

Quadrant – I

Milk Cookery

Objectives:

- explain the various changes which take place in milk on heating
- apply this information while making preparations from milk
- identify the different methods by which curdling of milk takes place
- apply this information while handling milk

INTRODUCTION

Changes that take place in milk on cooking can be broadly classed in two categories as per type of agent and chemical affected

Effect of heat on the milk proteins and fats.

Effect of various agents on milk proteins(coagulation of milk)

Effect of heat on milk

The physical and chemical properties of the constituents of milk decide the behavior of milk during its use in food preparation. Proteins of milk which lowers the surface tension of milk gets accumulated on the surface of milk and makes a liquid/air interface, when milk is heated in an open pan a scum or skin forms over the surface of the milk due to this liquid/air interface . At first this skin is rather thin and mobile but is gradually altered so that it becomes tenacious and tough enough to be removed with a stirring rod or spoon. This scum is a combination of coagulated albumin and globulin in which fat particles gets entangled to make it tough and tenacious.

When foods are cooked in milk the milk not only foams readily but the scum tends to hold the steam formed in heating the milk; the pressure of steam pushes the scum and causes milk to boil over.

Heating milk with added substances

Different added substances exhibit different changes in milk.

Heating milk with sugars-On heating the added sugars react with proteins. Protein of milk and sugar combines to form a protein-sugar complex of glucosidal nature. This protein sugar complex is a condensation of an amino acid with an aldehyde or ketone group of the sugar. When dextrose, lactose, or fructose is heated with skim milk or freshly precipitated casein, a dark brown color is formed in the product. As the temperature rises the dextrose and casein becomes firmly attached to each other and no amount of washing can remove the sugar. Most of the biruet action of the skim milk is lost. It has been found that as the reaction becomes more alkaline the appearance of the brown color is more rapid. The length of heating in connection with the temperature is important as relatively high temperatures for a short period gave only slight development of the brown color. It is almost impossible to retain the natural color of fresh milk in the condensed milk products, for some brown discoloration occurs in the unsweetened and sweetened product whether made from whole or skim milk.

Heating of milk for a sufficient time at high enough temperatures decomposes the lactose, decomposition of lactose forms acid products, and rises its acidity. That's why when milk is heated with sucrose the increasing acidity inverts some of the sucrose to dextrose and laevulose, with the development of a brownish color. One example of this is in the cooking of caramels, more brown color developing with long slow cooking of the sucrose and milk. Another instance where this is used to advantage is in making caramel pudding by boiling, in the can, sweetened condensed milk for three hours or longer. The can and contents are chilled. On opening the can it is found that the contents have developed the brown color of caramelized products and are thickened to the consistency of a pudding.

Heating milk with vegetables and fruits- The slight acidity of some vegetables combined with the heating of the milk may tend to bring about coagulation of milk. Besides this the salt and the tannin contents of the vegetables are probably the principal causes of coagulation. Some vegetables contain larger amounts of tannin than others. Tannin is a dehydrating agent and brings about denaturation of hydrophilic milk proteins, after denaturation the hydrophilic is sensitive to small amounts of electrolytes and precipitation occurs readily. Tannins are unable to bring about dehydration of the

protein in an alkaline medium; therefore the addition of soda in small amounts to the milk in which the vegetable is cooked prevents coagulation of the milk.

Highly acidic vegetables like tomatoes are when combined with milk to make cream of tomato soup, coagulation may occur. The acidity of tomatoes varies somewhat, but is about pH 4.4 to 4.6. If the amount of tomato added to the milk is great enough to lower the pH of the mixed milk and tomato to 4.8 to 4.6, the casein is precipitated without heating.

Heating fruits and milk- When milk or cream is added to fruit, clotting often occurs. This is usually due to the acidity of the fruit, some fruit enzymes are also responsible for hydrolysis of lactose and a resultant acid production which causes milk to curdle.

Effect of heat on Reaction Of Milk

The pH of freshly secreted milk is 6.6 that are it is nearly neutral to litmus. The freshly secreted milk contains carbon dioxide. The amount of this gas in the milk decreases during milking and the subsequent handling of the milk, while the percentage of oxygen and nitrogen increase. For this reason the Titratable acidity decreases for a time in milk exposed to the air, that is oxygen and nitrogen of air gets entered in the milk and carbon-di-oxide gets out in external environment.. Confined milk does not show as great a decrease in Titratable acidity as the exposed milk, for the percentage of carbon dioxide lost is smaller. When milk is heated at the boiling point or at temperatures above or near the boiling point the Titratable acidity at first decreases owing to the loss of carbon dioxide, and then increases due to breakdown of lactose. The hydrogen-ion increase and the later increase in Titratable acidity is due to the formation of acids from constituents of the milk. The amount of acid produced depends upon the time and temperature of heating, a greater amount of acid being produced with a longer heating period and with higher temperatures.

Effect of heat on Maillard reaction on milk proteins

No enzymatic glycation of amino group and carbonyl group of an amino acid and a carbohydrate is Maillard reaction. It is the extremely complex reaction that usually takes place during food processing or storage. In the case of milk, lactose reacts with the free amino acid side chains of milk proteins

(mainly ϵ -amino group of lysine residue). This reaction is performed in early, intermediate, and advanced stages and forms enormous kinds of Maillard reaction products. This reaction results in the formation of browning compounds (melanoidins).

The Maillard reaction shows various effects on milk proteins such as bioavailability, solubility, forming property, emulsifying property, and heating stability. In addition, the formation of flavor compounds and browning compounds is caused as the consequences of the Maillard reaction between lactose and milk proteins.

As for the effect of the Maillard reaction on the bioavailability of milk proteins, various studies were performed. Generally, in the Maillard reaction in milk, lactose mainly reacts with ϵ -amino group of lysine residue of milk proteins. Thus, the lysine loss by the Maillard reaction increases with a severity of heat treatment. The modified lysine cannot be available as a nutrient any more.

Coagulation Of Milk

Protein in milk is in dispersed or colloidal form. Any condition which disrupts colloidal state of milk proteins is responsible for curdling or coagulation of milk. The slightly basic pH of milk supports this colloidal status, when this pH becomes acidic due to any reason milk protein casein which is present as calcium caseinate in milk gets denatured resultantly colloid state of milk gets disrupted and a semisolid is formed, which is known as curd and the process is known as curdling of milk.

The coagulation of milk can be carried out by following agents or conditions

by inducing acidity to milk

by application of heat

Acids and milk

Curdling of milk can occur by any agent which changes pH of milk may be acid or enzyme. Acetic acid, citric acid or any other acid can bring forth such a change, similarly enzymes from micro-organisms (accidentally or incidentally incorporated) or purposely added can cause such a change. The chief agents employed for creation of acidity in milk are

rennet

acids

Rennet coagulation

Milk may be coagulated by the addition of rennet. Rennet is an extract that is usually obtained from the inner lining of the stomachs of calves and lambs. The rennet contains an enzyme called rennase or rennin.

Mechanism of rennin clotting- The clotting of milk by rennet is brought about in two steps, the first being the action of rennin on the casein and the second the precipitation of the changed casein. Rennin reduces the charge of the calcium caseinate micelle and thus reduces the stability of the casein sol. and precipitates it from milk in this precipitate most of the fat and high molecular weight particles are entangled resultantly a separated mass is obtained.

Factors affecting action of rennin- Several factors influence the activity of the rennin in bringing about coagulation. These may be listed as follows:

- temperature for rennin action

- heating the milk before the addition of rennin

- hydrogen-ion concentration

- concentration of casein, calcium, and phosphate ion

Temperature for rennin action- The optimum coagulation by calf rennin is about 40° to 42°C. Below this temperature coagulation is less rapid and no clotting occurs below 10° to 15°C. Also no clotting occurs above 60° to 65°C. The clot is softer at low temperatures and tougher and stringy at high temperatures. By optimum is meant the temperature at which coagulation takes place most rapidly for a definite concentration of rennin and milk.

Effect of previously boiling the milk upon rennin coagulation- If milk is boiled and then cooled before the rennin is added, the rate of coagulation is retarded and a much softer, more flocculent clot is obtained. Pasteurization also affects the rate of coagulation of the milk and the type of clot formed by rennin but not to the extent that boiling does.

Heat increases the electric charge on the casein micelles or the cataphoretic velocity of the casein solution. The fact that rennin does not form as firm a clot with milk that has been previously heated indicates that rennin reduces the charge on the casein particles but not sufficiently to form a firm clot.

This offers a colloidal explanation of why the addition of active cations (as calcium chloride) to heated milk causes the rennin to coagulate the milk normally.

Hydrogen-ion concentration- The reaction of the milk affects the rapidity of coagulation and the character of the curd formed. Ordinarily when the reaction of the milk is alkaline coagulation does not occur. This is shown by the addition of a small amount of soda to milk before the addition of junket. The optimum hydrogen-ion concentration for rennin activity has been reported to lie in the zone between pH 5.99 and 6.40.

Concentration of casein, calcium, and phosphate ion - In addition to rennin, cations are necessary to bring about coagulation of milk. Because casein and calcium are so closely involved in milk, the cation calcium is important in bringing about coagulation. Hence, it is to be expected that the concentration of both casein and calcium markedly affect both the rate of coagulation and the character of the clot. If milk is diluted with sufficient water, clotting is both delayed and incomplete, the clot being soft. If calcium chloride is added to the water, diluted milk clotting properties are restored, which suggests that the concentration of calcium ions is more important than that of the casein ions.

Acid Coagulation

Casein can exist either in acid or in an alkaline solution, but does not dissolve in water, with the consequence that the sol ordinarily flocculates when neutralized. Either the acid produced during fermentation or acids added to milk precipitate the casein. The casein is least soluble at its isoelectric point pH 4.6. If enough acid is added to lower the pH below 4.6, casein salts, such as casein chloride or casein lactate, are formed. If these salts are soluble, the casein goes into solution. Hence the largest yield of precipitated casein is near the isoelectric point. Acid in milk can be produced by

Micro-organisms

Added acids

Milk coagulation by micro-organisms- Fermentation, or the production of lactic acid from lactose by bacteria, takes place in milk that is allowed to stand under favorable conditions. True lactic acid fermentation is brought about by the *Streptococcus lactis* and certain other organisms, lactic acid being the principal end-product, other products being present in only small amounts. In mixed lactic

acid fermentation, or when other organisms in addition to *S. lactis* are present, the end-products may include acetic, propionic, lactic, succinic, formic, and butyric acids, carbon dioxide, hydrogen, acetone, and ethanol. As fermentation increases, acidity is reached at which the action of most bacteria is suppressed. When fermentation is checked at pH 4.8 to 5.0, the bacteria consists chiefly of *Streptococcus lactis*.

Factors affecting rate of fermentation-The rate of fermentation depends chiefly upon the temperature at which the milk is held. At low temperatures, on account of retardation of bacterial action, it takes place slowly. Fermented milk, allowed to stand at a fairly high temperature, undergoes a second lactic acid fermentation brought about by the *Lactobacillus bulgaricus* organisms. Some of these types of bacteria form a high percentage of acid and the hydrogen-ion concentration may reach pH 3.23.

Changes occurring during acid precipitation- During fermentation chemical and physical changes occur in the milk. The flavor becomes acid. The calcium caseinate is changed to casein. During this process calcium is split off and forms soluble calcium lactate. In addition some dicalcium phosphate is converted into monocalcium phosphate. Curdling or clotting occurs when the acidity reaches about pH 5.3. During the clotting process the hydrogen-ion concentration does not increase. Milk clotted by fermentation is often called clabbered milk. Its flavor and aroma may vary, depending upon the types of bacteria producing the fermentation.

Addition of acids to milk- when any acid is added to boiling milk it gets coagulated. Cheese, such as cottage cheese, when clotted by acid coagulation, loses a large proportion of its calcium. The calcium salts become soluble more rapidly than the phosphorus; hence a larger proportion of the calcium than of the phosphorus is lost in the whey. Casein precipitated by rennin retains most of its insoluble salts, hence has a larger proportion of calcium than the acid precipitated casein.

Heat Coagulation

The term heat coagulation refers to the so-called "denaturation" of the protein, by which it is rendered insoluble.

Lactalbumin- The lactalbumin of milk forms a flocculent precipitate when heated for 30 minutes.

Casein- Casein is not coagulated by heat at ordinary temperatures or when heated for short periods,

though the heating may alter the casein. It is necessary to heat milk about 12 hours at 100°C. To bring about coagulation. It takes approximately 1 hour at 135°C. And approximately 3 minutes at 155°C. The time and temperature vary somewhat with different milks.

The rate of coagulation depends upon the concentration of the casein as well as the time and the temperature of heating.

Fat- Fat particles aggregate on heating which acts as nuclei about which coagulation of the casein can proceed. In un-homogenized milk the fat affects the coagulation time and temperature but slightly. But when a milk of higher fat content is homogenized the fat clumps may act as nuclei about which the casein may gather during heating. With increase in homogenization pressure as well as fat content, other conditions being the same, a marked decrease in stability to heat is noted. In homogenized milk the maximum stability to heat coagulation occurs if homogenization is carried out at 80°.

The role of salts in heat coagulation of milk- In heat coagulation of milk, the milk salts play an important role, for the salt equilibrium is altered by heat. When milk is boiled precipitation of part of the calcium phosphate occurs. Salts are the main factor in heat coagulation of fresh milk. Electrolytes have a marked effect upon the stability of colloids. In precipitating a hydrophilic colloid divalent and trivalent ions are generally more effective than monovalent ones. In the milk are found the monovalent cations, sodium and potassium; the monovalent anion, chlorine; the divalent cations, calcium and magnesium; and the trivalent anions, phosphate and citrate. The coagulation of milk on heating may be due to an excess or a deficiency of calcium and magnesium. They explain this as follows. "The casein of the milk is most stable with regard to heat when it is in combination with the calcium. If the calcium combined with the casein is above or below this optimum, the casein is not in its most stable condition. The calcium of the milk distributes itself between the casein, citrates, and phosphates chiefly. If the milk is high in citrate and phosphate content, more calcium is necessary in order that the casein may retain its optimum calcium content after competing with the citrates and phosphates. If the milk is high in calcium there may not be sufficient citrates and phosphates to compete with the casein to lower its calcium content to the optimum. In such cases the addition of citrates or phosphates makes the casein more stable by reducing its calcium content. The magnesium functions by replacing the calcium in the citrates and phosphates.