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CHARACTERIZATION OF GLYCEROL RESIDUE FROM A PALM KERNEL OIL METHYL ESTER PLANT

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ABSTRACT

Glycerol residue, a by-product of glycerol refining from a palm kernel oil methyl ester plant, was characterized using standard test methods. The selected parameters were the contents of glycerol, ash, moisture and matter organic non-glycerol (MONG) and pH. It was found to contain, on average, 20.2% glycerol, 64.3% ash, 3.0% moisture, 12.4% MONG at pH 12.8. Fatty acids (6.6%) were isolated and comprised mainly C8:0 (30.3%), C10:0 (9.4%) and C12:0 (40.8%).

Keywords: characterization, glycerol residue, palm kernel oil methyl ester.

INTRODUCTION

The Malaysian palm-based oleochemicals industry is growing rapidly and producing an increasing array of products like fatty acid methyl esters, fatty alcohols and glycerine (Mohtar *et al.*, 1998). In the production, by-products are produced, many of them potentially useful. For example, palm kernel oil methyl ester residue is a potential source of sterols (Ooi *et al.*, 1993). Glycerol pitch, a distillation foot from glycerol refining, contains up to 70% glycerol which can be easily recovered by conventional chemical treatment (Hazimah and Ooi, 2000). However, the glycerol residue from a methyl ester plant has never been studied.

The transesterification of palm kernel oil produces glycerol residue (*Figure 1*) - about 1 t day^{-1} by a particular plant alone. This large amount of residue is a loss and poses a disposal problem as glycerol residue is a waste under Schedule S181 of the Environmental Regulations in Malaysia. Currently, this waste is stored in drums and disposed off in landfills.

It is obviously advantageous, both environmentally and economically, to recover the products in the waste for use. This research was therefore undertaken to characterize the glycerol residue from a palm kernel oil methyl ester plant and recover its valuable components.

MATERIALS AND METHODS

Materials

Twelve samples of glycerol residue (GR1 to GR12) were obtained from a local multinational oleochemicals company (from glycerol refining in the production of palm kernel methyl esters). The samples varied from light to dark brown granules or paste. All the chemicals (sodium chloride, sodium formate, sodium hydroxide, sodium metaperiodate and sodium sulphate anhydrous), reagents (boron trifluoride, concentrated sulphuric acid and ethylene glycol) and solvents (hexane and acetone) used were of analytical grade.

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Analyses

All the analyses were performed in duplicate according to the standard methods below:

Analysis	Method
Glycerol content (Titrimetric method)	ISO 2879-1975
Ash content	ISO 2098-1972
Moisture content	PORIM Test Method p2.1 (Siew, 1995)
*MONG	ISO 2464-1973 (slightly modified)

Notes: *MONG - matter organic non-glycerol.
In ISO 2464-1973, MONG is defined as 100 - (% glycerol content + % water content + % ash content). In this study, the *water content* (obtained by the Karl Fischer method) was replaced by *moisture content* (obtained by the oven method) because glycerol residue is a solid substance which water content cannot be detected by a coulometric titrator.

pH

A solution of 20% glycerol residue in 100.0 ml distilled water was measured with a pH meter (Mettler Toledo, MP220).

Isolation and Analysis of Crude Fatty Acids

The crude fatty acids were isolated from the glycerol residue by conventional acid hydrolysis followed by phase separation. The fatty acid composition (FAC) of the crude fatty acids was analysed using a Hewlett Packard HP 6890 gas chromatograph. The FAC was calculated as normalized percentages from the peak areas. A SUPELCO SP-2340 (60 m x 0.25 mm x 0.20 µm) column was used for the analysis. The temperature programme was as follows: 120°C initial temperature, ramp rate 3°C min^{-1} and final temperature of 185°C for 20 min. The injector and detector temperatures were set at 240°C. Nitrogen was used as the carrier gas (0.8 cm^3 min^{-1}) and about 1.0 µl of the derived crude fatty acids was injected into the gas chromatograph. The fatty acids were injected as their methyl ester derivatives, prepared according to PORIM Test Method p3.4, or the Boron Trifluoride Method (Siew, 1995).

RESULTS AND DISCUSSION

The analyses of the glycerol residue are shown in *Table 1*.

Glycerol Content

The average glycerol content was 20.2% (range 8.0% to 36.3%), higher than the 12% - 18% in sweet water from fat splitting, 10% - 14% and 18% - 30% in spent soap lye from kettle saponification and continuous saponification, respectively, and 20% - 25% in the raw glycerine from trans-esterification (Anderson and Hedtke, 1996).

Ash Content

The mean ash content was 64.3% (range 57.9% to 75.5%). Inorganic matter such as common salt (NaCl) was included in the ash. As the glycerol residue was

TABLE 1. CHARACTERISTICS OF GLYCEROL RESIDUE FROM A PALM KERNEL OIL METHYL ESTER PLANT

Batch	Contents of parameters characterized				
	Glycerol (%)	Ash (%)	Moisture (%)	MONG (%)	pH
GR1	17.7	58.7	5.9	17.7	12.8
GR2	17.1	58.5	11.2	13.2	12.6
GR3	19.0	62.8	5.9	12.3	12.7
GR4	8.0	75.5	0.5	16.1	12.9
GR5	11.9	72.3	1.1	14.7	12.4
GR6	8.8	73.1	1.3	16.8	10.4
GR7	23.1	66.1	2.0	8.8	13.5
GR8	36.3	57.9	1.2	4.6	13.6
GR9	29.7	58.3	1.2	10.2	13.5
GR10	17.7	67.3	2.3	12.7	12.8
GR11	19.2	62.2	2.7	15.9	12.9
GR12	33.5	59.2	1.1	6.2	13.5
Average	20.2	64.3	3.0	12.4	12.8

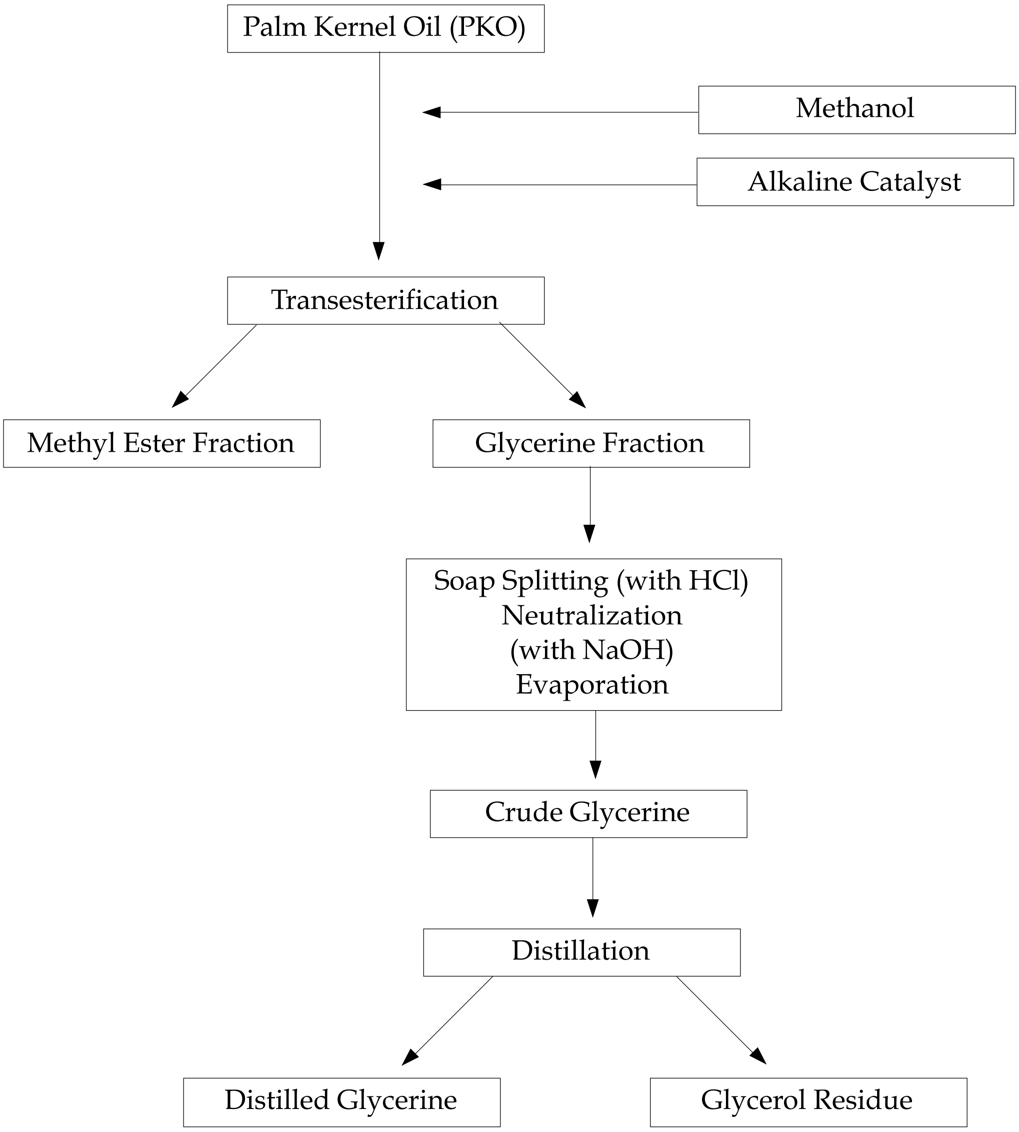

Figure 1. Flow diagram of transesterification leading to generation of glycerol residue in a palm kernel methyl ester plant.

from a methyl ester plant, the salt was formed during the acidification (soap splitting) and neutralization (*Figure 1*).

Ash was the largest component in the glycerol residue. Considerable salt had dissolved in the aqueous solution and was not removed during the evaporation. After the distillation, the salt was precipitated and concentrated in the glycerol residue.

Moisture Content

The average moisture content was 3.0% but highly variable (range 0.5% to 11.2%). As glycerol is hygroscopic, it absorbs moisture from its surroundings. In the production of methyl ester, the glycerol residue is discharged from the bottom of the distillation vessel where it is in high vacuum and high temperature (about 180°C). The fresh glycerol residue is therefore dry and should remain so if immediately stored in sealed containers. The high moisture in GR1 (5.9%), GR2 (11.2%) and GR3 (5.9%) was probably due to the fact that they were stored in unsealed containers during which they absorbed moisture. Hence, some moisture is to be expected if a sample is improperly stored. Proper storage should give a dry product undegraded from (bacterial) fermentation, oxidation and other processes.

Matter Organic Non-glycerol (MONG)

The average MONG was 12.4% (range 4.6% to 17.7%), mainly soap. About 6.6% fatty acids were recovered as soap. The raw glycerine from methanolysis of crude palm kernel oil (CPKO) contained some soap and methyl esters. When refined as in *Figure 1*, some of its fatty acids were released as the soap was split, and some of the methyl esters dissolved, or became suspended, in the glycerine solution. These (free) fatty acids and methyl esters then reacted with the excess NaOH in the subsequent neutralization to re-form soap which remained in the glycerol residue after distillation. In addition, the MONG may have included the polymerized compounds of glycerol (diglycerol and triglycerol) formed in the distillation (at about 180°C) and catalysed by the sodium hydroxide (Garti *et al*., 1981).

pH

The mean pH of the glycerol residue was 12.8 (range 10.4 to 13.6). The alkaline nature was due to its soap content and excess NaOH from neutralization in the refining of glycerol in the methyl ester plant (*Figure 1*).

Crude Fatty Acid Fractions

Crude fatty acids (from light to dark brown in colour) constituted 6.6% of the glycerol residue (range 2.7% to 10.7%) (*Table 2*). The variability might have resulted from differences in the duration of distillation, efficiency of soap splitting or fatty acid and methyl ester separation in the glycerol refining.

The composition of crude fatty acids (*Table 2*) was calculated from the GC chromatograms (from the normalized percentages based on the peak areas), a typical one of which is shown in *Figure 2*. The most common fatty acids were C12:0, C8:0 and C10:0 (*Table 2*). The short chain acids (C6:0 and C8:0) accounted for 34.5%, medium chain acids (C10:0, C12:0 and C14:0) 56.5%, long chain unsaturated acids 5.5% and long chain saturated acids 3.1% of the fatty acid component *(Table 3)*. Thus, the medium and short chain fatty acids predominated, as they are highly soluble in glycerol or aqueous solution. Furthermore, the raw material used in the methyl ester plant was palm kernel oil which contained only about 0.3% C6:0, 4.4% C8:0 and 3.7% C10:0. The long chain saturated fatty acids were low as they were only sparingly soluble in aqueous solution and glycerol.

TABLE 2. WEIGHT PERCENTAGES AND FAC OF CRUDE FATTY ACIDS ISOLATED FROM GLYCEROL RESIDUE

Batch	Weight (%)	Fatty acid (%)								
		C6:0	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2
GR1	10.5	4.0	38.3	13.7	31.6	5.4	2.0	0.6	3.9	0.4
GR2	2.7	3.7	30.0	12.2	45.4	4.5	1.2	0.3	2.3	-
GR3	5.7	5.5	32.0	7.3	44.9	5.2	1.5	0.3	2.5	0.3
GR4	10.7	5.9	33.3	8.2	37.6	6.0	2.4	0.7	4.8	0.4
GR5	9.7	4.5	28.3	8.3	37.3	6.9	3.4	1.2	7.9	1.3
GR6	9.8	4.1	28.5	8.7	37.6	7.0	3.4	1.2	7.8	1.2
GR7	5.4	5.0	35.2	9.9	39.9	5.1	1.6	0.4	2.7	0.4
GR8	3.9	3.6	30.6	9.8	43.9	5.9	1.9	0.5	3.3	0.5
GR9	4.8	3.9	29.4	8.9	42.7	6.8	2.5	0.6	4.7	0.4
GR10	4.7	4.8	30.4	8.5	40.0	6.8	2.6	0.7	5.3	0.7
GR11	7.6	2.4	19.8	7.4	44.4	9.6	4.3	1.3	8.9	0.8
GR12	4.1	3.5	28.3	9.5	44.7	6.7	2.2	0.5	4.1	0.4
Average	6.6	4.2	30.3	9.4	40.8	6.3	2.4	0.7	4.9	0.6

TABLE 3. MEAN FAC OF CRUDE FATTY ACIDS ISOLATED FROM GLYCEROL RESIDUE BY CHAIN LENGTH

Fatty acids	Percentage (%)
Short chain C6:0 and C8:0	34.5
Medium chain C10:0, C12:0 and C14:0	56.5
Long chain, saturated (C16:0 and C18:0)	3.1
Long chain, unsaturated (C18:1 and C18:2)	5.5

As shown in *Table 4*, the content of short chain fatty acids in the isolated crude fatty acids (34.5%) was higher than in CPKO (4.7%) and CPKO methyl esters (3.5%). In contrast, the medium chain fatty acids were only 56.5% of the isolated crude fatty acids compared to 67.6% in CPKO and 63.7% in CPKO methyl esters. This was because the raw glycerine from methanolysis of CPKO contained appreciable amounts of soap and methyl esters. During soap splitting in refining the glycerol, some of the short and medium chain fatty acids were released from the soap, and mixed or dissolved in the polar glycerine. Similarly, some of the short and medium chain fatty methyl esters also dissolved or became suspended in the glycerine phase without

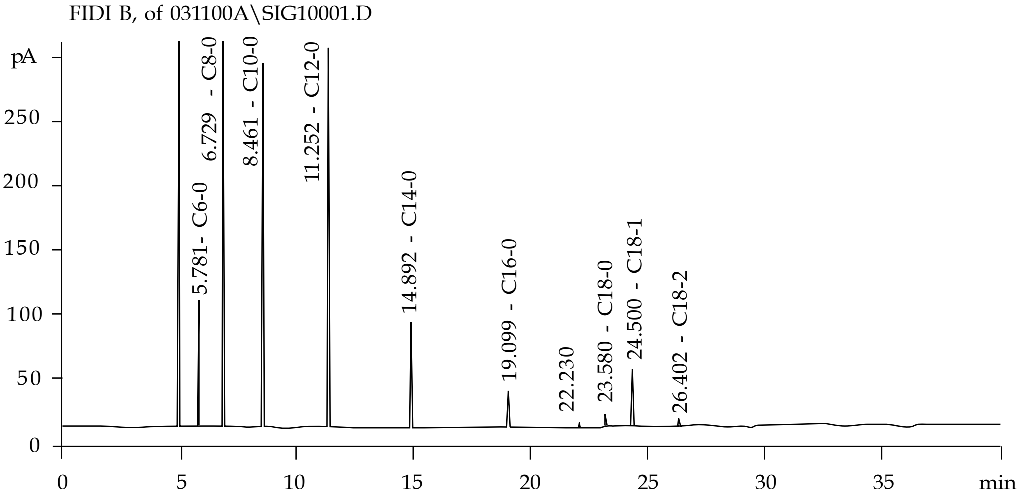

Figure 2. Typical GC chromatogram of fatty acid methyl esters of the crude fatty acid fraction isolated from glycerol residue (GR1).

TABLE 4. FAC OF CRUDE PALM KERNEL OIL (CPKO), METHYL ESTER OF CPKO (ME OF CPKO) AND CRUDE FATTY ACIDS (CFA) ISOLATED FROM GLYCEROL RESIDUE (%)

	Fatty acid										
Sample	**C6:**	**C8:0**	**C10:0**	**C12:0**	**C14:0**	**C16:0**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0**
CPKO[a]	0.3	4.4	3.7	48.3	15.6	7.8	2.0	15.1	2.7	0.2	-
ME[b]of CPKO	0.5	3.0	2.8	44.9	16.0	10.1	2.4	17.1	2.8	0.2	0.2
CFA[c]	4.2	30.3	9.4	40.8	6.3	2.4	0.7	4.9	0.6	-	-

Sources: [a]Siew and Berger (1981).
[b]Choo and Ma (1996).
[c]This study.

separation. These dissolved fatty acids and methyl esters then reacted with excess sodium hydroxide in the subsequent neutralization to re-form soap which concentrated in the glycerol residue after the distillation in refining. Therefore, the glycerol residue is a good source of short and medium chain fatty acids, although the acids recovered may need to be refined.

CONCLUSION

Twelve samples of glycerol residue, GR1 to GR12, showed large variation in the contents of glycerol, ash, moisture, MONG and crude fatty acids. Salt (64.3%), glycerol (20.2%) and fatty acids (6.6%, present as soap) were the three main valuable components of glycerol residue, accounting for 91.1% of the residue. The main fatty acids were C12:0 (40.8%), C8:0 (30.3%) and C10:0 (9.4%).

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