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CRUDE GLYCERINE RECOVERY FROM GLYCEROL RESIDUE WASTE FROM A PALM KERNEL OIL METHYL ESTER PLANT

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ABSTRACT

Eight samples of glycerol residue (GR1-1 to GR1-8) from one batch (GR1) were subject to chemical and physical treatments to recover crude glycerine, crude fatty acids and salt. The average weight percentages of the recovered components were: crude glycerine 33.9%, crude fatty acids 10.5% and salt 65.2%. The average composition of the recovered crude glycerine was: glycerol 51.4%, ash 13.8%, water 8.9% and matter organic non-glycerol (MONG) 25.9%. Crude glycerines with pH from 1-2 and 5-7 were produced. Chemical treatment at low pH (1-2) was better as it increased the glycerol and reduced the ash contents in the recovered crude glycerine. However, the MONG content was slightly increased. The treatment also increased the recovered salt and reduced the crude glycerine (giving a crude glycerine with lower dissolved salt and higher glycerol), but did not affect the recovery of crude fatty acids.

Keywords: crude glycerine, recovery, glycerol residue, palm kernel oil methyl ester.

INTRODUCTION

The oleochemicals industry in Malaysia is expanding strongly and producing an increasing array of products. However, the by-products of the industry, although potentially useful, are largely wasted.

In the production of palm kernel oil methyl esters, large amounts of glycerol residue are produced from glycerol refining - about 1 t day^{-1} by a particular plant alone. With the demand for methyl esters and fatty alcohols expected to increase greatly, the amount of glycerol residue generated will also rise. As most of this residue is dumped in landfills, it would be advantageous if its valuable components can be recovered for use.

Glycerol residue contains 20.2% glycerol, 6.6% fatty acids (as soap) and 64.3% salt (Yong *et al.*, 2001). Thus, 91.1% of it is potentially useful. In this study, processes were developed for their recovery by chemical and physical means, and their subsequent refining by distillation.

MATERIALS AND METHODS

Materials

Glycerol residue was obtained from a local oleochemicals company, the waste from glycerine refining in a palm kernel oil methyl ester plant. From one batch, eight samples (GR1-1 to GR1-8) of 1 kg each were taken. All the reagents (sulphuric acid 95% - 97% and ethylene glycol) and chemicals (sodium formate, sodium hydroxide and sodium metaperiodate) used were of analytical grade.

Recovery of Crude Glycerine

The eight samples were subject to chemical and physical treatment. Initially, they were acidified by dilute sulphuric acid (6% solution made by diluting 30 ml concentrated acid to 500 ml volume with

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distilled water) to split the soap and neutralize the residual NaOH contained in them. The charred substances produced were filtered off. The samples were then decanted to recover the crude fatty acids, and the aqueous glycerine solutions neutralized by 50% sodium hydroxide against the sulphuric acid. Subsequently, they were evaporated to concentrate the glycerine solutions. The salt crystallizing out was removed by decanting. To purify and concentrate the solutions further, they were solvent extracted and filtered to remove the residual salt. Finally, they were evaporated to obtain the crude glycerine. The chemical and physical treatments to recover crude glycerine from glycerol residue are shown schematically in *Figure 1*.

By varying the amounts of dilute sulphuric acid and 50% sodium hydroxide used in the acidification and neutralization, the crude glycerines were produced with pHs of 1.2, 1.3, 2.1, 5.4, 6.2, 6.3, 6.8 and 7.0, respectively (see *Table 1*).

Analytical Methods

The recovered crude glycerines were characterized in duplicate by the parameters below, obtained by the methods of analysis given:

(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).

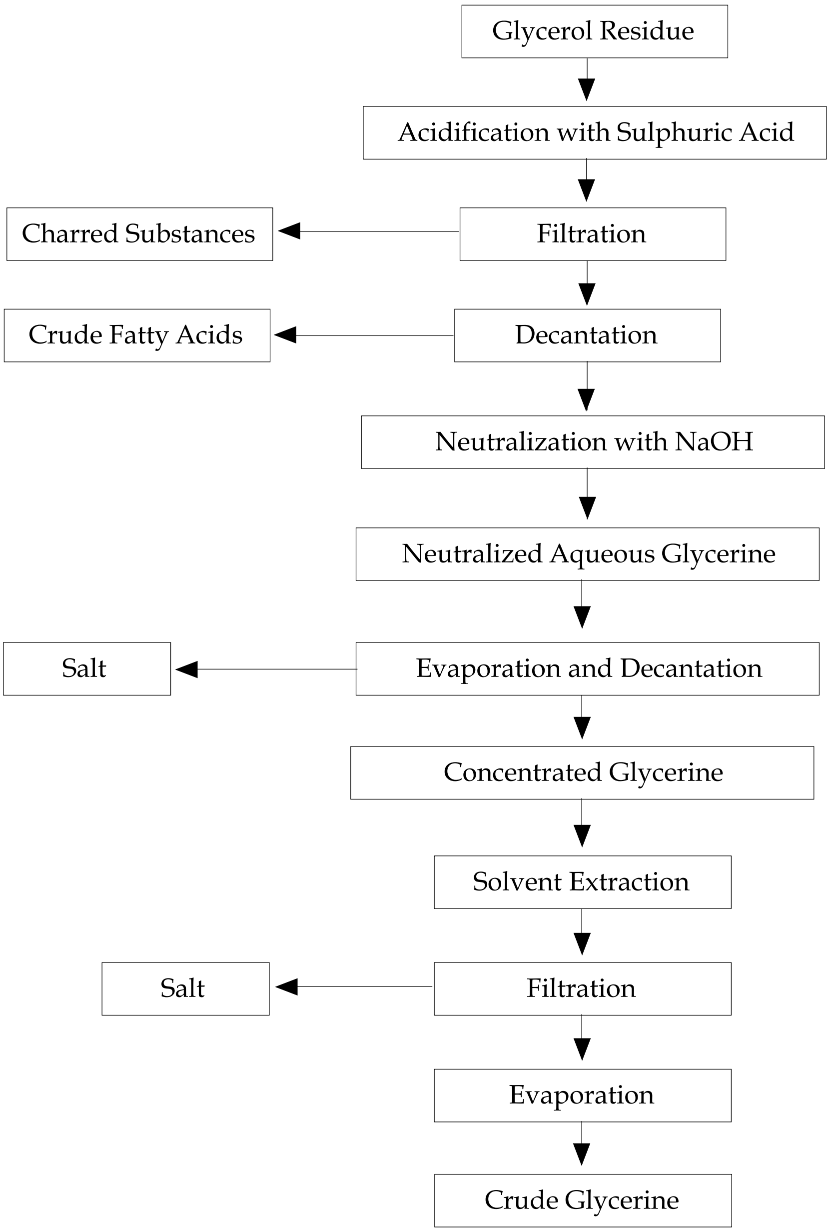

Figure 1. Schematic diagram of the chemical and physical treatments to recover crude glycerine from glycerol residue.

(e) pH (20%). Determined by dissolving 20.0 g crude glycerine in 100.0 ml distilled water, and measuring with a pH meter (Mettler Toledo, MP220).

(f) Infrared spectroscopy analysis. Analysis by a MAGNA IR 550 spectrophotometer. The samples were analysed as thin films on a potassium bromide pellet.

RESULTS AND DISCUSSION

Chemical Treatment

As the glycerol residue contained 64.3% ash, mainly sodium chloride, NaCl (Yong *et al.*, 2001), H_2SO_4 and NaOH were chosen as the reagents for the chemical treatment. This was because the sodium sulphate (Na_2SO_4) formed was less soluble in the aqueous solution of neutralized glycerine saturated with NaCl (Helmold, 1993; Thomas, 1983) and would crystallize out for easy recovery by subsequent evaporation and decanting, considerably reducing the dissolved salt in the crude glycerine.

Composition of the Recovered Components

The crude glycerine samples (CG1-CG8) recovered were dark brown viscous liquids which precipitated salt after a week's storage. The crude fatty acids were a light brown liquid with a pungent smell. The precipitated salt was white to slightly yellow. In this paper, only the recovery and characterization of the crude glycerine are discussed.

The components recovered from the samples of glycerol residue are shown in *Table 2*. The average crude fatty acids recovered was 10.5% (w/w) of the glycerol residue, with a narrow range of 9.1% to 11.2%.

The average crude glycerine recovered was 33.9% (range 30.7% to 37.8%). This was higher than expected considering that the glycerol residue had only 17.7% glycerol, and could have been a spurious result as the crude glycerine contained considerable MONG and water. Increasing the pH of the chemical treatment increased the dissolved salt in the crude glycerine (*Figure 2* and *Table 3*) and consequently

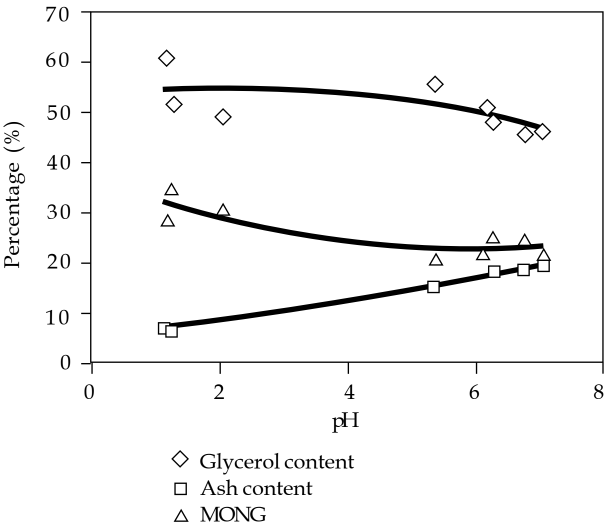

Figure 2. Effect of pH in the chemical and physical treatments on the composition of crude glycerine recovered from glycerol residue (each point is the mean of duplicate analyses).

TABLE 1. COMPOSITIONS OF THE GLYCEROL RESIDUE (GR1) AND THE CRUDE GLYCERINE RECOVERED

Sample	Parameter				
	Glycerol (%)	Ash (%)	Water (%)	MONG (%)	pH
GR[a]	17.7	58.7	5.9[b]	17.7	12.8
CG1	60.9	6.8	4.1	28.2	1.2
CG2	51.7	6.6	7.3	34.5	1.3
CG3	55.7	15.3	8.4	20.7	5.4
CG4	51.1	15.6	11.3	21.9	6.2
CG5	47.1	19.8	11.2	21.9	7.0
CG6	49.4	8.7	11.1	30.7	2.1
CG7	46.7	18.8	10.5	24.0	6.8
CG8	48.8	18.7	7.5	25.1	6.3
Average	51.4	13.8	8.9	25.9	-

Notes:

[a] Glycerol residue (GR1).

[b] Moisture content of glycerol residue (GR1), determined by PORIM Test Method p2.1 (Siew, 1995).

increased the apparent recovery of crude glycerine (*Figure 3*).

Salt was the largest component recovered, with an average of 65.2% (range 57.5% to 73.9%). This was in fact higher than the ash (which included all the salt) content in the glycerol residue of 58.7%, and implied that some Na_2SO_4 was formed in the recovery process and some water retained in the salt. The salt was mainly NaCl (from the glycerol residue) and some Na_2SO_4 (from the chemical treatment).

As high pH increased dissolved salt in the crude glycerine, a low pH conversely reduced the dissolved salt (*Figure 2*). This was due to the excess H_2SO_4 reacting with NaCl during the evaporation to form both sodium hydrogen sulphate ($NaHSO_4$) and Na_2SO_4. The $NaHSO_4$ and Na_2SO_4 were less soluble in the aqueous solution containing NaCl, and consequently crystallized out during the evaporation and decanting. Hence, the crude glycerine recovered at low pH contained less salt.

This occurrence agreed with the formation of Na_2SO_4 and HCl with $NaHSO_4$ as an intermediate by adding 93% - 96% H_2SO_4 to NaCl in a Mannheim furnace at 650°C (Helmold, 1993; Thomas, 1983). Helmold (1993) found that Na_2SO_4 could also be produced from dilute H_2SO_4 and NaCl in a spray evaporator. Therefore, limiting the quantity of NaOH used in the neutralization is essential to avoid the formation of Na_2SO_4 and to allow the excess H_2SO_4 to reduce the dissolved salt in the crude glycerine.

About 0.3% (w/w) charred substance was obtained. The overall weight percentage of recovered components was 109.9% - more than the weight of the glycerol residue. This was due to the chemical treatment producing Na_2SO_4, which was also *recovered*, and some water in the recovered salt and crude glycerine.

Characterization of the Recovered Crude Glycerine

Glycerol content. The average glycerol content was 51.4% (range 46.7% to 60.9%), about three times the 17.7% in the glycerol residue (*Table 1*). Nevertheless, this was still low compared to the contents in sweet water (88.0%) and soap lye (80.0%) (*Table 4*) because there remained some salt and water in the crude glycerine. As stated earlier, the salt content was strongly influenced by the pH of the chemical treatment (*Figure 2* and *Table 3*) - a high pH increasing the dissolved salt.

The crude glycerine contained very high MONG (25.9%) because the glycerol residue was collected from the bottom of the distillation vessel (in the refining plant) where some of the glycerol had

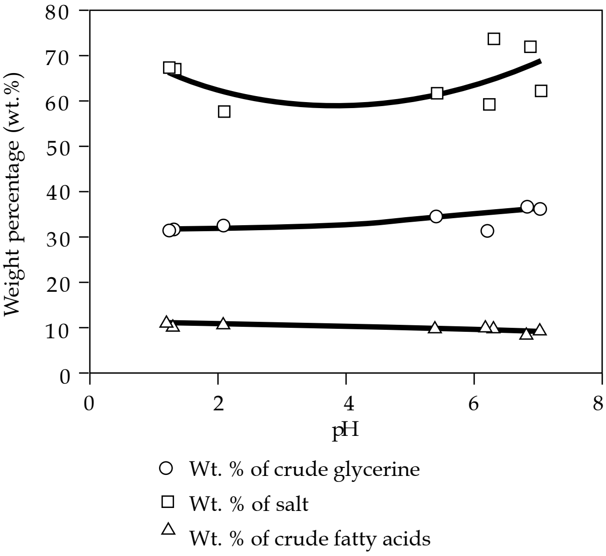

Figure 3. Effect of pH in the chemical and physical treatments on the recovery of components from glycerol residue.

TABLE 2. COMPOSITION OF COMPONENTS RECOVERED FROM GLYCEROL RESIDUE

Sample	Fraction (wt. %)			
	Crude fatty acids	Crude glycerine	Salt	Charred substance
GR1-1	11.2	30.7	67.1	0.2
GR1-2	10.4	31.1	66.9	0.3
GR1-3	10.8	35.1	61.9	0.2
GR1-4	10.8	31.9	59.4	0.3
GR1-5	10.2	36.7	62.6	0.3
GR1-6	10.6	32.6	57.5	0.1
GR1-7	9.1	37.8	72.0	0.3
GR1-8	10.7	35.5	73.9	0.3
Average	10.5	33.9	65.2	0.3

TABLE 3. COMPOSITION OF CRUDE GLYCERINE RECOVERED FROM GLYCEROL RESIDUE UNDER ACIDIC (pH 1-2) AND SLIGHTLY ACIDIC (pH 5-7) CONDITIONS

Treatment	Parameter				
	Glycerol (%)	Ash (%)	Water (%)	MONG (%)	pH
Acidic crude glycerine (pH 1-2)[a]	54.0	7.4	7.5	31.1	1.5
Slightly acidic crude glycerine (pH 5-7)[b]	49.9	17.6	9.8	22.7	6.3

Notes:
[a]Averages of samples CG1, CG2 and CG6.
[b]Averages of samples CG3, CG4, CG5, CG7 and CG8.

TABLE 4. COMPARISON OF THE BRITISH STANDARD SPECIFICATIONS FOR CRUDE GLYCERINE AND THE TYPICAL COMPOSITION OF RECOVERED CRUDE GLYCERINE FROM GLYCEROL RESIDUE

	BS 2621:1979 Soap lye crude glycerol[a]	BS 2622:1979 Hydrolyser crude glycerol[a]	Crude glycerine from glycerol residue[b]
Glycerol %	80.0	88.0	51.4
Ash % (max)	10.0	1.0	13.8
MONG % (max)	2.5	1.5	25.9
Water % (max) (Karl Fischer method)	10.0	-	8.9
Propane 1,3 diol (TMG) % (max)	0.5	0.5	-
Arsenic (ppm or mg kg^{-1}) (max)	2.0	2.0	-
Sugars (max)	Nil	Nil	-

Notes:
[a]Woollatt (1985).
[b]Average results from this study.

polymerized to diglycerol and triglycerol in the high temperature of distillation (180°C). This was a favoured reaction as the caustic soda (NaOH) used for neutralization in the refining was also a catalyst for polymerization. With the formation of diglycerol and triglycerol, it would have been unlikely for the glycerol content in the crude glycerine to be higher than those in soap lye and sweet water.

Ash content. The average ash content was 13.8%, with a range of 6.6% to 19.8% - less than a quarter of that in the glycerol residue (58.7%) (*Table 1*). The content was variable because of the earlier stated dependency of the salt content on the pH of the chemical treatment (*Figure 2* and *Table 3*).

Water content. The average water content was 8.9% (range 4.1% to 11.3%) (*Table 1*), higher than in the glycerol residue of 5.9% (*Table 1*). The glycerol residue was discharged from the bottom of the distillation vessel where, in the high vacuum and high temperature (180°C), it was dry and should have remained so if immediately and properly stored sealed. On the other hand, the crude glycerine, produced by evaporating water from neutralized aqueous glycerine, still contained considerable water unless subject to more stringent drying than was done in this study.

Matter organic non-glycerol (MONG). The average MONG was 25.9% (range 20.7% to 34.5%) **-** higher than in the glycerol residue (17.7%) (*Table 1*). This was expected as MONG from the glycerol residue was concentrated in the crude glycerine. In addition, the low pH chemical recovery increased the MONG further (*Figure 2* and *Table 3*) because of formation of acrolein (Hedtke, 1996), oxidation of glycerol to glyceraldehyde and dihydroxyacetone, and the crystallization of salt from the solution to produce a low volume of crude glycerine with high MONG and glycerol and low ash (dissolved salt).

Infrared Spectra of the Crude Glycerine

The typical infrared spectrum of acidic (pH 1 - 2) crude glycerine is shown in *Figure 4*. There was O-H stretching at 3400 cm^{-1}, C-H stretching at 2880 and 2940 cm^{-1}, C=O stretching from 1650 to 1740 cm^{-1}, C-O-H bending at 1400 to 1460 cm^{-1}, C-O stretching from 1040 to 1120 cm^{-1} and O-H bending at 920 cm^{-1} which indicated the presence of glycerol and some impurities. The crude glycerines with lower ash (acidic crude glycerines CG1, CG2 and CG6) showed IR absorption at 1737 to 1739 cm^{-1} whereas those with high dissolved salt (the slightly acidic crude glycerines CG3, CG4, CG5, CG7 and CG8) only showed strong absorption bands at 1595 to 1648 cm^{-1}.

CONCLUSION

The crude glycerine recovered had higher glycerol (51.4% *vs*. 17.7%), water (8.9% *vs*. 5.9%) and MONG (25.9% *vs*. 17.7%) but lower ash (13.8% *vs*. 58.7%) than the glycerol residue. Its ash and MONG contents were higher and glycerol content lower than the standard specifications for commercial crude glycerine from spent soap lye and sweet water.

The recovery of fatty acids was not affected by the pH of the chemical treatment, but the contents of glycerol, ash and MONG in the crude glycerine, and salt and the crude glycerine itself recovered were very much so affected. There were three main factors involved: (1) H_2SO_4 decreased the solubility of NaCl (from the glycerol residue), crystallizing it out, (2) NaOH neutralized H_2SO_4 to decrease its effect on NaCl, and (3) formation of extra salt, *i.e.* Na_2SO_4 by H_2SO_4 and NaOH.

Excess H_2SO_4 was preferred for the recovery as it reduced salt in the crude glycerine. This process is particularly suitable for recovering crude glycerine from a dilute source (10% - 20% glycerol) with high NaCl (60% - 70%), such as glycerol residue.

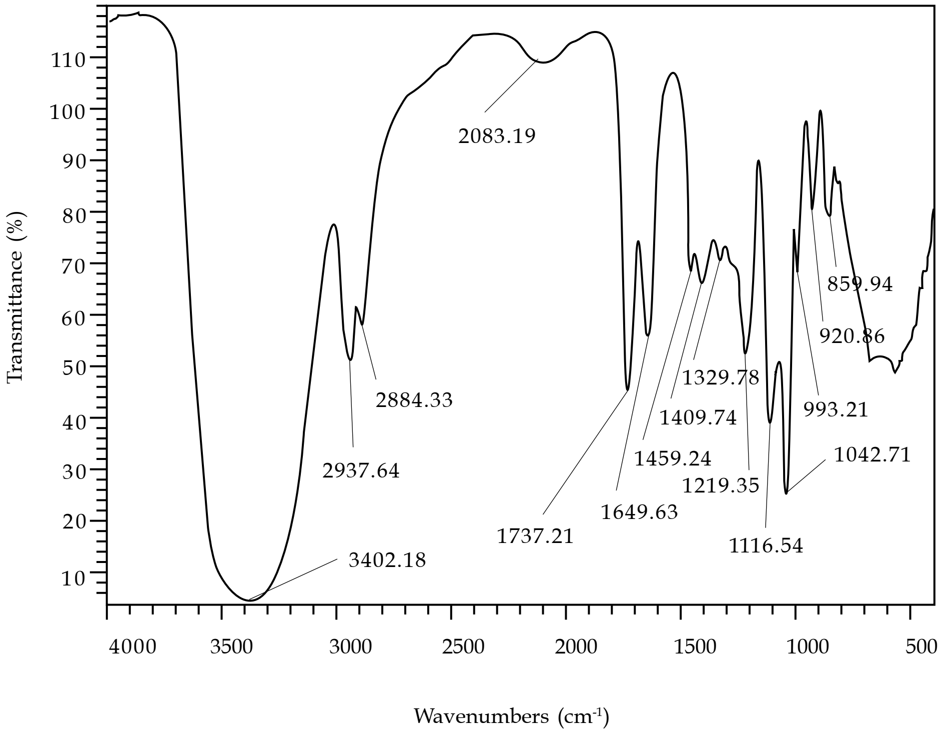

Figure 4. Typical infrared spectrum of acidic crude glycerine, CG6 (pH 1-2).

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