

MAILLARD BROWNING

Heat induced changes in dairy products involve lactose associated with browning.

Lactose may isomerize or react with protein in milk.

Reducing sugar, lactose condenses with the caseins and whey proteins of milk systems is the Maillard or non-enzymatic browning reaction (glycosylation of proteins entailing covalent addition of sugar moieties to specific amino acids).

Interaction between a carbonyl of lactose and an amino group (in foods, principally the ϵ -NH₂ group of lysine in proteins) to form a glycosamine (lactosamine) which subsequently undergo an Amadori rearrangement to form a 1-amino-2-keto sugar (Amadori compound).

EARLY STAGE REACTION

REACTANTS : PROTEIN AND REDUCING SUGARS

Nitrogen atom of an amino compound and carbonyl group of an aldehyde or ketone in food systems.

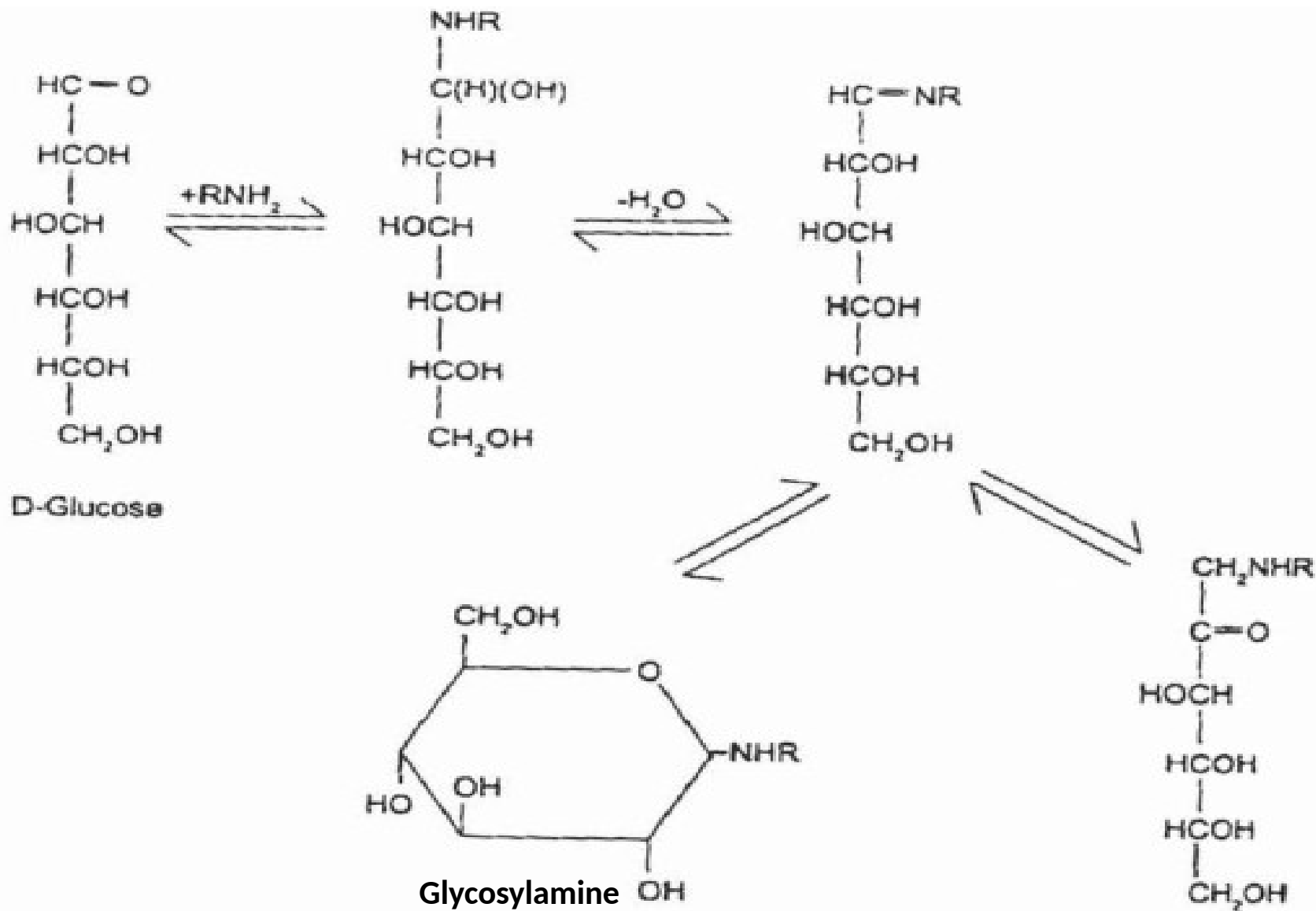
Elimination of a molecule of water to form a Schiff's base



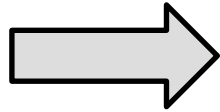
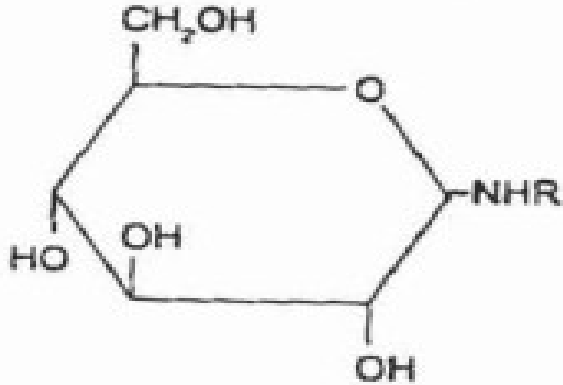
Form an unstable condensation N-substituted glycosylamine intermediate

(This intermediate either hydrolyzed to the parent amino acid and reducing sugar or react via a spontaneous rearrangement to form the corresponding keto- (α -1-amino-1-deoxy-2-ketose) or aldo (α -2-amino-2-deoxyaldose) derivative depending on whether the parent sugar is an aldose or a ketose respectively (Amadori rearrangement).

SUGAR-AMINE CONDENSATION



AMADORI REARRANGEMENT



**1-amino 2-keto sugar
(Amadori compound)**

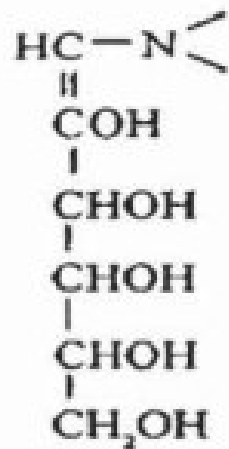
Formation of uncoloured amadori compound (1-amino-2-keto sugar) from glycosylamine with loss of nutritive value and no observable colour or flavour changes.

The Amadori compound may be degraded via either of two pathways, depending on pH, to a variety of active alcohol, carbonyl and dicarbonyl compounds. Dehydration of the Amadori compound by the loss of water molecules to form furfurals (at low pH) and reductones (at high pH).

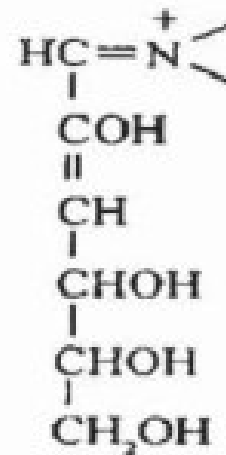
The final stage consists of the conversion of furfurals, fission products, reductones and strecker aldehydes into melanoidins pigments with further involvement of amines.



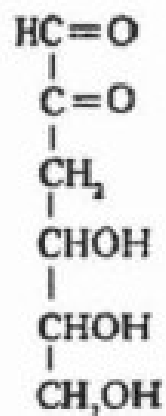
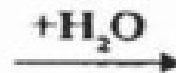
Amadori product



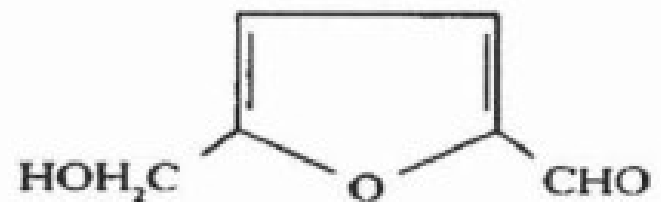
1,2-Eneaminol



2,3-Enol

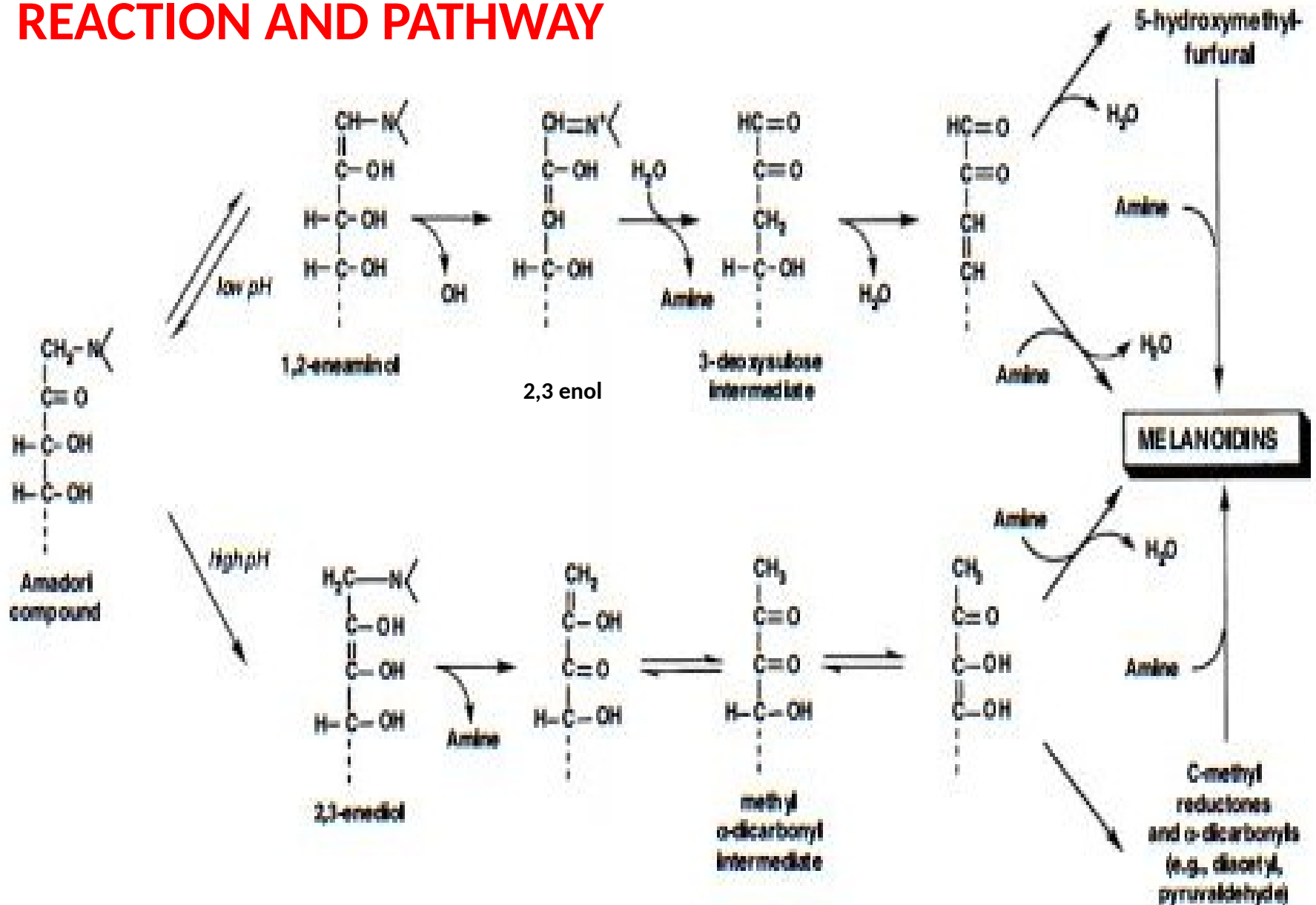


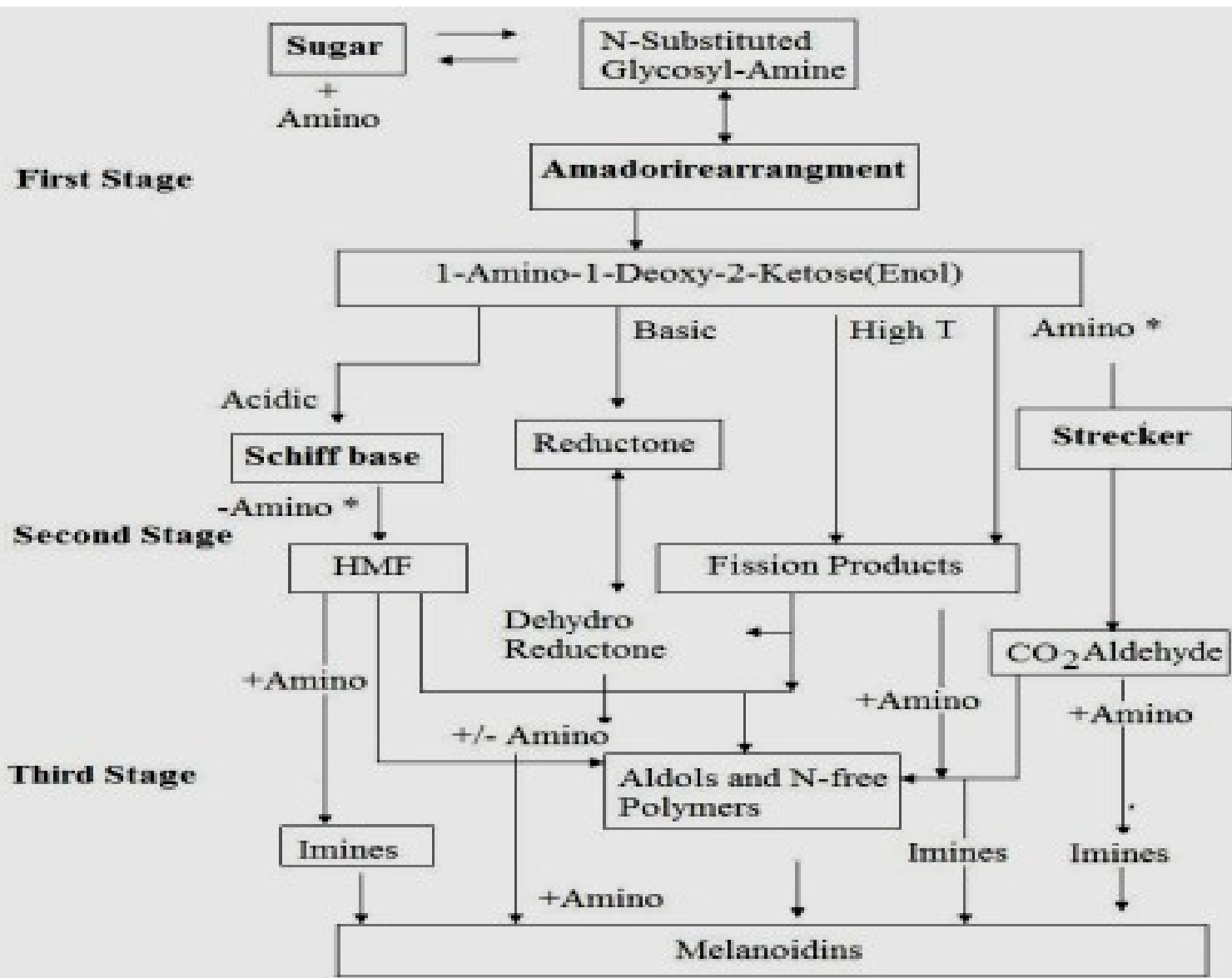
3-Deoxyhexosulose



5-Hydroxymethyl-2-furaldehyde

REACTION AND PATHWAY





MALLAIRD BROWNING PATHWAY

EFFECTS OF MAILLARD BROWNING

Lactose and casein are the two principal reactants in the browning of milk products.

The Maillard-type browning require relatively low energy of activation and direct caramelization has a rather high energy of activation.

Roller-dried products showed significant losses in lysine content, due to the contact with the drums with high temperatures.

The protein-carbohydrate complex or its decomposition products result in the production of reducing substances, fluorescent substances and disagreeable flavour materials.

SIGNIFICANCE OF MAILLARD BROWNING

Desirable consequences in many foods e.g., coffee, bread crust, toast, french fried potato products.

Consequences in milk products are negative (brown colour, off-flavours, slight loss of nutritive value (lysine), loss of solubility in milk powders). The final polymerization products (melanoidins) are brown and hence dairy products which have undergone Maillard browning are discoloured and aesthetically unacceptable.

Detrimental to the organoleptic, nutritional and functional qualities of the product. Some of the by-products of Maillard browning have strong flavours (furfural, hydroxymethylfurfural) which alter the typical flavour of milk.

Favorable for the preparation of products like khoa where milk is heated in the presence of sucrose to produce brown product with a pleasant flavour.

Generates flavour during the manufacture of ghee or clarified butter and milk chocolate.

FACTORS AFFECTING MAILLARD BROWNING

Reactants: Low molecular wt. reactants tend to react more readily than high molecular weight reactants. Glucose is more reactive than lactose and contribute to the increased rate of browning in lactose hydrolyzed milks. Cheese containing a high level of residual lactose or galactose (inability of a starter to utilize galactose), it is susceptible to Maillard browning, especially during cooking e.g., Mozzarella cheese on pizza.

pH: Maillard reaction increases with increasing pH, maximum up to 9-10 depending upon the type of amino acids involved. The browning of pure Amadori product is also accelerated at alkaline pH values.

Moisture content and a_w : Water may influence the rate of reaction by controlling the viscosity of the liquid phase and by dissolution concentration or dilution of reactants. Browning may also occur in grated cheese during storage if the cheese contains residual sugars; the water activity of the cheese ($a_w \sim 0.6$) is favourable for the Maillard reaction

Phosphate and citrate buffers accelerate the Maillard reaction up to 15 fold.

CARAMELIZATION

Non-amino or non-enzymatic browning reaction. Limited significance in milk and milk products.

This process consists of heating sugar (removal of water) slowly at high temperatures (pyrolysis) to around 170 C, the molecules break down and reform into compounds with a characteristic brown colour and flavour.

During baking, caramelization contributes to nutty flavour and colour. During the process, volatile chemicals such as diacetyl are released, producing the characteristic caramel flavour.

Caramel colouring is a dark, bitter-tasting liquid used in food colouring and beverages.

Three main components of caramel called caramelan, caramelen and caramelin prepared from sucrose:

- Caramelan is brown brittle, deliquescent solid having a bitter taste, melts between 136 C-144 C and it is readily water soluble.**
- Caramelen is a brown substance much darker than caramelan and melts at 153.5-154 C.**
- Caramelin (much darker) exists in three modifications namely, soluble in cold water, soluble only in boiling water and insoluble in all ordinary solvents.**