

CASEIN PRODUCTS

Casein is the principal protein found in cow's milk from which it has been extracted commercially for most of the 20th century. It is responsible for the white, opaque appearance of milk in which it is combined with calcium and phosphorus as clusters of casein molecules, called "micelles".

The major uses of casein until the 1960s were in technical, non-food applications such as adhesives for wood, in paper coating, leather finishing and in synthetic fibres, as well as plastics for buttons, buckles *etc.* During the past 30 years, however, the principal use of casein products has been as an ingredient in foods to enhance their physical (so-called "functional") properties, such as whipping and foaming, water binding and thickening, emulsification and texture, and to improve their nutrition.

In New Zealand, casein is precipitated from the skim milk that is produced after centrifugal separation of whole milk. The skim milk may be acidified to produce acid casein or treated with an enzyme, resulting in the so-called rennet casein. The precipitated casein curd is separated from the whey, washed and dried. Water-soluble derivatives of acid caseins, produced by reaction with alkalis, are called caseinates.

INTRODUCTION

The amount of casein in cow's whole milk varies according to the breed of cow and stage of lactation, but is generally in the range 24-29 g L⁻¹. Casein contains 0.7-0.9% phosphorus, covalently bound to the protein by a serine ester linkage. Casein is consequently known as a phospho-protein. All the amino acids that are essential to man are present in casein in high proportions, with the possible exception of cysteine. Thus, casein may be considered as a highly nutritious protein.

Casein exists in milk in complex groups of molecules (sometimes referred to as calcium phospho-caseinate) that are called "micelles". The micelles consist of casein molecules, calcium, inorganic phosphate and citrate ions, and have a typical molecular weight of several hundred million. In terms of physical chemistry, the casein micelles may be considered to exist in milk as a very stable colloidal dispersion. The caseins, as proteins, are made up of many hundreds of individual amino acids, each of which may have a positive or a negative charge, depending on the pH of the [milk] system. At some pH value, all the positive charges and all the negative charges on the [casein] protein will be in balance, so that the net charge on the protein will be zero. That pH value is known as the isoelectric point (IEP) of the protein and is generally the pH at which the protein is least soluble. For casein, the IEP is approximately 4.6 and it is the pH value at which acid casein is precipitated. In milk, which has a pH of about 6.6, the casein micelles have a net negative charge and are quite stable. Although casein has been shown to consist of several individual casein components, referred to as α_{s1} -, α_{s2} -, β - and κ -casein, each having slightly different properties (which are caused by small variations in their amino acid content), only the commercial product, which contains all of these components, is considered in this article.

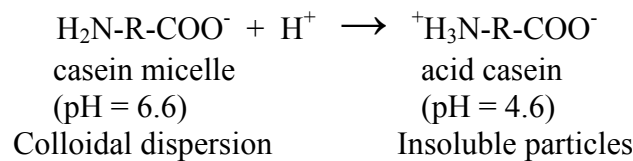
EXTRACTION OF CASEIN FROM MILK

Separation

Casein is extracted from milk using the processes outlined in **Figures 1** and **2**. Whole cow's milk (with a typical fat content of 4.65% - see Figure 1 in the introductory article) is first separated by means of centrifuges that produce cream (for the manufacture of butter or other milkfat products - see the article on milkfat products) and skim milk. Skim milk can thus be considered as the raw material from which casein products are made.

Precipitation

The operations involved in the precipitation of casein in New Zealand are shown in **Figure 1**. Precipitation by means of acidification can be considered in terms of simple chemistry as follows, R being the casein protein:



In the case of enzyme coagulation of casein, there is no change in the pH of the milk. Instead, the addition of a specific enzyme, *chymosin*, which is found in the stomach of newborn calves, specifically cleaves a highly charged portion from the κ -casein, called glycomacropeptide. That action causes the remainder of the κ -casein (now called *para- κ -casein*) to lose its considerable power in stabilising the micelles in milk, and the result is the formation of a three-dimensional gel network or clot of the casein in the presence of calcium ions. This reaction is essential in the manufacture of virtually all cheese types and in the production of rennet casein.

Wet-processing operations

When the casein has been precipitated, the mixture is heated (a process known in the dairy industry as "cooking"). Heating of the precipitated casein causes the particles to shrink and expel moisture (whey) (rather like a sponge), and also to agglomerate together to form clumps of curd. The curd is then separated from the whey and washed several times with water in vats prior to mechanical dewatering by pressing or centrifuging.

Drying and dry processing of casein

The dewatered curd, with a moisture content of about 55%, is dried by means of hot air using either fluidised bed driers with multiple decks or pneumatic-conveying ring driers to produce a dry casein having a moisture content of 10-12%. The warm, unmilled casein is then subjected to several dry processing steps (**Figure 2**), including cooling (usually by air conveying), "tempering" or conditioning to ensure that moisture is distributed evenly between large and small particles, milling, sifting (to produce coarse, medium and fine mesh particles), blending (to ensure uniformity) and bagging. The 25 kg bags of casein are placed on pallets and stored ready for shipping.

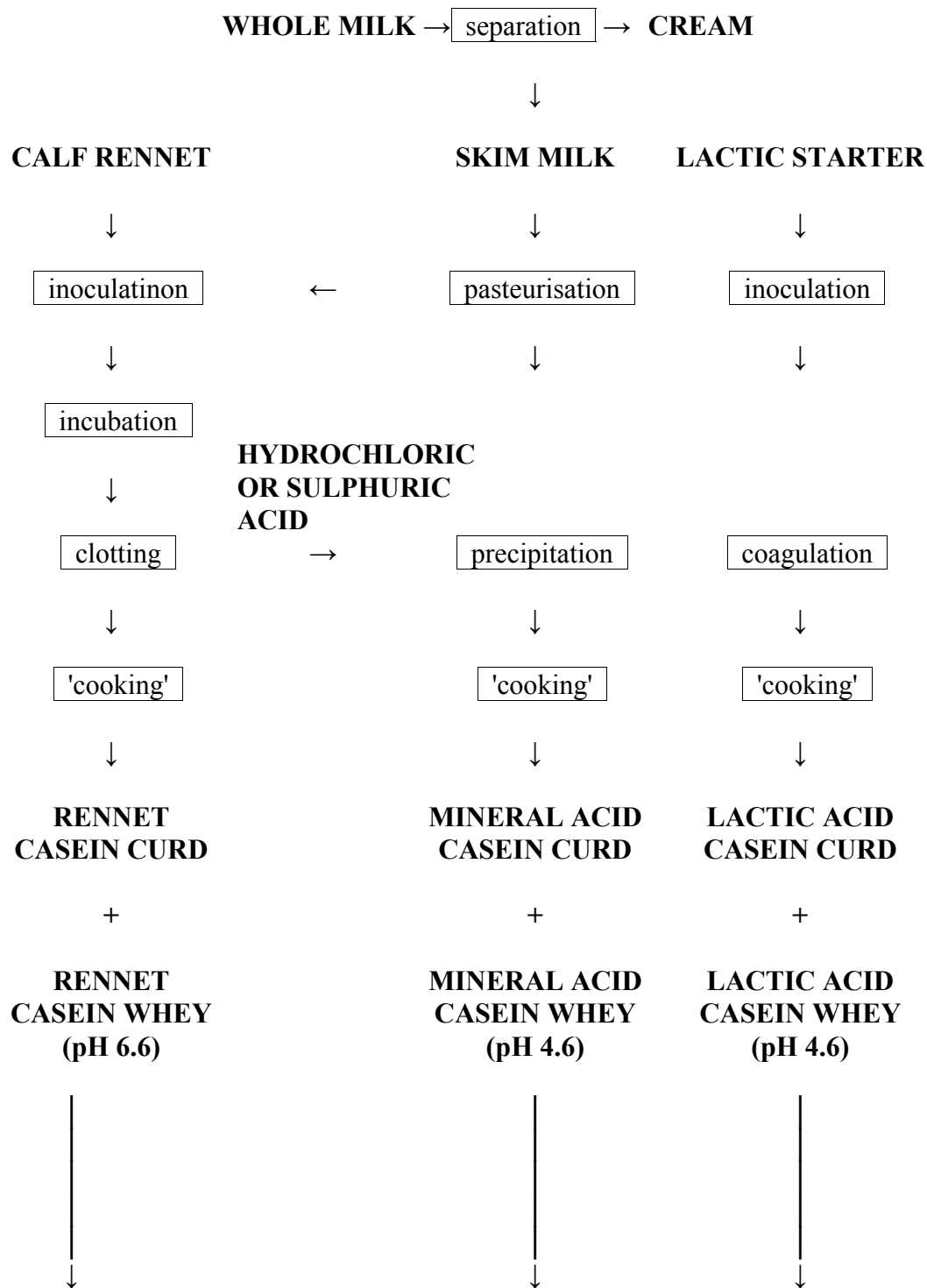


Figure 1 - Processing steps involved in the precipitation of acid and rennet caseins from milk.

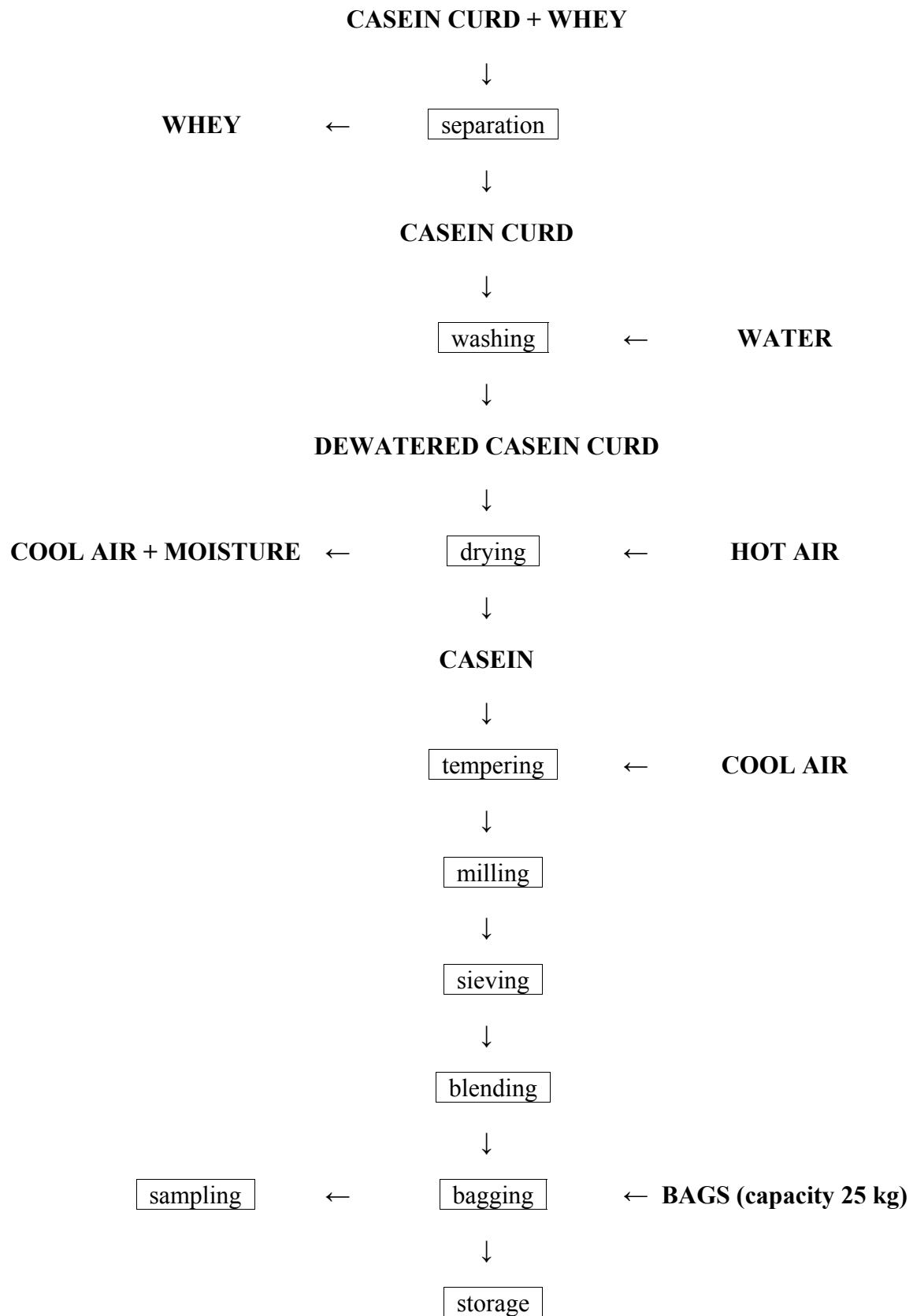


Figure 2 - Processing operations in the washing and drying of caseins.

Types of casein

As indicated above, two basic types of casein - acid and rennet - are produced in New Zealand. They are named in accordance with the coagulating agent employed. Three types of acid casein are made commercially: lactic, hydrochloric and sulphuric acid caseins. In New Zealand, lactic acid casein has been the most common casein product, although larger quantities of sulphuric acid casein have been produced in recent years. In Australia and Europe, the most common precipitant for acid casein is hydrochloric acid, which is a by-product of the chemical industry and hence is relatively cheap. In New Zealand, however, which has a very small chemical industry, hydrochloric acid is relatively expensive. On the other hand, sulphuric acid is relatively cheap, being produced in comparatively large quantities by the fertiliser industry for use in the manufacture of superphosphate. Consequently, virtually all mineral acid casein made in New Zealand is precipitated using sulphuric acid. The properties of the different types of acid casein are very similar and, for most applications, the acid caseins can be used interchangeably.

For the manufacture of rennet casein, several different coagulants are now available. These include chymosin (previously known as “rennet” or “rennet extract”), the milk-clotting enzyme extracted from the stomachs of young calves, and a number of so-called microbial rennets, which are enzymes that have been produced by means of microbial fermentation techniques. The caseins produced using any of these enzyme preparations are all known as rennet casein, and all have similar properties. However, their properties are noticeably different from those of acid casein.

Acid casein manufacture

Figure 1 outlines the steps involved in the precipitation of the acid caseins.

Lactic acid casein

For the manufacture of lactic acid casein, skim milk (pH 6.6) is first pasteurised (72°C for 15 s). It is then cooled to setting temperature (22-26°C) and inoculated with several strains of lactic acid-producing bacteria, known as “starters” (*e.g. Lactococcus lactis* sub-species *cremoris*, 0.1-0.2% of milk volume). The milk is incubated, without agitation, in large silos (each with a capacity of up to 250 000 L) for a period of 14-16 h. During this period, some of the lactose in the milk is converted to lactic acid by the starter (shown by a simple equation in **Figure 3**) and the pH is reduced to about 4.6, causing coagulation of the casein (and the milk). This takes the form of a soft gel and is generally referred to in the industry as “coagulum” or “coag”.

The fermentation of lactose to lactic acid in the manufacture of lactic acid casein is not as simple as that shown in **Figure 3**, however, and a number of other compounds are produced as well, *e.g.* diacetyl ($\text{CH}_3\text{COCOCH}_3$), acetoin ($\text{CH}_3\text{CHOHCOCH}_3$) and benzoin ($\text{C}_6\text{H}_5\text{COCHOHC}_6\text{H}_5$). These are present in relatively small amounts and do not generally present any serious problems.

After the pH of the milk has reached 4.6-4.7, the coagulum is “cooked” (*i.e.* heated), usually by means of a combination of indirect heating (through a heat exchanger) and steam injection, to a temperature of 50-55°C. After a brief period of residence in a “cooking” line and “acidulation” vat, the resultant curd is separated from the whey, washed and dried, as outlined above.

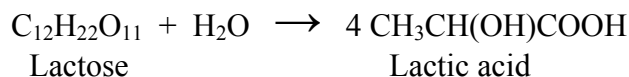


Figure 3 - Simple equation showing the conversion of lactose to lactic acid.

Mineral acid casein

For the precipitation of mineral acid casein, pasteurised skim milk at a pH of 6.6 is mixed thoroughly with dilute (0.25 mol L⁻¹) acid at a temperature of about 20°C to a pH of approximately 4.6. In this case, because of the very vigorous agitation and the short mixing time, the casein is precipitated as very fine, individual particles in a liquid serum (whey), unlike the gel/coagulum formed in lactic acid casein manufacture. The acidified milk mixture is then cooked and processed further in a manner similar to that described for the production of lactic acid casein.

Rennet casein manufacture

When rennet casein is made, the skim milk is not acidified. Hence, the pH remains at 6.6 throughout the manufacturing process. Following pasteurisation of the skim milk, it is cooled to a setting temperature of about 29°C, and calf rennet or microbial rennet is added (ratio by volume: 1 of rennet to about 7000 of skim milk) and mixed in thoroughly (**Figure 1**). During the first stage of renneting, the enzyme specifically cleaves one of the bonds in κ-casein, releasing part of the protein chain that is commonly referred to as glycomacropeptide. This action destabilises the casein micelles and, in the second stage of the reaction, they form a three-dimensional clot with some of the calcium ions that are present in the milk. The renneting process usually takes place in a period of 20-40 min under the conditions (pH and temperature) described above. The clotted milk may then be cooked and the casein processed in a manner similar to that described for lactic acid casein.

Yield

The yield of commercial casein is about 3 kg/100 kg skim milk.

MANUFACTURE OF CASEINATES

Caseinates may be produced by reaction under aqueous conditions of acid casein curd or dry acid casein with any one of several different dilute alkalis, as outlined in **Figures 4 and 5**.

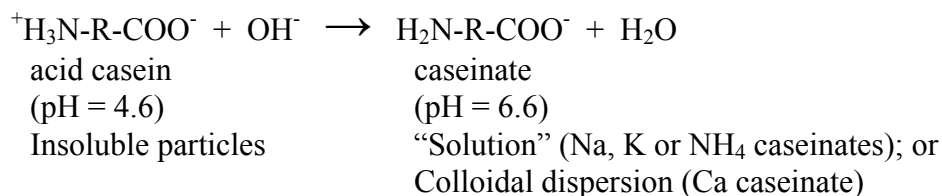


Figure 4 - Simple equation showing the neutralisation of acid casein with alkali (where R represents casein protein).

The resulting homogeneous solution may be spray dried to produce a caseinate powder having a moisture content of 3-6%, depending on the manufacturing conditions and customer requirements.

Spray-dried sodium caseinate

The most common alkali used in the manufacture of spray dried sodium caseinate is sodium hydroxide. It is mixed (as an aqueous solution with a typical concentration of 2.5 M) with a slurry of the casein curd or powder in water. The usual amount of sodium hydroxide needed is about 2% (w/w) of the casein solids.

The casein curd is milled (**Figure 5**) using one or more colloid mills to reduce the size of the individual particles so that they will dissolve rapidly, and is then mixed with the alkali using high shear. In producing solutions of sodium caseinate for spray drying, it is important to achieve the maximum possible concentration of solids for economic reasons, as the more water there is to evaporate, the higher is the energy cost. Concentrated solutions of sodium caseinate (> 15% solids), however, are very viscous, and require powerful agitators and pumps for mixing and fluid transfer. The use of high temperatures (60-95°C) during the later dissolving stages is of practical benefit, as the viscosity of sodium caseinate solutions decreases with temperature. However, there is still a delicate balance between what is mechanically achievable and what is economically practicable during the commercial production of sodium caseinate.

Other caseinates

The manufacture of potassium and ammonium caseinates is very similar to that of sodium caseinate, although, in the case of ammonium caseinate, a lot of the ammonia is evaporated from the solution during the drying process. A solution of sodium caseinate, like those of potassium and ammonium caseinates, has a straw-like colour and is completely different in appearance from milk. Solutions of calcium caseinate, on the other hand, are very white and opaque - even whiter than milk, and they are less viscous than solutions of the other caseinates. Calcium caseinate solutions are produced by adding a slurry of lime (calcium hydroxide) in water to a casein curd-water mixture and reacting the combined slurries at a relatively low temperature (< 45°C) until the neutralisation reaction is completed. Use of higher temperatures before neutralisation is completed is likely to result in precipitation or coagulation of the partly reacted calcium caseinate, with probable dumping of the contents of the reaction vessel.

All caseinate powders have a white appearance.

COMPOSITION OF CASEIN PRODUCTS

The typical composition of well-washed acid casein is shown in **Table 1**. As noted earlier, when the same manufacturing operations are used, the caseins produced from lactic, sulphuric or hydrochloric acid precipitation are almost indistinguishable from one another. Table 1 also shows that rennet casein differs from acid casein particularly in ash content and in the pH of a water extract. During the acidification process in the manufacture of acid casein, the calcium and inorganic phosphate (that are associated with the casein micelle in milk) are dissolved and leached from the curd leaving only the organic phosphorus and a small residue of calcium. Rennet casein contains about 3% calcium and approximately 1.4% phosphorus.

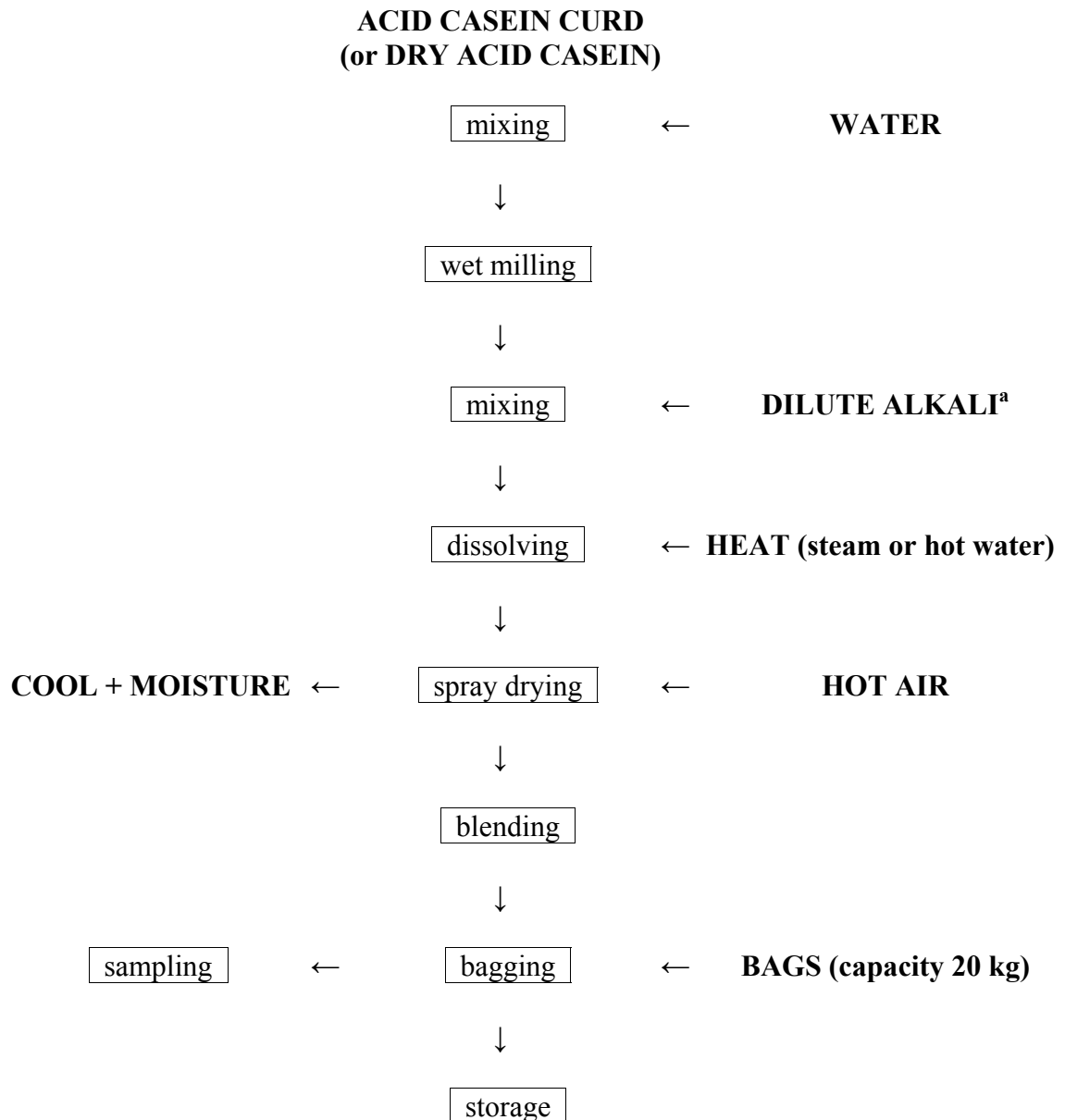


Figure 5 - Processing steps involved in the manufacture of sodium caseinate from acid casein curd or dry acid casein (Note^a: in this case, sodium alkali would be used.).

The composition of sodium and calcium caseinates is also shown in **Table 1**. As they are spray-dried products, their moisture content is much lower than that of the caseins, and their protein content is consequently higher. With a pH generally in the range 6.5-7.0, sodium caseinate will usually contain 1.2-1.4% sodium, whereas the calcium content of calcium caseinate is generally in the range 1.3-1.6%.

Table 1 - Composition of casein and caseinates

Component	Acid casein	Rennet casein	Sodium caseinate	Calcium caseinate
Moisture (%)	11.4	11.4	3.8	3.8
Protein (%)	85.4	79.9	91.4	91.2
Ash (%)	1.8	7.8	3.6	3.8
Lactose (%)	0.1	0.1	0.1	0.1
Fat (%)	1.3	0.8	1.1	1.1
Sodium (%)	< 0.1	< 0.1	1.2-1.4	< 0.1
Calcium (%)	0.1	2.6-3.0	0.1	1.3-1.6
pH	4.6-5.4	7.3-7.7	6.5-6.9	6.8-7.0
pH of whey after separation of curd	4.3-4.6	6.5-6.7	-	-
Solubility in water (%)	0	0	100	90-98

PROPERTIES OF CASEIN PRODUCTS

Solubility

Acid and rennet casein are insoluble in water. Virtually all applications of casein products require them to be dissolved first. Consequently, before use, acid casein must be dissolved using an alkali to produce a solution with a pH of 6.5 or higher. The caseinates mentioned in the previous sections are used for food and pharmaceutical applications. For non-food, technical applications, acid casein may be dissolved in other alkalis such as borax or ammonia, usually to a somewhat higher pH (7.5-9.5, or higher) than that used for edible applications.

Water absorption and viscosity

Casein products can absorb substantial amounts of water, so they can modify the texture of dough or baked products, serve as the matrix former in cheese-type products, produce specialised plastic materials, or increase the consistency of solutions such as soups. They are good film-formers and find use in whipping and foaming applications, and in emulsions of fats or oils in water.

Nutrition

The nutritional quality of a protein is determined primarily by its essential amino acid content. For adult man, eight amino acids are essential, *i.e.* they must be supplied in the diet. These are isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine; the infant requires histidine as well. In comparison with an “ideal” reference protein composition that was developed by the FAO in 1973, casein contains an adequate supply of all the essential amino acids with the possible exception of the sulphur-containing amino acids methionine and cysteine.

FOOD USES OF CASEIN PRODUCTS

The uses of casein products in foods are summarised in **Table 2**.

Table 2 - Edible applications of casein products

Bakery	Cheese products
Coffee whiteners and creamers	Confectionery
Cultured milk products, yoghurt <i>etc.</i>	High fat powders, shortenings and spreads
Ice cream and frozen desserts	Infant foods
Instant breakfasts and beverages	Meat products
Nutritional food bars	Pasta
Pharmaceuticals	Soups and gravies
Sports drinks	Whipped toppings

Casein is generally not consumed as a food on its own. Casein products are used mainly as ingredients in foods for the purpose of either modifying the physical properties of that food product or providing nutritional supplementation to it. As a consequence, they usually form a relatively minor proportion of the food. The function and use level of casein in the different food product groups listed in **Table 2** are shown in **Table 3**.

TECHNICAL (NON-FOOD) USES OF CASEIN PRODUCTS

Casein has been used commercially in non-food technical applications since the mid-19th century, initially in adhesives and water-based paints. These applications have multiplied during the 20th century and a list of current use categories is shown in **Table 4**.

Table 3 - Function and use level of casein products in foods

Food category	Casein product	Use level^b	Function
Baked products	Casein, caseinates	1-25%	Nutrition, water binding
Cheese products	Rennet casein, acid casein, caseinates	2-25%	Fat and water binding, texture, matrix formation
Coffee whiteners	Sodium caseinate	1-10%	Fat emulsification
Confectionery	Caseinates (whole and hydrolysed)	1-25%	Texture
Cultured products	Sodium caseinate	2-3%	Fat emulsifier, stabiliser
High fat powders	Sodium caseinate	up to 10%	Fat emulsifier
Ice cream	Sodium caseinate	1-5%	Texture, stabiliser
Infant foods	Whole or hydrolysed casein ^a	1-25%	Nutrition
Instant breakfasts and beverages	Sodium caseinate	2-30%	Nutrition
Meat products	Sodium caseinate	3-20%	Nutrition, fat emulsifier, water binding, texture
Nutritional food bars	Casein, caseinates	10-20%	Nutrition, texture
Pasta and snacks	Casein, caseinates	5-20%	Nutrition, texture
Pharmaceuticals	Casein, caseinates, hydrolysed casein	5-95%	Nutrition
Soups and gravies	Sodium caseinate	5-20%	Nutrition, thickener
Sports drinks	Sodium caseinate	2-10%	Nutrition
Whipped toppings	Sodium caseinate	5-10%	Film former, fat emulsifier, stabiliser, bodying agent

Note^a: Hydrolysed casein (“hydrolysates”) is derived from whole casein by reacting it in solution with a proteolytic enzyme. Hydrolysates are generally used in nutritional, pharmaceutical or medical applications where the whole protein is not readily digestible.

Note^b: Typical or estimated values.

Table 4 - Technical uses of casein

Acid casein	Rennet casein
Adhesive for wood, <i>e.g.</i> plywood; adhesive for foil laminates and paper	Plastics in the form of buttons, buckles, imitation tortoiseshell (combs and hairclips), imitation ivory (knife handles and piano keys), fountain pen barrels, shoehorns, dominoes, novelties
Coatings for paper and cardboard	
Horticultural spreaders	
Joint cements in wallboard	
Leather tanning	
Paints	
Photo-resist	
Stock foods	
Synthetic fibres	
Textile sizing	

GLOSSARY

acidulation	A period of time (5-10 minutes) when the mixture of cooked casein curd and whey is gently stirred in a vat before separation of curd and whey for further processing.
blending	Mixing of milled and sifted dry casein particles to achieve uniformity in composition and properties prior to bagging and storage.
α_{S1} -casein, β -casein, κ -casein	Fractions of whole casein that have very slight differences in amino acid composition.
caseinate	The water-soluble, neutralised (salt) form of acid casein. The most common are sodium and calcium caseinates.
chymosin	The more scientifically correct name for rennet.
coagulum/"coag"	A term describing the gel formed in milk after its acidification to pH <i>ca.</i> 4.6 using lactic starter bacteria.
colloid mill	A powerful mill with very fine tolerances used for wet-milling of aqueous slurries of casein curd.

cooking	The heating of coagulated or clotted or acidified milk, usually by steam injection or by means of a heat exchanger.
dewatering	Separation of casein curd and wash water, often by mechanical means.
glycomacropeptide	The fragment (or peptide) that is split off the casein during the action of rennet (or chymosin).
para- κ -casein	The casein remaining after the action of rennet or chymosin.
proteolytic	Causing breakdown of protein bonds.
rennet	A proteolytic enzyme found in the fourth stomach of a young calf. It is used in the manufacture of cheese and rennet casein, when it splits off a small fragment (known as glycomacropeptide) from the casein.
starter	A culture of several defined strains of bacteria that are added to milk to convert some of the lactose (milk sugar) to lactic acid during the manufacture of cheese and lactic acid casein.
tempering	A period of time when casein from the drier is mixed and held in storage bins to allow time for the equilibration of moisture among all the particles.

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