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CHARACTERIZATION OF A BY-PRODUCT OF PALM OIL MILLING

Keywords: Sludge palm oil; characterization; headspace-gas chromatography; iodine value, free fatty acid; peroxide value; phenols and by-product

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The characteristics of sludge palm oil, a by-product of the palm oil milling process, were analysed using six quality parameters for oils and fats. Volatile analyses namely headspace gas chromatography and simultaneous distillation-extraction, were also carried out to help characterize the oil. Results from the 'six parameter' determinations showed that the oil had on average a moisture content of 0.99%, free fatty acid 44.43% (as palmitic acid), peroxide value 9.98, iodine value 49.81, saponification value 197.47 and unsaponifiable matter 0.350 per cent. The headspace gas distillation extract showed the presence of aldehydes, ketones, alkanes, furan, phenols, carboxylic acids and esters.

INTRODUCTION

The extraction of oil from the fruits of the oil palm is carried out as shown in *Figure 1*. Of course this process is not 100% efficient. There are oil losses at various stages of milling, particularly in the sterilizer and sludge separator. The discharges from these units are mixed in a sludge pit from which the oil is recovered.

More oil can also be recovered from the effluent pond treating the combined sterilizer condensate and separator sludge. The quality of the recovered oils is inferior and they are therefore sold cheaply. Such oils, which are collectively termed sludge palm oil (SPO), can be used for non-edible applications such as the production of laundry soap, fatty acids, candles and other item. Hence there is a need to specify the quality of SPO in order to distinguish it from other palm oil products.

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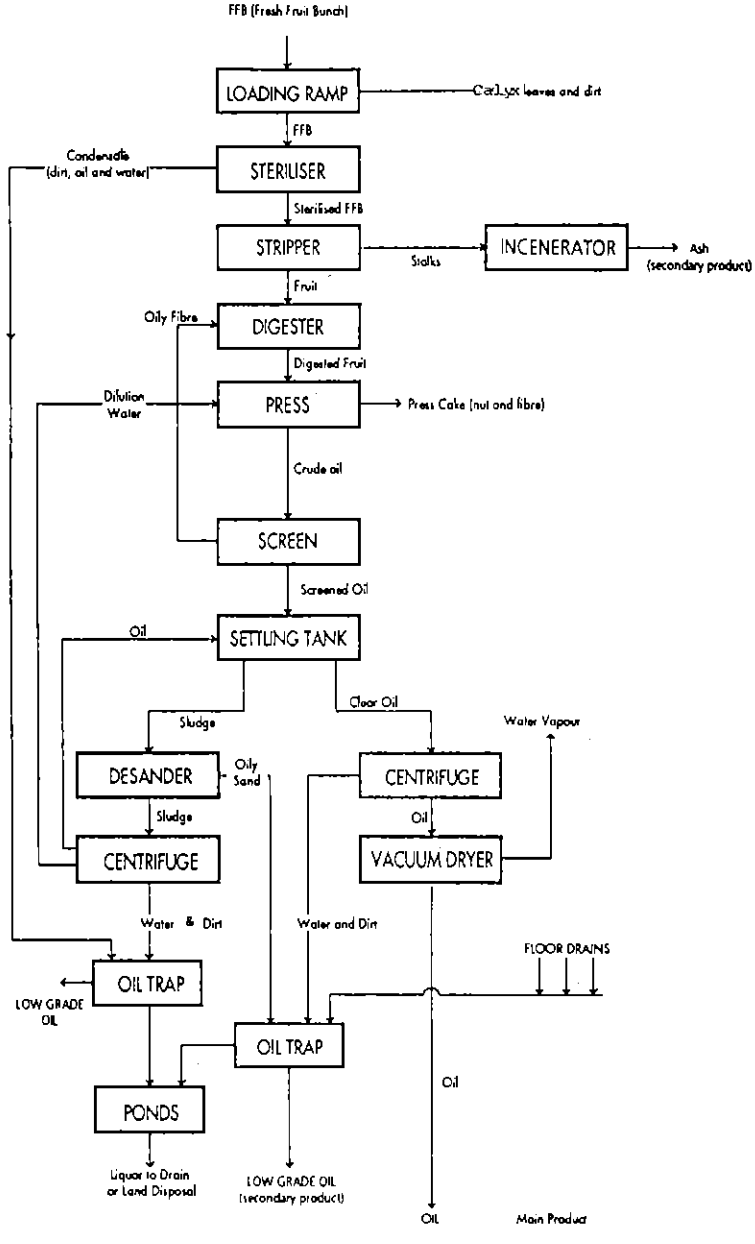


Figure 1. Schematic flow diagram of palm oil milling.

The present work was carried out to determine the characteristics of SPO. Samples were collected from various palm oil mills and analysed for moisture content, free fatty acid content, peroxide value, iodine value, saponification value and unsaponifiable matter.

Analysis of volatiles is widely used to characterize food (Koller, 1987; Nisperos-Carriedo *et al.*, 1992 and Blanch *et al.*, 1992), oils (Fritsch and Gale 1977; Dupuy, *et al.*, 1977; Evans and Selke, 1972; Evans *et al.*, 1969; Selke, *et al.*, 1977; Waltking and Zmachinski, 1977; Warner *et al.*, 1978; Williams and Applewhite, 1977); meat (Barbiere *et al.*, 1992; Baloga *et al.*, 1990; Wu and Liou, 1992) fruits (Flath *et al.*, 1990; Peppard, 1992; Perez *et al.*, 1992; Takeoka *et al.*, 1990; Takeoka *et al.*, 1992), and milk products (De Frutos, *et al.*, 1991), leaves (Potter and Fagerson, 1990; Leino, 1992; Sheen *et al.*, 1991), flowers (Loughrin, 1990) and drinks (Shimoda and Shibamoso, 1990). One of the techniques used to analyse volatiles is the headspace-gas chromatographic (HS-GC) method. Another is the Likens-Nickerson simultaneous distillation-extraction (SDE) gas chromatographic method. In this study both methods were used to analyse SPO volatiles qualitatively to determine whether this parameter could be used in the characterization of SPO.

MATERIALS AND METHODS

Materials

The SPO samples were obtained from palm oil mills located in the northern, western, central and southern regions of Peninsular Malaysia. Most of them were collected from the sludge pit and effluent pond after the processing of palm fruits (harvested in 1990) by means of twin-screw presses which were fabricated locally. The SPO was collected by scooping it from the effluent pond or by pumping it from the sludge pit into drums.

A total of thirty-three samples of SPO were collected and analysed for the six parameters listed below.

Quality parameter measurements

Moisture content, free fatty acid (FFA) peroxide value (PV), iodine value (IV), saponification value and unsaponifiable matter were determined using the PORIM Test Methods (Siew, 1988).

Headspace-Gas Chromatographic analysis

5 g of sample was weighed into a 12-ml vial which was then tightly sealed (Kuntom *et al.*, 1992). The vial was placed in a Hewlett-Packard Model 19395A headspace sampler (Palo Alto, CA) fitted with a 1-ml sampling loop. The sample vial was thermostatted in a carousel mounted on a silicon oil bath at 80°C and equilibrated for 30 minutes.

The headspace sampling operation was carried out under the following conditions: valve temperature and loop temperature 45°C, vial pressurization at 28 bar, carrier gas helium flow rate 8 ml/min, pressurization time 10 seconds, and venting time 10 seconds. The SPO volatiles were collected in the sampling loop and injected into a Hewlett Packard gas chromatograph Model 5890 via the transfer line which was maintained at 45°C.

Gas chromatographic separation of the volatiles in the headspace was carried out under the following conditions: column head pressure for the carrier gas 15 psi, initial temperature 40°C, rate of increase of temperature 10°C/min, final temperature 200°C, detector temperature 250°C, injector temperature 250°C, capillary column Supelco SPB-5 (cross-linked SE 54) with i.d. 0.32 mm and length 30 m (Supelco, Bellefonte, FA), hydrogen 18 psi, air 60 psi, make-up gas 27 ml/min, split flow ratio 1:4, septum purge 5ml/minute.

Likens-Nickerson simultaneous distillation-extraction

A simultaneous distillation-extraction apparatus (J & W Scientific, Folsom, CA) was used to extract the volatiles from SPO. 50 g of the sample was placed in a three-necked round-bottomed flask and 150 ml distilled water were added. The oil-water mixture was heated to 120°C in the oil bath (connected to the right side of the Likens-Nickerson head); 30 ml pentane in a pear-shaped flask was placed in a warm (60°C) water bath (connected to the left side of the Likens-Nickerson head). The steam distillation-extraction was carried out for 6 hr, after which the pentane phase was

separated and evaporated under a stream of nitrogen until the total volume was 2.0 ml. For analysis, 0.3 µl of the concentrated sample was injected into the gas chromatograph.

The volatiles were analysed in a Hewlett Packard gas chromatograph 5890 series II (Palo Alto, CA) with mass selective detector (MSD) 5971A (Palo Alto, CA) using a Hewlet-Packard HP-5 column (Avondale, PA.) of 0.2 mm i.d., length 25 m and 0.33 µm film thickness. Column head pressure was 13psi and the injector temperature was 250°C. Initial temperature was 40°C (5 min) programmed to 100°C (5 min) at 8°C/min and then at 16°C/min till the final temperature of 220°C. The MSD was equipped with a monolithic quartz hyperbolic quardrupole mass filter, and electron impact ion source at a voltage of 70 eV.

RESULTS AND DISCUSSION

The results from the determination of the six parameters on the 33 samples of sludge palm oil are summarized in *Table 1.*

Moisture content

The average moisture content was 0.99% and the values obtained ranged between 0.05% and 2.0 per cent. The standard deviation was 0.55 per cent.

Free Fatty Acid (FFA)

The mean FFA value was 44.43% with a standard deviation of 24.86 per cent. The range of FFA values was from 2.21% to 88.34 per cent. Two samples, SL8 and SL20, had less than 10% FFA, within the range of values for crude palm oil. The low FFA values of these SPO samples indicated that they had been collected soon after the oil palm fruits were processed. SPO collected fresh from the sludge pit can have a free fatty acid content of 3%–5% while samples collected at the pond contain at least 30% free fatty acid. The overall range of FFA values obtained in this work was very wide: 30% of the samples had FFA values greater than 60%, while 60% had values below 45 per cent. Since the average value was 44.43%, a value of < 45% but > 5% FFA should be suitable as a specification for SPO.

Peroxide value (PV)

The average peroxide value of the 33 SPO samples was 9.98 units, with a standard deviation of 8.55; the range was from 1.36 to 44.48. Two samples, SL1 and SL27, had PV of < 2.00; however this does not mean that their quality was necessarily good. Low peroxide values also indicate that hydroperoxides formed earlier might have been degraded into secondary oxidation products. In fact some of the SPO samples with low PV had a high FFA content (*Table 1*), indicating that they had undergone hydrolytic deterioration. The coefficient of variation for this analysis was extremely high (85.67) showing a large variation in the quality of SPO samples. It is suggested that the specification for this parameter be in the range of 1.36–21.81. This is because sample SL13 was only one with the value 44.48. It was most probably highly deteriorated, oxidatively as well as hydrolytically (FFA 25.20%).

Iodine value

The mean IV of the SPO samples was 49.8 with a standard deviation of 3.99 and a range from 40.2 to 55.9 units. The coefficient of variation was low (< 10). The lowest values observed (around 40) may have been due to a higher content of stearin, a consequence of solidification of the SPO samples during cooling.

Saponification value

The 33 SPO samples analysed had an average saponification value of 197.47 (mg KOH/g oil) with a standard deviation of 5.06 units, and a range from 173.82 to 197.86. The coefficient of variation was 2.6 per cent. This parameter could be used to specify SPO palm oil.

Unsaponifiable matter

The mean value for this parameter was 0.348% with a standard deviation of 0.191. Individual values ranged between 0.082 and 0.90 per cent.

Of the six parameters for which the 33 samples of SPO were analysed only IV and saponification value had low coefficients of variation. The others had high coefficients of variation, especially PV. This shows that the

TABLE 1. QUALITY PARAMETERS ANALYSED ON 33 SAMPLES OF SPO

Sample code	Moisture (%)	FFA (%)	Peroxide Value (meq/kg)	Iodine Value	Saponification Value (mg KOH/g oil)	Unsaponifiable matter (%)
SL1	0.75	29.9	1.8	53.5	185	0.25
SL2	2.08	71.7	2.7	51.3	190	0.31
SL3	0.90	32.7	16.8	53.1	180	0.20
SL4	1.35	34.5	5.2	55.0	194	0.49
SL5	1.24	86.2	3.4	40.2	182	0.91
SL6	1.72	83.1	8.0	41.8	188	0.27
SL7	1.21	36.6	21.8	55.2	183	0.33
SL8	0.83	5.3	12.6	55.9	187	0.19
SL9	0.90	35.9	5.2	51.6	190	0.29
SL10	1.71	17.9	6.1	53.4	182	0.36
SL11	0.92	35.5	8.1	52.9	189	0.23
SL12	1.18	36.6	20.1	54.2	185	0.08
SL13	1.85	25.4	44.5	55.6	186	0.24
SL14	1.39	88.3	7.6	44.0	192	0.32
SL15	1.66	63.2	20.3	48.7	187	0.19
SL16	0.54	27.6	14.6	49.9	180	0.34
SL17	1.72	79.7	9.6	53.6	194	0.16
SL18	0.94	30.7	2.1	49.7	182	0.41
SL19	0.51	69.7	17.4	48.8	182	0.20
SL20	1.34	2.2	12.8	51.4	186	0.30
SL21	0.17	42.8	10.8	49.5	187	0.29
SL22	0.16	42.8	12.1	47.3	191	0.44
SL23	0.18	43.3	11.5	46.7	191	0.33
SL24	0.28	44.4	6.2	46.5	198	0.42
SL25	0.63	29.1	7.1	49.5	190	0.38
SL26	0.27	22.0	2.8	50.6	189	0.24
SL27	0.70	32.8	1.4	50.2	190	0.51
SL28	0.88	19.8	3.3	49.1	189	0.82
SL29	0.65	48.8	2.2	48.3	191	0.83
SL30	0.05	13.5	15.8	49.3	189	0.17
SL31	1.38	84.2	4.8	43.8	173	0.51
SL32	1.49	83.8	5.6	43.6	193	0.29
SL33	1.09	66.0	5.1	49.3	194	0.26
Mean	0.99	44.4	10.00	49.8	198	0.35
Standard Deviation	0.5	24.86	8.55	3.99	5.06	0.19
Range	0.05–2.08	2.2–88.3	1.4–44.5	40.2–55.9	174–198	0.08–0.91
Coefficient of variance	50.5	55.9	85.5	8.0	2.6	54.3

quality characteristics of SPO can vary greatly. The magnitude of variation might relate to whether the samples were collected fresh from the sludge pit or long after discharge into the pit. Another factor is the comingling of the fresh discharge with other materials already in the sludge pit.

Headspace GC analysis

The headspace chromatographic profile of SPO is shown in *Figure 2*. The identities of the peaks are listed in *Table 2*. Tetradecane, eicosane, tetradecanol, tetradecanoic acid and 1-methyl-1-propyl hexanedioc acid were most likely breakdown products of the fatty acids of

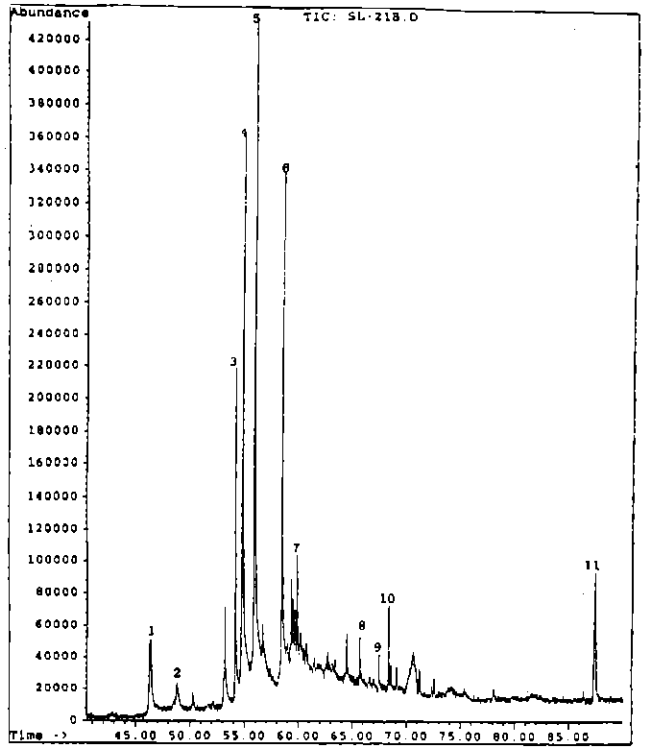
TABLE 2. COMPOUNDS IN THE HEADSPACE FO SLUDGE PALM OIL

No.	Retention Time	Compounds
1.	46.37	Unknown
2.	48.83	Tetradecane
3.	54.18	Unknown
4.	54.84	Diethyl-1,2-benzene dicarboxylic acid ester
5.	55.92	2,2,4-Trimethyl-penta-1,3-diol diisobutyrate
6.	58.47	2-Methylpropyl hexanedioic acid ester
7.	59.88	Eicosane
8.	65.71	1-Tetradecanol
9.	67.44	Tetradecanoic acid
10.	68.37	1-Methyl-1-propyl hexanedioic acid
11.	87.43	Diethyl phthalate

the glycerides. Other peaks could possibly be due to the degradation of the unsaponifiable compounds. The phthalate was most probably contributed by the plastic container holding the sample (Tan, 1989).

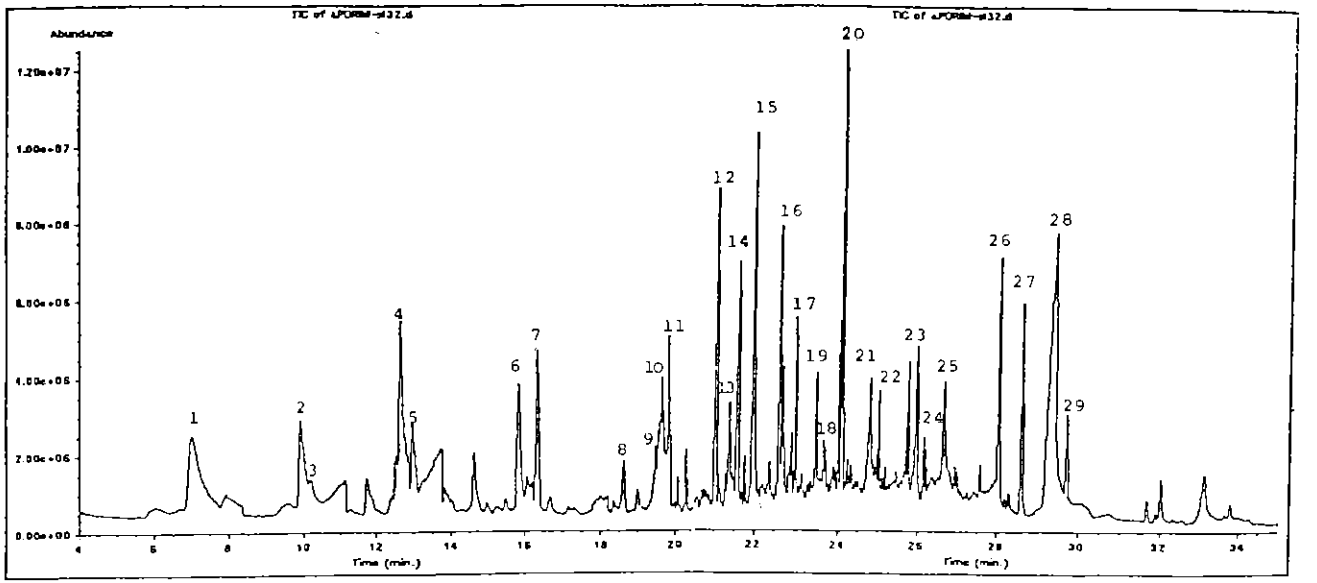
Simultaneous distillation-extraction

The chromatographic profile of the extract is shown in *Figure 3*. *Table 3* shows the compounds identified in the steam distilled extract: these were aldehydes, furans, ketones, phenols, hydrocarbons and carboxylic acids. The two phenolic compounds present were 2-methoxy-4-methylphenol and 4-ethoxy-2-methylphenol, both most probably derived from the tocopherols or tocotrienols. α-Ionone is most probably a breakdown product of carotene. These compounds could not be used to characterize SPO because crude palm oil would contain the same breakdown products.



1 – Unknown
2 – Tetradecane
3 – Unknown
4 – Diethyl-1,2-benzene dicarboxylic ester
5 – 2,2,4-trimethylpentan-1,3-diol diisobutyrate
6 – 2-methylpropyl hexanedioic acid ester
7 – eicosane
8 – 1-tetradecanol
9 – Tetradecanoic acid
10 – 1-methyl-1-propyl hexanedioic acid
11 – Diethyl phthalate

Figure 2. Total ion chromatogram of the low grade palm oil.



1 – Hexanal
2 – 2-heptanone
3 – Heptanal
4 – 2-pentylfuran
5 – octanal
6 – 2-nonanone
7 – nonanal
8 – 2-nonenal
9 – 2-methoxy-4-methylphenol
10 – dodecane
11 – Decanal
12 – Decenal
13 – 4-ethoxy-2-methoxyphenol
14 – Tridecane
15 – Decadienal
16 – *Trans*-2-undecenal
17 – Tetradecane
18 – Alpha-ionone
19 – 1-pentadecene
20 – Pentadecane
21 – Dodecanoic acid
22 – Eicosane
23 – 2-heptadecanone
24 – Hexadecanol
25 – Tetradecanoic acid
26 – 1,2-benzenecarboxylic acid, bis (-2-methylpropyl)
27 – Methyl hexadecanoate
28 – Hexadecanoic acid
29 – Ethyl hexadecnoate

Figure 3. Total ion chromatogram of Likens-Nickerson steam-distilled extract of the low grade palm oil.

TABLE 3. COMPOUNDS IDENTIFIED IN THE STEAM DISTILLATE EXTRACT OF SLUDGE PALM OIL

No	Retention Time	Compounds
1	7.004	Hexanal
2	9.912	2-Heptanone
3	10.250	Heptanal
4	12.650	2-Pentylfuran
5	12.954	Octanal
6	15.851	2-Nonanone
7	16.356	Nonanal
8	18.625	2-Nonenal
9	19.633	2-methoxy-4-methylphenol
10	19.681	Dodecane
11	19.861	Decanal
12	20.054	2-Decenal
13	21.380	4-Ethoxy-2-methoxy-phenol
14	21.603	Tridecane
15	21.985	Decadienal
16	22.601	*Trans*-2-undecenal
17	22.978	Tetradecane
18	23.462	Alpha-ionone
19	24.008	1-Pentadecene
20	24.103	Pentadecane
21	24.804	Dodecanoic acid
22	25.019	Eicosane
23	25.885	2-Heptadecanone
24	26.139	Hexadecanal
25	26.641	Tetradecanoic acid
26	28.051	1,2-Benzene dicarboxylic acid bis(-2-Methylpropyl)
27	28.627	Methyl hexadecanoate
28	29.422	Hexadecanoic acid
29	29.723	Ethyl hexadecanoate

CONCLUSION

Based on the values in *Table 1*, sludge palm oil would have the following charateristic: moisture content < 2%, FFA 5%–45%, PV 1.36–21.81 meq/kg and IV of 40.2–55.9. The observed ranges appear to be narrower than those reported by Tan *et al.* (1982).The saponification value and unsaponifiable matter should be in the range of 173.82–197.86 (mg KOH/g oil) and 0.082%–0.910% repectively.

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