

Purification of crude glycerol derived from waste used-oil methyl ester plant

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Abstract—The purification of crude glycerol from a biodiesel plant using waste used-oil as a raw material was carried out on a laboratory scale by using the combined chemical and physical treatments based upon repeated cycles of acidification to the desired pH within the range of 1–6 using 1.19 M H_2SO_4 , allowing phase separation and harvesting of the glycerol-rich middle phase followed by neutralization of the harvested glycerol phase with 12.5 M NaOH. Subsequently, the glycerol-enriched fraction was extracted by ethanol. The results indicated that increasing the pH of the acidification step led to an increased yield of the glycerol-rich layer and decreased amount of inorganic salt and free fatty acids phase. Under strong acid conditions, large quantities of fatty acid and salt in the glycerol-enriched fraction were eliminated and, at pH 1, high purity glycerol (~93.34%) with relatively low contaminant levels (0.00045% (w/w) ash and 5.16% (w/w) MONG) was obtained.

Key words: Crude Glycerol, Purification, Biodiesel, Glycerol-rich Layer, Waste

INTRODUCTION

Glycerol, or propan-1, 2, 3-triol, is an important commercial by-product of the biodiesel production process from the transesterification reaction of triglycerides, from spent or new vegetable oils or fats and waste oil, with alcohols, like methanol and ethanol, in the presence of a homogeneous base catalyst like NaOH or KOH [1–3] and acid catalyst [4]. In general, the production of every 10 kg of biodiesel yields approximately 1 kg of crude glycerol (10% (w/w)) [5], and currently the world's capacity for biodiesel production is increasing dramatically including within Thailand, where the recent yearly increase is 40% from less than 1.5×10^6 liters/day in 2007 to an expected 2.1×10^6 liters/day in 2008. Any further increase in biodiesel production rates will significantly raise the quantity and surplus of crude glycerol and partially purified glycerol in the environment. In contrast to the surplus of glycerol and impure glycerol, high purity glycerol is an important industrial feedstock for applications in the food, cosmetic and pharmaceutical industries, as well as other more minor uses, but it is costly to refine crude glycerol, especially for medium- and small-sized plants [6]. The conventional process used to recover or purify crude glycerol is based upon the chemical and physical treatment. For example, Ooi et al. [7] attempted to recover crude glycerin, crude fatty acids and salt from the glycerol residue waste derived from a palm kernel oil methyl ester plant by using 6% (v/v) H_2SO_4 . They reported that chemical treatment at a low pH was better as it increased the glycerol and reduced the ash contents in the recovered crude glycerin. However, the matter organic non glycerol (MONG) content was slightly increased. The treatment also increased the recovered salt and reduced the crude glycerin proportions, and did not affect the recovery of crude fatty

acids, but despite this was relatively suitable for recovering crude glycerine from a dilute glycerol source (10–20% (w/w) glycerol) with a high NaCl (60–70% (w/w)) presence, such as that found in glycerol residues. Yong et al. [8] reported the recovery of crude glycerin from glycerol residues by a simple distillation at 120–126 °C and 0.04–0.4 mbar to yield around 141.8 g glycerin/kg glycerol residue (~14% yield) at an acceptable purity of 96.6% (w/w) glycerol, with 0.03% (w/w) ash, 1% (w/w) H_2O and 2.4% (w/w) MONG as contaminants. Hazimah et al. [9] used the combined process of chemical and physical treatment (acid protonation, ether and ethanolic extractions, filtration and distillation) to recover glycerol and diglycerol from glycerol pitch, recovering high purity glycerol (~99.1–99.8% (w/w)) with low contaminants (0.11–0.80% (w/w) H_2O , 0.054% (w/w) ash and 0.56% (w/w) soap). Using other glycerol sources, such as spent soap lye, Israel et al. [10] found that the amount of the recovered glycerin and residual salts depended upon the quality of the spent lye and the technology employed in the recovery treatment.

In this work, the purification of crude glycerol from the transesterification reaction of a waste used-oil of the biodiesel plant was carried out by using a combination of the chemical and physical treatment with solvent extraction because of its easy in operation, low operating cost, high efficiency and its possibility to reuse the used solvent. The effect of pH in the acidification stage of the purification system on the properties of the purified crude glycerol was explored.

EXPERIMENTAL

Crude glycerol was obtained from a local biodiesel plant in Thailand that utilized waste used-oil as the raw material for biodiesel production via the alkali mediated transesterification process. During the purification step at a laboratory-scale experiment, 1 kg of crude glycerol was acidified by the addition of 1.19 M H_2SO_4 (98%, Mallinckrodt) to the desired pH, left for a while until the solution

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Table 1. Characteristics of crude and enriched glycerol, according to BS standards, from a waste used-oil biodiesel plant, and compared to that of commercial glycerol

Parameters	BS 2622:1979 [4]	Commercial glycerol (Fisher)	Crude glycerol	Purified crude glycerol
pH		6.97	10-11	7.03-7.12
Glycerol content (%)	>80	99.98	27.31-30.25	92.90-93.78
Ash content (%) (ISO 2098-1972)	<1.0	0.0002	2.96-3.34	0.0004-0.0005
Water content (%) (ISO 2097-1972)	No	0.01	5.10-8.20	1.5
Matter organic non glycerol (MONG) (%) (ISO 2464-1973)	<1.5	0.0008	50.50-61.81	4.72
Density at 20 °C (g/cm ³) (ISO 2099-1972)		1.2671	1.0181	1.25-1.25
Viscosity at 40 °C (cSt) (ASTM D 445)		267.70	42.41	201-207
1,3-propanediol (%)	<0.5	0	0	0
Color		Clear	Dark brown	Light brown

phase separated into three distinct layers, which is a top layer of free fatty acids, the middle glycerol-rich layer and the bottom inorganic salt rich layer. The top layer was removed by slow decantation and the middle layer then harvested and filtered. After selective harvesting of the middle layer, it was neutralized with 12.5 M NaOH (98%, Carlo) and evaporated at 105 °C for 2 h to eliminate the residual water followed by filtration to eliminate the precipitated salt. The enriched glycerol was then extracted with excess C₂H₅OH (99.9%, Merck) to encourage the precipitation of the salts for 10 min, harvesting the glycerol-ethanol solution and filtered again to eliminate the crystallized salt. The purified crude glycerol was then obtained after evaporation of the ethanol at 80 °C for 20 min.

The concentration of glycerol was analyzed by high performance liquid chromatography (HPLC: Shimadzu LC-10ADvp) with a RID-10A refractive index detector, and by FTIR. For the HPLC analysis, the stationary phase was a Pinnacle II C18 column (240×4.6 mm) and the mobile phase was a 96.7 : 3.3 (v/v) ratio of 5 mM H₂SO₄: pure methanol, passed through the column at 0.6 ml/min. The water content was measured following the standard method ISO 2097-1972 by using the volumetric Karl Fisher titration. Ash content was analyzed according to the standard method ISO 2098-1972 by burning 1 g glycerol in muffle furnace at 750 °C for 3 h. For MONG, it was calculated by the difference from a hundred of the previous three compositions (100 – (% glycerol content + % water content + % ash content)). The pH of the glycerol solution was measured by pH meter (Mettler Toledo, MP220). In addition, FTIR (DF3C206A, Thermo), GC/MS (6890N, Agilent of GC/Pegosees III, Lego of MS) and ¹³C-NMR (400 MHz, Mercury 400, Varian, USA) based analysis of the samples were used to analyze the characteristics of the crude starting and purified final glycerol.

RESULTS AND DISCUSSION

1. Characteristics of the Original Crude Glycerol from Waste Used-oil Biodiesel Plant

The original crude glycerol from the waste used-oil methyl ester

plant was a dark brown liquid with a high pH, in the range of 10-11, and a low density and viscosity compared with commercial glycerol. Indeed, it was found to only contain between 27.31-30.25% (w/w) glycerol with a high content of ash, water and MONG contaminants, as summarized in Table 1. The ash content (2.96-3.34% (w/w)) was largely composed of inorganic matter, such as sodium salts, that originated from the utilized catalyst (NaOH) in the transesterification process, while the water content (5.10-8.20% (w/w)) might be attributed to the absorption of moisture from its surrounding during the production process. By far the largest contaminant was MONG (50.50-61.81% (w/w)), which indeed exceeded the glycerol levels, and was generated by the contamination of soap, methanol and methyl esters in the glycerol residue from the biodiesel production process. During the acidification and phase separation based purification stage, some of the fatty acids were released as soluble soap, and some of methyl esters dissolved or suspended in the glycerol solution. These free fatty acids and methyl esters then reacted with the excess NaOH in the subsequent neutralization step to re-form soap which remained in the glycerol residue [6]. The composition of the crude glycerol was analyzed by FTIR and compared to commercial glycerol (Fig. 1(b)). The main functional groups of commercial glycerol, including the O-H stretching at 3,350 cm⁻¹, C-H stretching at 2,880 and 2,930 cm⁻¹, C-O stretching at 2,100 cm⁻¹, C-O-H bending at 1,400 to 1,460 cm⁻¹, C-O stretching from 1,450 cm⁻¹ (primary alcohol) to 1,100 cm⁻¹ (secondary alcohol), O-H bending at 920 cm⁻¹ and also the H₂O blending at 1,650 cm⁻¹ were clearly resolved. However, the spectra of the original crude glycerol obtained from the waste used-oil biodiesel plant (Fig. 1(a)) additionally showed strong FTIR peaks at 1,580 cm⁻¹ and 1,740 cm⁻¹, and a small band at 3,050 cm⁻¹, indicating the presence of some impurities. The sharp band at 1,580 cm⁻¹ represented the presence of COO⁻ function of soap. The small band at 3,050 cm⁻¹ indicated the presence of unsaturated C=C compound(s), supported by the positive result attained with the Baeyer test by KMnO₄ (data not shown). The sharp peak at 1,740 cm⁻¹ indicated the presence of C=O compound(s) of an ester or carboxylic acid of fatty acid. The crude

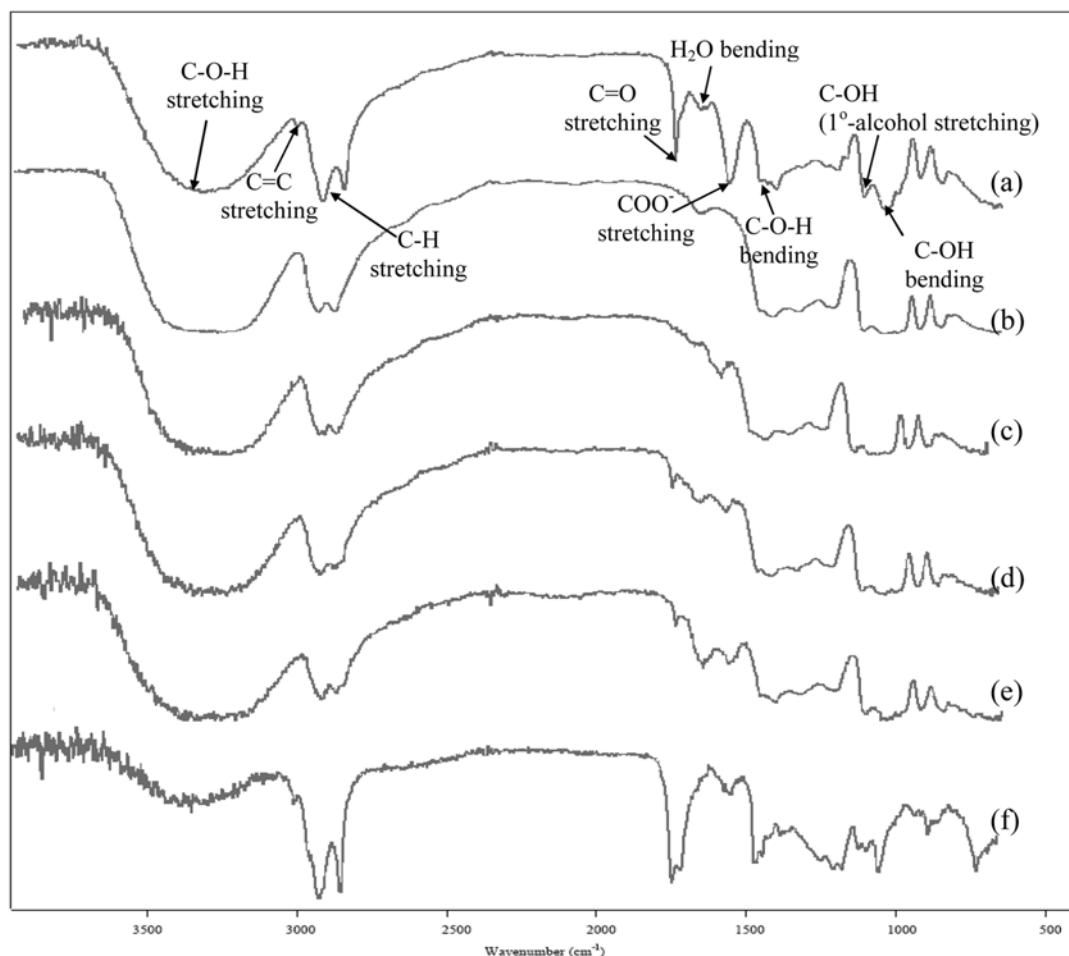


Fig. 1. Representative FTIR spectra of the crude glycerol (a), a commercial glycerol solution (b), and the purified crude glycerol with the acidification stage performed at a pH of 1.0 (c), 2.2(d), 3.5 (e) and 6.0 (f).

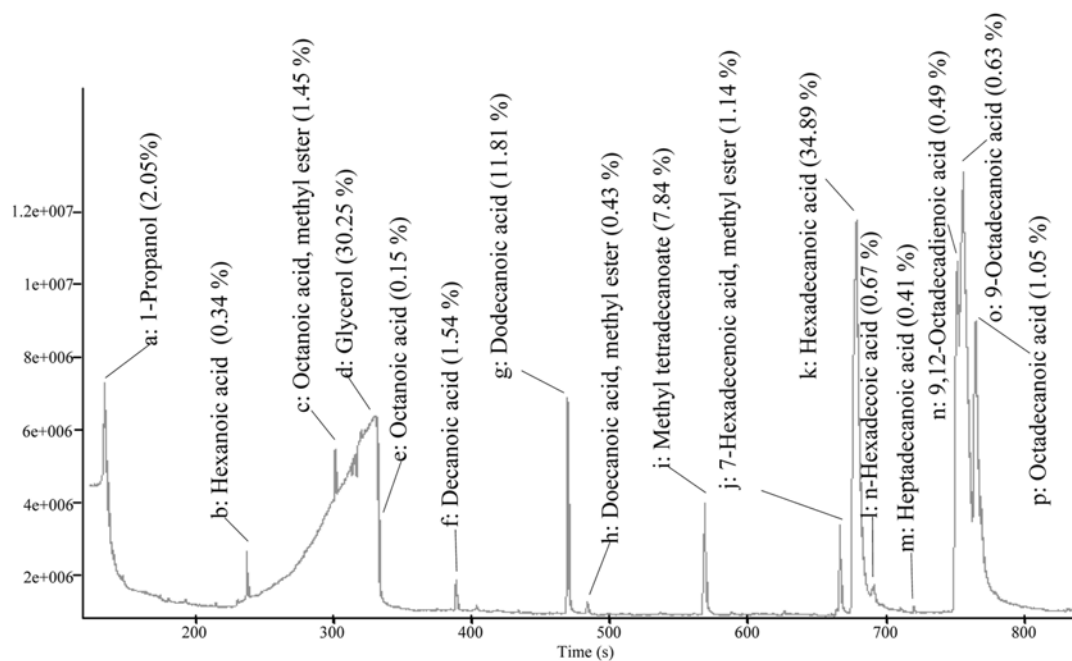


Fig. 2. Representative GC/MS spectra of the crude glycerol obtained from the waste used-oil biodiesel transesterification plant.

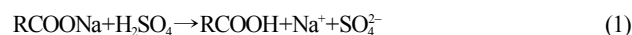
glycerol was also characterized by GC/MS (Fig. 2), which revealed that while the principal compound found in the original crude glycerol was glycerol, in agreement with the data in Table 1, the main fatty acids and methyl esters contaminating the crude glycerol were the saturated aliphatic fatty acid compounds, hexadecanoic acid or palmitic acid (34.89% (w/w)), dodecanoic acid or lauric acid (11.81% (w/w)); methyl tetradecanoate (7.84% (w/w)) and unsaturated aliphatic fatty acid compounds such as octadecenoic acid or oleic acid (1.05% (w/w)).

2. Composition and Characteristics of the Purified Crude Glycerol

After the addition of H_2SO_4 to the original crude glycerol to the desired final pH, it automatically phase separated into three distinct layers, the inorganic salt layer on the bottom, a glycerol-rich layer in the middle and the free fatty acid layer on the top. The inorganic salt layer and the free fatty acid layer were removed by gravitational decantation and filtration. The glycerol-rich layer contained methanol, methyl esters and a significant amount of soap, formed by the reaction of the alkaline catalyst (in this case NaOH) and the waste used-oil substrate. Fig. 3 shows the fraction of all distinct layers at all investigated pH values. It can be seen that increasing the pH during the acidification step from 1.0 to 6.0 led to an increase in the volume of glycerol-rich layer from 60.7 to 89.6%, but concomitantly decreased the catalyst-sulfate and free fatty acid layers from 0.87 to 0.04% and 38.5 to 10.3%, respectively. This might be attributed to the fact that the strong acid condition can neutralize the alkaline catalyst, which precipitated out as the bottom layer, and also achieve the hydrolysis to insoluble (uncharged as protonated) free fatty acids as the top layers.

To obtain high purity glycerol, the glycerol-rich layer was then neutralized with NaOH and extracted with ethanol as mentioned in the experimental section. The FTIR spectrum of the purified crude glycerol at various pH values in the range of 1.0-6.0, compared with the spectra of the commercial glycerol and the crude glycerol, revealed the principal functional groups of all glycerol solutions were similar

(Fig. 1). Namely, each preparation had the peaks of the O-H stretching at $3,350\text{ cm}^{-1}$, C-H stretching at $2,880$ and $2,930\text{ cm}^{-1}$, C-O stretching at $2,100\text{ cm}^{-1}$, C-O-H bending at $1,400$ to $1,460\text{ cm}^{-1}$, C-O stretching from $1,450\text{ cm}^{-1}$ (primary alcohol) to $1,100\text{ cm}^{-1}$ (secondary alcohol), O-H bending at 920 cm^{-1} and also H_2O blending at $1,650\text{ cm}^{-1}$. However, all the purified crude glycerol samples, from all pH values, revealed a much smaller peak at $1,580\text{ cm}^{-1}$, representing the presence of COO^- function of soap, than the original crude glycerol, and this was reduced to a greater extent as the pH in the acidification stage of the glycerol purification was reduced. This was attributed to the fact that the acidification of the crude glycerol helps to reduce and convert the soap bulk to insoluble protonated (uncharged) free fatty acids, according to reaction (1).



Under strong acidic conditions, large amounts of free fatty acid were separated. In addition, the strong FTIR bands at $1,710$ and $3,050\text{ cm}^{-1}$ in the original crude glycerol, indicating the presence of unsaturated aliphatic of carboxylic acid compound(s), were extremely reduced under strong acidic enrichment conditions and even disappeared in the spectra of the glycerol purified at pH 1.0. This emphasized that a large amount of impurities were eliminated under these acidic conditions.

Indeed, the pH of the acidification stage during the chemical treatment had a significant effect on the composition of the purified crude glycerol (Fig. 4). The ash contents in the purified crude glycerol were lower than the original level in crude glycerol from the waste used-oil biodiesel plant, but were lower still when treated at a low pH than when treated at a higher pH. This might be due to the excess sulfate ions from the ionized H_2SO_4 , added during the acidification stages, complexing with the sodium ions from the contaminated salts in the crude glycerol to form the relatively insoluble Na_2SO_4 in aqueous solution, particularly at a low pH, and consequently crystallized out during the phase separation and evaporation steps [8]. Hence, the crude glycerol purified at a low pH con-

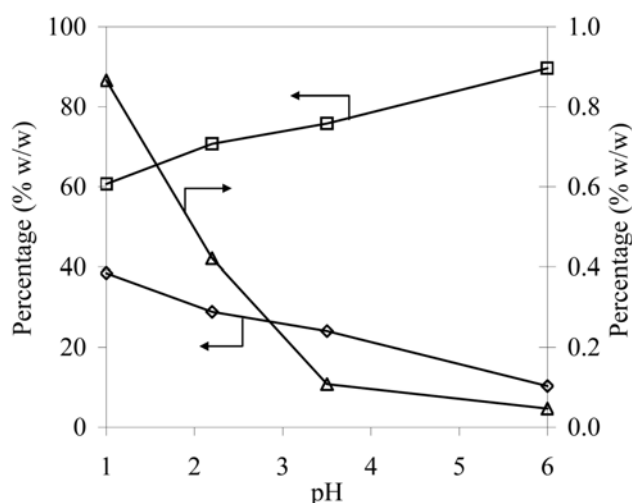


Fig. 3. Weight fraction of the three distinct phases (layers), the top free fatty acid layer (◇), the middle glycerol-rich layer (□), and the bottom inorganic salt layer (△), obtained from the H_2SO_4 acidification stage of glycerol purification at different pH values.

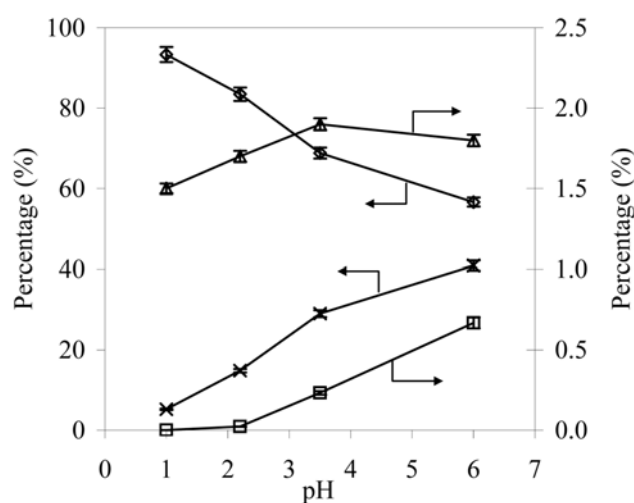


Fig. 4. Effect of pH in the acidification stage of glycerol purification, from the crude glycerol liquid obtained from a waste used-oil biodiesel plant, upon the composition of the purified crude glycerol; assayed as glycerol content (◇), ash content (□), water content (△) and MONG (×) content.

tained less salts, measured in terms of ash content. For MONG, its fraction in the purified crude glycerol, at all pH values used in the acidification mediated phase separation stage, was lower than that in the crude glycerol before treatment. Increasing the pH of the purification system led to an increase in the MONG content, because a large amount of free fatty acid was separated from the crude glycerol under strong acid conditions, leading to a lower amount of MONG in the purified crude glycerol. Nevertheless, it is difficult to completely eliminate MONG contamination in the purified crude glycerol by this methodology for two reasons. First, the re-formation and contamination of the glycerol by soap formed from the reaction between excess NaOH in the neutralizing stages and the dissolved short (C_{6-8}) and medium chain (C_{10-14}) fatty acids, generated from the soap hydrolysis in the acidic stages and then dissolved in the polar glycerol phase rather than partitioned into the upper free fatty acid phase, or the reaction with some of the short and medium chain methyl esters dissolved or suspended in the glycerol phase [3]. Second, the degradation of glycerol to acrolein as the temperature exceeds 60°C , during the purification step [9]. The water content changed slightly, within the range of 1.5–1.8% (w/w), during the purification process. The glycerol content, of course, decreased in content with the increasing pH of the acidification stages in the purification system, since at a low pH large quantities of fatty acid and salt were eliminated resulting in a concomitant increase in the relative glycerol content.

The ^{13}C -NMR of commercial glycerol demonstrated the signal at 66.4 and 74.3 ppm, indicating the presence of the aliphatic carbon of the 1°- and 2°-alcohol of the glycerol molecule, respectively (Fig. 5). With respect to the spectrum of the original crude glycerol, in addition to the expected glycerol-derived signals at 66.4 and 74.3 ppm it had additional signals at 184 ppm of carboxyl compounds ($-\text{COOH}$), 131 ppm of unsaturated aliphatic of hydrocarbon ($-\text{C}=\text{CH}-$), 49.5 ppm of alpha methyl ester compounds, 39 ppm of alpha aliphatic carbon of carboxyl group ($-\text{CH}_2\text{COOH}$), 20–35 ppm of aliphatic carbon in long chain hydrocarbon compounds $[-\text{CH}_2-\text{CH}_2-]_n, n=6-16$ and 16 ppm of methyl group ($-\text{CH}_3$), indicating the presence of contaminants in the crude glycerol. After the chemical and physical purification, however, the purified crude glycerol revealed only the glycerol-derived signals only at 74.3 and 66.4 ppm, similar to the

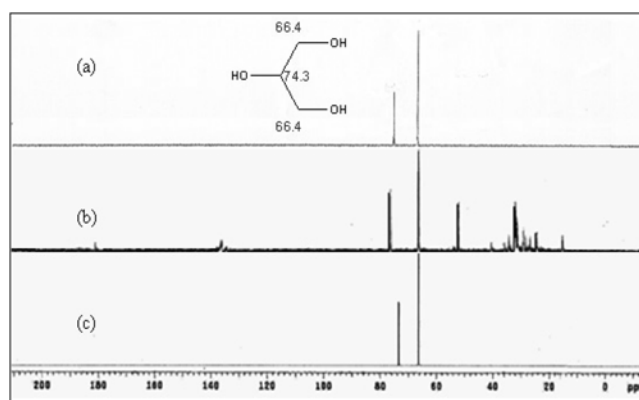


Fig. 5. Representative ^{13}C -NMR spectrum of a commercial glycerol (a), the crude glycerol (b) and the purified crude glycerol at pH 1 (c).

commercial glycerol. Thus, the chemical and physical purification outlined in this work was effective at purifying the original crude glycerol from the waste used-oil biodiesel plant to a level that is close to that of commercial glycerol, at least at a laboratory scale.

Table 1 also shows the characteristics of the purified crude glycerol obtained in this work compared with the BS standard and commercial glycerol. Although the amount of glycerol and ash in the purified crude glycerol was in the range of the BS standard, the quantities of water and MONG were still higher than the acceptable values. To increase the purity of the purified crude glycerol and decrease amount of water and MONG, the further work should be performed with the non-polar organic solvent such as hexane or diethyl ether to eliminate the free fatty acid or with polar solvent such as isopropanol to extract glycerol from the glycerol-rich phase. With respect to the color of the purified crude glycerol derived from this work, it is light brown liquid. Therefore, further work such as adsorption process should be carried out to reduce its color.

Table 2 summarized the properties of the purified crude glycerol of this work compared with the other works. It can be seen that the chemical and physical treatments are effective not only for the crude glycerol obtained from the biodiesel plant with the virgin oil such as

Table 2. Comparison of purified crude glycerol properties obtained from this work with other works

Author (s)	Source of crude glycerol	Purification procedure	Glycerol (% w/w)		Ash (% w/w)		MONG (% w/w)		Water (% w/w)	
			(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Asher and Simpson [11]	Soap lye solution	Ion extraction	7.5	82.5	13	7				
Ooi et al. [7]	Transesterification of palm kernel oil	Chemical and physical treatment	17.7	51.4	58.7	13.8	17.7	25.9	5.9	8.9
Hazimah et al. [9]	Fatty acid plant	Chemical and vacuum distillation	70	99.3	4	7				
Schaffner et al. [12]	Synthetic solution	Bipolar electrodialysis	65	95	2	0.054	4	0.56	4	0.45
This work	Transesterification of waste used-oil	Chemical and physical treatment	28.56	93.34	2.65	0.00045	56.13	5.16	6.7	1.5

(a) Concentration of glycerol and impurities content in the original crude glycerol

(b) Concentration of glycerol and impurities content in the purified crude glycerol

palm kernel oil but also for the waste used-oil. However, the weight percent of purified crude glycerol from this work was higher than that from the work of Ooi et al. [7] of around 1.82 fold. This might be attributed to the utilization of different solvent during the extraction step. With respect to the effect of purification procedure, it seems to be that our treatment was more effective than the ion extraction [11] but less effective than that of bipolar electrodialysis [12] and chemical and vacuum distillation [9]. However, the former has very low original glycerol content (7.5% w/w) and the latter has very high glycerol content (70 and 65% w/w). It is difficult to mention which procedure is the best. Nevertheless, the chemical and vacuum distillation is the 2-step purification including chemical method and vacuum distillation requiring high temperature (110-120 °C) and low pressure (0.1-3 mbar), which is hard to control in actual operation. For the ion extraction and bipolar electrodialysis, their performance strongly depends on the concentration of impurities in crude glycerol. In the presence of high impurity content, some contaminated ions such as Na^+ and fatty acid can deposit on the membrane surface leading to lower the purification efficiency.

CONCLUSIONS

The purification of glycerol from a crude glycerol containing (27-30% (w/w)), derived from a waste used-oil biodiesel transesterification plant, was achieved using the combined approach of chemical and physical treatments. The original high content of ash, water and especially MONG was successfully removed. The main fatty acid and methyl ester contaminants in the crude glycerol were hexadecanoic acid, dodecanoic acid and methyl tetradecanoate. Acidification with H_2SO_4 led to phase separation into three distinct layers, a free fatty acid top layer, a glycerol-rich layer middle layer and an organic salt layer at the bottom. Increasing the pH during the acidification step led to an increased glycerol yield but at the cost of purity with increased salt (ash) and free fatty acid contamination levels. An acceptably high purity level of glycerol (~93.34% (w/w)) with low contaminants (0.00045% (w/w) ash and 5.16% (w/w) MONG) was obtained at pH 1. To encourage the results of this part in actual application in small or medium industrial plant scale, some work

to still needs be established as mentioned above. In addition, the environmental costs of the disposal of the waste components and costs of acid-alkali rounds plus chemical extraction need to be explored.

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