

Review Article

Food Browning, Its Type and Controlling Measures: A Review Article

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Abstract

Browning, an important reaction generally occurring during processing and storage of food. Sensory and nutritional qualities of fruits and vegetables are degraded and even consumer's purchase of fresh-cut products is discouraging due to browning. Depending on the food type, quality of food is affected either positively or negatively by browning. During enzymatic browning, phenolic compounds are oxidized by PPO, this reaction incorporates a particular importance in fruits, vegetables, and seafood. Non-enzymatic browning is referred as Maillard reaction, it takes place between free amino and carbonyl group. Food browning occurring due to degradation of carbohydrates is called as caramelization. Various physical and chemical treatments have potential to inhibit browning, in fruits and vegetables products. Variety of natural products and their extracts are known to hinder browning of certain products, such as onion, lemon etc. Browning results in numerous significant implications on the food business concerning to nourishment, technology and financial expenses.

Keywords: Antioxidants, Caramelization, Chelating agents, Maillard reaction, Polyphenol oxidase (PPO)

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Introduction

Browning is a process in which the food turns brown due to the chemical reactions taking place within the food. It may be desirable or undesirable. In spite of the fact that there are several ways via which food chemically changes over the long run.

In browning process common change observed in food during pre-preparation, processing, or storage of food is development of brown colour. Degree of its occurrence varies in some food material. Thus, the extent of reaction and the food item, results in variation in food's colour from pale yellow to dark brown or black. During browning, in some food colour and flavour developed are highly desirable and also associated with the delicious, highly acceptable, and quality product. In various cases browning reactions even contributes in aroma, flavour and colour of the product for instance, in bread, chips, roasted nuts and other processed foods.

Dehydrated food such as milk, eggs, dry fruits, cut fruits, citrus fruit juice concentrates, canned milk etc commonly shows the undesirable effects of browning reactions. The variation in colour is from light cream to black while coconut develops a saffron colour. Depending on the extent to which the browning reaction has progressed the off-colour and off-odour develops in the food. The flavours may vary from mild to very bitter flavour.

Even in the food where browning is desired, controlled browning is essential as extreme browning can produce an undesirable product. Browning has numerous significant implications on the food business concerning to nourishment, technology and financial expense [1].

Browning specifically falls into 2 main categories:

- Enzymatic Browning
- Non-Enzymic Browning

Enzymic Browning

Enzymic browning is an oxidative reaction that occurs generally in fruits and vegetables, by the enzyme polyphenol oxidase causing them to turn brown. For enzymic browning to occur, action of enzyme and oxidation are required. So, when tissue is exposed to air it results in brown coloured pigment 'melanin' production as a result of series of biochemical reactions. Generally, enzymic browning is a chemical reaction which involves polyphenol oxidase (PPO), catechol oxidase, and other enzymes that result in formation of melanin and benzoquinone from natural phenols. Enzymatic browning requires exposure to oxygen so it is also referred as oxidation of foods. It begins with the oxidation of phenols by polyphenol oxidase into quinines [2].

For instance, in case of apple, enzyme phenolase and phenol are present in the cell, and when apple is sliced, they are exposed to oxygen in the air. The phenol is converted into melanin which posses brown colour, by enzyme phenolase (**Figure 1**).

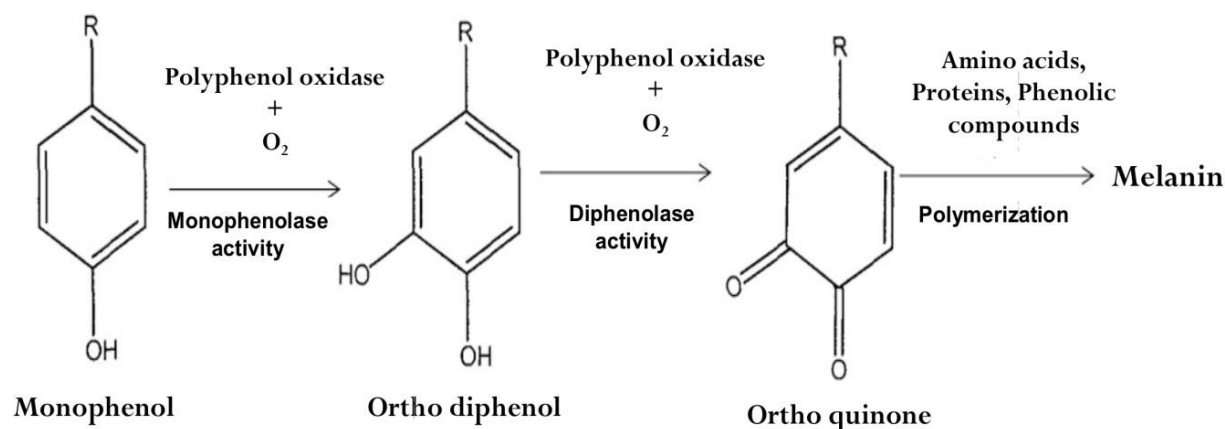


Figure 1 Melanin production in presence of oxygen.

The quinone is initial product of oxidation, which frequently condenses and results in production of melanin (insoluble brown polymers).

Polyphenol oxidase (PPO) was first discovered by Schoenbein in 1856 in mushrooms. Polyphenol oxidase is a copper-containing enzyme that catalyses or causes the oxidation of phenol compounds. It even speed up the process when pH is between 5-7. PPO enzyme is present in some bacteria, fungi, arthropods, plants and all mammals.

In fruit and vegetables rate of enzymatic browning is determined by following factors [3]:

- Concentration of PPO
- Concentration of phenolic compounds present
- pH level and temperature
- Oxygen accessibility of the tissue.

Enzymatic browning is common in:

- Fruits - Apple, Pear, Peach, Banana
- Vegetables - Potato, Brinjal, Lettuce
- Cereals - Wheat flour
- Sea food - Shrimps, Spiny lobster, Crabs

Development of colour and flavour in coffee, cocoa beans, tea and even in dried fruit such as figs and raisins shows beneficial effect of enzymatic browning, whereas, apples, potatoes, bananas, brinjal, lettuce, avocados and some crustaceans such as shrimp are examples of non-beneficial effect of enzymatic browning. Major enzyme responsible for the formation of melanosis is polyphenols oxidases (PPO).

Non Enzymatic Browning

Non-enzymatic browning is a process in which brown coloured polymer is formed in the food, but without the involvement of enzymes. Non-enzymatic browning has two main forms:

- Caramelization
- Maillard reaction.

Caramelization or Sugar browning occurs during high temperature treatment of different types of sugar over their melting point, providing a caramel-like flavour. In other words, caramelization could be called as a process which involves pyrolysis of sugar. It is widely used in various cooking processes to get the desired nutty flavour and the brown colour. As caramelization process occurs, volatile chemicals are emitted, and results in production of the characteristic caramel flavour.

The Maillard reaction occurs under mild conditions, but sugars are generally caramelized at temperatures above 120°C. When sugar is heated via dry heat, the granulated sugar molecules melt at circa 160°C with continued heating, the melted sugar will gradually turn brown and form caramelized sugar. In this process heat generated, pulls water out

of the sugar molecules, resulting in formation of furfural derivatives and its surface reaches temperature above 100°C where the browning and flavour development begin [4].

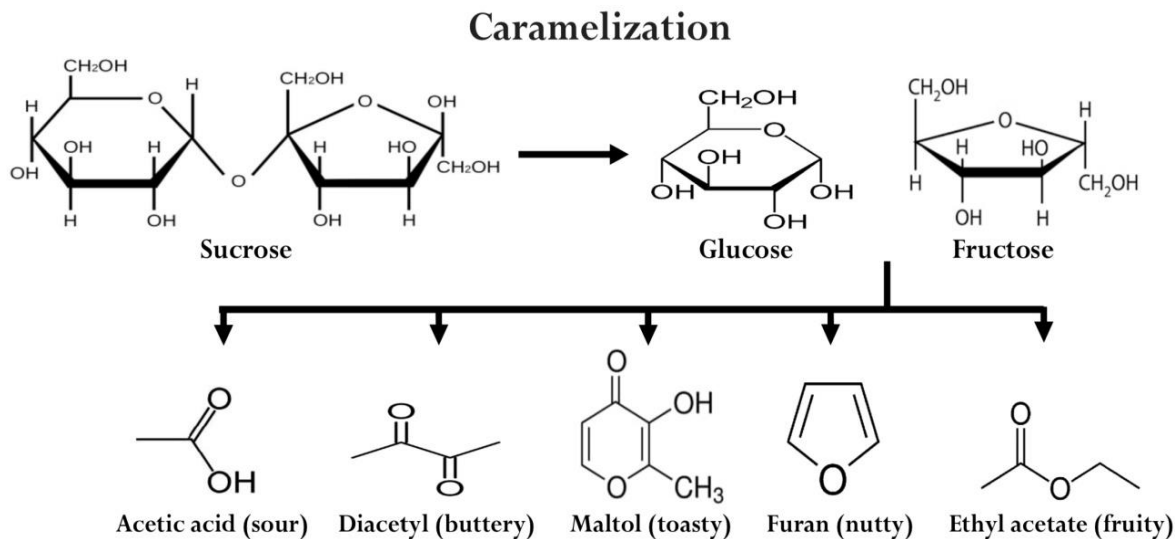


Figure 2 Sucrose decomposition leading to formation of caramel.

For example, caramelization of table sugar to brown nutty flavoured substances such as furan and maltol. Caramelization of table sugar (**Figure 2**) i.e. sucrose commence at high temperature resulting in melting of sugar followed by foaming (boiling). Firstly, glucose and fructose are formed by decomposition of sucrose, followed by condensation where sugars lose water and react with one other, ultimately forming hundreds of new aromatic compounds having a wide range of complex flavours.

Flavours of Caramel

- Diacetyl (2,3-butanedione) is responsible for a buttery flavour.
- Esters and lactones give sweet rum like flavour.
- Furans have nutty flavour.
- Maltol responsible for toasty flavour.

Caramelization reaction occurs in several products such as, jams, canned fruit products, fruit juices and concentrates, soft drinks, honey, and sugar syrups. Without using additives aromatic caramel and caramelized sugar syrups are produced, while some additives are used for caramel colour production. So, caramel colour is also used as a colourant in beverages and food [5].

Maillard reaction is a chemical reaction that takes place between the amine group of a free amino acid and the carbonyl group of a reducing sugar [1], usually with the addition of heat. It is browning of food on heating or on storage due to chemical reaction. This reaction produces flavour when food is cooked.

Common examples of food products that undergo maillard reaction are breads, steaks, and potatoes. Maillard reaction is one of the important sources for generating artificial flavours for processed food within the flavouring industry [6]. The sugars react with the amino acid and results in production of variety of odors and flavours, depending upon type of amino acid used.

Three major stages of Maillard reaction are

The early stage - In this stage there is condensation of primary amino groups of amino acids with the carbonyl group of reducing sugars (aldose), with loss of a molecule of water, leading to formation of a Schiff's base and Amadori rearrangement (**Figure 3**) which results in formation of so called Amadori compound [7]. Amadori compound is used as a source for several compounds which are essential for the development of distinctive flavours, aromas, and brown polymers.

The intermediate stage - In this stage Amadori compound breakdown and there is formation of degraded products, reactive intermediates (3-deoxyglucosone) and volatile compounds (formation of flavour). The 3-

deoxyglucosone is involved in cross-linking of proteins to a large extent at faster rates than glucose itself and in addition degradation results in formation of two known advanced products:

- 5-hydroxymethyl2-furaldehyde
- Pyraline

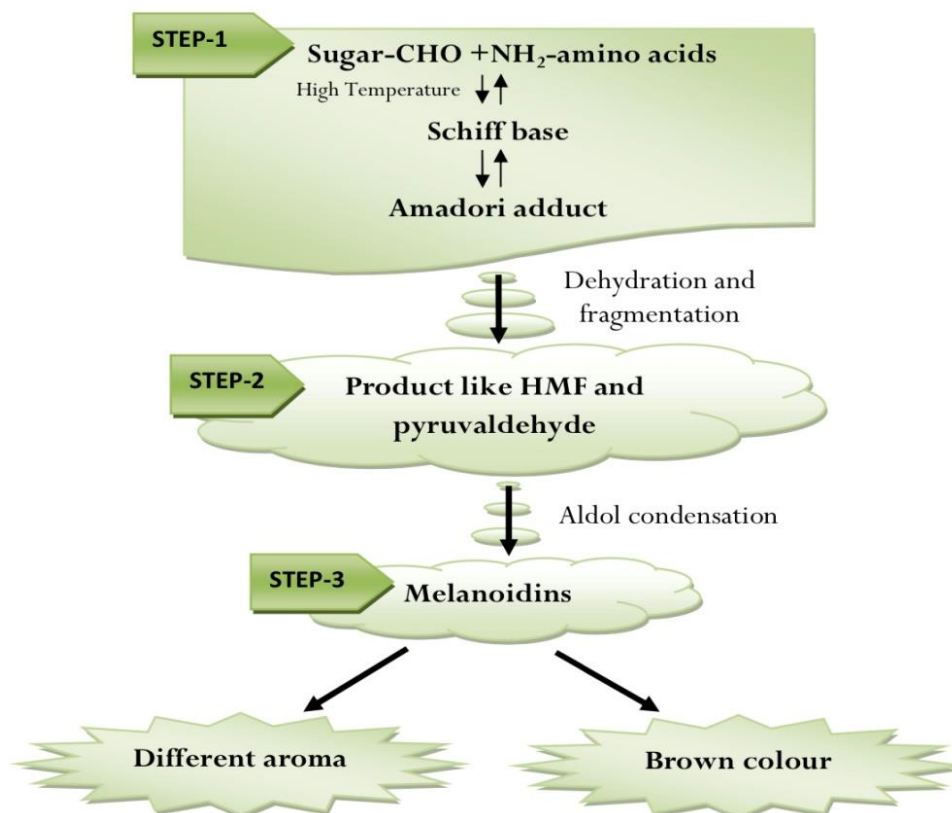


Figure 3 Three major stages of Maillard reaction

The final stage - In this stage nitrogen-containing brown polymers and copolymers are produced which are known as melanoidins [8].

During heat treatment, acrylamide is formed as an outcome of maillard reaction between amino acids and reducing sugars of food component. Major amino acid in potatoes and cereals i.e. asparagine is an essential contributor in acrylamide production. At 180°C temperature when all 20 amino acids are heated separately for about 30 min., formation of acrylamide will be observed in case of asparagine [9].

In fruit and vegetable products non-enzymatic browning can be inhibited by:

- Reduction of reducing sugar content in the products
- Controlling the water activity in dehydrated foods
- Using sulfites
- Giving glucose oxidase treatment
- Reduction of amino nitrogen content in the products
- Refrigerating the products
- Packaging the products with oxygen scavengers

The non-enzymatic browning in food depends on products composition, e.g., pH, water activity, heavy metal ions, moisture content, exposure to oxygen, presence of inhibitors, maillard precursors or ascorbic acid, storage time, temperature etc. [10, 11].

Browning Control

The measures to control browning are classified as:

- Physical methods
- Chemical methods

Physical methods

- **Heat treatment**- Blanching or roasting are examples of heat treatment that destroy the reactants and denatures the enzyme which are responsible for browning in food. Blanching at 93°C for about 2 min. inactivate PPO enzyme and improves the transfer of water vapour from the skin e.g. light coloured raisins [12]. Blanching is an essential treatment in manufacturing of wine [2], storing of nuts and bacon, processing of tea, preparation of vegetables for freezing preservation [13] and so on.
- **Cold treatment** - Refrigeration and freezing are the most widely recognized methods of storing food, preventing it from decay. Browning enzymes activity such as rate of reaction, drops at low temperatures [14]. Thus, refrigeration helps fresh fruits and vegetables to retain their initial appearance, colour and flavour. Refrigeration is also used during retailing and distribution of fruits and vegetables.
- **Oxygen elimination** - For enzymatic browning oxygen is essential, thus disposing of oxygen from the surroundings enables to sluggish down the browning in food. Withdrawing air or supplementing it with other gases (e.g. N₂ or CO₂) during preservation, such as in vacuum-packaging or modified atmosphere packaging [14], wine or juice bottling [3], using impermeable films or edible coatings, dipping into salt or sugar solutions and keeping food away from direct contact with oxygen [15]. Impermeable films composed of plastic or other materials prevent exposure of food to oxygen and also avoid moisture loss. There is an escalating activity in developing wrapping materials impregnated with antioxidants, antimicrobial and antifungal substances, for example, chitosan, butylated hydroxytoluene (BHT), lysozyme, butylated hydroxyanisole (BHA), nisin, tocopherols and natamycin [16, 17]. Edible coatings can be made of lipids, proteins, polysaccharides, vegetable skins, plants or other natural products [18].
- **Irradiation** - Food irradiation using gamma rays, x-rays and electron beams is another technique to expand the food shelf life. Ionizing radiation suppresses the vitality of microorganisms liable for food spoilage, and delays the sprouting and maturation of fruits and vegetables [15]. By managing the dosage of radiation, browning can be reduced. If the dose of ionizing radiation is more than 1 kGy, it will introduce diverse type of physiological disorders in food products. When food is treated with ionizing radiation there is production of free radicals. These free radicals are capable of reacting with various food constituents and induce undesirable side effects, for instance tissue darkening, lipid oxidation, and decreased vitamin content.

Chemical methods

- **Acidification** - Browning enzymes, show dynamic results at a particular gamut of pH. For instance, at pH 5-7 PPO shows optimal activity and is hindered beneath pH 3 [15]. Acidifying agents and acidity regulators are widely used as food additives to retain a desired pH in food products. Acidulants, for instance citric acid, ascorbic acid, and glutathione are also used as anti-browning agents.
- **Antioxidants** - Numerous antioxidants are used as food additives in food industry. They react with oxygen and suppress the commencement of browning process [15]. Antioxidants also interfere with intermediate the products of following reactions and inhibit formation of melanin. Some of the antioxidants that are also studied for their anti-browning properties are ascorbic acid, 4-hexylresorcinol, N-acetylcysteine, cysteine hydrochloride, L-cysteine, erythorbic acid, glutathione etc.
- **Chelating agents** - Copper is required by polyphenol oxidase enzyme for its proper functioning, thus copper-chelating agents restrain the activity of PPO enzyme. Numerous chelating agents are used in various fields of food industry, such as, citric acid, polycarboxylic acids, porphyrins, sorbic acid, polyphosphates, EDTA, hinokitiol [15, 17]. Hinokitiol is utilized in coating materials for food packaging.
- **Sulfites** - It is quite helpful in managing browning but due to their adverse effects on health they are subjected to regulatory restrictions. Since ancient times numerous sulfiting agents (sodium sulfite, sulfur dioxide, sodium and potassium bisulfites and metabisulfites) have been added to food to prevent enzymatic and non-enzymatic browning, control microbial growth in wine, grape and other products, act as bleaching agents such as in cherries, antioxidants, or reducing agents, carry out various technical functions [19, 20]. As per Food and Drug Administration Act of 1988, sulfiting agents are not mutagenic, teratogenic or carcinogenic in laboratory animals, but some people are sensitive to sulfite due to acute allergic reactions.
- **Ascorbic acid** - Before quinones undergo a reaction to form brown pigment, ascorbic acid convert quinones back into phenolic compounds, thus inhibit enzymatic browning, by hindering PPO [21]. Ascorbic acid inhibits enzymatic browning even after having no direct interaction with PPO enzyme that is by reducing oxidized substrates [22]. In frozen and fresh-cut fruits like, peaches and apples, ascorbic acid and its isomer erythorbic are commonly utilized as enzymatic browning inhibitor. These compounds are added to syrup or

dipping in this solution is given to fruits. Sometimes the browning inhibitors are present in combination with organic acid for instance, citric acid and calcium salt [10]. Penetration of ascorbic acid, enhance the browning inhibition by treating under vacuum or pressure rather than dipping or spraying. [19].

- **Sulfhydryl-containing amino acids** - Stable-colourless compounds are formed in milk and in pear concentrate by cysteine as it prevents formation of brown pigment by reacting with quinones to form intermediates [23, 24]. For inhibiting browning cysteine is also used as an important ingredient [25]. Browning of apple, fresh fruit juices etc can be managed by N-acetylcysteine which works as efficiently as sulfites [26].

Other methods

- **Natural agents** - Browning of certain products can be hindered or slow down by natural products and their extracts, for instance, onion, pineapple, lemon, and white wine [15]. Effective anti-browning properties exhibited by onion and its extract hinder PPO activity. In apples and bananas browning can be seized by the application of pineapple juice. Lemon juice incorporated in pastry dough makes product look brighter, this impact clarifies the anti-browning properties of ascorbic and citric acids present in lemon juice. Enzymatic browning also slow down in the cut fruits when treated with honey [27].
- **Genetic modification** - Arctic apples have been genetically modified for silencing the expression of PPO, which not only delay the browning effect but also improve eating quality of apple.
- **Chemical agents** - Certain chemical agents are quite effective in inhibiting browning (**Table 1**) such as, inorganic halides, edible coating, protease enzymes, zinc chloride etc.

Table 1 Chemical browning inhibitors

Browning inhibitors	Role	Source
Inorganic halides	Renowned inhibitors of PPO	[21]
Zinc chloride	Effective browning inhibitor, especially when used in combination with ascorbic acid, calcium chloride and citric acid	[28]
Calcium	Retarding the non-enzymatic browning in dehydrated potatoes	[28]
Sodium chloride	Commercial browning inhibitor and generally regarded as safe but limited by its effect on product taste	[21]
Edible coating	Avoid enzymatic browning of mushroom slices	[29]
Protease enzymes	Inhibit browning of apples, potatoes, shrimp, and plum juice	[30]

Conclusion

Browning occurs particularly during manufacturing, processing and storage of food (fruit, fish, meat and vegetable products). Browning is desirable in some products like bread crust, meat, cocoa, coffee, raisins, prunes etc. and even prolong their shelf life. In some products sensory properties such as colour, flavour and softness besides nutritional properties are decreased due to browning. PPO is essential enzyme of food industry, responsible for browning, resulting in decline of nutritive value and acceptance among consumer's leading to economic losses. So, managing browning is an important key to enhance the product value, to diminish post-harvest losses and to preserve the quality of the food. Various physical and chemical methods have been used for inhibiting browning such as blanching, freezing, irradiation, acidification, refrigeration etc. However natural products like lemon, onion, pineapple etc are also used for slowing down the browning. Inclusion of natural resources, attention to health benefits, and sustainability should be considered utmost important while developing anti-browning agents. Genetically modified food, is a hope in food industries, for reducing the polyphenol oxidase activity and thus ultimately decreases browning. Production of Arctic apples is an example of such accomplishments in food engineering. Researchers are above all interested in studying the management or control or inhibition of browning and the various methods that could ultimately prolong the shelf life.

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