Review Article

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Natural Antioxidants in Bakery Products

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Abstract

Most processed foods contain different ingredients that can easily undergo oxidation. While all compounds possess the ability to undergo oxidation, fats present in these foods in general have the greatest tendency to lose electrons. Auto-oxidation of lipids in food triggered by exposure to light, heat, ionizing radiation, metal ions or metallo-protein catalysts can have a deteriorating effect on the food color, flavor, texture, quality, wholesomeness and safety. However, both natural and synthetic antioxidants have long served as preservatives, used to prevent oxidation reactions, which lead to browning, and rancidity in foods. Major sources of naturally occurring antioxidants are fruits, vegetables and whole grains, spices etc. The beneficial properties of these natural antioxidants have been used in different bakery products. Baked products have popularities in the populace because of their availability, ready to eat convenience and having good shelf life. The purpose of this review is to explore the natural antioxidants, their action mechanism and the potentialities of being used in bakery industry.

Keywords: Bakery Products; Antioxidants; Natural Antioxidants; Food Sources.

Introduction

Bakery industry in India is considered as one of the major food processing industry with an annual demand of over 2758 MT [1]. The Indian bakery industry is passing through an impressive growth phase where it is trying to cater to health and wellness demands of its consumers. Among the bakery products, the most consumed is bread, followed by cakes and biscuits which are also greatly appreciated. India is known to be the second largest manufacturer of biscuits. A variety of products have entered the Indian bakery industry during the last two decades, which have contributed to the change in consumer tastes. Today urban middle and upper class Indians' tastes for bakery products are not restricted merely to bread, biscuit and cake but also to other products including burger, pizza, muffin, doughnut, etc. They are the most popular food consumed by all age groups and are gaining popularity as processed foods because of their availability, ready to eat convenience, and comparatively good shelf life [2]. The search for quality makes this sector a very competitive niche market. Responding to this positive demand, bakery industry has seen a revolution, over the past few decades. The small artisan bakeries have made way for high technologically upgraded bakery industry. As in other global markets, industrial mono-production took over from high variety bakeries to specialized bakeries in India too. Productivity became the key of success. Newer baking technologies were developed to respond better to new market requirements [3]. New materials and ingredients were introduced in products composition while research generated a constant and impressive progress. Continuous improvement in baking technology has immensely contributed in creation of better quality product, development of nutritionally superior product and economic consideration.

However, bakery products, like many processed foods, are subjected to physical, chemical and microbiological changes. Shelf-life is a major consideration in developing, producing and marketing food products. It refers to the time during

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which a product remains acceptable to a consumer in terms of sensory characteristics. There are many factors influencing shelf-life of a product viz., moisture loss, spoilage due to micro organisms, enzymatic changes and oxidation [4]. Processed foods contain fats and oils which oxidize slowly during storage. In general, baked goods have a short shelf-life, but for products such as biscuits, this can be extended from a few days to several weeks, or months, if packaged correctly. Many biscuits are characterized by their crispness and as a result need low moisture content. In addition, products that contain fat should be protected from light, air, and heat to prevent development of 'off' flavours due to rancidity. Fat, being an integral ingredient of bakery products, is susceptible to oxidation leading to the development of rancidity and off-flavour. However antioxidants have been found to enhance shelf life of baked foods [5]. It helps prevent the oxidative deterioration of fats and oils in foods [6]. Since ancient times it has been in practice to use antioxidants in baked foods. The form of antioxidant (powder or solution), method and time of incorporation are particularly important for the dispersion of antioxidant and ultimately stabilization of the product.

Owing to their wide range of availability, a huge number of compounds have been proposed to possess antioxidant activity. However of this diverse collection, only a few can be used in food products. The use of antioxidants in food products is controlled by regulatory laws of a country or international standards [7]. According to FSSAI regulations plant based antioxidants like fruits, herbs and spices etc., may be used in milk ice, frozen dessert, ice cream, cream cheese, cottage cheese, processed cheese and cheese spread, shrikhand, bread, ready-to-eat vegetables, frozen vegetables, frozen fruits/fruit products, soybean sauce, culinary pastes /fruits and vegetable sauces, tomato ketchup and tomato sauce, vegetable juices and soups, pickles, synthetic vinegar, mango chutney, pasta products, fruits and vegetable chutney and meat products (canned chopped meat, canned cooked ham) [8]. However, upper limit of their application is not specified.

Classification of Antioxidants

The antioxidants in food systems may be classified by using diverse indicators. Depending on the origin and the methods of production, food antioxidants may be natural or synthetic . The inclusion of natural sources of antioxidants could be an effective strategy for improving oxidative stability of processed foods and would be a better and more consumer-friendly alternative to synthetic additives.

Natural and Synthetic Antioxidants

Natural antioxidants occur naturally in many foods and are essential for our health. They include vitamin C found in fruits and vegetables and vitamin E found in seeds and nuts. Some vitamins (ascorbic acid and α-tocopherol), many herbs and spices (rosemary, thyme, oregano, sage, basil, pepper, clove, cinnamon, and nutmeg), and plant extracts (tea and grape seed) contain antioxidant components as well. Natural antioxidants or photochemicals antioxidants are secondary metabolites of plants . The total antioxidant capacity of plant materials such as culinary herbs, spices, vegetables, as well as fruits and oilseed products reflects concentrations of ascorbic acid (vitamin C), alphatocopherol (vitamin E), beta-carotene (vitamin A precursor), various flavonoids, and other phenolic compounds [9,10]. Phyto chemicals have been found to possess huge functional activities, such as protection against lipid oxidation, inhibition of cancer cell proliferation, and regulation of inflammatory and immune response [6]. Among the phyto chemicals, phenolic compounds were found to play major role in protection against oxidation. These antioxidants are of high or low molecular weight, can differ in their composition, their physical and chemical properties and in their mechanism and site of action.

Synthetic phenolic antioxidants (butylated hydroxyanisole [BHA], butylated hydroxytoluene [BHT], and propyl gallate), on the other hand, effectively inhibit oxidation, for e.g.: chelating agents such as ethylene diamine tetra acetic acid (EDTA) can bind metals reducing their contribution to the process. Synthetic antioxidants have been used as antioxidants for foods since the beginning of this century [11,12].

While use of synthetic antioxidants (such as butylated hydroxytoluene and butylated hydroxyanisole) to maintain the quality of ready-to-eat food products has become commonplace, consumer concern regarding their safety has motivated the food industry to seek natural antioxidants. The antioxidants that have caused health problems, for some people, are primarily synthetic [13].

Mechanism of Action: Natural and Synthetic Antioxidants

Oxidation reactions can produce free radicals, which start chain reactions that damage cells. Antioxidants terminate these chain reactions by removing free radical intermediates, and inhibit other oxidation reactions by being oxidized themselves. The oxidation of lipids proceeds through three different

stages: initiation, propagation, and termination. Hydro-peroxides and secondary oxidation products (aldehydes, ketones, acids, etc.) are responsible for the rancid aroma and off-flavors in foods [12]. The different factors that catalyse lipid oxidation are the presence of oxygen and metal ions, heat, and light. To prevent, minimize, or slow down the rate of lipid oxidation, oxygen and metal catalysts must be removed or sequestered to render them non-reactive. The food prone to oxidation must be stored at low temperatures and/or shielded from light. To prevent the oxidation, antioxidant acts effective way by acting at different stages of lipid oxidation such as initiation, propagation, and termination [14].

The natural antioxidants are the chain breaking antioxidants which react with lipid radicals and convert into more stable products. They are primarily phenolics that may occur in all parts of plants such as fruits, vegetables, nuts, seeds, leaves, roots and barks. They scavenge harmful free radicals, which are implicated in the most common cancers and other degenerative diseases including poor brain function [15,16]. Various natural substances were used, but were soon replaced by synthetic chemicals, which are cheaper, more easily available, of consistent quality, and have greater antioxidant activity [12].

The synthetic antioxidants, on the other hand, are phenolic compounds that perform the function of capturing free radicals and stopping the chain reactions for example butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tertiary butyl hydroquinone (TBHQ) [17,18].

Table 1: Comparison of natural and synthetic antioxidants [5,64]

Synthetic antioxidants	Natural antioxidants
Advantages : • Have well established mechanism of action and more efficiency. • Has stability in varied processing time and temperature. • Simple purification stages. • Cost of production less than natural sources.	**Advantages :** • Higher acceptability as considered safe for health. • GRAS certification as safe for consumption. • No positive results for toxicological studies till date. • Besides antioxidant property, act as colouring agents too.
Disadvantages: • Positive results for some toxicological studies. • May impart unwanted colour, aftertaste and flavour. • Use regulated by PFA, FSSAI.	**Disadvantages:** • Expensive purification and distillation process. • Properties of different prepations differ if not purified. • Maynot be atable under high temperature and processing time • Action mechanism is not well established.

Food Sources of Natural Antioxidants

Plants contain a variety of substances called "phytochemicals" that owe to naturally occurring components present in plants. The phytochemical preparations in preventing lipid oxidation have tremendous potential for extending shelf life of food products. The major sources of naturally occurring antioxidants are fruits [19], vegetables, whole grains [20], green and black tea, coffee, wine, beer, herbs and spices [5,21,22].

Essential oils from various spices, oilseeds, brans etc have also been qualified as natural antioxidants and proposed as potential substitutes of synthetic antioxidants in food preservation. *Zingiber officinale* contains a number of antioxidants such as beta-carotene, ascorbic acid, terpenoids, alkaloids, and polyphenols such as flavonoids, flavones glycosides, rutin, etc. [23].

A study to evaluate efficiency of *Zingiber officinale* essential oil as antioxidant agent and use in cake preservation as a natural plant preservative due to the harmful effects of synthetic antioxidants reported that cakes treated with *Zingiber officinale* essential oil in three levels (0.3%, 0.4%, 0.5%), had good antioxidant activity at 0.5% incorporation level in comparison with the control samples (without any synthetic and natural antioxidant agents). However, its activity was less than that of synthetic ones TBHQ as antioxidant agent. Results showed that this essential oil could be used as natural antioxidant in food stuffs especially those containing lipid [24].

Natural Antioxidants from Foods used in Bakery Products

Cereals

Studies have been carried out to find potential sources of natural antioxidants in wheat breads with incorporation of various cereal flours [37]. The incorporation of barley increased the antioxidant properties of the breads and the sensory evaluation showed differences among sensory attributes, depending on the barley variety used [38]. In another

study it was found that the buckwheat could be incorporated into wheat bread to get better functional composition and improved antioxidant properties in bread [48].

Baking had a negative impact on antioxidant properties of gluten-free breads and polyphenol content was generally found to be reduced in the bread. It was reported that in the case of wheat bread replaced with 40% barley flour, the amount of free phenolic compounds decreased by up to 23.5% during the baking process, while the amount of bound phenolic increased [26,27]. At the same time, the measured antioxidant activities were relatively stable during the baking process. The addition of phenols-rich materials with wheat bread is an effective technique to improve the antioxidant potential of the final product [28,29]. Wholegrain buckwheat flour is a good source of phenols and possessed good antioxidant activity [28]. Buckwheat bread had a highest content of phenolic compounds [30]. The addition of buckwheat flour to wheat flour can increase total phenols concentration and improve antioxidant status of bread. Baking temperature influenced the loss of total phenols in wheat flour more than in buckwheat flour and increase of antioxidative activity in bread samples by the formation of products of Maillard's reaction [31]. These interactions between added phenolic and bread proteins, and starch influenced the antioxidant capacity, protein and starch digestibility or functional properties of fortified bread [32,33]. Bioavailability of phenolic and antioxidant activities thermal processing can increase the bioavailability of phenolic, and increase antioxidant activities [29]. In another such study, biscuits treated with natural antioxidants (Barnyard millet) received higher sensory score during storage, than control and BHA [34].

Legumes, nuts and oilseeds

A good number of studies have reported the antioxidant activities of many legumes, such as yellow and green peas, chickpea, lentils, common beans (pinto, great northern, navy, black, dark red kidney, light red kidney, red Mexican, pink and alubia bean), fava beans, beach bean, and yellow and black soybeans . Flaxseed, sunflowers, soybean, cottonseed, and canola antioxidants typify the antioxidants from oil seeds. An important group of antioxidants includes the sterols. These compounds have been shown to prevent thermal oxidative degradation of oils. The antioxidants of confectionery and oil sunflowers include phenolic acids, tocopherols and sterols while purple hulled varieties contain significant concentrations of anthocyanins. Tocopherol homologues are phenolic antioxidants that occur naturally in vegetable oils and provide some protection against oxidation by terminating free radicals [35]. The average tocopherol content in sunflowers was found to be 649 ppm [36] with 94% as α-tocopherol and β-tocopherols each accounting for 3% of the total.

A novel fortified biscuit was successfully produced incorporating flaxseed and it was observed as the concentration of flaxseed (10%) increased the moisture, fat, ash, protein showed gradual increase whereas dietary fibre showed a rapid increase and however, carbohydrate content was decreased. The antioxidant activity, phenolic concentration was linearly increased as the fortification was increased [37].The principle effect of flaxseed in humans and animal nutrition are the high levels of alpha linolenic acid (ALA c18; 3 n-3) in its oil and the high fibre in the seed. The total flax plant is approximately 25% seed and 75% stem and leaves. The flaxseed is 35% oil, of which 55% is ALA, a polyunsaturated, n-3 type fatty acid.

Fruits and Vegetables

Plant products are rich in natural antioxidants and functional components which have been suggested to curtail oxidation of foods [38,39,40]. In agreement, many studies showed that adding vegetables to burgers and emulsions improved their oxidative stability and shelf life . Fruits are rich source of vitamin C, carotenoids and polyphenolic compounds [22,41,42]. It has been reported that apples have very strong antioxidant activity, inhibit cancer cell proliferation, decrease lipid oxidation, and lower cholesterol [43]. Dried fruits are widely used in confectionaries, bakery products and sweet industries. Raisin containing bakery products are reported to stay fresher for a longer period. Addition of raisins at 12% (flour basis) inhibited mold growth and increased the shelf-life of wheat bread by 1–3 days [45].

Potato *(Solanum tuberosum)* is considered as a good source of antioxidants such as ascorbic acid, α-tocopherol and polyphenolic compounds. However, most studies have been focused on the antioxidant activity of phenolic compounds in potato [44]. Over 20 compounds of quercetin and kaempferol were found in cabbage [22].

Furthermore, the antioxidant activity of onion *(Allium cepa)* and onion scales has been studied in lipid oxidation models and in radical scavenging assays. Both yellow and red onions were poor

antioxidants towards oxidation of methyl linoleate in contrast to their high antioxidant activity towards oxidation of LDL [44]. Vegetables containing natural antioxidants may be an effective natural substitute for prolonging the shelf life of breads. Adding vegetables reduced lipid oxidation in bread. Carrot, beetroot and broccoli reduced protein oxidation and tomato increased it, whilst beetroot and broccoli improved shelf life. The addition of carrot, tomato and broccoli to bread showed equivocal effects on oxidative stability during gastrointestinal digestion and at times appeared to induce it. Beetroot can also be a functional ingredient for the production of bakery and confectionery products, especially cakes and related products because of its high mineral contents. Beetroot has antioxidants called betalains. A study of beetroot powder incorporated (20%) value added cakes; found that total antioxidant activity increased from 5.5 to 47% and Folic Acid from 0.24 to1.9 mg/ 100g with the increase in beetroot powder incorporation Beetroot consistently showed positive effects on macronutrient oxidation during storage [47].

In yet another study, researchers used three plant foods viz., amla (*Emblica officianalis*), drumstick leaves (*Moringa oleifera*) and raisins (*Vitis vinifera*) as sources of natural antioxidants [46]. All the three extracts exhibited a high percentage of antioxidant activity evaluated using b-carotene–linoleic acid in vitro system, compared to synthetic antioxidants. Biscuits prepared by addition of natural extracts were subjected to sensory studies and chemical analysis. Biscuits treated with natural antioxidants, extracted from raisins and drumstick leaves received higher panel scores during storage period of 6 weeks, than control, butylated hydroxyl anisole (BHA) and amla extract incorporated biscuits. Addition of plant extracts from the three plant foods gave an excellent antioxidant effect on the biscuit compared with the effect of BHA, as the % increase in both peroxide and acid values after 6 weeks were lower than that of the control and BHA treated samples. Extracts from drumstick leaves and *amla* were more effective in controlling lipid oxidation during storage.

Vegetables containing natural antioxidants may be an effective natural substitute for prolonging the shelf life of breads. In biscuits, addition of purified extracts of marjoram, mint and basil is reported to have an excellent antioxidant effect compared with the effect of BHA [48].

Spices

Herbs and spices have been used for centuries to preserve foods and to make them more accepatable and appetizing [49]. Many leaf spices are reported to contain biologically active constituents that impart antioxidant, anticarcinogenic and antimicrobial properties to foods [46,50]. Natural aromatic plants and spices have been widely used in many food products including dairy and bakery products [51]. The most commonly used spices in bakery products are cinnamon, mint, mace, cloves, poppy and sesame[46]. The antioxidant activity of herbs and spices is most often due to phenolic acids, phenolic diterpenes, flavonoids, volatile oils and phenyl-propanoids [52,53] (Table 2).

Table 2: Natural antioxidants present in herbs and spices

Sl. No	Group of Phytochemicals	Chemical compound
1	Phenolic Acids	Gallic, protocatechuic, caffeic, and rosmarinic acids
2	Phenolic Diterpenes	Carnosol, carnosic acid, rosmanol, and rosmadial
3	Flavonoids	Quercetin, catechin, naringenin, kaempferol, epicatechin, gallate epigallocatechin gallate and rutin
4	Volatile Oils	Eugenol, carvacrol, thymol, menthol, safrole, 1,8-cineole, *a*-terpineol, p-cymene, cinnamaldehyde, myristicin and piperine
5	Phenylpropanoids	Thymol, eugenol, carvacrol, p-cymene
6	Curcuminoids	Curcumin, demethoxycurcumin ,bis-demethoxy curcumin

Turmeric (*Curcuma longa* L.) is another popular spice containing natural antioxidants, and is reported to possess numerous medicinal properties including antioxidant, anti-protozoal, anti-tumour, anti-inflammatory and anti-venom activities [54]. The major bioactives in turmeric are polyphenols, including curcumin, which is well known, besides other polyphenols, for its strong antioxidant activity [55]. Curcumin is a yellow coloured phenolic pigment and is an effective antioxidant that can scavenges superoxide radicals, hydrogen peroxide and nitric oxide from activated macrophages. It is used as an antioxidative and antimycotic agent in butter cakes [56].

Extracts of *Garcinia* and turmeric powder have been reported to be suitable for use in biscuits as natural antioxidants [5].The quality and antioxidant

properties of bread containing turmeric (Curcuma longa L.) Cultivated in South Korea was studied by some researchers [57] and they found that total phenolic contents of breads significantly increased with the addition of turmeric powder. Breads containing turmeric powder also showed good antioxidant activity as tested by the b-carotene-linoleate bleaching assay. A 4% substitution of wheat flour with turmeric powder showed acceptable sensory scores which were comparable to wheat bread. Breads containing turmeric powder can thus be developed as a health-promoting functional food.

Radical scavenging activity (RSA) of coriander seed oil and oil fractions were investigated and it was found that coriander seed oil and its fractions exhibited the strong RSA and can use as a natural antioxidant in lipid-containing foods [58].

In another study, by three different bioassays, indicated that extract and oil of leaves and seeds of coriander has strong antioxidant activity and thus, probably prevent oxidative deterioration of food [59].

The extract of coriander leaves was added to refined sunflower and groundnut oils heated to frying temperature and were kept for four weeks. This plant had good antioxidant activity and it is stable at high temperatures and can be used as substitutes for synthetic antioxidant. Other studies reported, antioxidant and antimicrobial effects of chamomile essential oil in cake preparation were evaluated during 75 days of storage.

The results showed that, the sample containing chamomile at 0.15%, had good antioxidant and antimicrobial activity in comparison with the control samples (without any synthetic and natural antioxidant and antimicrobial agents) ($p<0.01$). But its activity was less than that of synthetic ones (TBHQ and potassium sorbate as antioxidant and antimicrobial agent) ($p<0.01$).

In sensory evaluation, the sample containing chamomile at 0.05% had higher score in flavor, taste and overall acceptability than the samples at 0.15 and 0.1% ($p<0.05$) [60]. Bread samples exhibited higher antioxidant activity than control after addition of some aromatic and medicinal plants (garlic, coriander, sumac, fennel, marjoram, thyme and cardamom) as natural antioxidants[61].

Similar studies on biscuits incorporated with spearmint and peppermint clearly indicated the antioxidant efficiency of different mint forms in preventing the onset of rancidity in biscuits during storage suggesting the retention of bioactive components of mint [62].

Conclusion

The role of antioxidants in today's food systems is constantly expanding, given the level of processing and handling that many foods encounter on their way from farm to the fork. Antioxidant content in foods has achieved prominence on many food labels, including baked products. As long as they are consumed in moderate concentrations, natural antioxidants have been proven to have many positive health effects, such as preventing plaque formation in the arteries and preventing other chronic conditions such as cancer and heart disease.

These beneficial properties have put natural antioxidants on the forefront of recent food advertising, and public levels of awareness concerning natural antioxidants and their positive effects have increased significantly. This in turn has resulted in the increased global interest in finding new and safe antioxidants from natural sources. The challenges in using natural antioxidants derived from food, however, is their strong flavor and aroma and the exorbitant cost of extraction. More research will have to be undertaken in various areas to improve utilization of plant based sources as antioxidants and to increase their availability and efficacy specifically in areas of:

- Refinement in extraction and isolation methods
- Optimization in extraction processes in terms of cost benefit feasibility,
- Optimizing the synergistic effect of combining natural antioxidants,
- Isolation and identification of unexplored phytochemicals responsible for antioxidant activity
- Standardization of novel processes to reduce strong aroma and flavor in the extracts especially from herbs and spices.

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