻¹ with resolution of 4 cm⁻¹ and 100 scans. The specific surface area and pore size distribution of silica and ZnCl₂-Activated carbon were measured by nitrogen adsorption-desorption isotherm using BET method [8]. X-ray diffraction was used to determine the phase of silica. The scanning rate was 20 min in the 2θ diffraction angle between 20° and 80°.

D. Biodiesel Production via Base-Catalyzed tranesterification

400 g of palm oil was added into 1000 mL of round bottom flask equipped with condenser. After the oil was heated to 65 °C, 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.

E. Biodiesel Purification

Crude biodiesel was purified via two types of adsorbents; ZnCl₂-Activated carbon (the ratio of RHA to ZnCl₂ is 0.25:1,

1:1, and 2:1) and extracted silica from rice husk ash with 120-200 meshes size. The purification process was achieved via two processes; in the presence of methanol and without methanol.

Adsorption in the presence of methanol

After tranesterification, the bottom glycerol was separated from crude biodiesel via gravitational settling and the crude biodiesel was then brought to purification process. The experiment was carried out 50°C and five amount of adsorbents: 1, 3, 5, 8, and 10% wt. in a batch experiment with sample size of 50 mL with a 150 rpm speed agitator and immersed in a water bath for 10 min. The Adsorbent was removed from biodiesel by polishing through a filter with sizes 0.45 micrometer, the purified biodiesel was analyzed by titration and GC method. All purification conditions were done in duplicate.

Adsorption without methanol

After the bottom glycerol was separated, the crude biodiesel was transfer to the Rotary evaporator at 50 °C for methanol removing. The crude biodiesel was then brought to purification process. The four amounts of adsorbents: 0.5, 1.0, 1.5, and 2.0% wt. were applied to purify crude biodiesel with the same condition as adsorption in the presence of methanol.

F. Adsorption isotherm

For adsorption isotherm study, In a 50 mL glass bottle, 50 g of crude biodiesel was added in to varied amounts of adsorbents (1-10 % wt.) with stirring rate at 150 rpm at 50 °C and contact time for 10 min. Then, the adsorbent was removed by membrane filtration (Millipore fulture, 0.45 micrometer) and the glycerine content were analysed by using titration method.

G. Regeneration of adsorbents

The used adsorbents were regenerated by washing with methanol (10X50ml).

H. 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).

III. RESULTS AND DISCUSSIONS

A. Characteristic of prepared adsorbents

Oxygen surface groups and iodine and methylene blue

adsorption numbers surface area, pore diameter, and pore volume of ZnCl₂-Activated carbon and extracted silica were determined and presented in Table 1. It can be seen that Each 1.0 mg of iodine adsorbed equals to 1.0 m² of ZnCl₂-Activated carbon (1:0.25, 1:1, and 1:2 ratios of RHA: ZnCl₂) and extracted silica surface area. Iodine adsorption numbers of adsorbents are showed in Table 1. It can be seen that 1:2 ratio of ZnCl₂-Activated carbon had higher surface area compared to other ratio and extracted silica. It can be explained that increasing the amount of ZnCl₂ effected to increase the surface area of activated carbon from 31.44 to 890 nm. This is because high acidity of ZnCl₂-Activation helps to increase the porous structure through further removal of volatiles. The adsorption of methylene blue is attributed to its meso porosity. MB values of the ZnCl₂-Activated carbon (1:0.25, 1:1, and 1:2 ratios of carbon: ZnCl₂) were much lower than those of the IAN. This means that ZnCl₂-Activated carbon have micro porous structures. The lowest adsorption of methylene blue is attributed to extracted silica meso porosity. This also confirm by BET method.

TABLE I

CHARACTERISTIC OF ADSORBENTS

Ratio (RHA: ZnCl ₂)	Iodine number (mg/g)	Methyl line blue (mg/g)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
RHA	-	-	31.44	0.0380	4.831
1:0.25	468.78	40.90	593.24	0.2637	1.7783
1:1	579.60	44.98	670.35	0.3351	1.9997
1:2	600.10	45.46	890.80	0.4210	1.8905
RHA burnt at 700 °C	-	-	2.205	0.0034	6.2244
Extracted Silica	76.49	37.32	126.72	0.207	6.34

The FTIR spectrum of extracted silica is showed in Fig. 1(A) 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 [10,11]. The band present at 3400 cm⁻¹ is due to the O-H stretching of the silanol SiOH groups on the silica surface [8, 10]. Therefore, the infrared analysis indicates that the RHA adsorbent is a material with high content of SiO₂ and very

low content of organic components.

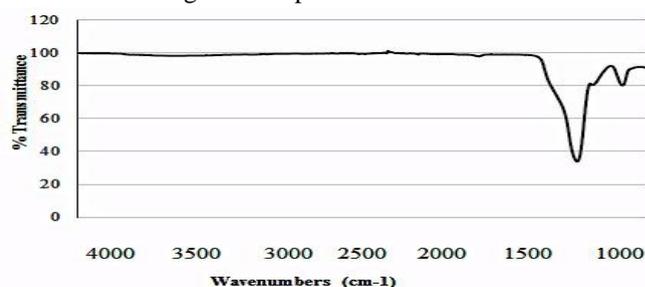


Fig. 1. (A) FTIR spectrum of extract silica produced from RHA

XRD pattern of RHA (Fig. 1(B)) shows sharp phases. These sharp peaks suggested characteristic of crystallization.

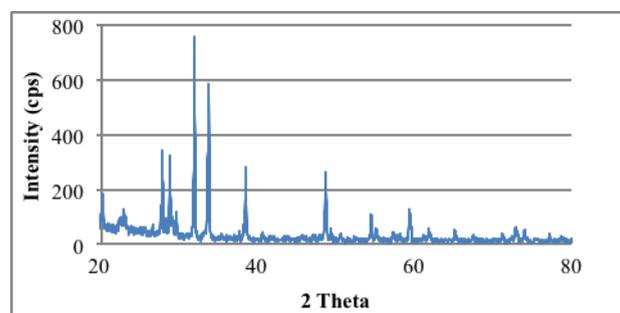


Fig. 1 (B) XRD diffractogram of extract silica produced from RHA.

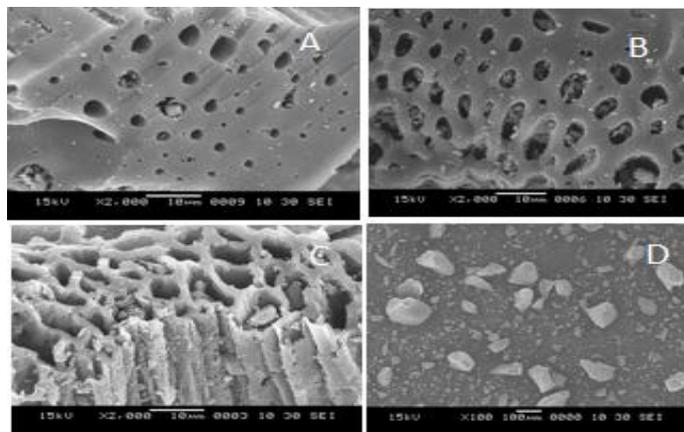


Fig. 2. Scanning electron micrograph of (a) RHA: ZnCl₂_0.25:1 (b) RHA: ZnCl₂_1:1; (c) RHA: ZnCl₂_1:2 ; (d) extracted silica (magnification 2000X)

The scanning electron macrograph of ZnCl₂-Activated carbon and extracted silica are shown in Fig. 2., RHA: ZnCl₂_1:2 shows higher surface roughness (porosity) than RHA: ZnCl₂_1:1 and RHA: ZnCl₂_1:2 .The extracted silica shows smooth surface due to it is crystalline structure

B. Purification of biodiesel over adsorbents

From Fig. 3 it could be seen that ZnCl₂-activated carbon (1:0.25, 1:1, and 1:2 ratios of RHA: ZnCl₂) and extracted silica

showed the efficiency to remove glycerine. In the present of methanol, 89 % of glycerin was removed from crude biodiesel by using 5% wt. of 1:2 ratio of RHA: ZnCl₂, at 50 °C with 150 rpm of agitation speed for 10 min. However, the color of treated biodiesel was dark.

In the present of methanol, 5 % wt. of 1:2 ratios of ZnCl₂ - activated carbon and extracted silica, at 50 °C with 150 rpm of agitation speed for 10 min. showed the best result on glycerine removal. About 89 % of glycerine content was dramatically removed via both adsorbents. However, the color of treated biodiesel via ZnCl₂ -Activated carbon was dark. This can be explained considering that lower surface area of extracted silica has the same efficiency with ZnCl₂-Activated carbon because it 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 [10]. Purified biodiesel via both adsorbents passed the biodiesel standards (Table 2).

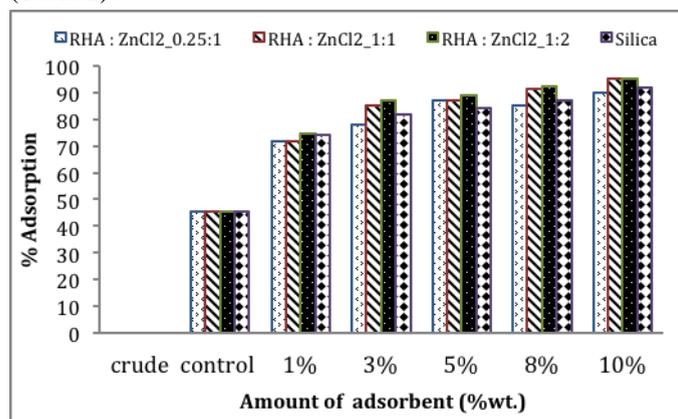


Fig. 3. Ionahtem htiw lavomer nirecylyg no tnuoma tnebrosla fo tceffe ta50 °C with 150 rpm of agitation speed for 10 min.

TABLE II

QUANLITYS OF PURIFIED BIODIESEL IN THE PRESENT OF METHANOL

Properties	ZnCl ₂ -Activated carbon		Silica	
	5% (wt.)	10% (wt.)	5% (wt.)	10% (wt.)
Acid value (mgKOH/g) (<0.5 mgKOH/g)	0.126	0.134	0.146	0.158
Free glycerol (%m/m) (< 0.02)	8.43×10^{-4}	1.48×10^{-3}	1.54×10^{-3}	6.58×10^{-4}
Mono-glyceride (%m/m) (< 0.80)	0.44	0.41	0.39	0.39
Di-glyceride (%m/m) (< 0.20)	0.03	0.03	0.03	0.03
Tri-glyceride (%m/m) (< 0.20)	-	-	-	-
Total glyceride (%m/m) (< 0.25)	0.12	0.11	0.11	0.10

Adsorption without methanol: After the methanol was removed, the glycerin dissolved in crude biodiesel has reduced. The results from Fig.4. and Table 3 shows that by using 1.5 % wt. of both adsorbents (1:2 ratio of ZnCl₂-Activated carbon and extracted silica), the quantities of purified biodiesel passed the biodiesel standards .

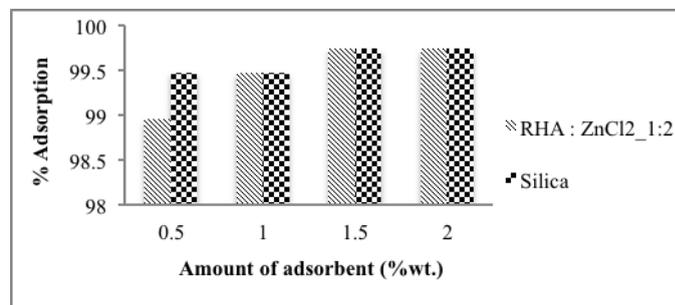


Fig. 4. Effect of amunt of adsorbent on glycerine removal without ta lonahtem50 °C with 150 rpm of agitation speed for 10 min.

III ELBAT

QUANLITYS OF PURIFIED BIODIESEL WITHOUT METHANOL

Properties	ZnCl ₂ -Activated carbon		Silica	
	1.5 %wt.	2.0 % wt.	1.5 %wt.	2.0 % wt.
Free glycerol (%m/m), (< 0.02)	5.92×10^{-3}	3.62×10^{-3}	8.22×10^{-3}	5.39×10^{-4}
Mono-glyceride (%m/m), (< 0.80)	0.29	0.48	0.50	0.43
Di-glyceride (%m/m) (< 0.20)	0.03	0.03	0.03	0.03
Tri-glyceride (%m/m) (< 0.20)	-	-	-	-
Total glyceride (%m/m) (< 0.25)	0.13	0.13	0.14	0.12

C. Adsorption isotherm of adsorbents

TABLE IV
A DSORPTION ISOTHERM.

Adsorbents	Langmuir				Freundlich		
	a (mg/g)	b (l/mg)	R ²	R _L	K _F (l/g)	1/n	R ²
ZnCl ₂ - Activated carbon	1000	5.20×10^{-5}	0.975	0.798	0.055	0.975	0.968
silica	166.67	5.78×10^{-4}	0.896	0.289	0.300	0.768	0.844

From Table 4 The adsorption isotherm of ZnCl₂ - Activated carbon and extracted silica were fit to Langmuir equation. It can be explained that the glycerin is strongly attracted

to adsorbents surface. This adsorption involves the attachment of only one layer of glycerin to adsorbents surface. This Langmuir equation is also describes chemisorption process [12].

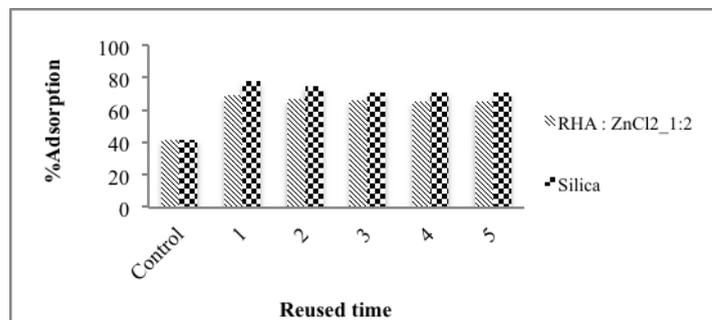


Fig. 5. Comparison of regeneration of ZnCl₂-Activated carbon and extracted silica from RHA on glycerine removal at 50 °C with 150 rpm of agitation speed for 10 min.

From Table 5 and Fig.5., It was found that extracted silica show better result on biodiesel impurities removal than ZnCl₂-Activated carbon. The properties of purified biodiesel especially the free glycerol, mono-glyceride, and di-glyceride were lower than that purified using The ZnCl₂-Activated carbon. It can be said that extracted silica is a good adsorbent for the purification of biodiesel compare to ZnCl₂-Activated carbon. Moreover, it can be regenerated and can be reused up to 5 times.

TABLE V
PURIFIED BIODIESEL OVER REGENERATED ADSORBENTS

Process	Free glycerol (%m/m) (< 0.02)	Mono-glyceride (%m/m) (< 0.80)	Di-glyceride (%m/m) (< 0.20)	Tri-glyceride (%m/m) (< 0.20)	Total glycerol (%m/m) (< 0.25)
ZnCl ₂ -Activated carbon					
(1)	0.028	0.48	0.03	-	0.16
Silica					
1	6.30 × 10 ⁻⁴	0.4	0.03	-	0.11
3	0.012	0.35	0.03	-	0.14
5	6.30 × 10 ⁻⁴	0.46	0.03	-	0.09

IV. CONCLUSIONS

In purifying the biodiesel, the adsorbents from rice husk ash can be used instead of water. By using extracted silica, emulsion, drying of final product and waste water treatment can be omitted. ZnCl₂-Activated carbon and extracted silica from rice husk ash can be used for the purification of crude biodiesel production via base catalyzed transesterification. As the results, the study showed that extracted silica shows better results. Treating

biodiesel via ZnCl₂-Activated carbon resulted in dark color of biodiesel, while extracted silica gave clear biodiesel. At least 5% wt. of extracted silica with contact time of 10 min. regenerated in order to decrease glycerol and soap content. The results show that the free glycerol level fulfill the requirement of EN 14214 standard.

ACKNOWLEDGMENT

The authors would like to acknowledge the assistance and support given by Department of Environmental science and department of chemistry faculty of Chulalongkorn University for support the GC, BET, IR XRD instrument.

REFERENCES

- i. Atadashi I.M., Aroua M.K., Aziz A.A., High quality biodiesel and its diesel engine application: A review; *Renewable & Sustainable Energy Reviews*, **14**, PP 1999–2008, 2010
- ii. Nicolae S., (2010), A Study using classical or membrane separation in the biodiesel process; *Desalination* **250**, 1070-1072.
- iii. Berrios M., Skelton R.L., (2008), Comparison of purification methods for biodiesel, *Chemical Engineering Journal* **144**, 459-465.
- iv. Della VP., Kuhn L., Hotza D., (2000), Rice husk ash as an adsorbent source for active silica production, *Material Letters* **57**, 818-821.
- v. Kalapathy U., Proctor A., Shultz J., (2000), A simple method for production of pure silica from rice hull ash, *Bioresource Technology* **73**, 257-262.
- vi. Liou T.H., Wu S.J., (2009), Characteristics of microporous/ mesoporous prepared from rice husk under base- and acid- treated conditions, *Journal of Hazardous Materials* **171**, 693–703.
- vii. Kalderis D., Bethanis S., Paraskeva P., Diamadopoulos E., (2008), Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times, *Bioresource Technology* **99**, 6809-6816.
- viii. Marcia CM., Candice SF., Bruna O., Edilson VB., Elina BC., (2012), Rice husk ash as an adsorbent for purifying biodiesel from waste frying oil, *Fuel* **92**, 56-61.
- ix. Chandrasekhar S., Pramada PN., (2006), Rice husk ash as an adsorbent for methylene blue-effect of ashing temperature, *Adsorption* **12**, 27-43.
- x. Meida RM., Pantano CG., (1990), Structural investigation of silica gel films by infrared spectroscopy, *J Appl Phys* **68**, 4225-32.
- xi. Costa TMH., Gallas MR., Benvenuti EV., Jornada J. D., (1997) Infrared and thermogravimetric study of high pressure consolidation in alkoxide silica gel powders, *J Non-Cryst Solids*, **220**, 195-201.
- xii. Adamson, Arthur W. (1979), *A Textbook of Physical Chemistry*, ; 2nd Edition, Academic Press, New York.