

Comparison and Combination of Solvent Extraction and Adsorption for Crude Glycerol Enrichment

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Abstract- A comparative study of enrichment of crude glycerol via solvent extraction and adsorption was performed at a laboratory at 30 °C. Effect of various parameters on the properties of the obtained glycerol including glycerol-, ash- and contaminant contents and color, was explored. The results showed that the enrichment of glycerol by solvent extraction was significantly affected by the solvent type and ratio of solvent to pre-treated crude glycerol. The use of *n*-C₃H₇OH at a ratio of 2.0 was given the highest purity of glycerol, but the lowest color reduction. However, use of C₄H₁₀O at a ratio of 1.0 was given the low glycerol content but the highest color removal. On the other hand, adsorption with activated carbon was given poor glycerol purity of 70.3 wt.% but its color was decreased more than 97.1%. The combined process of extraction with *n*-C₃H₇OH at a ratio of 2.0 was followed by activated carbon adsorption and it was given the highest glycerol purity with the color removal to a clear solution. In addition, the cost analysis of crude glycerol enrichment by the combined approach was also explored.

Keywords- Crude glycerol, Transesterification, Enrichment, FAME (Fatty Acid Methyl Ester), MONG (Matter Organic Non-Glycerol)

1. Introduction

Glycerol or propan-1, 2, 3-triol (also glycerin or glycerine) is a trivalent alcohol that is widely used in diverse applications including in the cosmetic, paint, automotive, food, tobacco, pharmaceutical, pulp and paper, cleaning materials, detergents, wetting agents, emulsifiers, skin protectives, asphalt, ceramics, photographic products, wood treatment, adhesives, leather and textile industries or as a feedstock [1-2]. It can be produced by either microbial fermentation [3], or by chemical synthesis from petrochemical feedstocks, such as the oxidation or chlorination of propylene [2], or can be recovered as a by-product of soap production by saponification or biodiesel production by transesterification of triglycerides from vegetable oils or animal fats [4].

Due to the fast development and commercialization of biodiesel in many countries, a large amount of glycerol is produced [5]. Within Thailand, the recent increase in biodiesel production is increased from less than 2.1×10^6

l/day in 2008 to an expected 8.4×10^6 l/day in 2012 [6]. Stoichiometrically, glycerol is produced at 10 wt.% of the total biodiesel production [7]. Thus, any further increase in biodiesel production rates will significantly raise the quantity and surplus of crude glycerol as waste in the environment. The crude glycerol discharged from biodiesel production plants consists not only glycerol but also various chemicals such as water, organic and inorganic salts, soap and alcohol, traces of glycerides and vegetable colors [4]. Thus, there have been various studies focusing on the glycerol enrichment and refining. For example, Ref. [8] pointed out that a simple vacuum distillation at 120-126 °C and 0.04-0.4 mbar pressure was effective to recover a high purity of glycerol (~ 96.6%) from crude glycerine that contained high levels of salt and matter organic non-glycerol (MONG). To avoid foaming, the pH of crude glycerine was adjusted as < 5. However, this process is energy intensive due to the high specific heat capacity of glycerol and so has a high-energy input requirement for vaporization under the low pressure [9]. By using the electrochemical technique, Ref. [10]

reported that the EUR2C-7bip electrolyzer allowed 80% demineralization of a 65 vol.% glycerin solution from diester wastes with faradic efficiencies of 47% and 35% for sulphuric acid (H_2SO_4) concentrations of 2 M and 3 M, respectively, and an energy cost of 0.5 kWh/kg of pure glycerin. After concentration, a 95% pure glycerin solution was obtained with less than 2 wt.% mineral content. The selective removal of ions-contained within the glycerol was performed using an ion-exchange technique. Ref. [11] demonstrated that the macroporous resin Amberlite 252 was effective to remove sodium ions from glycerol/water solutions with a high salt concentration. A strongly basic anionic-exchange resin (Amberlite IRA-420) could be used for chloride removal, whilst a strongly acidic ion exchanger (Amberlite IR-120) exhibited higher selectivity for potassium and sodium ions [12]. By using a physicochemical approach, a neutralization step was first performed to remove the excess homogeneous catalyst as well as the un-reacted free fatty acids (FFAs) from the crude glycerol, and then the level of free ions from the salt and catalyst were reduced by passage through ion exchange resins [13]. The acidification of crude glycerol by H_2SO_4 in the pH range of 1-6 can alter the properties of obtained crude glycerol [14], where increasing the pH in the acidification step led to an increased yield of the glycerol-rich layer and decreased amounts of residual inorganic salt and FFAs. Under strong acid conditions, large quantities of FFAs and salt in the glycerol-enriched fraction were eliminated. At pH = 1, high purity of the glycerol (~93.34%) with a relatively low content of ash (0.00045 wt.%) and MONG (5.16 wt.%) was obtained. Hájek and Skopal [4] pointed out that the utilization of phosphoric acid (H_3PO_4) in the acidification step can produce the useful fertilizer potash phosphate (KH_2PO_4). Accordingly, Ref. [15] claimed that the step-by-step purification of glycerol by saponification, acidification and neutralization can simultaneously produce high quality FFAs, glycerol and potassium phosphate (KH_2PO_4 , K_2HPO_4) from crude glycerol derived from the transesterification of waste cooking oil. Based on this process; KH_2PO_4 , K_2HPO_4 , glycerol and FFAs with a purity of 98.0%, 98.1%, 96.1% and 99.6% were obtained, respectively.

In this study, comparative and combinative ability of glycerol enrichment via solvent extraction and activated carbon adsorption was performed at a the laboratory temperature of 30 °C. Effect of various parameters on the properties of enriched crude glycerol including glycerol-, ash- and other contaminant contents as well as color were investigated. Finally, the operating cost related to the cost of chemical/material for crude glycerol enrichment by both enrichment processes was estimated.

2. Experimental Proceses

Crude glycerol was obtained from a local fatty acid methyl ester (FAME) production plant in Thailand that utilizes waste used-oil as the raw material for biodiesel production via the alkali mediated “*transesterification*” process. It was dark brown solution with a high viscosity and it can change to a semi-solid substance during the long

storage. Thus, prior to use, the crude glycerol was slowly melted at around 40-60 °C.

2.1. Pre-treatment of Crude Glycerol

Due to the presence of organic and inorganic contaminants in the crude glycerol such as soap, fatty acid esters of glycerol, mineral salt, water and residual FAME, it was first pre-treated according to the procedure of Ref. [16]. Namely, the crude glycerol was acidified by the addition of H_3PO_4 (85%, Qrec) to a pH of 2.5 and shook at constant rate of 200 rpm (CTL, model SK electric shaker) for 1 h. Then, it was left for 12 h until the solution had phase separated into the three distinct layers of a top FFA-rich layer, the middle glycerol-rich layer and the bottom inorganic salt-rich layer. All layers were separated from each other by slow decantation. Subsequently, the middle glycerol-rich layer was neutralized by the addition of 12.5 M NaOH (98% Merck) to pH 7.0, left for a while and then filtered to eliminate the precipitated salt. The pre-treated crude glycerol was obtained after drying at 110 °C for 15 h [16].

2.2. Enrichment of Pre-Treated Crude Glycerol

The enrichment of pre-treated crude glycerol was carried out by two main procedures including solvent extraction and adsorption. For the first one, various types of solvents including polar solvent (methanol (99.99% CH_3OH , Merck), ethanol (99.9% C_2H_5OH , Merck), propanol (99.99% *n*- C_3H_7OH , Fisher Scientific)) and non-polar solvent (hexane (99.79% C_6H_{14} , Honey well) and diethyl ether (99.7% $C_4H_{10}O$, Panreac)) were utilized at different volume ratios of solvent to pre-treated crude glycerol in the range of 0.5-4.0. For the second one (with the polar solvents), the pre-treated crude glycerol was mixed with the selected solvent and volume ratio by shaking at 200 rpm for 4 h and then left for 2 h to encourage the phase separation into the glycerol-alcohol phase on the top and the crystallized salt on the bottom. The top layer was separated from the bottom layer by slow decantation and the enriched glycerol was obtained after evaporation of the solvent at 95 °C for 12 h. For the extraction with the non-polar solvents, a similar procedure was carried out except the non-polar contaminant-solvent phase was observed on the top and the glycerol-rich phase was observed on the bottom. The slow decantation was carried out and the enriched crude glycerol was obtained after evaporation of free water at 95 °C for 12 h.

For the adsorption, the commercial activated carbon (Rankem, India) at the ratio of activated carbon to pre-treated crude glycerol in the range of 33-167 g/l was used in this work. The particle size, BET surface area, pore size and micropore volume of the utilized activated carbon were 0.1-0.3 nm, 898 m^2/g , 0.239 nm and 0.539 cm^3/g , respectively. Prior to use, the activated carbon was dried at 105 °C to eliminate free moisture. The selected dose of activated carbon was added to a 250-ml flask containing 150 ml of pre-treated crude glycerol and shaken at a constant 200 rpm. Finally, the adsorbent was separated by vacuum filtration and the properties of the enriched glycerol were analyzed.

2.3. Analytical Procedures

The glycerol content was analyzed by the High Performance Liquid Chromatography (HPLC: Agilent 1100) with a RID-10A refractive index detector. The stationary phase was a Pinnacle II C18 column (240 × 4.6 mm) and the mobile phase was a 99.9:0.1 (v/v) ratio of 10 mM H₂SO₄: pure CH₃OH, passed through the column at 0.5 ml/min. Ash content was analyzed according to the standard method (ISO 2098-1972) by slowly eating 2 g of glycerol on a hot plate to eliminate the free moisture and volatile matter. When no further mist was generated, the glycerol was burnt in a muffle furnace at 750 °C for 10 min. The residue was cooled down to room temperature and weighed. The quantity of water and MONG measured in terms of contaminants was calculated by the difference in weights as;

$$\text{Contaminant (wt.\%)} = 100 - [\text{Glycerol content (wt.\%)} + \text{Ash content (wt.\%)}] \quad (1)$$

The pH of the glycerol solution was measured with a pH meter (Mettler Toledo, MP220). The color of glycerol was measured by a UV/Vis spectrophotometer (Jasco, V-530) at a wavelength of 487 nm. The density and viscosity were measured by using a pycnometer and Oswald viscosity according to ISO 2099-1972 and ASTM D 445, respectively. The composition of the crude, pre-treated and enriched crude glycerol were analyzed by gas chromatography coupled mass spectrometry (GC/MS) on a 6890N GC-MS system (Agilent of GC/Pegosees III, Lego of MS).

3. Results and Discussion

3.1. Characteristics of the Crude Glycerol and Pre-Treated Crude Glycerol

The original crude glycerol obtained from the waste used-oil FAME biodiesel production plant was a dark brown liquid (Fig. 1(a)) with a high pH in the range of 9.5-9.8 and a low density and viscosity (Table 1) compared to that of the commercial glycerol (density and viscosity of commercial glycerol are 1.2671 g/cm³ and 267.70 cSt, respectively [14]). It contained a very low glycerol content (29.8 wt. %),

acceptable level of ash (7.90 wt. %), and has a relatively high contaminant (62.3 wt. %). The ash was largely composed of inorganic matter such as sodium salts that originated from the NaOH catalyst used in the *transesterification* process. The large quantity of contaminant might be attributed to the absorption of moisture from its surroundings during the production process and by the contamination of soap, methanol, fatty acid-glycerol esters and residual FAME from the production process. During the phase separation process, some of the fatty acids and FAME can dissolve or suspend in the glycerol solution, which can consequently react with the excess NaOH during the neutralization step to form suspended soap in the crude glycerol [17]. The composition of the crude glycerol derived from the waste used-oil FAME production plant was then analyzed by a GC/MS apparatus. Besides glycerol, the crude glycerol contained various compounds (Fig. 2(a)) including FFAs and derivatives such as lauric acid, methyl myristate, myristic acid, methyl palmitoleate, methyl palmitate, palmitic acid, methyl linoleate, oleic acid and methyl stearate which are the main components of vegetable oil.

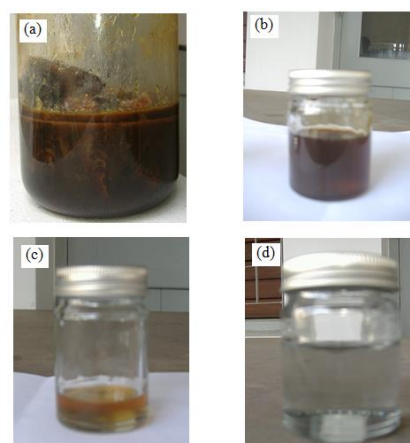


Fig. 1. Color of the (a) crude glycerol obtained from the FAME biodiesel production plant, (b) pre-treated crude glycerol, (c) enriched crude glycerol by solvent extraction with *n*-C₃H₇OH at a volume ratio of solvent to pre-treated crude glycerol of 2.0 and (d) enriched crude glycerol by adsorption with activated carbon at ratio of activated carbon to pre-treated crude glycerol of 67 g/l glycerol.

Table 1. Characteristics of the crude, pre-treated and enriched crude glycerol.

Parameters	Standard [7]	Crude glycerol	Pre-treated crude glycerol ^a	Crude glycerol enriched by chemical extraction with:		Crude glycerol enriched by adsorption ^d	Crude glycerol enriched by the combined sequential chemical extraction and adsorption	
				<i>n</i> -C ₃ H ₇ OH ^b	C ₄ H ₁₀ O ^c		<i>n</i> -C ₃ H ₇ OH + adsorption ^e	C ₄ H ₁₀ O + adsorption ^f
pH		9.5-9.8	7.0-7.2	5.5-6.0	5	5	4	4
Glycerol content (wt. %)	≥ 80	29.8 ± 0.14	51.9 ± 0.15	97.9 ± 0.02	86.6 ± 1.66	68.9 ± 0.11	99.0 ± 0.12	87.0 ± 0.01
Ash (wt. %)	≤ 10	7.90 ± 0.5	23.4 ± 1.1	0.86 ± 0.07	12.4 ± 0.06	17.0 ± 0.13	0.995 ± 0.00	10.8 ± 0.11
Other contaminant (wt. %)	≤ 10	62.3 ± 1.04	24.8 ± 0.16	1.29 ± 0.05	1.03 ± 0.31	14.1 ± 0.17	0.01 ± 0.00	2.25 ± 0.04
Density at 20 °C (g/cm ³)		1.03 ± 0.024	1.27 ± 0.03	1.28 ± 0.05	1.27 ± 0.02	1.245 ± 0.03	1.30 ± 0.00	1.25 ± 0.01
Viscosity at 40 °C (cSt)		48.3 ± 0.172	53.8 ± 1.29	na ^g	na	na	na	na
Color (Pt-Co unit)		484,855 ± 10,499	221,575 ± 7,257	15,440 ± 1,072	6,570 ± 641	1,030 ± 25	310 ± 81	285 ± 90

^a Pre-treatment by acidification with H₃PO₄ at pH= 2.5.

^b at volume ratio of solvent to pre-treated crude glycerol of 2.0

^c at volume ratio of solvent to pre-treated crude glycerol of 1.0

^d at weight by volume of adsorbent to pre-treated crude glycerol of 67 g/l

^e at volume ratio of solvent to pre-treated crude glycerol of 2.0 and adsorption at activated carbon dose of 67 g/l

^f at volume ratio of solvent to pre-treated crude glycerol of 1.0 and adsorption at activated carbon dose of 67 g/l

Meanwhile, the excess H_2PO_4^- (ionized from H_3PO_4) can couple with the Na^+ salts in the crude glycerol to form the relatively insoluble NaH_2PO_4 in glycerol [16], resulting in the formation of an inorganic salt layer on the bottom of the aqueous solution. As demonstrated in Table 1, the pre-treatment by acidification with H_3PO_4 altered the characteristics of the crude glycerol. The pH of the pre-treated crude glycerol was slightly lower at 7.0-7.2, the density increased 1.23-fold to 1.273 g/cm^3 (near that of pure glycerol), whilst the viscosity was only slightly increased. The appearance of the acid pre-treated crude glycerol was changed to a brown liquid (Fig. 1(b)), or some 2.2-fold lower (Table 1). The contaminant content was decreased 2.51-fold to 24.8 wt.%, resulting in an increase in the glycerol content to 51.9 wt. %. However, the ash content increased almost 2.96-fold in comparison with the original crude glycerol, probably due to the fact that the generated phosphate salt (NaH_2PO_4) remains partially soluble in the crude glycerol-containing water ($1.6 \text{ g/100 ml H}_2\text{O}$), leading to the contamination of this salt in the pre-treated crude glycerol. In terms of the chemical composition, the acidification stage can partially or totally remove different FFAs and derivatives such as 2 hexadecanoyl glycerol, methyl linoleate, methyl myristate, methyl palmitate, methyl palmitoleate, methyl palmitate, methyl stearate, 2 monooleoyl glycerol and oleic acid (Fig. 2(b)).

According to previous reports, the addition of a mineral acid such as H_2SO_4 [14] or H_3PO_4 [16] to crude glycerol can cause automatic phase separation into two or three distinct layers comprised of a FFA layer on the top, a glycerol-rich layer on the middle and an inorganic salt layer on the bottom. This is because the H^+ from the mineral acid can protonate the soap bulk to insoluble FFAs (Eq. (2)), which consequently separate out as a top layer due to their low density and low polarity compared to the polar glycerol.



where R is the variable hydrophobic core of the fatty acids.

3.2. Enrichment of the Pre-Treated Crude Glycerol via Solvent Extraction

To further increase the glycerol content in the crude glycerol, the pre-treated crude glycerol was then subjected to solvent extraction. Three types of polar solvent (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and $n\text{-C}_3\text{H}_7\text{OH}$) and two types of non-polar solvent (C_6H_{14} and $\text{C}_4\text{H}_{10}\text{O}$) at different volume ratios in the range of 0.5 to 4.0 were utilized at constant extraction time of 4 h and shaking rate of 200 rpm. As demonstrated in Fig. 3(a), in the presence of polar solvent, the glycerol content in enriched crude glycerol increased as the increase of volume ratio of solvent to pre-treated crude glycerol up to 2.0. This is because large quantity of polar solvent can extract large amount of glycerol from mineral salts and other contaminants. However, further increase volume ratio greater than 2.0 cannot enhance higher glycerol content in enriched crude glycerol. Oppositely, it decreased the glycerol content in enriched crude glycerol. This might be due to the fact that an excess solvent can contaminate or dissolve in enriched crude glycerol, resulting to the reduction of glycerol content.

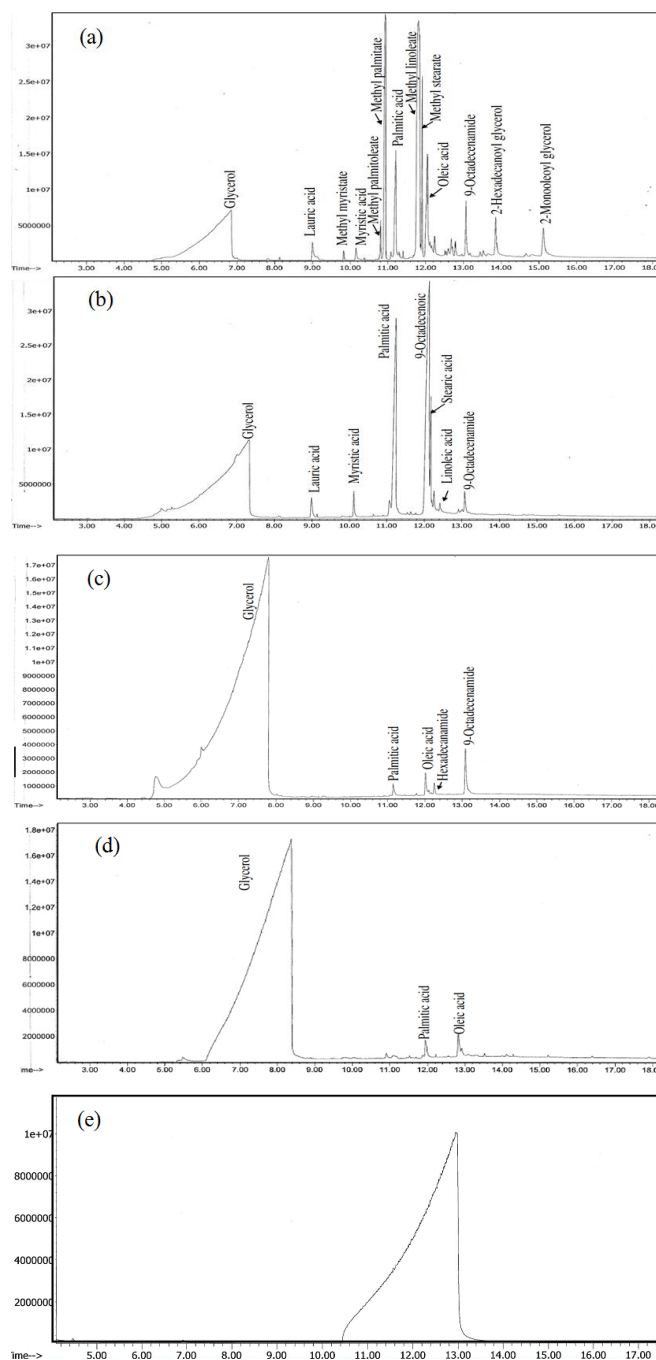


Fig. 2. Representative GC/MS spectra of the (a) original crude glycerol as obtained from the FAME biodiesel plant, (b) pre-treated crude glycerol and (c,d) enriched crude glycerol following solvent extraction with (c) $n\text{-C}_3\text{H}_7\text{OH}$ at a volume ratio of solvent to pre-treated crude glycerol of 2.0 or with (d) $\text{C}_4\text{H}_{10}\text{O}$ at a volume ratio of solvent to pre-treated crude glycerol of 1.0, and (e) adsorption with commercial activated carbon.

At volume ratio of 2.0, the highest glycerol content was observed in the enriched crude glycerol extracted by $n\text{-C}_3\text{H}_7\text{OH}$ (97.9 wt. %). With respect to the efficiency of non-polar solvent (Fig. 3(b)), using different volume ratio of $\text{C}_4\text{H}_{10}\text{O}$ and pre-treated crude glycerol in the range of 0.5-4.0 cannot alter the glycerol content in enriched crude glycerol, whilst increasing the volume ratio of C_6H_{14} and pre-treated

crude glycerol resulted to the slight increase of glycerol content in enriched crude glycerol. For all ratios, the utilization of $C_4H_{10}O$ as a solvent gave a more extraction efficiency in comparison to C_6H_{14} . The glycerol content in enriched crude glycerol extracted by $C_4H_{10}O$ was greater than that extracted by C_6H_{14} for all ratios. This is because the $C_4H_{10}O$ had a higher water solubility compared with C_6H_{14} (~6.89 and 0.001 for $C_4H_{10}O$ and C_6H_{14} , respectively [18]), resulting to a high content of water in extract phase (solvent-rich phase) and low content in raffinate phase (glycerol-rich phase). Considering the effect of solvent types and ratios on the color of enriched crude glycerol, it was evidenced that the color of enriched crude glycerol decreased of around 91.0-97.0 % in comparison to that of pre-treated crude glycerol as demonstrated in Fig. 4. This is because the utilized solvent can extract contaminants or color-generating compounds from glycerol, resulting to the reduction of color in enriched crude glycerol. Among the utilized solvents and ratios, the most color reduction (97.0 %) was observed by the utilization of $C_4H_{10}O$ at the volume ratio of solvent to pre-treated crude glycerol of 1.0, while the lowest color reduction was observed by the utilization of $n-C_3H_7OH$ as a solvent (93.0 % at the ratio of 2.0). The optimal extraction conditions for enriching the glycerol were thus $n-C_3H_7OH$ at a volume ratio of solvent to crude glycerol of 2.0 in terms of the obtained glycerol purity, but with $C_4H_{10}O$ at a corresponding volume ratio of 1.0 in terms of the color reduction. The main composition in enriched crude glycerol by solvent extraction with $n-C_3H_7OH$ and $C_4H_{10}O$ were glycerol as demonstrated in Fig. 2(c) and 2(d), respectively. As also exhibited in Table 1, the glycerol content in enriched crude glycerol by solvent extraction with $n-C_3H_7OH$ increase of around 3.28-fold, while the ash content, contaminants and color decreased of approximately 9.19-, 48.29- and 31.40-fold, respectively in comparison to the original crude glycerol. With regard to the characteristic of enriched crude glycerol by solvent extraction with $C_4H_{10}O$, the quantities of glycerol and ash in enriched crude glycerol increase of around 2.91-, and 1.56-fold, respectively. The amount of contaminants changed slightly whereas the color of crude glycerol decreased of approximately 73.79-fold.

Based on the obtained results in this part, it is difficult to decide which solvent is better between $n-C_3H_7OH$ and $C_4H_{10}O$ because the former solvent can enhance the highest purity of enriched crude glycerol (97.9 wt.%), but lowest color reduction (93.0 %), whilst the latter solvent can facilitate the low glycerol content (86.6 wt.%), but highest color reduction (97.0 %).

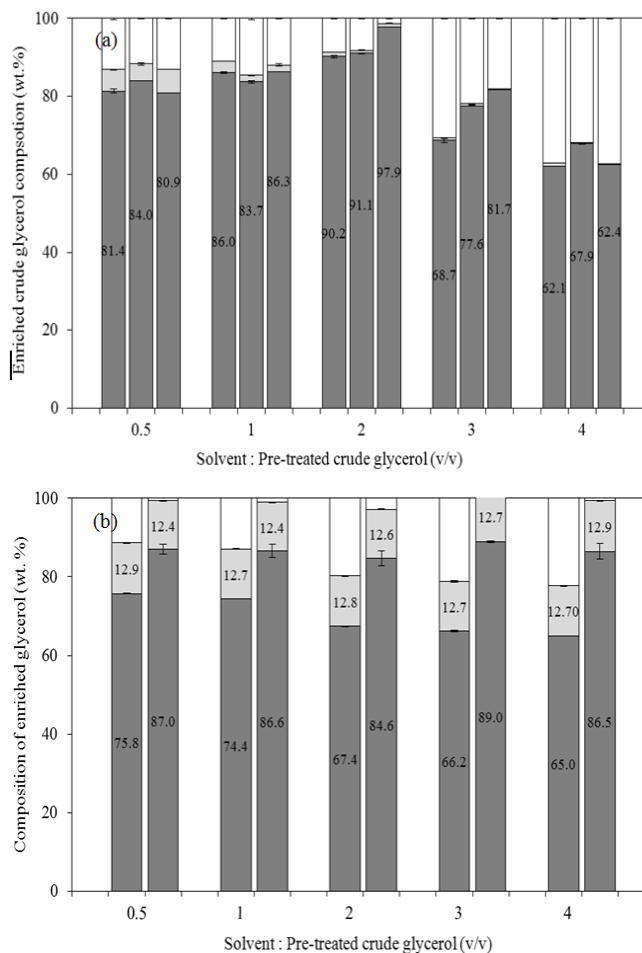


Fig. 3. Effect of solvent to pre-treated crude glycerol ratio on glycerol (■), ash (■) and other contaminant (□) contents in enriched crude glycerol purified by solvent extraction via (a) polar solvents: CH_3OH (left bar), C_2H_5OH (middle bar), $n-C_3H_7OH$ (right bar) and (b) non-polar solvents: C_6H_{14} (left bar), $C_4H_{10}O$ (right bar).

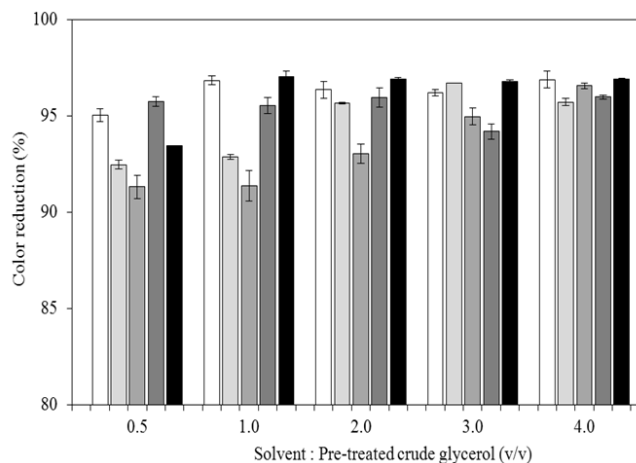


Fig. 4. Effect of solvent to pre-treated crude glycerol ratios on color of enriched crude glycerol purified by solvent extraction via CH_3OH (□), C_2H_5OH (■), $n-C_3H_7OH$ (■), C_6H_{14} (■) and $C_4H_{10}O$ (■).

3.3. Enrichment of Pre-Treated Crude Glycerol via Adsorption

The enrichment of pre-treated crude glycerol was carried out by the adsorption with commercial activated carbon at different dose in the range of 33-167 g/l during the adsorption time of 15-180 min at constant shaking rate of 200 rpm. The results evidenced that the glycerol and ash contents in enriched crude glycerol increased from initial content as the increase of adsorption time and reached their plateau after 15 min (data not shown). Further increase the adsorption time cannot enhance a more glycerol and ash reduction, they were equilibrated after 15 min. This observation could be explained by the theory of adsorption process. That is, the adsorbate molecules (mineral salt) have to first transport from the bulk solution to the surface of the adsorbent (activated carbon) and then adsorb onto the adsorbent surface [19]. The former stage occurs on the adsorbate-free surface, so the adsorbate molecules arriving the surfaces of adsorbent may attach instantly, resulting in a fast reduction of mineral salt substance. The rate of adsorption during this period may be dominated by the transportation of pollutant molecules from the bulk solution to the adsorbent surfaces. On the other hands, the latter stage occurs on the adsorbate-covered surface and the rate of adsorption during this period may be controlled by the adsorption kinetics. Thus, the rate of adsorption may be slow depending on the quantity of free active site of adsorbent. In our case, the fast adsorption rate occurred during the former period consistently with the adsorption theory. No more adsorption during the latter period might be attributed to the equal rate of adsorption and desorption of mineral salt on activated carbon surface [20]. Regarding to the effect of ratio of activated carbon to pre-treated crude glycerol, the adsorbent dose slightly affected the content of glycerol as well as ash contents in enriched crude glycerol as demonstrated in Fig. 5. However, increasing the adsorbent dose in the range of 33-167 g/l glycerol resulted to a slight decrease in the glycerol content. Nevertheless, a higher dose can achieve a higher color reduction.

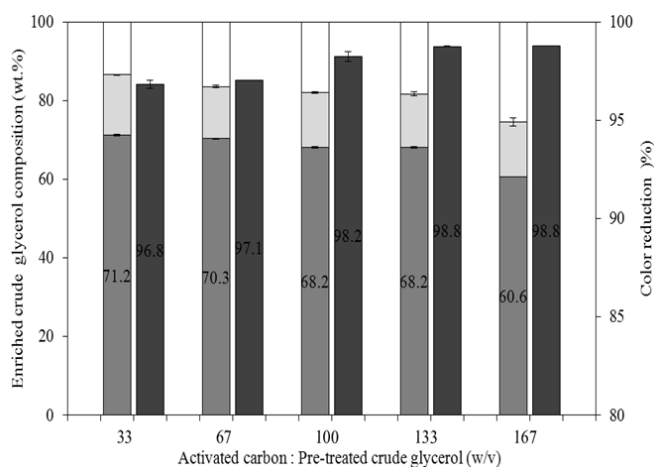


Fig. 5. Effect of activated carbon to pre-treated crude glycerol ratios on composition of enriched crude glycerol (left bar) including glycerol (■), ash (■), and other contaminant (□) contents and color (right bar) purified by adsorption with activated carbon at 180 min.

A clear color of glycerol with greater than 97% color reduction is being obtained with the commercial activated carbon at 67 g/l glycerol at 180 min. The characteristics of the enriched crude glycerol with the process by the adsorption with activated carbon were also demonstrated in Table 1. The glycerol and ash contents in enriched crude glycerol increased of approximately 2.31- and 2.15-fold, while the contaminants and color decreased of approximately 4.42 -and 471-fold, respectively in comparison to the original crude glycerol. The composition of enriched crude glycerol obtained by the enrichment by adsorption with activated carbon at the dose of 67 g/l as displayed in Fig. 2(e). The principle composition is glycerol.

To further increase the glycerol purity and decrease the color in the enriched glycerol, a sequential process of extraction with either $n\text{-C}_3\text{H}_7\text{OH}$ or $\text{C}_4\text{H}_{10}\text{O}$ at volume ratio of solvent to pre-treated crude glycerol of 2.0 or 1.0, respectively, was followed by activated carbon adsorption at 67 g/l glycerol. A significant increase in the glycerol purity was obtained (up to 99.1%) after the combined sequential process of $n\text{-C}_3\text{H}_7\text{OH}$ extraction and carbon adsorption, while only a slight increase in the glycerol content was obtained in the case of the corresponding process of $\text{C}_4\text{H}_{10}\text{O}$ extraction and carbon adsorption (Table 1). Surprisingly, the color of glycerol obtained in both combined processes was not reduced as much as that by the adsorption with activated carbon alone (Table 1). This might be due to the complete elimination of water and MONG levels, leaving a more heavily enriched crude glycerol. The properties of the crude glycerol enriched by our proposed approach compared with that of the other published reports were summarized in Table 2. Direct comparison is difficult since the initial glycerol content in each crude glycerol source as well as the contaminants was different and depended on the type of raw material used in the process. Regardless, using waste used-oil as a raw material for biodiesel production generates a low-grade crude glycerol, and it was noticed that our combined approach was more efficient to enrich crude glycerol than the simple distillation [21], the electrodialysis [10], a combined process of neutralization, microfiltration and ion exchange resin [13], the saponification and neutralization procedures [4] and a step-by-step chemical enrichment [15].

The operating cost of chemical/material used in glycerol enrichment by either solely chemical extraction or adsorption and a combined process were estimated based on the properties of utilized crude glycerol as well as the developed enrichment approach, and summarized in Table 3. For the acidification step, two types of chemical substance were used; H_3PO_4 and NaOH . The yield of this step was approximately 65%. With respect to the enrichment of pre-treated crude glycerol by either chemical or process, the chemical enrichment by $\text{C}_4\text{H}_{10}\text{O}$ was cheaper than that of $n\text{-C}_3\text{H}_7\text{OH}$ (8.09- and 11.4 USD/l for $\text{C}_4\text{H}_{10}\text{O}$ and $n\text{-C}_3\text{H}_7\text{OH}$, respectively) while the cheapest cost (0.59 USD/l) was observed in case of adsorption process. However, the yield of enriched crude glycerol was in the reverse order as demonstrated in Table 3. The chemical extraction with $n\text{-C}_3\text{H}_7\text{OH}$

Table 2. Comparison of the enriched glycerol properties obtained from this work and other works.

Author(s)	Sources of crude glycerol	Glycerol (wt.%)		Ash (wt. %)		Contaminant (wt.%)		Color
		w_i	w_f	w_i	w_f	w_i	w_f	
Yong et al [21] ^a	Residual glycerol from chemical and physical treatment of olive oil	50.4	96.60	17.0	0.03	32.6	3.4	-
Schaffner et al [10] ^b	Synthetic solution	65	95	2	0.054	8	1.01	-
Isahak et al [13] ^c	Palm oil <i>transesterification</i> (homogeneous catalyst)	96.66	97.47	-	-	3.34	2.53	-
Hájek and Skopal [4] ^d	<i>Transesterification</i>	56.4-58.9	86	-	-	-	-	-
Kongjao et al [14] ^e	<i>Transesterification</i> of waste used-oil	28.6	93.3	2.7	0.00045	68.8	6.7	light brown
Javani et al [15] ^f	<i>Transesterification</i> of waste used-oil	-	96.08	-	-	-	-	-
This work ^g	<i>Transesterification</i> of waste used-oil	29.8 ± 0.14	99.01 ± 0.12	7.90 ± 0.5	1.013 ± 0.04	62.3 ± 1.04	na	almost clear

w_i initial content of glycerol and impurities in the crude glycerol

w_f final content of glycerol and impurities in the crude glycerol

^aBy simple distillation

^bBy electro dialysis

^cBy combination process of neutralization, microfiltration and ion exchange resin

^dBy saponification and neutralization procedures

^eBy acidification by H₂SO₄

^fBy step-by-step chemical enrichment

^gPurify at volume ratio of solvent to pre-treated crude glycerol of 2.0 and adsorption at activated carbon dose of 67 g/l

^hNot detected

Table 3. Operating cost analysis of chemical/material for glycerol enrichment via chemical extraction and physical adsorption processes.

Estimated cost for 1 liter glycerol enrichment	Quantity of used chemical/material (l or g)	Actual cost of chemical/material (USD)	Quantity of obtained glycerol (l)
I. Pre-treated crude glycerol by acidification			
H ₃ PO ₄	0.2	2.71	0.650
NaOH	0.375	2.42	
II. Enrichment of glycerol via chemical extraction or physical adsorption			
Extraction with <i>n</i> -C ₃ H ₇ OH	1.30	11.4	0.624
Extraction with C ₄ H ₁₀ O	0.65	8.09	0.507
Physical adsorption with activated carbon	0.215	0.59	0.232
III. A combined process of chemical extraction and physical adsorption			
Extraction by <i>n</i> -C ₃ H ₇ OH and adsorption with activated carbon			
Extraction with <i>n</i> -C ₃ H ₇ OH	1.30	11.4	0.416
Physical adsorption with activated carbon	20.6	0.57	
Extraction by C ₄ H ₁₀ O and adsorption with activated carbon			
Extraction with C ₄ H ₁₀ O	0.65	8.09	0.338
Physical adsorption with activated carbon	16.73	0.46	
Summary			
Enrichment cost by extraction with <i>n</i> -C ₃ H ₇ OH (USD/l crude glycerol)			16.6
Enrichment cost by extraction with C ₄ H ₁₀ O (USD/l crude glycerol)			13.2
Enrichment cost by extraction with activated carbon (USD/l crude glycerol)			5.72
Enrichment cost by extraction with <i>n</i> -C ₃ H ₇ OH and adsorption with activated carbon (USD/l crude glycerol)			17.1
Enrichment cost by extraction with C ₄ H ₁₀ O and adsorption with activated carbon (USD/l crude glycerol)			13.7

C₃H₇OH provided the highest yield of enriched crude glycerol and the adsorption process donated the lowest yield. By using a combined approach, the chemical extraction with *n*-C₃H₇OH and adsorption was more expensive than that of the chemical extraction with C₄H₁₀O and adsorption of around 28.6%. However, more yield of enriched crude glycerol was obtained in the former approach. For the whole enrichment process, based on equal quantity of crude glycerol, it was noticed that the adsorption process was cheapest process (5.72 USD/l crude glycerol) while a combined process of chemical extraction with *n*-C₃H₇OH and adsorption was the most costly (17.1 USD/l crude glycerol). The different cost of both approaches was around 11.40 USD/l. Based on the quantity of an obtained enriched crude glycerol, the operating cost of both approaches was increased to 26.4 and 41.2 USD/l enriched crude glycerol, respectively. According to this analysis, it seemed to be that

the operating cost of glycerol enrichment increased with the increase of enrichment step, while the yield of enriched crude glycerol decreased.

4. Conclusion

The enrichment of crude glycerol derived from a waste used-oil FAME biodiesel plant was performed by solvent extraction and adsorption. For the solvent extraction, types of solvent as well as the volume ratio played an importance role on the purity and color of enriched crude glycerol. Among the utilized solvent and ratio, the *n*-C₃H₇OH at the volume ratio of solvent to pre-treated crude glycerol of 2.0 was the best of the evaluated solvents, yielding a glycerol purity of 97.9 wt.% and reducing the color level by around 93.0%, whereas extraction with C₄H₁₀O at its optimal ratio of 1.0 yielded a higher color removal efficiency (97.0%) but a

lower glycerol purity (86.6 wt.%). For the adsorption process, the adsorption with activated carbon was poor at improving the glycerol purity (70.3 wt.%), but it can decrease the color in the glycerol by 97.1% at 67 g/l. A combined process of solvent extraction with $n\text{-C}_3\text{H}_7\text{OH}$ followed by adsorption gave a high glycerol purity (99.0 wt.%) and reduction in the color (99.1%), but it was costly (41.2 USD/l enriched crude glycerol). Thus, the operation should be balanced between its enrichment efficiency and operating cost.

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