A STUDY OF THE NATURE OF OIL RECOVERED FROM SPENT EARTH OBTAINED FROM THE PHYSICAL REFINING OF PALM OIL

Keywords: Palm oil; physical refining; spent bleaching earth; solvent extraction; characteristics of extracted oil.

OOI, T L; BADRI, M AND ASMA, D*

The characteristics of oils extracted with solvents from spent earth used to bleach palm oil were investigated. It was found that the total oil extracted from spent earth by petroleum ether (SE-P) followed by chloroform (SE-C) accounts for 26.3% of the total weight of spent earth. The extracted oils were slightly brownish red and brownish respectively. The unsaponifiable matter in SE-P and SE-C amounted to 1.39% and 1.60% respectively. The FFA content of both extracts was high, about 22 per cent. However there was no significant difference in the fatty acid composition or carbon number between palm oil, SE-P and SE-C. The phosphorus contents of SE-P and SE-C were found to be 11.2 ppm and 10.1 ppm respectively, while the iron and copper present in SE-P were found to be at 2.1 ppm and 0.04 ppm respectively.

INTRODUCTION

Today, practically all fully refined palm oil products in Malaysia and Indonesia are produced by physical or steam refining. One of the by-products of this process is spent bleaching earth. *Figure 1* shows schematically the steps involved in the physical refining process for palm oil. At present the spent earth is mostly disposed of in landfills. The quantity of the oil retained in the spent earth normally ranges between 0.5% to 1.8% by weight of the oil processed.

The treatment of the spent earth obtained in the physical refining of palm oil, and recovery of oil from it, were described and discussed by Wong (1983). Analyses of phospholipids and

*Palm Oil Research Institute of Malaysia
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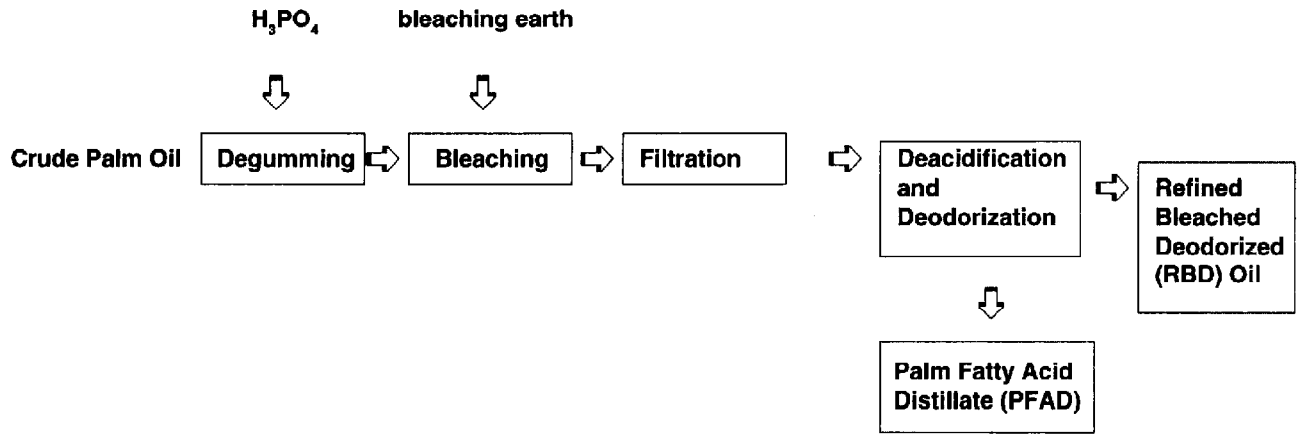


Figure 1. Physical (steam) refining process.

glycolipids in the recovered oil have been reported by Goh *et al.* (1982) and Yamaoka *et al.* (1989) respectively. The content of glycolipids was found to be 3.8% of the recovered oil.

Recently, some companies have shown interest in the production of edible grade oil products by further refining the palm oil extracted from spent bleaching earth. Therefore it could obviously be of importance to understand the characteristics of the extracted oil; it is the purpose of this paper to describe some recent analyses of the characteristics of the oil extracted by petroleum ether (60°C–80°C) and by chloroform from the spent earth.

MATERIALS AND METHODS

Materials

The spent earth used in this study was obtained from Southern Edible Oil Industries (M) Sdn. Bhd.

All solvents used were of analytical grade.

Methods

Extraction of oil from spent earth

About 200 g of spent earth was weighed in a conical flask and 300 ml of petroleum ether (60°–80°C) was then added. The mixture was shaken for 5–6 minutes and was later vacuum filtered. The residue was washed twice with 300 ml of petroleum ether each time. The filtrates were combined and the solvent was removed using the roto evaporator. The petroleum ether extract obtained was labelled SE-P.

The residue from petroleum ether extraction was further extracted three times, with 300 ml of chloroform each time. This chloroform extract was labelled SE-C. *Figure 2* shows a flow chart for the extraction of oil from spent earth.

The residual spent earth (after the extractions) was air dried in the fume cupboard and weighed.

Determination of unsaponifiable matter in extracted oil

A 5 g sample of the extracted oil was weighed accurately in a round bottomed flask. 30 ml of ethanol and 5 ml of aqueous potassium hydroxide (50% KOH by weight) were added, together with some anti-bumping granules. The mixture was refluxed for one hour. Then 40 ml of hot distilled water was added followed by 40 ml of cold distilled water. The mixture was allowed to cool to room temperature. It was then poured into a separating funnel and the transfer completed by rinsing the flask with a further 50 ml of ethanol.

50 ml of petroleum ether was added to the funnel and the mixture was shaken vigorously for one minute, then allowed to settle

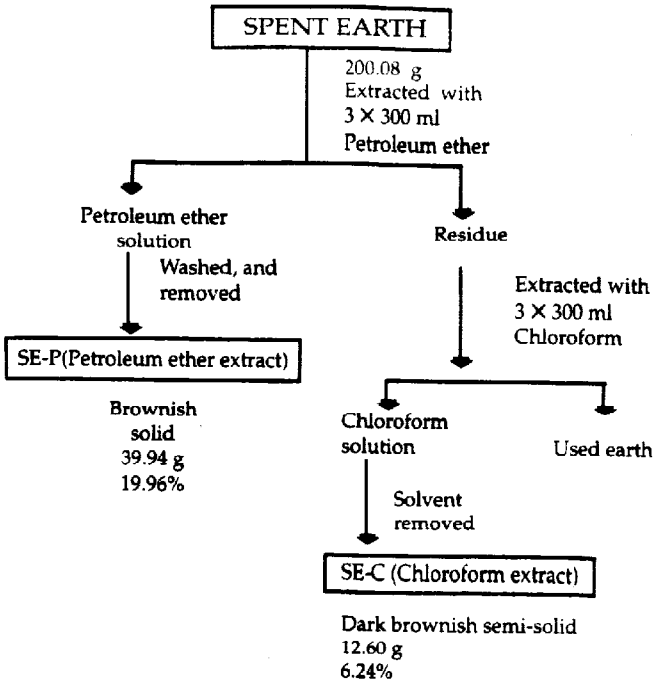


Figure 2. Flowchart of the extraction of oil from spent earth.

until two clear layers were observed.

The ether layer was collected and the aqueous layer was extracted five more times using 50 ml of petroleum ether each time.

The combined extract was washed repeatedly by vigorous shaking with 25 ml of distilled water containing 10% ethanol each time. Washing was discontinued when the water was neutral to phenolphtalein.

The petroleum ether extract was dried with anhydrous sodium sulphate. Then it was placed in a weighed round bottomed flask and the solvent was removed using the roto evaporator.

GC analysis of sterols in the unsaponifiable matter of the extracts

The conditions used for gas chromatography were as follows:

Instrument	: Shimadzu GC-9A PTF fitted with flame ionization detector
Column	: 3% OV-1 packed column, 2.5 m × 3 mm
Column temperature	: 270°C
Injector/detector temperature	: 330°C
N_2 gas flow rate	: 40 ml/min

Determination of percentage of free fatty acids in extracted oil

0.3 g of sample was weighed into a conical flask and dissolved in 50 ml of neutralized isopropyl alcohol. 0.5 ml phenolphathalein (0.1 in ethanol 95%) was added. The flask was placed on a hot plate and the temperature was regulated at 40°C. The sample was shaken gently and titrated with 0.1 N sodium hydroxide to the first permanent pink colour. The percentage FFA was calculated (as palmitic acid) using the formula:

$$\text{FFA} = \frac{25.6 \times N \times t}{W}$$

where N = normally of sodium hydroxide
t = titre in ml of sodium hydroxide
W = Weight of sample used in grams

Measurement of colour of extracted oil using Lovibond Tintometer

Extracted oil was heated to 60°C and homogenized with a stirrer before use. Then it was poured into a one inch Lovibond cell. Colour measurement was carried out using a Lovibond Tintometer Model E.

Analysis of extracted oil by thin layer chromatography

The sample was spotted on a small thin layer chromatographic plate (plastic sheet, Kieselgel G F_{254}). The developing solvent used was hexane: diethyl ether: formic acid (6:4:0.1 V/V/V). Crude palm oil was used as a reference. The plate was sprayed with 2,7 dichlorofluorescein.

Measurement of absorbance of extracted oil at max 233 nm, 269 nm and 446 nm

0.1 g of sample was weighed accurately (± 0.001 g) in a 25 ml volumetric flask, then dissolved in iso-octane. Absorbances at λ_{max} 233 nm,

269 nm and 446 nm were measured using a Hitachi UV-spectrophotometer Model 120–60.

Determination of phosphorus content of extracted oil

Total phosphorus content (ppm) of extracted oil was determined by charring and ashing in the presence of magnesium oxide followed by colorimetric measurement as phosphovanadomolybdic complex (IUPAC Fifth Edition: Method II. D.16.2).

Determination of iron and copper content of extracted oil

The iron content (ppm) and copper content (ppm) of the extracted oil were determined using the Perkin Elmer Atomic Absorption Spectrophotometer, model 373 and model 1100B respectively.

Determination of fatty acid composition of extracted oil

Preparation of methyl ester of fatty acids from samples for GC analysis

Approximately 0.3 g of sample was weighed into a 50 ml round bottomed flask. 6 ml of 0.5 N methanolic sodium hydroxide solution was added, and the mixture was refluxed for 20 minutes. 1 ml of methanolic boron trifluoride solution (20% in methanol, Merck) was added through the top of the condenser, and the mixture was boiled for two minutes more. About 3 ml of n-heptane was added, and boiling was continued for another one minute.

The reaction mixture was allowed to cool to room temperature before removing the condenser. A small amount of saturated sodium chloride solution was added and the flask was swirled gently several times. More saturated sodium chloride solution was added to bring the liquid level into the neck of the flask. The upper layer of heptane solution was then transferred into a test tube and a small amount of anhydrous sodium sulphate was added. This solution was then injected directly into the gas chromatograph.

Gas chromatography analysis of the methyl esters

The conditions used were as follows:

Instrument : Shimadzu GC-9A PTF fitted with flame ionization detector

Column : 10% SP-2340 glass packed column, 3 m × 3 mm

Column temperature : 185°C

Injector/Detector temperature : 230°C

N_2 gas flow rate : 50 ml/min

Carbon number analyses of extracted oil

Two drops of homogenized sample were placed in a vial, dissolved in about 5 ml of hexane and then injected directly into the gas chromatograph.

The conditions used were as follows:

Instrument : HP 5890

Column : HT 5

Column temperature : 300°C–350°C, 4°C/min

Injector/detector temperature : 380°C

N_2 gas flow rate : 15 ml/min

RESULT AND DISCUSSION

Figure 3 shows the appearance of the original spent earth used in this study (left) and the earth after oil has been extracted using petroleum ether followed by chloroform (right).

It was found than when 200 g of spent earth was extracted, the total oil recovered (SE-P, 39.94 g, and SE-C, 12.60 g) weighed 52.54 g which accounted for 26.3% of the weight of the spent earth used.

The dark colour of the spent earth was evidently due to the oil and colour components adsorbed, because after they were removed by the solvents, the colour of the resulting earth was similar to that of the fresh bleaching earth used in the refining industry. The loss of oil due to retention by the earth as calculated from our results, was found to be comparable to that reported in practice (Wong, 1983).

The oil extracted with petroleum ether followed by chloroform was brownish red in colour. The oil extracted with petroleum ether alone was lighter in colour.

The unsaponifiable matter determined in the SE-P and SE-C extracts was found to amount to 1.39% and 1.60% respectively. These figures are higher than the average amount (about 1%) of unsaponifiable matter normally present in crude palm oil. Sterols were found to be among the unsaponifiable components in these extracts, as determined by gas liquid chromatography. From the GC analysis, it was found that the major sterol present in SE-P and in SE-C was β-sitosterol. One of the functions of bleaching earth is to adsorb the products of carotene degradation and other impurities in the oil, including sterols. Some of the minor components have been found to be selectively adsorbed by the earth (Siew, 1984) and rice husk ash (Ooi, 1991). *Figure 4* shows the GC chromatogram for the sterol analysis of the samples.

The free fatty acid of content SE-P was found to be 21.51% and that of SE-C was 22.67%; these are quite high values. This was probably due to the acidic nature of the earth which causes the hydrolysis of the oil.

The colour indices of the SE-P extract as determined using the Lovibond Tintometer were as follows:

Extract	SE-P
Blue	–2.0
Yellow	–60.0
Red	–24.0

Size of the Lovibond cell: 1 inch

Colour measurement was not carried out on SE-C because of its darker colour.

The thin layer chromatography of the extracts showed the presence of triglycerides, diglycerides, monoglycerides and fatty acids. Similar results were also observed for crude palm oil which was used as reference. These are, of course, the expected results since the major components of crude palm oil are glycerides and fatty acids. *Figure 5* shows a typical thin layer chromatogram of SE-P and SE-C.

Oxidative changes in the oil were monitored using UV spectrophotometric measurements at wavelengths 233 nm and 269 nm. The absorbance at 233 nm of SE-C was 3.3, higher than that of SE-P (2.4). The absorbances at 269 nm for SE-P and SE-C were 0.9 and 3.7 respectively. These results indicate that the extract of SE-C contained a larger amount of primary and secondary oxidation products than SE-P, presumably because, as a polar solvent, chloroform has a high dissolution affinity for the primary and secondary oxidation products from the earth.

Figure 3. Spent earth (left) and the earth after oil extraction with petroleum ether and chloroform (right).

The phosphorus contents in SE-P and SE-C were found to be 11.2 and 10.1 ppm respectively, while the iron and copper contents of SE-P were found to be 2.1 ppm and 0.04 ppm respectively. The average phosphorus contents in crude palm oil and in refined bleached deodorized palm oil are around 16.2 ppm and 5.4 ppm respectively. The iron and copper contents of crude palm oil average 4.4 ppm and 0.06 ppm respectively, while of RBD palm oil average 1.0 ppm and 0.01 ppm respectively (Siew, 1984).

Table 1 summarizes the characteristics of SE-P and SE-C, while *Table 2* and *Table 3* show the fatty acid composition and carbon number analyses of SE-P and SE-C respectively. It can be seen that there is no significant difference in the FAC and carbon number between crude palm oil and SE-P and SE-C. This is consistent with the finding of Siew *et al.* (1984), that the refining process had no effect on the fatty acid or triglyceride composition of the oil.

CONCLUSION

From these preliminary studies it can be seen that the quality of the recovered oil is inferior in that:

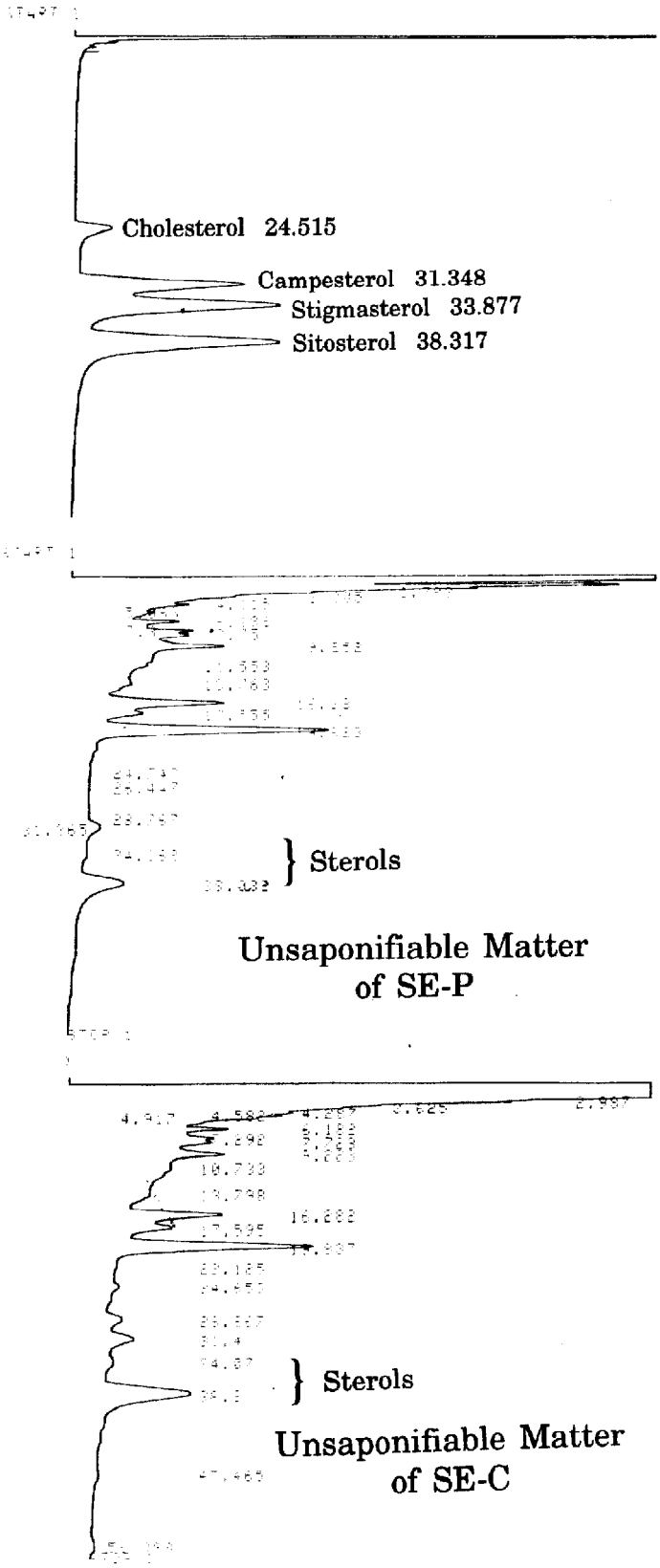


Figure 4. Gas chromatograms of standard sterol mixture and unsaponifiable matter in extracted oil.

TABLE 1. SOME CHARACTERISTICS OF SE-P AND SE-C

	SE-P	SE-C	Crude Palm Oil
Percentage oil extracted	20.6	6.3	–
Unsaponifiable matter (%)	1.4	1.6	1.0
FFA (%)	21.5	22.7	2–5
Colour (Lovibond)	24.0R 60.0Y 2B	n.d.	–
Absorbance at 233 nm	2.4	3.3	1.26
Absorbance at 269 nm	0.9	3.6	0.28
Absorbance at 446 nm	0.1	1.0	–
P(ppm)	11.2	10.7	10–18
Fe(ppm)	2.1	n.d.	4–10
Cu(ppm)	0.04	n.d.	0.05

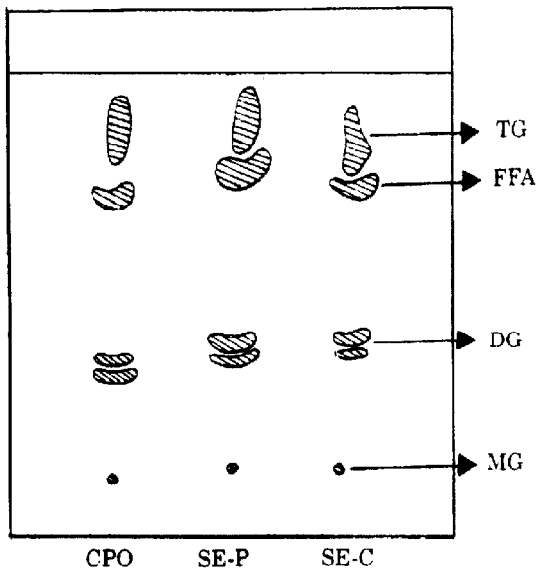
n.d. – not determined

TABLE 2. FATTY ACID COMPOSITION OF CRUDE PALM OIL AND EXTRACTED OIL

Sample	C12	C14	C16	C18	C18:1	C18:2
CPO	0.2	1.1	45.9	4.3	39.8	7.9
SE-P	0.3	1.2	46.0	4.8	39.1	7.8
SE-C	0.3	1.2	47.4	5.0	38.1	6.9

TABLE 3. CARBON NUMBER ANALYSIS OF CRUDE PALM OIL AND EXTRACTED OIL

Sample	C44	C46	C48	C50	C52	C54	C56
CPO	0.1	0.9	9.0	43.3	36.8	9.4	0.5
SE-P	0.1	0.9	9.5	44.1	35.8	9.0	0.6
SE-C	0.7	0.7	9.6	43.3	37.2	8.8	0.4



TG : Trigylycerides
FFA : Free fatty acids
DG : Diglycerides
MG : Monoglycerides

Figure 5. Analytical TLC of crude palm oil, SE-P and SE-C.

- FFA is high, about 22%.
- The content of unsaponifiable matter is high, 50% more than that of crude palm oil.
- The degree of oxidation of the oil is high.
- The extracts are brownish.

The results indicate that the oil extracted from spent bleaching earth may be difficult to re-refine to good quality and stability

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