

Effects of Short-Term Exposure to Sunlight on the Quality of Some Edible Vegetable Oils

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Abstract: The effects of ambient sunlight on the quality of oven-dried palm, palm kernel, groundnut and soybean oils were determined by exposing them to sunlight for 25 days. Physico-chemical measurements made at 5th day intervals shown that their relative density, viscosity, peroxide, refractive index and free fatty acids values increased in the order soybean oil>groundnut oil>palm oil>palm kernel oil, while their iodine values were found to decrease in the same order. The increase/decrease in each of the values were significant when compared to those found for their respective unexposed (i.e., control) oil samples. The variation of the values between the exposed and the unexposed samples in each oil was correlatable to the degree of unsaturation in the oil. There was reduction of colour intensity in all of the exposed oil samples.

Key words: Sunlight, soybean oil, groundnut oil, palm oil, palm kernel oil, photo-oxidation

INTRODUCTION

Vegetable oils form a good part of human diet, providing concentrated sources of energy and essential nutrients (Min, 1983). They are often displayed under direct sunlight in open markets and under fluorescent light in the supermarkets. Such exposures can result in the production of off-flavours, colour defects as well as loss of nutritional quality of the oils (Ihekoronye and Ngoddy, 1988; Sanders, 1983; Mecollum, 1956). In the process, the essential fatty acids and vitamins present in the oils are oxidized and their nutritive values reduced.

When oils are exposed to sunlight their π -bond contents become photoxidized (Fekarurhobo *et al.*, 2005; Ullah *et al.*, 2003). In the process, oxygen reacts with the double bonds of fatty acids to form peroxides and/or free radicals in the presence of light (Przybylski, 2005) (Fig. 1). Indeed, the oxidation levels of vegetable oils are important quality criteria in food chemistry because oxidation increases their toxicity by the formation of products such as hydroperoxides, aldehydes, ketones, etc (Muik *et al.*, 2005; Harold and Kirk, 1981).

The rate of photoxidation is affected by some factors such as the presence of oxygen, intensity of radiation, degree of unsaturation and temperature. In general, the higher the unsaturation, the more the oil is susceptible to oxidative rancidity. However, the susceptibility of vegetable oils to photoxidation is not only due to high concentration of the unsaturated fatty acids. The oils also, contain pigments (as chlorophyll) and their

Table 1: Fatty-acid-type compositions of the oils

Types	Palm kernel oil	Groundnut oil	Soya bean oil	Palm oil
Saturated	85	17	15	53
Mono unsaturated	13	61	25	38
Poly unsaturated	2	22	60	9

USDA Handbook (1979)

decomposition products, which can act as photosensitizers to generate singlet Oxygen (1O_2) in the presence of light and atmospheric triplet oxygen (Barr *et al.*, 2002; Nawar, 1972). 1O_2 , being a strong electrophile, reacts with the π bonds of unsaturated fatty acids to form the initial hydroperoxides, which can break down and form free-radicals to initiate autoxidation (Chan, 1987).

Natural antioxidants found in many fruits and vegetables, which include β -carotene, ascorbic acids, tocopherol, which can act as 1O_2 quenchers, help to reduce the rate of photoxidation in the oils.

Soybean oil, groundnut oil, palm kernel oil and palm oil are popularly used in food preparations. Their fatty acid type compositions vary therefore, their degrees of susceptibility to sunlight are expected to be different. The fatty acid compositions of the vegetable oils are shown in Table 1 (USDA, 1979). The extent of deterioration of the oils reflects the molecular changes effected by their exposure to sunlight. The degree of the molecular alterations can be studied by monitoring changes in physico-chemical parameters such as peroxide value, iodine value, free fatty acids, refractive index, relative density and viscosity.

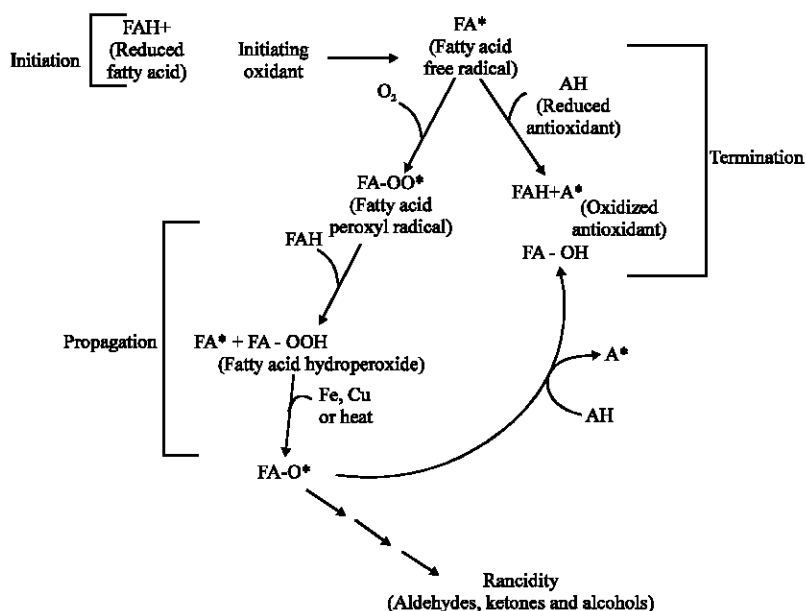


Fig. 1: The free radicals in the presence of light

MATERIALS AND METHODS

Oil extraction: Seeds were purchased from mile 3 market in Port Harcourt. They were cleaned and all except the palm fruits were milled. The milled groundnuts and palm kernels were Soxhlet extracted with petroleum spirit (60-80), while the milled soybean oil was extracted with straight-run gasoline (40-60). Palm oil was traditionally extracted. The oils were dried in the oven at 105°C for 2 h.

Irradiation: One hundred milliliter each of the 4 oil samples were irradiated under natural sunlight in transparent Pyrex glass beakers in the months of December to July. Non-irradiated oil samples were kept in opaque bottles in a dark chamber to serve as control.

Measurement of quality parameters: The quality parameters studied were peroxide value, free fatty acid, refractive index, iodine value, viscosity and relative density. The parameters were measured before irradiation and at 5th day intervals for both the irradiated and unirradiated samples.

RESULTS AND DISCUSSION

The results obtained are shown in Table 2 and Fig. 2-7.

The physical changes observed in the oils are shown in Table 2. They include the separation of liquid and solid phases in palm oil sample after exposure for 5 days, the

appearance of a thin crust on the surface of the palm oil after exposure for 5-10 days, the disappearance of this crust from the surface of the exposed oil after 10 days of exposure, the formation of a sludge at the bottom of the oil and increase in thickness of the oil samples with exposure duration. The observations may be attributed to photolysis/photoxidation. Such physical changes observed in the exposure of crude oil to sunlight were similarly explained (Fekarurhobo *et al.*, 2005).

The colour lightening observed in the oils may be as a result of loss of colour pigments. All natural fats and oils contain colour pigments (e.g., chlorophyll and carotenoids), which are highly oxidizable because of their π bond contents. Such changes have been reported (George, 1997; Daling, 1988; Nawar, 1972).

Figure 2-7 show that all the parameters (except iodine value, which decreased) increased with exposure duration.

Relative density and viscosity: Relative density values increased at the end of the exposures by 0.033, 0.025, 0.017 and 0.016 for soybean, groundnut, palm and palm kernel oils, respectively. The viscosity values also, increased on exposure by 86.41, 58.12, 24.10 and 21.86 for soybean, groundnut, palm and palm kernel oils, respectively. The increase in the values of these parameters may be as a result of photo-oxidation, which results in the formation of higher molecular weight compounds. Such increases have been reported by Carlson *et al.* (1976) and Hoffman (1989). The increases, which are in the order, soybean > groundnut > palm >

Table 2: Physical observations

Exposure duration (days)	Physical changes observed
0-5	The exposed and unexposed palm oil samples separated into liquid and semi solid phases No significant physical change was observed in the other oil samples
5-10	Irradiated samples were slightly lighter in colour than shielded samples. Palm oil samples formed thin crusts on the surfaces and a thick sludge at the bottom of the oil. The crust/sludge was thicker in the shielded sample
10-15	The thin crust on the palm oil surface disappeared. Irradiated oil samples were noticeably lighter in colour
15-20	The irradiated oil samples became thicker. The thickness was most in the irradiated soybean oil
20-25	Irradiated soybean oil became jelly-like

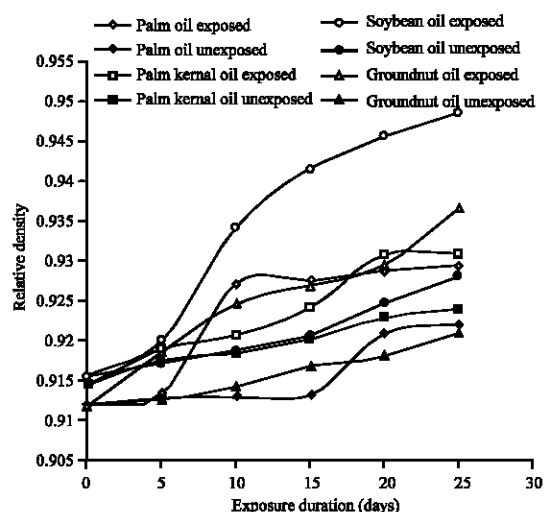


Fig. 2: Plot of relative density vs. exposure duration

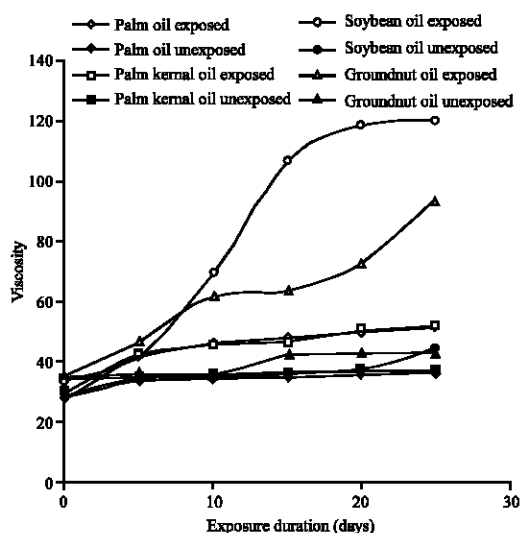


Fig. 3: Plot of viscosity vs. exposure duration

palm kernel oils, may be a reflection of the degree of unsaturation in the oil samples (Table 1).

Peroxide value: The peroxide value (meq kg^{-1}) increased on exposure by 125.39, 101.82, 59.99 and 48.22 for soybean, groundnut, palm and palm kernel oils, respectively.

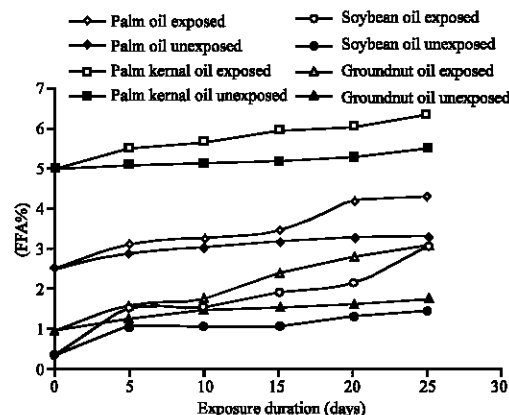


Fig. 4: Plot of free fatty acid vs. exposure duration

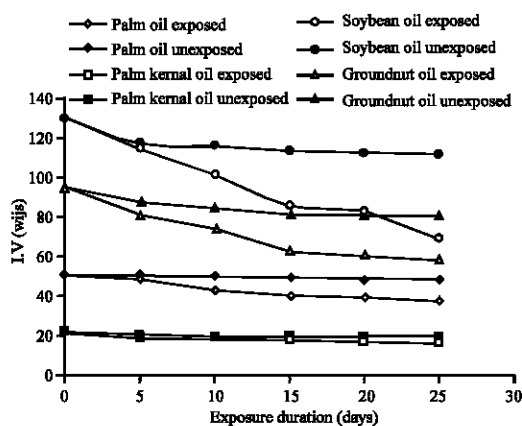


Fig. 5: Plot of iodine value vs. exposure duration

The increases in peroxide values of the oils indicate their deterioration during exposure to sunlight. Such increases have been reported (George, 1997; Zeb and Ahmad, 2004) and were ascribed to the degree of unsaturation of the oils. Thus, the order of increase in the peroxide values observed in the current exposure agrees with the degree of unsaturation in the oils (Table 1).

Iodine value (Wij's): Iodine values of the oil samples decreased by 60.22, 36.60, 13.05 and 4.67 for exposed soya bean, groundnut, palm and palm kernel oils, respectively. The decrease in iodine value may be as a result of loss of

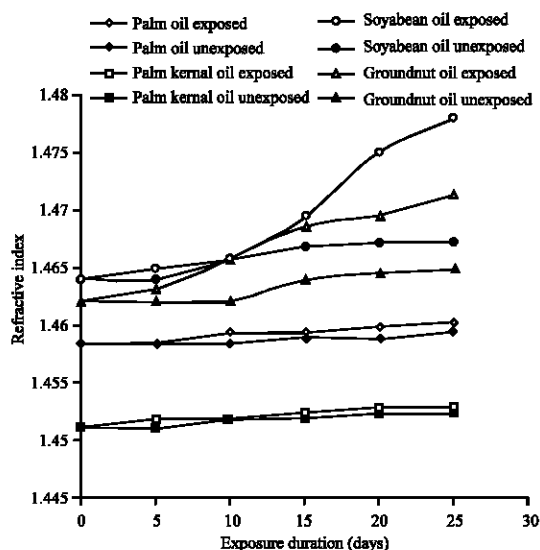


Fig. 6: Plot of refractive index vs. exposure duration

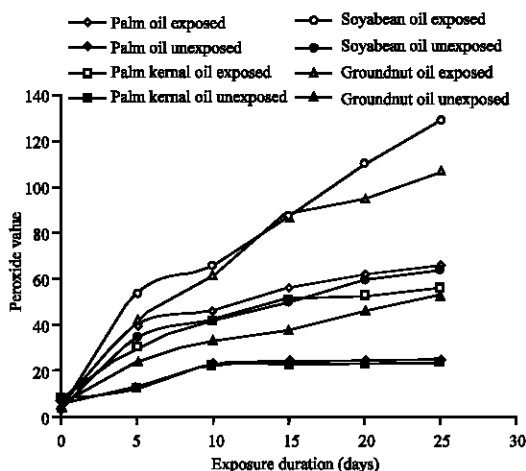


Fig. 7: Plot of peroxide value vs exposure duration

unsaturation as the π -bonds become oxidized with exposure of the oils. The order of decrease in the values while, it agrees with the order of unsaturation in the oils, also corresponds to earlier findings by Zeb and Ahmad (2004).

Refractive index: The refractive indices of the four oil samples changed only slightly throughout the exposures as can be shown in Fig. 6. The values increased by 0.014, 0.0092, 0.0019 and 0.0018 for soybean, groundnut, palm and palm kernel oils, respectively. The results confirm earlier observations that irradiation does not have much effect on the refractive indices of the oils (Sattar and deMan, 1976; Zeb and Ahmad, 2004). The

trend in the increases is the same as that observed in the other parameters, presumably reflecting the degree of unsaturation in the oils.

Free Fatty Acids (FFA%): The results of the percentage free fatty acids of the oil samples (Fig. 4) show that the values increased by 2.72, 2.13, 1.79 and 1.40 for soybean, groundnut, palm and palm kernel oils, respectively. The fact that the trend in the increases is the same as the order of unsaturation in the oils suggests that functional group interconversion in the triglycerides alone cannot explain the result.

The observation that changes also occurred in the control samples suggests that a more plausible explanation is that the carbon-carbon π -bonds oxidize to give the free fatty acids. Thus, other factors such as temperature may also have contributed to the formation of the free fatty acids.

CONCLUSION

Exposure of soybean, palm, palm kernel and groundnut oils to sunlight accelerated their oxidation. The increasing change in the parameters measured indicates that the oils deteriorated on exposure to sunlight. Further studies however, are needed to identify the specific products formed and to determine their possible health implications.

REFERENCES

- Barr, D.G. Reynhout and J. Guzinski, 2002. Measuring oxidation in cooking oil using EPR Spin Trapping, EPR division of Bruker Biospin Corp. Billerica, MA 01821 and Kalsec Inc. Kalamzoo, M/49005-0511. pp: 1-4. <http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/39096.pdf>.
- Carlson, D.J., T. Suprunchuk and D.M. Wiles, 1976. Photooxidation of unsaturated oils, effect of singlet oxygen quenchers. J. Am. Oil Chemist Soc., 53: 656-659. ISBN: 0003-021x. <http://www.science-direct.com/science>.
- Chan, H.W.S., 1987. The Mechanism of Autoxidation In: Chan, H.W.S. (Ed.). Autoxidation of Unsaturated Lipids, Academic Press Inc. Orlando. www.scribd.com/doc/13569723/VitaminHandbook.
- Daling, P.S., 1988. A study of the chemical dispensability of fresh weathered crude oils. Proceedings of the Eleventh Arctic and Marine Oil Spill Programme Technical Seminar, June 7-9, pp: 481-499. ISBN: 0381-4459. www.nrt.org/production/NRT/NRTweb.nsf/.../SA/Isb-bib.pdf.

- Fekarurhobo, G.K., F.G. Obomanu, W.A.L. Izonfuo, N. Boisa and U. Uzoezie, 2005. Photo-degradation of a Nigerian crude oil. *J. Nig. Environ. Soc.*, 2: 306. ISBN: 1596-7751.
- Hoffman, G., 1989. The chemistry of edible fats in: Chemistry and technology of edible oils and fats and their high fat products. Academic Press, pp: 3-22. www.bioline.org.br/request?ft02017.
- Harold, E. and R. Kirk, 1981. Pearson's Chemical Analysis of Food. 8th Edn. Churchill Livingstone, Edinburgh, London, pp: 543.
- Ihekoronye, A.I. and P.O. Ngoddy, 1988. Integrated Food Science for the Tropic, Macmillan Publishers, London, pp: 59-80. ISBN: 0-333-38883-6.
- Jeorge, M., 1997. Natural antioxidants for preventing colour loss in stored Paprika. *J. Food Sci.*, 65(5): 1017-1022. ISBN: 0022-1147. <http://www.bioline.org.br/request?ft02017>.
- Mecollum, E.V., 1956. A history of nutrition, Riverside Press, Cambridge MA, USA, May 18, pp: 50-60. www.canna-net.info/foodscripts/count_article.asp?Article_code=11018220.
- Min, D.B., 1983. Analysis of flavour qualities of vegetable oils by gas chromatography. *J. Am. Oil Chemists Soc.*, 60: 544. <http://www.springerlink.com/content/u8t23vo4618127q1>.
- Muik, B., B. Lendl, A. Molina-Dioz and M. Ayora-Canada, 2005. Direct monitoring of lipid oxidation in edible oils by Fourier transform Raman spectroscopy. *Chem. Phys. Lipids*, 132: 173-182.
- Nawar, W.W., 1972. Effect of ionization radiation on lipids In: Progress in the Chemistry of Fats and Other Lipids, 13: 91-118. ISBN: 0003-021x. DOI: 10.1007/BF02633572. <http://www.springerlink.com/content/033005x742113799>.
- Przybylski, R., 2005. Canola Oil: Physical and Chemical Properties, Council Publications, Canada. <http://www.canola-council.org/Pubs/Physprop.html>.
- Sanders, T.A.B., 1983. Nutritional Significance of Rancidity. In: Foods, Allen, J.C. and J. Hamilton, (Eds.). Applied Sci. Publications, New York, pp: 59-66. DOI: 10.1016/j.jfoodeng.2007.05.029. <http://linkinghub.eslevier.com/retrieve/pii/S0260877407003159>.
- Sattar, A. and J.M. DeMan, 1976. Stability of edible oils and fats to fluorescent light irradiation. *J. Am. Oil Chemist Soc.*, 63: 473-477. ISBN: 003-021x. DOI: 10.1007/BF02636815. <http://www.springerlink.com/content/92t5xvv701344378>.
- Ullah, J., M. T. Hamayoun, M. Ahmad, Ayub and M. Zafarullah, 2003. Effect of light, natural and synthetic antioxidants on stability of edible oil and fats. *Asian J. Plant Sci.*, 2 (17-24): 1191-1194. ISBN: 1682-3974. www.scialert.net/qredirect.php?doi=ajps.2003.1192-1194&linkin=pdf.
- USDA, 1979. Composition of Fats and Oils. United States Departments of Agriculture (U.S.D.A) Handbook 8-4, Government Printing Office, Washington DC, USA,
- Zeb, A. and T. Ahmad, 2004. The effect of high dose irradiation on the quality parameters of edible oils. *Pak. J. Biol. Sci.*, 7 (6): 943-946. ISBN: 1028-8880. <http://eprints.kfupm.edu.sa/91466>.