BROWNING IN FOODS

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ABSTRACT

Browning is a serious problem particularly in respect of dehydrated foodstuffs. Taking into consideration the operational theatres in which our Forces are deployed at present, the supply of dehydrated material has become a necessity. In view of this the problem of browning in the processed foods has assumed added importance. Browning results in the development of off-flavours and odours and loss in nutritive value. Various causes leading to enzymic and non-enzymic browning are described as also a brief account of the current theories of browning. Methods of minimising browning and increasing storage life of precooked foods are given.

Introduction

One of the principal causes of deterioration in processed foods on storage is the development of brown to brownish black colours, commonly referred to as “Y” browning. Browning results in the loss of original flavour, odour, texture and nutritive value of the food. During the Second World War there were several military operations in varied hot, humid and tropical climates and consequently the preservation of processed foods and food concentrates presented a great problem to the Defence Services. Browning in stored foods was one of the main problems confronted with. After the War this experience gave much impetus to intense research activity in the Defence Research Laboratories and other institutions all over the world to understand the fundamental causes of browning and to evolve methods of prevention thereof. Large number of research papers have been published mostly from the laboratories in U.S.A., U.K., Australia and some Asian countries. The present review does not purport to be an exhaustive one, but it will deal with the various important aspects of browning and its prevention in brief.

The following varieties of foods and their products are known to undergo browning on storage:

(a) Vegetables (Cabbage, potatoes, cauliflower)
(b) Fruits and fruit-juices (Citrus fruits and their juices)
(c) Meat and meat products (Beef, mutton, pork)
(d) Fish and fish products
(e) Eggs
(f) Milk and milk products.
As a result of browning, changes in nutritive value along with deterioration in palatability, loss of colour, odour and flavour have been reported in detail\(^1,2\). For instance in the case of badly deteriorated milk powder the biological value of 85 (for the unstored control) for the young rat had fallen to 65-70 and by supplementing lysine the original value was attained\(^1\). This shows the deficiency in this essential amino-acid that has developed during storage. In most of the cases browning is undesirable; however, in rare instances like caramel production in candies, browning is desirable and is deliberately caused to have the desirable flavour and attractive colour while retaining its suitable consistency or structure\(^2\).

**Types of browning**

(a) **Enzymic browning—Causes and Prevention**

It is enzyme catalysed and occurs mostly in freshly cut fruits and vegetables. It is not as serious as non-enzymic browning. Hence a brief mention of the causes of enzymic browning and its prevention will be sufficient. It is mainly an oxidative process catalysed by enzymes. Examples are the oxidation of catechol-type polyphenols to o-diquinones by polyphenolase, and of ascorbic acid to its dehydro derivative by ascorbic acid oxidase. Enzymic browning has been earlier reviewed\(^3\). The most effective means of prevention of enzymic browning is either by blanching and/or treatment with sulphur-dioxide (sulphiting), whereby enzyme activity is almost completely inhibited. Recently\(^4\) boric acid and its salts have been reported to inhibit enzymic browning.

(b) **Non-enzymic browning—Causes and Theories**

It is the development of brown colour in processed stored foods in which enzyme activity is almost absent. World wide importance to this problem is evident from the earlier reviews\(^5\)–\(^20\) dealing with one or other aspect of non-enzymic browning.

This phenomenon is highly complicated due to many varied factors and conditions and the important factors are given below and current theories of browning (hereafter referring to non-enzymic type) are indicated:

(i) **Maillard reaction (carbonyl-amino reaction)**—It is one of the principal causes of browning. It is essentially a reaction between the reducing sugar and amino acid or protein. Maillard was the first to observe that simple sugars and amino acids react to form brown products. Maillard reaction followed by polymerisation leading to melanoidins (brown pigments) is responsible for this type of browning. The chemistry of Maillard reaction has been studied in much detail\(^16\), and continues to be the subject of recent investigations\(^21\)–\(^23\). Although at one time Maillard reaction was thought to be solely responsible for browning, it is now well-established that there are other equally important causes. The theory of Maillard reaction is as follows:

There are two types of condensations:—

1. Controlled condensation between reducing sugars and amino acids leading to N-substituted glycosylamines and/or occasionally their Amadori rearrangement products.
(2) Typical Maillard reaction of the amino group of amino acids followed by other more complex changes leading to the formation of brown pigments and polymers.

Histidine, threonine, phenylalanine and lysine are the most affected amino acids.

(ii) L-Ascorbic acid—L-ascorbic acid has been reported to be responsible for browning in foods. The theory is that ascorbic acid and related compounds are oxidised yielding 'active' compounds which either polymerise or react with amino acids to yield brown products. This theory is mostly valid for fruits and fruit juices.

(iii) Furfural and furfural derivatives—The breakdown of pentoses and hexoses lead to furfural and 5-hydroxymethyl furfural which either polymerise or condense with amino acids and then polymerise forming brown products. The presence of these active aldehydes have been reported to lead to browning.

(iv) Carbohydrates and non-nitrogenous acids—Based on the studies on apricots Bedford was the first to disprove the classical Maillard reaction theory for browning. Haas and Stadtman confirmed the above findings by using ion-exchange resins for the separation of basic, acidic and neutral fractions of apricot extracts. The following reactions were reported to lead to browning:

1. Reaction between nitrogenous constituents and sugars.
2. Reaction between nitrogenous constituents and organic acids.
3. Reaction between sugars and organic acids.
4. Reaction involving organic acids only.

Other workers have also supported the above findings.

(v) Proteins and protein hydrolysates—The reactions of proteins, protein derivatives and model substances with glucose solutions have been studied in detail and are reported to lead to browning depending upon temperature and pH. Studies on Bovine serum albumin, dried human plasma and vitamin test casein have been made. The above investigations point out that proteins and protein hydrolysates cause browning.

(vi) Polyphenols—A novel type of browning through the condensation of polyphenols and amino acids resulting in hydroxy-indoles, which are potential precursors in browning, has been reported. This is of interest since 5:6-dihydroxy-2-indole carboxylic acid is known to be an intermediate in melanin formation.

(vii) Metals and metal complexes—Barnes and Kaufmann first reported that traces of copper materially accelerate the rate of browning. Copper-protein complexes are reported to promote browning.

(viii) Radiations—Ionising radiations have been reported to induce and accelerate browning in foods.
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(ix) Miscellaneous—The following chemicals are reported to cause and/or accelerate browning in foods:

(a) 2:4-Dichlorophenoxyacetic acid
(b) Chlorogenic acid
(c) β-carotene
(d) Urea
(e) B-Vitamins
(f) Di- and tri-ketones
(g) Fertilisers
(h) Aldehydes from oxidation of fish oil
(i) Unsaturated acids.

In addition, kinetic and thermal energy are also causative in browning.

Methods for the study of browning

For identifying some of the reaction products and for estimating their speeds of formation the following methods are used (see Ellis for collective references):

(i) Chromatography
(ii) Spectroscopy (ultraviolet and infrared)
(iii) Potentiometric titration
(iv) Colorimetric methods
(v) Cryoscopy
(vi) Polarography
(vii) Radioactive tracer technique
(viii) Estimation of water formed
(ix) Hydrolysis with pancreatin followed by determination of amino acids by ninhydrin.

The last method is reported to be a very satisfactory one.

Conditions favourable to browning

Maillard reaction is known to be enhanced with increase in temperature and pH. Studies of browning in vegetables, wheat germ, meat and fruit juices confirm the above finding. Moisture content and relative humidity affect browning considerably. Even though oxygen is not indispensable for Maillard reaction, it plays a considerable part in browning in natural systems. Sugar phosphates, copper salts, ionising radiations and kinetic and thermal energy accelerate browning.

Conditions unfavourable to browning

Browning due to Maillard reaction is minimised either in the absence of moisture or by the use of very dilute solutions. Low pH and low temperature are reported to reduce browning. L-lysine and the pentoses are reported to be the most chromogenic in browning reactions. The removal of free reducing sugar either by continuous leaching with water or by enzymic method is reported to minimise browning. Live cells
of *Lactobacillus pentaaceticum*, with D-ribose oxidase activity, are known to inhibit browning in fish. Glucose oxidase has been used to counteract the browning of eggs during drying. Another method uses a simple amino acid which preferentially reacts with the reducing sugars forming colourless and more soluble melanoids than those formed from proteins present in dried eggs. By this method the nutritive value of the eggs is not affected. Amino acids except cysteine maintain the solubility of the dried egg powder but accelerate the development of fluorescence and colour. Cysteine not only retards the development of fluorescence and colour but also maintains the solubility of the powder. An unusual method is the continuous extraction of apricots with ethyl acetate and as long as the extraction continues there is no browning.

**Inhibitors of browning**

By the addition of certain chemicals browning is known to be inhibited. The most widely used is sulphur-dioxide which acts as an antioxidant in the preservation of vitamin-C and inhibits browning. Best results were obtained if sulphur-dioxide is applied as a dry spray and if at the same time moisture content was lowered to 4 per cent. The use of a salt solution, L-ascorbic acid and a sulphiting agent has been patented, and it is described to be a better method than using sulphite alone because of better flavour in the resultant product.

The following chemicals are known to inhibit browning:

(i) Formic acid
(ii) Urea
(iii) Thiourea
(iv) Benzoaldehyde
(v) Formaldehyde
(vi) Hydroxylamine
(vii) Hydrazine
(viii) Semicarbazide
(ix) Sodium borohydride
(x) Sodium metabisulphite
(xi) Sodium sulphite
(xii) Sodium dithionite (sodium hydrosulphite).

A combination of sulphite and calcium chloride has been reported to be most effective than either compound in retarding browning. No explanation could be given to the effect of calcium chloride; but it causes a small depression in the pH value of the substrate and may block free amino groups. The dehydrating action of calcium chloride may also have an effect in taking up traces of moisture, which may persist after drying.

The mechanism by which sulphurous acid inhibits browning is not yet completely understood. The facile combination of sulphur-dioxide with active aldehydes (e.g. furfural) may be significant in this connection. The sulphite content markedly decreases with time and this has been attributed to reversible binding.
Browning in different categories of processed foods—Causes, prevention and storage

To inhibit browning in different processed foods the methods of preservation are given below:

In general, low moisture content, pH, temperature and relative humidity, packing in inert atmospheres like carbon dioxide or nitrogen and addition of inhibitors (mostly sulphiting agents) considerably minimise browning.

(a) Vegetables—

The vegetables are usually preserved through one of the following methods:

(i) Canning (tin and glass containers)

(ii) Freezing (storage at $-17.8^\circ C$)

(iii) Dehydration and

(iv) Pickling.

Of these methods dehydration affords the best storage stability. The preservation of dehydrated vegetables in general and potatoes in particular is of potential interest to military requirements.

Vegetables contain significant amount of free amino acids, simple sugars (glucose, fructose) and polysaccharides as also ascorbic acid and hydroxy acids which are potential causative agents for browning. Good keeping properties in dried vegetables are attained by selecting the material with low moisture content, low reducing sugar content, and gas packing in nitrogen or carbon-dioxide to minimise destruction of carotenoids and ascorbic acid. According to one method a small bag of quicklime is kept inside the container of vegetables, to achieve and maintain a very low humidity. Sodium bisulphite is added before drying thereby increasing resistance to browning. The addition of 0.25% sulphur-dioxide at the moment of canning greatly reduces the browning in pickled pasteurised cabbage. Storage of potatoes in a small soundly constructed unheated brick building protected from draughts and with restricted ventilation leads to the development of less reducing sugar content and to less browning compared to potatoes stored in field clamps. The use of sodium metabisulphite of concentration 0.5 to 1.0% (W/V) at pH 5.3-6.0 was found to be most effective in retarding browning of potatoes.

For the storage of peeled potatoes the following methods are recommended:

(i) Scalding by water or high radio frequency method; Infrared heating is less satisfactory.

(ii) Scalding or irradiating after packing. This reduces bacterial spoilage.

(b) Fruits and fruit juices—

In general sulphur treatment (exposure to burnt sulphur fumes) or dipping in sulphite solutions of fruits before drying followed by removal of water in the tissues with dry hot air is adopted. This treatment not only minimises browning but also protects the nature of fruit flavours. Five basic treatments in the prevention of browning in apples is as follows:

(i) Treatment with sulphur-dioxide or sulphurous acid

(ii) Vacuumising in salt solution
(iii) Blanching in sucrose and dextrose solutions
(iv) Vacuumising in ascorbic acid syrup solution
(v) Blanching in steam.

As in the case of vegetables, fruits are generally preserved through canning, freezing or dehydration; they are also converted to jams, jellies and marmalades. Fruit juices are generally preserved by canning, freezing, dehydration and the incorporation of chemical additives like sodium benzoate and sorbic acid. In a recent International Symposium on ‘Fruit Juice’ concentrates at Bristol the browning of glucose syrups were reported to be a minimum at pH 3.0 and depended on the amount of protein present156. Rapid formation of 5-hydroxy-methyl furfural occurs at pH 1.0. In citrus concentrates sulphur-dioxide is reported to strongly inhibit browning. The role of ascorbic acid in browning in fruit concentrates has been discussed154. A recent review97 considers many factors to be responsible for browning in commercial glucose syrups. The preservation of fruits and vegetables had been given in detail102.

Meat and meat products

Canning, dehydration, freezing and curing are some of the common methods of preservation of meat and meat products. The onset of browning in meats has been shown to be due to Maillard reaction98,100. Browning in meats was found to be independent of oxygen concentration but was retarded by low moisture content99. The non-oxidative deterioration due to Maillard reaction in freeze-dried beef has been studied and possible methods of increased storage are given100. Browning in meat has been shown to be minimised when it is stored at 50°C in nitrogen containing 500 parts per million sulphur-dioxide and glucose is removed by fermentation or treatment with glucose oxidase101. The use of yeast fermentation to remove reducing sugars has been reported to slow down browning in dehydrated cooked pork mince during storage in air101a.

Fish and fish products

Salting, curing, canning, semidrying and freezing are the common methods of fish preservation.

The browning in fish has been shown to be by Maillard reaction103. The need for eliminating as much moisture as possible to avoid brown colouration has been stressed by Stansbury but not by Cutting and Reay104b. The latter investigators emphasised the need for nitrogen packing to reduce fat oxidations. Recently the investigation carried out in Japan104 on dehydrated fish show that browning in marine products is closely related to the aldehydes derived from fish oil.

According to Stansbury Maillard reaction in dehydrated fish could cause a significant decrease in nutritive value by decreasing availability of essential amino acids. However, feeding trials with certain dehydrated fish preparations indicated no loss in nutritive value or in digestibility though 50% of the thiamine and 65% of the riboflavin were destroyed. The danger of growth of moulds, yeasts and bacteria in dehydrated fish stored at rather high relative humidities has been pointed out105.
Eggs and egg products

On storage dried whole egg develops an unpleasant flavour, a brownish colour, insolubility, fluorescence and loss of aerating power. Chemically free amino acid content falls along with reduction in pH and reduction in the small amount of glucose present. General conditions for rapid deterioration show a marked resemblance to those required by Maillard reaction. On closer examination it has been found that the changes in egg white is a typical Maillard reaction between glucose and cephalin.

Changes in egg white are attributed to autooxidation of the unsaturated fatty acids of the egg lipids.

Milk and milk products

Maillard reaction has been observed to be responsible for browning in milk. Combination of protein with lactose even below 80°C resulted in the formation of humine-like substances without apparent browning and at higher temperatures of 90°C-100°C, the thermal decomposition of proteins leads to acidity followed by marked increase in the number of basic amino groups, which combine with lactose resulting in browning. Not all the browning reactions in a typical sample of commercial evaporated milk is attributable to Maillard reaction; part of the browning may be due to carotenoids naturally present in raw pigments and partly to an increased solids content. Recently Japanese workers have studied the composition and qualities of market milk caramels the effect of aeration on some properties of stored milk caramels and have evolved a colorimetric method of determination of Maillard reaction products. The sensitivity of milk to browning has been reported to be increased by ionising radiations and prior removal of carbonyl compounds are reported to prevent such browning. Pasteurising, drying and skimming milk are some of the usual methods of preservation of milk and milk products.

The study of the phenomenon of browning in general and particularly in fish, eggs and milk and their respective products is yet in its infancy and more investigations are necessary to understand further the causes of browning and to evolve methods of prevention thereof.

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