PURIFICATION OF CRUDE GLYCEROL BY SOLVENT EXTRACTION AND ADSORPTION IN BIODIESEL PRODUCTION FROM JATROPHA OIL

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1. Introduction

Crude glycerol is a byproduct of biodiesel production through the transesterification reaction of plant oil, for example, jatropha oil as an inedible oil that substitutes for edible oil and waste cooking oil, with alcohol. Crude glycerol is basically produced at 1 kg for each 10 kg of biodiesel, which faces an oversupply problem caused by the intensification of biodiesel industry. The increasing supply of glycerol motivates the emergence of two main glycerol consumer markets, the first is utilization of high amounts but lower qualities of crude glycerol in industrial sectors such as chemical products and additives for automotive fuels, and the second is demands of high quality of glycerol in mainly foods, pharmaceutical and cosmetic products [1]. Although the food, pharmaceutical and cosmetic industries are among the largest consumption markets, one of the major difficulties in utilization of glycerol in these products is its low degree of purity, affecting its physical and chemical properties.

Crude glycerol from biodiesel production contains kinds of non-glycerol organic matters and presents a dark brown color. The general characteristics of crude glycerol from biodiesel production was shown in Table 1 [2].

Table 1 Characteristics of crude glycerol from biodiesel production

pH	9.08±0.01
Glycerol Content (wt. %)	36.7±0.49
Ash Content (wt. %)	4.31±0.027
Water Content (wt. %)	14.7±0.90
Matter Organic Non-glycerol (wt. %)	44.0±0.44
Color	Dark Brown

In general, the purification of glycerol derived from biodiesel comprised of three steps. The first involves the removal of non-glycerol substances by saponification using strong alkali, continued with neutralization through adding strong acid to produce free fatty acids. The next step is to remove alcohol from glycerol stream by evaporation. The final step is refining step with diverse methods such as vacuum distillation, ion exchange, and membrane separation, during which desired degree of glycerol can be achieved, however, these methods faced difficulties such as high energy-intensive input corresponding to the high heat capacity of glycerol, or poor durability of exchange materials and membranes that leads to high costs. As an alternative method, combination of solvent extraction and adsorption is considered since there is not enough studies, in addition, it allows glycerol purification to be performed under less hazardous conditions and is more cost saving.

The main objective of this study is to purify crude glycerol by solvent extraction and adsorption in biodiesel production from jatropha oil. This purification process is achieved by firstly equilibrium extraction of model crude glycerol to move fatty acid, secondly equilibrium adsorption of model crude glycerol using jatropha shell activated carbon to remove colored compound.

2. Equilibrium extraction of model crude glycerol to remove fatty acid
2.1. Experimental

The equilibrium extractions of model crude glycerol to remove oleic acid using heptane were carried out. Oleic acid was used because it accounted for the highest fatty acid composition in jatropha oil. Heptane was selected as solvent, because it showed favorable performance in the recovery of fatty acids and did not have the environmental or health concerns. The experimental conditions of the equilibrium extractions are summarized in Table 2.

Table 2 Experimental conditions of equilibrium extraction

Feed		Glycerol + Oleic Acid
Mass of Feed	[kg]	3×10^{-2}
Mass Fraction of Oleic Acid	[-]	1×10^{-2}-3.5×10^{-2}
Solvent		Heptane
Mass Ratio of Solvent to Feed, E_0/R_0	[-]	0.5-4
Hot Stirrer		
Temperature	[K]	298
Frequency of Shaking	[rpm]	300
Time	[h]	48

The specified amounts of feed and solvent were brought into contact in conical flasks with screw caps and shaken on the hot stirrer under specified temperature. According to previous study in the laboratory, 48 hours of contact was sufficient to reach equilibrium of the extraction process [3]. After reaching equilibrium, two phases were separated into raffinate phase and extract phase in a separating funnel. All phases were analyzed by gas chromatograph (GC) to determine their compositions.

2.2. Results and discussion

The material balance of oleic acid for the equilibrium extraction was given by following expression with mass and compositions of respective phase,

$$R_0 x_{OA,0} - R_1 x_{OA,1} = E_1 y_{OA,1}$$

The left side represented mass decrease of oleic acid in feed phase. It was equal to right side representing mass increase in solvent phase.

The fractional removal of oleic acid, r_{OA}, was defined by following equation with ratio of mass increase of oleic acid in extract phase at equilibrium to initial mass of oleic acid in feed phase.

$$r_{OA} = E_1 y_{OA,1} / R_0 x_{OA,0}$$

The distribution coefficient of oleic acid, K_{OA}, was defined by following equation with ratio of mass fraction of oleic acid in extract to raffinate phase at equilibrium,

$$K_{OA} = y_{OA,1} / x_{OA,1}$$

Figure 1 showed the relation of fractional removal of oleic acid, r_{OA}, to initial mass faction in feed phase, $x_{OA,0}$, and mass ratio of solvent to feed, E_0/R_0, respectively. Oleic acid was successfully extracted and removed. With the rise of $x_{OA,0}$ and E_0/R_0, the fractional removal of oleic acid, r_{OA}, increased at equilibrium. Under the condition that mass fraction of oleic acid in feed, $x_{OA,0}$, was 3.5×10^{-2} and mass ratio of solvent to feed, E_0/R_0, was 4, the fractional removal of oleic acid was highest.

Figure 2 showed the relation of distribution coefficient of oleic acid, K_{OA}, to the mass fraction of oleic acid in raffinate phase, $x_{OA,1}$, at equilibrium. With the rise of $x_{OA,1}$, the distribution coefficient of oleic acid, K_{OA}, decreased. This could be explained by the polarities of each component in the equilibrium extraction. Polarity of oleic acid was decided by the electronegativity difference in C-H bonds of oleic acid, when it was less than 0.9, the bonds were considered nonpolar. C-H bonds were nonpolar since carbon and hydrogen had similar electronegativity values, which were 2.5 and 2.1, respectively. Electronegativity difference between carbon and hydrogen was not great enough to make the bond polar. Therefore, C-H bonds existed in molecular structure made oleic acid to be nonpolar and easy to be extracted from the polar glycerol phase into nonpolar heptane phase. In general, with the rise of $x_{OA,1}$ at equilibrium, which indicated more oleic acid soluble in raffinate phase rather than extract phase, so distribution coefficient K_{OA} decreased. Under the condition that mass fraction of oleic acid in feed phase, $x_{OA,0}$, was 3.5×10^{-2} and mass ratio of solvent to feed, E_0/R_0, was 4, the distribution coefficient of oleic acid was highest.

3. Equilibrium adsorption of model crude glycerol to remove colored compound
3.1. Experimental
3.1.1. Preparation of jatropha shell activated carbon

Jatropha shell sample was collected from jatropha plantation in Thailand. Sample was washed and dried overnight, crushed and sieved into desired size between 0.425~1.7 mm. Next, sample was impregnated with 4 mol/L of phosphoric acid for 6 hours at 358 K, and dried for 24 hours at 383 K. 20g of sample was thermally treated in an electrical furnace using experimental conditions in Table 3, to produce activated carbon (AC).
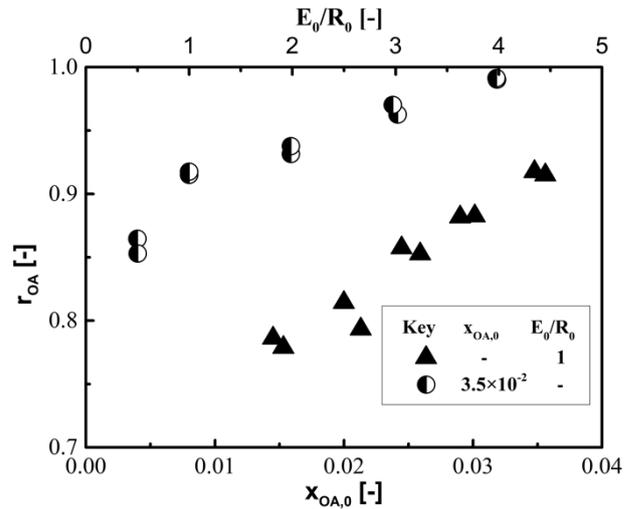
Fig. 1 Relation of fractional removal of oleic acid, r_{OA}, to initial mass fraction in feed phase, $x_{OA,0}$, and mass ratio of solvent to feed, E_0/R_0
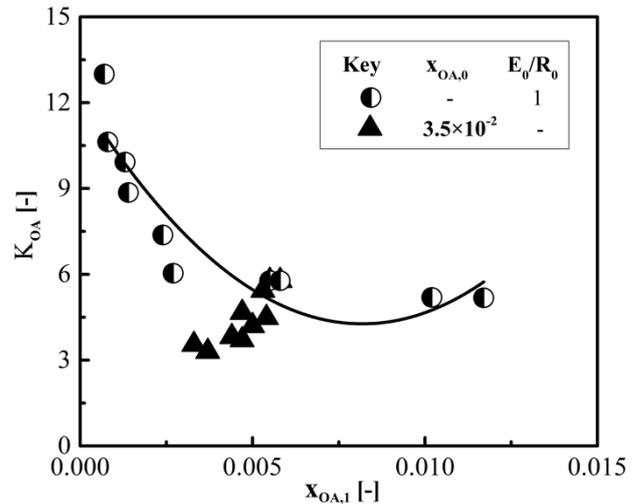
Fig. 2 Relation of distribution coefficient of oleic acid, K_{OA}, to mass fraction in raffinate phase, $x_{OA,1}$

Table 3 Experimental conditions of pyrolysis treatment

Feed		Jatropha shell
Particle Size	[mm]	0.425~1.7
Mass of Feed	[kg]	2×10^{-2}
Atmosphere		Nitrogen
Flow Rate of Atmosphere	[mL/min]	150
Temperature	[K]	673, 1073
Holding Time	[h]	1

The activated carbon made from jatropha shell was analyzed using high performance gas and vapor adsorption instrument (BELSORP Max) to determine its specific surface area, total pore volume and pore size distribution.

3.1.2. Equilibrium adsorption of model crude glycerol

The equilibrium adsorption of model crude glycerol to remove glutamic acid using jatropha shell activated carbon was carried out in the experimental conditions in

Table 4.

Table 4 Experimental conditions of equilibrium adsorption

Feed		Glycerol + Glutamic Acid
Mass of Feed	[kg]	$2.5×10^{-2}$
Mass Fraction of Glutamic Acid	[-]	$3×10^{-4}$-$1.5×10^{-2}$
Adsorbent		Jatropha Shell Activated Carbon
Mass of Adsorbent	[kg]	$1×10^{-4}$
Hot Stirrer		
Temperature	[K]	298
Frequency of Shaking	[rpm]	300
Time	[h]	120

The specified amounts of feeds were brought into conical flasks with $1×10^{-4}$ g of jatropha shell activated carbon and shaken on the hot stirrer for 120 hours under specified temperature. After reaching equilibrium, the liquid phase and solid phase were separated by filtration, and the liquid phase was analyzed using ultraviolet visible (UV) spectrophotometer at 210 nm of wavelength to determine their compositions.

3.2. Results and discussion

3.2.1. Characteristics of jatropha shell activated carbon

The yield of activated carbon, $Yield$, was calculated by the mass of activated carbon before and after pyrolysis treatment as shown in the expression,

$$Yield = M_{after}/M_{before}$$

The specific surface area and total pore volume of activated carbon were calculated on the basis of BET plot [4]. Two samples indicated type IV adsorption isotherms and the results marked the development of mesopores and micropores. Activated carbon treated at 673 K (AC-673) has larger adsorption amounts than activated carbon treated at 1073 K (AC-1073). This indicated that larger specific surface area had been formed with AC-673.

The characteristics of activated carbon samples were summarized in Table 5.

Table 5 Characteristics of activated carbon

Activated Carbon	$Yield$	Specific Surface Area (m2/g)	Total Pore Volume (cm3/g)
AC-673	0.793	801.18	0.523
AC-1073	0.182	238.47	0.252

3.2.2. Equilibrium adsorption of model crude glycerol

The material balance of glutamic acid was given by following expression,

$$C_0L_0 = CL + qS$$

The fractional removal of glutamic acid, r_{GA}, was defined by following equation,

$$r_{GA} = (C_0L_0 - CL)/C_0L_0$$

The performance of glutamic acid adsorption was evaluated with Langmuir adsorption isotherm,

$$q = (q^*K_LC)/(1 + K_LC)$$

Figure 3 and 4 showed the fractional removal of glutamic acid, r_{GA}, from the model crude glycerol with respect to different glutamic acid amounts in feeds, C_0, using activated carbon. Glutamic acid was successfully removed from model crude glycerol. The fractional removal of glutamic acid, r_{GA}, decreased as the increment of glutamic acid amounts in feeds, C_0, which pointed out better adsorption performance of the activated carbon samples in relatively lower concentration of glutamic acid. Comparing the adsorption performance of AC-673 and AC-1073, AC-673 was able to treat model feeds with higher glutamic acid concentration, which could be explained by its larger specific surface area.
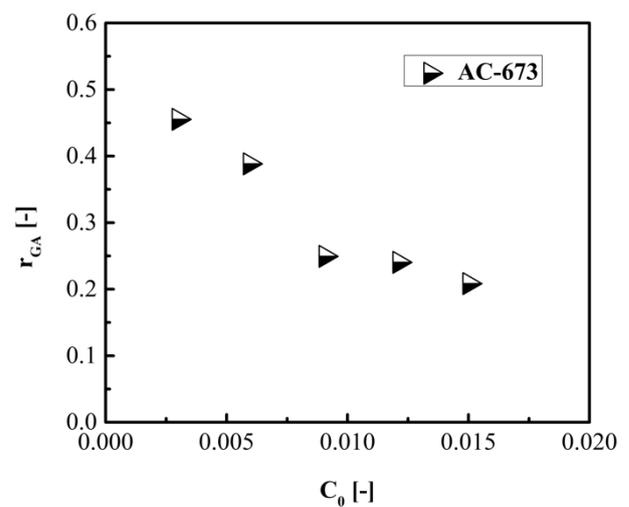
Fig. 3 Fractional removal of glutamic acid, r_{GA}, on AC-673
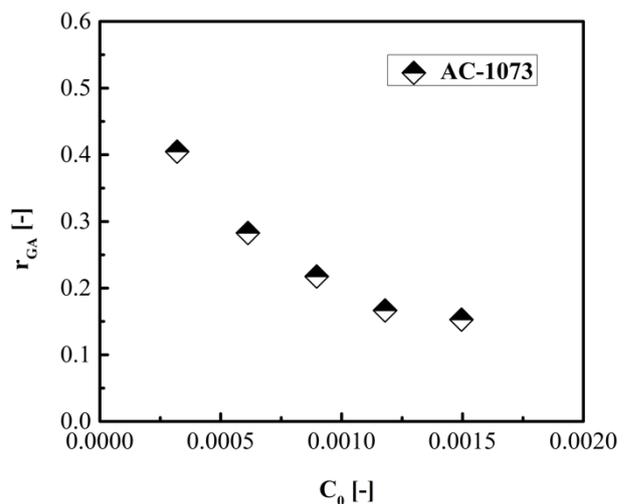
Fig. 4 Fractional removal of glutamic acid, r_{GA}, on AC-1073

Figure 5 and 6 showed the equilibrium adsorption isotherms of glutamic acid using the activated carbon samples. The fitting of Langmuir isotherm to the experimental data was finished on the software Origin Lab.

The results of adsorption isotherm followed the Langmuir model. The Langmuir parameters for the adsorption isotherm on respective activated carbon were summarized in Table 6.

Table 6 Langmuir parameters for adsorption isotherm

Adsorbent	Langmuir Parameter	
	q^* (kg/kg-AC)	K_L
AC-673	0.88	390
AC-1073	0.06	5496

Figure 7 showed the general schematic diagram of purification of crude glycerol. Crude glycerol was firstly treated with heptane by solvent extraction, then heptane phase was distillated to separate the solvent and extracts, through which heptane was recycled, glycerol phase was secondly treated with jatropha shell activated carbon obtained from pyrolysis of jatropha shell to produce purified glycerol, and spent activated carbon could be combusted to provide energy for additional treatments.

4. Conclusion

Based on the results from this study, a method to purify crude glycerol by solvent extraction and adsorption in biodiesel production from jatropha oil was proposed. The equilibrium extraction of model crude glycerol using heptane could remove fatty acid. The equilibrium adsorption of model crude glycerol using jatropha shell activated carbon could remove glutamic acid.

Nomenclature

x: mass fraction of component in feed phase [-], y: mass fraction of component in solvent phase [-], R: mass of feed phase [kg], E: mass of solvent phase [kg], r: fractional removal of component [-], K: distribution coefficient of component [-], C: mass fraction of component in liquid phase [-], L: mass of liquid phase [kg], q: adsorbed amount at equilibrium [kg/kg-AC], S: mass of activated carbon [kg], q^*: saturated adsorbed amount at equilibrium [kg/kg-AC], K_L: Langmuir constant, 0: at initial, 1: at equilibrium

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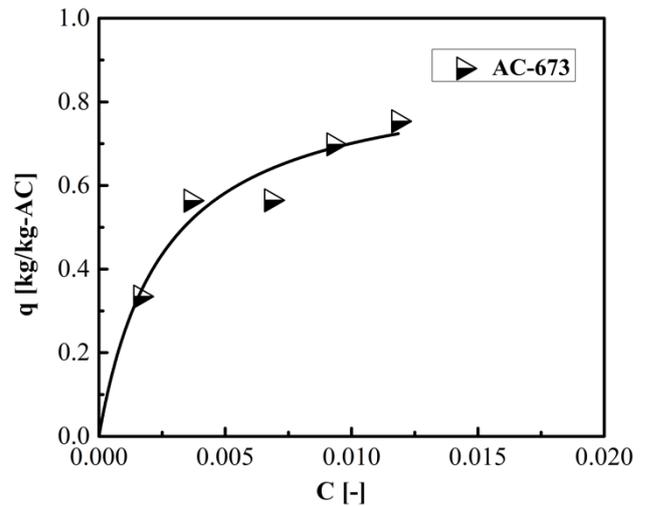
Fig. 5 Adsorption isotherm of glutamic acid on AC-673
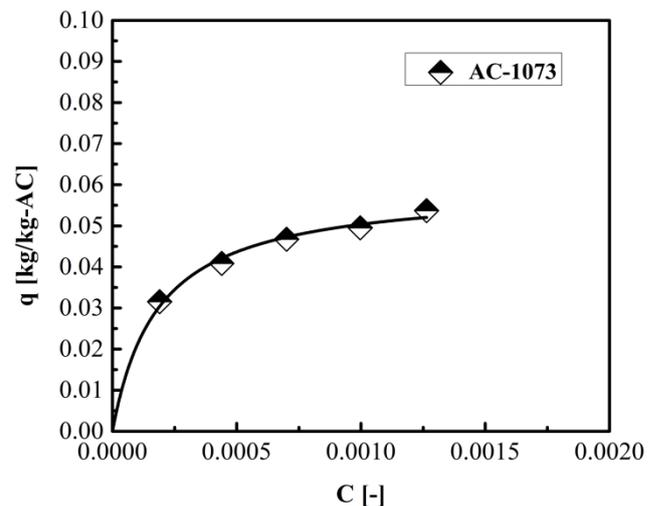
Fig. 6 Adsorption isotherm of glutamic acid on AC-1073

Fig. 7 Schematic diagram of purification of crude glycerol from biodiesel production