Journal of Oil Palm Research Vol. 13 No. 2, December 2001, p. 39-44

REFINING OF CRUDE GLYCERINE RECOVERED FROM GLYCEROL RESIDUE BY SIMPLE VACUUM DISTILLATION

YONG, K C*; OOI, T L; DZULKEFLY, K*;**
WAN YUNUS, W M Z* and HAZIMAH, A H**

ABSTRACT

Glycerol residue obtained from the refining of glycerol in a palm kernel oil methyl ester plant is a schedule waste and can be processed to recover its glycerol. On average, 141.8 g (14.2%) distilled glycerine (97% purity) were recovered from 1 kg glycerol residue by a simple vacuum distillation at 120°C - 126°C and 4.0 x 10^{-1} - 4.0 x 10^{-2} mbar pressure. The pH for the distillation was kept <5 in order to avoid foaming. The characteristics of the distilled glycerine were: 96.6% glycerol, 0.03% ash, 1% water (Karl Fischer method), 2.4% matter organic non-glycerol (MONG) and pH 3.5.

Keywords: refining, crude glycerine, glycerol residue, vacuum distillation.

INTRODUCTION

Palm kernel oil methyl ester plants in Malaysia generate large amounts of glycerol residue from glycerol refining - about 1 t day^{-1} by a particular plant alone. It is classified as a waste under Schedule S181 of the Environmental Regulations in Malaysia, and stored in drums and disposed off in landfills.

In a previous study (Yong *et al.*, 2001), glycerol residue was found to contain 20.2% glycerol, 6.6% fatty acids (as soap) and 64.3% salt. A process to recover the glycerine, fatty acids and salt has been developed (Ooi *et al.*, 2001). In this paper, refining the crude glycerine recovered from glycerol residue by a simple vacuum distillation and characterization of the distilled glycerine are described.

MATERIALS AND METHODS

Materials

The crude glycerine was recovered from glycerol residue from a local oleochemicals company by chemical and physical treatment according to the method of Ooi *et al.* (2001). All the reagents - hydrochloric acid (37%), sulphuric acid (95% - 97%) and ethylene glycol, and chemicals - sodium formate, sodium hydroxide and sodium metaperiodate - used were of analytical grade.

Glycerine Distillation

Three samples of the crude glycerine (CG1, CG2 and CG3) were vacuum distilled to produce distilled glycerine (DG1, DG2 and DG3) and the residue (distilled bottom) (DB1, DB2 and DB3).

A known amount (*Table 1*) of the crude glycerine was placed in a three-neck round bottom flask fitted with a vacuum release apparatus and thermometer, and connected to a condenser. A magnetic bar was used for stirring to reduce the temperature difference between the top (glycerol vapour) and bottom (silicon oil bath) of the flask. A

---

* Department of Chemistry, Faculty of Science and Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
** Malaysian Palm Oil Board, P.O. Box 10620, 50720 Kuala Lumpur, Malaysia.

cold trap cooled by liquid nitrogen was placed between a vacuum pump (Edward, Model: RV 12, England) and a collecting flask connected to the condenser. The cold trap was kept a constant temperature (<0°C) to avoid any variation in the pressure. A silicone oil bath was used to heat the crude glycerine to the required temperature (*Table 1*). The heat generated by the oil bath was conserved in the distillation equipment by covering it with aluminum foil for insulation. The glycerine distilled over at a top temperature of 120°C -126°C (the bottom temperature was 165°C - 190°C) and pressure of 4.0×10^{-1} - 4.0×10^{-2} mbar, and was collected in a flask. The condenser was cooled to 8°C in a cooler (Grant, Type: C1G, England) to condense the glycerol vapour. Some of the water from the crude glycerine was retained in the liquid nitrogen cold trap. The distilled bottom was collected from the three-neck round bottom flask and weighed and kept in containers.

Characterizing the Distilled Glycerine

The distilled glycerine was characterized by its contents of glycerol, ash, MONG, water and soap. Its pH and infra-red spectrum were also obtained. The analyses were done in duplicate by the methods below:

(a) Glycerol content. Standard method ISO 2879-1975.

(b) Ash content. Standard method ISO 2098-1972.

(c) MONG. Standard method ISO 2464-1973.

(d) Water content. Determined using a DL 37 coulometer (Mettler Toledo, Switzerland) validated with a standard containing 0.1% water (Hydranal, Riedel-de Haen, Germany).

(e) Soap content. Distilled glycerine (1.0 g) was dissolved in 50 ml distilled water and a few drops of bromophenol blue indicator (0.04% w/v H_20) added. The solution was titrated with 0.1N HCl until a permanent fluorescent yellow. The soap content was calculated by:

$$\text{Soap content} = \frac{\text{normality of HCl x volume of HCl x 15}}{\text{Weight of sample}}$$

(f) pH. A solution of 20.0 g distilled glycerine in 100.0 ml distilled water was measured with a pH meter (Mettler Toledo, MP220).

(g) Infrared spectroscopic analysis. The infrared spectrum of distilled glycerine was analysed from a thin film on a potassium bromide pellet using a Nicolet MAGNA IR 550 Spectrometer.

RESULTS AND DISCUSSION

Distillation

There are three possible reactions that may reduce the yield of glycerol in the distilled glycerine:

(a) Polymerization of the glycerol at high pH (in excess NaOH and high temperature, >200°C) to form polyglycerol (Garti *et al.*, 1981; Ikuya *et al.*, 1990; Lutz *et al.*, 1998), which concentrates in the distilled bottom.

(b) Dehydration of the glycerol at low pH (Hedtke, 1996; Monick, 1960) to form acrolein (bp. 52°C), which is then lost in the cold trap.

(c) Moderate oxidation of the glycerol to form glycerose, a mixture of glyceraldehyde and dihydroxyacetone (Jungermann, 1991; Monick, 1960).

However, by proper control of the pH of the crude glycerine, and the temperature and pressure of distillation, these unwanted reactions can be minimized. Vacuum distillation was used so that the glycerine distilled over at a lower temperature and pressure than would otherwise have been necessary.

Table 1 shows the fractions obtained from the crude glycerine distilled. On average, 41.8% glycerine was recovered. This was a reasonable amount from the glycerol content of 50.4% in the crude glycerine (*Table 2*) as some of the glycerol was lost in the side reactions described or remained in the distilled bottom

The distilled bottom, a dark brown solid, constituted 41.8% of the crude glycerine. This large amount was due to the high contents of salt (17.0% w/w) and MONG (24.0% w/w) (polyglycerol, sugar components, free fatty acids and partial glycerides) in the crude glycerine (*Table 2*) which did not distill over.

About 16.5% of the crude glycerine was lost, most of it water (8.6%). Dehydration of the glycerol to form acrolein in the acidic distillation condition would also have contributed to the loss because acrolein (bp. 52°C) is a volatile chemical.

Infrared Spectrum of the Distilled Glycerine

A typical infrared spectrum of the distilled glycerine is shown in *Figure 1*. The spectrum was almost similar to that of pure glycerol but with a broader absorption band at 3379 cm^{-1}. This was probably due to the hydroxyl groups from water and

TABLE 1. TEMPERATURES AND PRESSURES OF VACUUM DISTILLATION AND THE MASS BALANCES AND APPEARANCES OF THE DISTILLED FRACTIONS RECOVERED FROM CRUDE GLYCERINE

Sample of crude glycerine	Top and bottom temperature[a] (°C)	Pressure (mbar)	Crude glycerine used for distillation (g)	Distilled fractions							
				Distilled glycerine			Distilled bottom			Losses[b]	
				Mass (g)	Weight percentage (wt. %)	Appearance	Mass (g)	Weight percentage (wt. %)	Appearance	Mass (g)	Weight percentage (wt. %)
CG1	122-126 170-190	4.0×10^{-2}	206.3	92.5	44.8	Clear liquid	71.7	34.8	Dark brown solid	42.1	20.4
CG2	120-122 165-180	$1.5\text{-}4.0 \times 10^{-1}$	150.6	57.8	38.4	Clear liquid	74.9	49.7	Dark brown solid	17.9	11.9
CG3	120-124 170-180	2.0×10^{-1} to 4.0×10^{-2}	190.2	80.0	42.1	Clear liquid	77.6	40.8	Dark brown solid	32.6	17.1
Average	-	-	-	-	41.8	-	-	41.8	-	-	16.5

Notes: [a] Top temperature is the temperature of the glycerol vapour in the three-neck round bottom flask and bottom temperature, the temperature of the silicon oil bath.

[b] Loss = mass of crude glycerine distilled - (mass of recovered distilled glycerine + mass of distilled bottom).

TABLE 2. CHARACTERISTICS OF THE CRUDE GLYCERINE USED

Glycerine[a]	Parameters of characterization				
	Glycerol (%)	Ash (%)	Water (%)	MONG (%)	pH
CG1	55.7	15.3	8.4	20.7	5.4
CG2	47.1	19.8	11.2	21.9	7.0
CG3	48.5	16.0	6.1	29.4	4.6
Average	50.4	17.0	8.6	24.0	-

Source: [a]Ooi *et al.* (2001).

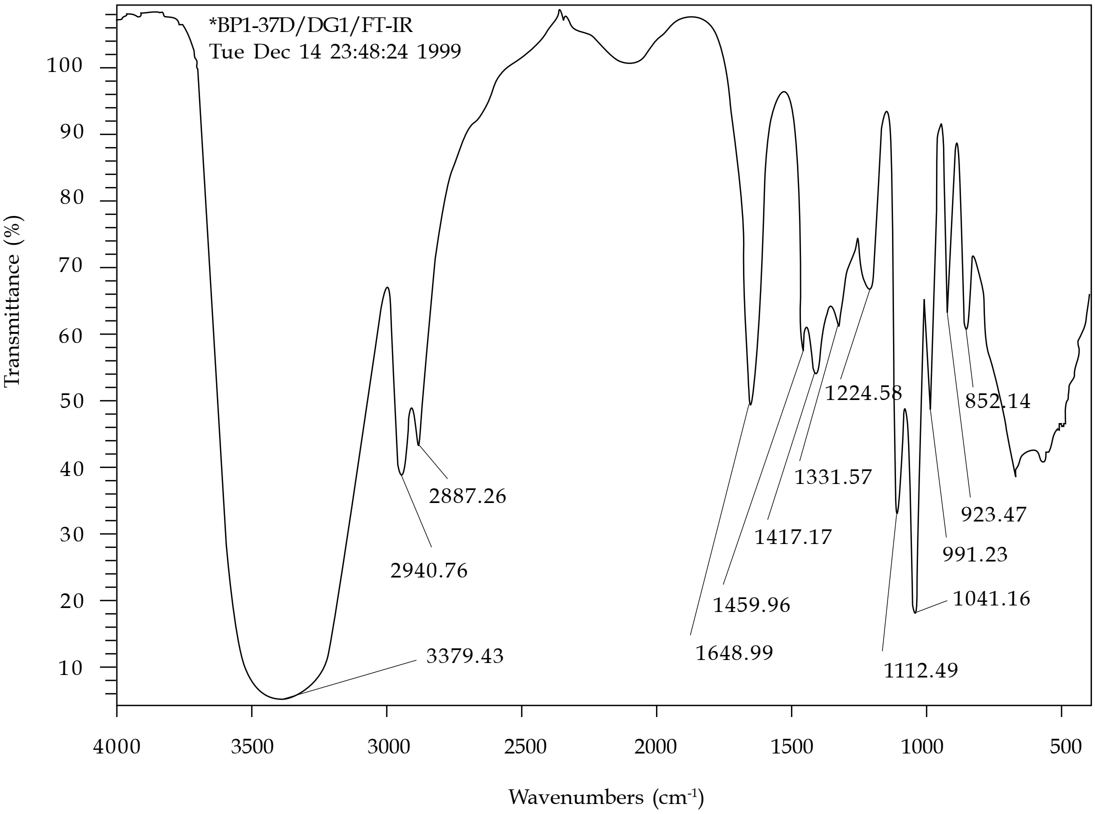

Figure 1. Typical infrared spectrum of distilled glycerine (DG2) obtained from high vacuum distillation of crude glycerine (CG2).

the glycerol molecules as the distilled glycerine still contained about 1% water. The presence of some impurities (2.4%) was shown by the absorption peak at 1649 cm^{-1} (C=O group), corresponding to the oxidation products of glycerol (*e.g.* glyceraldehyde, dihydroxyacetone) and/or free fatty acids.

Characterization of the Distilled Glycerine

***Glycerol* content.** The average glycerol content of the distilled glycerine was 96.6% (*Table 3*). Thus, the crude glycerine with 50.4% glycerol was successfully refined to a considerably higher purity by the simple vacuum distillation.

Ash content. The average ash content of the distilled glycerine was 0.03%, markedly lower than the 17.0% in the crude glycerine (*Tables 2* and *3*). Salts, such as sodium chloride and sodium sulphate, mainly constituted the ash, and the distillation had effectively removed them. Salts are inorganic chemicals with strong ionic bonding, and hence high boiling points. They are not easily distilled over and therefore remained mostly in the distilled bottom.

pH. The distillation was done at pH 4 to 5. Foaming was the main problem at >pH 5. Initially, CG1 (pH 5.4) and CG2 (pH 7.0) were distilled at their own pHs but foamed easily with their pHs rising to 6.9

(CG1) and 8.1 (CG2). They were then acidified to pH 5.0 (CG1) and 4.5 (CG2), and re-distilled without foaming. CG3 (pH 4.6) was distilled throughout without foaming.

The foaming was caused by the formation of soap in the high temperature of distillation. The glycerol residue contained 6.6% crude fatty acids, mainly the short and medium chain acids - C6:0 4.2%, C8:0 30.3%, C10:0 9.4% and C12:0 40.8% - as they were highly soluble in glycerol and water. During the recovery of crude glycerine from the glycerol residue, trace amounts of the short and medium chain fatty acids were retained in the crude glycerine.

At the high temperature, the free sodium hydroxide reacted with the fatty acids to form short and medium chain soaps which foamed easily. A higher pH obviously indicates more sodium hydroxide and more formation of soap. The sodium hydroxide also accelerated the polymerization of glycerol to polyglycerol as it is a catalyst for polymerization (Garti *et al.*, 1981). Thus, the best pH for distilling the crude glycerine was below 5, at which all the soap was converted to free fatty acids, obviating foaming.

Soap content. The distilled glycerine was free of soap (*Table* 3). This was expected as the distillation was done at pH 4.5 to 5 in which any soap present would have been hydrolysed. In addition, the distilled glycerine had an even lower pH of 3.2 to 3.9 (*Table 3*).

Water content. The average water content in the distilled glycerine was 1.0%, considerably less than in the crude glycerine (8.6%) (*Tables* 2 and 3). The low water content was due to the high vacuum used vaporizing the water, which then condensed in the liquid nitrogen cold trap. Thus, the vacuum and cold trap also functioned as a dessicant for the distilled glycerine.

Matter Organic Non-glycerol (MONG)

The average MONG in the distilled glycerine was 2.4%, much reduced from the 24% in the crude glycerine. MONG in the crude glycerine comprised mainly partial glycerides, free fatty acids, oxidation products and the polymerized compounds of glycerol. These impurities mostly remained in the residue although some distilled over, especially at

TABLE 3. CHARACTERISTICS OF THE DISTILLED GLYCERINE RECOVERED

Distilled glycerine	Parameters of characterization					
	Glycerol (%)	Ash (%)	Water (%)	MONG (%)	Soap (%)	pH
DG1	97.3	0.04	0.7	2.0	nil	3.2
DG2	95.0	0.04	1.8	3.2	nil	3.3
DG3	97.5	0.02	0.4	2.1	nil	3.9
Average	96.6	0.03	1.0	2.4	nil	3.5

TABLE 4. AMOUNTS OF CRUDE GLYCERINE, DISTILLED GLYCERINE AND DISTILLED BOTTOM RECOVERED FROM 1 kg OF GLYCEROL RESIDUE

Sample	Crude glycerine[a] (g)	Distilled glycerine		Distilled bottom	
		Distilled glycerine[b] (wt. %)	Distilled glycerine[c] (g)	Distilled bottom[d] (wt. %)	Distilled bottom[e] (g)
CG1	350.9	44.8	157.2	34.8	122.1
CG2	366.7	38.4	140.8	49.7	182.2
CG3	302.4	42.1	127.3	40.8	123.4
Average	340.0	41.8	141.8	41.8	142.6

Notes:
[a] Weight of crude glycerine recovered from 1 kg glycerol residue (Ooi *et al.*, 2001).
[b] Weight percentage of glycerine recovered from crude glycerine.
[c] Estimated by multiplying the weight of recovered crude glycerine by the weight percentage of distilled glycerine.
[d] Weight percentage of distilled bottom from crude glycerine.
[e] Estimated by multiplying the weight of recovered crude glycerine by the weight percentage of distilled bottom.

>126°C. The probable components of MONG in the distilled glycerine were short and medium chain fatty acids and the oxidation products of glycerol, *e.g.* dihydroxyacetone, glyceraldehyde, hydroxy pyruvic aldehyde and tatronic dialdehyde. The MONG content in the distilled glycerine can be further reduced by purification, *e.g.* ion exchange, deodorization and bleaching. However, no purification was carried out in this study.

CONCLUSION

Vacuum distillation is a simple and efficient process to recover glycerol from crude glycerine with high contents of salt and MONG. On average, 141.8 g glycerine were recovered from 1 kg glycerol residue, leaving 142.6 g distilled bottom. The distilled bottom comprised mainly salt, high boiling MONG and some glycerol. The crude glycerine was distilled at 120°C - 126°C and 4.0×10^{-1} - 4.0×10^{-2} mbar pressure to produce 96.6% glycerine. The optimum pH for the distillation was <5 in which foaming was obviated.

ACKNOWLEDGEMENTS

The authors would like to thank the Director-General of MPOB for permission to publish this paper, Dr Ma Ah Ngan (Director of Engineering and Processing Division), Dr Salmiah Ahmad (Head of Advanced Oleochemical Technology Centre) and Andy Chang Kwong Choong for their valuable comments, Asma Don, Sapiah Hashim, Zamiah Hasman and the personnel in the Advanced Oleochemical Technology Centre for their technical assistance. This work was supported in part by a scholarship from the *Pasca Siswazah* of Universiti Putra Malaysia to the first author.

REFERENCES

GARTI, N; ASERIN, A and ZAIDMAN, B (1981). Polyglycerol ester: optimization and techno-economic evaluation. *J. Amer. Oil Chem. Soc. Vol. 58*: 878-883.

HEDTKE, D (1996). Glycerine processing. *Bailey's Industrial Oil and Fat Products: Industrial and Consumer Non-edible Products from Oils and Fats* (Hui, Y H ed.). Fifth edition, Vol. 5. John Wiley & Sons, Inc., New York. p. 275-308.

IKUYA, N; SHIGEO, O and KAZUO, M (1990). Production of high-purity diglycerol. J. P. patent 2169536A2.

JUNGERMANN, E (1991). Chemical reactions of glycerine. *Glycerine, A Key Cosmetic Ingredient* (Jungermann, E and Sonntag, N O V eds.). Marcel Dekker Inc., New York. p. 97-112.

LUTZ, J; BERNHARD, G; REINHARD, B and VOLKMAT, J (1998). Process for the production of diglycerol. U. S. patent 5710350.

MONICK, J A (1960). Trihydric and polyhydric alcohol. *Alcohol, their Chemistry, Properties and Manufacture* (Monick, J A ed.). Reinhold Book Corporation, New York. p. 365-445.

OOI, T L; YONG, K C; DZULKEFLY, K; WAN YUNUS, W M Z and HAZIMAH, A H (2001). Crude glycerine recovery from glycerol residue waste from a palm kernel oil methyl ester plant. *Journal of Oil Palm Research Vol.13(2)*. In press.

YONG, K C; OOI, T L; DZULKEFLY, K; WAN YUNUS, W M Z and HAZIMAH, A H (2001). Characterization of glycerol residue generated from a palm kernel oil methyl ester plant. *Journal of Oil Palm Research Vol. 13 (2)*. In press.