32) DETERIORATIVE REACTIONS IN DRIED FRUITS & VEGETABLES

Reactions occurring during drying can result in quality losses, particularly nutrient losses and other deteriorations caused by browning reactions. Reactions during drying may be classified as browning reactions and nutrient losses. Moreover, there occur also structural changes, which affect quality of dried fruits and vegetables.

I. Browning Reactions

Browning reactions in foods are of widespread occurrence, and become evident when food materials subjected to processing or to mechanical injury. They are important in terms of the alteration of appearance, flavour, and nutritive value. Browning is considered to be desirable if it enhances the appearance and flavour of a food product in terms of tradition and consumer acceptance like in the cases of coffee, maple syrup, beer, and in toasting of bread. However, in many other instances, such as fruits, vegetables, frozen and dehydrated foods, browning is undesirable as it results in off-flavours and colours. Therefore it is important to know the mechanisms and inhibition methods of browning reactions. Another significant adverse effect of browning is the lowering of the nutritive value of the food article (1).

Rate of browning reactions depends on temperature of drying, pH and moisture content of the product, time of heat treatment, and the concentration and nature of the reactants. Rate increases with increasing temperature, and the increase is faster in systems high in sugar content. For moisture contents above 30 %, a decrease in reaction rate is caused by dilution; whereas below 30 %, decrease is caused by the intrinsic ability of sugars to lower water activity (1, 2).

There are two main mechanisms of browning reactions: (i) Non-enzymatic browning (Maillard reactions, caramelization, ascorbic acid oxidation), (ii) Enzymatic browning (2).

I. 1. Enzymatic Browning

Enzymatic browning is caused by a group of enzymes collectively called “phenolase” or “polyphenol oxidase”. This type of browning occurs in many fruits and vegetables, such as potatoes, apples, and bananas, when the tissue is bruised, cut, peeled, diseased, or exposed to any number of abnormal conditions. The injured tissue rapidly darkens on exposure to air, due to the conversion of phenolic compounds to brown melanins (1, 3).

Phenolase group includes such enzymes as phenoloxidase, catecholase, tyrosinase and ascorbinase. Phenolase is extensively distributed in plants such as roots, citrus fruits, plums, bananas, peaches, pears, melons, olives, tea, mushrooms, and others. It has a molecular weight of 128,000 and a copper content of 0.2 %, amounting to 4 Cu molecules to each enzyme molecule. The freshly prepared enzyme contains cupper in the cuprous form, but it slowly oxidizes to the cupric form on aging. This change thus not results in any loss of activity. Phenolase in the pure form is colourless. Concentrated solutions of phenolase are most stable at the neutral pH. But, heating for a short time at 60°C inactivates enzyme. Phenolase is also inhibited by substances, which form stable complexes with copper such as H₂S, KCN, CO or p-aminobenzoic acid (2).
In plants, there are a large number of naturally occurring o-diphenolic compounds, which are oxidizable by phenolase. Actually the mechanism of action of phenolase on o-diphenolic compounds is very complicated. Since the copper is the prosthetic group of the enzyme, it has been postulated that the activity of phenolase is based on the change of the copper from the cupric to the cuprous state. Simply phenolase catalyse the oxidation of colourless phenolic compounds into o-quinones, which are red to brown in colour. O-quinones are precursors of the brown colour in cut fruits and vegetables. When they combine with amino acid derivatives, highly collared complexes forms (1).

The initial reaction, involving the conversion of the phenolic compound to the corresponding quinone, is dependent upon the presence of the phenolase, its copper prosthetic group, and oxygen. Advantage may be taken of this in order to control or prevent enzymic browning in foods. This type browning is a serious problem during the dehydration process where any injury to the plant tissue, sustained through the use of heat or through poor handling procedures, can result in phenolase activation (2).

I. 1. 1. Control of Enzymatic Browning

I. 1. 1. 1. Heat

The application of heat to the food article at a high temperature for an adequate length of time will inactivate phenolase and all other enzymes present. Several problems may arise through the use of heat. The fruit or vegetable becomes cooked, and this in turn leads to unfavourable texture changes and the development of off-flavours. Such problems may occur for instance in the processing of pre-peeling potatoes, apples, pears, and peaches (1).

There is a close relationship between temperature and time with respect to the heat-treatment of foods. These factors themselves depend upon the amount of enzyme. It is therefore essential to control the heating time very carefully at high temperatures, so that the enzymes are inactivated while avoiding significant changes in flavour and texture. A balance should be worked out in terms of each particular raw material and desired food product (1).

I. 1. 1. 2. Sulfur dioxide and sulfites

Sulfur dioxide and sulfates, usually sodium sulfate, sodium bisulfite, and sodium metabisulfite, are powerful inhibitors of phenolase, and are widely used in the food industry. One can employ gaseous sulfur dioxide or dilute aqueous solutions of the sulfites. The gas will penetrate at a faster rate into the fruit or vegetable, but the sulfite solutions are easier to handle, as in the form of a dip in the processing plant, or as a spray. There are advantages and disadvantages in the use of sulfur dioxide or sulfites. They can be used in cases where the application of heat would result in undesirable textural changes and the development of off-flavours. They have antimicrobial properties and also assist in preserving vitamin C. However, their use in food material may result in an objectionable flavour and door, or may bleach the natural colour of the food. It is toxic at high levels, and can be detected organoleptically. Perhaps the most serious disadvantage of using sulfur dioxide or sulfites in foodstuffs is their adverse destructive effect on vitamin B or thiamine. In spite of these drawbacks, this group of phenolase inhibitors is widely used in food processing, due mainly to the effectiveness and low cost of these substances (1, 4).
I. 1. 1. 3. Acids

This is a widely used method for controlling enzymatic browning. The acids employed are among those, which occur naturally in tissues, particularly citric, malic, phosphoric and ascorbic acids. In general their action is to lower tissue pH and thus to decrease the rate of enzymatic browning. The optimum pH of phenolase lies within the range 6-7, and below 3 there is virtually no enzymatic activity (2).

Citric acid, often in conjunction with ascorbic acid or sodium bisulfite, has long been used as a chemical inhibitor of enzymic browning. Cut fruit, such as peaches is often immersed in dilute solutions of these acids prior to processing. Citric acid possesses a double inhibitory effect on phenolase, not only by lowering the pH of the medium, but also by chelating with the copper moiety of the enzyme (2).

A much more significant inhibitor of phenolase is ascorbic acid. It does not have a detectable flavour at the concentration used, nor does it possess a corrosive action upon metals; in addition, its vitamin value is well known. Ascorbic acid reduces the o-quinones formed by phenolase to the original o-dihydroxphnolic compounds, which in turn prevents the formation of brown substances (2).

I. 2. Non-Enzymatic Browning

In the preparation and processing of foods, one is soon acquainted with the phenomenon of browning associated with heated and stored products. In contrast to those reactions discussed in the previous section, these do not require enzymic catalysis and are referred to as non-enzymatic.

In general, browning reactions are deleterious to the nutritional value of the food concerned, and can occur during processing as well as during storage of food products. It is therefore imperative to arrest these reactions, thereby not only preventing any nutritional changes, but also other changes which might render the food unacceptable to the consumer (1).

Non-enzymatic browning occurs in dried foods during protracted storage (2).

There are three main reaction pathways: (i) Maillard reaction, (ii) Caramelization, (iii) ascorbic acid oxidation (1).

I. 2. 1. Maillard Reaction

This reaction was reported by a French chemist, Maillard (1912), who observed the formation of brown pigments or melanoidins when heating a solution of glucose and glycine. The reaction was subsequently referred to as the "Maillard Reaction" and similar reactions between amines, amino acids, and proteins with sugars, aldehydes, or ketones have also been established. The Maillard reaction appears to be the major cause of browning developing during the heating or prolonged storage of foods (1).

The Maillard reaction is the action of amino acids and proteins on sugars. The carbohydrate must be a reducing sugar because a free carbonyl group is necessary for such a combination.
The end product is the melanoidins, which are brown pigments. The mechanism of reaction has three stages (2):

(i) Initial stage (colourless)
   a. Sugar-amine condensation
   b. Amatory rearrangement

(ii) Intermediate stage (colourless to yellow)
   c. Sugar dehydration
   d. Sugar fragmentation
   e. Amino acid degradation

(iii) Final stage (highly collared)
   f. ado condensation
   g. aldehyde-amine polymerization, formation of heterocyclic nitrogen compounds.

The carbonylamino reaction can occur in acidic or alkaline media, although it is favoured under the more alkaline conditions. A number of studies have demonstrated an increase in reaction rate with a rise in pH. The relationship between the reaction rate and pH would therefore render those foods of high acidity less susceptible to this reaction, e.g., pickles (1).

The role of buffers in nonenzymic browning has been shown to increase the rate of browning for sugar-amino acid systems as a result of their influence on the ionic environment in which the reaction takes place. The temperature dependence of this reaction has been demonstrated in a number of quantitative studies, where increased rates were reported with a rise in temperature. This reaction proceeds readily in aqueous solution, although complete dehydration of the reactants results in a rapid halt in the process (1).

Reducing sugars are essential ingredients in this reaction, providing the necessary carbonyl groups for interaction with the free x-amino groups. The reaction, itself, is not confined to monosaccharides but can also proceed in the presence of reducing disaccharides, i.e. maltose and lactose. Non-reducing sugars, however, cannot participate unless the glycosidic bond is cleaved, thereby liberating its constituent reducing monosaccharides capable of entering the reaction. The order of reactivity appears to be greater for aldopentoses than for aldonexoses, whereas reducing disaccharides exhibit considerably less activity (2).

I. 2. 2. Caramelization

This process is another example of nonenzymic browning involving the degradation of sugars in the absence of amino acids or proteins. It was soon established that when sugars are heated above their melting points they darken to a brown coloration. This soon associated with changes in flavor. The main disadvantage of this reaction is the production of unpleasant, burned, and bitter products which can arise if this process is allowed to proceed uncontrolled. This reaction may be slowed down by bisulfites, which react with sugar to decrease the concentration of aldehydic form (2).
I. 2. 3. Ascorbic Acid Oxidation

A further mechanism appears to operate during the discoloration of dehydrated vegetables in which ascorbic acid is involved. The formation of dehydroascorbic acid and diketogluconic acids from ascorbic acid is tought to occur during final stages of the drying process and is capable of interacting with the free amino acids, nonenzymatically, producing the red-to-brown discoloration. This reaction may involve Strecker degradation (1).

I. 2. 4. Inhibition of Non-enzymatic Browning

Several of factors can affect the formation of collared complexes in food products. Among these are pH, temperature, moisture content, time, concentration and nature of reactants (2).

The rate of browning increases with rising temperature. Since these reactions have been shown to have a high temperature coefficient, lowering of the temperature during the storage of food products can help to minimize these processes (1).

Those reactions being moisture dependent for optimum activity can be inhibited by reducing the moisture content through dehydrating procedures. In attempting to carry out these procedures one must ensure that the dehydrated product is suitable for sale in that form, and that the product is suitably packaged so as not to permit moisture uptake during storage.

Since the Maillard reaction is generally favoured at the more alkaline conditions, if this type of browning is involved, lowering of the pH might provide a good method of control (1).

Gas packaging is extremely useful in excluding oxygen by using an inert gas. This reduces the possibility of lipid oxidation, which in turn could give rise to reducing substances capable of interacting with amino acids. While this reaction does not appear to influence the initial carbonylamino reaction, exclusion of oxygen is thought to effect other reactions involved in the browning process (1).

Chemical inhibitors have been used to advantage in limiting browning reactions during the production and storage of a variety of foods. Among those widely used are sulfites, bisulfites, thiols, and calcium salts (1).

Sulfites proved successful in controlling a variety of browning processes. Bisulfites inhibit the conversion of D-glucose to S-hydroxymethyl-furfural, as well as the conversion of ascorbic acid to furfural by complexing through the reducing group. Consequently the formation of furfurals is blocked, thus preventing the production of the colored pigments. They can also block the carbonyl group of the reducing sugars involved in the carbonylamino reaction (3).

Calcium chloride was reported to be a possible inhibitor of browning. Its inhibitory effect is due to the chelation of calcium with the amino acids (1).

Although the various inhibitors discussed can prevent to varying degrees of success browning from occurring, it is important to realize that the nutritional value of the foods could still have been seriously reduced. The initial stages of the Maillard reaction, for example, the carbonylamino reaction could still have rendered the amino acids unavailable even though no browning is visible during this stage. However to be certain that this stage is the one inhibited is extremely difficult to ensure.
II. NUTRIENT LOSSES
Dehydrated fruits and vegetables are good sources of energy, vitamins, protein and vitamins since they are concentrated in these nutrients. However some vitamin potency, especially the heat sensitive vitamins, may be lost during drying. The extent of vitamin destruction depends mainly on the pretreatments done before drying, the drying method, and the storage conditions after drying. Vitamin A and C are sensitive to oxidative degradation, whereas thiamine is sensitive to heat and sulfuring and riboflavin is light sensitive (5).

Processing steps that affect nutrient in drying are pretreatments, especially sulfuring, blanching, drying and storage. Sulfur dioxide is a strong reducing agent, which causes a total destruction of thiamine, whereas it protects oxygen sensitive vitamins like vitamin A and vitamin C. Sulfur dioxide enhances approximately 50% retention of vitamin C during drying. Moreover, it decreases the loss of carotene during drying as low as to 10-15 % (5).

Blanching is an essential step for minimizing nutrient losses. It stabilizes pectins, so that higher rehydration capacity and lower rehydration losses are achieved. Blanching inactivates enzymes, thereby decreases carotene and thiamine loss appreciably. On the other hand it causes loss of ascorbic acid (2).

The drying process itself has a very important effect on nutrient quality of the product. Drying time, temperature and oxygen availability during drying are critical aspects with respect to vitamin loss. During drying, loss of fat-soluble vitamins (vitamins A and E) is due to reactions of oxidation products of lipids (peroxides and radicals) with vitamins. Sun drying causes large losses in carotene and ascorbic acid. Rapid drying is important for the retention of greater amounts of ascorbic acid. In spray drying and freeze drying nutrient losses are minimum. Since proteins are heat sensitive, overheating during drying may reduce the PER (protein efficiency ratio) and make proteins unavailable to body (5).

Storage temperature and packaging materials are important for nutrient losses. Ascorbic acid is easily lost under aerobic storage conditions. Therefore, storage under carbon dioxide atmosphere is used to protect ascorbic acid and carotene contents. In general, niacin, vitamin B and pyrodoxine are stable during drying (6).

III. PHYSICAL CHANGES
A factor often greatly affecting the drying rate of the product is the shrinkage of the solid as moisture is removed. Fibrous materials such as vegetables and other foodstuffs do undergo shrinkage during drying. The most important affect of shrinkage is that there may be developed a hard layer on the surface, which is impervious to the flow of liquid or vapour moisture and slows the drying rate. In many foodstuffs, if drying occurs at too high temperatures, a layer of closely packed shrunken cells, which are sealed together, forms at the surface. This presents a barrier to moisture migration and is known as ‘case hardening’. Sometimes to decrease the effects of shrinkage, it is desirable to dry with moist air, which decreases the rate of drying so that the effects of shrinkage on hardening at the surface are greatly reduced (5).

In dried fruits and vegetables, shrinkage influences textural properties of the product. Since it results in casehardening, it resists or prevents full rehydration. Sometimes, a freeze/thaw cycle prior to dehydration is used to improve rehydration characteristics of dried products. The
effect of freeze/thaw cycle can be attributable to increased internal porosity caused by cavities left by large ice crystals (5).

Changes in textural properties of the product is determined by the integrity of cell wall and the relative mobility of cell wall content upon breakage of cell wall.

**IV. STORAGE STABILITY**

When discussing storage stability, one is concerned with the organoleptic, physical, and chemical changes that take place in the dried fruit and vegetables during storage and the rates at which these changes occur. Darkening and loss of flavour are the major types of deteriorations of dried fruits and vegetables in storage (7).

Sulfur dioxide content, storage temperature, light, packaging material, moisture content, antimicrobial treatment and trace elements are major factors affecting storage stability. Only free sulfite is effective in retarding the formation of pigment materials. During storage, the loss of sulfur dioxide determines the practical shelf life of the dried product with respect to spoilage through non-enzymatic browning. Storage of products at semitropical or summer temperatures requires residual sulfites to prevent darkening and flavour bittering, and to make the dried fruit less favourable medium for growth of microorganisms. Sulfur dioxide helps to maintain a light, natural colour during storage. Darkening rates during storage is inversely proportional to sulfur dioxide content. Therefore, any condition accelerating sulfur dioxide loss, in turn, accelerates the darkening of the product. One way to retard sulfite loss, thereby darkening, is the addition of oxygen scavenger pouch to the sealed packed sulfured dried fruit (7).

Storage temperature is of vital importance in relation to maintenance of quality. Storage of dried fruits and vegetables should be at relatively low temperatures to maximize storage life. There is an important effect of temperature on loss of sulfur dioxide from the dried product during storage. A 20°F increase in temperature increases the rate of sulfur dioxide loss approximately 3 times. Moreover at higher temperatures, the rate of change in flavour also increases (6, 7).

Light, during storage, is detrimental for quality. It causes a reduction in carotene content, increases the rate and amount of sulfur dioxide loss, and thereby increases the rate of darkening. In addition, it also affects riboflavin content (2).

Packaging material used and the package environment is another major factor in terms of storage stability. The type of package used varies with expected storage conditions. Packaging may be done under vacuum, nitrogen or atmospherically (6).

Dried foods have a moisture content below 20 % and a water activity 0.7 or below. They are hard and firm, resistant to microbial deterioration. There are critical water activities for some products below which browning is minimized. Storage stability increases with decreasing moisture content. But, it was also reported that the maximum rate of deterioration of dried fruits occurs at a moisture content of 5-8 % moisture (8).

Dried fruits and vegetables must be protected from rodents and insects during storage. Fumigation is often used to prevent insect infestation during storage and before packaging. In addition to fumigation, antimycotic agents (fungistats) are used to stabilize most prunes and figs against meld growth at 30-35 % moisture. Sorbic acid and sorbate salts are used as dips.
or sprays to prevent moulding; sulfur dioxide or sulfite salts are used to preserve fruits during drying from colour changes and browning, and to ward off insects. Potassium sorbate dip is the most effective one. The effectiveness depends on pH of the product (7, 8).

Some salts and metals are detrimental to nutritive value, flavour and storage quality. Raw materials may be exposed to these trace elements during washing or pretreatment. Calcium has a firming effect on texture; iron and copper combine with tannins to cause blackening and may accelerate degradation of ascorbic acid. Sodium, magnesium and calcium sulfates impart bitter flavour. Certain salts of zinc, cadmium and chromium have toxic effects (2).

V. REFERENCES


