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Paper Title: TECHNOLOGY OF MILK AND MILK PRODUCTS

Module – 32: Technology of dairy byproducts-1: Caseinates

INTRODUCTION

With a content of 0.7 - 0.9% phosphorus, covalently bound to the casein by a serine ester linkage, casein as a phospho-protein is a member of a relatively rare class of proteins. Moreover, due to high proportions of essential amino acids, casein is nutritionally excellent protein. Its protein efficiency ratio reported is 2.5, which is mostly unaffected by the processing conditions usually employed during the dairy operations. Casein has some rather unique properties and cannot be replaced by other proteins in certain food application. Edible casein and caseinates are long established dairy by-products finding use in many dairy and food products.

Acid casein is insoluble in water. Its soluble form caseinates may be prepared from freshly precipitated acid casein curd or from dry acid casein by reaction with dilute solution of alkali (such as sodium, potassium, calcium or ammonium hydroxide). Sodium caseinate is the most commonly used water-soluble form of casein and is used in the food industry. The two main reasons for using sodium caseinate as an ingredient in foods are its functional properties and nutritive value. Sodium caseinate is valued for its ability to emulsify fat in the production of modified dairy products such as coffee whiteners, whipped cream and ice cream. It also possesses very good water binding and whipping properties. Industries of meat processing, baking and modified dairy products are the largest consumer of sodium caseinate. The various food products in which sodium caseinate is used consist of various kinds of sausages, meat-based and milk-based instant breakfasts, modified milk, whipped cream, coffee whiteners, non-dairy creams, desserts, sauces, soups, bread, doughs, crackers (biscuits), dietetic products and various protein-enriched products. Other casein products, used in a descending order in the food industry are calcium caseinate, potassium caseinate, other caseinates, and, finally, pure casein.

Other soluble forms of casein are produced using phosphates, carbonates, and other salts as the solubilizers. Magnesium caseinate is prepared from casein and a magnesium base or basic salt such as magnesium oxide, magnesium hydroxide, carbonate or phosphate or by ion exchange. Compounds of casein with aluminium may be prepared for medicinal use or for use as an emulsifier in meat products. Heavy metal derivatives of casein, which have been used principally for therapeutic purposes, include those containing silver, mercury, iron and bismuth. Iron and copper caseinates have also been prepared by ion exchange for use in infant and dietetic products.

MANUFACTURING PROCESS

For the manufacturing of caseinates, fresh acid casein curd is preferred over dried casein as a raw material, since the former yields caseinates with blander flavour than does the latter. Caseinates prepared from dry casein will also incur the additional manufacturing costs associated with drying, dry processing, bagging and storage of casein prior to its conversion to sodium caseinate. However, in countries, which import casein, buyers may still prefer to purchase casein and produce their own sodium caseinate rather than purchase sodium caseinate. Casein should have low calcium content (< 0.15% dry basis) in order to produce a caseinate solution with a low viscosity, and a low lactose content (< 0.2% on dry matter basis) to produce sodium caseinate with the best colour, flavour and nutritional value.

Sodium Caseinate

Irrespective of the starting material used, the main difficulties experienced in the conversion of acid casein to the manufacture of sodium caseinate consists of formation of a casein suspension, solubilization of casein using sodium hydroxide, and drying of the sodium caseinate produced.

Problems in drying sodium caseinate are: (a) very high viscosity of sodium caseinate solutions of moderate concentration, which limits the solids content for spray drying to 20% (b) the formation of a relatively impervious, jelly like viscous coating on the surface of casein particles which impedes their dissolution on addition of alkali.

To overcome the former difficulty, it is essential that the pH and temperature are controlled during conversion as these influence viscosity, while the latter can be overcome by reducing the particle size by passing a curd-water mixture through a colloid mill prior to addition of alkali.

After the final casein wash, the curd may be dewatered to about 45% solids and then remixed with water (to 25 to 30% total solids) before entering the colloid mill. The temperature of the emerging slurry should be below 45°C, since it has been observed that milled curd can re-agglomerate at higher temperatures.

Addition of alkali: The most commonly used alkali in the production of sodium caseinate is sodium hydroxide, with strength of 2.5 M or 10%. The quantity of NaOH required is generally 1.7-2.2% by weight of casein solids in order to reach a final pH, generally about 6.7.

Other alkalis, such as sodium bicarbonate, or sodium phosphates, may be used, but the amounts required and their cost both are greater than those of NaOH. They are therefore, generally used only for specific purposes, such as that in the manufacture of citrated caseinates.

The dissolving time of the alkali is directly related to the particle size of curd and the particle size reduction prior to addition of sodium hydroxide rather than afterwards produces a more rapid reaction. Consequently, the curd is passed through a colloid mill prior to addition of the alkali.

Generally the slurry is collected in a jacketed tank provided with an effective agitator and also integrated in a circular system with a high capacity pump. The addition of diluted alkali must be carefully controlled with the aim of reaching a final pH of about 6.7. Preferably, the alkali is dosed into the recirculation line just upstream of the pump. Once the alkali has been added to the slurry, it is important to raise the temperature as quickly as possible to 60–75°C to reduce the viscosity.

Dissolving: The viscosity of sodium caseinate solution is a logarithmic function of the total solids concentration. Hence, each dissolving vat must be equipped with a powerful agitator and a high speed circulatory pump. Other important factors which affects viscosity of sodium caseinate are temperature, pH, calcium content of curd, type of alkali used and seasonal and genetic factors.

Care should be taken to avoid holding the hot (> 70°C) concentrated sodium caseinate solution for extended periods prior to drying, since it is possible for brown colour to develop in the solution due to reaction between the protein and residual lactose. During the dissolving operation, the incorporation of air should be kept to a minimum since caseinate solutions form very stable foams.

Drying: The homogenous sodium caseinate solution is usually spray dried in a stream of hot air. For efficient atomization, the sodium caseinate solution must have a constant viscosity when it is fed to the spray dryer. It is a common practice to minimize the viscosity by preheating the solution to 90-95 °C just prior to spray drying.

The moisture content of spray dried sodium caseinate should be less than 5% for satisfactory storage.

The total solid content of the solution destined for spray drying ranges between 20 and 22% and only occasionally may be as high as 25%. The low solids content of the feed solution produces spray dried powder with a low bulk density. It may vary from 0.25 g/ml to 0.4 g/ml.

Generally pressure nozzle dryers, operating at 100–250 bars produce a caseinate with higher bulk density than from the disc atomizing dryers.

Ammonium/Potassium/Citrated Caseinate

Ammonium and potassium caseinates may be prepared by a method similar to that used for the production of sodium caseinate by substituting ammonium hydroxide or potassium hydroxide for sodium hydroxide. Citrated caseinate can be prepared by a method similar to that used for the preparation of spray dried sodium caseinate by using a mixture of trisodium citrate and tripotassium citrate in place of sodium hydroxide.

Calcium caseinate

In contrast to the translucent, viscous, straw coloured sodium, potassium and ammonium caseinate solutions, calcium caseinate forms micelles in water, producing an intensely white, opaque, milky solution of relatively low viscosity. Calcium caseinates are much less soluble and have poorer functional attributes than sodium caseinate.

The preparation of calcium caseinate follows the same general lines as for sodium caseinate with a couple of important exceptions. Calcium caseinate solutions are liable to be destabilized by heating, especially at pH values below 6. The sensitivity decreases with an increase in pH or a decrease in the concentration and is manifested as a reversible heat gelation. During the dissolving process, it has been found that the reaction between acid casein curd and calcium hydroxide (the alkali which is most commonly used in the production of calcium caseinate) proceeds at a much slower rate than between curd and sodium hydroxide. To increase the rate of reaction between casein and calcium hydroxide, the casein may first be dissolved completely in ammonia. Calcium hydroxide in sucrose solution is then added and the calcium caseinate solution is dried. Most of the ammonia evaporates during the process. The calcium caseinate obtained by this process has moisture content of 4.5%, protein 84%, sucrose 5.8% and calcium 1.0% with nutritional properties similar to those of the original casein.

Other Caseinates

Magnesium caseinate is prepared from casein and a magnesium base or basic salt such as magnesium oxide, magnesium hydroxide, carbonate or phosphate. Compounds of casein with aluminum may be prepared for medicinal use or for use as an emulsifier in meat products. Heavy metal derivatives of casein, which have been used principally for therapeutic purposes, include those containing silver, mercury, iron and bismuth. Iron and copper caseinates have also been prepared by ion exchange for use in infant and dietetic products.

Composition of Caseinates

The quality standards for sodium caseinate vary from country to country. The typical composition of sodium and calcium caseinate, produced from well-washed acid casein, is shown in Table 1.

Table 1: Typical composition of caseinates

	Sodium caseinate	Calcium caseinate
Moisture (%)	3.8	3.8
Protein (N x 6.38) (%)	91.4	91.2
Ash (%)	3.6	3.8
Lactose (%)	0.1	0.1
Fat (%)	1.1	1.1
Sodium (%)	1.2-1.4	< 0.1
Calcium (%)	0.1	1.3-1.6
Iron (mg/kg)	3-20	10-40
Copper (mg/kg)	1-2	1-2
Lead (mg/kg)	< 1	< 1
pH	6.5-6.9	6.8-7.0

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