

Oxidative Stability of Oils and Fats with Natural Antioxidants: A Review

Manju V. Nehra and Amanjyoti

Department of Food Science and Technology
Chaudary Devi Lal University,
Sirsa-125055 (Haryana)

Abstract—Oils and fats are important part of the human diet and more than 90% of global production is used as food or as ingredients in food products. They are rich source of energy; they contain fatty acids, antioxidants, antifoaming, anti-surfactant, less amount of meal etc. Vegetable oils play important functional and sensory roles in food products and they act as carriers of fat-soluble vitamins (A, D, E and K). Lipids are protected against oxidation by addition of antioxidants that remove the free radicals and reactive oxygen species.

Oxidative stability of oils is the resistance to oxidation during processing and storage (Guillen and Cabo 2002). Resistance to oxidation can be expressed as the period of time necessary to attain the critical point of oxidation, whether it is a sensorial change or a sudden acceleration of the oxidative process (Silva *et al.*, 2001). Oxidative stability is an important indicator to determine oil quality and shelf life (Hamilton, 1994) as low-molecular weight off-flavor compounds are produced during oxidation. The off-flavor compounds make oil less acceptable or unacceptable to consumers or for industrial use as a food ingredient. Oxidation of oil also destroys essential fatty acids and produces toxic compounds and oxidized polymers. The problem of ensuring a high quality of lipids and lipid-containing products and prolonging their storage time is directly associated with their optimum stabilization by addition of suitable antioxidants. There is a growing interest in natural antioxidants found in plants because of the world-wide trend towards the use of natural additives in food and cosmetics (Yanishlieva *et al.*, 2006).

Lipid oxidation has been recognized as the major problem affecting edible oils, as it is the cause of important deteriorative changes in their chemical, sensory and nutritional properties. Oxidation normally proceeds slowly at the initial stage and then a sudden rise occurs in the oxidation rate. The period of time which marks this change in the oxidation rate is called induction period or induction time. Oxidation may occur in foods during harvesting, processing and storage, giving rise to the development of off-flavours, loss of essential fatty acids, fat-soluble vitamins and other bioactive, and formation of potentially toxic compounds, thus making the lipid or lipid-containing foods unsuitable for consumption (Shahidi and Zhong, 2010).

Keywords: Oxidative Stability, Antioxidants, Free Radicals, Shelf life, Bioactive.

Phytochemicals are a big group of non-nutrient substances present in vegetables and fruits which are biologically active and have important role in health promoting impacts. Several compounds in this group are antioxidants, processing to the fact that these compounds have a capacity to protect cells and bio-macromolecules neutralizing free radicals and prevent against oxidative degradation and certain human diseases (Rubalya *et al.*, 2009; Vertuani *et al.*, 2004). The term antioxidant originally was used to refer specifically to a chemical that prevents the consumption of oxygen.

In the last 15-20 years, special attention has been given to the use of natural antioxidant in important food and industrial processes (Tomaino *et al.*, 2005). Early research on the role of antioxidants in biology focused on their use in preventing the oxidation of unsaturated fats (Rubalya and Neelamegam, 2008). Antioxidants are important for human health and to prevent the oxidation of food containing lipids. The antioxidants are believed to play major role in body defense system against reactive oxygen species (ROS), which are the harmful byproducts generated during normal metabolism and in pathological conditions. Oils and fats are important part of the human diet and more than 90% of global production is used as food or as ingredients in food products. They are rich source of energy; they contain fatty acids, antioxidants, antifoaming, anti-surfactant, less amount of meal etc. Vegetable oils play important functional and sensory roles in food products and they act as carriers of fat-soluble vitamins (A, D, E and K). Lipids are protected against oxidation by addition of antioxidants that remove the free radicals and reactive oxygen species.

Antioxidants significantly delay or inhibit oxidation of oxidizable substrates at low concentration, compared to the higher contents of lipids and proteins in foods (Halliwell and Gutteridge 2001). Antioxidants for foods should be reasonable in cost, nontoxic, stable, effective at low concentration, have carry-through, and should not change flavor, color, and texture of the food matrix (Schuler, 1990). The effects of antioxidants on the oxidation of foods are dependent on their concentration (Frankel *et al.*, 1996), polarity, and the medium (Cuvelier and

others 2000; Samotyja and Malecka 2007), and also the presence of other antioxidants (Decker, 2002).

The synthetic antioxidants are less expensive than natural antioxidants. It is generally accepted that natural antioxidants are more potent, more efficient and safer than synthetic antioxidants.

Synthetic antioxidants are widely used as food additives to prevent rancidification, owing to their high performance, low cost and wide availability. Hence synthetic antioxidants, such as Butylatedhydroxytoluene (BHT), Tertiary butyl hydroquinone (TBHQ), 2,4,5- trihydroxybutyrophenone (THBP), Octylgallate (OG), Nordihydroguaiaretic acid (NDGA) and Butylatedhydroxyanisole (BHA) are used in edible vegetable oil. These antioxidants that are being used as preservative in the food industry may be responsible for liver damage and carcinogenesis; for this reason, interest in the use of natural antioxidants has increased.

Fruits and vegetables contain significant levels of biologically active components that impart health benefits beyond basic nutrition (Oomah&Mazza, 2000). Polyphenols are secondary plant metabolites which were earlier considered as anti-nutrients because some (tannins) were shown to have adverse effects in human metabolism, but recently the recognition of antioxidative properties of these phenolics has evoked a rethinking towards the health benefits of these secondary metabolites (Bravo, 1998). Polyphenols account for the majority of antioxidant activity when compared with ascorbic acid in fruits (Wang et al., 1996; Deighton et al., 2000). The antioxidant properties of phenolics is mainly because of their redox properties, which allow them to act as reducing agents, hydro- gen donors and singlet oxygen quenchers (Rice-Evans et al., 1997). The replacement of synthetic antioxidants by natural ones may have benefits due to health implications and functionality. The protection that fruits and vegetables provide against several diseases has been attributed to the various antioxidants, vitamin C, vitamin E, α -tocopherol, beta carotene and polyphenolic compounds (Abushita, Hebshi, Daood&Biacs, 1997; Aruoma, 1998). In living systems, dietary antioxidants (α -tocopherol, beta-carotene, ascorbic acid) and endogenous enzymes (superoxide dismutase, glutathione peroxidase, catalase) protect against oxidative damage.

Solvent extraction is more frequently used for isolation of antioxidants and both extraction yield and antioxidant activity of extracts are strongly dependent on the solvent, due to the different antioxidant potential of compounds with different polarity (Julkunen-Tiito, 1985; Marinova and Yanishlieva, 1997). Polar solvents are among the most employed solvents for removing polyphenols from water. Ethyl acetate and diethyl ether have been used for extraction of low molecular weight phenols from oak wood (Fernaandez de SimoA n, CadahoaAa, Conde and GarcoAa-Vallejo, 1996) and the polyphenols extracted with ethyl acetate from natural materials were reported to have strong antioxidant activity

(Marinova&Yanishlieva). Ethanol and water are the most widely employed solvents for hygienic and abundance reasons, respectively. Since the activity depends on the polyphenol compounds and the antioxidant assay, comparative studies for selecting the optimal solvent providing maximum antioxidant activity are required for each substrate. Less polar solvents such as ethyl acetate, provided slightly more active extracts than mixtures with ethanol or methanol, or methanol alone for tamarind seed coats (Tsuda, Watanabe *et al.*, 1994) although ethanol and methanol extracts also presented high lipid peroxidation-inhibiting activity, comparable to tocopherol. Selective extraction of more polar compounds was reported to enhance the antioxidant activity of lentil husk extracts (Muanzaet *al.*, 1998). Lower IC50 values for the DPPH radical (amount of antioxidant required for causing a 50% reduction in the absorbance of DPPH) were observed for butanol extracts, followed by those in ethyl acetate. Those obtained with methanol-water were less efficient.

Julkunen-Tiito (1985) found a different behaviour in the extraction of different compounds and total extractable polyphenols (TEP). Maximum total phenolics extraction yields were attained with methanol, whereas 50% acetone extracted more selectively leucoanthocyanins and no significant effects were observed in the extraction of glycosides. Also, for extracts from burdock roots, water (regardless of the temperature used) yielded the greatest amount of extract and exhibited the strongest antioxidant activity (Duh, 1998). Azizahet *al.* (1999) reported maximum antioxidant activity from cocoa by-products (cocoa powder, cocoa nib, cocoa shell) in the methanol, followed by mixtures of chloroform, ether and dichloroethane or chloroform, methanol and dichloroethane.

Velasco and Dobarganes (2002) studied the oxidative stability of virgin oil. Virgin olive oil has a high resistance to oxidative deterioration due to both a triacylglycerol composition low in polyunsaturated fatty acids and a group of phenolic antioxidants composed mainly of polyphenols and tocopherols. Polyphenols are of greater importance to virgin olive oil stability as compared with other refined oils which are eliminated or drastically reduced during the refining process. They also studied the main aspects related to the oxidative stability of virgin olive oil during storage as well as at the high temperatures of the main processes of food preparation, i.e., frying and baking. Differences between oxidation pathways at low and high temperature are explained and the general methods for the measurement of stability are commented on. The compounds contributing to the oxidative stability of virgin olive oils are defined with special emphasis on the antioxidative activity of phenolic compounds.

Reference

- [1] Abushita, A. A., Hebshi, E. A., Daood, H. G. and Biacs, P. A. (1997). Determination of antioxidant vitamins in tomatoes. *Food Chemistry*, 60, 207-212.

- [2] Aruoma, O. I. (1998). Free radicals, oxidative stress and antioxidants in human health and disease. *Journal of the American Oil Chemists' Society*, 75, 199-212.
- [3] Azizah, A. H., NikRuslawati, N. M., & Swee Tee, T. (1999). Extraction and characterization of antioxidant from cocoa by-products. *Food Chemistry*, 64, 199-202.
- [4] Cuvelier ME, Bondet V. and Berset C. 2000. Behavior of phenolic antioxidants in a partitioned medium: structure-activity relationship. *J Am Oil Chem Soc* 77:819-23.
- [5] Decker EA. 2002. Antioxidant mechanisms. In: Akoh CC, Min DB, editors. *Food lipids*. 2nd ed. New York: Marcel Dekker Inc. p 517-42.
- [6] Deighton, N., Brennan, R., Finn, C. and Davies, H.V. (2000). Antioxidant properties of domesticated and wild *Rubus* species. *Journal of the Science of Food and Agriculture*, 80, 1307-1313.
- [7] Duh, P.-D. (1998). Antioxidant activity of Burdock (*Arctium lappa* LinneA), its scavenging effect on free-radical and active oxygen. *Journal of the American Oil Chemists' Society*, 75, 455-461.
- [8] Fernandez de Simo A n, B., Cadahoa, E., Conde, E., & Garco Aa-Vallejo, M. C. (1996). Low molecular weight phenolic compounds in Spanish oakwoods. *Journal of Agricultural and Food Chemistry*, 44.
- [9] Frankel, E.N, Huang, S.W, Prior, E. and Aeschbach, R. 1996. Evaluation of antioxidant activity of rosemary extracts, carnosol and carnosic acid in bulk vegetable oils and fish oils and their emulsions. *J Sci Food Agric* 72:201-8.
- [10] GUILLEN, M.D. and CABO, N. 2002. Fourier transform infrared spectra data versus peroxide and anisidine values to determine stability of edible oils. *Food Chem*. 77, 503-510.
- [11] Halliwell B. and Gutteridge J.M.C. 2001. *Free radicals in biology and medicine*. 3rd ed. New York: Oxford Univ Press Inc.
- [12] Hamilton, R.J. The chemistry of rancidity in foods. 1994; In: *Rancidity in foods*. 3rd ed. London: Blackie Academic & Professional. P. 1-21.
- [13] Julkunen-Tiito, R. (1985). Phenolic constituents in the leaves of northern willows, methods for the analysis of certain phenolics. *Journal of Agricultural and Food Chemistry*, 33, 213-217.
- [14] Marinova, E. M. and Yanishlieva, N.V. (1997). Antioxidative activity of extracts from selected species of the family Lamiaceae in sunflower oil. *Food Chemistry*, 58, 245-248.
- [15] Muanza, D., Robert, R. and Sparks, W. (1998). Antioxidant derived from lentil and its preparation and uses. US Patent. US5762936. Naczka, M., Amarovicz, R., Sullivan, A., & Shahidi, F. (1998). Current research developments on polyphenolics of rapeseed/canola, a review. *Food Chemistry*, 62, 489-502.
- [16] Oomah, B.D. and Mazza, G. 2000. Functional foods. In: Francis, F.J. (Ed.), *The Wiley Encyclopedia of Science and Technology*, vol. 2, 2nd ed. Wiley, New York, NY, pp. 1176-1182.
- [17] Rice-Evans A. C. Measurement of total antioxidant action as a marker of antioxidant status in vivo. *Proceedings and limitations. Free Radical Research* 33 (2000) 59-68.
- [18] Rubalya VS, Neelamegam P. and Gayathri K. 2009. Estimating Antioxidant Stability in Sunflower and Rice Bran Oil on Heating Using In-vitro Analysis, *Biomedicine*, 29 (1), 31.
- [19] Rubalya V.S. and Neelamegam PA. 2008. Study of Rheological Behaviour and Oxidative Stability of Rice Bran and Corn Oil Using FTIR Spectra, *International J. of Pure and Applied Physics*, 4, 77.
- [20] Samotyja U. and Malecka M. 2007. Effects of blackcurrant seeds and rosemary extracts on oxidative stability of bulk and emulsified lipid substrates. *Food Chem* 104:317-23.
- [21] Schuler P. 1990. Natural antioxidants exploited commercially. In: Hudson B.J.F., editor. *Food antioxidants*. New York: Elsevier Applied Science. p 99-170.
- [22] Shahidi, F. and Zhong, Y. 2010. Lipid oxidation and improving the oxidative stability. *Chemical Society Reviews* 39 (11): 4067-4079.
- [23] Silva, F.A.M., Borges, F. and Ferreira, M.A. (2001). "Effects of phenolic propyl esters on the oxidative stability of refined sunflower oil." *J Agric Food Chem* 49: 3936-41.
- [24] Tomaino A, Cimino F, Zimbalatti V, Venuti V, Sulfaro V, De Pasquale A, Saija A. 2005. Influence of Heating on Antioxidant Activity and the Chemical Composition of some Spice Essential Oils, *Food Chem.*, 549.
- [25] Tsuda, T., Watanabe, M., Ohshima, K., Yamamoto, A., Kawakishi, S. and Osawa, T. (1994). Antioxidative Components Isolated from the Seed of Tamarind (*Tamarindus indica* L.). *Journal of Agricultural and Food Chemistry*, 42(12), 2671-2674. doi:10.1021/jf00048a004
- [26] Velasco, J. and Dobarganes, C. (2002). *European Journal of Lipid Science and Technology*, 104(9-10), 661-676. doi:10.1002/1438-9312(200210)104:9/10<661::aid-ejlt661>3.0.co;2-d
- [27] Vertuani, S., Angusti, A. and Manfredini, S. 2004. The Antioxidants and Pro-antioxidants Network: An Overview, *Current Parma Des*, 14, 1677.
- [28] Wang, H., Cao, G. and Prior, R. L. (1996). Total antioxidant capacity of fruits. *Journal of Agricultural and Food Chemistry*, 44, 701-705.
- [29] Yanishlieva, N. V., Marinova, E. and Pokorný, J. (2006). *Natural antioxidants from herbs and spices. European Journal of Lipid Science and Technology*, 108(9), 776-793. doi:10.1002/ejlt.200600127.