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Glycerol Residue — A Rich Source of Glycerol and Medium Chain Fatty Acids

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Abstract: Glycerol residue, a by-product of glycerol refining from a palm kernel oil methyl ester plant, was found to be a good source of glycerol and medium chain fatty acids. From analyses of twelve samples, it was found to contain, on average, 20.2 % glycerol and 6.6 % fatty acids. The fatty acids comprised mainly C8:0 (30.3 %), C10:0 (9.4 %) and C12:0 (40.8 %).

Key words: glycerol residue, glycerol, medium chain fatty acid, palm kernel oil

1 Introduction

Lauric oils are the main sources of short chain (C6 - C8) and medium chain (C10, C12 and C14) fatty acids. The major commercial lauric oils available in the world are coconut and palm kernel oil (1). Cuphea seed oils have been found to contain up to 93 % capric acid. In 2002, the world production of coconut and palm kernel oils were 3,106,000 tonnes and 2,975,000 tonnes respectively and they contributed to about 5.0 % of the world production of fats and oils (2).

Typical fatty acid composition of palm kernel oil and coconut oil are shown in **Table 1**. It can be seen that the total percentage of C6-C10 fatty acids of palm kernel oil and coconut oil are in the range of 8.4% and 15 % respectively.

The short hydrocarbon chain of short and medium chain fatty acids make them more hydrophilic and possess special interfacial properties which makes them suitable for the application in detergent, cosmetics, soaps, lubricants, metalworking fluid/cutting fluid additive, additive for plastic, biocide and others. Other uses include the production of medium chain triglycerides (MCT). MCT has been found to possess medicinal and nutritional importance (3,4). The preparation of some polyglycerol ester of short and medium chain length fatty acids is another important area of applications and they have been found to show promising application in surface activity, emulsification and solubilisation of oil and water system (5).

Malaysia is the world's largest palm oil and palm kernel producer. Most of the palm kernel oil produced are normally used as a raw materials for the production of oleochemicals. It is normally used to produce methyl esters via transesterification of palm kernel oil. The esters are then used as intermediates for the production of oleochemicals derivatives such as fatty alcohol and derivatives. In the process, sweetwater is produced as one of the by-products. Upon distillation, it results in the production of a distillation bottom (DB), which is currently of no usage and use it for landfill. This waste is normally called glycerol residue. So far to our knowl-

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Table 1 Fatty Acid Composition of Palm Kernel Oil and Coconut Oil (%).

Fatty acids	Palm kernel oil	Coconut oil
C6	0.3	0.5
C8	4.4	7.8
C10	3.7	6.7
C12	48.3	47.5
C14	15.6	18.1
C16	7.8	8.8
C18	2.0	2.6
C18:1	15.1	6.2
C18:2	2.7	1.7
C18:3	0.1	0.1

edge, no reports or patents have reported the composition of this waste. Therefore, it is the purpose of this paper to report our findings for this waste product.

2 Experimental Procedures

2·1 Materials

Twelve batches of glycerol residue (GR1 to GR12) were obtained from a local oleochemical company. The residues were generated by the glycerol refining process of a palm kernel oil methyl ester plant. The glycerol residues consisted of light to dark brown granule or paste. All chemicals and solvents used in this study were of analytical grades.

2·2 Glycerol Content

Glycerol content was analysed by titrimetric method according to standard method ISO 2879- 1975.

2·3 Isolation and Analysis of Crude Fatty Acids

The crude fatty acids were isolated from glycerol residue by using conventional acid hydrolysis process, followed by phase separation. The fatty acid composition of crude fatty acids was analyzed by using a Hewlett Packard, HP 6890 gas chromatograph. The fatty acid composition of the sample was calculated by the normalized percent method. The column used was SUPELCO SP-2340 (60 m × 0.25 mm × 0.20 μm) and the oven temperature was programmed from 120℃ to 185℃ at ramp rate of 3℃ min^{-1}. The injector and detector temperatures were set at 240℃. Nitrogen was used as carrier gas (0.8 $cm^3 min^{-1}$) and about 1.0 μL of sample was injected into the gas chromatograph for analysis. The fatty acid was injected as methyl ester derivative, which was prepared according to the PORIM Test Method p3.4, boron trifluoride method (6).

3 Results and Discussion

3·1 Generation of Glycerol Residue

Methyl ester of palm kernel oil was produced by transesterification of crude palm kernel oil with methanol in the presence of an alkaline catalyst. The completion of the reaction resulted in a heterogeneous mixture of methyl esters and glycerine phase, which were immiscible and could readily be separated in a settling tank.

The glycerine phase contained methanol, methyl ester and a significant amount of soap (which was formed by the reaction of the alkaline catalyst and the palm kernel oil). The methanol was recovered for reuse. The soap in the crude glycerine was removed in the soap splitting step where the glycerine was acidified with diluted hydrochloric acid. The released free fatty acids (which was immiscible in the glycerine solution) was removed by gravitational settling and decantation.

The excess hydrochloric acid was removed by subsequent neutralization step where the hydrochloric acid was neutralized by diluted sodium hydroxide solution (caustic soda). In this step a considerable amount of sodium chloride was formed in the glycerine solution. The acidified and neutralized glycerine solution was then concentrated in a drying process before it was subjected to distillation to produce distilled glycerine and glycerol residue (distillation residue, generated as waste material). The flow diagram of the transesterification of crude palm kernel oil leading to the generation of glycerol residue is presented in **Fig. 1**.

3·2 Glycerol and Fatty Acid Content of Glycerol Residues

Twelve batches of glycerol residue (GR1 to GR12) have been studied to determine their composition and characteristics. The results of the analyses of glycerol and fatty acid contents in twelve batches of glycerol residue samples are shown in **Table 2**.

3·3 Glycerol Content

The average glycerol content of the glycerol residues was 20.2%. It ranged from 8.0% to 36.3%. The amount

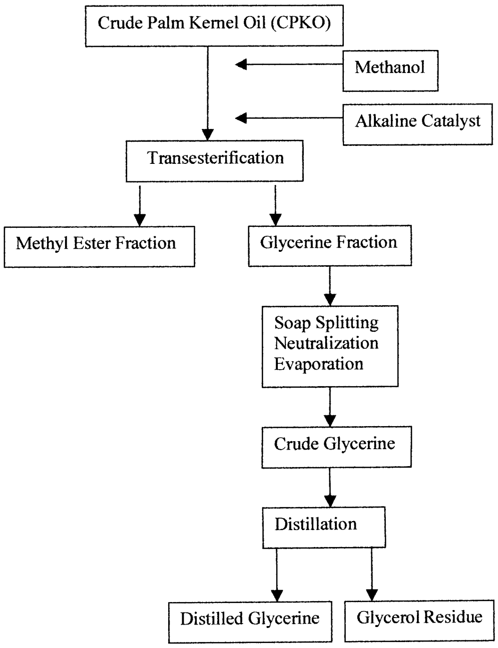

Fig. 1 Flow Diagram of the Transesterification Process Leading to Generation of Glycerol Residue in a Palm Kernel Methyl Ester Plant.

Table 2 Glycerol and Fatty Acid Contents of Glycerol Residues*.

Glycerol residue	Glycerol (%)	Fatty Acids (%)
GR1	17.7	10.5
GR2	17.1	2.7
GR3	19.0	5.7
GR4	8.0	10.7
GR5	11.9	9.7
GR6	8.8	9.8
GR7	23.1	5.4
GR8	36.3	3.9
GR9	29.7	4.8
GR10	17.7	4.7
GR11	19.2	7.6
GR12	33.5	4.1
Average	20.2	6.6

*Determination was done in duplicate and average value was taken

of glycerol content for samples GR 4, GR 5 and GR6 was lower than the others because it was known from the company that distillation of glycerol was carried out immediately after servicing the plant and attempts to optimize the process. The average content of 20.2% is significant as compared to 12-18% of glycerol in the raw glycerine solution of the fat splitting process, 10-14% in the kettle saponification, 18-30% in the continuous saponification process and 20-25% in the transesterification process (7).

3·4 Crude Fatty Acid Fractions

The average weight percentage of the crude fatty acid fractions, which were isolated from glycerol residue was 6.6%. The values ranged from 2.7% to 10.7% as shown in **Table 2**. The crude fatty acids isolated from the twelve different batches varied from light to dark brown liquid. The weight percentage of crude fatty acids varied widely from batch to batch. The variation might be caused by the differences in the duration of distillation and the efficiency of the soap splitting or fatty acid and methyl esters separation in glycerol refining process.

The fatty acid compositions of the crude fatty acids (**Table 3**) were calculated from the GC chromatograms (normalized percent based on peak area). The typical GC chromatogram of crude fatty acid components is shown in **Fig. 2**. The results show that C12:0, C10:0 and C8:0 fatty acids are prominent in the crude fatty acid fractions. **Table 4** shows that in the fatty acid fraction, short chain fatty acids (C6:0 and C8:0) accounted for 34.5%, medium chain fatty acids (C10:0, C12:0 and C14:0) for 56.5%, long chain unsaturated fatty acids (C18:1 and C18:2) for 5.4% and long chain saturated fatty acids (C16:0 and C18:0) for 3.1%. The short and medium chain fatty acids predominated in the glycerol residue, as they are highly soluble in glycerol or aqueous solution. Furthermore, the raw material used in the methyl ester plant was palm kernel oil in which contained 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.

Also 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%). In contrast, the medium chain fatty acids were only 56.5 % of the isolated crude fatty acids compared to 67.6 % in CPKO.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, mixed or dissolved in the polar glycerine. Similarly, some of the short and medium

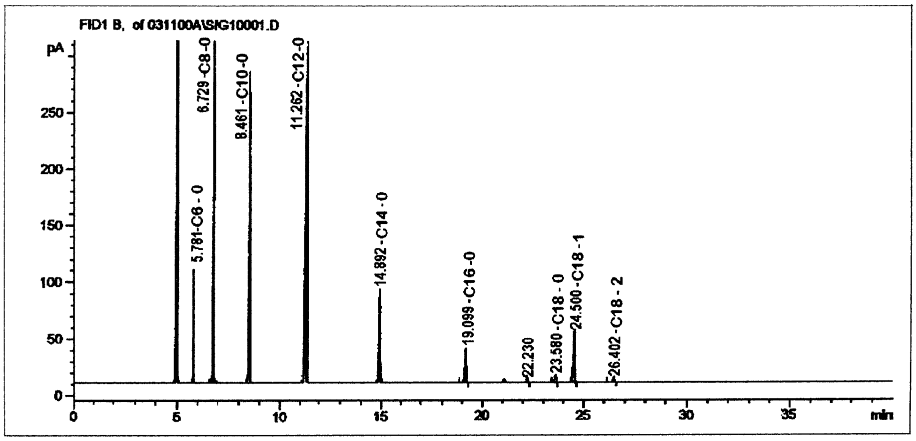

Fig. 2 Typical GC Chromatogram of Fatty Acid Methyl Esters of Crude Fatty Acid Fraction Isolated from Glycerol Residue (GR1).

Table 3 Fatty Acid Composition of Crude Fatty Acids Isolated from Glycerol Residue.

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

Table 4 Fatty Acid Composition of Crude Palm Kernel Oil (CPKO) and Crude Fatty Acids (CFA) Isolated from Glycerol Residue (%).

sample	Fatty acid									
	C6:0	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
CPKO[a]	0.3	4.4	3.7	48.3	15.6	7.8	2.0	15.1	2.7	0.1
CFA[b]	4.2	30.3	9.4	40.8	6.3	2.4	0.7	4.9	0.6	—

Sources: [a] Siew and Berger (9)
[b] This study

chain fatty methyl esters also dissolved or became suspended in the glycerine phase without separation. These dissolved fatty acids and methyl esters then reacted with excess sodium hydroxide in the subsequent neutralisation to reform 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.

4 Conclusion

From the twelve batches of glycerol residue analysed, GR1 to GR12. It showed besides the high glycerol content (average about 20.2 %) , glycerol residue can also provide a good source of short and medium chain fatty acids, however, the recovered crude fatty acids may need further purification. The weight percentage of the glycerol and crude fatty acids varied from batch to batch. The average weight percentage of the isolated crude fatty acids is 6.6%. The main components of crude fatty acids are C8:0 (30.3%), C10:0 (9.4%) and C12:0 (40.8 %).

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