Characterization of Palm Acid Oil

Ainie Kuntom*, **Wai-Lin Siew** and **Yew-Ai Tan**
Chemistry and Technology Division, Palm Oil Research Institute of Malaysia, Ministry of Primary Industry, Kuala Lumpur, Malaysia

Palm acid oil (PAO) is a by-product obtained from the alkaline refining of palm oil. It is used for making laundry soaps and for producing calcium soaps for animal feed formulations. The properties and composition of PAO may differ according to variations in the palm oil feedstock and the alkaline refining process. Because information on the characteristics of PAO is limited, this investigation aims to establish the properties of this product. Quality and oxidative parameters of 27 samples of PAO were determined. The six parameters analyzed were moisture and free fatty acid content, peroxide value, iodine value, saponification value and unsaponifiable matter. Headspace-gas-chromatographic (HSGC) analysis and gas-chromatographic analysis of the extract from Likens-Nickerson steam distillation of the samples were also carried out. Mean moisture content was 0.98%, free fatty acids 62.6% (palmitic acid), peroxide value 4.1 meq/kg, iodine value 50.2, saponification value 186 and unsaponifiable matter 0.53. HSGC profiles of a few samples showed the presence of one to three peaks, while the steam distillation extract showed the presence of aldehydes, ketones, furans and acids.

KEY WORDS: Acids, aldehydes, FFA, furans, IV, ketones, palm acid oil, PV, saponification value, unsaponifiable matter and headspace-GC volatiles.

Crude palm oil obtained from the mesocarp of the palm fruit must be processed before it is used in edible applications. Processing involves refining, bleaching and deodorizing the oil. There are two types of refining, namely physical and alkaline/chemical refining. Physical refining involves steam distillation under vacuum (2–6 mm Hg) at 240–260°C. Alkaline refining (Fig. 1) involves neutralization with alkali such as caustic soda. One of the by-products of alkaline refining is soapstock, which contains some emulsified neutral oil. The soapstock is easily separated from the neutralized oil by density-difference or centrifugal separation. Acidification of the soapstock gives the acid oil. The main components of palm acid oil (PAO) are free fatty acids (FFAs), neutral oil and moisture.

PAO is exported from Malaysia to Europe, Japan, India and other countries. For the year 1991, PAO export from Malaysia totalled 37,154 million tons. In Africa, India and some other countries, it is used for making laundry soaps. It also is used to produce calcium soaps for animal feed formulations. At the moment, the Malaysian Custom Department defines PAO as oil with high FFAs, obtained from the soapstock of alkaline refining through acidolysis, usually with sulfuric acid. This definition is not specific enough, and therefore, there is a need to draw up certain specifications for a clear definition of PAO. With this in mind, PAO was subjected to a few quality and oxidative analyses besides determination of volatiles.

Analysis of volatiles is widely used to characterize food (1–3), oils (4–11), meat (12–14), fruits (15–19), milk products (20), leaves (21–23), flowers (24) and drinks (25). One of the methods used to analyze volatiles is the headspace gas-chromatographic (HSGC) method. Another method is the Likens-Nickerson simultaneous distillation–extraction (SDE) gas-chromatographic method. In this study, both methods were used to analyze PAO volatiles qualitatively to assess if this parameter could aid characterization of this oil.

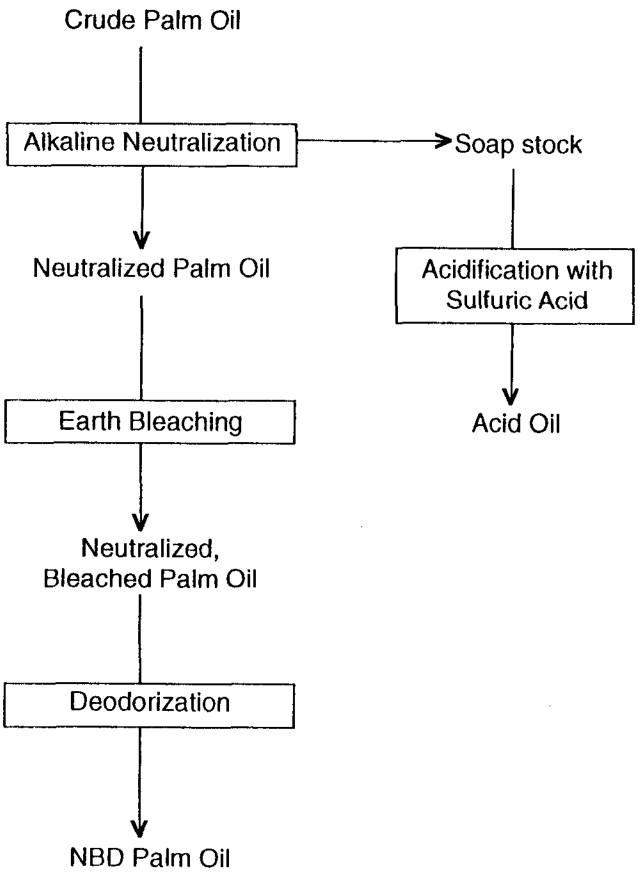

FIG. 1. Flow diagram of alkaline-refining process of crude palm oil. NBD Palm Oil, neutralized, bleached, deodorized palm oil.

EXPERIMENTAL PROCEDURES

Materials. PAO samples were derived from alkali-refining (Alfa Laval, Westfalia, Germany) of oil palm fruits, *Elaeis guineensis*, harvested in the year 1990. The samples were collected from refineries located in the North, West, Central and South of Peninsula Malaysia. In Malaysia, only eight refineries produced neutralized, bleached, deodorized palm oil by this process.

Quality and oxidative parameter measurements. For moisture content, loss of moisture was measured according to a PORIM Test Method 1988, p 5.2 (26). For FFA, the acid value of the samples was determined according to the PORIM Test Method 1988, p 2.5 (26). Peroxide value (PV) determination was in accordance to the PORIM Test Method 1988, p 2.3 (26). For IV, PORIM Test Method

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*To whom correspondence should be addressed.

1988, p. 3.2 (26) was used. The saponification value of the samples was measured by PORIM Test Method 1988, p. 3.1 (26). For unsaponifiable matter, PORIM Test Method 1988, p 2.7 (26) was used.

HSGC analysis (27). A PAO sample (5 g) was weighed into a 12-mL vial and then tightly sealed. The vial was placed in a Hewlett-Packard Model 19395A headspace sampler (Palo Alto, CA) with a 1-mL sampling loop installed in this model. The vial containing PAO was thermostated in a carousel mounted in a silicone oil bath at 80°C and equilibrated for 30 min. The headspace sampling operation was carried out under the following conditions: valve temperature and loop temperature 45°C, vial pressurization 28 bar, carrier gas helium flow rate 8 mL/min, pressurization time 10 s and venting time 10 s. The PAO volatiles were collected in the sampling loop and injected into a Hewlett-Packard Model 5890 gas chromatograph *via* the 45°C transfer line.

Gas chromatographic separation of the headspace gas sample was conducted under the following conditions: helium carrier gas head pressure of 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, 0.32 mm i.d. and 30 m length; Supelco, Bellefonte, PA), hydrogen 18 psi, air 60 psi, make-up gas 27 mL/min, split flow ratio 1:4, septum purge 6 mL/min.

Likens-Nickerson simultaneous distillation–extraction. A J&W Scientific (Folsom, CA) simultaneous distillation–extraction apparatus was used to extract the volatiles. The extraction was carried out according to the instructions enclosed by the manufacturer. The PAO sample (50 g) was placed in a three-necked round-bottomed flask and 150 mL distilled water was added. The oil/water mixture was heated to 120°C in the oil bath, and 30 mL pentane in a pear-shaped flask was placed in the warm (60°C) waterbath. The steam distillation–extraction was carried out for 6 h.

PAO samples were steam-distilled, and the volatiles were extracted with pentane. The pentane was then evaporated under a stream of nitrogen until the total volume was 2.0 mL, and 0.3 μL of the sample was injected into the gas chromatograph.

The volatiles were analyzed on a Hewlett-Packard gas chromatograph 5890 series II with a mass selective detector (MSD) 5971A (Palo Alto, CA) and a Hewlett-Packard HP-5 column (Avondale, PA) of 0.2 mm i.d., 25 m length and 0.33 μm film thickness. Helium carrier gas head pressure was 13 psi 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 to the final temperature of 220°C. The MSD was a quadrupole, with electron impact at a voltage of 70 eV.

RESULTS AND DISCUSSION

The results of the six-parameter analysis of 27 samples of PAO are discussed below.

Moisture content. Table 1 lists the average moisture content of the 27 samples of PAO studied. The values ranged between 0.15–2.16% with a mean value of 0.98%.

FFA. The mean FFA of 27 samples is given in Table 1, and the value was 62.6%. The range was 27.6–81.2%. On the average, the FFA value of PAO was above 50% with the exception of two samples, A05 and A029, which had low values of 38.1 and 27.6, respectively.

TABLE 1

Quality and Oxidative Parameters of Palm Acid Oil

Parameter	Mean value of 27 samples	Standard deviation	Range
Moisture content (%)	0.98	0.53	54.08
Free fatty acid (%)	62.6	11.5	18.49
Peroxide value (meq/kg)	4.1	3.8	92.68
Iodine value	50.2	5.3	10.56
Saponification value	186	5.6	3.01
Unsaponifiable matter	0.53	0.42	79.25

PV. Table 1 lists the PVs for the PAO samples. The mean value was 4.1 meq/kg with a range of 1.9–20.7. On average, the PV of acid oil was less than 5. Two samples, A020 and A025, had slightly higher PVs of 6.9 and 5.3, respectively; while another two samples, A019 and A029, had high PVs of 10.6 and 20.7, respectively.

IV. The range of IVs of the PAO samples studies is shown in Table 1. The mean value was 50.2 meq/kg, indicating the presence of a reasonable amount of unsaturated fatty acids. The IVs ranged between 39.2–57.6.

Saponification value. The mean saponification value of the PAOs studied was 186 and the range was 172–197 (Table 1).

Unsaponifiable matter. Three PAO samples, A017, A027 and A028, had a slightly higher unsaponifiable matter of more than 1.00 (Table 1). The mean value was 0.42 and the values of 27 samples ranged between 0.04–1.67.

The six parameters, namely, moisture content, FFA, PV, IV, saponification value and unsaponifiable matter can be useful as specifications of PAO.

Headspace analysis. In this experiment, the headspace procedure used was the static method. The chromatographic headspace profiles of 27 samples of PAO showed three profile types as illustrated in Figure 2. Fourteen percent of the samples had profile type (a), 82% profile type (b) and 4% profile type (c). These three profile types suggest that the quality of PAO varies slightly, depending most probably upon processing conditions. Samples with profile type (b) with only a few minor peaks can be projected as good-quality PAO. This is supported by the low PV of less than five for these samples. On the other hand, samples with profiles of type (a) and (c) are likely to be samples that have deteriorated slightly. On this basis, the headspace chromatographic profile can be used as an indicator of the quality of PAO.

SDE analysis. Figure 3 shows the gas chromatogram of the SDE profile of PAO. Table 2 lists the compounds identified in the distillate. Volatiles consisted of alkanals, alkanones, alkylfurans, alkenals, carboxylic acids, alkadienals and hydrocarbons (28–34). Three unique ketone compounds, 6,6-dimethyl-2,10-undecadione, α-ionone (29) and geranyl acetone, most probably resulted from the degradation of carotenoids. The potential use of these ketone compounds as a characterization tool seems

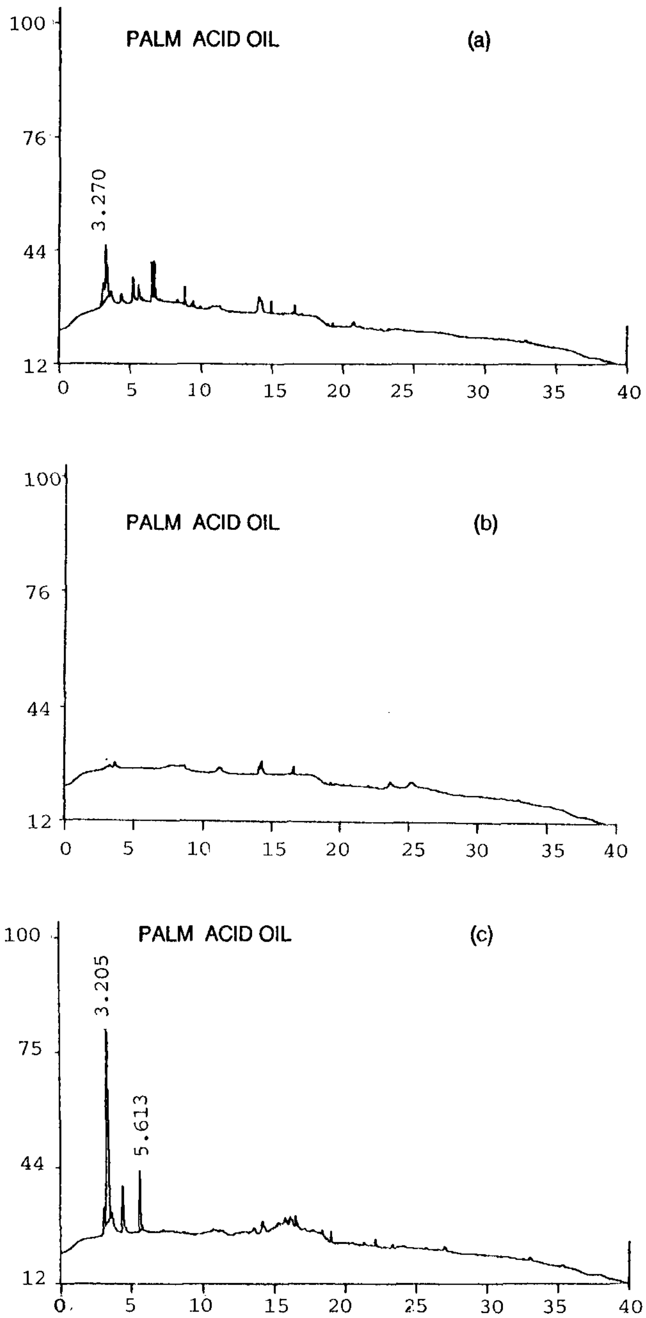

FIG. 2. Headspace chromatographic profiles of palm acid oil: (a) 14%, (b) 82% and (c) 4%.

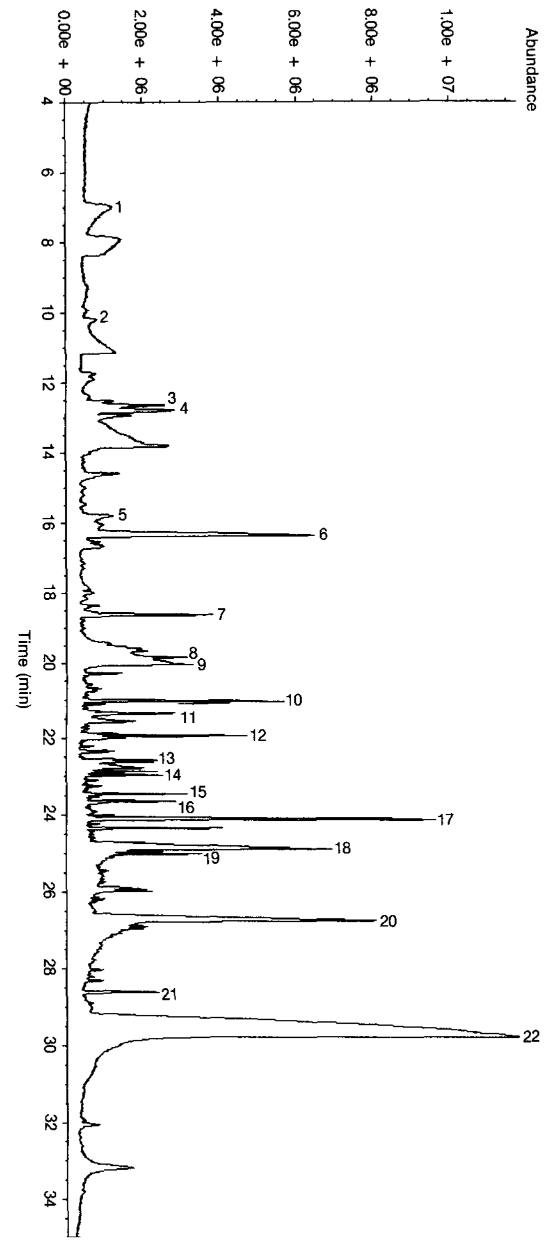

FIG. 3. Chromatographic profile of Likens-Nickerson steam distillate of palm acid oil, 1 = hexanal, 2 = heptanal, 3 = 2-pentylfuran, 4 = octanal, 5 = 2-nonanone, 6 = nonanal, 7 = 2-nonenal, 8 = dodecane, 9 = decanal, 10 = 2-decenal, 11 = 6-,6-dimethyl-2,10-undecadione, 12 = decadienal, 13 = *trans*-2-undecenal, 14 = tetradecane, 15 = α-ionone, 16 = geranyl acetone, 17 = pentadecane, 18 = dodecanoic acid, 19 = eicosane, 20 = tetradecanoic acid, 21 = methyl hexadecanoate, 22 = hexadecanoic acid.

practical but for the fact that, if carotenoids were their presumed source, crude palm oil would also contain the same compounds. An analysis of the SDE volatiles of crude palm oil is now in progress to verify the source of these ketones.

In summary, it is proposed that PAO should have the following specifications: FFA >50%, PV <5, moisture content <2%, IV between 40–50, saponification value 72–197 and unsaponifiable matter of 0.04–1.67. These values are based on the mean and ranges of 27 samples analyzed.

TABLE 2

Compounds Identified in the Steam-Distilled Extract of Palm Acid Oil

Peak number	Retention time (min)	Compounds
1	7.0	Hexanal
2	10.250	Heptanal
3	12.643	2-Pentylfuran
4	12.788	Octanal
5	15.758	2-Nonanone
6	16.375	*n*-Nonanal
7	18.637	2-Nonenal
8	19.608	*n*-Dodecane
9	19.750	*n*-Decanal
10	21.019	2-Decenal
11	21.353	6,6-Dimethyl-2,10-undecadione
12	21.936	2,4-decadienal
13	22.531	*trans*-2-undecenal
14	22.965	Tetradecene
15	23.453	Alpha-ionone
16	23.640	Geranyl acetone
17	24.108	Pentadecane
18	24.878	Dodecanoic acid
19	25.011	Eicosane
20	26.736	Tetradecanoic acid
21	28.603	Methyl hexadecanoate
22	29.746	Hexadecanoic acid

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REFERENCES

1. Koller, W.D., *Preconcentration by Using Static-Head-Space Technique for Mass Spectrometric Identification, Flavor Science and Technology*, edited by M. Mattens, G.A. Dalen and H. Russwam Jr., John Wiley & Sons Ltd., New York, 1987, p. 191.
2. Nisperos-Carriedo, M.O., E.A. Baldwin, M.G. Moshomas and P.E. Shaw, *J. Agric. Food Chem. 40*:2464 (1992).
3. Blanch, G.P., J. Tabera, J. Sanz, M. Heraiz and G. Reglero, *Ibid. 40*:1046 (1992).
4. Evans, C.D., and E. Selke, *J. Am. Oil Chem. Soc. 49*:106 (1972).
5. Evans, C.D., G.R. List, R.L. Hoffmann and H. Moser, *Ibid. 46*:501(1969).
6. Selke, E., W.K. Rohwedder and H.J. Dutton, *Ibid. 54*:62 (1977).
7. Britsch, C.W., and J.A. Gale, *Ibid. 54*:225 (1977).
8. Dupuy, H.P., E.T. Rayner, J.I. Wadsworth and M.G. Legendre, *Ibid. 54*:445 (1977).
9. Waltking, A.E., and H. Zmachinski, *Ibid. 54*:454 (1977).
10. Williams, J.L., and T.H. Applewhite, *Ibid. 54*:461 (1977).
11. Warner, K., C.D. Evans, G.R. List, H.P. Dupuy, J.I. Wadsworth and G.E. Goheen, *Ibid. 55*:252 (1978).
12. Barbueru, G., L. Bolzoni, G. Parolari, R. Virgili, R. Buttini, M. Careri and A. Mangra, *J. Agric. Food Chem. 40*:2389 (1992).
13. Wu, C.M., and S.E. Liou, *Ibid. 40*:838 (1992).
14. Bologa, D.W., GA. Reineccius and J.W. Miller, *Ibid. 38*:2021 (1990).
15. Peppard, T.L., *Ibid. 40*:257 (1992).
16. Flath, R.A., D.M. Light, E.B. Jang, T.R. Mon and J.O. John, *Ibid. 38*:1060 (1990).
17. Perez, A.G., J.J. Rios, C. Sanz and J.M. Olias, *Ibid. 40*:2232 (1992).
18. Takeoka, G.R., R.G. Buttery and R.A. Flath, *Ibid. 40*:1925 (1992).
19. Takeoka, G.R., R.A. Flath, T.R. Mon, R. Ternaishi and M. Guentert, *Ibid. 38*:471(1990).
20. De Frutos, M., J. Sanz and I. Martinez-Castro, *Ibid. 39*:524 (1991).
21. Potter, T.L., and I.S. Fegerson, *Ibid. 38*:2054 (1990).
22. Leino, M.E., *Ibid. 40*:1379 (1992).
23. Sheen, L.Y., Y.H. Tsai Ou and S.J. Tsai, *Ibid. 39*:939 (1991).
24. Loughrin, J.H., T.R. Hamilton-Kemp, R.A. Henderson and F. Hildebrand, *Ibid. 38*:455 (1990).
25. Shimoda, M., and T. Shibamoso, *Ibid. 38*:802 (1990).
26. PORIM Test Methods, compiled by Palm Oil Research Institute of Malaysia, Kuala Lumpur, 1988, Methods p 2.3, p 2.5, p 2.7, p 3.1, p 3.2, p 5.2.
27. Kuntom, A., H. Kifli and K.H. Chen, *J. Am. Oil Chem. Soc. 69*:614 (1992).
28. Gaddis, A.M., R. Ellis and G.T. Curie, *Ibid. 38*:371(1961).
29. Hoffmann, G., and J.G. Keppler, *Nature 125*:310 (1960).
30. Dirinck, P., L. Schreyen, L. de Schroenmaker, F. Wychuyse and N. Schamp, *J. Food Sci. 42*:645 (1977).
31. Badings, H.T., *Neth. Milk and Dairy J. 14*:215 (1960).
32. Dirinck, P., A.H. Kuntom and N. Schamp, *Progress in Flavor Research 1984*, edited by J. Adda, Elsevier Science Publishers B.V., Amsterdam, 1985, p. 505.
33. Dirinck, P., A.H. Kuntom and N. Schamp, *Proceedings of the Second European Conference on Food Chemistry*, Rome, 15–18 March 1983, p. 183.
34. Kuntom, A.H., P.J. Dirinck and N.M. Schamp, *Elaeis 1*:53 (1989).

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