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RECOVERY OF GLYCEROL AND DIGLYCEROL FROM GLYCEROL PITCH

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ABSTRACT

Glycerol pitch is one of the wastes generated by the Malaysian oleochemicals industry. A recovery technique which involved an acid-based extraction was developed in which the pitch was separated into three components - crude glycerol containing diglycerol, fatty acids and inorganic salts. The crude glycerol was subjected to vacuum distillation to produce pure glycerol, leaving behind an undistilled fraction rich in diglycerol. Several analyses, such as glycerol content, ash content, moisture content and acidity, and Fourier transform infra red (FTIR) and high performance liquid chromatography (HPLC) were employed to determine the purity and the compositions of glycerol pitch and the products thus isolated from the waste. The analyses showed that the glycerol pitch comprised 55%-65% glycerol, 15%-25% diglycerol, and less than 10% each of fatty acids and inorganic salts. The method developed is simple and suitable for the recovery of glycerol and diglycerol in the waste.

Keywords: glycerol pitch, diglycerol, polyglycerol, sweet water.

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INTRODUCTION

With the abundant supply of both palm and kernel oils as raw materials locally, the Malaysian palm oil industry has begun producing oleochemicals to add value to the basic products. The demand for oleochemicals is strongly related to the standard of living – rising with affluence and environmental consciousness. From an ecological point of view, the prospects for renewable resources are bright as natural products are increasingly favoured by consumers. Malaysia is now a leading producer of oleochemicals in the world.

Glycerol pitch is a waste from the oleochemicals industry, generated from fatty acid plants in the refining of sweet water to pure glycerol. Sweet water normally requires chemical treatment for the removal of dissolved or suspended fatty acids, oxidized fatty acids, colour materials and various nitrogenous materials prior to the evaporation stage.

Sweet water from the splitting unit is usually taken to a settling tank, where the separated fatty acids are first skimmed off. The remaining solution is then air-agitated and undergo chemical treatments to further remove the insoluble materials such as adsorbed fatty acids, metal salts and others. The resultant aqueous fraction is then concentrated. A pure and refined glycerol is obtained by high vacuum distillation of the concentrate (Whalley, 1995), and the residue left is called glycerol pitch. The refining process of sweet water to pure glycerol may differ from one plant to another.

Glycerol pitch is classified as a *scheduled waste* by the Malaysian Department of Environment (DOE). Scheduled waste means any waste falling within the category of wastes listed in the First Schedule of the Environmental Quality (Scheduled Wastes) Regulations 1989 which came into force on 1 May 1989. Disposal of combustible wastes like glycerol pitch has been a major problem to the community especially in urban and densely populated areas (Corey, 1969). Burning the waste can literally means converting it into acrolein, a highly volatile compound and well-known for its toxicity and very hazardous to life. Currently in Malaysia, Kualiti Alam Waste Management Centre is the only body

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handling these scheduled wastes where disposal and its treatment are carried out at prescribed premises only with a certain amount of charges imposed for every tonne of waste disposed off. The cost for landfill is ~RM 500 and incineration ~RM 810-RM 3600 t^{-1}.

The glycerol pitch which is usually very alkaline (pH >10) is a viscous gel with a colour ranging from brown to dark brown although its appearance and composition vary from plant to plant. It contains glycerol, diglycerol, fatty acids and inorganic salts. The Malaysian Palm Oil Board (MPOB) is exploring the potential of the various wastes generated by the oleochemicals industry in the hope of recovering useful by-products from them. Hence, this study was undertaken to recover useful by-products from glycerol pitch.

MATERIALS AND METHOD

Fourier transform infra red (FTIR) spectra were recorded on a NICOLET MAGNA-IR 550 Spectrometer. The liquid samples were determined as liquid films (neat) and the solid samples using potassium bromide (KBr) pellets. The absorptions were expressed as wave numbers (cm^{-1}).

Gas Chromatography (GC) chromatograms were recorded by HP 6890 Series GC system with the following conditions:

column: open tubular fused silica column coated with SP 2340 (60 x 0.25 mm)
oven temperature: 185°C (isothermal)
injector temperature: 240°C
detector temperature: 240°C
carrier gas: H_2, 0.8 ml min^{-1}
make-up gas: N_2, 30 ml min^{-1}
split ratio: 1:100
injection volume: 1μl

High performance liquid chromatography (HPLC) chromatograms were obtained from a JASCO PU-980 Intelligent HPLC Pump and JASCO RI-930 Intelligent RI Detector. Samples of ~5% concentration were prepared by dissolving 500 mg of each in 10 ml distilled water in 10 ml volumetric flasks. The analyses were expressed in minutes of retention time (R_t). The following conditions were employed throughout the analyses:

stationary phase (column): hypersil 10 μ NH_2 (4.6 mm x 250 mm)
detector: for refractive index (RI)
temperature: 30°C
mobile phase (solvent system): acetonitrile:water (85:15)
flow rate of mobile phase: 1 ml min^{-1}
sample injected: 20 μl

The test methods below were used for analysis of the glycerol pitch and the products isolated from it. The purified glycerol was analysed by the industry.

Moisture:	PORIM AOTC 01/96 (Karl Fisher)
Glycerol:	ISO 2879-1975(E)
Ash:	ISO 2098-1972 (E)
Colour:	PORIM p4.1 (1995)
Acidity:	ISO 1615 – 1976 (E)

Recovery Method

In a typical laboratory-scale experiment, 100 g of glycerol pitch dissolved in 150 ml distilled water were acidified to pH ~2 using concentrated sulphuric acid (H_2SO_4) added in portions. The mixture was allowed to settle for 30-45 min and partition into two layers. The fatty acid layer (top layer), which contained a tar-like solid or paste, was skimmed off and the aqueous layer filtered to further remove any solid material. The fatty acids obtained were ~5.5 g. To ensure complete removal of the fatty acid fraction, the filtrate was transferred to a 500 ml separatory funnel and extracted with diethyl ether. The ether extracts were combined and concentrated in *vacuo* to give another ~0.3 g of the fatty acids. The aqueous layer was placed in a 500 ml beaker and neutralized to pH ~7 using 50% NaOH solution. The resultant mixture was transferred to a 500 ml round bottom flask with filtration to remove any residual solid material. The water was then removed in *vacuo* to give a mixture crude of glycerol and inorganic salts. About 30-40 ml chilled MeOH were added and the sample allowed to stand at room temperature for ~30 min followed by refrigeration for another 30 min to ensure complete precipitation of the salts. The inorganic salts were filtered off and washed with chilled MeOH. They were air-dried and weighed ~6.7 g. The MeOH extracts were combined and concentrated in *vacuo* to give ~78.5 g crude glycerol.

Vacuum Distillation

The crude glycerol samples (~10 g) obtained from above were subjected to vacuum distillation at 0.1 to 3 mbar, and heated in an oil bath at 140°C - 160°C. The distillates (~7.7 g) were usually obtained at ~110°C-120°C, depending on the stability of the vacuum applied. The purified glycerol obtained was slightly yellowish.

RESULTS AND DISCUSSION

The glycerol pitch from different factories differed considerably in viscosity and colour which can range from brown to dark brown. The FTIR spectra of the glycerol pitch were recorded and compared to that from pure glycerol (*Figure 1*). The presence of soap

(COO^- functionality) was indicated by the absorption frequency at ~1580 cm^{-1} which was absent in pure glycerol. The glycerolic moiety of the pure compound is evidenced by the absorption peak at 1500-1200 cm^{-1}, assigned to overlapping of the C-H in-planes and O-H bending in the glycerol molecule. The presence of the OH group in all the samples was evidenced by the fundamental mode of OH stretching at 3500-3000 cm^{-1} and 1630 cm^{-1} (Silverstein *et al.*, 1981). The FTIR of the crude glycerol (R-G) recovered from glycerol pitch also showed similar absorption patterns.

The recovery technique separated the glycerol pitch into its various components - crude glycerol (70%-80%), fatty acids (<10%) and inorganic salts (<10%). Further analysis of the crude glycerol fraction and glycerol pitch by HPLC indicated the presence of diglycerol (15%-25%). Analysis of the residue from the vacuum distillation also showed the presence of diglycerol. For comparison, the HPLC chromatograms of commercial polyglycerol and glycerol pitch are shown in *Figures 2* and *3* respectively. In the chromatograms, glycerol appears at R_t ~7.8 min, diglycerol at R_t ~13 min and triglycerol at R_t between 20-30 min. The diglycerol could have been formed during the vacuum distillation when the crude glycerol was heated to a high temperature especially in the presence of either some acid or caustic.

The analysed composition of glycerol pitch is summarized in *Table 1*. The characteristics of the crude glycerol and its purified glycerol are shown in *Table 2*. For comparison, the characteristics of commercial glycerol are also given.

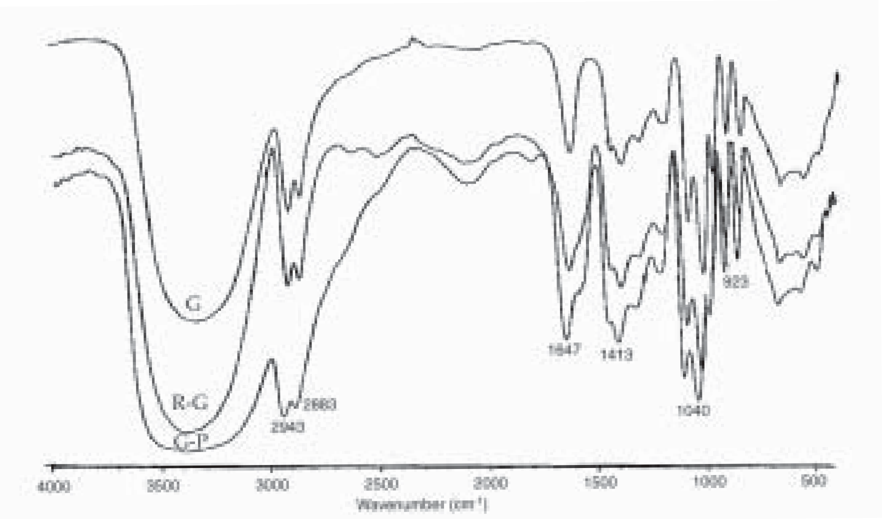

Figure 1. Fourier transform infra red (FTIR) spectra of pure glycerol (G), crude glycerol (R-G) and glycerol pitch (G-P).

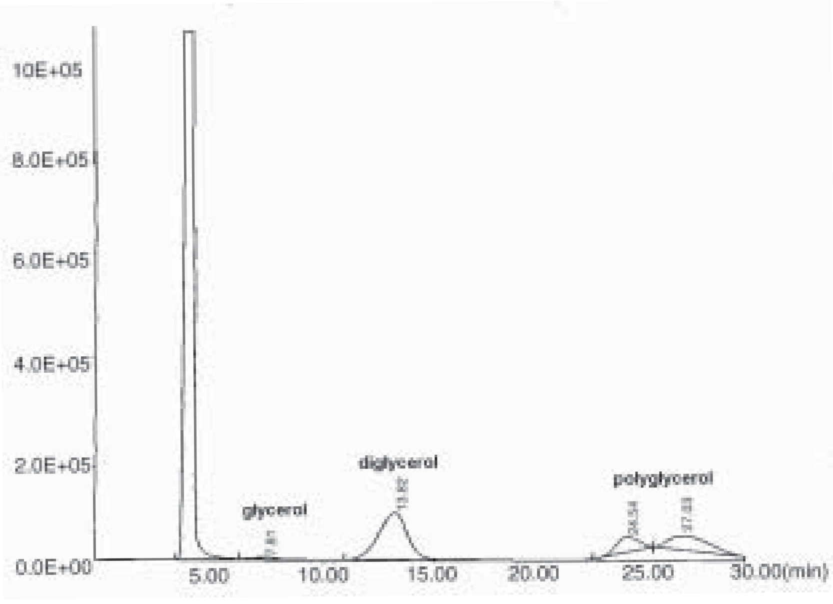

Figure 2. High performance liquid chromatography (HPLC) chromatogram of commercial polyglycerol.

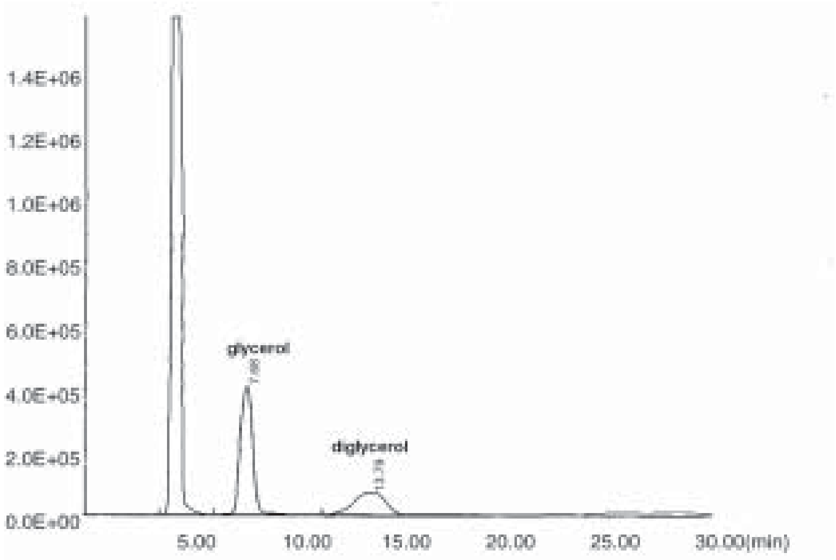

Figure 3. High performance liquid chromatography (HPLC) chromatogram of glycerol pitch.

The fatty acids isolated were very dark and tar-like. The fraction was analysed by GC and the fatty acid composition (FAC) shown in *Table 3*. The FAC varied considerably from one sample to another, especially in the C8 acids. No further work was done on this fraction since it was only present at 4%-6%.

As a commodity chemical, glycerol is widely used as a solvent or drug carrier in pharmaceutical and medicinal products, as a humectant in cosmetics, toiletries and other personal care products. Glycerol is also used in the making of paper and explosives. Polyglycerol and its corresponding esters are widely

TABLE 1. COMPOSITION OF GLYCEROL PITCH (%)

Glycerol	Fatty acids	Inorganic salts	Diglycerol-rich fraction
55 to 65	< 10	< 10	15 to 25

Note: * Seven samples from three fatty acid plants were analysed.

TABLE 2. CHARACTERISTICS OF CRUDE GLYCEROL AND PURIFIED GLYCEROL FROM GLYCEROL PITCH AND COMMERCIAL GLYCERIN

Parameter	Crude glycerol	Purified glycerol	Commercial* glycerin
Glycerol content (%)	60 - 80	99.1- 99.8	99.2 - 99.98
Moisture/H_2O (%)	1.5 - 6.5	0.11- 0.80	0.14 - 0.29
Ash (%)	1.5 - 2.5	0.054	< 0.002
Soap (%)	3 – 5	0.56	n.a
Acidity	0.7 - 1.3	0.10-0.16	0.04 – 0.07
Chloride	n.d.	1 ppm	0.6 – 9.5 ppm
Colour (APHA)	Dark	34-45	1.8-10.3

Note: *Mohtar *et al.* (2001).

TABLE 3. FATTY ACID COMPOSITION OF GLYCEROL PITCH

Fatty acid chain length	Percentage (%)
C8:0	0.5 – 26.5
C10:0	0.5 – 1.2
C12:0	0.5 – 2
C14:0	1.2 – 1.5
C16:0	1.2 – 2
C18:0	0.5 – 12
C18:1	20 – 24
Others	30 – 55.3

Note: * Three samples were analysed.

used as food additives, emulsifiers, anti-spattering agents and for anti-clouding in cooking and salad oils. The process of converting glycerol to polyglycerols has been one of major advancement in the chemical conversion of glycerol to polyglycerol. Polyglycerols can be prepared by polymerization of glycerol, in the presence of an alkaline or acid condensation catalyst (Seiden and Martin, 1976). The use of glycerol and polyglycerol for manufacturing of urethane foam is on the increase. Foams made from glycerol derivatives are flexible, resilient and age well in humid conditions (Croy and Dotson, 1997).

CONCLUSION

Although glycerol pitch is a waste generated from the fatty acid plant, it is rich in glycerol and diglycerol, and therefore a worthwhile source of feedstock for recovery of useful chemicals.

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