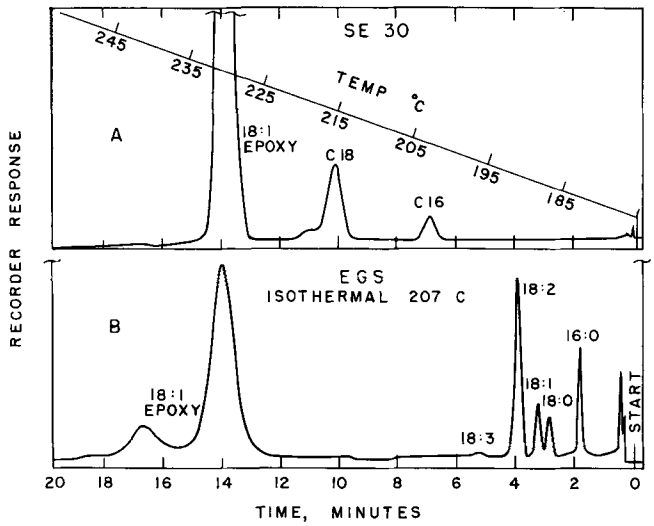

FIG. 2 Chromatograms of *Vernonia anthelmintica* seed oil methyl esters.

A. Temperature programmed, SE-30 stationary phase (see text).

B. Isothermal, EGS stationary phase (see text).

The analysis of the *Vernonia anthelmintica* seed oil methyl esters by two procedures is given in Table II. One analysis was obtained by combining data from the SE-30 and EGS columns as described in this paper. The other was determined from data obtained from the EGS column only but where an internal standard and correction factors were applied as described in a previous publication (1). The agreement was good. However, the combined SE-30 + EGS procedure requires considerably less calculation and we believe the analysis can be more readily reproduced.

TABLE II

GLC Analysis of *Vernonia anthelmintica* Seed Oil

Components	Method A [a]	Method B [b]
	%	%
16:0	2.52	1.94
18:0	1.37	1.40
18:1	1.88	2.05
18:2	8.10	7.86
18:3	0.26	0.30
18:1 epoxy [c]	76.7	76.4
Other fatty acids	1.35	2.31
Unsap.	7.76	7.76

[a] SE-30 (programmed) and EGS (isothermal); see text for columns and conditions.

[b] EGS (isothermal) + internal standard (15:0) + correction factors (1).

[c] Oxirane value = 3.87 = 75.1% as methyl expoxyoleate.

Preliminary studies indicate that the procedure may be applicable to the analysis of commercial epoxidized oils such as epoxidized soybean or linseed oils. We have had limited success with this type oil but find some unidentified peaks on the chromatogram when di- and possibly tri-epoxy compounds are present.

REFERENCES

1. Barford, R. A., S. F. Herb, F. E. Luddy, P. Magidman, and R. W. Riemenschneider, JAOCS *40*, 136–138 (1963).
2. Herb, S. F., P. Magidman, and R. W. Riemenschneider, *Ibid. 37*, 127–129 (1960).
3. Magidman, P., S. F. Herb, R. A. Barford, and R. W. Riemenschneider, *Ibid. 39*, 137–142 (1962).
4. Stahl, E., G. Schröter, G. Kraft, and R. Renz, Pharmazie *11*, 633–637 (1956).
5. Morris, L. J., R. T. Holman, and K. Fontell, J. Lipid Res. *2*, 68–76 (1961).
6. Durbetaki, A. J., Anal. Chem. *28*, 2000–2001 (1956).
7. Miwa, T. K., K. L. Mikolajczak, F. R. Earle, and I. A. Wolff, *Ibid. 32*, 1739–1742 (1960).
8. VandenHeuvel, W. J. A., C. C. Sweeley, and E. C. Horning, J. Am. Chem. Soc. *82*, 3481–3482 (1960).
9. VandenHeuvel, W. J. A., C. C. Sweeley, and E. C. Horning, Biochem. Biophys. Res. Commun. *3*, 33–36 (1960).
10. Anders, M. W., and G. J. Mannering, J. Chromatog., *7*, 258–260 (1962).
11. Rosenfeld, R. S., M. C. Lebeau, S. Shulman, and J. Seltzer. *Ibid. 7*, 293–296 (1962).

[Received August 20, 1963—Accepted December 9, 1963]

Some Problems in Improving Tropical Materials Utilized by the United Kingdom Oilmilling Industry [1]

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Abstract

This paper considers palm oil, palm kernels, and peanuts imported to the U.K., mainly from Nigeria. The origin of the oil palm and the peanut plant, their commercial development, and the antiquity of the use of palm oil is discussed, and a brief description is given of the manner in which the crops are handled and processed in West Africa.

By the control of lipolysis, due to 1) the presence of lipases in the fruit, 2) chemical hydrolysis, and 3) the lipolytic action of moulds, oil with about 1% fatty acid may be marketed; most Nigerian peasant-produced oil is below 5%. It is mainly edible, but not easily bleached. This is due to oxidation caused by lipoxidases in the fruit, and oxidation by air catalysed in the presence of metals, especially iron. By control of these factors Nigerian oil of excellent bleachability may be prepared.

Palm kernels suffer from acidity and browning. Development of acidity is ascribed to kernel breakage with concomitant development of lipolytic moulds and bacteria. Non-enzymic browning is mentioned.

Nigerian peanut oil from the 1951–52 crop averaged 5.63% free fatty acid content (FFA) compared with 1.46% for 1960–61. This improvement is largely due to improved methods of decortication. Some preliminary studies are reported concerning mould growth on kernels stored under West African conditions and work on toxicity associated with certain batches of peanuts, caused by the mould, *Aspergillus flavus*.

Introduction

THE U.S. GROWS most of its oilseeds, in contrast to the U.K. where much is imported from former colonies. Consequently, unique problems have arisen in the effort to use mainly peasant-grown tropical oilseeds, with storage and transportation to oil mills in the U.K.

Palm Oil

The tree *Elaeis guineensis* yields possibly one of

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the first edible oils used by man. Friedel (1) in 1897 examined some Egyptian tomb fat from Abydos, ca. 3,000 B.C., and concluded that it might be palm oil. Various theories about the Sahara desert in ancient times suggest there was trade between Abydos and West Africa (2). More recently the Tropical Products Institute examined a tomb fat from Abydos using GLC for fatty acids, and paper chromatography for the sterols. This fat is similar in composition to that examined by Friedel and our results indicate it is palm oil.

The oil palm was described by some of the earliest European visitors to West Africa (3). Thus, when Welsh (4) visited Benin in the 16th Century he found there "a good store" of soap smelling like "beaten violets." This was doubtlessly made from bleached palm oil perfumed with oxidized carotenoids.

However, palm oil trade with Europe did not begin until early in the 18th Century. In 1790 some 130 tons of oil were imported by the U.K., and by the middle of the 19th Century the trade was well established (5,6). Today palm oil is an important part of edible fats and world trade is ca. 600,000 tons annually, with ca. 200,000 tons from Nigeria. World production of oil, much of which is used in Africa, must be considerably higher since world exports of kernels total almost a million tons (7).

The palm is found in tropical Africa, roughly between 15°N and 10°S. It is a feathery tree, up to 60 ft in height, and carrying a tuft of 20–25 leaves on its crown (8,9,10,11,12,13). The fruit is olive-shaped and weighs 3–20 g, but grows in bunches weighing 10–50 lb. At maturity the fruit color varies from almost white to black.

The well cultivated plant may bear in two years, but in Nigeria the first crop is usually harvested the fourth year, and 10–12 years are required for full production.

Many systems of classification have been proposed (14,15,16), but for commercial purposes the three main types are based on the thickness of the shell: 1) *dura,* with a thick shell; 2) *tenera,* with a thin shell and a ring of fibers surrounding the nut; and 3) *pisifera,* with no shell.

The *deli* fruit of Malaya is the *dura* type but contains a large proportion of pulp to kernel.

The amount of fruit in a bunch varies but is usually ½–⅔ of its wt. The amount of oil in the fruit is 45–50%.

The origin of the oil palm is still controversial (17, 18) but it probably came from West Africa (19), perhaps near the Gulf of Guinea. Certainly man has been one of the main factors in the distribution of the palm, and the dense grove palms (20) so characteristic of the oil belt in Nigeria, may have been from trees planted around African homesteads where soil fertility was enhanced. Plantations are a more recent development. The bulk of oil exported from Nigeria is produced by Africans from trees growing in a semi-wild condition.

Processing the oil. Palm oil is extracted by a variety of methods (21,22,23,24,25). Some primitive African methods use practically no apparatus; others involve trampling the fruit in canoes. A popular method is to sterilize the fruit in boiling water and then press out the oil in a hand press. More recently (26) there have been attempts to introduce hydraulic presses, and on well organized plantations the fruit is processed by mechanized operations involving stripping the fruit from the bunch, after sterilization with high pressure steam, digestion by stirring the sterilized fruit, and pressing out the oil in cage presses, or continuously in screw presses. Centrifuges are also used, mainly in the Pioneer Oil Mills which were designed for cooperative use by the peasant. Some idea of the progress in mechanization in Nigeria over the past decade can be obtained from the following comparative peasant-production figures (27).

	1950	1960
	%	%
Primitive	92.2	25–30
Hand presses	6.7	65
Pioneer Mills	1.1	5–10

Quality and Yield of Oil. The yield by these methods varies considerably. In the more primitive processes only 40–55% of the total oil in the fruit is recovered, but hand presses are usually ca. 65% efficient. Recently introduced manual hydraulic presses are almost 90% efficient; higher efficiencies are obtained in plantation mills.

The quality of the oil varies widely. Primitive methods often produce poor quality, although a large proportion measures up to the minimum edible standard of less than 5% FFA calculated as palmitic acid. Plantation oil in Nigeria is better and more uniform with 1.5–4% FFA. But oil produced by the most primitive process can be of high quality if sufficient care is exercised.

Bleachability of the oil is important in addition to FFA content. Since 1900 the demand for palm oil has come from the edible trade, so low acidity and good bleachability are essential. In the U.K., oil is bleached by earth and also by special heat processes. However, Nigerian oil is generally inferior in bleachability to oil from the Far East; this difference discounts Nigerian oils often as much as $4 per ton. The causes of this difference (Difference 40 units; see footnote (b) Table I) have been investigated (28) and shown to be caused mainly by oxidation.

The color in the crude oil is almost entirely carotenoids, with ca. 20% alpha-carotene, 65% beta-carotene, and 15% lycopene. The gross amount of coloring matter from different types of fruit varies, being 100 ppm (calculated as beta-carotene) or less in the oil from *albescens* fruit, to about 2,500 ppm from dark-colored fruit. Most Nigerian oil contains 300–2,000 ppm, usually in the range 1,000–1,300 as compared with 500 or less in Malayan oil (29).

Preliminary studies showed that samples collected in Nigeria with a high absorption ca. 230 mμ were difficult to bleach. Since absorption at this wavelength is associated with the presence of conjugated dienes, resulting from oxidation, it was tentatively concluded that oxidation during processing might be causing inferior bleachability. Samples of virgin oil were then prepared in Nigeria with great care and showed excellent bleachability. When these same samples were heated to ca. 105C under a current of air for an hr they became difficult to bleach, but only when iron or other metals were present. Since samples of Nigerian oil from native producers often had poor bleachability even with low iron content, it was concluded that deterioration in bleachability could be due to causes other than atmospheric oxidation. It was later established that enzymic deterioration occurred during fruit collection. In peasant production of palm oil the fruit often lies by the roadside for hr or even days before collection. The enzyme lipoxidase, present in a wide range of vegetable material, affects the coupled oxidation of carotenoids and unsaturated fatty acids. Ex-

TABLE I

Comparison of Specially Prepared Commercial Congo Oil and Experimentally Produced Nigerian and Cameroons Oil with Fair Average Quality Nigerian Edible Grade

Sample	F.F.A. as palmitic %	Peroxide value ml 0.002N sodium thiosulphate	Absorption[a] at 230 mμ	Carotene content mg/kg ppm	Residual color[b] after bleaching		
					With earth 105C	With heat	With heat and earth
Congo super oil S.P.B. from Lukumete	1.0	0	1.84	553	9	83	24
Specially prepared Eastern Nigerian oil	0.1 –3.0	0 –2.1	1.58–1.78	622–1547	3–32	38–108	16–29
Specially prepared Cameroons oil							
Series A	0.3 –0.4	0	1.52–1.77	478–946	4–9	78–105	16–22
Series B	0.9 –1.5	0 –2.3	1.45–2.26	339–757	3–25	80–84	17–25
Typical Nigerian oil	1.67–4.23	0.4–6.6	2.71–3.29	812–1573	30–102	69–140	45–88

[a] Extinction coefficient of 230 mμ %, 1-cm cell determined spectrophotometrically.
[b] Given as 10 x red Lovibond units + yellow Lovibond units, for 1-in. cell.

periments showed that, as with atmospheric oxidation, enzymic oxidation causes marked deterioration in bleachability. Field and other experiments confirmed these findings.

The nature of the coloring matter remaining after earth bleaching was also investigated; it appears that compounds are formed by the combination of oxidized fatty acids, with oxidized carotenoids, and that these compounds are difficult to bleach. This theory is still under examination.

Fickendey (30) in 1910 correctly attributed the development of acidity in palm fruit to the presence of a fat-splitting enzyme; but he also established that acidity could develop from infection and subsequent growth of micro-organisms. This latter finding appears to have been largely disregarded.

Recently the Tropical Products Institute has collaborated with the West African Stored Products Research Unit (W.A.S.P.R.U.) and University College, Ibadan, in the study of the nature of organisms found in palm oil and their importance to its lipolysis (31, 32). Moulds are often present in commercial oil; the four most frequently found were *Paecilomyces,* two species of *Aspergillus,* and *Rhizopus,* which were found in 10–20% of the oils examined.

Samples of sterile wet palm oil, inoculated with these moulds and stored at tropical room temperatures for 8 weeks, showed marked acid increase as compared with control samples. The increase in acidity varied 0.5–3.2%, being greatest for the mould *Aspergillus niger.*

By application of these findings, an improved quality of palm oil with low acidity, good bleachability and, incidentally, a higher melting point is now possible. See Table I.

Palm Kernels

Palm nuts with shell thickness dependent on the kind of fruit are a by-product of the palm oil industry (33).

Some kernels were exported to Liverpool as early as 1849, and today Nigeria is the main producer, accounting for about half of the world trade (34), ca. 900,000 tons annually. Some kernels are milled in the country of origin, but the bulk are milled in Europe. As received in the U.K. they have the defects of high acidity and color.

The cause of the acidity has been correlated with the amount of broken kernels, and some preliminary studies have been made of the incidence of fungi. Species of *Aspergillii,* notably *Aspergillus flavus,* are common and these have high lipolytic activity. Moulds must play an important part in causing the observed lipolysis (35,36,37).

Discoloration of the kernels (38) may be due to non-enzymic browning involving a reaction between fat aldehydes and sugars. The aldehydes could result from the auto-oxidation of some of the fatty acids present in palm kernel oil and the resultant brown substances would then be soluble in palm kernel oil (39,40). Further work on this subject is required.

Peanuts

The origin of the oil palm is to be sought in West Africa, but the groundnut or peanut most probably came from the area of Paraguay, Brazil, and the Argentine drained by the Parana River (41). It is likely that our modern peanut, *Arachis hypogaea,* is a derivative of a wild perennial strain of *Arachis.* Certainly peanuts were cultivated in Peru before the Spanish conquest, indicated by finds in tombs at Ancon near Lima. The Spaniards carried the plant to Mexico, France, Spain, and eventually to the Pacific and the Far East. It was brought to Africa by Portuguese slave traders who used the nuts as rations in their ships (42).

Present production. Today, ca. 37 million acres of land are planted to peanuts, producting ca. 8 million tons of shelled nuts. World trade in kernels is ca. 1 million tons, and in most years 400,000–500,000 tons come from Nigerian small peasant farms (43).

The peanut is an annual of the Legume family. After fertilization the small stalk bearing the flower is elongated and the fertilized ovaries are pushed into the ground where the seed pod develops. Two main types of plant are commonly distinguished, the erect, bunch, or upright and the spreading, trailing, or runner type (44,45).

At harvesting, the whole plants are usually cured in stocks or windrows. The pods are then separated and further dried if necessary. In Nigeria the decorticated nuts are stored in pyramids until they are transported by train and ship to Europe.

A few years ago the Nigerian peasant pounded the pods for decortication in a wooden mortar and a typical sample of nuts so decorticated contained 30% "wholes," 35% "halves" and 35% "brokens." Hand winnowing was then applied with a loss of fine peanut dust, estimated as 2–3%. The Tropical Products Institute suggested the use of mechanical decortication, preferably by a hand-operated machine (46, 47).

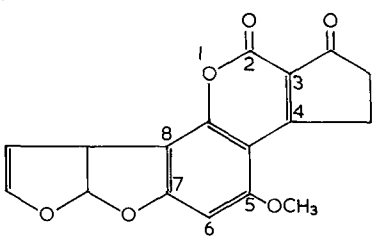
After the introduction of these small decorticators in Nigeria, exportable kernels now are at least 70% whole nuts. Improvement in quality has been spectacular. Whereas the 1951–52 crop averaged 5.63% FFA, the 1960–61 averaged only 1.46% (calculated as oleic acid).

Measures also have been taken to reduce insect attacks (48,49), and although this may have improved the acidity of the crop the main cause of lipolysis was probably breakage of kernels with increased growth of moulds and bacteria (50,51). Samples collected at

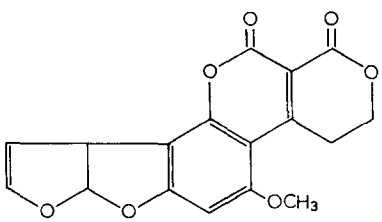
random from the pyramids in 1961 showed mould counts of 1,500–320,000 colonies/g.

Aspergillus flavus was the most common; most of the isolates belonged to 10 species of this genus. However, the study of moulds in the lipolysis of peanuts was interrupted by another problem.

In Britain during 1960, outbreaks of an apparent new disease occurred in young turkeys (52) and caused over 100,000 deaths in a few months. Investigations (53,54) showed the common factor was peanut meal from a large overseas consignment. Control feeding experiments (55,56,57) confirmed the toxicity of this meal and further studies led to the isolation of the toxic factor, which was found (58) to be a metabolite from the growth of the mould *Aspergillus flavus*. This metabolite was subsequently found (59, 60,61) to consist of at least four fluorescent compounds which have been termed Aflatoxin B1 and B2 and Aflatoxin G1 and G2. B1 and G1 have been shown (62) to be:



AFLATOXIN B_1



AFLATOXIN G_1

Aflatoxin is resistant to the ordinary processes used in extracting oils from nuts and therefore persists in the expeller cake and solvent extracted meal. The small amount which passes into the oil is removed during refining. Even in the more highly toxic samples of cake and meal aflatoxin is present, only to the extent of a few ppm.

Sensitive chemical tests (63,64) and biological methods (65) of assay have been elaborated by the Tropical Products Institute and the Central Veterinary Research Laboratory in England.

A. flavus, of which the aflatoxin-producing organism is a particular strain, can be isolated from many stored, dried foodstuffs (66) and is common in tropical soils. It is one of the most rapidly growing of the moulds and requires more moisture than certain others. At tropical temperatures it will grow at 80–85% relative humidity and above, which is equivalent to a moisture content above 9% in decorticated peanuts, and about 16% for cake or meal (67). The extent to which the mould itself is present appears to be an uncertain guide to the amount of toxin, and only a few of the pyramid samples mentioned above were found to be even mildly toxic. Careful harvesting and storage of peanuts, and grading to preclude mouldy nuts will prevent trouble. In doubtful cases tests can easily be applied.

While the main theme has been the problems of oilseeds grown in the tropics and processed in Europe, it is a matter of pride to be able to report the impact of the British oil milling industry upon the static and ancient practices of Nigeria. In a century, increased yields per acre, spectacular improvements in quality, and large valuable exports testify to the progress that has been made.

REFERENCES

1. Friedel, M. C. Compt. Rend. *124*, 648–653 (1897).
2. Mauny, Raymond, "Tableau Geographique de l'ouest Africain au Moyen Age." Memoires de l'Institut Francais d'Afrique-Noire No. 61, Ifan-Dakar, 1961, pp. 248, 429.
3. Fickendey, E., and H. M. Blomendaal, "Olpalme," Walter Bangert, Hamburg, 1929, p. 97.
4. Hakluyt "Voyages" (A description of a voyage to Benin in 1588–89, by James Welsh), Dent, London, Vol. 4, 1927, p. 297.
5. Chevalier, A., "Documents sur le Palmier à Huile," Les Végétaux Utiles de L'Afrique Tropicale Francaise, Fasc. VII, Paris, 1910.
6. Seeman, B., "Popular History of the Palms," London, 1856, p. 191.
7. Commonwealth Economic Committee, "Vegetable Oils and Oilseeds," No. 12, Her Majesty's Stationery Office, London, 1962.
8. Bauhin, J., "Historia Plantarum Universalis," Part I, Liber 3, Cap. 159, 1650.
9. Jacquin, N. J., "Selectarum Stirpuim Americanarun Historia," 1763, p. 280.
10. Adam, J., "Le Palmier à Huile." Paris, 1910.
11. Johnson, R. M., and W. D. Raymond, Colonial Plant Animal Prod. *4*, 14–23 (1954).
12. "Investigations into the African Oil Industry," Bull. Imp. Inst. *7*, 357–394 (1909); *11*, 206 (1913); *15*, 57 (1914).
13. "The Cultivation of the African Oil Palm with Special Reference to the East Indies," *Ibid. 18*, 209–252 (1920).
14. Farquhar, J. H. F., "The Oil Palm," Crown Agents, London, 1913.
15. "The Oil Palm: Its Culture, Manuring and Utilization," International Potash Institute, Berne, 1957.
16. Proceedings of the Conference on Oil Palm Research, held at the Oil Palm Research Institute, Colonial Office, H.M.S.O., London, 1949.
17. Cook, O. F., Nat. Hort. Mag. 10–31 (1940).
18. Cook, O. F., Sci. Monthly, Lond. *54*, 577–580 (1942).
19. Chevalier, A., Rev. Bot. Appl. *14*, 187 (1934).
20. Waterston, J. M., J. W. African Inst. Oil Palm Res. *I*, 24–59 (1953).
21. Faulkner, O. T., and C. S. Lewin, "Native Methods of Preparing Palm Oil—II," Second Ann. Bull. Dep. Agr., *Nigeria*, 3–17 (1923).
22. Faulkner, O. T., "Palm Oil Control Factories," First Ann. Bull. Dep. Agr., Nigeria, 18–27 (1922).
23. Gray, J. E., "Native Methods of Preparing Palm Oil," *Ibid.* 29–50 (1922).
24. Barnes, A. C., "Native Methods of Preparing Palm Oil–III," Third Ann. Bull. Dep. Agr., Nigeria, 3–10 (1924).
25. Barnes, A. C., Bulletin of the Dept. of Agriculture, 1924, and Second Bulletin, 1925.
26. West African Institute for Oil Palm Research Quarterly Progress Report No. 39 (Dec. 1961) Hand Press Operation Report.
27. Raymond, W. D., J. Inst. Agr. Eng. *3*, 74 (1960).
28. Ames, G. R., W. D. Raymond, and J. B. Ward, J. Sci. Food Agr. *4*, 194–202 (1960).
29. "Variations des Characteristiques de Certaines Huiles de Palme," Ser. Sci. Inst. Rech. Huiles, No. 9, Paris, 1956. "Etudes sur le Carotene de l'Huile de Palme," Ser. Sci. Inst. Rech. Huiles, No. 8, Paris, 1955.
30. Fickendey, E., Tropenpflanzer *14*, 560–570 (1910).
31. Coursey, D. G., Oléagineux *15*, 623–30 (1960).
32. Coursey, D. G., and H. W. O. Eggins, *Ibid. 16*, 227–33 (1961).
33. Eckey, E. W., "Vegetable Fats and Oils," Reinhold Publishing Corporation, New York, 1954, p. 339–343.
34. Commonwealth Economic Committee, "Vegetable Oils and Oilseeds," No. 12, Her Majesty's Stationery Office, London, 1962, pp. 130–142.
35. Coursey, D. G., E. A. Simmons, and Ann Sheridan, Private Communication, May, 1962.
36. Coursey, D. G., Oléagineux *16*, 385–8 (1961).
37. W.A.S.P.R.U. Annual Report, 28 (1959).
38. West African Institute for Oil Palm Research Quarterly Progress Report No. 36, p. 9; No. 38, p. 8.
39. McWeeny, D. J., Private Communication, July 1962.
40. Some Observations on the Discolouration of Palm Kernels," W.A.S.P.R.U. 1960.
41. Dubard, Marcel, Bull. Mus. Hist. Nat., Paris, 340 (1960).
42. Badami, V. K., J. Mysore Agr. Expt. Union *15*, 141–154 (1935).
43. Commonwealth Economic Committee "Vegetable Oils and Oilseeds," Her Majesty's Stationery Office, No. 12, London, 1962, pp. 24–44.
44. Adam, J., "L'Arachide," Paris, 1908.
45. "The Peanut, the Unpredictable Legume," National Fertilizer Association, Washington, D. C., 1951.
46. Raymond, W. D., Colonial Plant Animal Prod. *2*, 265–274 (1951).
47. Annet, M. E., "Le Probleme du decortiquage des Arachides en Afrique Occidentale Françoise," Rev. Bot. Appl. *11*, 730–8 (1931).
48. Raymond, W. D., Colonial Plant Animal Prod. *4*, 200–235 (1954).
49. Davey, P. M., D. W. Hall, P. L. K. Coveney, W. D. Raymond, and J. A. Squires, Trop. Sci. *1*, 296–307 (1959).
50. Whiston, A., R. S. Hay, and W. D. Raymond, Trop. Sci. *1*, 149–181 (1959).
51. Ramanathan, K. M., R. Nataragan, and D. M. Samuel. Indian Oilseeds J. *6*, 95 (1962).
52. Blount, W. P., Turkeys, *9*, 52 (1961).
53. Asplin, F. D., and R. B. A. Carnaghan, Vet. Rec. *73*, 1212 (1961).
54. Loosemore, R. M., and L. M. Markson, *Ibid. 73*, 813 (1961).
55. Carnaghan, R. B. A., and K. Sargeant, *Ibid. 73*, 726–727 (1961).
56. Sargeant, K., Ruth Allcroft, and R. B. A. Carnaghan, *Ibid. 73*, 865 (1961).
57. Sargeant, K., J. O'Kelly, R. B. A. Carnaghan, and Ruth Allcroft, *Ibid. 73*, 1219–1223 (1961).

58. Sargeant, K., A. Sheridan, J. O'Kelly, and R. B. A. Carnaghan, Nature *192*, 1096–1097 (1961).
59. Van der Zijden, A. S. M., W. A. A. Blanche Koelensmid, J. Boldingh, C. B. Barrett, W. O. Ord, and J. Philp, *Ibid. 195*, 1060–1062 (1962).
60. Nesbitt, Brenda F., J. O'Kelly, K. Sargeant, and Ann Sheridan, *Ibid. 195*, 1062–1063 (1962).
61. De Iongh, H., R. K. Beerthius, R. O. Vles, C. B. Barrett, and W. O. Ord, Biochim. Biophys. Acta *65*, 548–551 (1962).
62. Asao, T., G. Büchi, M. M. Abdel-Karder, S. B. Chang, Emily L. Wick, and G. N. Wogan, J. Amer. Chem. Soc. *85*, 1706 (1963).
63. Coomes, T. J., and J. C. Sanders, Analyst *88*, 209–213 (1963).
64. Broadbent, J. H., J. A. Cornelius and G. Shone, *Ibid. 88*, 214–216 (1963).
65. "Toxicity Associated with Certain Batches of Groundnuts." Report of the Interdepartmental Working Party on Groundnut Toxicity Research (London) 1963, Appendix B, p. 2–3.
66. Milner, M., and W. F. Geddes, "Storage of Cereal Grains and Their Products," edit. by Anderson, J. A., and A. W. Alcock, 165, Amer. Assoc. Cereal Chem., St. Paul, Minnesota, 1956.
67. Austwick, P. K. C., and G. Ayerst, Chem. Ind., 55–61 (1963).

[Received July 25, 1963—Accepted September 9, 1963]

Factors Affecting the Rate of Deterioration in the Frying Qualities of Fats.[1] I. Exposure to Air

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Abstract

The effect of heating fats in air and the effect of heating fats in an inert atmosphere were compared, and the relationship of air to changes in the frying characteristics of fat studied. The frying characteristics of a fat did not change to an extent that is commercially significant even after 48 hr heating at 375F in the absence of air; fats heated under identical conditions but in the presence of air, changed radically. It was found, also, that fat which had changed appreciably in frying characteristics when heated in air did not continue to change significantly when heated further under nitrogen. Hence, presence of oxygen was shown to be a necessary condition for the deterioration of the frying qualities of fat at frying temp. Rate of change of the frying characteristics was found to be directly proportional to the degree of exposure of fat surface to the oxygen.

Introduction

IN RECENT YEARS the specific chemistry of fat deterioration at the elevated temp of frying has been the subject of considerable study (1–4,7,8) and it is likely that, with the aid of the newer methods of analysis now available to the oil chemist, it will not be long before the mechanisms and products of this deterioration are known, at least qualitatively. Our laboratory has been concerned with frying fat both as a heat transfer medium and as an important ingredient of the fried food, and, therefore, we have concentrated on the functional effects of deterioration on product quality and the methods of minimizing them rather than the specific chemistry.

This paper is concerned with factors that affect the rate of fat deterioration in the frying system, and more specifically thermal oxidation; it excludes other factors resulting from contamination of the fat by the fried product.

Although today it is generally agreed that the deteriorative mechanism for fats heated in air is autoxidative and proceeds through free radical processes, there has been some suggestion (1) that purely thermal reactions are also operative to a degree that would have functional significance. Our purpose in this work, therefore, was twofold: 1) to test the extent to which non-oxygenated thermal changes could affect chemical and physical properties of fat which relate to its frying performance, and 2) to find out how the rate of oxidation as measured by these same properties was affected by conditions under which the fat was heated.

Materials and Methods

Fat used throughout this study was a portion of a commercially prepared batch of partially hydrogenated lard of iodine #55–60, stabilized by the addition of antioxidants (Tenox 2, Eastman Chem. Prod. Co. Tenox 2 contains 20% butylated hydroxyanisole, 6% propyl gallate, 4% citric acid and 70% propylene glycol and was used at a concn of 0.05%.).

In all cases in which reference is made to heating in an atmosphere of nitrogen, the preparation of the samples was as follows: the fat in the reaction vessel was heated and stirred by means of a magnetic stirrer hot plate at 140F while drawing a vacuum until the fat was degassed as evidenced by the absence of bubbles (approximately one hr). While still exhausting, oxygen-free, prepurified nitrogen was passed into the reaction vessel through a tube opening well below the surface of the sample for a period of about 5 min. The vessel was brought to atmospheric pressure by removing it from the vacuum system while continuing to flush with nitrogen. Both intake and exhaust ports were then closed simultaneously to seal the reaction vessel, retaining an atmosphere of nitrogen.

Samples were heated in a radiant-wall oven, thermostatically maintained at 375±2F. Temp variations due to location of samples in the oven did not exceed 1F. Reported heating times were taken from the moment samples were placed in the oven to the moment they were removed. A minor but constant error was, therefore, introduced because the time of heating up to the desired temp was not specially treated.

Various fat properties were monitored throughout this work, but only viscosity and titratable acidity were observed constantly. Previous work in this laboratory (9) had demonstrated a high correlation between these two properties and performance characteristics. Actual frying tests were performed in those experiments in which fats were heated in nitrogen because we had no similar experience with fats heated under this condition.

Titratable acidity (Free Fatty Acids), iodine number, and peroxide value were determined by the AOCS Official Methods (5).

Viscosity was determined in a steam jacketed pipet, fabricated in this laboratory, by timing the flow of 20 ml fat at 212F. The pipet was calibrated with NBS viscosity standards (6) covering the range of viscosities experienced in this work.

[1] Presented at the AOCS Meeting in New Orleans, 1962.