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MINI-REVIEW

Role of antioxidants in stability of edible oil

Dipak Patil

Department of Chemistry, Sardar Vallabhbhai Patel Arts and Science College, Ainpur, Jalgaon, Maharashtra. 425507, India.

*Corresponding Author:

Dipak Patil (Ph.D)
Email: dbpatil37@gmail.com

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Abstract

In response to the considerable increase in research publications in the field of antioxidant in last few years, this article is an attempt to introduce antioxidants for stabilization of edible oil. Present paper discusses the term antioxidant, their types and role, especially in edible oil. Like human being, food also needs to protect itself by oxidation. Antioxidants are kind of additives that are essential in oils to avoid the process of lipid oxidation that results in off-flavor development. As oxidation in food is a chain process, trace amount of antioxidant is required to retard the process of oxidation. Plant extracts were found as source of antioxidant due to their high contents of phenolic compounds; hence these are widely used to retard lipid oxidation in foods.

Keywords: Antioxidant, stability, vegetable oil, natural extract.

Introduction

An antioxidant, is any substance, present at low concentrations compared to oxidizable substrate; significantly preventing or delaying the oxidation of the substrates (Halliwell, 1995). Food antioxidant is specially formulated to prevent or retard oxidation of oxidizable materials such as fats (Frankel and Meyer, 2000).

Free radicals produced by oxidation reactions can start chain reactions that lead to further oxidation by chain reaction. Antioxidants terminate these chain reactions by removing free radical intermediates and inhibit other oxidation reactions by themselves being oxidized (Saha and Tamrakar, 2011). Antioxidants act as "free radical scavengers" and thereby prevent damage done by these free radicals. Food components such as lipids are very susceptible to oxidation, which results in detrimental changes to the color, odor and nutritive value of the food products. Antioxidants prevent such changes by retarding or slowing down the process of oxidation or rancidity. Fat deterioration can be divided into four types (Stuckey, 1980).

i. Hydrolysis: It leads triacylglycerols to the formation of free fatty acids and glycerol, often characterized by a soapy flavor.
ii. Rancidity: A term widely used in the food industry which covers a large number of objectionable off-flavor volatile components generated from the auto-oxidation of polyunsaturated fatty acids.
iii. Reversion: It is a type of flavor and odor degradation usually associated with the oxidation of certain highly unsaturated vegetable oils (e.g. soybean oil) and fish oils. This flavor degradation is attributed to oxidation of linolenic acid, and other ω-3 fatty acids.
iv. Polymerization: It is a term usually employed to describe the cross- linking of unsaturated fats between two carbon atoms.

Conditions that promote formation of free radicals

Cooking of food, especially frying may create formation of free radicals. Ingestion of pesticides causes more oxidative stress in the body and should be neutralized by enough antioxidants available in the diet or through supplementation. Any smoker and people who may inhale secondary smoke should supplement their diet with vitamin C. When exposed to abnormal ozone levels, normal metabolism may not be able to cope with the extra free radicals accumulated. People who are exposed to sunlight for longer time (sunbathing, skiing, yachting etc.) also require diet supplemented with extra antioxidants.

Although oxidation reactions are essential for life, they can also be harmful; hence plants and animals maintain complex systems of multiple types of antioxidants; such as vitamin C, E as well as enzymes, such as, catalase, superoxide dismutase, and various peroxidises (Alok *et al*., 2014). Low levels of antioxidants or inhibition of the antioxidant enzymes causes oxidative stress and may damage or kill cells.

Mechanism of antioxidant

Generally, the oxidation of fats or oils involves a free radical mechanism. This process can be induced catalytically by light, temperature, enzymes, metals, and microorganisms with the reaction involving free radicals or active oxygen species.

In case of unsaturated fatty acid, formation of free radical takes place by abstraction of allylic hydrogen. The resultant radical becomes very susceptible to attack by oxygen to form peroxide free radicals. These free radicals serve as strong initiators and promoters of oxidation by extracting hydrogen from another fatty acid molecule which triggers propagation (Fig. 1).

In the final stage of fatty acid oxidation, the primary oxidation products of rancidity formed are hydroperoxides. These hydroperoxides are quite unstable and subsequently degrade into smaller chain organic compounds such as aldehydes, ketones, alcohols and acids, the secondary oxidation products of rancidity. It is the latter compounds which actually render fats and oils rancid and unacceptable and unsuitable for food purposes.

Triplet oxygen lipid oxidation, a free radical process, has been extensively studied during the past 70 years. However, triplet oxygen oxidation does not fully explain the initiation step of lipid oxidation. Singlet oxygen is involved in the initiation of triplet oxygen lipid oxidation, because singlet oxygen can react directly with double bonds without the formation of free radicals (van Aardt *et al*., 2004). During the last 40 years, attention has been given to singlet oxygen oxidation of foods, because, the rate of singlet oxygen oxidation is much greater than that of triplet oxygen oxidation, and singlet oxygen oxidation produces compounds absent in triplet oxygen oxidation due to the different reaction mechanisms (Min and Boff, 2002). Interaction with light, sensitizers, and oxygen is mainly responsible for singlet oxygen formation in food (Bradley and Min, 1992). On the other hand, triplet oxygen reacts with unsaturated fatty acids by abstracting allylic hydrogen. Once hydrogen is removed, a pentadienyl radical intermediate is formed. The energy required for the removal of hydrogen varies at different carbon atoms. The relative reaction ratio of triplet oxygen with oleic, linoleic, linolenic acid for hydroperoxide formation is 1:12:25, which is dependent on the relative difficulty for the formation of the free radical in the molecule (Min and Boff, 2002). The reaction rate of the triplet oxygen with linolenic acid is approximately twice as fast as that of linoleic acid because linolenic acid has two pentadienyl groups in the molecule while linoleic acid has one pentadienyl group (Min and Boff, 2002).

The classical mechanism for free radical oxidation of unsaturated fatty acids involves hydrogen abstraction at the allylic carbon to produce delocalized three carbon allylic radicals. Phenolic substances (antioxidant) functioned as free radical acceptors and could terminate free radicals at the initiation stage. Hindered phenolics like BHA (Butylated hydroxyanisole), BHT (Butylated hydroxytoluene), TBHQ (tertiary butylhydroquinone), and tocopherols, as well as polyhydroxy phenolics like propyl-gallate are primary antioxidants, which delay or inhibit the initiation step by reacting with a lipid free radical or by inhibiting the propagation step by reacting with the peroxy or alkoxy radicals (Fig. 2). This is why trace amount of antioxidant is required to protect the matter from oxidation.

Function of antioxidants

Antioxidants mixed with food materials have the potential to control damaging free radicals by scavenging. The wide array of solid and liquid antioxidant blends are available in the market necessitates consideration of the following factors before utilizing a particular antioxidant in a food.

i. The type of food to be stabilized.
ii. The need for carrying through from the oil to the cooked food product.
iii. The ease of antioxidant solubility and disposition into the fat phase of the product (Patil *et al*., 2011a).
iv. The presence of metal ions and possibility of discolouration.
v. The relative severity of processing (e.g. baking versus frying) and the legality of a specific antioxidant for a specific antioxidant application (Min and Boff, 2002).

Antioxidants

Different synthetic antioxidants such as TBHQ, BHT, BHA, tocopherols etc. have been used in foods to prevent deterioration during storage, transportation and discoloration from oxidation (Thorat *et al.,* 2013). The primary antioxidants act as follows (Adegoke *et al*., 1998):

i) They can terminate the free radical chain by donating hydrogen to free radicals and converting them more stable products.
ii) They can form lipid-antioxidant complexes by reacting with lipid radicals.
iii) They may either delay or inhibit the initiation step by reacting with a lipid free radical or inhibit the propagation step by reacting with peroxy or alkoxy radical.

Synergistic antioxidants

Synergism may be defined as two or more agents working together to produce a result not obtainable by any of the single agents independently. The word synergy or synergism comes from two Greek words: *erg* meaning "to work" and *syn* meaning "together"; hence, synergism is a "working together" (Kim *et al*., 2010). These antioxidants decompose the hydrogen peroxide formed during the reaction of primary antioxidant with free radicals and hence, are used significantly with primary antioxidants. Examples of synergistic antioxidants include phosphates, sulphites, thioesters etc. In the food industry both natural and synthetic antioxidants are used. Recently, there is an increased demand for natural antioxidants, these are present in the plant kingdom and can be useful to enhance the oxidative and flavor stability of frying oils (Kochhar, 2000). Natural antioxidants are considered as more efficient and safer than those are from synthetic origin. Fish oil which is important source of n-3 polyunsaturated fatty acids like EPA and DHA (Patil and Nag, 2011), is highly susceptible to oxidation; synthetic antioxidants have been replaced by natural antioxidant to stabilize them (Maqsood *et al*., 2012).

Synthetic antioxidants, such as Butylated hydroxytoluene (BHT), Tertiary butyl hydroquinone (TBHQ), 2,4,5- trihydroxybutyrophenone (THBP), Octyl gallate (OG), Nordihydroguaiaretic acid (NDGA) and Butylated hydroxyanisoleb (BHA) are widely used in edible vegetable oil to prevent rancidification, due to their high Performance and lower cost. These antioxidants are used as preservative in the food industry; however, some reports suggest that, these may be responsible for liver damage and carcinogenesis; hence, interest in the use natural antioxidants in the food industry has been increased (Kim *et al*., 2010).

When compared to synthetic antioxidants**,** natural antioxidants have the following advantages,

i) They are readily acceptable by the consumers.
ii) They are considered to be safe.
iii) These natural antioxidants (not the synthetic chemical antioxidants) are identical to the food in which people ate for hundreds of years or mixed with their food.

Natural extracts as antioxidants for stability of edible oil

Since food habits worldwide are generally based on deep fried foods, oxidative-resistant (resistance to oxidation of lipids) oils are desired and demanded (İnanç and Maskan, 2012). This demand can be fulfilled conveniently by the addition of antioxidants into the frying oils. Several reports are available in literatures that highlight the use of plant derived compound or extracts as natural antioxidants in food products. Some of these plant extracts are summarized in Table 1; those are reported as potential source of natural antioxidants in stabilizing the edible oils. Natural extracts are also used for the stabilization of bio-fuel. Chung *et al*. (2012) reported stabilization of Jatropa oil for twelve months by using propyl gallate, BHA and garlic extract. Patil *et al*. (2011b) reported the production of gallic acid which is a well known antioxidant from Bahera seed coat, whose methanolic extract acts as antioxidant on lipid samples. Bera *et al*. (2004) reported ajowan (*Trachyspermum ammi*) as an antioxidant for stabilizing flaxseed and bahera (*Terminalia bellirica*) oil. From their study, although TBHQ showed higher thermal stability and comparable in cost with ajowan; the latter is preferred for use as a natural antioxidant in food as it is a spice that is being used in traditional food preparation.

In some studies, instead of plant extract, essential oils those are having high oxidative stability are used with edible oil as an antioxidant. Antioxidant effect of thyme and lavender essential oil (Bensmira *et al*., 2007) on sunflower oil was studied at frying temperatures (150, 180, 200 °C) and a significant difference in essential oil treated and untreated oil samples was observed. Antioxidant effects of essential oil from cassia (Du and Li, 2008) was found to be most effective in palm oil, during frying process. Similarly, essential oils from rosemary, clove and cinnamon (Özcan and Arslan, 2011) were shown to have stronger antioxidant effect than the control and among them cinnamon oil was the most effective on retarding lipid oxidation of crude oils, followed by clove and rosemary oils. Recently, Proestos *et al*. (2013) studied antioxidant capacity of some selected popular aromatic plants and their essential oil in Greece, with respect to their total phenolic content, antioxidant capacity, and oxidative stability.

As discussed above, essential oils have some sort of oxidative stability as compare to edible oil, mostly they are less active than synthetic antioxidant; moreover they themselves need to stabilize. Some important essential oils are well discussed by Inanc and Maskan (İnanç and Maskan, 2012).

Table 1: List of different extract as an antioxidant.

Extract	Oil	Temperature	Reference
Oleoresin rosemary extract, sage extract	Palm olein	Frying	Jaswir *et al*. (2000)
Potato peels extract	Soybean	45 °C	Rehman *et al*. (2004)
Greek sage and summer savory	Virgin olive, refined olive, sunflower, commercial oil blend	Frying	Kalantzakis and Blekas (2006)
Bahera seed coat	Flaxseed, Refined olive, lard	100-120 °C	Bera *et al.* (2007)
Garlic extract	Sunflower	185 °C	Iqbal and Bhanger (2007)
Pomegranate peel extracts	Sunflower	185 °C	Iqbal *et al.* (2008)
Pandanus amaryllifolius leaves extract	Palm olein	Frying	Nor *et al.* (2008)
olive tree leaves extract	Sunflower	Frying	Chiou *et al.* (2009)
Curcuma longa (turmeric) leaf extract	Palm olein	Frying	Mohd Nor *et al.* (2009)
Potato peels and sugar beet pulp extracts	Sunflower and soybean	70 °C	Mohdaly *et al.* (2010)
Blackcurrant seeds	Soybean	60 °C	Samotyja and Małecka (2010)
Majorana syriaca	Refined corn	Frying	Al-Bandak and Oreopoulou (2011)
Drumstick leaves extracts	Soybean	180 °C	Arabshahi-Delouee *et al.* (2011)
Chlorophyll pigments extracted from Chemlali olive leaves	Refined olive	50 °C	Jaber *et al.* (2012)
Methanolic extracts of some Cameroonian spices	Crude soybean oil	65 °C	Womeni *et al.* (2013)
Moringa oleifera Leaf	Butter oil	63 °C	Nadeem *et al.* (2013)

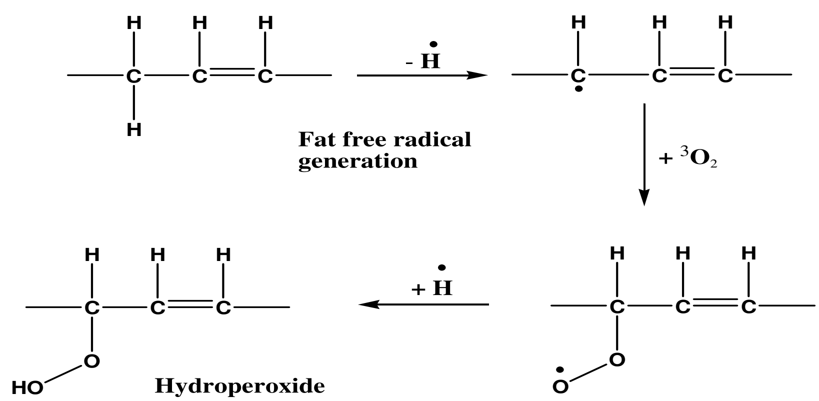

Fig. 1: Formation and propagation of free radical.

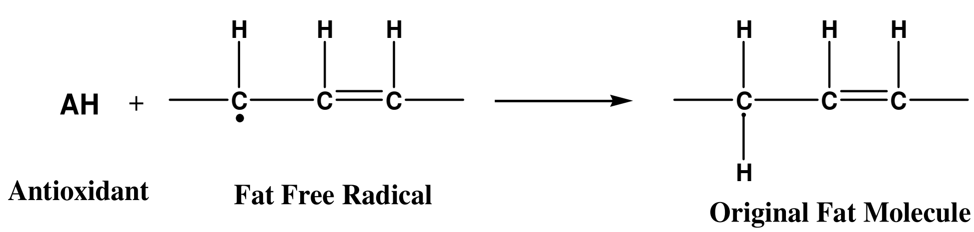

Fig. 2: Termination of free radical by antioxidant.

Conclusion

Evaluation of existent literature on stability of edible oil is discussed and various natural extracts used for the stability of edible oil is addressed systematically. Considering the vast literature on the stability of edible oil, it is important to avoid oxidative changes or deterioration. Many of the plant based antioxidants are being used as spices and condiments, which have antioxidant properties; their use can be showcased and encouraged for the use in food industries. Moreover, the plant essential oils can also be considered as the alternative to chemical antioxidants, considering the fact that there is lots of public awareness and demand for chemical free food products. Further research is required to develop or find new antioxidant for stabilization of edible oils.

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