

BY-PRODUCTS TECHNOLOGY



Vijay Kumar

By-Products Technology

Course Developer

Vijay Kumar

Dairy Technology Division
NDRI, Karnal

Luck is not in your hands
But decision is in your hands
Luck can't make your decision,
But your decision can make luck....

EDITOR



AGRIMOON.COM

All About Agriculture...

Course Outlines 4 (3+0+2)

Module 1: Introduction

- Lesson 1. By-products and issue involved in their utilization
- Lesson 2. Global status, availability and utilization of dairy by-products
- Lesson 3. Indian status, availability and utilization of dairy by-products

Module 2: Skim milk and its by-products

- Lesson 4. Physico-chemical characteristics of skim milk
- Lesson 5. Casein: classification & specifications
- Lesson 6. Basic principles of edible acid casein manufacture
- Lesson 7. Continuous manufacturing of hydrochloric acid casein
- Lesson 8. Manufacture of lactic casein
- Lesson 9. Manufacture of rennet casein
- Lesson 10. Industrial uses of caseins-1
- Lesson 11. Industrial uses of caseins-2
- Lesson 12. Manufacture of sodium caseinate
- Lesson 13. Manufacture of other caseinates
- Lesson 14. Production of casein hydrolysates
- Lesson 15. Enzymatic production of casein hydrolysates
- Lesson 16. Debittering of protein hydrolysates
- Lesson 17. Co-precipitates: Introduction and basic principles for production
- Lesson 18. Manufacture of co-precipitates
- Lesson 19. Physico-chemical properties of co-precipitates

Module 3: Processing and Utilization of whey

- Lesson 20. Physico-chemical characteristics of whey
- Lesson 21. Manufacture of condensed whey products
- Lesson 22. Manufacture of dried whey
- Lesson 23. Physico-chemical properties and utilization of condensed and dried whey products
- Lesson 24. Whey beverages
- Lesson 25. Fermented whey beverages
- Lesson 26. Fermented products from whey-1
- Lesson 27. Fermented products from whey-2
- Lesson 28. Electrodialysis process for demineralisation
- Lesson 29. Ion exchange process for demineralisation
- Lesson 30. Demineralisation of whey and its utilization
- Lesson 31. Methods of whey protein recovery from whey
- Lesson 32. Manufacture of whey protein concentrates by molecular separation processes
- Lesson 33. Physico-chemical properties of whey protein concentrates
- Lesson 34. Manufacture of crude lactose

Lesson 35. Refining of lactose

Lesson 36. Uses of lactose

Lesson 37. Lactose hydrolysis

Lesson 38. Applications of hydrolysed lactose

Module 4: Functional properties of milk protein products

Lesson 39. Functional properties of whey proteins

Lesson 40. Functional properties of casein products

Module 5: Food application of milk protein products

Lesson 41. Food application of milk protein products-1

Lesson 42. Food application of milk protein products-2

Module 6: Butter milk

Lesson 43. Physico-chemical characteristics of buttermilk and its preservation

Lesson 44. Utilization of buttermilk

Module 7: Ghee-residue

Lesson 45. Ghee-residue and its characteristics

Lesson 46. Ghee-residue: Processing and utilization

Module 8: Nutritional characteristics of by-products

Lesson 47. Nutritional characteristics of skim milk and its by-products, buttermilk & ghee-residue

Lesson 48. Nutritional characteristics of whey and its by-products

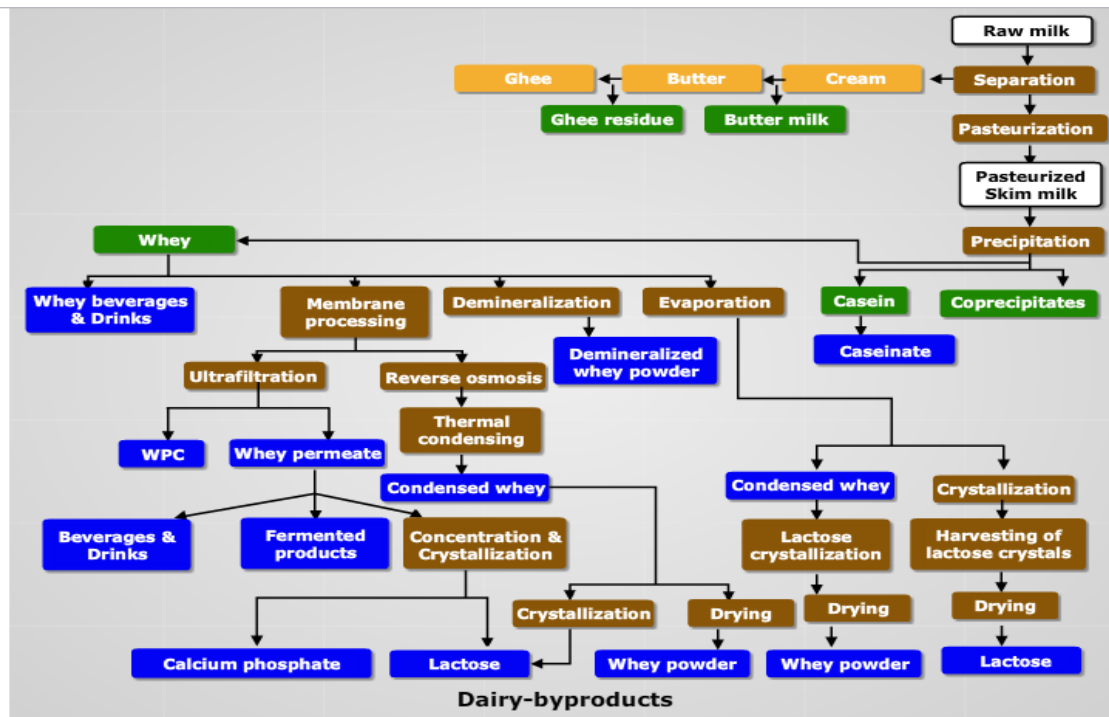
Lesson 1

BY-PRODUCTS AND ISSUES INVOLVED IN THEIR UTILIZATION

1.1 Introduction

A dairy by-product may be defined as a product of commercial value produced during the manufacture of a main product. Skim milk, buttermilk, ghee residue and whey are the main dairy by-products as shown in Fig.1.1. Utilization of dairy by-products improves plant economy, makes valuable nutrients available for humans and reduces environmental pollution originating from dairy waste. Conversion of edible substances into non-food items is not ordinarily justifiable, especially in countries, where there is an overall shortage of milk supplies. It has always been realized that economic disposal of by-products is an essential prerequisite to profitable dairying. Each and every component of milk must be judiciously processed into edible form for the obvious reason of its unique nutritional value. These by-products are, therefore, receiving increasing attention for their proper utilisation by the research workers all over the world. However, it should be recognized that just because it is technically feasible for any dairy by-product to be processed into interesting by-products, it does not mean that we can utilize it. Processing of by-products needs to be economically feasible, if one is to invest capital and resources into a programme to utilize them. Therefore, further emphasis needs to be put on cost effective processing and utilization technologies of dairy by-products.

In some countries like India, the most of problems associated with the production and utilization of dairy by-products are: a low per capita availability of milk, higher proportion of buffalo milk, poor quality of raw milk, lack of organized manufacture of products, lack of adequate technology, high cost of new technologies, lack of in-house R & D, lack of proper infrastructure, lack of indigenous equipments and plants etc. Before setting up a by-product factory, it is important to consider the economical aspects of the plant, because sometimes the cost of manufacture of the by-product may be more as compared to the by-product and, therefore, the setting up of the by-product plant is not economically feasible. But with advancement in science and technology as also the automation of plants, the economic feasibility of these can be improved.



1.2 Skim Milk and Its By-Products

Skim milk is produced by separation of cream from milk in dairy processing. Skim milk is rich in solid not fat (SNF) content and is used for standardization of milk, preparation of skim milk powder and coffee whitener. It is regarded as a by-product only when it is either not economically utilized or has to be utilized for the manufacture of derived by-products like casein in small quantities.

1.2.1 Casein and caseinates

These are prepared from skim milk and used in food preparations, specialized foods and manufacture of plastics etc. The technology of production of caseins from cow milk is well established. But when the milk is from buffalo or other animal origin, some technological modifications are required in the manufacture of casein from them. The R & D work on this aspect is very limited and is not available freely. This has been one of the limitations for production of edible casein from milk sourced from animals other than cow. Further, it is very difficult to control all the processing parameters when this product is manually prepared. For good quality product, large, mechanical and automatic plants have been developed. For using these plants economically, there has to be some minimum handling of milk of about 2 lakh litres per day. Also there should be facilities for proper utilization of whey that emerges in large quantity. Unless these conditions are met, casein production may not be techno-economically feasible. Additionally, in many countries, the technology and manufacturing plants need import that is costly and not all the time convenient.

The economic constraints for the production of spray dried caseinates are their high drying cost, low bulk density and high packaging, storage and transportation costs.

1.2.2 Co-precipitates

The technology of production of co-precipitates from skim milk is well established all over the world. However, their poor solubility especially of the high calcium co-precipitates, has been mainly responsible for their non-acceptability and so non-production on commercial scale.

1.2.3 Protein hydrolysates

Protein hydrolysates are the breakdown products of protein in the form of peptides and amino acids as a result of hydrolysis of protein either by acid, alkali or proteolytic enzymes. Acid and alkali hydrolysis of protein results in complete or partial destruction of some and racemisation of most of amino acids. These processes also pose problem of removing residual acid from hydrolysates. Bitterness, which is a natural consequence of enzymatic hydrolysis of protein, is the main hindrance in the production of an acceptable protein hydrolysate. Expert specialized knowledge of different available proteolytic enzymes is necessary for developing good quality protein hydrolysates through enzymatic hydrolysis.

1.3 Whey and Its By-Products

Whey, the greenish translucent liquid is obtained during the manufacture of *cheese, casein, chhana, paneer, chakka* and *co-precipitates* and has been viewed until recently as one of the major disposal problems of the dairy industry. Due to the presence of significant amount of organic matter (6-7% total solids) in the form of protein, lactose, fat, minerals and water-soluble vitamins, its disposal causes environmental pollution. The biological oxygen demand of whey is very high (40,000 mg/kg or more), constituting a major economical burden to be disposed of as a waste material.

The quantity of whey produced is sometimes not sufficient to utilize it economically. Hence, the utilization of whey is not taken up in a significant way in such circumstances. Further, in view of the low total solids content of whey, there has been a gross lack of interest in its utilisation compared to other fluid by-products of dairy industry. However, due to high cost of processing and handling, a large amount of whey is disposed off as raw whey.

However, whey being a source of precious nutrients like lactose, whey proteins, minerals and vitamins, some economical prepositions have been evolved to utilize it. Utilization of this by-product in the human food chain is now being predominantly favoured due to the economic opportunities provided by the milk nutrients contained in whey. It is the base material for manufacture of not only nutritional products like whey protein concentrates (WPC) and lactose, but also the base for manufacture of whey drinks and dietetic beverages.

Despite significant gains in the amount of whey being processed, a large amount of current whey production still is disposed of as raw whey. Much of this represents production of small plants, where the cost of purchasing, processing as well as the subsequent transportation and handling clearly exceeds the value of any whey product that might be produced. In small plants, the choice remains some form of disposal, be it municipal treatment, spreading raw whey on local farmlands for its nutrient value or feeding to local livestock. Further, acid whey, like cottage cheese whey, because

of high mineral content and low pH, poses considerable difficulties in utilization and, therefore, mostly remains unutilized. Neutralization is possible; however, the process adds to the expense, changes the whey characteristics, and introduces more sodium ions. The high level of minerals (0.7-0.8%) present in whey also restricts their commercial utilization in many applications. A major problem with many whey-based products is their salty flavour owing to their high mineral content.

1.3.1 Whey drinks

A variety of whey based beverages consisting of plain, carbonated, alcoholic and fruit flavoured have been successfully developed and marketed all over the world, because they hold great potential for utilizing whey solids. The predominant types of new whey drinks are based on blends of fruit juices and whey. Other types of whey-containing beverages currently available on the market in various countries include products from deproteinated 'milk serum', fermented dairy-type beverages containing whey, and flavoured milk-type products containing whey or whey components. Manufacture of fermented whey beverages such as soft drinks, whey wine, beer like products and low alcoholic beverages appear to be most economical and viable process for returning the wasted milk nutrient into value added products among various innovative microbiological process of whey utilization. Although alcoholic whey beverages may still be available in certain local markets, products like whey beer and whey wine appear to be of limited importance. Whey-based liqueurs may become an important product in the near future.

Whey drinks contain valuable and nutritious whey proteins, but do not have large market value; they can be utilized only on small scales. Technological problems may be encountered also when the desired formulation contains additional components that interfere with processing or final product quality. Flavour losses with some fruit juices containing whey drinks may be encountered in UHT processing of the product, especially in the direct type machines employing a flash cooling vacuum chamber.

1.3.2 Concentrated and dried whey

Drying extends the shelf life of the whey, simultaneously reducing its weight and volume. This reduces the cost of transporting and storing the product. The advantage of processing whey into powder is that there are no by-product residues to be treated separately. Basic disadvantages include expensive equipment and energy, both of which requires a large processing capacity yet command relatively low prices for the final product when compared to other products such as whey protein concentrates. The evaporation of large quantity of water to convert the whey to dried form is found to be uneconomical with the conventional evaporators due to high evaporation cost. In the manufacture of dried whey more than 50% of energy consumed is required at evaporation stage therefore the cost of energy required for the evaporation of whey is a major factor determining the production of whey powder. Hence it is important for the economic production of whey powder to ensure that evaporators are operating at their maximum capacity and efficiency.

1.3.3 Ultrafiltration processing of whey

Separation of whey proteins is typically achieved by ultrafiltration (UF) or diafiltration to produce whey protein concentrates (WPC), which have many applications in the food industry. By UF process, a highly functional WPC is produced as the primary end product for a wide variety of applications as a substitute for non-fat dry milk and other protein ingredients. Increased production of whey protein concentrate warrants its greater application in food products.

UF membrane technology is economically feasible only for large scale processing of whey, because the product yield is very low. Although UF of whey has been in commercial use since 1972, the industry has been slow to adopt it because the process generates a UF permeate as a by-product rich in lactose and minerals that creates a waste disposal problem, almost equal in magnitude to the disposal of whole raw whey.

1.3.4 Demineralized whey

Ion-exchange and electrodialysis processes are used to demineralize whey. These processes can be utilized only for large scale operation and their high capital cost, high running cost and the problem of resultant effluents are the main limitations of these processes. Economic feasibility of production of demineralized whey lies in its utilization in value added products only.

1.3.5 Lactose

Lactose production from whey can be economically feasible only when it is produced on large scale. Generally, sweet whey is preferred because of its high lactose and low ash content. In case of acid whey, neutralisation is necessary. This will change the whey characteristics and also increase the cost of manufacture. Lactose can be produced by using UF permeate as a raw material, but UF permeate, particularly the acid whey permeate, has a very high calcium content. Removal of approximately 50% calcium is necessary to avoid difficulties during evaporation, which makes the process costly.

1.3.6 Milk Mineral products

These products are prepared by precipitation of calcium phosphate in whey UF permeate under suitable conditions of concentration, pH, time and temperature. The crystals that first precipitate quickly undergo solid state transitions depending on the conditions to which they are subjected. It is necessary to grow calcium phosphate particles to sufficient size to recover them in a good yield by centrifugation and filtration. Milk mineral products rich in natural calcium and phosphate are valuable nutritional supplements in today's osteoporosis-sensitive world and are used as a natural calcium supplement in a growing range of food products including milks, yoghurts, canned milk powders and confectionary and health foods. However, their commercial production needs further boost.

1.4 Buttermilk

Buttermilk is the by-product of butter industry. Buttermilk is produced when butter is made by churning cream or whole milk curd. Buttermilk, as a by-product, has very important place in dairy industry and needs proper attention for its judicious utilization. The high nutritional value of buttermilk and increasing public awareness concerning the environmental pollution warrants for the economic utilization of this important by-product. Sweet cream buttermilk that is produced in organized sector is preferred for processing and utilization in different products. The spray dried buttermilk powder is less free flowing and dusty because of high fat content in comparison with skim milk powder. The high fat content reduces the shelf-life of the powder during storage. Desi buttermilk is an important domestic beverage, but it is mainly produced in unorganized sector in small and scattered quantities and is mostly utilized at domestic level.

1.5 Ghee-Residue

Ghee-residue is brownish sediment obtained by filtration of ghee after heat clarification. Major portion of ghee-residue in countries like India is obtained in small quantities, particularly from the scattered small scale household production of desi ghee in villages, which remains unutilized. Ghee-residue from ghee produced at organized sector or at commercial level can be utilized for the manufacture of chocolate burfi, samosa filling etc., but potentiality of its full utilization is yet to be explored.

***** 😊 *****

Lesson 2

GLOBAL STATUS, AVAILABILITY AND UTILIZATION OF DAIRY BY-PRODUCTS

2.1 Introduction

In recent years, there has been wide spread and increasing interest throughout the world in creating newer channels for the utilization of by-products of the dairy industry. The production of by-products like casein, caseinates, co-precipitates, protein hydrolysates, whey protein concentrates, lactose, whey beverages, low lactose powder and many others have prominence in advanced dairy countries. The western dairy industry especially American and European and also of Australia and New Zealand have been the harbingers in the utilisation of by-products. They have developed technologies for the utilisation of by-products, developed large automated plants and also developed users for by-products in dairy and food industry. A large range of milk protein products is presently recovered from milk. It is likely that this range will be extended in the future as methods developed to effect separation of individual caseins and whey proteins become commercial. The main area of application of milk protein products will continue to be as functional ingredients in formulated foods, it is likely that there will be increased use of milk protein-based products in dietary, pharmaceutical and medical products.

2.2 Skim Milk and Its By-Products

The way in which the skimmed milk is utilized has changed dramatically. Firstly the proportion of supplies used for direct feeding to livestock has declined from over 50% in 1960 to only 11% in 1979. More of it was used for the manufacture of skim milk powder (which was the main way of utilization of skim milk from 14% in 1960 to 53% in 1979). Presently, skim milk is mostly utilized either in standardization of milk for the manufacture of main dairy products or preserved by removing moisture in spray dried form. The skim milk when utilized in either of these two forms or consumed as liquid is not considered a by-product. It is regarded as a by-product, only when it is either not economically utilized or has to be utilized for the manufacture of derived by-products like casein in small quantities. In 2002, about 6 million tonne of skim milk was utilized for casein production.

2.2.1 Casein and caseinates

Estimated production of casein was 3.5-4.3 lakh tonnes in 2005 (Fig.2.1). The large producers of casein are New Zealand, Netherlands and Germany. The world market of casein/caseinates used in the food industry fluctuates between 2 to 2.5 lakh tonnes. The biggest importer of casein is United States of America, where food casein demand can be estimated at 20,000 tonnes per year and caseinates demand at 27,000 tonnes per year. About 20% of this demand is for nutraceutical applications. The second biggest importer is Japan. A lot of casein is utilized for the manufacture of imitation cheeses. Total export of casein and caseinates from New Zealand reached 1.34 lakh tones in 2004.

Casein production is approx. 3.5-4.3 lakh tonnes

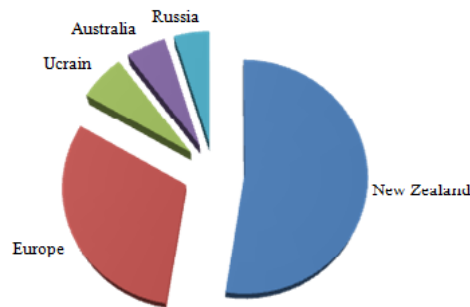


Fig. 2.1 World casein production-2005

2.2.2 Co-precipitates

The manufacture of co-precipitates has several advantages like increased yield and higher nutritional value over that of casein. However, it has never been commercially exploited to any great extent.

2.2.3 Milk protein hydrolysates

Today protein hydrolysis has assumed a new dimension in the food industry. Milk protein hydrolysates find extensive use in nutritional, dietetic and formulated foods, where a pre-digested form of protein is needed.

2.3 Whey and Its By-Products

Whey is the largest by-product of dairy world. In 2008, Global production of liquid whey from cheese and casein was estimated at about 186 million MT. The EU and US produce about 70% of whey in the world. Cheese whey accounts for nearly 95% of total whey. The continuing annual growth in the production and consumption of cheese and coagulated milk products represents the generation of about two percent additional quantities of whey globally every year. Whey trade has grown from approx. 860,000 MT in 2005 to more than 1,010,000 MT in 2008, corresponding to an annual growth of 5-6%, US and EU accounting for approx. 80% of global whey trade followed by China and Canada (Fig.2.2). In Rest of world, the Asian countries represent a major market. Some South American countries, Mexico and Russia are clearly emerging markets. In 2008, large export of whey was from west to east. In the East, Japan, Korea, Thailand and Indonesia are major whey importers.

The processing options for whey utilization fall into four main areas

- Those concerned with simple removal of water (spray or roller drying to yield whey powder).
- Those concerned with increasing the ratio of protein in the end product (ultrafiltration for manufacture of whey protein concentrates, fractionation processes for the manufacture of protein isolates, heat treatment for the production of lactalbumin).
- Those concerned with utilization of lactose in whey (treatment with lactase or heat/ acid for lactose-hydrolyzed products, fermentation to a number of products such as lactic acid, citric acid and microbial biomass proteins).
- Those designed to alter the mineral composition of the product (electrodialysis and ion-exchange for the manufacture of demineralised products).

Whey proteins and lactose are clearly mainstream ingredients. Many of the whey protein fractions and lactose derivatives are still at a very early market development stage.

Total whey market ~ 770,000 MT

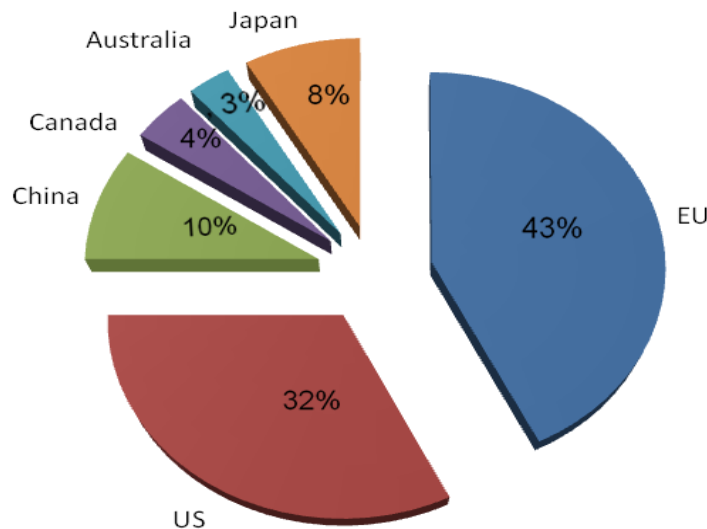


Fig. 2.2 Global overview of major whey markets

Today, modern industrial processing techniques such as membrane processing, new drying methods, hydrolysis, electrodialysis, ion-exchange, fermentation and protein fractionation, among others, have converted whey into a major source of numerous ingredients with differing functional and nutritional properties finding increasing utilization in various branches of the food and dairy industry. Membrane processes are continuous molecular separation processes that do not involve either a phase change or inter-phase mass transfer. Therefore, energy requirements of membrane processes are very low compared with other processes such as evaporation. Further, easy, simple and economical operation, improved recovery of constituents and better yield of products are other advantages for which membrane processes are valued. A membrane separation system separates an influent stream into two effluent streams known as the permeate and the concentrate. The permeate is the portion of the fluid that has passed through the semi-permeable membrane. Whereas the concentrate stream contains the constituents that have been rejected by the membrane.

The main membrane systems in ascending order of pore size are: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). In a broader sense RO is essentially a dewatering technique, NF a demineralization process, UF a method for fractionation and MF a clarification process. The principal application of nanofiltration is for separation of mineral ions in the 10^{-9} m size exclusion range. UF membranes retain only macromolecules or particles larger than 1-20 nanometers. This process typically employs membranes with molecular cut-off in the range of 10000 - 75000 D. MF processes are designed to separate particles in the so called micrometer range, that is suspended particles of 0.1-10 micrometers.

The predominant driving force behind the development of whey utilization has been stringent regulations imposed by the environmental pollution agencies all over the world. Other aspect relates to economic return from whey, which contains almost half the solids of original milk. Table 2.1 gives the production of major whey products. The market for whey products is estimated to be about \$ 6.5 billion in sales globally. During the last few years, many new products have been launched including bakery, confectionery, dessert, ice creams, snacks etc. The number of new products launched has grown, on average, approx. 15% per annum from 2002-2008. In 2008, out of top five countries (USA, UK, Japan, Brazil and Germany), USA was the number one producer of whey products.

Table 2.1. Production of Whey and Modified Whey Products in the United States in 2005 (USDA)

Product	Quantity (MT)
Condensed whey solids	53,460
Dry whey	550,173
Human use	524,570
Animal feed	23,308
Lactose and mineral reduced whey solids	45,789
Lactose	369,328
Whey protein concentrate (WPC)	213,862
Human use	189,309
Animal use	24,553
WPC 25–50% protein	148,733
WPC 50–90% protein	65,129
Whey protein isolate (>90% protein)	15,337

2.3.1 Condensed and dried whey

By far the single largest use of whey solids, on global basis, is in the form of whole dry whey and it continues to grow. This is whole whey that has been condensed and spray dried as such or after blending with certain other liquid ingredients. These powdered whey products are marketed as commodity ingredients for a variety of food and animal applications. The feed industry may be the largest consumer of dried whey and whey products.

Considerable advancements have been made in condensing and drying equipments for energy conservation and for the production of better quality product. A significant trend in the last two decades has been the increasing interest in RO for removing water from whey. Small plants concentrate whey by RO for shipment to the larger plants. Medium sized plants concentrate whey by evaporation for large drying plants. Large plants concentrate their own whey plus outside sources whey to high solids for lactose crystallization and drying.

During 1990-2000, four countries accounted for more than 80% of world dry whey production. United States was the largest dry whey producer, with an average share of more than 31 % of annual world dry whey production. France followed with an average share of 28%. Netherlands averaged a 15% share, and Germany averaged slightly less than 10% of the world production. EU accounted for more than 60% of world dry whey production. Combined, United States and EU accounted for more than 90% of world dry whey production.

Global exports of dried whey are dominated by the EU and United states, which together accounted for approximately 64% of world export in 2002. Australia ranked third among leading dry-whey exporting countries with 66,000 MT, or 11 percent of the world exports. Dry whey is imported in several countries, most of which are developing countries. China ranked as the world's leading importing country of dry whey, importing 138,000 MT in 2002, accounting for 25 % of global imports.

2.3.2 Demineralised whey

At the other end of the spectrum, a small percentage of utilized whey (less than 5%) is demineralised by ion exchange or electro dialysis prior to spray drying to produce dry demineralised whey for specialized uses including whey protein based infant formulas and other medical and nutritional products that require lactose, special nutritional quality of whey proteins and low mineral content.

2.3.3 Whey drinks

Liquid whey has been utilized for the manufacture of wide range of beverages and soups over the years, as a result of which a number of such products are available to consumers. The utilization of whey into various vegetable based soups and fruit beverages is one of the most attractive avenues for the utilization of whey. Cheese whey has successfully been tried in the manufacture of mixed vegetable, mushroom, tomato and spinach soups, whereas, paneer whey is suited for mango, lemon, banana and pineapple beverages.

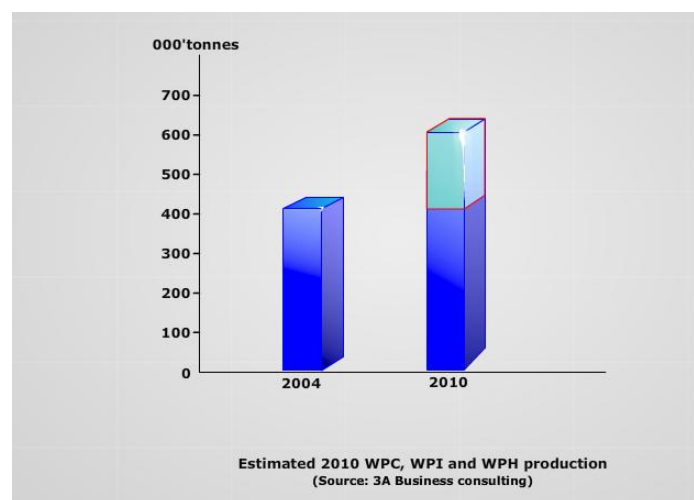
Commercial interest in fermented whey beverages has increased in several European countries notable Germany, Holland, Australia and Switzerland, possibly as a result of health consciousness of the modern consumers. Alcoholic whey beverages are available in certain local markets. Products like whey beer and whey wine appear to be of limited importance.

2.3.4 Lactose production

The production of lactose from whey continues to be one of the most important forms of whey's utilisation. The global market for lactose based goods is valued at over \$ 3 billion. Europe is the largest producer of lactose followed by United States. In 2006, the production of lactose was 850,000 MT in Europe and 317,000 MT in United States. In 2008, the global lactose market was worth roughly US \$ 1.5 billion. During 2005-2008, market volume for lactose increased up to 8% and its market value up to 25%. Total market volume for lactose products was approx. 1,652,000 MT globally in 2008.

2.3.5 Whey protein concentrates

New Zealand is the largest manufacturer of WPC by ultrafiltration (UF) process in the world. By UF process, a highly functional WPC is produced as the primary end product for a wide variety of applications as a substitute for non-fat dry milk and other protein ingredients. The estimated production of WPC, WPI and WPH in 2010 is given in Fig.2.3.



The global whey protein market was worth roughly US \$ 3.8 billion in 2008. During 2005-2008, market volume of whey protein increased up to 3% and market value up to 24% (Fig. 2.4). Food consumption of whey proteins, WPC and WPI was estimated approx. 190,000 MT, 85,000 MT and 14,500 MT respectively. Whey protein fractions such as lactoferrin, α -lactalbumin and colostrum/IgG alongside galacto-oligosaccharides (GOS) are showing interesting new application opportunities and significant annual growth rates. For instance GOS is growing annually by an impressive 15 per cent.

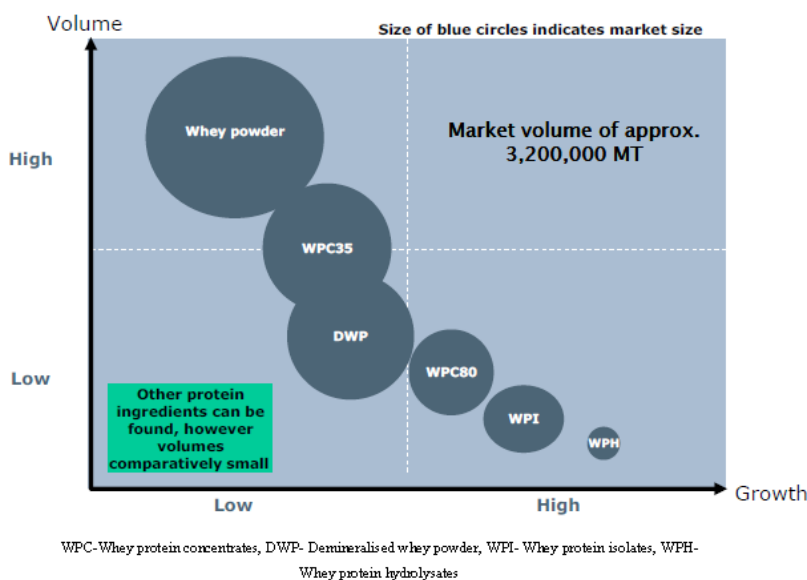


Fig. 2.4 Global whey protein market in 2008
(Source: 3A Business Consulting)

2.3.6 Fermented products

The lactose in whey can be converted by fermentation by a variety of organisms to products ranging from lactic acid to flavouring materials, but the identification of the most cost effective means for its utilization is still awaited by most dairy companies world wide. Up to some extent, alcohol is produced from the fermentation of lactose. Three plants in New Zealand are in operation presently producing alcohol cost effectively by the fermentation of lactose.

2.4 Buttermilk

The worldwide production of buttermilk could be considered close to that of butter production, which was estimated at around 8.6 million tonnes in 2006. In the United States, the commercial use of buttermilk was mainly for the baking industry (39%), prepared dry mixes (33%), and for the dairy industry (23%) during 2002.

2.5 Butter Oil/Ghee-Residue

Butter oil/ ghee-residue is not generally used anywhere in the world. A sincere R & D work and a strong willingness on the part of manufacturer is required to develop food uses of butter oil/ ghee-residue and put it in the market place.

***** 😊 *****

Lesson 3

INDIAN STATUS, AVAILABILITY AND UTILIZATION OF DAIRY BY-PRODUCTS

3.1 Introduction

A low per capita availability of milk, higher proportion of buffalo milk, poor quality of raw milk, lack of organized manufacture of products, lack of adequate technology, high cost of new technologies, lack of in-house R & D, lack of proper infrastructure, lack of indigenous equipments and plants etc. have been the problems mainly associated with the production and utilization of dairy by-products in India. It is only after economic liberalization and de-licensing of the dairy industry in 1993, that dairy by-products, which were mostly neglected by the dairy plants earlier started receiving due attention. A number of by-products based dairies with large automatic and continuous manufacturing plants have been set up. India's import and export of dairy by-products during 2008-2010 is shown in Fig.3.1.

3.2 Skim milk and Its By-products

In India, skim milk is mostly utilized either for standardization purposes or preserved in spray dried form. Only a very small quantity of skim milk, mostly of substandard quality, has to be used as by-product. A small percentage of this is disposed off in drain particularly during flush season.

3.2.1 Casein and caseinates

Production of edible casein is an economically feasible proposition, only when the whey thereby produced is efficiently and economically utilized. This has been one of the main reasons why edible casein was not produced seriously in India before 1995. Most of the requirement of this by-product, even for industrial uses, was met through import. During the last 15 years, there has been an entry of a few large automatic and continuous manufacturing plants in India for the manufacture of edible casein, lactose and whey protein concentrates. Presently, most of the casein produced is being exported, but eventually with the assured Indian market, the product would be diverted for internal consumption also. Manufacture of caseinates is yet to pick up on commercial scale in India.

3.2.2 Co-precipitates

Manufacture of co-precipitates was not taken up in India at any time.

3.2.3 Milk protein hydrolysates

Milk protein hydrolysates are prepared from casein and whey protein. In India, there lies a great scope for making improvement in the quality of the protein hydrolysates being prepared.

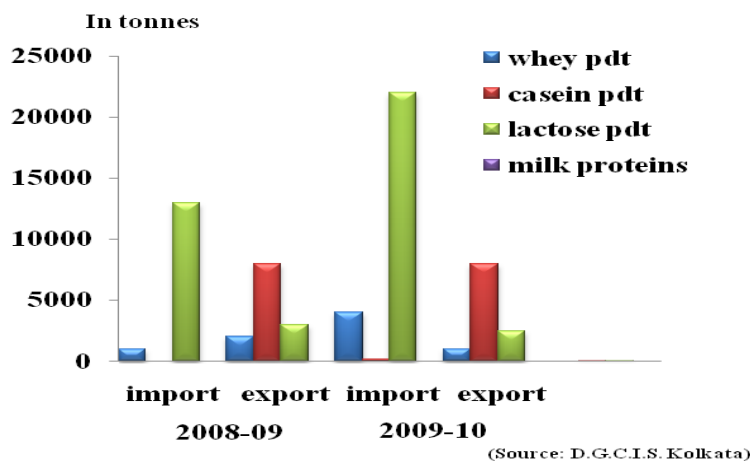


Fig. 3.1 Data on India's import and export of dairy by-products during 2008-2010

3.3 Whey and Its By-products

In India, there has been a tremendous increase in the production of cheese and coagulated milk products resulting in a proportionate increase in whey. Many large scale by-product manufacturing plants are processing whey to prepare WPC, lactose and demineralised whey powder in India. In India, the major source of whey (above 70%) is from the production of *chhana* and *paneer*, the production of which is mostly scattered over numerous small holdings. In the absence of systematic surveys/statistics, the predicted value for total whey production in India is estimated at 5 million tonnes per annum.

3.3.1 Concentrated and dried whey

Condensing and drying of whey has still not been adopted by any dairy plant in India.

3.3.2 Whey drinks

A number of refreshing whey drinks and beverages have been developed in India that include *whevit*, acidowhey, whey-based fruit beverages, whey-based soups, whey-based lassi and whey-based sports beverage. These beverages are preferably prepared from *paneer/chhana* whey, which is acidic and has low protein content (0.4%). In India, some organized manufacturers have initiated production of whey based beverages and soups and these products are fast becoming popular.

3.3.3 Demineralisation

In India, whey demineralisation is done in few plants. About 4 dairy plants have installed electro dialysis process and one plant has installed ion exchange process.

3.3.4 Ultrafiltration processing

UF is one of the most potential technologies for processing of whey to recover whey proteins in India. In India, all the lactose, the total production capacity being about 15,000 tonnes per annum, is produced from UF permeate.

3.4 Buttermilk

Buttermilk is the by-product obtained during the manufacture of butter. The exact amount of buttermilk production in India is not estimated. However, based on conversion of 6.5% of total milk production into creamery butter, it can be estimated that over 0.4 million tonnes of buttermilk is produced in organized sector annually as a by-product. In addition, a substantial amount of *lassi* (sour buttermilk) is also produced during the manufacture of *makkhan* directly from fermented milk (curd). Total annual production of buttermilk in India is estimated at 35 million tonnes. Sweet cream buttermilk resembles skim milk in gross chemical composition and is usually admixed with bulk of skim milk for further spray drying or even product manufacture in dairy plants. Desi buttermilk, on the other hand, has long been an important domestic beverage in India. It has high nutritive and therapeutic value. It also finds its way in the preparation of a host of items such as kadhi, dhokla and idli. Also a number of state dairy federations and private plants sell salted and spiced buttermilk in 200 ml pouches. Surat-based Sumul does business out of selling buttermilk (*chhach*) in and around the city. "Sumul chhach" in 500ml packs reaches practically every nook and corner of Surat, covering over 850 retail outlets. In the summer, an average sale of chhach is around 45,000 litres a day.

3.5 Ghee-Residue

Mostly dairy plants in India have not been utilising Ghee-residue profitably except for fat extraction; most of the Ghee-residue goes to waste. Only a few dairy plants are utilising Ghee-residue (GR) in chocolate sweet manufacture. According to one estimate, about 33 percent of total milk produced in the country is diverted for ghee making (Dairy India, 2007). Taking an average yield of GR as one-tenth the quantity of ghee produced, at present level of ghee production (30.4 million tonnes), the GR produced works out to more than 3 million tonnes per annum.

***** 😊 *****

PHYSICO-CHEMICAL CHARACTERISTICS OF SKIM MILK

4.1 Introduction

Skim milk is a by-product obtained during the manufacture of cream. It is rich in solid not fat content and has high nutritional value. This milk is also referred as non-fat, fat free or defatted milk.

4.2 Physico-chemical Characteristics of Skim Milk

4.2.1 Chemical composition

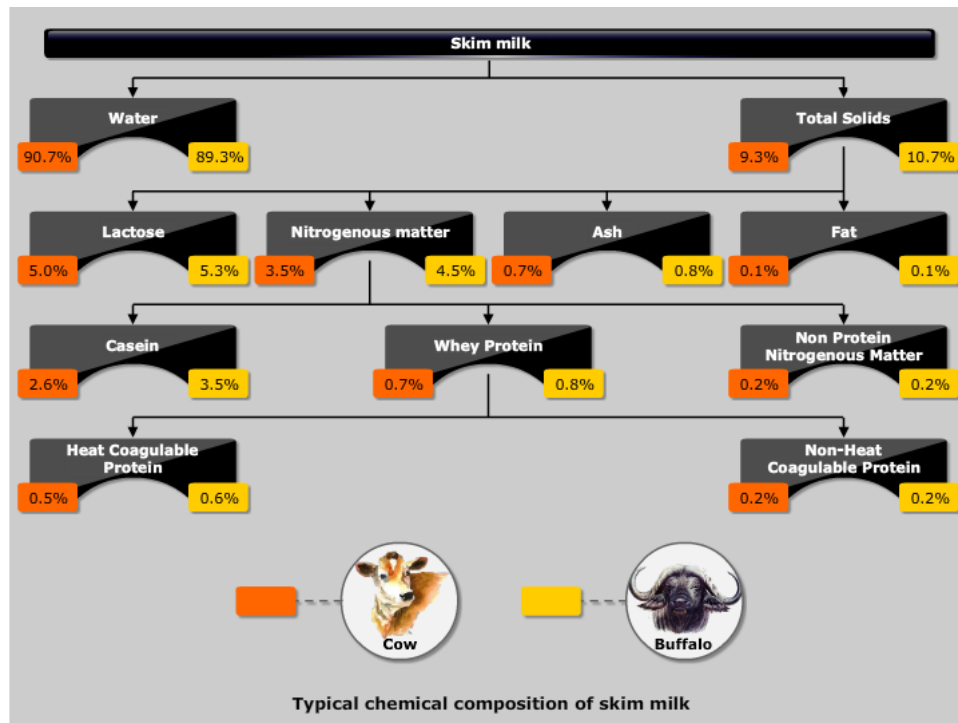
Skim milk and cream are the products of whole milk separation through a cream separator. As per FSSAI (2011) skimmed milk means the product prepared from milk from which almost all the milk fat has been removed mechanically and it should have not more than 0.5% fat and minimum 8.7% milk SNF. A fat content in skim milk below 0.1% is desirable. Buffalo skim milk contains higher total solids i.e. about 10.7% including higher lactose and protein mainly casein content as compared to cow skim milk having about 9.3% total solids. Typical chemical composition of skim milk is shown in Fig.4.1.

4.2.2 Density/ Specific gravity

The density of milk is a resultant of the densities of its components complicated by variations in the ratio of solid to liquid fat and in the degree of hydration of the proteins. Thus the density of a given specimen of milk is determined by its percentage composition, by its temperature and processing treatments. Specific gravity of skim milk at 15.5°C is 1.036.

4.2.3 Viscosity

The viscosity of the milk depends on the temperature and on the amount and state of dispersion of the solid components. Representative values at 20°C for skim milk is 1.5 cP. It is evident that the caseinate micelles are the most important contributors to the viscosity. There is decline of viscosity from 5 to 30°C, reflecting a decrease in voluminosity of the caseinate micelles. Above 30°C, the decrease is less marked until about 65°C, where the whey proteins begin to be denatured.



4.2.4 Surface and interfacial tension

The area of contact between two phases is called “interface”, or especially if one of the phases is gaseous, the “surface”. Properties of interfaces and surfaces are determined by the number, kind and orientation of molecules located in them. Surface tension of skim milk at 20°C is 51 dynes cm⁻¹.

4.2.5 Electrical conductivity

Electrical conductivity of milk is mainly due to Na, K, and Cl etc. The fat globules of milk reduce the conductivity by occupying volume and by impeding the mobility of ions. Thus the conductivity of the whole milk is less than that of skim milk by about 10%. The production of acid by bacterial action, of course, increases the conductivity of milk. Temperature control is important in the measurement, since the conductivity increases about 0.0001 ohm⁻¹ cm⁻¹ per °C rise in temperature.

4.2.6 Refracting index

Refracting index of a substance is defined as the ratio of the speed of light in a vacuum to its speed in that substance. One consequence of refraction is to change the direction of a light ray as it enters or leave the substance. Measurement of this bending gives a direct measure of refractive index. Refractive index of skim milk falls in the range of 1.3440-1.3485.

4.2.7 Solubility

Between pH 3.5 and 5.5, caseins are very insoluble which restricts its use in low pH foods.

4.2.8 Heat stability

Skim milk normally withstands heating at 140°C for 20 min, while concentrated skim milk (20% TS) is usually stable at 120°C for 20 min. Heat induced interaction between β-Lg and *k*-casein plays a major

role in determining the heat stability and rennet clotting behavior of milk.

4.2.9 Heat capacity and thermal conductivity

The heat capacity of a substance is the quantity of heat required to raise the unit temperature of a unit mass. It is usually expressed in terms of $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$. Thermal conductivity is the rate of heat transfer by conduction through unit thickness across unit area of substance for a unit difference of temperature.

Skim milk exhibits a small but definite linear increase in heat capacity between 0 and 50°C from about 0.933 to 0.954 $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$. There is a marked decrease in heat capacity as the total solids contents of the sample is increased. Dried skim milk products have heat capacities of 0.28 to 0.32 $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$ in 18 to 30°C temperature range.

***** 😊 *****

Converted in PDF By:



AGRIMOON.COM

All About Agriculture...

Lesson 5

CASEIN: CLASSIFICATION & SPECIFICATIONS

5.1 Introduction

Casein, the principal protein in milk, has been produced commercially for more than a century. Edible casein is a long established dairy by-product finding its use as an ingredient in many dairy and food products. The general development in technologies and the new uses in foods have ever increased the production and demand of this by-product. Its manufacture differs from that of non-edible casein (also called industrial casein) in that it is produced under sanitary conditions. Further, during its manufacture, food grade chemicals are to be used and sufficiently heat treated to make it safe for human consumption. Appropriate National and International standards for this by-product call for rigorous control during its manufacture. The intensive investigation in manufacturing technologies over the years and the introduction of efficient plant designs, have immensely improved the technology of caseins.

5.2 Classification

5.2.1 Classification based on coagulant

5.2.1.1 Acid casein

Acid casein can be further classified as follows:

- Direct acidification with mineral acids: Hydrochloric acid casein, sulphuric acid casein etc.
- Lactic casein: Produced by growth of lactic starter culture.

5.2.1.2 Rennet casein

Rennet casein is obtained by using rennet as the coagulant.

5.2.2 Classification based on use

Based on use of casein, it can be classified as 'edible casein' or 'industrial casein'.

5.3 Specifications

5.3.1 Standards for edible casein

There are a number of National and International standards for chemical and microbiological quality of edible casein.

5.3.1.1 National Standards

a) FSSAI (2011) Standards

According to Food Safety and Standards Authority of India (FSSAI - 2011) Standards, edible casein products mean the products obtained by separating, washing and drying the coagulum of skimmed milk. Edible acid casein means the product obtained by separating, washing and drying the acid precipitated coagulum of skimmed milk. Edible non-animal rennet casein means the product obtained after washing and drying the coagulum remaining after separating the whey from the skimmed milk which has been coagulated by non-animal rennet or by other coagulating enzymes. The products shall be white to pale cream or have greenish tinge; free from lumps and any unpleasant foreign flavour. They may contain food additives permitted in these regulations. They shall conform to the microbiological requirements prescribed in Annexure - I and shall conform to the requirements as given in Table 5.1.

Table 5.1 FSSAI (2011) compositional standards for edible casein

Requirements	Acid Casein	Non-animal rennet Casein
Moisture	Not more than 12.0 percent m/m	Not more than 12.0 percent m/m
Milk Fat	Not more than 2.0 percent m/m	Not more than 2.0 percent m/m
Milk Protein (Nx6.38) on dry weight	Not less than 90.0 percent m/m	Not less than 84.0 percent m/m
Casein in Protein	Not less than 95.0 percent m/m	Not less than 95.0 percent m/m
Ash including P ₂ O ₅	Not more than 2.5 percent m/m	Not less than 7.5 percent m/m
Lactose	Not more than 1.0 percent m/m	Not more than 1.0 percent m/m
Free Acidity	Not more than 0.27 percent	-

b) BIS Standards

According to BIS Standards, casein shall be prepared from skim milk of either cow or buffalo or a mixture of both. Casein shall be nearly white or pale cream in colour and shall have no undesirable odour or any foreign matter. It shall be free from any added colour or preservative. The size of the particles shall be such that 100 percent by weight of casein shall pass through 500-micron IS Sieve. The material shall also comply with the requirements given in Table 5.2.

5.3.1.2 International Standard (FIL-IDF 45, 1969)

The International Standard (FIL-IDF 45, 1969) defines the quality of edible acid casein (Table 5.2). Dry casein is usually in the form of a coarse powder of white to cream-yellow colour that has the odour and flavour of pure milk.

Table 5.2 National and International Standards for edible acid casein

Requirement for edible casein	International Standards (FIL-IDF 45:1969)		BIS Standards (IS:1167-1965)
	Extra grade	Standard grade	
Moisture, % by weight, max.	12	12	10
Total ash, % by weight, (on dry basis), max.	-	-	2.5
Copper, max.	5 ppm	5 ppm	-
Lead, max,	5 ppm	5 ppm	-
Iron, max.	20 ppm	20 ppm	-
Acid insoluble ash, % by weight (on dry basis) max.	-	-	0.1
Fat % by weight (on dry basis) max.	1.7	2.25	1.5
Nitrogen, % by weight (on dry basis), min.	-	-	14.5
Protein, % by weight (on dry basis), min.	95	90	-
Total acidity in terms of ml. of 0.1 N NaOH/g.	-	-	6-14
Free acidity in terms of ml of 0.1 N NaOH, max.	0.20/g	0.27/g	5.6/10 g
Lactose, % by weight, max.	0.2	1	-
Bacterial counts, per g, max.	30,000	100,000	50,000
Coliform count, max.	Negative in 0.1g		10 per g
Mould count, per g, max.	-	-	50
Moulds and Yeasts, per g, max.	50	100	-
Thermophillic organisms, per g, max.	5,000	5,000	-
Optional Requirements			
Staphylococci (beta haemolytic coagu- lase positive), per g.	Negative	Negative	-
Salmonella, per 100 g.	Negative	Negative	-

5.3.1.3 European Communities Standards

According to official standards of European countries, 'edible rennet casein' means edible casein obtained by precipitation using the technological adjuvants listed in Table 5.3 (d) which comply with the standards laid down in Table 5.3.

Table 5.3 European Communities Standards (237/30, 1983) for edible rennet casein

a)	Essential factors of composition	
1.	Maximum moisture content	10% by weight
2.	Minimum milk protein content calculated on the dried extract of which minimum casein content	84% by weight 95% by weight
3.	Maximum milk fat content calculated on the dried extract	2% by weight
4.	Minimum ash content (P ₂ O ₅ included)	7.50% by weight
5.	Maximum anhydrous lactose content	1% by weight
6.	Maximum sediment content (burnt particles)	22.5 mg in 25 g
b)	Contaminants	
	Maximum lead content	1 mg/kg
c)	Impurities	
	Extraneous matter (such as wood or metal particles, hairs or insect fragments)	Nil in 25 g
d)	Harmless technological adjuvants suitable for human consumption	
	–rennet	
	–other milk-coagulating enzymes	
e)	Organoleptic characteristics	
1.	Odour	No foreign odours
2.	Appearance	Colour ranging from white to creamy white; the product must not contain any lumps that would not break up under slight pressure.

5.3.2 Standards for industrial casein

The International Standard (FIL-IDF 45, 1969) defines the quality of casein destined for industrial use (Table 5.4). The mineral content is substantially lower in acid casein than in casein coagulated with proteolytic enzymes.

Table 5.4 International Standards (FIL-IDF 45:1969) for quality of industrial casein

Component (max)	Rennet Casein			Acid Casein		
	Extra Grade	First Grade	Standard Grade	Extra Grade	First Grade	Standard Grade
Moisture (%)	12.0	13.0	13.0	12.0	12.0	13.0
Milk fat (%)	--	--	--	2.0	2.25	2.5
Milk fat (% on dry basis)	1.0	1.25	1.50	2.25	2.5	3.0
Ash (%) (P ₂ O ₅ included)	--	--	--	2.3	2.5	3.0
Ash (% on dry basis)	7.5	7.5	7.0	2.5	2.7	3.3
Free acid (ml of 0.1N NaOH/g total solids)	--	--	--	0.33	0.88	1.32
Sediment/10 g (mg)	--	--	--	15.0	22.5	--

Lesson 6

BASIC PRINCIPLE OF EDIBLE ACID CASEIN MANUFACTURE

6.1 Introduction

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. As the initial pH value of the milk is decreased from 6.5, casein starts losing its colloidal dispersibility and stability and begins to precipitate at pH 5.3. Maximum precipitation takes place at pH 4.6, which is the isoelectric point of casein. Ion exchanges to replace cations in deproteinated whey with hydrogen ions has been applied in reducing the pH to about 1.8 prior to using the treated whey as the precipitant for acid casein. More recently, it has been proposed that ultrafiltration be used to increase the protein content of skim milk to 5-7% and to produce a permeate which is treated by cation exchange and then used to precipitate the casein. These techniques avoid incorporating the anions of hydrochloric or sulphuric acid in the whey resulting from casein manufacture and so aim to increase the value of the whey as a raw material for further processing. Casein may also be coagulated by other means, particularly proteolytic enzymes.

6.2 Processing Principle

Efficient separation of fat from milk is essential in production of edible casein. Fat needs to be reduced to the level less than 0.05%. Further, achievement of the microbiological standards for edible casein requires pasteurization of either or both the milk and the curd. The basic operations in the production of casein are the same irrespective of the type of casein produced. Such operations consist of the precipitation of the curd and its washing, pressing, and drying.

6.2.1 Precipitation

Casein exists in milk as a calcium caseinate-calcium phosphate complex. When an acid is added to milk, this complex is dissociated. As the pH of milk is lowered, the calcium is displaced from the casein molecules by hydronium ions, H_3O^+ and the calcium phosphate associated with the complex is converted into soluble Ca^{2+} ions and $H_2PO_4^-$ ions. At about pH 5.3, the casein begins to precipitate out of solution and at the isoelectric point of casein (about pH 4.6), maximum precipitation occurs. At this pH, all the calcium is solubilized. Not only is the calcium from the caseinate molecule removed, but also the calcium phosphate is liberated to the soluble form. This makes it possible to wash these soluble salts from the curd and achieve low ash content in the final product.

It might be expected that all the casein in milk would be precipitated simply by adding sufficient acid to bring the pH value to approximately 4.6. However, the reaction of acid with caseinate complex is not instantaneous and the pH will tend to rise slowly with time. Therefore, ample time should be allowed for achieving equilibrium conditions. When casein is precipitated from skim milk by the direct addition of acid, the temperature and pH of precipitation and the mechanical handling of the curd during its formation are very important in determining the subsequent properties of the curd.

Casein precipitated by acid usually includes the name of the acid in its description e.g. hydrochloric acid casein, lactic acid casein etc. but may simply be called acid casein. Any of the acid precipitation processes (hydrochloric acid casein, sulphuric acid casein or lactic casein process) can be used to produce edible quality casein. The choice of method for reducing the pH of skim milk to precipitate casein is largely governed by economics.

6.2.1.1 Temperature of precipitation

The kind of curd formed is quite sensitive to heat. Curd precipitated at temperature below 35°C is very soft and fine, and consequently, is slow to settle and difficult to wash without loss. Precipitated at temperatures between 35 and 38°C, the curd is coarse provided stirring is not too fast. Stirring is necessary to distribute the acid uniformly, but rapid stirring at temperatures below 38°C produces a curd so fine that it settles very slowly during drainage and washing and may be lost to some extent in the whey and washings. Much more rapid equilibrium, more complete precipitation and, therefore, better yields are obtained by rapid and complete mixing before precipitation. The curd can be made firm in either of two ways; by heating to a temperature above 38°C; or the pH lowered to 4.1. Curd precipitated at about 43°C has a texture resembling chewing gum, being stringy, lumpy and coarse, containing practically no fine particles, and separating cleanly from the whey.

High-grade casein, low in ash and readily soluble, is made by the grain-curd process, provided pH value and temperature are closely controlled. The best product is made by the use of hydrochloric acid, but lactic and sulphuric acids may be used successfully. The temperature of precipitation of the skim milk should be held close to 37°C for hydrochloric acid curd.

6.2.1.2 Stirring during precipitation

When acid is being added to skim milk, stirring is necessary to distribute the acid uniformly, but rapid stirring at temperatures below 38°C produces a curd so fine that it settles very slowly during drainage and washing and may be lost to some extent in the whey and washings. Much more rapid equilibrium, more complete precipitation and, therefore, better yields are obtained by rapid and complete mixing before precipitation.

6.2.2 Drainage of whey

After the precipitation has been completed and the curd has settled, whey should be removed from contact with the curd as soon as possible. The longer the curd stands in contact with the whey, the more difficult it is to wash out acids, salts, whey protein and lactose, as the freshly broken curd tends to anneal itself, thereby enclosing these constituents within a protein film.

6.2.3 Washing

The most positive quality improvement in casein is achieved through efficient washing. Improperly and insufficiently washed casein has a high acidity, is less soluble, has a lower adhesive strength, and develops a yellowish colour on drying when compared to properly washed casein. Significant amounts of lactose, minerals and acids are trapped within the curd, which prevents their ready removal during washing of the curd. It is important to keep the mineral content, particularly that of calcium, as low as possible in acid casein to maintain high solubility and low viscosity of the casein. It is necessary to allow sufficient holding time during each washing stage to permit diffusion of these whey components from the curd into wash water. The diffusion rate depends on the size and permeability of the curd particles, and the purity, amount and rate of movement of the wash water. Smaller size and better permeability of the curd particles are important for efficient washing. Three separate washes of casein curd are required with contact times of 15-20 min each. As soon as the whey is removed from the curd, wash water should be added equal in quantity to whey that has drained off. The curd should be well stirred in the wash water either by rakes or by mechanical agitators, but care should be taken not to break the curd into fine particles. Firm and friable curd particles are required to avoid creation of excessive fines. Rubbery and plastic curds cannot be washed effectively. A marked increase in the efficiency of washing can be achieved by removal of as

much whey as possible at the whey off stage. Even small amounts of whey contamination in wash water can cause a sharp decrease in washing efficiency.

An important consideration in the design and operation of a casein washing system is minimization of fine casein particles in the wash water. Processing conditions must be chosen to give firm casein curd particles at precipitation and to avoid shattering them during washing. Counter-current washing with a low wash water ratio assists in minimizing losses by restricting the opportunity for loss to one effluent wash-water flow and by minimizing the volume of such water that has to be processed to effect fines recovery.

6.2.3.1 pH of wash water

The pH of wash water should be about 4.6 for first two washings to avoid the formation of a gelatinous layer over the curd particles in excessively acid water and softening and redispersion of the curd in alkaline waters. Gelatinous layer if formed over the curd particles inhibits drainage of salts and lactose from the particles. The adjustment of same pH of wash water as that of casein facilitates in maintaining the equilibrium. For pH adjustment, sulphuric acid is preferred, as casein is much less soluble in this acid, than in hydrochloric acid. The third wash should be given with neutral water.

6.2.3.2 Temperature of wash water

Casein curd has the usual property of acting somewhat like a sponge in water, contracting to expel water when heat is applied (syneresis) and relaxing when the water temperature is lowered. On the application of heat, the curd also becomes hard and rubbery, while cold water softens it and causes the curd to be quite fragile and readily broken. The temperature of the first wash should be about the same as the precipitation temperature to give good curd shrinkage. In practice, it is usual to adjust the temperature of last wash water to 32-40°C for better expulsion of water during subsequent pressing.

6.2.4 Pressing

The objective of pressing the curd is to reduce its moisture content and thus minimising the energy required for removal of remaining water by drying. If the pressing has not been adequate, the subsequent grinding will give lumps of curd that will dry on the outside to give hard, impervious surface that prevents the escape of moisture from the inside, a condition known as case hardening. The pressing of the curd should not be for less than 12 to 15 h with 34 kg/cm² pressure.

The proportion of water in washed curd and its ease of removal depend upon the type of curd made. Precipitation of the curd at pH of 4.1-4.3, and the curd well-washed in waters, also of the proper pH and at temperatures of 41°C would give a firm, friable curd which would drain well and press well. The final moisture content is usually 55-60%.

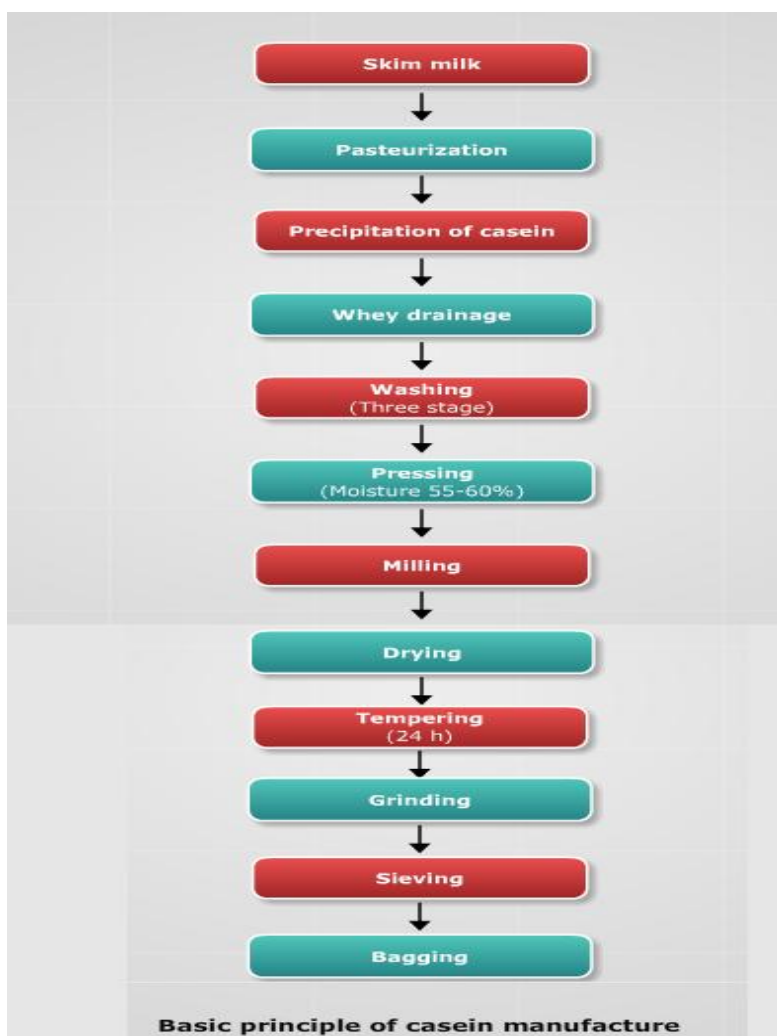
6.2.5 Milling and drying

Pressed curd is liable to deterioration by action of moulds and bacteria and therefore, should be shredded and dried as promptly as practicable. The pressed curd is milled to produce particles of uniform size and surface for drying. Otherwise, uneven drying occurs. Large particles or lumps may dry on the outside forming a hard, impervious outer surface that prevents the diffusion of the remaining moisture from the interior of the particle. The kind of grinder used is dictated by the kind of drier used. To produce a stable, storable product that meets the internationally recognized compositional standards for edible grade product, the casein curd is dried to <12% moisture in any

one of variety of drier types. Dried casein is relatively hot as it emerges from the drier and the moisture content of individual particles varies. Therefore, it is necessary to temper and blend the dried product to achieve a cooled final product of uniform moisture content. Proper control of temperature and humidity of air coming in contact with the curd are the essentials of efficient drying of casein. A temperature of 52-57°C for the air entering a tunnel drier is suitable for any type of curd. Higher temperatures may be used for well-washed curd, but they are not recommended because of the risk of discolouration and defects in the sensory attributes of the dried casein and impairing its solubility. Especially during the early stages of drying, it is desirable to circulate a portion of the air so that the surface of the particle will not become fully dried while the interior is still moist. Care should be taken that the temperature in the drier does not rise above 57°C towards the end of the drying when comparatively small amounts of water are being evaporated. Drying once started should not be interrupted, but should continue until the percentage of moisture is approximately 8%. Properly dried casein has much the same fine, granular characteristics as the properly ground curd from which it is made.

6.2.6 Tempering, grinding, sieving and bagging

Tempering means the holding of the casein for a period (24 h) to allow efficient cooling, hardening of the casein and evenness of moisture throughout the batch. Casein shows variation in moisture content during a day's run as it comes from the drier. Agitation is necessary for efficient tempering. The most efficient tempering consists of recirculating the dried casein by pneumatic conveyance. It has the advantage that air used for transport of the casein assists in cooling the curd.



The cool, tempered casein is ground. The casein must be cooled before grinding because warm casein is plastic and causes "burn on" of the rollers. An object of the grinding and sieving operation is to produce the highest proportion of the product in the size range desired by the buyer.

6.2.7 Yield

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

***** 😊 *****

Lesson 7

CONTINUOUS MANUFACTURING OF HYDROCHLORIC ACID CASEIN

7.1 Introduction

The use of mineral acids has the advantage of completely continuous operation with no holding time for coagulation. Hydrochloric acid is most commonly used as a precipitant as it is usually available at a reasonable low price and is known to produce high quality casein. When sulphuric acid or hydrochloric acid is used to precipitate curd, it should be diluted before being added to the skim milk; otherwise local action of the acid may injure the curd, even though the agitation is rapid. Within reasonable limits, the more dilute the acid, the better will be quality of casein produced. In practice, hydrochloric acid is used in dilutions ranging from 1 part in 3 to 1 part in 9 and sulphuric acid is diluted 1 part in 20.

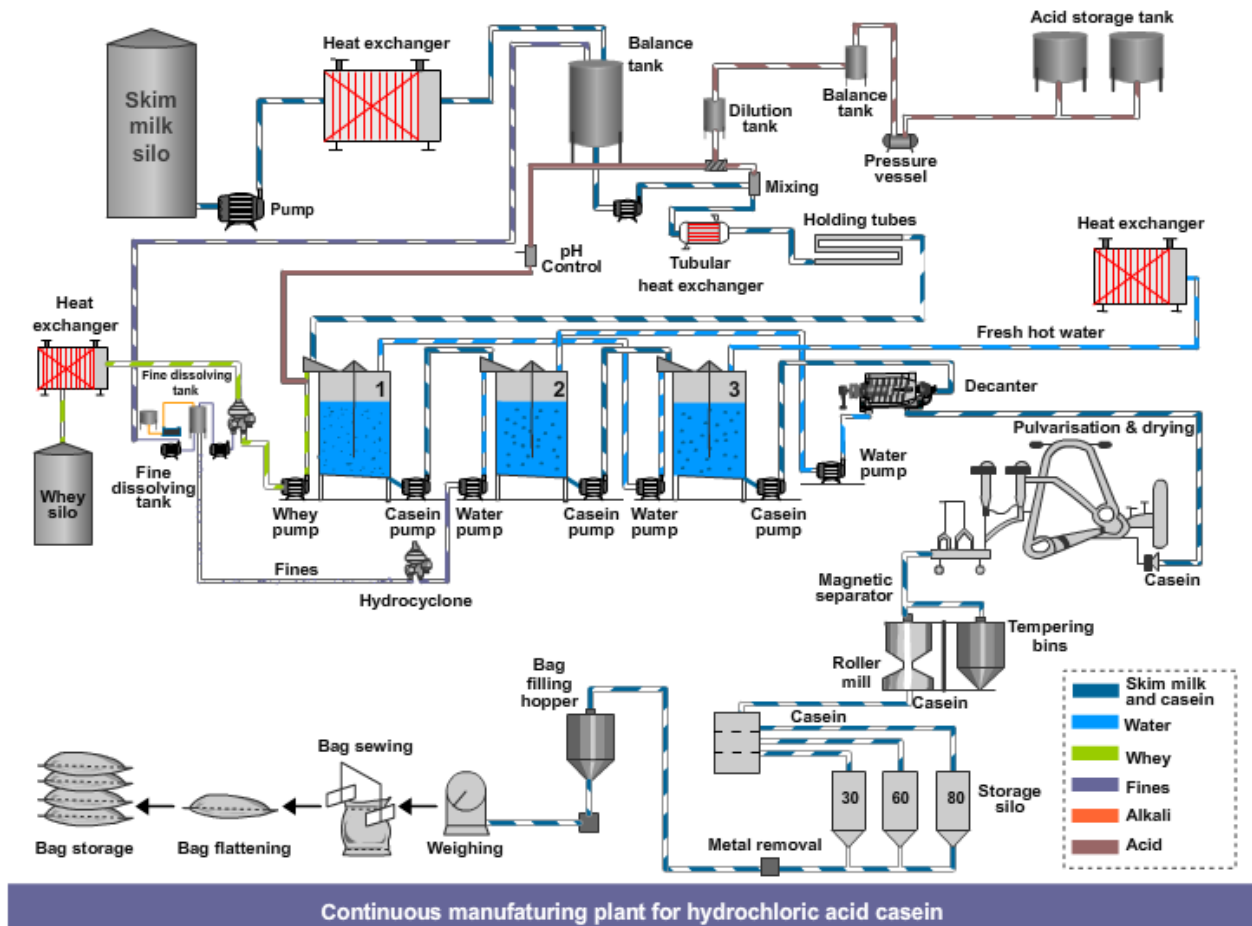
7.2 Continuous Manufacturing Process

Due to the advance in technology and automation, continuous casein manufacturing plants have taken over the batch processes for large production. These plants, not only, reduced manufacturing costs, but also elevated the status of casein for both industrial and food uses. A large casein plant with continuous hydrochloric acid precipitation having a capacity of 14000 l per h requires only one person to operate it. A typical continuous casein manufacturing plant is shown in Fig.7.1.

7.2.1 Precipitation

Thorough and rapid mixing of milk and acid is achieved by spraying dilute (1.3-1.4 N HCl) acid under pressure into skim milk flowing in the opposite direction and the rate of coagulum formation is reduced by lowering the mixing temperature to as low as 25°C (mostly, 30-35°C) to ensure that equilibrium conditions are attained before coagulation begins. It has been reported that on mixing acid and milk at 43-46°C, coagulation occurs in less than 0.1 sec and that the curd is fibrous and sticky - equilibrium state of pH cannot be attained before coagulation of curd, resulting in high ash content in casein.

The pH is stabilized by using accurate measuring pumps to ensure a constant flow of milk and acid. The mixer (acid & milk) should be designed in such a way that the acid injection into the flowing milk would induce turbulence and produce a rapid and complete mixing of both liquids. In this way a close contact between the milk and the acid prior to onset of coagulation is ensured.



Steam injection is then automatically regulated to give the desired coagulation temperature and a holding or acidulation tube is used to ensure complete coagulation and agglomeration of the curd prior to separation of the curd and whey. This method reduces fines losses to less than 1% of the casein and still allows regulation of precipitation pH and temperature to give curd with the desired physical properties for further processing.

7.2.2 Drainage of whey

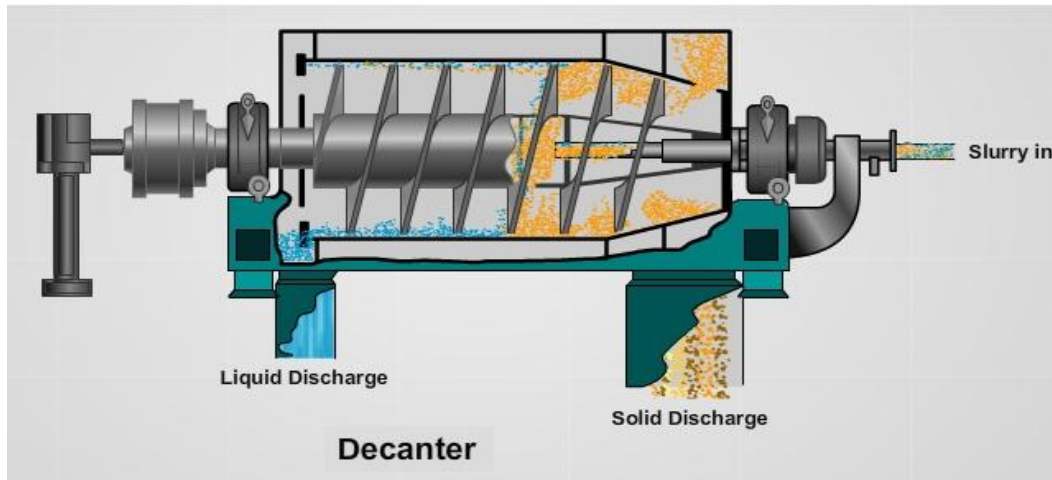
After precipitation, casein curd is concentrated by passage over stationary, inclined and fine mesh screens, which remove between 70 to 90% of the whey. Several dairy companies have installed and are successfully operating, roller presses and lately decanters for dewheying. Hydroclones or automatic desludging separators may be used to recover casein fines from whey and wash water, which may then be dissolved in sodium hydroxide and recycled for coagulation or may be recycled directly to the hot wash water.

7.2.3 Washing

For continuous washing of casein curd, the most common procedure is to use multi-stage washing system involving as many as five washing stages (mostly 3 stages), in which curd and wash water travel counter-current to each other and are separated between stages using screens. These tanks are of sufficient capacity to permit an average holding time of 20 to 30 min. This system reduces both the volume of water needed and the loss of casein fines.

7.2.4 Pressing

Continuous curd pressing is done in mechanically driven roller presses, belt or by passing through decanters, where water is sufficiently expelled for subsequent economical drying. The properties of the casein curd following washing should be such as to allow for maximum dewatering under the conditions of operation of the dewatering machine while at the same time maintaining the curd in a suitable condition for subsequent drying. The physical properties of the curd are also influenced by dewatering temperature, which should be about 39°C in case of roller press and decanter centrifuge (Fig.7.2).



7.2.5 Drying, tempering & grinding

Pneumatic ring driers, which consist essentially of a large, stainless steel, ring-shaped duct through which high-velocity, heated air and moist, disintegrated casein curd is circulated continuously, are now widely used to dry casein. The short residence time of the product in the drier avoids heat damage and individual curd particles are dried to relatively uniform moisture content before exiting with the spent air *via* a manifold into product separators. The drying air may be heated by direct combustion of propane or natural gas.

Following drying, tempering and blending, the casein is ground in roller or pin-disc mills to produce the small-size particles required by users of casein. Milled material is separated on screens to products of desired particle-sized range and oversized material which is re-cycled for further milling.

A drying technique referred to as 'attrition drying', based on the principle of grinding and drying in a single operation, is now widely used in casein plants since it allows the production of casein product closely resembling spray dried casein. The drier consists of a fast revolving, multi-chambered rotor and a stator with a serrated surface. Turbulence, vortices and cavitation effect in the drier result in highly efficient grinding, which pulverizes the curd into very small particles with a large total surface area. These particles are simultaneously dried in a hot air stream that passes through the drier concurrently with the curd. The dried casein is very fine: no particle is larger than 600 µm, about 80% are smaller than 150 µm and the overall average particle size is about 100 µm. The particles have good wettability and dispersibility in water because they are irregularly shaped and many contain cavities due to the rapid evaporative process.

***** 😊 *****

Lesson 8 MANUFACTURE OF LACTIC CASEIN

8.1 Introduction

Lactic acid casein can be prepared either of direct acidification or by lactic fermentation process. In terms of cost of acid, a lactic fermentation process is attractive especially when, with large-scale processing by modern methods, the tendency for higher capital and operational costs are minimized. In New Zealand, lactic acid casein has been the most common casein product. Lactic casein is isoelectrically precipitated from skim milk at about pH 4.6 mostly by the lactic acid produced by starter bacteria growing on lactose. Commercial lactic casein is free flowing granular powder of light cream colour.

8.2 Traditional Batch Method of Lactic Casein Manufacture

In lactic casein production, lactic acid is produced in skim milk by lactose fermentation using cultures of *Streptococcus lactis* and/or *Streptococcus cremoris*. The steps involved in production of lactic casein, are given in Fig.8.1.

8.2.1 Precipitation and curd formation

Coagulation of skim milk is performed in cheese vats. The pasteurized milk is cooled to 22-26°C and inoculated with about 0.5% starter of mixed strain (*S. cremoris* being the major culture) and incubated for 14-16 h. Mixed starters, composed largely of *S. cremoris* have been used successfully in New Zealand for many years, probably because of the build of the bacteriophages resistant strains. During incubation period, the starter ferments some of the lactose to lactic acid. As the pH of the skim milk falls slowly under quiescent conditions, the colloidal calcium phosphate in the casein micelles progressively dissolves and a casein gel network or coagulum with good water holding capacity is formed as the isoelectric pH of the casein is approached. The slow coagulating cultures are desirable as they exhibit less proteolysis and increased protein yield. The precise rate of acid production by the starter is not important as coagulation usually takes place several hours before processing begins and at about pH 4.5, the culture is in stationary phase of growth.

Traditionally, undefined mixed starters containing a gas producing component, usually "*Leuconostoc spp* or *Streptococcus diacetylactis*" have been used. A certain level of gas production is required to produce a type of curd particle that can be cooked and washed easily. The dried casein obtained from such gassy curd can be ground more easily. Too much gas production however will shatter the curd resulting in an increase in casein fine losses. Important factors in multiple strain starter selection are:

- i. The component strains must not produce inhibitory substances.
- ii. It is necessary to select the strain, which demonstrates the resistance to a wide variety of phages and maintain that resistance during long term commercial use. Strains should be phage unrelated, that is, each strain in the multiple starters should be insensitive to phages, which attack any of the strains present.
- iii. The multiple strain culture should be maintained in a deep frozen state.



8.2.2 Cutting of curd, cooking and dewheying

The set coagulum is cut with cheese knives and the agitation of the curd is started after about 2 minutes of cutting. Steam is then injected into the vat jacket at controlled rate (sufficient to raise the temperature by 0.5°C/min) to cook the casein curd to 50-60°C for whey syneresis, to facilitate the separation of curd and whey and to create a curd firm enough for subsequent processing.

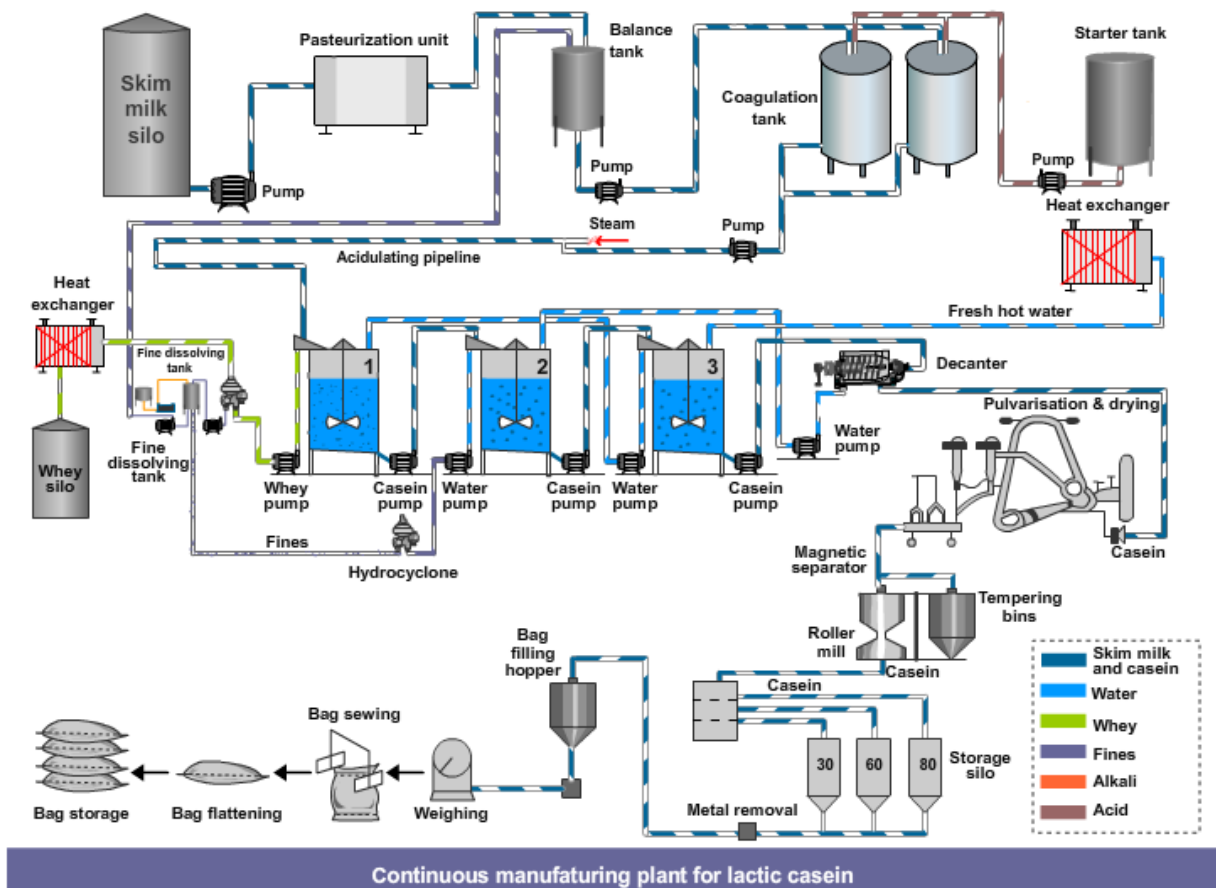
Whey syneresis is further assisted by gentle agitation of the curd for about one hour during cooking. The curd is then allowed to settle and the whey drained off.

8.2.3 Washing

The washing of lactic casein curd is done in the same way as for mineral acid casein except that a higher temperature (70°C or more) is necessary at some stage of washing to pasteurize the curd. Usually, a temperature of 75-77°C is used during second washing. After washing, the wash water is drained and the casein curd is pressed, milled and dried the same way as during the manufacture of hydrochloric acid casein.

8.3 Continuous Manufacturing Process

A more sophisticated method that reduces amount of labour and time and wash water requirement has been developed in New Zealand. This method is characterized by incubating the skim milk with starter culture in large silos (each with a capacity of up to 250 000 l) for a period of 14-16 h, which causes coagulation of milk. The curd formed is pumped and simultaneously heated to 50-60°C by direct steam injection. Further processing steps are similar to that are used in the continuous manufacture of hydrochloric acid casein. The flow diagram of the continuous lactic casein manufacture is illustrated in Fig.8.2.



***** 😊 *****

Lesson 9

MANUFACTURE OF RENNIN CASEIN

9.1 Introduction

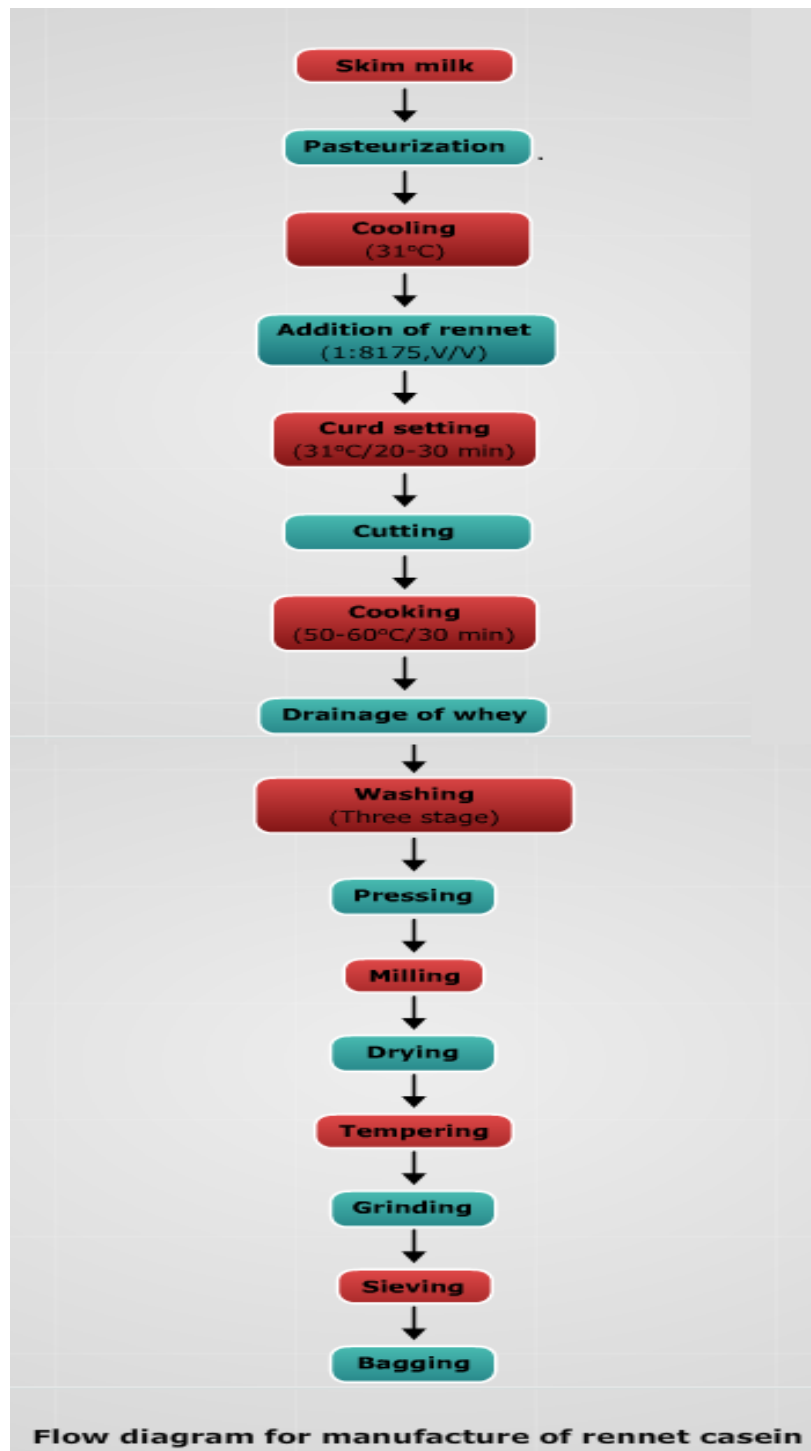
Rennin casein is obtained by the enzymatic coagulation of skim milk. Rennin casein has characteristic bland, stable flavor and high nutritional value. Industrially, rennet casein is used for the production of plastic. There is growing interest in the use of rennet casein as a food ingredient partly because of its suitability for use in making cheese analogues and partly because of its flavour stability. For the manufacture of rennet casein, several different enzyme preparations 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 rennet, 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. Rennet obtained from calf stomach has been used traditionally in the production of rennet casein, but high costs, shortages of calf rennet and being considered non-vegetarian, have encouraged dairy products manufacturers to seek acceptable alternatives. Rennet substitutes are now being widely used. Porcine pepsin, bovine gastric extracts or microbial rennet from *Mucor miehei* and *Mucor pulsillus* compares very favourably with calf rennet for the manufacture of rennet casein.

9.2 Rennin Action

The coagulation of the casein by rennin is a two-stage process. In the first stage, enzyme hydrolyses the Phe-Met (residue 105-106) bond of **k-casein** macromolecule splitting it into para **k-casein** and glycomacropeptide. The hydrophilic glycomacropeptide is released into the whey. This action destabilizes the casein micelles. In the second stage of the reaction, the remaining para **k-casein** forms a three dimensional clot in the presence of calcium ions.

9.3 Traditional Batch Manufacturing Process

High quality milk is used for the preparation of rennet casein, since milk of poor quality with developed acidity will have some of its calcium solubilized, which will result in poor curd. Poor microbiological quality of milk also results in a plastic of dark brown colour. It is important that the milk is separated efficiently because even small amount of fat in skim milk is detrimental to the quality of rennet casein prepared. In the traditional batch method, skim milk is pasteurized at 72°C for 15 s, cooled to 31°C and added with sufficient quantity of calf rennet (1: 4500) to give setting time of 20-30 min (Fig.9.1). The mixture is stirred vigorously for 10 s and then left to stand unstirred at 31°C for setting.



9.3.2 Cutting of curd, Cooking and Dewheying

The set coagulum is cut with cheese knives and the agitation of the curd is started after about 2 minutes of cutting. Steam is then injected into the vat jacket at controlled rate (sufficient to raise the temperature by 0.5°C/min) to cook the casein curd to about 50-60°C with continuous gentle agitation. Cooking of curd is further continued for 30 min at 50-60°C. Cooking process promotes whey syneresis, facilitates separation of rennet casein curd and whey, improve curd strength for further processing and minimize potential curd losses as fines during rennet casein manufacture. After the cooking process, the casein curd is allowed to settle and the whey is drained out.

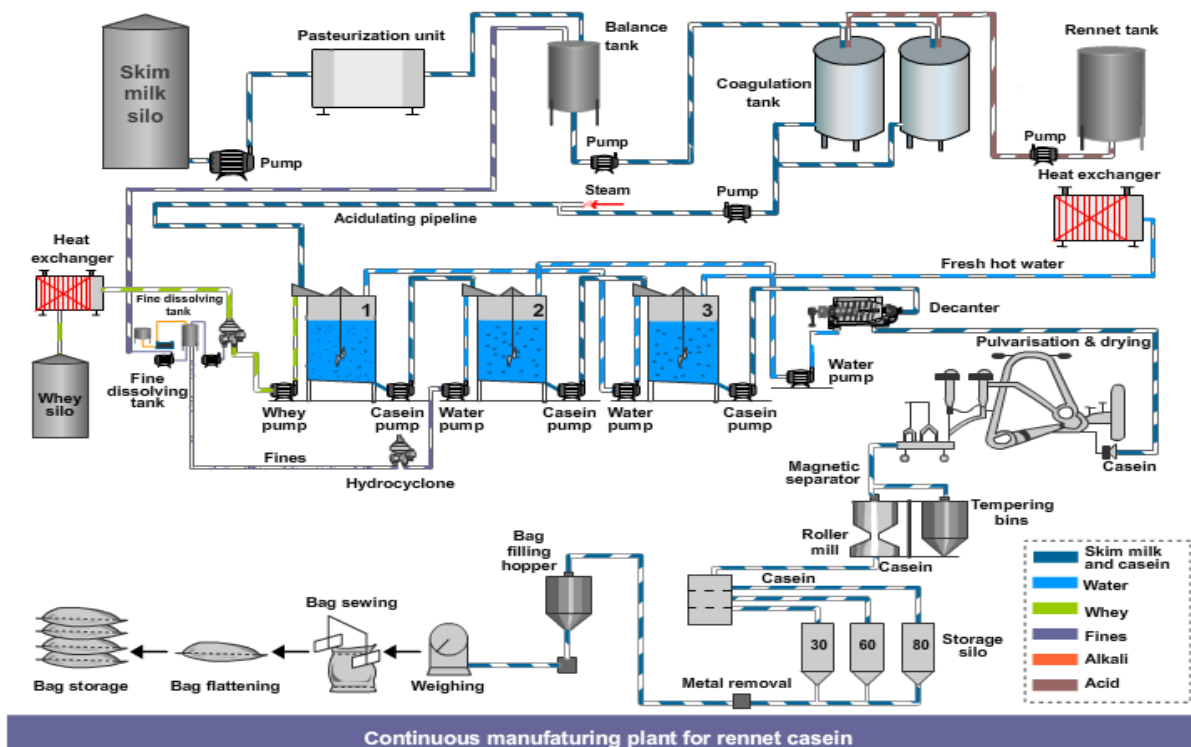
9.2.3 Washing and dewatering

After dewheying, the curd is washed with water to remove lactose, whey protein and soluble minerals, the same way as lactic acid casein curd. Washing is influenced by particle size distribution, wash water temperature, number of washings, holding time at each washing stage and degree of agitation. A typical wash water temperature profile for a four stage washing system is 30, 60, 75 and 30°C. After washing, rennet curd is dewatered to 60-70% moisture by pressing it for 10-12 h, usually overnight. Mechanical presses are usually employed for this purpose, and then the casein dried and packed in similar manner as hydrochloric acid casein.

9.3 Production of Rennet Casein by Continuous Process

In continuous rennet casein production process (Fig. 9.2), the rennet (1:7000 to 1: 8175) is mixed with skim milk stored in large silos (each with a capacity of up to 250 000 L) for setting of curd. When the coagulum has progressed to the desired stage, the gel is broken by agitation to give optimally sized curd particles for further processing and then pumped from the coagulation silo to a cooking pipe, where direct steam is injected to raise the temperature to 50-55°C. The pipe length is such as to hold the curd/whey mixture for about 45 sec for whey syneresis. After cooking, the processing steps of the rennet curd are same as for the continuous manufacture of lactic acid casein.

In continuous method, less rennet is required, less steam is required for cooking, higher processing rates is feasible and labour requirements are lower. Also, rennet casein, produced by the continuous cooking process, retains less than half the fat retained by batch-cooked rennet casein. When separated from whey, the curd is firmer than that from the batch process. When plastic is made from the rennet casein by continuous cooking, it has better clarity due to its lower fat content, but generally has gas pin-holes than did plastic prepared from traditional rennet casein.



9.4 Effect of Manufacturing Variables on Colour of Rennet Casein Plastics

The manufacturing variables that has the greatest influence on the colour of both rennet casein and rennet casein plastics are heat treatment of the milk and number of washes. Pasteurization or similar heat treatment of the milk used for casein manufacture leads to rennet casein plastics with a darker brown colour than plastics produced from unpasteurized milk. So, the rennet casein intended for use in plastics should preferably be made from unpasteurized skim milk. High lactose content in poorly washed casein also leads to brownish colour in plastics. Iron in skim milk or wash water can also discolor (reddish brown) the plastic, especially if the iron content of the casein exceeds 10mg/kg.

***** 😊 *****

Lesson 10

INDUSTRIAL USES OF CASEINS-I

10.1 Introduction

Casein is unique amongst dairy products in that it has a long history of use in foods and in non-food industrial or technical applications. The major uses of casein until the 1960s were in technical, non-food applications. Considerable efforts are being made to prepare more and more food and pharmaceutical grade casein during the past 35 years, not only because it gives better return, but also because it is an excellent protein nutritionally and functionally. Still, a sizable amount of casein for non-food uses is being prepared for industrial and technical applications. Due to their high amount of polar groups, caseinate also shows good adhesion to different substrates such as wood, glass or paper and this hydrophilicity makes caseinate films excellent barriers to non-polar substances such as oxygen, carbon dioxide and aromas. Considering different properties, caseinate-based polymers can be used in several technical applications such as protective coating and foams, paper coating, adhesives or injection moulding disposables. The specific properties of casein relevant for technical applications are listed in Table 10.1. An excess of fat present in casein may make the casein unsuitable for certain uses. In paper coating it may result in faulty imprints, in plastics it would prevent binding of the individual components, and in glues it would decrease their adhesive strength.

10.2 Application of Casein in Glues

Casein glues came to be used extensively in Europe probably in the 1890s, but they did not become widely known in the United States until 1917. When that country became involved in the First World War, a need arose for water-resistant glue for the construction of military aircraft which were made mostly of wood. Interest was aroused in casein glue, especially for plywood, and this led to a thriving industry in its manufacture. Although animal glues had been commercially important for wood gluing long before casein was used, it was difficult to make them water-resistant and their durability was consequently often poorer than that of casein. By the time aircraft construction had shifted largely to metal, casein glue was firmly established in other woodworking industries.

For marketing purposes, casein glues have been classified as (a) prepared glues and (b) wet-mix glues. Prepared glues were sold in the form of dry powders which contained all the necessary ingredients except water. The proportion of powder to water was usually about 1:2 by weight and even large batches could be prepared with a mechanical mixer in less than 30 min. Once mixed, the glues generally had to be used within a working day. Wet-mix glues were prepared by mixing together ground casein, water and additional chemicals according to the formula.

Table 10.1 Principle technical applications of casein

Product	Property	Applications	Remarks/importance
Coating	Film forming ability Adhesion Technical properties	Paints Ink Paper Packaging Leather finishing Textile coating	Still used in some paints Still used Still used To be developed Historical Historical
Adhesive	Good processability Bond strength Water resistance obtained by cross linking	Water based glue	Historical Still used in some few applications
Plastic	Strength Good mechanical properties Water resistance obtained by cross linking	Rigid plastic Disposable Fibre Coating, Film/foil in packaging application	Historical Historical Historical To be developed Laboratory scale
Surfactant	Surface tension Stability of interface	Emulsifier, detergent	Enhancement by chemical modification

Besides casein and water, an alkali must be used to dissolve the casein. This is often sodium hydroxide and provides the third ingredient in simple glue. Lime may be added if the glue is to be water resistant. The lime promotes cross-linking of the casein and, over a period of several hours, will cause a casein glue to form an irreversible jelly which is insoluble in water. Various additives may be employed to change the properties of casein glues, e.g., sodium silicate prolongs the working life of the glue while addition of a soluble copper salt such as copper chloride increases the water resistance of the glue after it has dried. Preservation of solutions of casein glue against putrefaction and mould growth may be accomplished by using chlorophenol derivatives, for instance, and the viscosity of solutions of casein glues may be reduced by addition of a viscosity-modifying agent such as urea or ammonium thiocyanate.

Casein glue is used for gluing timber in internal woodwork, such as laminated beams and arches and in interior doors, plywood, wood particle board and in bonding of Formica laminate to timber. Casein adhesives may also be used for bonding paper, in packaging and in foil laminating, in holding the seam of a cigarette together, in the seaming of paper bags, in the assembly of milk cartons and in securing the abrasive strip on the covers of match boxes.

10.3 Casein as an Adhesive in Coating Paper and Cardboard

Coated paper was developed to satisfy the needs of printers for a paper upon which illustrations, especially fine halftones, could be reproduced satisfactorily. The coating is prepared by mixing mineral material with a solution of an adhesive and applying this mixture in a thin, even layer to the surface of a sheet of paper. The function of the adhesive is to bind the coating material so firmly that it will not be removed or 'picked' off during printing. The coating material, which covers the individual fibres on the paper surface and also fills any hollows between them, forms a surface which is receptive to printing ink. After calendering (polishing), the surface of the coated paper is smooth,

even and continuous which is needed for high quality reproduction of illustrations, in particular. Casein is still a preferred binder for cast-coating and in enamel grades of coating. It is also used in coating stock, label stock and bleached kraft board for food cartons.

10.4 Casein in Sizing

In such utilizations, casein acts as a binder for the coating material, generally a mixture of mineral materials, which is applied as a thin layer on the surface of the material. Casein glue has long been used as a sizing material, sometimes for the sealing of absorbent surfaces prior to subsequent treatment. The film-forming ability of casein is retained even when deposited from a very dilute solution, and casein sizings have been used on such diverse products as shot-gun shells, heels of ladies' shoes, in varnishes, in paper making, leather finishing and textile manufacture.

Casein has also been applied to wool to reduce its felting properties and to artificial textile materials such as Nylon in order to ensure successful wearing or knitting.

The casein film may be given a high degree of water resistance by the inclusion of 'hardeners', either in the solution or by post-application to the film. Casein then becomes a permanent finish which can be applied to paper to enhance its snap, lustre or stiffness.

10.5 Paper Industry

The hydrophobic/hydrophilic balance of casein increases its affinity for pigments, its ink-binding properties and its adhesion to various substrates. In the paper industry, casein is used as size for high quality glazed papers or for fine halftone illustrations. Water resistance can be achieved by exposure to formaldehyde vapours or by dipping in concentrated solutions of formaldehyde. Formaldehyde or dialdehyde are crosslinking agents which bind free amino groups to protein to give a three dimensional network. For example, wallpaper becomes water washable by adding a coating of casein solution brushed over with a solution of formaldehyde. With high solid contents (china clay, kaolin, chalk...) coating solutions become too viscous, so in some applications, flow modifiers are added to enhance the casting process. Viscosity can be lowered by reducing the molecular weight of caseins and by denaturing the protein. This can be achieved by addition of urea, by alkaline or enzymatic hydrolysis, or by disulphide bond reducing agents such as mercaptoacetic acid or 2-mercaptoethanol. Pigments can be directly mixed with the formula to obtain coloured size and coatings. In the middle of the twentieth century, paper and board coating accounted for the major uses of casein. Nowadays casein is still used in high quality paper finishing and for enamel grades of paper, but a decline in the use of casein in paper coating can be mentioned due to casein's high costs.

10.6 Textile Industry

For producing casein fibres for textiles, acid casein is dissolved in an alkali, such as sodium hydroxide, at a concentration of about 200 g/litre, and the solution is then forced through a spinneret into a coagulating bath. The bath usually contains acid, inorganic salts and often heavy metal salts. The fibres thus formed resemble wool, except that they have a lower tensile strength and do not 'felt' (i.e. shrink on washing) like wool. The dissolved salt produces a large osmotic pressure and causes a

considerable shrinkage in the diameter of the freshly extruded filaments. It also reduces the tendency of the filaments to stick together. Aluminium sulphate is used in such coagulating baths and can also be employed with formaldehyde for stretching and hardening the fibres. The hardening of the fibres is very important since the strength of the wet casein fibres is generally less than half that of the dry fibres. Amongst the more successful hardening process developed is acetylation.

The principal proprietary casein fibres which were developed throughout the world in the decade from 1936 to 1945 included: *Aralac* (National Dairy Products Corp., USA), *Casolana* (Co-op Condensfabriek Friesland, Netherlands), *Fibrolane* (Courtaulds Ltd., UK), *Lanital* and *Merinova* (Snia Viscosa, Italy). Of these, only *Fibrolane* and *Merinova* were still in production by 1971, though two other casein fibre products were being produced elsewhere (*Wipolan*, in Poland and *Chinon*, in Japan).

Casein fibres were used during and after the war years, usually in combination with wool and other fibres, such as cotton, viscose, rayon, etc., in a variety of products, such as flannel, woolen spun cloth (overcoats, blankets), felt hats (up to 25% casein fibre with wool), filling materials such as artificial horsehair, and in carpets and rugs. Bristles were also produced from casein fibres for use in brushes of various types. Caseins also combined with acrylates become a protective coating against greying of cotton. Chemically-modified caseins, either grafted with acrylate esters or crosslinked, are used as anti-static finishing of natural (wool, cotton and silk) and synthetic (polyester) textile fibres.

The importance of casein fibre for textiles has now declined in the face of competition from other fibres. However, co-polymer fibres containing casein have been prepared in Japan as a substitute for silk, which was still being undertaken during the preparation of this article.

10.7 Leather Industry

The use of casein in the leather industry is confined almost entirely to the last of the finishing operations, which consist in coating leather with certain preparations and then subjecting it to mechanical operations such as glazing, plating, brushing and ironing. After finishing in this way, leather is said to have been seasoned. Polyol plasticised casein is used in the finishing operations in the leather industry combined with additional components such as acrylates, phenol derivatives, pigments for coloured products or binders such as gelatine or sulfonated castor oil. For application to leather, casein is first dissolved in alkalis such as ammonia, borax, sodium hydroxide or trisodium phosphate or acids. An acid solution of casein (concentration, 1-6% by weight) produces a clear, bright finish for naturally-finished vegetable tanned leather, commonly known as russet leather, to which up to five coats may be applied. The particular properties of casein which make it desirable for these applications are: its film-forming properties, adhesive strength and viscosity-enhancing characteristics, which prevent the film from running before it has set. Casein is hard, but tends to be brittle, and it is for this reason that oils and glycerol may be added to the casein solution to increase its plasticity and reduce the brittleness of the film. A casein product, treated with a chlorocarbonate plasticizer, has been proposed to overcome the natural brittleness of casein on its own. Casein may also be incorporated with other binders such as shellac, carnauba wax, blood albumin, gelatin and

sulphonated castor oil. More recently, various acrylates have been used with casein (as graft co-polymers) in leather finishing.

***** 😊 *****

Converted in PDF By:



Lesson 11
INDUSTRIAL USES OF CASEIN-II

11.1 Introduction

Rennet casein is used exclusively for making casein plastics. The high mineral content of rennet casein results in its good adhesion and plastic characteristics. Casein plastic were first produced before the turn of century, after First World War, the manufacture of casein plastics increased all over World, since that time it is estimated that over 10,000 tonnes of casein plastic have been made throughout the World each year. Rennet casein plastic has retained a place in the market mainly because it can be dyed easily, giving colourful and lustrous products. Despite the introduction of newer plastic made chiefly from petro-chemical, rennet casein continuous to be used in this field is principally for the manufacture of buttons.

Due to low frequency of secondary structures (α -helix and β -sheets), caseins are mostly random coil polypeptides with a high degree of molecular flexibility able to form typical intermolecular interactions (hydrogen, electrostatic and hydrophobic bonds). This confers upon caseins good film-forming and coating abilities. The strongly amphipathic nature of caseins, arising from the balance of polar and non-polar amino acids residues, causes them to concentrate at interfaces to form a protein film. This confers upon casein good emulsifying and stabilizing properties. In this lecture, rennet casein plastic, casein based packaging films and biomaterials, application of casein as additive in paints, in rubber products and other miscellaneous products are discussed.

11.2 Rennet Casein Plastics

Rennet casein produces a plastic, which is far superior to that of acid casein. Rennet casein plastic was first available in France and Germany under the trade name of "Galalith®" in the early twentieth century but other casein plastics have been patented under the trade names of Erinoid® (UK), Aladdinite® (USA), Casolith® (Netherlands), Lactoloid® (Ja-pan) and Lactolithe® (France). The importance of casein plastics has now declined due to severe competition from synthetic plastics with better properties. In the production of casein plastic, the casein (if ungrounded) is milled, sieved through a screen with apertures of about 600 μm and mixed thoroughly with water to final moisture content between 20 and 35%. At this stage, filler such as titanium dioxide or zinc oxide may be added to produce either a white or opaque plastic, and dyes may also be included to produce coloured plastic. The wet casein is then stored for several hours or overnight to allow the water and casein to come to equilibrium and ensure uniform moisture content throughout the whole mixture. The extrusion mixture is then placed in a hopper feeding the extruder, which consists of a screw rotating in a water-cooled barrel. The casein mixture is delivered by the screw into a heated nozzle section, where it undergoes several compression and expansion stages and is consequently formed into casein plastic. Extrusion of the plastic mass generally occurs in the temperature range of 60-100°C to produce a smooth rod or strip sheet from the nozzle section. Extruders can be equipped with up to

three screws, which may feed casein with different dyes into a single nozzle section. By manipulation of the feed rates of the casein in each barrel and alteration of the design of the mixing head where the various streams of casein plastic merge, it is possible to produce many beautiful and intricate designs in the plastic.

The warm plastic, which emerges from the nozzle of the extruder is initially soft and pliable. This is immediately immersed in cold water, which has the effect of hardening the plastic and preventing or reducing the development of internal stresses. Rods of casein plastic are subjected to 'dowelling' after they have cooled. This process trims the surface irregularities to produce smooth rods of uniform diameter. These are sliced into discs (or 'button blanks') which are subsequently placed into a dilute solution of formaldehyde for several weeks in order to 'cure' or harden the plastic. The cured blanks are later dried, machined into buttons and finally polished, usually by mechanical tumbling in the presence of wood chips and oil seeds.

If sheet plastic from casein is required, rods of casein plastic are placed side by side in a heated hydraulic press and then subjected to high pressure. The casein plastic sheet so produced must still be cured in formaldehyde for periods varying from 1 week to 6 months, depending on the thickness of the plastic. Once cured, the plastic sheets may be dried carefully to avoid rupturing the material or setting up stresses and strains within it during the expulsion of excess moisture and formaldehyde. Sheets of casein plastic still tend to warp during this process and must be straightened in low pressure hydraulic presses. Even when hardened, casein plastic can absorb moisture and its moisture content can vary according to changes in humidity. This limits its use in large panels or long rods which can warp badly.

Even though many different treatments of casein and casein plastic have been made in an effort to overcome the problems outlined above, they have not caused a significant increase in the commercial production of casein plastic. Although articles fashioned from casein plastic have included knife handles ('imitation ivory'), combs, imitation tortoise shell, pens, shoehorns and dominoes, the present range of casein plastic articles is somewhat more limited and includes buttons, buckles, novelties and knitting needles. In spite of this limitation, casein plastic articles do take up a great range of dyes to produce very attractive patterns which are somewhat more difficult to reproduce in the more common plastics made from petrochemicals.

11.3 Casein in Paints

Casein has a long history of use in paints. As paint technology evolved, synthetic resin emulsions were produced in which the ratio of casein to drying oil was much lower than in the oil-phase reinforced casein paints. The casein became the thickener and emulsion stabilizer and only a minor portion of the binder. After World War II, styrene-butadiene latex paints were developed in which casein was used mainly as a thickener and stabilizer, generally at a level of 1-2% by weight of the finished paint.

In general, casein is used in paints for its ability to disperse both white and coloured pigments and its power to thicken the binder. It may also be used as a protective colloid, as a film former and to improve flow and levelling properties of the paint. The paints are marketed in both powder and paste form.

11.4 Casein in Rubber Products

One of the less well-known applications of casein is its use as a reinforcing agent and stabilizer for rubber used in motor vehicle tyres. Casein hardened by formaldehyde was used to replace part of the carbon black used in the vulcanizing of rubber. Measurement of such properties as resistance to breaking, extensibility, resistance to tearing, hardness and abrasion of rubber which contained, for instance, 18% carbon black and 10% casein were either similar to or better than those for rubber containing 28% carbon black and no casein.

The Dunlop Rubber Company Ltd. used casein with paraformaldehyde as a protective colloid to improve the stability of a dispersion of a resin-latex composition, which was used to treat textile fibres intended for reinforcing rubber products. Casein gave significantly greater adhesion of textile fibres to rubber compared with fibres without any added casein.

11.5 Casein-Based Packaging Films and Biomaterials

Transparency, biodegradability and good technical properties (barrier properties for a polar gas such as O₂ and CO₂) make casein films innovative materials for packaging. Nevertheless, casein-based materials have two major drawbacks in common with other protein-based biomaterials: limited mechanical properties and water sensitivity.

To overcome weakness and brittleness, plasticizers are added to enhance workability, elasticity and flexibility. Plasticizers reduce intermolecular hydrogen bonding while increasing intermolecular spacing. By decreasing intermolecular forces, plasticizers cause an increase in material flexibility but also a decrease in barrier properties due to increasing free volume. To summarise, an initially hard and brittle material becomes soft and flexible when plasticized enough.

For casein-based materials, the most common plasticizers are polyols, sugars or starches owing to their miscibility with the protein and their ability to enhance elasticity and flexibility. The incorporation of polyol-type plasticizers (glycerol and sorbitol) in protein-based films causes a decrease in tensile strength and an increase in ultimate elongation. The major difference between protein- (casein or whey protein) based films and synthetic films (LDPE, HDPE and PVC wrap film) concerns elongation at break. The maximum elongation is rather low in plasticized protein - based samples (less than 85%) compared with synthetic films (from 150% for plasticized PVC to 500% for LDPE), which may limit application domains for protein based films. Compared with starch-based materials, the most commonly used substitute for synthetic polymers, milk protein-based films exhibit better mechanical properties. The second drawback of caseinate films deals with their water sensitivity and water vapour permeability. Mixing the protein with oils, waxes or acetylated monoglycerides is an easy route to drastically reduce water sensitivity. Casein can also be

hydrophobised by attachment of hydrophobic ligands, generally alkyl groups incorporated by esterification or by using monofunctional aldehydes. Water sensitivity of caseinate films can also be reduced by crosslinking with (i) calcium ions (ii) transglutaminase (iii) γ -irradiation and (iv) formaldehyde or dialdehydes. As for other protein materials, casein based films are hydrophilic, making them excellent gas barriers to non-polar substances such as oxygen, carbon dioxide and aromas. Casein based films and biomaterials obtained from caseinates can find many applications in packaging in edible films and coatings for fruits and vegetables or in mulching films.

11.6 Miscellaneous Technical Applications of Casein

Casein presents good metal and ion binding properties, making it suitable for absorbing and recovering chromate in wastes from manufacturing processes such as electroplating and water purification. Amongst the large number of other technical (non-food) applications where casein has been used (or at least claimed to be used) are in cleaners and dish washing liquids, hair setting products and cosmetics and cheese marks. In cosmetics, caseinate is used as surface active agent in soaps and various cosmetics such as cold wave lotions, hair sprays and hand cream. Casein hydrolysates could also be active substances for skin hydration. However, little information is available about these applications and their markets, which seem rather limited.

In building and civil engineering, uses for casein are claimed in the preparation of bitumen emulsions, in light weight concrete, in gypsum wallboards, in the preservation and restoration of old stone buildings and as a foaming agent for de-icing equipment, roads and run ways. In printing, casein is claimed to be used as a film-forming transfer regulator in a thermal printing adhesive ink and as a binder for a printable coating on a foamed polystyrene sheet. Casein has been used in photo etching for the production of shadow masks for colour television sets, computer circuitry and electronic ignition components for motor vehicles. Cross-linked casein has been used for water purification and for recover of chromium from waste electroplating liquors. In agriculture and horticulture, casein has also been used in insecticide sprays (as a spreader), in fungicides (as an adhesive), as a fertilizer and in coated seeds (as an adhesive).

***** 😊 *****

Lesson 12

MANUFACTURE OF SODIUM CASEINATE

12.1 Introduction

The soluble form of casein, 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). For the manufacture of caseinates, fresh acid casein curd is preferred over dried casein as 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 the casein. However, in countries that import casein, buyers may still prefer to purchase casein and produce their own sodium caseinate. Casein should have a low calcium content ($< 0.15\%$ dry basis) in order to produce a caseinate solution with a low viscosity, and a low lactose content ($< 0.2\%$ dry basis) to produce sodium caseinate with the best colour, flavour and nutritional value. Control of the curd characteristics is also important to ensure rapid dissolution.

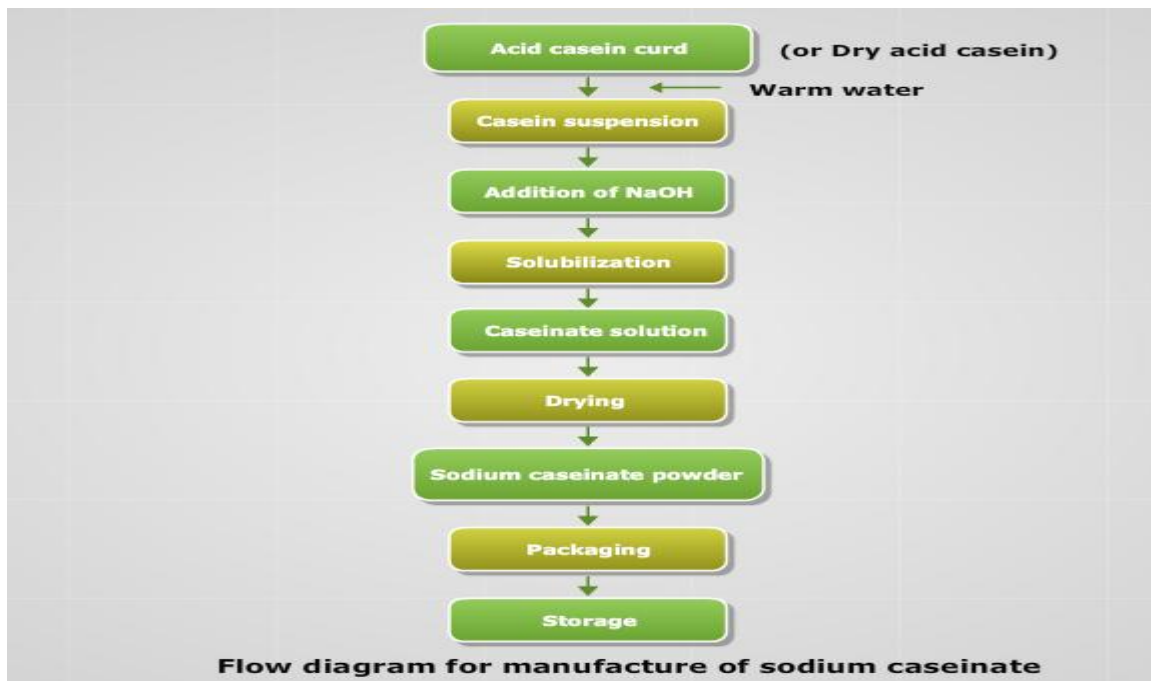
Sodium caseinate is the most commonly used water soluble form of casein and is used in wide range of processed food products as a source of protein, and for their physico-chemical, nutritional and functional properties.

12.2 Manufacture of Sodium Caseinate

Irrespective of the starting material used, the manufacture of sodium caseinate consists of: formation of a casein suspension, solubilization of casein using sodium hydroxide, and drying the sodium caseinate produced (Fig.12.1).

12.2.1 Casein suspension and solubilization

The fresh casein curd passed from a de-watering device (about 45% solids) is minced and the finely-divided curd mixed with water at 40°C to give a solid content of 25-30% solids. If dried casein is used, it is ground and held in water for sometime so that it absorbs water and becomes softened. Casein suspension is then passed through the colloid mill. The temperature of the emerging slurry, which may have the consistency of 'toothpaste', should be below 45°C, since it has been observed that milled curd can re-agglomerate at higher temperatures.



The main difficulties experienced in the conversion of acid casein to 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) 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.

12.2.2 Addition of alkali and pH control

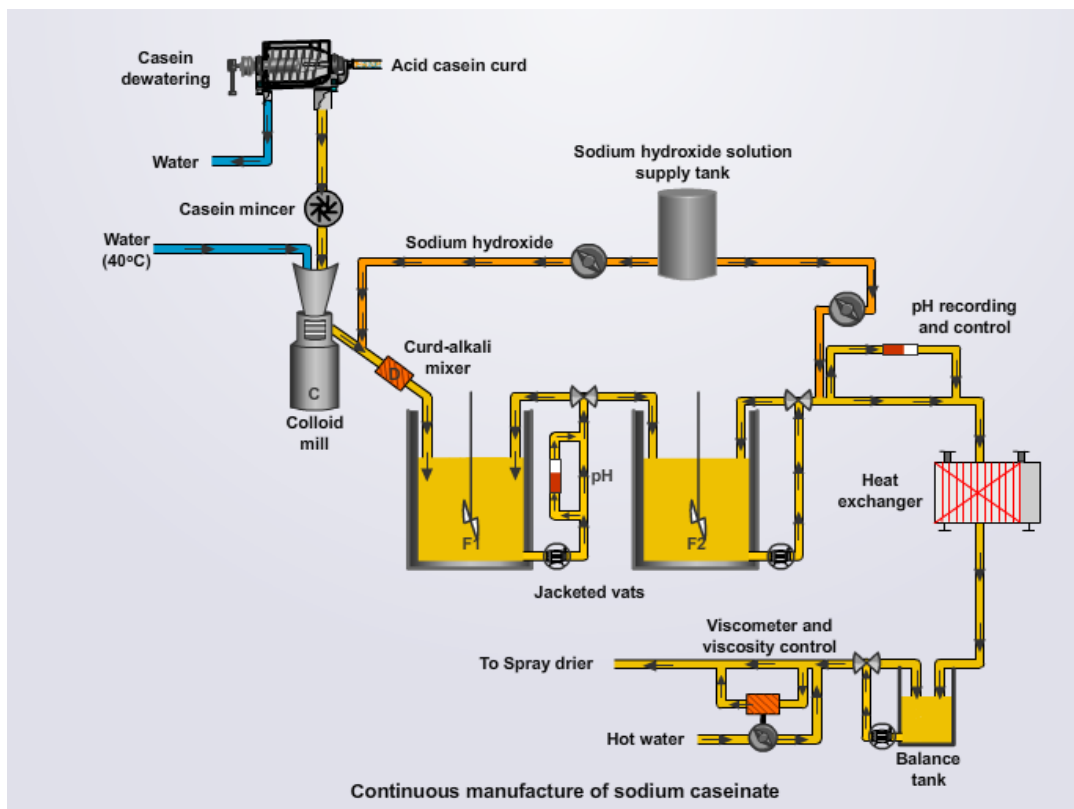
Sodium hydroxide solution with strength of 2.5 M is pumped into the casein slurry, emerging with the consistency of 'toothpaste' from the colloid mill at $>45^{\circ}\text{C}$. The quantity of sodium hydroxide required is generally 1.7-2.2% by weight of the casein solids. Other alkalis such as sodium bicarbonate or sodium phosphates may be used, but the amounts required and their cost is both greater than those of sodium hydroxide. Hence, they would generally be used only for specific purposes such as in the manufacture of citrated caseinates. The addition of the dilute alkali must be carefully controlled with the aim of reaching a final caseinate pH of 6.6-7.0 (generally about 6.7). The recommended technique for achieving the correct caseinate pH is to add sufficient alkali to bring the pH close to, but below, the specified value and then add the additional alkali needed towards the end of the dissolving operation. This technique is used for following main reasons

- Firstly, because reduction of the pH of a sodium caseinate solution by addition of acid is likely to cause localised precipitation of casein, and

- Secondly, the development of any off-flavours associated with localised conditions of high alkalinity is minimized.
- A third reason is the potential for formation of lysinolamine when the pH is excessively high (e.g. > 10).

12.2.3 Dissolving

The casein alkali mixture is transferred to first dissolving vat, where it is recirculated and/or pumped to a second dissolving vat where solubilisation is completed as the solution temperature is raised to about 75°C. An in-line pH meter is used to monitor and regulate the addition of the NaOH solution. The viscosity of sodium caseinate solutions is a logarithmic function of the total solid concentration. Each dissolving vat, therefore, must be equipped with a powerful agitator and a high speed recirculating pump (Fig.12.2 F₁, F₂). In addition to concentration, other factors which affect viscosity of sodium caseinate solutions are temperature (semi-logarithmic), pH, calcium content of the curd, type of alkali used and seasonal and genetic factors. Once the solution is prepared, it is important to raise the temperature as quickly as possible to 60-75°C to reduce the viscosity. However, 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. For this, all joints on pipes, especially on suction side of pumps, must be airtight and recirculation line must discharge below surface of liquid in dissolving vat. In view of the many variables which can affect the viscosity of sodium caseinate solutions, it is considered desirable to standardize them to a constant viscosity, rather than to a constant concentration, prior to drying.



12.2.4 Drying of sodium caseinate solution

The homogeneous sodium caseinate solution is usually spray dried in a stream of hot air. In order to ensure efficient atomization of the sodium caseinate solution, it must have a constant viscosity as it is fed to the drier. It is common practice to minimise the viscosity by preheating the solution to a temperature of 90-95°C just prior to spray drying. However, care should be taken to minimise the time for which the caseinate solution is at high temperature.

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 highest possible caseinate concentration is determined experimentally for every spray drier. At about 20% solid concentration of the sodium caseinate solution, approximately 4 kg of water need to be evaporated to produce 1 kg of powder. Hence, the solids output from a drier used for caseinate is about one quarter of that when used for drying of skim milk (feed concentration usually 45-50% solids). However, it is possible to increase the inlet air temperature in order to increase the water evaporation rate. Thus, while steam radiators may produce inlet air temperatures of up to 170°C, it is possible (with indirect oil heating or direct gas firing) to produce inlet air temperatures of up to 260°C. The warm spray dried sodium caseinate powder is cooled in a fluid bed drier. The low solids content of the feed solution produces a spray-dried powder with a low bulk density. It may vary from 0.25 g/ml to 0.40 g/ml. Generally, pressure nozzle dryers, operating at 100-250 bar, produce caseinate with a higher bulk density than that from disc atomizing dryers. The powder particles produced on disc dryers tend to be in the shape of hollow spheres. Since the powder is so light, the losses from the product recovery cyclones may be rather high, and it is, therefore, considered prudent to install bag filters for improved recovery. The moisture content of spray-dried sodium caseinate should be less than 5% for satisfactory storage and this appears to be consistent with many product specifications.

12.2.4.1 Alternative method of sodium caseinate drying

Other methods used to reduce cost, increase processing rate during caseinate manufacture and control the properties of the resulting powders, include:

- Production of roller dried sodium caseinate by feeding a mixture of curd (50-65% moisture) and an alkaline sodium salt (Na_2CO_3 or NaHCO_3) onto the drying drum of a roller-drier. Sodium caseinate with good flavour and a high bulk density could be produced by using the roller drier at relatively low steam pressure (i.e. low drying temperature).
- Production of granular sodium caseinate by lowering the moisture content of acid casein curd to < 40%, reacting the curd with Na_2CO_3 with agitation for up to 60 min and drying the resultant caseinate in a pneumatic ring drier or a fluidized bed drier. The resulting caseinate has a higher bulk density and improved dispersibility compared to spray and roller dried product.
- Drying a mixture of acid casein curd (45% dry matter) and Na_2CO_3 in an attrition drier to produce a product that looks like spray dried sodium caseinate but which has a much higher bulk density.
- Spray drying sodium caseinate solutions of higher solids content (up to 30%) in a drier fitted with a modified atomizer disc or preparation of concentrated caseinate solutions (33-47%

solids) by a modified procedure and drying these solutions in spray or roller dryers or by an extrusion drying method.

- Conversion of casein to caseinate in the presence of a limited amount of water using extrusion technique. Commercially, casein in powder form is introduced and transported with water continuously into an extruder machine. An alkaline reagent is introduced in second step and whole mixture subjected to intense kneading under pressure with a rise in temperature to initiate chemical reaction between casein and alkaline reagent. The mixture is subjected to second intense kneading under pressure and intense shear to finish off chemical reaction with temperature of mixture rising to cause mixture to melt and to obtain a viscous caseinate paste. It is then cooled with a degassing operation to reduce and adjust its temperature and viscosity. Finally caseinate paste is extruded at 70-90°C with 30-40% moisture to form a continuous strand of caseinate paste at outlet from extruder machine. A continuous thin sheet of caseinate paste is formed from strand. The sheet of caseinate is simultaneously cooled to a temperature below 20°C and cut longitudinally into a plurality of parallel strips. Strips are then cut into small sized pieces of caseinate.

***** 😊 *****

Lesson 13

MANUFACTURE OF OTHER CASEINATES

13.1 Introduction

Next to sodium caseinate, calcium caseinate is common and finds use in both pharmaceutical preparations and as a food ingredient. The specifications for this product vary with its end use, but they frequently include a limitation of the calcium content to within the range of 1.0-1.5%. Various countries have prescribed varying specifications for caseinates. 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.

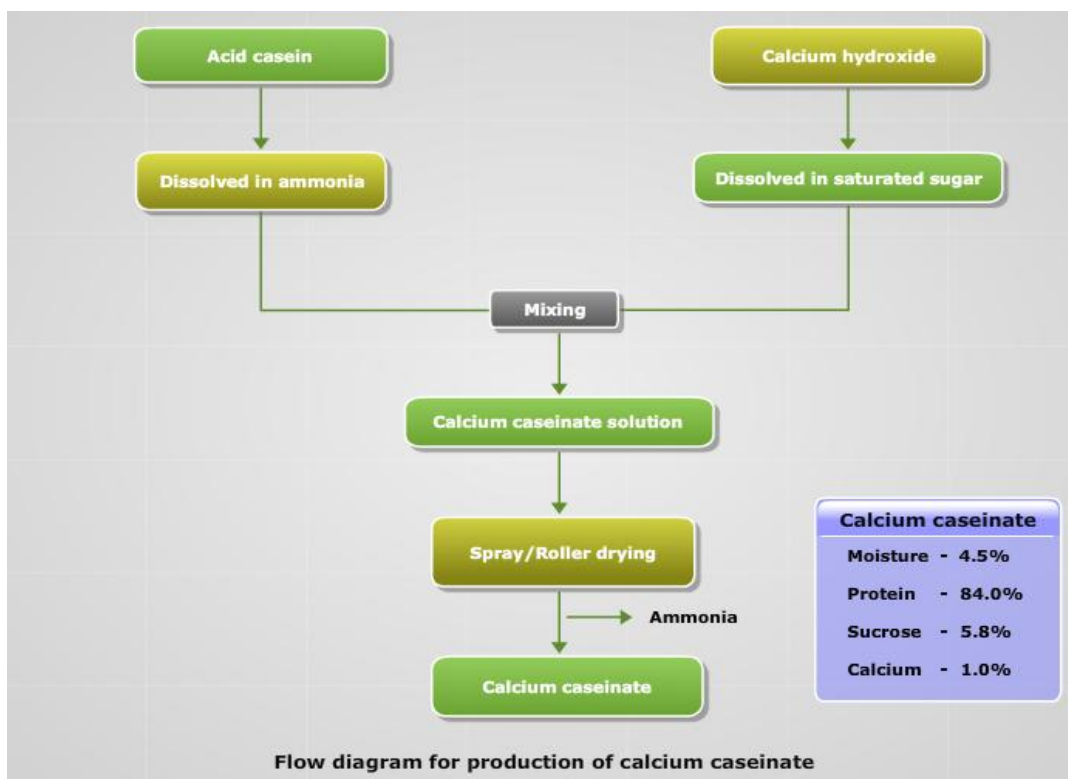
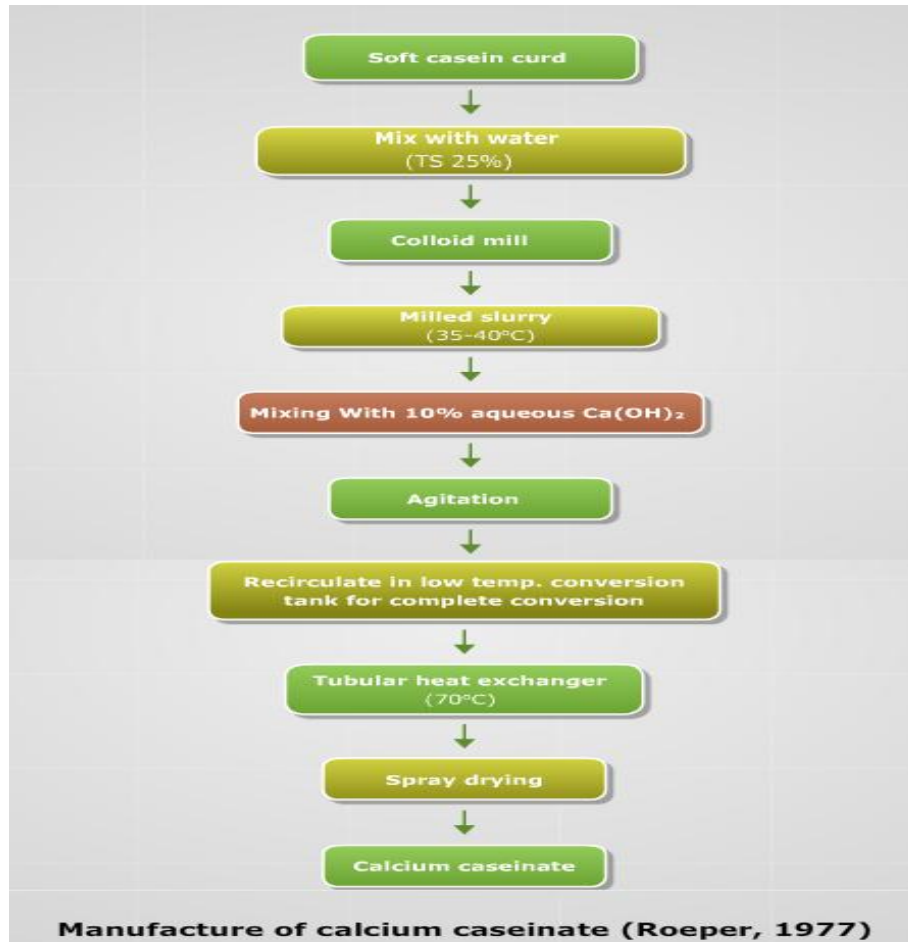
13.2 Calcium Caseinate

Its preparation follows the same general process as that used for sodium caseinate with one or two important exceptions. Calcium caseinate solution is destabilized on heating especially at pH values below 6. This sensitivity decreases with an increase in pH or a decrease in 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 most commonly used in the production of calcium caseinate) proceeds at a much slower rate than that between curd and sodium hydroxide. The temperature of conversion is a particularly important factor in determining the completeness of solubility (assessed from the amount of sedimentable matter) of the calcium caseinate. Therefore, the dissolving process must be closely monitored to ensure production of calcium caseinate with a good solubility.

The optimum process as recommended by Roeper (1977) is: pass 'soft' casein curd through a mixer to give evenly-sized particles, mix with water to about 25% total solids, pass the mixture through a colloid mill and adjust the temperature to give a milled slurry at 35-40°C; mix the slurry with a metered volume of 10% aqueous calcium hydroxide to give the desired final pH; agitate and recirculate in a low-temperature conversion tank until conversion is complete (>10 min); heat the dispersion in a tubular heat exchanger to 70°C and pump directly to a spray drier (Fig.13.1). Calcium caseinate then packaged and stored in a cool, dry place.

The common associated problems in the manufacture of calcium caseinate have led to an examination of alternative methods of producing calcium caseinate. Calcium hydroxide is soluble in sugar solutions and may, therefore, be used in this form for reaction with acid casein. In order to increase the rate of reaction between casein and calcium hydroxide, the casein may first be dissolved completely (and rapidly) in ammonia (Fig.13.2). Calcium hydroxide solution of sugars (sucrose, glucose, galactose, lactose or fructose) is then added and the solution of calcium caseinate dried by means of a roller drier. Most of the ammonia evaporates during processing, leaving a relatively pure

calcium caseinate (protein 84%, sucrose 5.8%, moisture 4.5%, calcium 1.0%) with nutritional properties similar to those of the original casein.



13.3 Ammonium/Potassium/Citrated Caseinates

Ammonium and potassium caseinates may be prepared by a method similar to that used for the production of sodium caseinate by substituting NH_4OH or KOH for NaOH . Granular ammonium caseinate may be prepared by exposing dry acid casein to ammonia gas and removing excess ammonia with a stream of air in a fluidized bed degassing system. Citrated caseinate has been 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 NaOH .

13.4 Other Caseinates

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.

13.5 Specifications of Caseinates

The quality standards for caseinates vary from country to country. As per FSSAI (2011), edible caseinate means the dry product obtained by reaction of edible casein or fresh casein curd with food grade neutralising agents and which have been subjected to an appropriate heat treatment. It shall be qualified by the name of the cation and the drying process used (Spray or Roller dried). The product shall be white to pale cream or have greenish tinge; free from lumps and any unpleasant foreign flavour, it may contain food additives permitted in these regulations. It shall conform to the microbiological requirements prescribed in Annexure - I. It shall conform to the requirements as given in Table 13.1.

Table 13.1 FSSAI (2011) compositional standards for edible sodium caseinate

Requirements	Caseinate
Moisture	Not more than 8.0 percent m/m
Milk Fat	Not more than 2.0 percent m/m
Milk Protein (Nx6.38) on dry weight	Not less than 88.0 percent m/m
Casein in Protein	Not less than 95.0 percent m/m
Lactose	Not more than 1.0 percent m/m
pH Value in 10% solution	Not more than 8.0

The typical chemical composition of caseinates is given in Table 13.2. Within a general pH range of 6.5-7.0, sodium caseinate will usually contain 1.2-1.4% sodium, while the calcium content of calcium caseinate is generally in the range, 1.3-1.6%.

Table 13.2 Typical composition of caseinates

Composition	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

***** 😊 *****

Lesson 14

PRODUCTION OF CASEIN HYDROLYSATES

14.1 Introduction

Protein hydrolysis is an ancient technology used for centuries all around the world. Today, protein hydrolysates have assumed a new dimension in food industry. The manufacture of protein hydrolysates is a well-established process for the utilization of protein rich food by-products, wastes and non-conventional food proteins. Historically, soy sauce was the first protein hydrolysate. The fundamental flavour characteristic of a protein hydrolysate is suggestive of meat flavour. Therefore, hydrolysates are used by packer, canners and other manufacturers to accentuate or to suggest the flavour of meat. Casein is an important substrate for the preparation of milk protein hydrolysates.

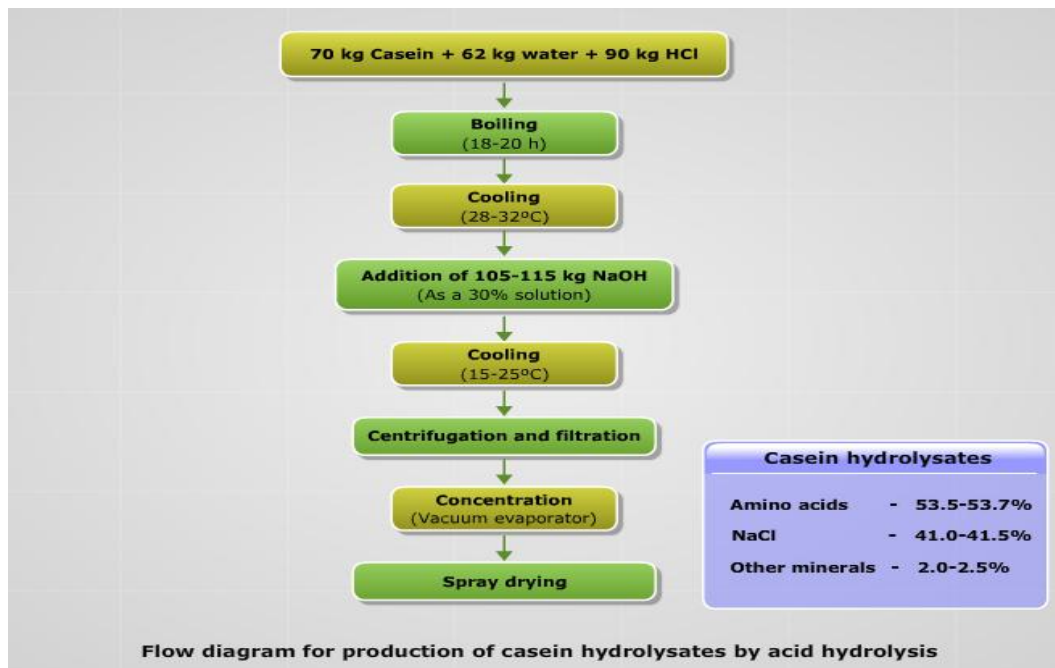
The extent of protein hydrolysis, which represents the extent of protein breakdown to peptides and amino acids, is expressed either as percent amino nitrogen or as degree of hydrolysis (DH). Degree of hydrolysis is the ratio of the number of peptide bonds cleaved and the total number of peptide bonds in the intact protein. In the manufacture of casein hydrolysates, per cent DH is one of the important controlling factors, which reflect on the product quality.

14.2 Processes of Casein Hydrolysates Manufacture

Basically, there are two methods for the manufacture of protein hydrolysates, viz. acid hydrolysis and enzymatic hydrolysis, however, there are also reports of use of alkali for the manufacture of hydrolysed protein.

14.2.1 Acid hydrolysis

In this process, casein or caseinates are allowed to react with arsenic-free hydrochloric acid (35-45%) or sulphuric acid for a period of 4-18 h. The reaction is carried out at higher temperature (80-100°C) either at atmospheric or higher pressure. Thereafter, the content is neutralized to pH 6.0-7.0 by an alkali. The product is then either concentrated or dried. The process details given in a patent comprises of mixing 70 kg casein with 62 kg water and 92 kg purified arsenic-free hydrochloric acid (sp.gr. 1.17 and 34% concentration), and boiling with stirring for approximately 18-20 h until casein is fully broken (Fig.14.1). This is followed by cooling to 28-32°C and gradual addition of 105-115 kg pure sodium hydroxide (as a 30% aqueous solution) to the mixture to bring the pH to 6.6-6.7. The neutralized mixture is then cooled to 15-25°C and then purified by centrifugation and filtration. The clear liquid is spray dried at 95-100°C obtaining a readily water soluble powder. It contains 53.5-53.7% amino acids, 41-41.5% NaCl and 2.0-2.5% other minerals.



Although acid hydrolysis has been used for preparing casein hydrolysates, the process has some limitations. The acid hydrolysis ordinarily entails the complete or partial destruction of some of the amino acids like tryptophan. This process also possess problem of removing residual acid from the products of hydrolysis. Neutralization of acid employed for hydrolysis result in the formation of salts which in turn becomes another limiting factor in food/ dietic applications.

Use of mont morillonite to inhibit discolouration, normally experienced during acid hydrolysis at high temperature, has been successfully tried. The hydrolysis of milk protein is carried out at 80-95°C by non oxidizing acids (e.g. HCl and/or H₂SO₄) in the presence of (i) orthophosphorus acid and/or its salts and (ii) acid activated mont morillonite. Similarly for preparing colourless, odourless and tasteless acid hydrolysate, suitable for pharmaceutical industry, use of methanol has been reported.

14.2.2 Alkalzne hydrolysis

This is another process of manufacturing casein hydrolysates. However, it is not effective method as it leads to the destruction of some and the recemisation of most amino acids. It also results in partial chemical hydrolysis, oligomerisation and destruction of functional groups of amino acid residues.

14.2.3 Enzymatic hydrolysis

Enzymatic hydrolysis of protein is preferred over acid or alkali hydrolysis as the former causes no destruction or racemization of the amino acids and nutritional quality of the original protein is retained. This process of hydrolysis of casein results in product with high content of water soluble nitrogen and low salt. Production of casein hydrolysates by enzymatic hydrolysis is given in detail in next chapter.

Lesson 15

ENZYMATIC PRODUCTION OF CASEIN HYDROLYSATES

15.1 Introduction

Proteolytic enzymes are used to produce casein hydrolysates. These enzymes have ability to hydrolyse proteins to peptides and amino acids. The chain length of peptides formed is dependent upon the extent of hydrolysis, condition of hydrolysis, type, concentration and activity of enzyme, and type of protein to be hydrolysed. Proteolytic enzymes could be obtained from plant (Papain, Ficin, Bromelain), animal (Pepsin, Trypsin, Rennin) microorganisms (Neutrase, Alcalase, Esperase, Pronase etc.).

15.2 Classification of Enzymes

On the basis of their specificity of action, enzymes can be classified into:

15.2.1 Endopeptidases

These enzymes have preference for certain side chains on amino acids adjoining peptide bond and are usually divided into three groups:

- i. Pepsin type of protease is characterized by a preference for amino acids with free carboxyl groups
- ii. Trypsin types are characterized by a preference for amino acids with basic group
- iii. Chymotrypsin types are characterized by a preference for amino acids with aromatic or bulky chains.

Papainase type enzymes (Papain, chymopapain, ficin, bromelain) are endopeptidases, but are difficult to classify under this scheme.

15.2.2 Exopeptidases

These are mostly microbial enzymes that split terminal amino acids from one end of the chain by hydrolysis of peptide bond. They can be further divided in two groups:

- i. Carboxy (exo) peptidases that act on the terminus of chain carrying free carboxyl group
- ii. Amino (exo) peptidases that start from the other end i.e. the terminus of chain carrying free amino group.

Choice of the protease for protein hydrolysis depends mainly on its specificity and also on its pH optimum, heat stability and the presence of activators or inhibitors. pH optima of pepsin, papain and pancreatin are 3.0, 7.0 and 8.0, respectively. Individual endopeptidases do not split all or even a majority of the peptide bonds in a protein system leading to the formation of bulky, hydrophobic acid

chains, which give bitter taste. Exopeptidases are reported to hydrolyse carboxyl and amino terminal amino acids of such peptides, thus eliminating the bitter taste.

15.3 Enzymatic Production of Casein Hydrolysates

Hydrolysis of casein has been mostly carried out as a single stage process (where enzyme is added once during the hydrolysis period) and a two-stage process (where two or more enzymes are added at subsequent intervals of hydrolysis). The general steps in the manufacture of protein hydrolysates include suspension of protein in appropriate amount of water, incubation with enzyme at appropriate pH and temperature in the presence of preservative like chloroform, pasteurize to inactivate enzymes, removal of insoluble material by centrifugation, concentration, drying and packing in moisture proof container.

15.3.1 Single stage hydrolysis

In single-stage hydrolysis process, the common enzymes used have been pepsin, papain, trypsin, pancreatin and microbial proteinases, though other proteolytic enzymes: Corolase PS, Corolase L10, Maxatase LS 400,000, Novozym 257 etc. can also be used. In one method, three enzymes - pancreatin, proteinase of *Aspergillus oryzae* and *Lactobacillus helveticus* were added to 10% casein solution and incubated at 50°C for 24 h. Inactivation of proteolytic enzymes was done by heating at 85°C for 15 min. The solution was cooled to 5°C and centrifuged at 1,200 x g for 20 min to remove the precipitate. About 91% of the total casein nitrogen remained in the supernatant.

15.3.2 Two stage hydrolysis

In a two stage process, combination of different enzymes have been used. Some of important two stage casein hydrolysis processes suggested are as follow:

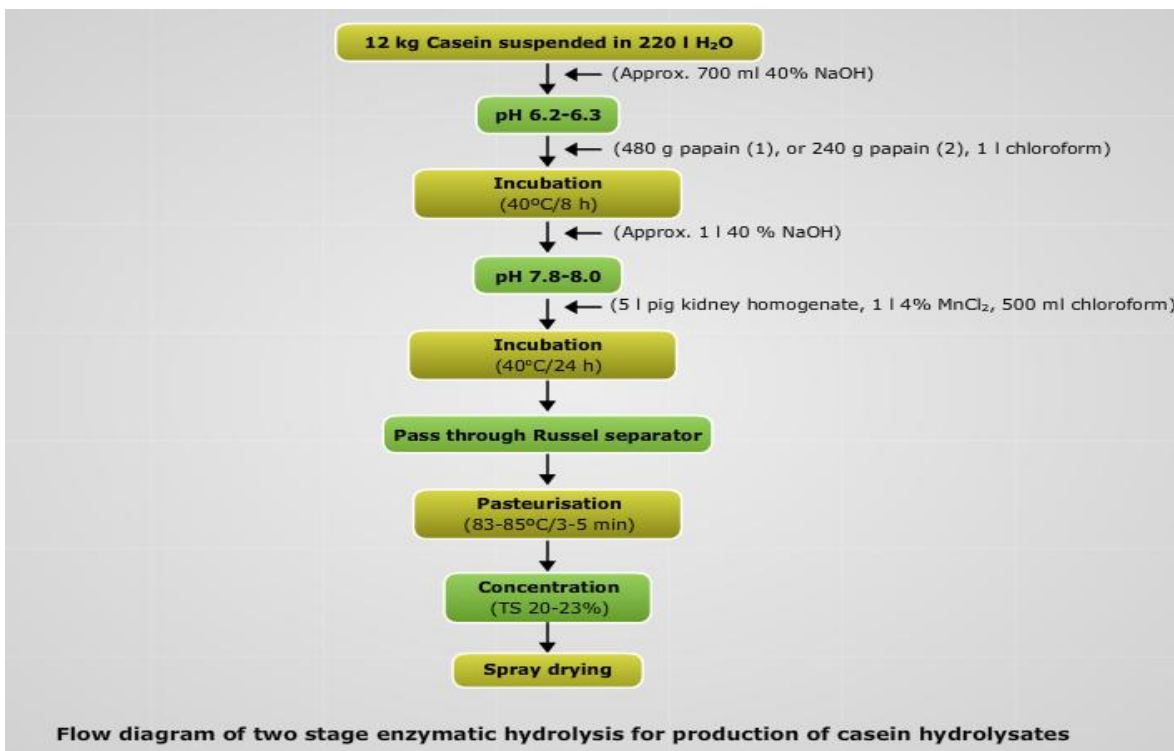
- Clegg *et al.* (1974) described a process for the production of enzymatic hydrolysate of casein. Twelve Kg of casein was suspended in 220 l water at pH 6.2-6.3 and digested with papain at 40°C for 8 h, and then with a pig kidney homogenate (serving as a source of exopeptidases) at pH 7.8-8.0 for 24 h. The hydrolysate was then passed through a Russel separator to remove insoluble material followed by pasteurization at 83-85°C for 3-5 min (Fig.15.1). After concentration up to 20-23% total solids in a Wiegand evaporator and holding at 60°C, the product was spray dried. The process was completed in 60 h. However, this was not an efficient process for production of debittered hydrolysate, as it is costly, time consuming and results in production of significant amount of free amino acids. First endopeptidase papain (4%) and then an exopeptidase leucine aminopeptidase (0.015%) are used to obtain casein hydrolysates with reduced bitterness and high (46%) free amino acids.
- Cogan *et al.* (1981) suggested use of papain, pepsin and Rhozyme enzymes.
- Khanna and Gupta (1996) reported enzymatic production of casein hydrolysates in a short hydrolysis period of 8 h. Sodium caseinate solution (10% TS) at pH 7.0 was observed to be optimum for hydrolysis with papain. Four percent papain in the first stage and 0.4% pancreatin in the second stage, each stage with 4 h of hydrolysis, were found to give optimum degree of hydrolysis (Fig.15.2). However, the casein hydrolysate so produced was definitely bitter. The bitterness was removed using activated carbon treatment. Minimum 15% activated carbon treatment was necessary for debittering the casein hydrolysate, though this treatment resulted in 40.90% N loss through adsorption on activated carbon. The yield and recovery of

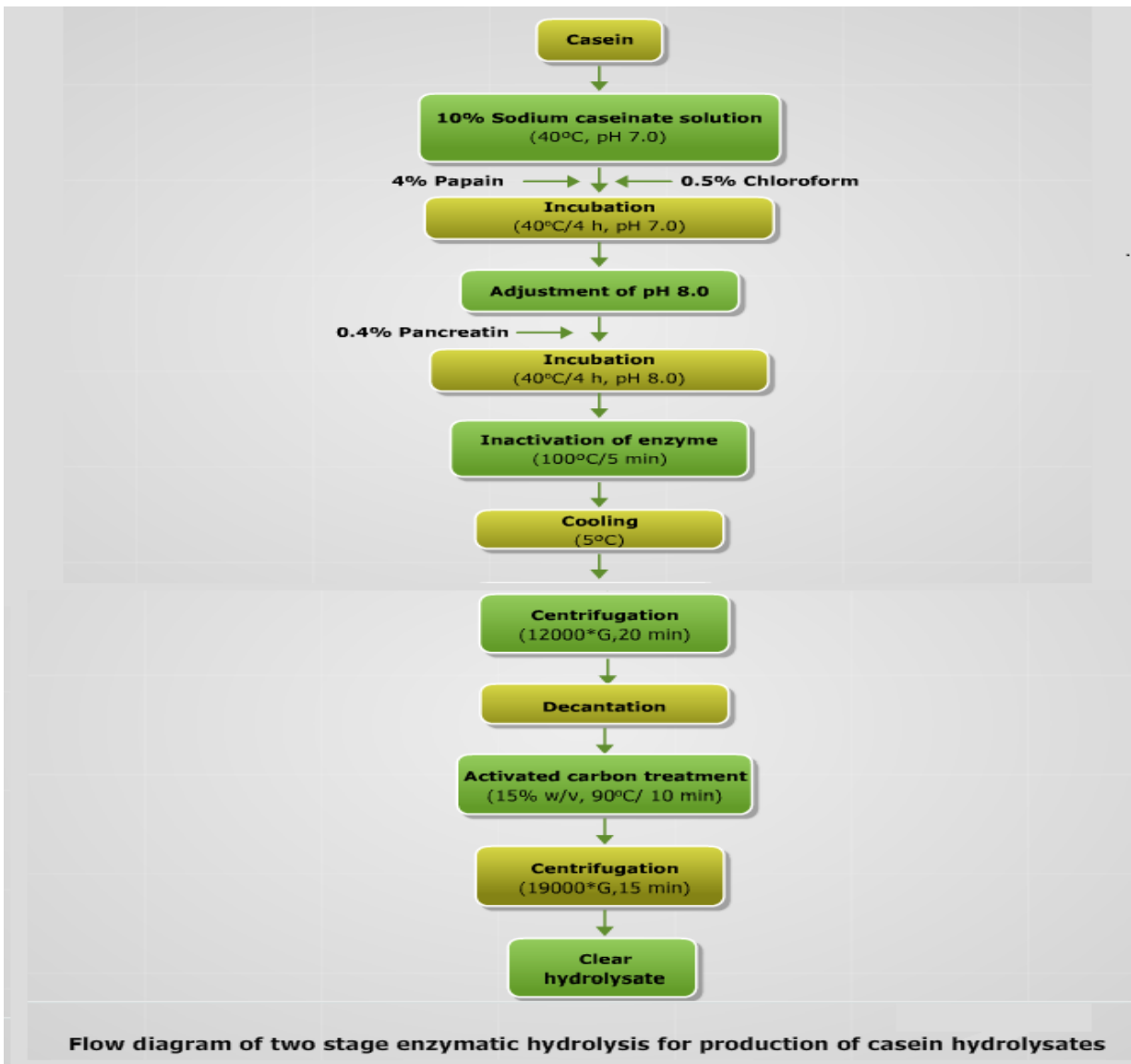
liquid casein hydrolysate were 47.98% and 46.23%, respectively. The liquid product had 10.25% TS, 1.93% nitrogen, 1.19% ash and a low viscosity of 1.99 cP at 20°C.

- Peptic pre-digestion of protein followed by hydrolysis with pancreatin or trypsin, papain followed by leucine aminopeptidase and pancreatin followed by pepsin have also been used.

15.4 Continuous Hydrolysis of Proteins in Membrane Reactor

The development of membrane technology has led to a new concept: continuous reaction and simultaneous separation of the product from the reaction mixture (Mannheim and Cheryan, 1990). A membrane module with the appropriate pore size and physicochemical properties is incorporated into the reactor, which contains the enzyme. Feed is continuously pumped into the reaction mixture while product is continuously withdrawn as the permeate. The molecular size of the product can be controlled by proper selection of the pore size of the membrane. The enzyme is recycled and reused, thus improving enzyme utilization and overall





productivity. The main system components include a vessel coupled in a semi-closed-loop configuration to a membrane module via a recirculation pump. Provisions are made for control of temperature, pH and agitation in the reaction vessel. The casein suspension is preadjusted to the required pH and temperature (in the food vessel) and pumped into the reaction vessel at a flow rate equal to the permeate flux. The reaction mixture is continuously recycled with a pump inserted in-line between the reaction vessel and the membrane module inlet. The membrane modules may be polysulfone hollow fibers of 5,000 and 10,000 molecular weight cut-off.

Chiang *et al.* (1995) worked on producing casein hydrolysate continuously by hydrolysis of bovine casein with protease type XXIII (from *Aspergillus oryzae*) in a pilot scale formed-in-place membrane reactor. A high percentage (> 99%) of TCA-soluble nitrogen in the hydrolysate (product) was achieved after 45 min at 37°C and pH 7. The product was completely soluble over pH range 2-9. Water sorption increased 4-6.5 times at water activity of 0.35-0.95 as compared with intact casein. The immunologically active casein and immunologically active whey proteins in the product were reduced 99 and 97%, respectively.

Lesson 16

DEBITTERING OF PROTEIN HYDROLYSATES

16.1 Introduction

Bitterness, which is a natural consequence of development of bitter-tasting components during enzymatic hydrolysis of protein, is the main defect that limits the use of protein hydrolysates for human consumption. Consequently, the reduction, prevention or removal of bitterness from protein hydrolysates has been investigated intensively. Debittering of the protein hydrolysates by different techniques like selective separation of bitter components, masking, enzymatic treatment and palstein reaction, are the key to the production of an acceptable protein hydrolysate, which can be used in the formulation of novel functional foods for geriatric, sports nutrition, weight control, anti milk allergic foods and for special medical diets like opiodic, anti hypersensitive and antimicrobial active foods.

16.2 Application of exopeptides

Free amino acids are much less bitter than the corresponding peptides, and the bitterness is highest when the hydrophobic amino acids are non-terminal. Bitter peptides in casein hydrolysates can be degraded by the application of carboxypeptidases into non-bitter peptides. Minagawa *et al.* (1989) reported that aminopeptidase T hydrolyses hydrophobic amino acid residues at N-terminal of peptides and proteins and hence remove bitter components from bitter peptides. Flavourzyme is the enzyme obtained from *Aspergillus oryzae* which has both exo- and endo- peptidase activity. This helps in debittering the protein hydrolysate.

Debittering methods using exopeptidases encounters certain limitations. The use of exopeptidases results in very high degree of hydrolyses. The hydrolysates will consist mainly of free amino acids and small peptides, resulting in high osmolality, which may limit its use.

16.3 Selective separation of bitter components

Selective separation of bitter components was first applied in 1952 for treating casein hydrolysate with activated carbon. This separation is based on the adsorption of hydrophobic group by means of the followings:

- Activated carbon
- Hydrophobic chromatography
- Hexylepoxy cellulose, soft glass fibre, flint glass powder or micro fibre paper
- Azeotropic mixture of secondary butanol and water
- Phenolic formaldehyde resin
- Aqueous ethanol

16.3.1 Activated carbon

The activated carbon treatment method has been found safe, promising and most effective in the elimination of the bitter taste. Activated carbon functions as a hydrophobic adsorbent and as such binds peptides and amino acids that are mainly hydrophobic and bitter tasting. This however results, in about 26% loss of protein nitrogen. The treatment of activated carbon lowers the bitterness of casein hydrolysates.

Bitterness in the hydrolysates obtained from Rhozyme 62 was eliminated by employing 0.5 g of activated carbon per g protein and storing it for 60 min at 25°C. However, such treatment was accompanied by a selective loss of tryptophan (63%), phenylalanine (36%), arginine (30%) and 26±2% of protein nitrogen due to adsorption of peptides and amino acids on to the activated carbon. As remedial measure, supplementation of the treated hydrolysates with the proper amounts of tryptophan and phenylalanine was suggested for the production of casein hydrolysates of acceptable taste and high nutritive quality.

Soluble casein hydrolysates for use in acid beverages could be obtained by stirring 5% casein hydrolysates solutions with 10% carbon of various kinds and mesh sizes at 22°C for 2 h or at 90°C for 10 min. Khanna and Gupta (1996) observed that minimum 15% activated carbon treatment was necessary for debittering the casein hydrolysate, though this treatment resulted in 40.90% N loss through adsorption on activated carbon. The yield and recovery of liquid casein hydrolysate were 47.98% and 46.23%, respectively. The liquid product had 10.25% TS, 1.93% nitrogen, 1.19% ash and a low viscosity of 1.99 cP at 20°C.

16.3.2 Hydrophobic chromatography

During chromatography, binding forces occurring between the structurally similar phenolic resin and peptide amino acid residues (containing aromatic/heterocyclic side chains) delay the emergence of these bitter components, permitting selective preparation of a non-bitter peptide hydrolysate. However, this method is reported to be impractical and costly for application to casein hydrolysates. Debittering by hydrophobic chromatography on hexyl Sepharose 6B has also been described.

16.3.3 Azeotropic mixture of secondary butanol and water

Selective extraction of bitter peptides using an azeotropic mixture of secondary butanol and water has also been observed to be very effective in reducing bitterness.

16.4 Masking

Masking of bitter compounds is advantageous over selective separation of bitter compounds as some of the bitter compounds are removed by separation technique. In masking, bitter peptides/components are retained for nutrition or medicinal property. A number of components have been shown to mask bitter taste of protein hydrolysates. These components are:

- Amino acids (aspartic acid, glutamic, taurine in acid solution and glycine)
- Fatty substances
- Cyclodextrin
- Gelatin
- Polyphosphates and starch

16.4.1 Amino acids

Masking of bitterness by adding acidic dipeptide and acidic amino acids like aspartic acid, glutamic acid and taurine have been reported. Glutamic acid or aspartic acid can be used to mask bitterness by weakening the bitter compound. Taurine in acid solution reduces bitterness without imparting sourness and is as effective as glutamic acid and aspartic acid.

16.4.2 Fatty substances

Fatty substances such as creaming powder, margarine and vegetable oil exert varying effect in their debittering effectiveness probably because of their affinity for hydrophobic compounds.

16.4.3 Cyclodextrin

Cyclodextrin can also mask bitterness because of its ability to wrap up the hydrophobic groups of bitter peptides, but its safety as a food additive still needs to be established. The bitterness from casein hydrolysates can be removed through treatment of 10% β - cyclodextrin.

16.4.4 Glycine

Glycine, an amino acid, has been characterized as sweet and has sweetness equivalent to a 0.45 percent sucrose solution at 0.30 percent in aqueous solution. Addition of 0.5 percent glycine in a protein hydrolysate could mask the bitterness, resulting in a sweet taste, which, however, may not always be desirable in the product.

16.4.5 Gelatin

Gelatin is as effective as cyclodextrin in debittering, although not as good as glycine. When gelatin is added along with the protein for hydrolysis, the enzymes used for hydrolysis (trypsin, chemotrypsin/ flavourze) also attack gelatin along with the desired protein. It seems that gelatin could donate hydrolysate substances including glycine, which are capable of masking bitterness.

16.4.6 Polyphosphates and starch

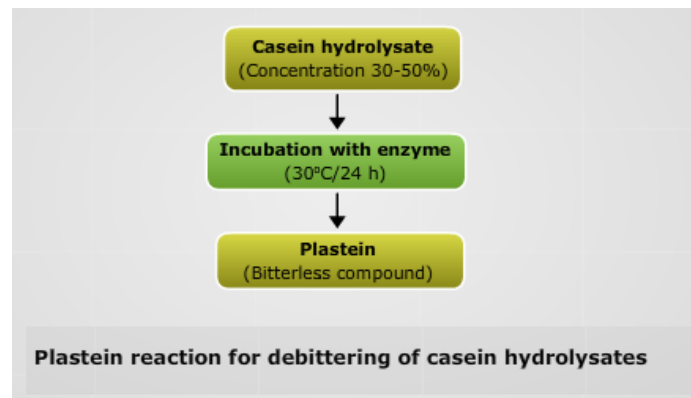
Addition of polyphosphates during the hydrolysis process could successfully mask the bitterness of casein hydrolysates; addition of hexametaphosphate @ 0.1% before hydrolysis is recommended.

Bitterness could be masked using gelatinized starch as the bitter peptides get hidden in the network structure of starch and thereby prevent them from reaching the bitter taste buds. To achieve this effect, it is necessary to heat the mixture of starch and bitter peptides.

16.5 Plastein reaction

The plastein reaction is a process in which proteins are broken down by proteolytic enzymes into a mixture of peptides and amino acids and are then resynthesized enzymatically into products which consists of insoluble, highly aggregated materials having different structural, compositional and functional properties from that of initial protein. The synthesis of plastein involves following steps:

- i. The protein is enzymatically hydrolysed to a low molecular weight mixture of peptides.
- ii. After hydrolysis, the impurities which cause undesirable odours, colours and flavours are removed. Hydrolysis, however, results in a characteristic bitterness which has been attributed to peptides with more than three amino-acids. This material serves as substrate for the third step of plastein synthesis.
- iii. During plastein synthesis, a high concentration of hydrolysate (30-50%) is incubated with an enzyme or heated to form viscous gel like material.



The plastein reaction has been claimed to yield the following advantages:

- i. Elimination of bitterness present in the hydrolysate.
- ii. Possibility of incorporating limiting essential amino acids into the plastein to form a protein like material with increased nutritional quality.
- iii. Improvement in the acceptability and nutritional quality of a protein, as well as, alternation in physical properties.
- iv. Facilitating the amino acids fortification in food by reducing loss during processing due to less solubility and thus helping in improving the amino-acid profile.

***** 😊 *****

Lesson 17

CO-PRECIPIATES: INTRODUCTION AND BASIC PRINCIPLES FOR PRODUCTION

17.1 Introduction

A co-precipitate of milk proteins may be defined as the product which separates as the solid phase after the heat treatment and precipitation of dairy fluid, or mixtures of dairy fluids, which contain both casein and heat coagulable whey proteins. The resultant product contains a significant proportion of the whey proteins and almost all the casein present in the raw material. Previously this name was confined to milk proteins only, but recent work has widened the term "Co-precipitates" in the sense that it covers the combination of milk proteins as well as the proteins derived from other biological systems. In the process of the manufacture of co-precipitates, up to 97% proteins have been reported to be recovered as compared to only 80% in casein manufacture (Muller *et al.*, 1967). The structure of co-precipitates and their characteristics are highly influenced by the production process. It has led to many patents covering the production of co-precipitates having specific characteristics for particular uses. The concept of controlling calcium content of co-precipitates to produce a series of products with different physical or functional properties was introduced by Muller *et al.*, (1967). The level of calcium in co-precipitate has major effect on its functional properties. The structure of co-precipitates and their characteristics are highly influenced by the production process. Control of calcium level is achieved by varying the amount of CaCl_2 added, changing the length of time at which the milk is held at about 90°C and varying pH of precipitation by acid for low and high calcium co-precipitates. The flexibility inherent in the co-precipitate process enables products to be produced, which vary in casein to whey protein ratio, solubility, ease of whipping, water binding, equilibrium moisture, viscosity and compatibility with other foodstuffs. Consequently, the range of application and properties of co-precipitates is large. Co-precipitates may be used as an ingredient in the preparation of various food products such as in dairy, meat, baked, confectionary, snack and animal and pet foods, either to contribute the desired functional properties or to improve the nutritional qualities of the products.

Co-precipitates are rich in proteins and low in lactose. They can be utilized for the manufacture of foods and beverages for lactose intolerant people or for fortification of infant foods without increasing the lactose and mineral contents. The cost of production of co-precipitates, as reported in the literature, is lower than that for skim milk powder and only slightly higher than that for casein.

17.2 Classification

Depending on the production process parameters, especially CaCl_2 quantity, pH value at precipitation and washing conditions, some authors classify co-precipitates in three varieties, each with differing amounts of calcium.

17.2.1 Muller *et al.*, (1967) classified co-precipitates in three varieties given below

17.2.1.1 Low-calcium co-precipitate

The calcium content in these co-precipitates is 0.5-0.8%.

17.2.1.2 Medium calcium co-precipitate

The calcium content in these co-precipitates is 1.5%.

17.2.1.3 High calcium co-precipitate

The calcium content in these co-precipitates is 2.5-3.0%.

17.2.2 Kozhev *et al.*, (1970) classified co-precipitates as

17.2.2.1 Acid co-precipitates

The calcium content in these co-precipitates is 0.8-1.0%.

17.2.2.2 Low calcium co-precipitates

The calcium content in these co-precipitates is 1.2-1.5%.

17.2.2.3 Medium calcium co-precipitates

The calcium content in these co-precipitates is 2.0-2.5%.

17.2.2.4 High calcium co-precipitates

The calcium content in these co-precipitates is 3.5-4.5%.

17.3 Basic Principle

Following precipitation of caseins from skim milk by acidification or renneting, the whey proteins remain soluble (in the whey). However, these can be precipitated in combination with the casein by first heating milk to such an extent that denature majority of the whey proteins and induce complexation of the whey proteins with casein, followed by precipitation of the milk protein complex by acidification to pH 4.6 or by a combination of added CaCl₂ and acidification. Precipitate of casein and whey proteins together from heated skim milk by acidification is termed as "co-precipitate". Thus co-precipitates of milk proteins are in principle formed by a two-stage process: i) Heat treatment of milk or a mixture of products which provide casein and whey protein, and ii) Precipitation of the proteins from the heated milk. The precipitated proteins are then separated from the serum, washed and dried.

In order to obtain the highest possible protein yield, it is necessary to heat the milk before the precipitation. Preheating to a temperature above 65°C promotes the interaction between β -lactoglobulin and *k*-casein, thus leading to complex formation between whey protein and casein. The complexed whey protein will then co-precipitate along with casein after the addition of the precipitating agent. For maximum protein recovery the heating temperature had to be at least 85°C. In addition to temperature, the time of heating also affects the protein yield. The interaction between β -lactoglobulin and *k*-casein changes the functional properties of the caseins considerably. Co-

precipitate is a total milk protein preparation with properties different from those of the native protein fractions.

The calcium concentration in co-precipitates can be maintained by changing basic parameters in the production process: a higher pH value at precipitation results in a higher calcium concentration in the product, while the longer retention time at high temperature decreases calcium concentration. It has been found that CaCl_2 concentration of about 0.2% of the skim milk quantity results in the highest recovery of milk proteins (> 95%) and in a low calcium content in the whey. The level of CaCl_2 required in milk for the precipitation of high calcium co-precipitate was found (Southward *et al.*, 1973) to be inversely related to the precipitation temperature. At 90°C, a concentration of 0.2% CaCl_2 in the milk was required for complete precipitation, whereas at lower temperature, it was found necessary to use up to 0.3% CaCl_2 .

***** 😊 *****

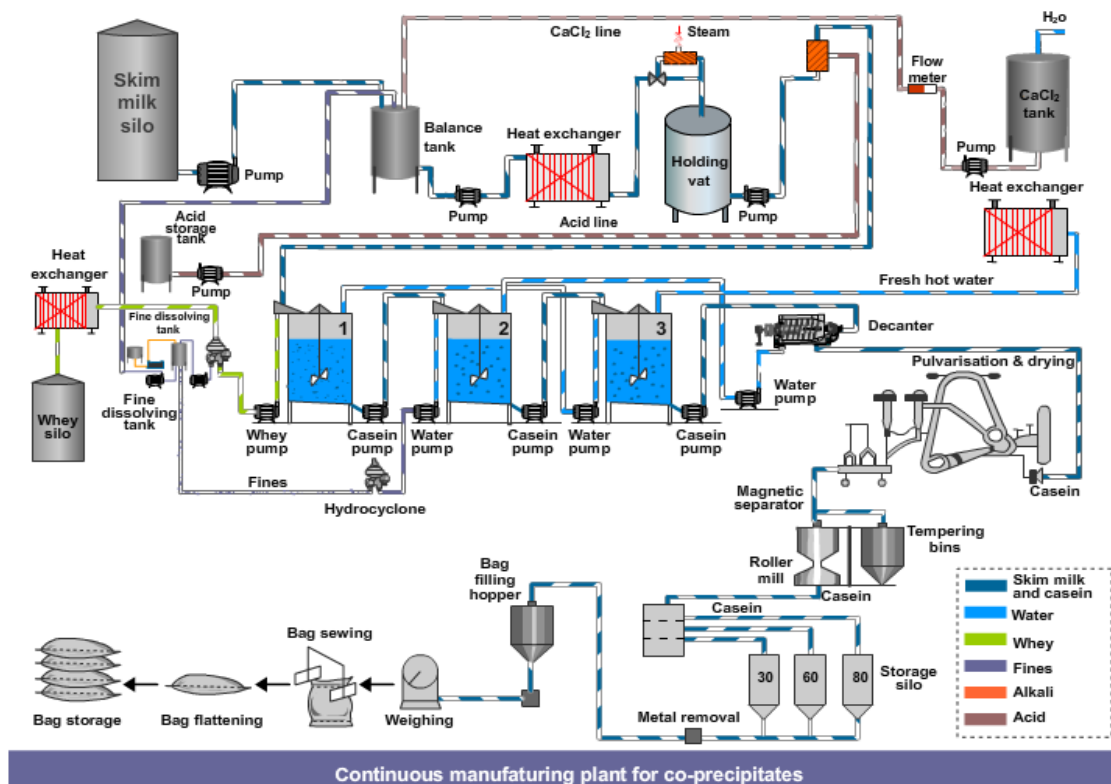
Lesson 18 MANUFACTURE OF CO-PRECIPITATES

18.1 Introduction

Early developments in the manufacture of co-precipitates occurred mainly in the USA and USSR. Co-precipitate manufacture was first reported in the USSR in early 1950s, the commercial potential of co-precipitates was developed in the 1960s and 1970s by research workers at the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO). This, and subsequent work, has been extensively reviewed (Muller, 1971, 1982, Southward and Goldman, 1975, Southward, 1985).

18.2 Manufacturing Process

The type of plant used for casein manufacture can be adopted for the manufacture of co-precipitates, by which it is possible to increase the protein recovery from 80-96% with a 28% reduction in B.O.D. of the whey. Fig.18.1 shows how the acid casein plant is modified for the manufacture of co-precipitates. The modification made it possible to use the plant for either casein or co-precipitate manufacture.



The manufacture of a range of co-precipitates with different calcium contents from cow milk as described by Muller *et al.*(1967) has been outlined in Fig.18.2.

18.2.1 Heating of buffalo skim milk

Buffalo skim milk is heated in double jacketed stainless steel vat to 90.6°C by indirect heating or by direct steam injection.

18.2.2 Holding and precipitation

The skim milk is held at varied holding times, depending on the type of co-precipitate desired, at 90.6°C by maintaining the temperature of hot water in the outer jacket at 93-94°C. The precipitation of co-precipitates is done at different pH ranges as follows:

18.2.2.1 Low calcium co-precipitates

For low-calcium co-precipitate production, 0.03% of CaCl_2 is added to skim milk; the mix is then preheated to a temperature of 65-75°C by passage through a plate heat-exchanger. In the next stage, a final temperature of 90°C is obtained by steam injection into the mix and this temperature is maintained for 15-20 minutes in a holding vat. Two-stage heat treatment is employed for the following reasons: (a) the Plate-heat exchanger is to be used re-generatively in commercial operations and hence recovery of heat from the whey is possible. This process of 'pre-heating' the milk is less expensive than entirely heating is done with steam; and (b) If the plate heat exchanger is the only means of used for heating milk, there would be a tendency for 'burn-on' to occur in the plates from slight precipitation of the milk proteins, especially at temperatures above about 68°C and at a pH of 6.3-6.5. After heat treatment, the hot skim milk is cooled and then the pH value is adjusted (pH 4.6) by injecting dilute hydrochloric acid (1:6) through a spray countercurrently to the direction of milk flow to provide full mixing. The mixture is transformed into curd in 20-25 seconds in a holding tube. The precipitate is then separated from the whey on an inclined 90-mesh screen, washed with water, pressed and dried. The calcium concentration of low calcium co-precipitates produced in this way is 0.1-0.5%.

In the production of low calcium co-precipitates with a calcium content of 0.5%, coagulation temperature 65°C produced slightly sticky and soft curd. Losses of fines in the whey are fairly high (about 1ml/100ml, representing some 2% of co-precipitate), but are much lower in the first wash water (approx. 0.1 ml/100 ml) which is usually heated to a temperature near 40°C and maintained at a pH of about 4.6. Total fines losses amounts to approx. 2.5% of the low co-precipitate.

18.2.2.2 Medium calcium co-precipitates

The same production process can result medium calcium co-precipitates (1.0-1.5% of calcium in the product) if 0.06% CaCl_2 is injected in the skim milk, and the mix is retained at a temperature of 90°C for 10-12 min and then precipitated at a pH value of 5.3. In the production of co-precipitates with a calcium content of 1.0-1.5%, coagulation temperature of 65°C produced the firmest and most manageable curd. The most robust curd is precipitated at a pH of 5.2-5.3. When losses of fine curd particles are approximately 0.3 ml/100 ml in both the whey and wash water, and accounted for about 2.1% of the weight of co-precipitate.

18.2.2.3 High calcium co-precipitates

For high-calcium co-precipitates production (2.5-3.0% of calcium in the final product), skim milk is heated at 90°C and retained at this temperature for 1-2 min, then 0.2% CaCl₂ is added. It is not necessary to add acid to adjust the pH value of precipitation. The firmest high calcium co-precipitate curds and the clearest whey's are produced from milk heated at pH 6.4 and 85°C for 6 min, when 0.2% CaCl₂ is injected into the hot milk and the temperature of the mixture is 77°C or higher. Under these conditions, the fines in the whey are reduced to a level of 0.1 ml/100 ml or approximate 0.2% by weight of co-precipitate. When, however, the coagulation temperatures fell below 73°C, the whey become cloudy and the fine losses increased to 0.4 ml/100 ml or approximate 0.8% by weight of the co-precipitate.

18.2.3 Drainage of whey

After the precipitation of the co-precipitate curd, it is allowed to settle and the whey removed after filtering through the stainless steel strainer covered with muslin cloth. Filtration is done to avoid loss of fine particles.

18.2.4 Washing

The co-precipitate curd is given 2, 3 or 4 washings with the acidulated water with 15 min holding time for each washing. In low calcium co-precipitate, the curd is washed in water (up to four batch washes, each of 400-500 litre) at a pH (usually pH 4.6) and at temperatures (usually 45 to 55°C).

In medium calcium co-precipitate, the curd is washed, dewatered and dried in a manner similar to that described for low co-precipitate. Temperature of the first wash water is generally varied between 45°C and 55°C and its pH is usually adjusted with dilute sulphuric acid to between 4.5 and 5.5 in order to assist in maintaining the firm structure of the curd. During this type of washing, the properties of fine curd losses is reduced in each succeeding wash.

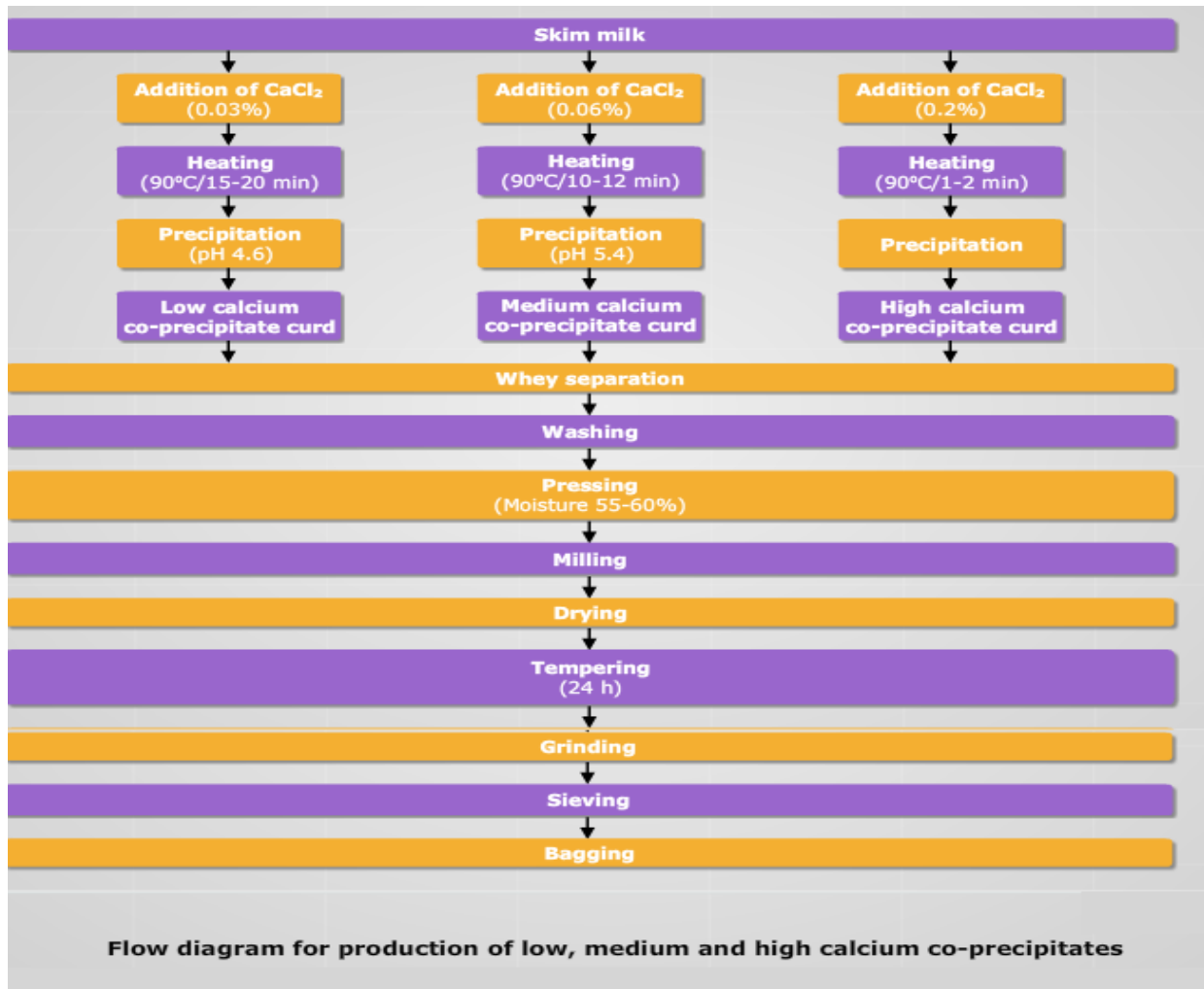
In high calcium co-precipitate, the temperature of the wash water is very important. When the wash water temperature is reduced to less than 60°C, the curd becomes very soft and mushy with a consistency similar to that of toothpaste. Wash water temperatures are therefore, adjusted to 60-75°C in the manufacturing of high calcium co-precipitates. Under these conditions, the losses of fine co-precipitate particles in the wash water, therefore any fines recovery amounted to approx. 0.5ml/100ml or about 2.5% by weight of the co-precipitate. No measurable fines losses are observed in the wash water effluent which is discharged for the centrifuge used to dewater the co-precipitate curd before it is dried. Combined fines losses from whey and wash water consequently represents about 2.7% by weight of the high calcium co-precipitate. Generally the wash water is acidified to pH 6.0 which is near the pH of the co-precipitate whey (pH 5.8-5.9).

18.2.5 Pressing

Pressing of curd is done with same principle as in casein. The curd can be subsequently de-watered using a decanter.

18.2.6 Drying

The co-precipitates is finally dried in a granular form, to a moisture content near 10% in a pneumatic conveying ring drier. A typical drier (F.W. Berk & Co. Ltd., London, England) has a water evaporation capacity of approx. 3.5 kg/h using inlet and outlet temperatures of 190°C and 90°C, respectively. After drying, the co-precipitates goes for tempering, milling, blending, bagging and storage in same manner as described for casein.



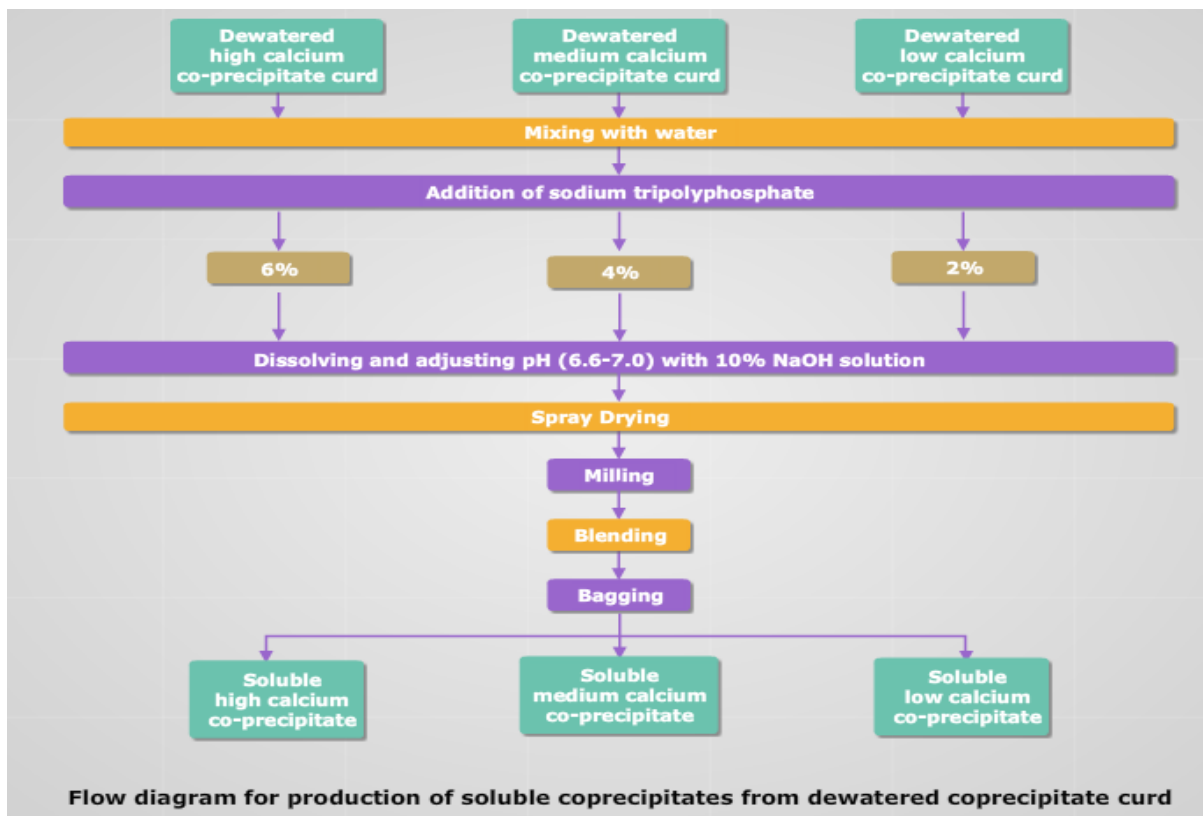
18.3 Manufacturing Process For Soluble Co-Precipitates

The solubility of co-precipitates depends on the calcium concentration in the product. Up to 90% of low calcium co-precipitates are soluble in water at a pH of 7.0, while high calcium co-precipitate is practically insoluble in water under the same conditions. In order to adequately dissolve medium-calcium co-precipitate at neutral pH, Smith and Snow (1968) added sodium tripolyphosphate, a calcium sequestering agent, to the mixture of co-precipitate and alkali. High calcium co-precipitate was dissolved at neutral pH by addition of sodium tripolyphosphate alone (6% on co-precipitate). The reason why complex phosphates such as sodium tripolyphosphate are so effective in dissolving medium and high calcium co-precipitate in water was ascribed to their calcium sequestering ability. When 2% sodium tripolyphosphate is included, high calcium co-precipitate solubility is

approximately 10%, but a 6% sodium tripolyphosphate addition increases the co-precipitate solubility up to 80% at a pH of 7.0.

Smith and Snow (1968) found that solution of low, medium and high-calcium co-precipitate (5% w/w) were stable to a heat treatment of 120°C for 20 min. The heat stability of similar co-precipitate solutions containing lactose, however, was generally lower than that of the co-precipitate solutions alone. Neutralization with alkali of low and medium calcium co-precipitates yielded products which were substantially water-soluble (e.g. C.S.I.R.O., 1968).

For spray drying, the wet curd of low, medium and high calcium co-precipitates are dispersed in water containing 2, 4 and 6 percent sodium tripolyphosphate (STPP) respectively, calculated on the dry weight basis of the curd. The mixture is heated in a water bath to about 85°C and continuous stirring is done for about 30 min. This heat treatment gives a pasteurization treatment to the co-precipitates. Slowly and slowly 2.5 N sodium hydroxide solution is added to the curd with constant stirring in such a way that pH did not rise to more than 7.0. The mixture is then passed through the mini-pulveriser in place of colloid mill. The redispersed material is then filtered through muslin cloth. The pH of the dispersion is adjusted to 7.0 at this stage. Then the material obtained is spray dried. The manufacturing processing for soluble co-precipitates is given in Fig.18.3.



***** 😊 *****

Lesson 19 PHYSICO-CHEMICAL PROPERTIES OF CO-PRECIPTATES

19.1 Introduction

The choice of manufacture of different calcium co-precipitate is influenced not only by consideration of yield and ease of manufacture, but also by the properties and intended use of the product. Co-precipitates with different calcium content have different physico-chemical properties.

19.2 Proximate Composition of Granular Co-precipitates

The proximate composition of granular (insoluble) co-precipitates, prepared from curd, which is washed twice in water, is shown in Table 19.1. The calcium content of a co-precipitate is determined mainly by its pH of precipitation (Muller *et al.*1967). The composition of co-precipitates is also affected by the extent of washing of the curd.

Table 19.1 Proximate compositional analysis of granular co-precipitates

Composition (%)	Co-precipitates		
	High calcium	Medium calcium	Low calcium
Moisture (%)	9.5	9.5	9.5
Fat (%)	0.6	0.7	0.9
Ash (%)	7.7	3.7	2.4
Protein (N x 6.38) (%)	81.7	85.6	86.7
Protein (dry basis) (%)	90.3	94.5	95.8
Lactose (%)	0.5	0.5	0.5
Calcium (%)	2.81	1.13	0.54
pH	6.5-7.2	5.6-6.2	5.4-5.8
pH of whey after separation of curd	5.8-5.9	5.1-5.3	4.9-5.1

The fat content of the co-precipitates increases from 0.6% to 0.9% as the pH of precipitation is reduced from 5.9 to 4.9. The high ash content of high calcium co-precipitate leads to a consequential reduction of 3-5% in the protein content of the product relative to lactic and acid caseins and low calcium co-precipitate.

19.3 Proximate Composition of Soluble Co-precipitates

Proximate compositional analysis and physical properties of soluble and dispersible co-precipitates are presented in Table 19.2.

Table 19.2 Proximate compositional analysis and physical properties of spray-dried soluble co-precipitates

Analysis	Product				
	A	B	C	D	E
Moisture (%)	4	4	4	4	4
Fat (%)	0.6	0.6	0.7	0.7	0.9
Ash (%)	13.5	10	5	6.7	4.1
Protein (N x 6.38) (dry basis) (%)	84.5	88.0	93.0	91.5	94.0
Lactose (%)	0.5	0.5	0.5	0.5	0.5
Calcium (%)	2.9	2.9	1.2	1.2	0.5
Sodium (%)	1.9	0.6	0.6	-	1.1
pH	7.1-7.2	6.5-6.9	6.6-7.2	6.6-7.2	6.6-7.2
Solubility (%)	92	72	70-90	95-98	97-98
Farinograph water absorption (%)	278	129	193	282	292

Product

- A. High calcium co-precipitate rendered soluble by the addition of sodium tripolyphosphate (6% w/w).
- B. High calcium co-precipitate rendered dispersible by the addition of sodium tripolyphosphate (2% w/w).
- C. Medium calcium co-precipitate, neutralized with sodium hydroxide.
- D. Product C containing additional sodium tripolyphosphate (2% w/w).
- E. Low calcium co-precipitate, neutralized with sodium hydroxide.

Soluble high calcium co-precipitate has very high ash content (13.5%) due in part to the presence of sodium tripolyphosphate and contains almost 2% sodium. Soluble low calcium co-precipitate has a composition similar to that of sodium caseinate. In order to render medium calcium co-precipitate substantially (> 90%) soluble at pH 7.5, it is necessary to use both, sodium hydroxide and sodium tripolyphosphate (or some other complex phosphate).

19.4 Physical Properties of Co-precipitates

The general physical properties of co-precipitates may be regarded as the physical properties of these products when examined alone or in water (dispersed or dissolved). These include pH solubility (in water, alkali or acid) and rate of solution, density, particle size, viscosity of solutions and colour of powder and solutions.

19.4.1 Solubility

Solubility of low-calcium co-precipitates in alkali over a range of pH values was similar to casein. Solubility is a characteristic of casein products such as co-precipitates which varies markedly under the influence of pH, agitation, mixing temperature, mixing time, the particle size and concentration of the casein product and the presence of other species such as dissolved salts. The solubility of co-

precipitates has generally been considered in the pH range from 6 to 10. However, it has been demonstrated that co-precipitates can also be dissolved in several different acids such as phosphoric, hydrochloric and citric acid at pH 2-3.

19.4.2 pH

The pH of a water dispersion of an insoluble co-precipitates is determined particularly by the pH of precipitation, which also affects its calcium content. It is also affected to some extent by the number of washes, and by the alkalinity of the wash water used, particularly in the manufacture of low calcium co-precipitate. Where co-precipitates are rendered substantially or partly soluble or dispersible in water by the addition of alkali and/or complex phosphates, the pH of these solutions is usually near 7.

19.4.3 Bulk density

The packing density (bulk density) of casein products such as co-precipitates can vary markedly depending on the method of manufacture. Granular, insoluble co-precipitates have approximately density 0.6 g/ml, depending on particle size, whereas the density of spray dried soluble co-precipitates can be much lower. Buchanan *et al.* (1965) found the density of a spray dried high-calcium co-precipitates containing 2% sodium tripolyphosphate to be 0.34 g/ml compared with 0.25 g/ml for sodium caseinate.

19.4.4 Viscosity

The viscosity of solutions of soluble co-precipitate in water at different concentrations, temperature and shear rates was measured by Hays, Muller and Fraser (1969). They found that low calcium co-precipitate had a viscosity similar to that of acid casein. The viscosity of medium and high-calcium co-precipitate solutions was found to be relatively high when the pH was above 7. The viscosity of solutions of low-calcium co-precipitate was affected by the heat treatment of the milk from which it was made.

19.4.5 Colour

Hays, Dunkerely & Muller (1969) found that pH, calcium and polyphosphate content of co-precipitate solutions were the factors which particularly affected its whiteness.

19.5 Flavour

The development of "gluey" off-flavours in low calcium co-precipitates was inhibited by the addition of 0.01-0.05% sodium metabisulphite. The flavour of co-precipitates tends to follow a similar pattern to that of the caseins, high calcium co-precipitates being more stable than low calcium (acid) co-precipitates and fresh curd soluble co-precipitates being better than those reconstituted from dry granular insoluble co-precipitates. The co-precipitates also exhibit 'cooked flavour' due to high heat treatment given.

The successful and potential uses of co-precipitates in food products will depend upon the

satisfactory functional properties of the proteins that are added in the food system so that in body, texture, flavour and nutritive characteristics etc. of the finished product are not adversely affected and remain acceptable to the consumers. The investigations conducted so far indicated that the co-precipitates are used mostly in a variety of food products in small proportions to improve their functional and nutritive properties.

***** 😊 *****

Lesson 20

PHYSICO-CHEMICAL CHARACTERISTICS OF WHEY

20.1 Introduction

There is wide variation in composition depending on milk supply and the process involved in the production of the whey. In general, whey produced from rennet-coagulated cheeses and casein is sweet whey, whereas the production of acid casein and fresh acid cheeses, such as Ricotta or Cottage cheese, yields acid whey. When we use rennet, most part of calcium and phosphorus of the casein complex remain with the curd. The ash content of the whey is, therefore, less than when the coagulating agent is acid, which transfers part of the phosphorus and most of the calcium to the whey. Production of *channa* and *paneer* yields medium acid whey. Based on acidity, whey can be conveniently classed into groups:

Sweet whey : Titrable acidity, < 0.20%, pH 5.8- 6.6.

Medium acid whey : Titrable acidity, 0.20-0.40%, pH 5.0-5.8.

Acid whey : Titrable acidity greater than 0.40%, pH < 5.0.

20.2 Chemical Composition of Different Types of Whey

Different types of whey produced during the manufacture of cheese, casein, *chhana*, *paneer*, *chakka* and co-precipitates vary in chemical composition and acidity (Table 20.1). It, in general, contains about half of the total solids of milk, and is a source of precious nutrients like lactose, whey proteins, minerals and vitamins.

Table 20.1 Composition of different whey systems

Constituents	Cheddar cheese	Acid casein	Rennet casein	Channa and paneer	Co-precipitates
Total solids (%)	6.7	6.9	6.7	6.4	6.1
Fat (%)	0.3	0.1	0.1	0.5	0.1
Protein (%)	0.9	1.0	1.0	0.4	0.3
Lactose (%)	4.9	5.1	5.1	5.0	5.1
Ash (%)	0.6	0.7	0.5	0.5	0.6
T.A. (%)	0.2	0.4	0.2	0.4	0.3

Whey is a multicomponent solution of various water-soluble milk constituents in water; the dry matter of whey consists primary of carbohydrate (lactose), protein (several chemically different whey proteins) and various minerals. Fat content of the freshly separated liquid whey may be up to 0.5-1% depending on the type of milk used and the efficiency of the cheese-making operation. Fat content of most acid whey from fresh cheeses such as cottage cheese or ordinary quarg is negligible as skim milk is used in the manufacture of these cheeses. The proximate composition of various whey may show significant variations due to many factors including the pretreatment of the cheese milk (heating, centrifugation, cultures used, mechanical handling, use of processing aids such as the yellow color, use of membrane processes); and the whey handling and pretreatment processes (pasteurization, pre concentration, recovery of casein fines).

Lactose, the principal component of the whey constitutes about 4.4-4.9% of the whey (almost 75% of the dry matter) depending on the whey type. Lower lactose content is usually found in the acid whey due to the fermentation process in which some of the lactose is converted to lactic acid. Although lactose is the most abundant material of whey, the most valuable whey component is the whey protein, constituting approximately 0.7% of the whey (about 9-11% of the dry matter). In addition, whey may contain about 0.2-0.3% of nitrogenous matter denoted as non protein nitrogen (principally inorganic compounds, urea etc): this is sometimes included with the true whey protein and reported as total whey protein ($N \times 6.38$). In many cases, like in the manufacture of co-precipitates, *channa* and *paneer*, high heat treatment is given to milk resulting in varying degree of whey protein precipitation along with the product. As a result, whey obtained from the production of such products will contain mainly the heat non-coagulable whey proteins and its total protein content will be substantially lower.

In addition to lactose and whey proteins, minerals constitute the third major component of dry matter of whey, which contribute to the electrical conductivity of whey. The mineral composition shows the greatest variations between different types of whey, together with pH and lactic acid content. In addition to lower pH and higher lactic acid (and correspondingly lower lactose) content, the acid cheese whey shows substantially higher calcium and phosphorus contents caused by the solubilization of the calcium-phosphate complex of the casein micelle at the acid pH range. In contrast, the calcium removal from the casein micelle does not occur during rennet clotting at pH 6.0 or higher; thus, much of the milk calcium is retained in the cheese rather than being lost in the sweet whey. The differences in acidity as well as the higher calcium content of the acid whey appear to be the main reason for variations in physico-chemical properties of different whey, including the substantially lower heat stabilities of acid whey in comparison to sweet whey.

20.3 Physical Properties

There is comparatively little data available on the detailed physical properties of whey.

20.3.1 Colour

Whey is the greenish translucent liquid. The greenish color of most traditional whey systems, regardless of the processing conditions used, is caused by the water-soluble and heat-stable riboflavin. However, riboflavin is sensitive to light as well as to ionizing radiation treatments and whey systems exposed to these conditions will show fading of the green color.

20.3.2 Flavour

Studies on the flavour of acid whey, based on eight flavour characteristics, have been reported by McGugan *et al.* (1979). When increasing concentration of whey were added to skim milk, 'brothiness' was first noted when 20% whey was added, and diacetyl, bitterness and sweetness at 40% addition. Volatile acidity, non-volatile acidity, saltiness and astringency were only noted in 100% whey. Neutralization of the whey resulted in a change in all flavour characteristics.

20.3.3 Surface tension

The surface tension of cheese whey has been shown to vary between 40,000 and 84,000 N/m, increasing with increasing total solids, and decreasing with temperature. It is possible that some of the observed variation is due to difference in lipid content of whey. According to one report, the surface tension of whey is low (42 dynes/cm) compared to 48 dynes/cm of skim milk.

20.3.4 Viscosity

The viscosity of whey at different temperatures has been presented in Table 20.2. The viscosity characteristics of whey and concentrated whey are important, not only in terms of evaporation efficiency, but also for operation such as lactose hydrolysis, which might be expected to function more efficiently if applied to concentrates. Lactose hydrolysis reduces viscosity and the degree of non-newtonian behaviour.

Table 20.2 Viscosity of whey at different temperatures (Viscosity in cP)

Temperature	Viscosity
10°C	1.71
20°C	1.26
40°C	0.82
80°C	0.68

20.3.5 Heat stability

The individual proteins in whey have a wide range of denaturation temperature, about 65-75°C. In general it has been found that, with higher TS, the denaturation of β -Lg slows down, but the denaturation of α -La increases. Increased lactose concentration reduced the denaturation of both proteins, perhaps as result of the formation of heat induced complexes. Increased calcium contents, up to 0.4 mg ml⁻¹, tended to slow denaturation, but above this level, little further effect was observed. The rate of denaturation of both proteins was slower at pH 4 than at pH 9. Other comparisons have shown that the method used for concentration may significantly affect the nature and detailed confirmation of whey proteins, with membrane processing having much less severe effects than conventional evaporation. The changes occurring in the proteins at these temperatures may partly explain the improvement in flux commonly obtained holding whey at 55°C before ultrafiltration.

20.3.6 Solubility

The solubility of lactose is only about 20 g/100 g water at room temperature and 60 g/100 g water at 60°C. Therefore, whey concentration to more than about 36-38% total solids results in formation of crystalline lactose. This is the principle of the lactose manufacturing process based on crystallization from highly concentrated whey.

***** 😊 *****

Lesson 21

MANUFACTURE OF CONDENSED WHEY PRODUCTS

21.1 Introduction

Whey is a highly perishable and its use in liquid form is limited to only small quantities. It can be preserved by removing its water and so the concentration and drying of whey assumes a special significance. With the development of membrane technology, it became economically feasible to concentrate whey using reverse osmosis (RO) to 28% TS retaining all functional properties of whey proteins. The potential use of RO can be as a pre-concentration step prior to transportation of whey concentrate to a central processing facility for further processing for the manufacture of whey powder, whey protein powder, demineralised whey powder and lactose. Whey concentration is carried out with the following objectives:

- a) Volume reduction for transport to other processing facilities.
- b) Pre-concentration for drying into whey powder.
- c) Manufacture of condensed whey: plain or sweetened.

21.2 Production of Concentrated Whey

Usually the whey is prepared as plain or sweetened condensed whey depending on its end use and its targeted shelf life. Various steps involved in the production of concentrated whey are as follows:

21.2.1 Clarification

The whey always has curd fines, which confer serious risk of blocking heat exchangers channels or fouling RO membranes. These curd fines also adversely affect the solubility properties and flavour of the end product. These curd fines are usually removed by a combination of treatments such as settling, screening and clarification. For large-scale operation, it is usual to employ a self-discharging clarifier with an enlarged solid-holding capacity. Also used commonly are the hydrocyclones, for recovering curd fines from whey.

21.2.2 Separation and pasteurization

In order to obtain flavour stability in concentrated whey, the whey is separated to remove fat. It is followed by whey pasteurization for optimum microbiological quality, to inactivate rennet and to ensure storage stability. It is then stored at 5°C till concentration and drying.

21.2.3 Concentration

The clarified and defatted whey may be concentrated economically with the integration of RO for pre-concentration and multi-effect evaporator. The main difference between evaporation and reverse osmosis is that evaporation removes water by the application of heat, which turns the water into steam followed by condensation of the vapour, whereas RO is a simple filtration process requiring mechanical energy. As compared to evaporation, RO takes place at low temperatures and consumes less energy (Table 21.1). However, RO concentration is limited by the osmotic pressure of the

concentrated solution and for whey, the maximum level is approx. 25-28% TS. RO concentration of whey will at some point become uneconomical to continue the concentration because of a low flux at higher concentration. Typical economically viable TS levels in RO concentration are 21% for sweet whey and 17% for acid whey.

Evaporation, on the other hand, is only limited by the solubility of the solutes at the evaporation temperature and thus a TS level of 60-65% is obtainable. The most modern concentration installation consists of a 5-7 stages evaporation system. By adding more stages to the evaporator, the specific steam consumption is reduced. A seven-stage plant consumes 50 % less steam than a three-stage plant.

Acid whey foams less during evaporation in evaporators than does sweet whey. When sweet whey is difficult to manage in the evaporator a small quantity of acid or a little fat may be added to break the foam.

Table 21.1 Energy cost of efficient evaporation v/s reverse osmosis for whey

Energy per tonne of whey	Efficient evaporation				RO Concentration		
	1 Stage	2 stage	7 stage	MVR	12%TS	18% TS	28% TS
Steam (tonnes)	0.62	0.14	0.09	0.03	-	-	-
Electricity (kWh)	0	3	3	25	3.6	8.8	9.6
Total equivalent (kWh)	387	90	60	44	3.6	8.8	9.6
Equivalent energy	192	46	31	35	3.6	8.8	9.6

Initial total solid in whey = 6%

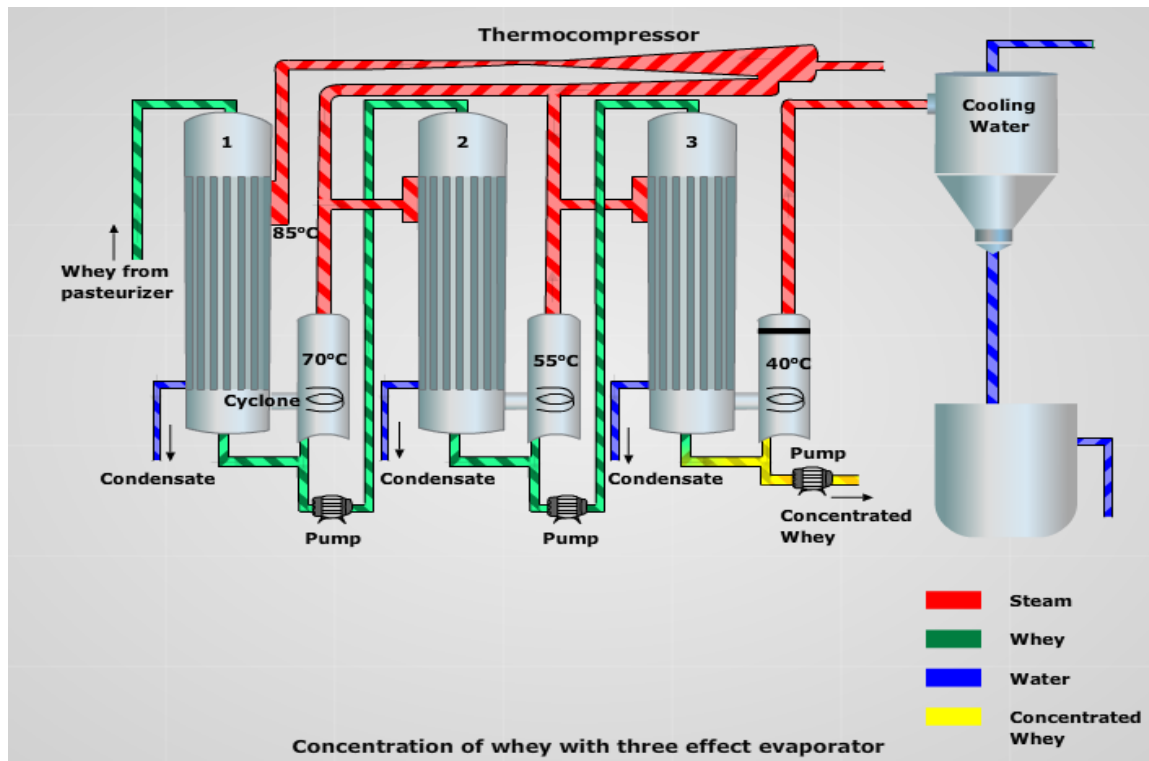
MVR- Mechanical vapour recompression

TS- Total solids

There is spontaneous lactose crystallization in vapour separator while concentrating whey to levels above 55% TS. This may be avoided by immediate removal of concentrated whey from the evaporator apart from controlling final total solids contents of whey and increasing the evaporation temperature in the last stage, where lactose is in most concentrated form. For this, the whey evaporators are sequenced in such a way that the higher solids are reached at higher temperature than that prevails in the last stage. For instance, a 7-Stage falling film evaporator can be sequenced 1-2-3-4-7-6-5, where the temperature (°C) in the respective stages is 68, 65, 61, 57, 50, 45, and 39°C.

21.3 Plain Condensed Whey

Plain condensed whey is prepared by pasteurizing the whey and drawing the hot liquid into the vacuum pan. The desirable degree of concentration of plain condensed whey is 35-50% total solids. Whey condensed to higher solids content (more than 55% TS) forms a gel after cooling and is not recommended to be used in any food or feed products due to its coarser texture and low solubility.

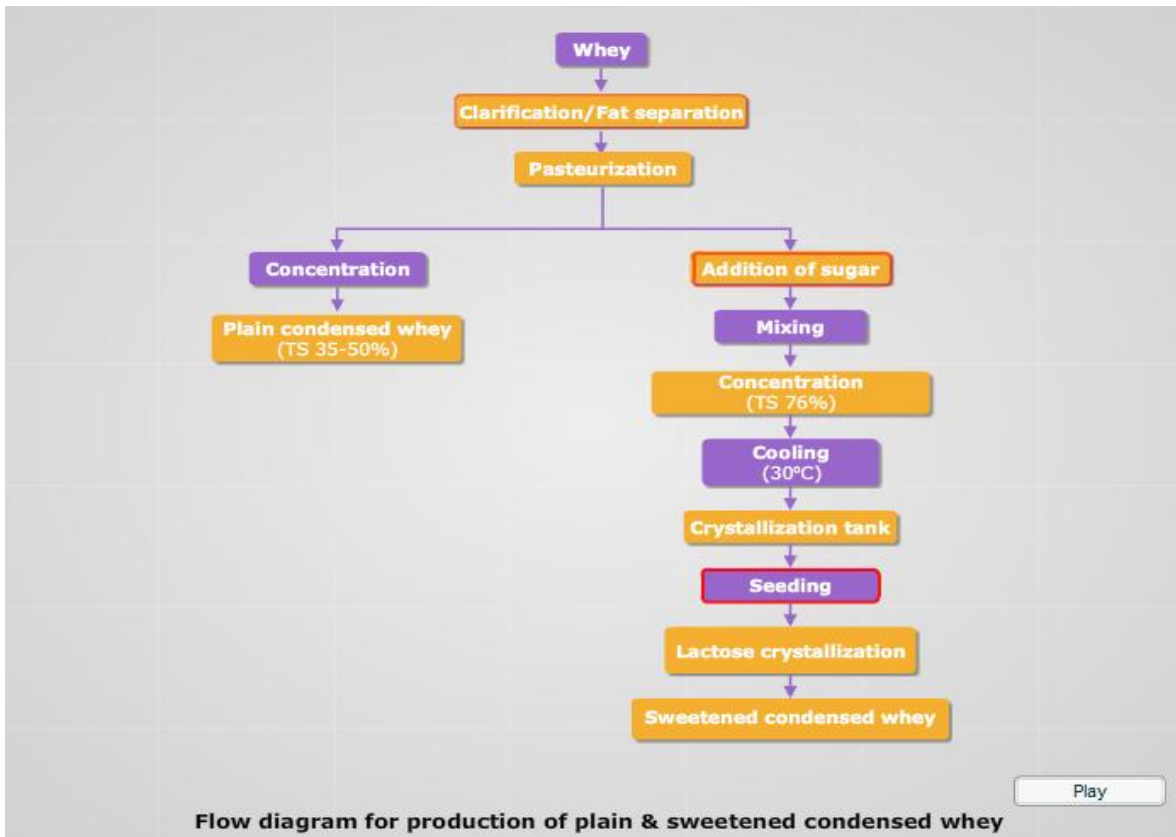


Plain condensed whey is also prepared as an intermediate product for whey powder making. For this purpose, the whey is concentrated to about 40-60% solids and lactose pre-crystallized before drying. For lactose crystallization, concentrated whey is cooled rapidly to 30°C using flash coolers and seeded with fine-grained α -lactose monohydrate crystals (crystal size of approximately 10 μ) at a level of about one kg per tonne of concentrate. The seeded mixture is stirred for 1 to 3 h in a crystallization tank at 30°C for mass and forced crystallization of lactose to a size lesser than 25 μ . Lactose crystallization may be continued by cooling up to 10°C for higher level of lactose crystallization.

21.4 Sweetened Condensed Whey

For the preparation of sweetened condensed whey, sweet cheese whey is mixed with sugar equal to the weight of solids in whey (about 6.7 kg sugar for 100 kg whey). The mixture is concentrated using multistage evaporators to at least 76% TS (Fig.21.2). The specific gravity of sweetened condensed whey at 50°C is 1.360 (38.4° Bé). For controlled lactose crystallization that is necessary for producing smooth texture product, the concentrate is then subjected to lactose crystallization by cooling up to 10°C, the similar way as explained under point 21.3. The lactose crystal size must be kept below 25 μ to produce a smooth rather than sandy texture. It may then be packed in barrels or cans. The product does not require any refrigeration for storage.

Sweetened condensed whey is somewhat salty and also has a characteristic whey flavour. Some desalting of the original whey by RO or other procedure would greatly improve flavour and utilization in certain foods. Sweetened condensed whey darkens and thickens in storage, but these changes do not develop to an objectionable level during the first year. The product must be utilized within one year of production to get full advantage of its functional and nutritional properties.



***** 😊 *****

Lesson 22

MANUFACTURE OF DRIED WHEY

22.1 Introduction

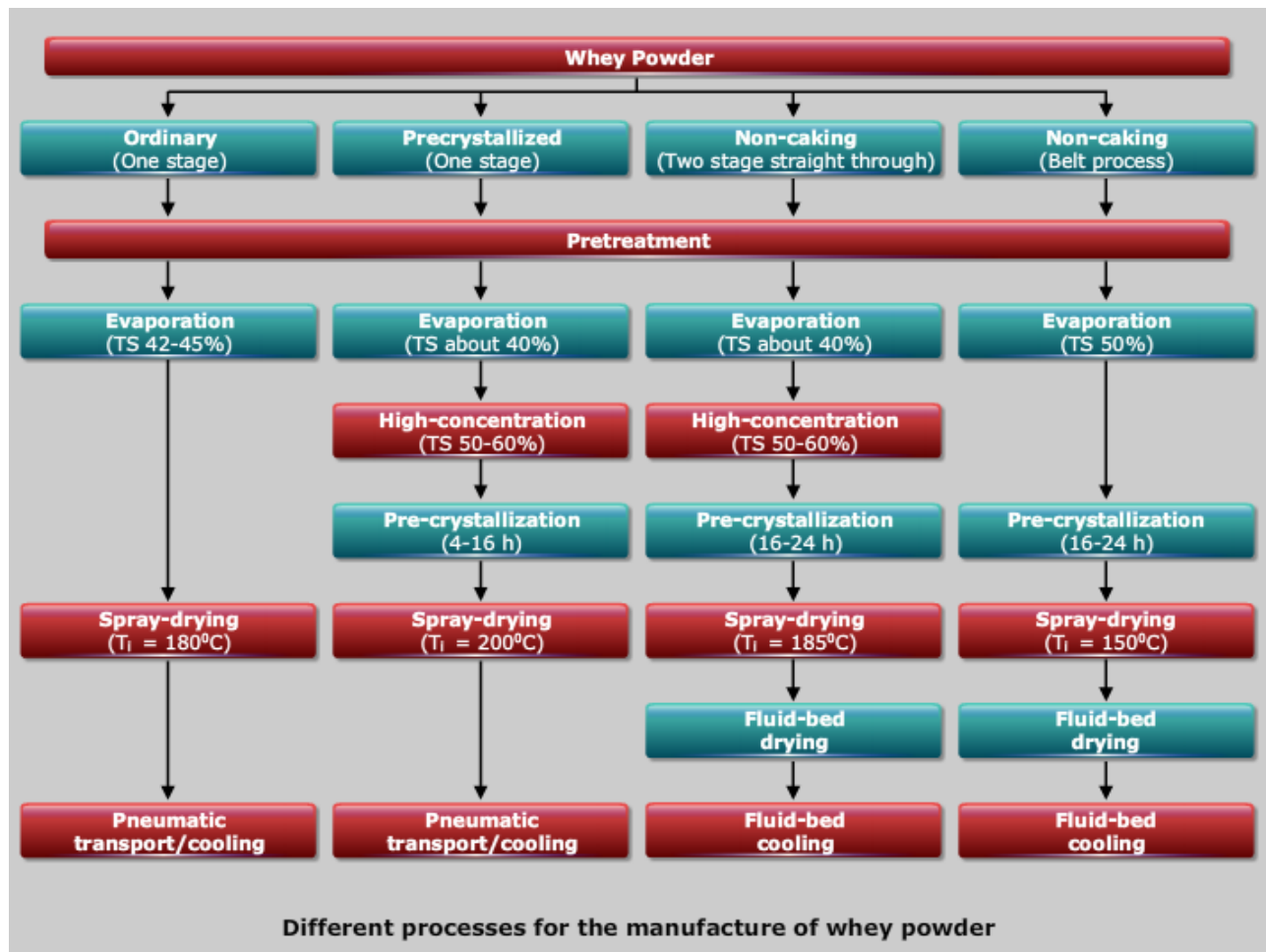
The trend in Western Europe is to preserve whey solids in the form of demineralised and delactosed whey powders. Whey powder is essentially produced by the same method as other milk powders. Whey powder production consists of three main operations: evaporation, crystallization, and drying. During evaporation whey is concentrated to 42-60% total solids. Lactose crystallization prior to drying for whey powder production is inevitable because amorphous lactose is sticky. This causes problems during drying as it results in a hygroscopic product, but this can be overcome by converting most of the lactose into crystalline α -hydrate form.

When dried conventionally without lactose crystallization, whey concentrates yield powder that are very hygroscopic and the manufacturer runs the risk of the powder caking on storage, or even in the drier. In addition, the efficiency of the drying is reduced, since it is not possible to concentrate whey to solids content greater than 42-45% total solids for a non-crystalline product. To avoid the caking properties of ordinary whey powder it is industrially important to encourage the majority of the lactose to crystallize into the non-hygroscopic α -lactose hydrate form. The advantage of lactose crystallization lies both in energy savings and in improved powder properties.

22.2 Drying of Whey

Recent trend in drying of whey is extensive use of spray drier that may be single stage, two-stage and more recently three-stage drying. The moisture content of whey powder ranges between 3.5-5%. Processes pertaining to the spray drying of whey for the manufacture of various types of whey powder are depicted in Fig.22.1.

Whey can be transformed into powder by using different technological processes, with the final product quality depending on applied technology. Powders produced by different methods vary considerably. Characteristics essential to powder quality are powder hygroscopicity and caking tendency. Since 100% lactose crystallization cannot be achieved, the target in whey powder production is to gain the largest possible portion of lactose in crystalline form, such as 90-95% α -lactose monohydrate.



Increased lactose crystallization in procedures 2, 3, and 4 (Fig 22.1) results in a decreased quantity of amorphous lactose and drying is performed at higher outlet air temperatures, allowing intensified evaporation of up to 60% total solids. The increase in the inlet air temperature by 10°C raises the outlet air temperature by 1°C.

22.2.1 Single-stage process

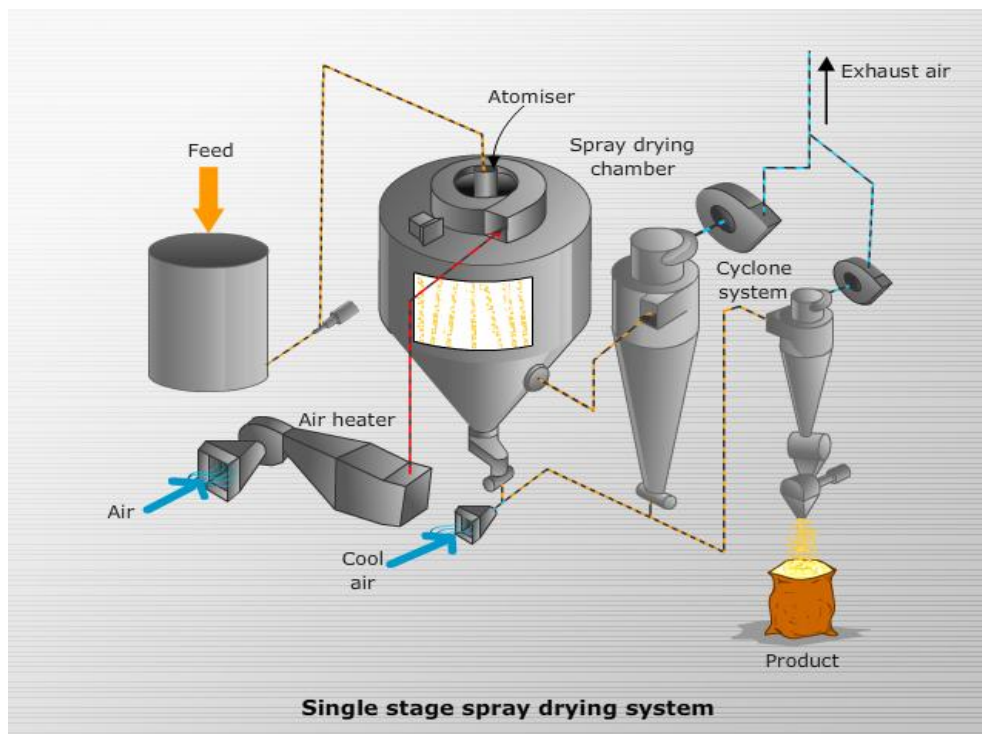
In single-stage drying, the product is dried to its final moisture content in the spray-drying chamber alone; sometimes pneumatic conveying system is adopted with one-stage drying system (Fig.22.2). Ambient air provides both the conveying and cooling of powder. If climatic conditions prevent powder temperature/residual moisture contents to be achieved with ambient air, the conveying air must be dehumidified and cooled to usually 8°C. In procedure 1 (Fig.22.2), concentrated whey is pumped into the spray drying chamber. Both spraying methods are used with a pressure or a centrifugal (rotating) atomizer. Inlet air temperature varies from 150 to 200°C with different procedures. Outlet air temperature is 85°C. As a general rule, outlet air temperature should be as low as possible, but high enough to prevent the powder from sticking and leaving a deposit (“fouling”) in the spraying chamber. Air, evaporated materials, and powder fines are directed through the system of cyclones, where powder particles are separated and returned into the process. Most of powder obtained at the chamber bottom and joined to the powder derived from the cyclone is cooled with cold air and pneumatically transported to sifting and packaging equipment. Powder obtained in such a way is very hygroscopic, with a high caking tendency. Hygroscopic whey powder exposed to room

conditions has a strong tendency to absorb moisture from the air and form hard cakes or lumps. For these reasons, careful control of drying conditions is necessary to reduce the production of undesirable hygroscopic product. Air flows, which permitted product to contact high temperature surfaces, such as the lip of inlet air duct, results in excessive scorched particles in the finished product.

Procedure 1, in addition to resulting in a highly hygroscopic product, is disadvantageous from an energy-saving point of view, because whey can be concentrated in evaporated only up to 45% total solids. However, since water evaporation in a multieffect vacuum evaporator is significantly cheaper than in a spray drier, the steam consumption for this procedure is 6.6 kg/kg whey powder.

By introducing lactose crystallization between the evaporation and drying process (Procedure 2) powder quality and process economy are improved. Controlled crystallization can be initiated by immediate flash cooling of condensed whey after evaporation to about 30°C. As far as possible slow agitation should start immediately and fine-grained α -lactose monohydrate at a level of about one kg per tonne of concentrate should be added. The holding time under these conditions should be 3-4 hours. Cooling of the concentrate should then start, the rate being about 3°C/h until 10°C is reached. Crystal size in the final crystallized concentrate should be mostly in the range 20-30 μm with the largest crystals not exceeding 50 μm .

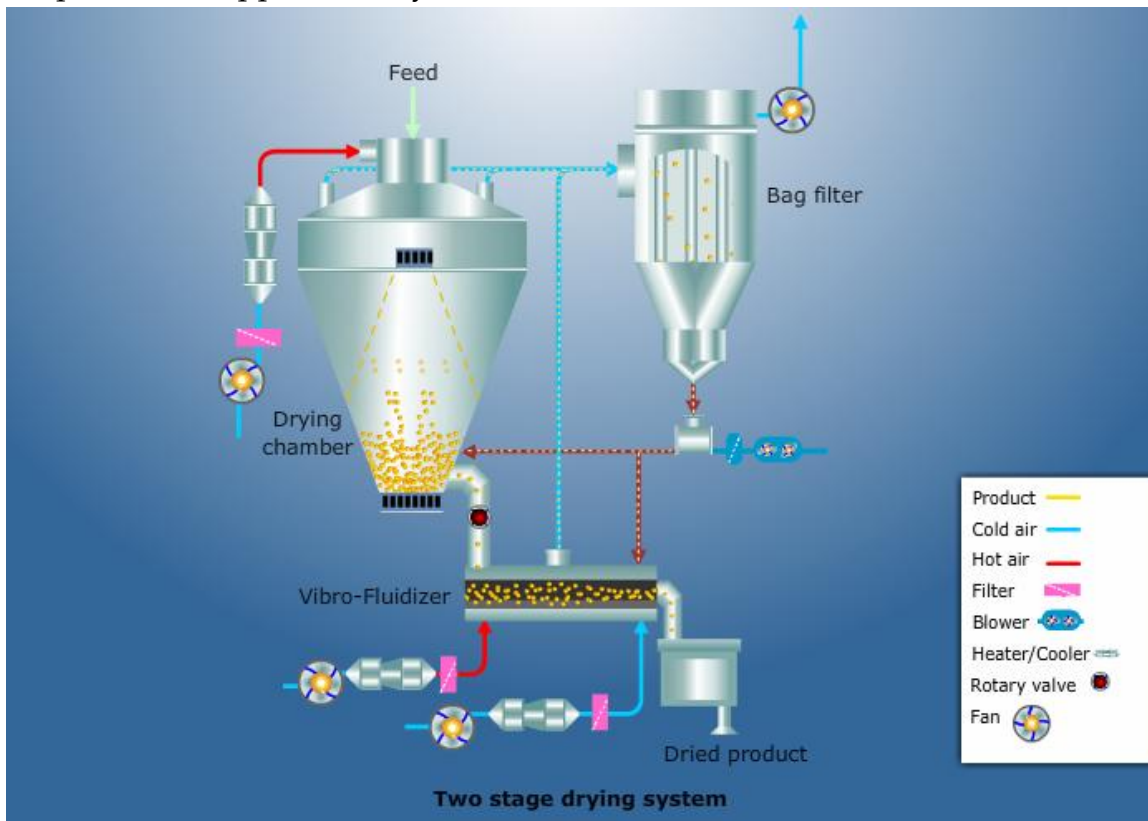
In the spray drier, it is possible to dry whey concentrate containing up to around 60% TS, when the lactose content has been subjected to a crystallization degree of 85-90%. Direct evaporation and drying costs in procedure 2 are thus lowered to 5.5 kg steam/kg of whey powder.



22.2.2 Two-stage process

The principle of two-stage drying is a combination of spray drying as the first - stage drying and fluid bed drying at the second stage (Fig.22.3). Final drying in the integrated fluid bed dryer ensures that the desired residual moisture is achieved. After final drying, the powder is cooled in a pneumatic conveying duct. The installations can be operated with both nozzle and centrifugal atomizers.

By two stage drying, it has been possible to obtain good quality powders and also with advantage regarding drying economy in the manufacture of non-agglomerated products. In this process normally, powders leave the chamber and enter the attached vibrating fluid bed drier with a moisture content of 5-7%. In the fluid bed, the air blown into the first section has an ambient temperature to stabilize the agglomerates, thus avoiding lumping of the thermoplastic powder. Air temperature in the second section is 100°C, where the excess moisture is removed from the powder, while in the third section the powder is cooled down with conditioned air of approximately 11°C, to prevent additional moisture absorption. This lowers drying costs. Fines are recovered in the spray drier and fluid bed cyclones collected and returned to the atomizing zone for agglomeration. This agglomeration gives a free flowing powder. In this process typical drying conditions are: feed preheating to 80°C, feed concentration of 50-60%, crystallization, and then drying at an inlet temperature of approximately 185°C.



22.2.2.1 Advantages

Two-stage drying allows for gentler handling of the product, thereby reducing product degradation. The biggest advantage over single-stage drying is the improved efficiency achieved by increasing the temperature difference between supply air and outgoing air. The energy required for drying is about 10 - 15 % lower than in the single-stage process. The cost of whey drying is reduced to 5.0 kg

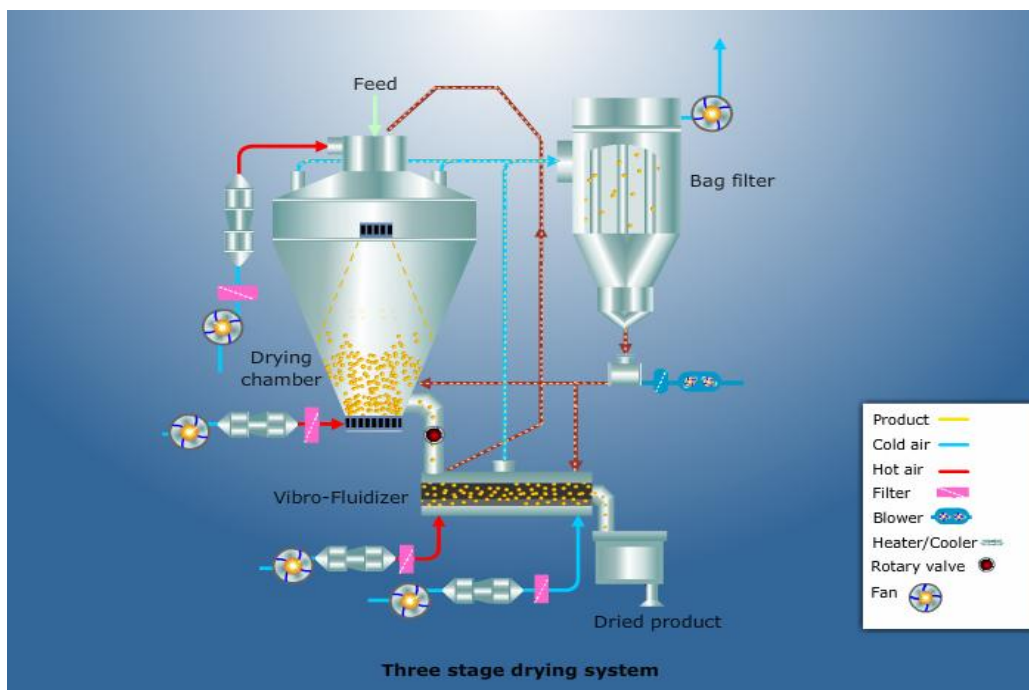
steam/kg of powder by application of two-stage processing.

22.2.3 Three-stage drying

The three-stage dryer involves transfer of the second drying stage into the base of the spray drying chamber and having the final drying and cooling conducted in the third stage located outside the drying chamber (Fig22.4). It consists of a main drying chamber, static integrated bed chamber and vibro fluidized bed chamber. In the main chamber primary drying of the droplets takes place in the main chamber as they fall from the atomizer to the base of the chamber. The second drying stage takes place as drying air is sucked through the powder layer. The moisture content of the powder falling on the integrated bed is 12–20 % depending upon the type of product. This second drying stage reduces the moisture content to 8-10 %. The moisture content is very important to achieving the exact degree of agglomeration of the product and porosity of the powder layer. The third and last drying stage takes place in the vibro fluidized bed dryer where the moisture contents of the powder reduces to 3to 5%. Fluidized bed chamber is supplied with heating and cooling section. Only a small amount of powder leaves the plant together with the drying and cooling air as fines. This powder is separated from the air in a cyclone. The powder is recirculated, either to the main chamber or to a point in the process appropriate to the type of product and the agglomeration required.

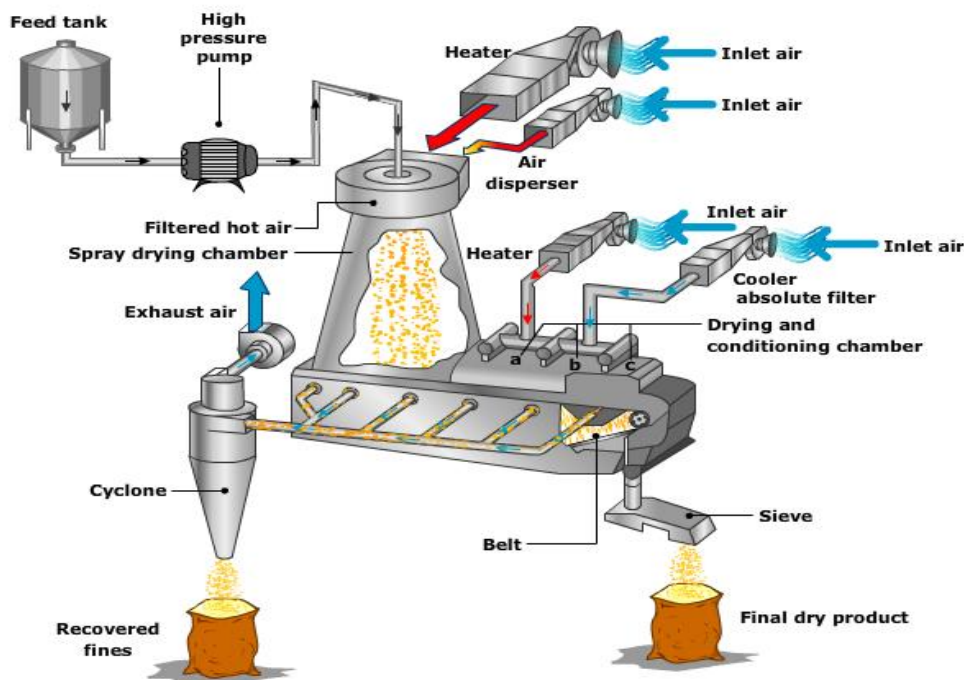
22.2.3.1 Advantages

This configuration allows the supply air temperature to be increased and the outgoing air temperature to be lowered. This reduces the specific energy requirement by a further 10-15%, improves particle agglomeration and reduces product degradation by using lower drying air temperatures compared with two-stage drying. A large number of plants installed work to this principle. Mass-produced products such as skim milk powder and whey powder are manufactured cost-effectively in this way.



22.2.4 Belt process

Lactic acid in dry form is very thermoplastic even at low temperature and difficult to dry by conventional spray drier. This means that this type of powder is extremely sticky during the spray drying process. The belt process is especially advantageous in drying lactic acid whey. The high moisture content of powder leaving the spray drying chamber ensures that crystallization will continue in the powder to an even greater extent than in the two-stage process using fluid bed drier. This crystallization is improved if the wet powder is kept at high moisture content for 10-15 minutes. This is conveniently done on a belt conveyor mounted between the chamber outlet and a fluid bed, where the final drying takes place. The resulting powder consists of large agglomerates, which has a low bulk density, but is extremely instant and have excellent non-caking properties. In order to avoid condensation in the cyclones, hot air is introduced into the exhaust system of the spray dryer to increase the relative humidity.

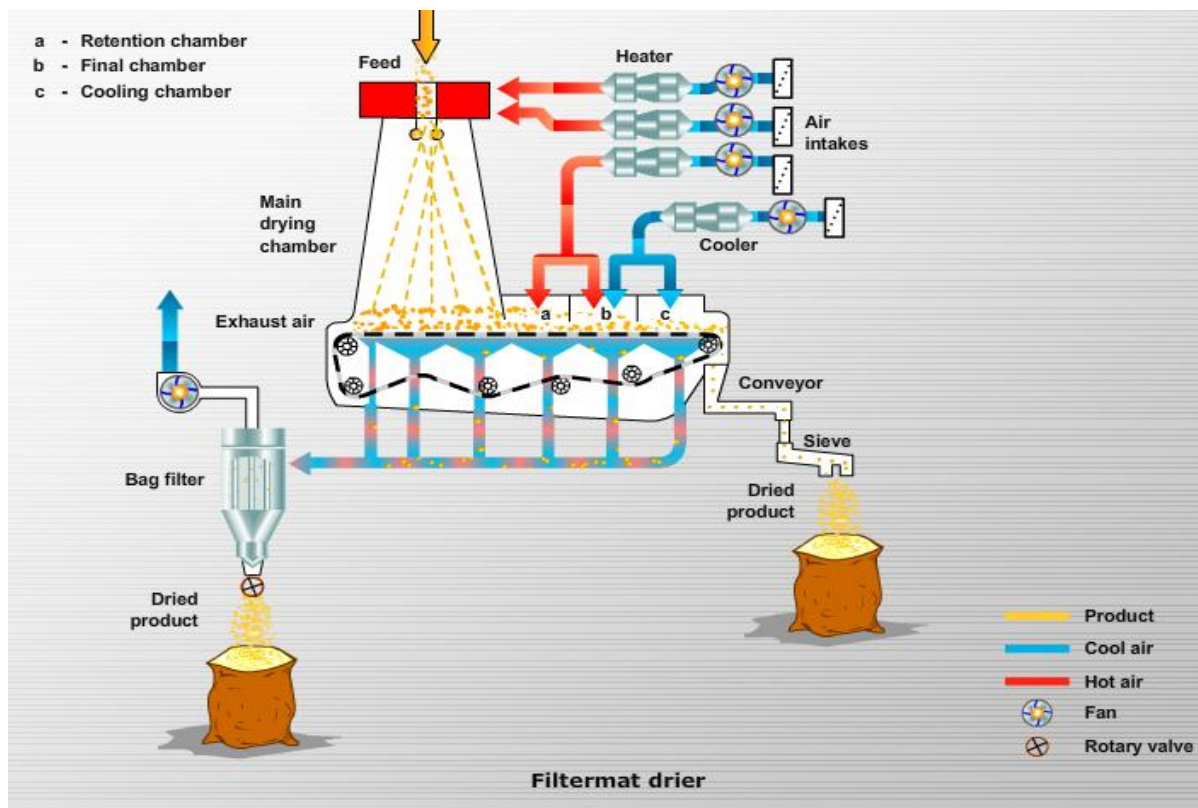


Belt system of acid whey drying

A spray belt dryer is shown in Fig.22.5. It consists of a main drying chamber and three smaller chambers for crystallisation, final drying and cooling. Typical drying conditions involve preheating to 80°C, feed concentration to 50%, spray drying at inlet temperature of 150°C and outlet temperature of 55°C to a moisture content of 12-15%.

22.2.5 Filtermat concept of drying

In filtermat drying system, the concentrate is atomized by pressure nozzle in a low profile drying chamber. Here the conveyor belt collects powder from bottom of the chamber (Fig.22.6). The conveyor belt contains three sections. First section for agglomeration and crystallization, second section contains warm air for drying and third section for cooling of powder.



22.3 Roller Drying of Whey

The technologically simpler and much less expensive roller drying technique can sometimes be used economically for the production of lower-quality whey powders (Peters, 2005), but its harsh heat treatment effects diminish the utility of this traditional technique for producing high quality whey-based powders.

Whey powder obtained by the roller drying method is very hygroscopic since most of the lactose is in amorphous form. It has a dark colour caused by the maillard reactions between proteins and lactose. Considering that the amino group in lysine takes part in these reactions, the quantity of available lysine is decreased by 30%. In addition, roller-dried whey powder is not easily soluble and has other negative characteristics. In spite of these negative effects the roller drying also have some advantages, such as low cost investment, relatively small space necessary for the operation, economical processing, and easy operation and maintainance. Some of the problems encountered in conventional roller drying may be eliminated by vacuum roller drying. In this type of drying the whey is dried at a temperature below 100°C at 91-98 KPa means that the effects of oxygen and high temperature are markedly reduced. The product has better properties than the whey powder obtained from roller drying under atmospheric pressure.

***** 😊 *****

Lesson 23

PHYSICO-CHEMICAL PROPERTIES & UTILIZATION OF CONDENSED AND DRIED WHEY PRODUCTS

23.1 Introduction

Composition of condensed and dried whey vary depending on the type of whey from which they have been prepared, pretreatment given to the whey, and the various processing steps followed in the production. By far the single largest use of whey solids on global basis is in the form of whole dry whey and it continues to grow. This is whole whey that has been condensed and spray dried as such or after blending with certain other liquid ingredients. These powdered whey products are marketed as commodity ingredients for a variety of foods for human and animals. Whey solids in the form of concentrated whey or whey powder are used in different food industries. Whey powder is also used as an ingredient in animal feed mixes as well, since it is a cheap source of high-quality proteins and carbohydrates.

23.2 Physico-chemical Properties of Condensed and Dried Whey Products

23.2.1 Condensed whey

Chemical composition of plain, sweetened condensed whey and condensed acid whey is given in Table 23.1.

Table 23.1 Chemical composition of condensed whey

Product	Constituent (%)					
	Sugar		Water	Ash	Fat	Protein
	Lactose	Sucrose				
Plain condensed whey	51.3	-	32.0	6.0	0.6	10.1
Sweetened condensed whey	28.7	38.0	24.0	3.4	0.3	5.6
Condensed acid whey	49.0	-	33.5	8.2	0.6	7.7

23.2.2 Whey powder

According to FSSAI (2011) Standards, whey powder means the product obtained by spray or roller drying sweet whey or acid whey, from which major portion of milk fat has been removed. It shall be of uniform colour with pleasant taste and flavour free from off flavour and rancidity. It may contain food additives permitted in these regulations. It shall conform to the microbiological requirements prescribed in Annexure - I. It shall conform to the requirements as given in Table 23.2. Other properties of whey powder are shown in Table 23.3.

Table 23.2 FSSAI (2011) compositional standards for whey powder

Requirements	Whey Powder	Acid Whey Powder
Moisture	Not more than 5.0 percent	Not more than 4.5 percent
Milk Fat	Not more than 2.0 percent m/m	Not more than 2.0 percent m/m
Milk Protein (N x 6.38)	Not less than 10.0 percent m/m	Not less than 7.0 percent m/m
Total Ash	Not more than 9.5 percent m/m	Not more than 15.0 percent m/m
pH (in 10.0% solution)	Not less than 5.1	Not more than 5.1
Lactose content expressed as anhydrous Lactose	Not less than 61.0 percent m/m	Not less than 61.0 percent m/m

Note: (i) Although the powders may contain both anhydrous lactose and lactose monohydrates, the lactose content is expressed as anhydrous lactose.

(ii) 100 parts of lactose monohydrate contain 95 parts of anhydrous lactose.

Table 23.3 Properties of whey powder

Properties	Ordinary whey powder	Precrystallized whey powder	Non caking whey powder (Straight through)	Non caking whey powder (Belt process)
Total moisture (%)	3-4	3-5	5-6	4-5.5
Free moisture (%)	3-4	1-2	1.5-2.5	1-2
Bulk density (g/cm ³)	0.6-0.7	0.6-0.7	0.55-0.65	0.4-0.5
Degree of cakeness (%)	100	40-100	0-5	0-5
Degree of Crystallization (%)	0.1	50-75	75-85	85-90

Whey powder easily accepts atmospheric moisture as a result of amorphous lactose content, proteins, and salts. Caking tendency is influenced by the degree of lactose crystallization, as well as the crystal number and size distribution. In ordinary whey powder, total lactose is in an amorphous form. Absorption of ambient moisture takes place until a balance with the powder moisture is achieved (e.g., approximately 30% moisture in the powder). Powder then loses its previous consistency and becomes viscous. The presence of moisture causes crystallization nuclei formation and lactose crystallization. As a result, vapor pressure of moist powder overcomes the pressure of the surrounding air, disturbing the balance and causing moisture desorption. The powder then undergoes solidification and can be used only as animal feed. In improved whey powders, where lactose precrystallization is implemented, these characteristics are much improved.

23.3 Utilization of Condensed and Dried Whey Products

Whey solids are used in dairy products, bakery goods, baby food, meat products, beverages, soups, sauces, dressings and creams. In addition, whey solids are used in animal feed mixes, as it is a cheap source of high-quality proteins and carbohydrate. Plain condensed whey and sweetened condensed whey may be used to make various whey candies such as 'wheyfers', whipped whey fudge, whey caramel and 'whey' taffy. The whipping properties of sweetened condensed whey is of value in many food preparations, say for example, ice cream, shakes, sherbets and bakery and confectionery

products. Uses of whipped sweetened condensed whey include making of fruit whips, certain candies and frozen dessert preparations. A sweet spread of good keeping quality, may be made by mixing equal weights of sweetened condensed whey and peanut.

23.3.1 In dairy products

US Government regulations permit replacement of up to 25% of the MSNF of ice cream formulation with good quality sweet or acid whey solid in accordance with good manufacturing practices. In ice creams, whey powder can successfully replace skim milk powder and is less expensive. It has been proven that this substitution, ranging from 0-20%, does not influence the taste, consistency, or melting point of ice cream. The application of condensed and dried whey in other dairy products is significant as well. In Norway, "Mysost" and "Primost" cheeses are produced from concentrated whey with 84% total solids. Dulce de leche, yoghurt and whipped cream substitute may also contain condensed or dried whey.

23.3.2 In bakery products

Concentrated whey and whey powder have worldwide industrial application in bread and other bakery products. For example, condensed hydrolyzed whey added to flour during bread making enhances consistency and results in better structure, porosity, freshness retention, and taste of the final product, while improving the nutritive value. Liquid whey concentrate and whey powder are used in breakfast cereals, bakery and fried food products, where the development of a golden brown crust is desired. Whey powder is used at up to 3% of the flour in the formulation to improve crust colour, crumb structure and tenderness of bakery products. Special additives for the bakery industry are produced with whey powder as the main ingredient. In macaroni, spaghetti, and other production, added whey dry matter improves viscosity and dough properties.

23.3.3 In confectionery products

Condensed whey is used with fruits, jams in various toppings, and spreads in confectionery. Other uses include caramels, fudge & fondants where usage is from 8-16% of the sugar to reduce sweetness, prolong shelf life and improve nutritional quality. Condensed sweetened whey is used in caramel production, which is 38% whey solids, 38% sucrose and 24% water. Sweetened condensed whey is used as economical substitute for NFDM solids ingredient in candies and confections. Whey products provide important functions by increasing background milk flavour improving texture and chewiness & producing characteristic colour and flavour. High lactose concentration in the condensed whey enhances golden brown colour of caramel. In milk chocolates, although whey is not included as optional ingredient, but whey solids, particularly demineralized whey solids, provides several advantages for manufacturing chocolate milk products. Concentrated whey in chocolate liquor are used frequently and found compatible and increase flavour and bloom resistance in chocolate coatings.

A mixture of equal parts of peanut butter and sweetened condensed whey will produce an attractive sweet filling or candy center. It may also be used as a sweet spread. The addition of sweetened condensed whey takes the sticky, clinging characteristic from peanut butter and gives it a smooth,

short type of body. The mixture is prepared by blending one pound of sweetened condensed whey for each pound of peanut butter to be treated.

23.3.4 In fermented products

Gandhi and Patel (1994) found that whey fermented with selected lactic acid bacteria could be concentrated up to 30% TS while retaining viable lactic acid bacteria at levels up to 10-30 cells/ml. The whey concentrate could be stored for up to 4 months at 5°C. Thus excess whey can be stored for up to 4 months in concentrated form and reconstituted as a fermented dairy beverage. Rodriguez *et al.* (2002) used concentrated whey and ultra filtered to get 3% true proteins. Thus was formed with yogurt cultures to get a fermented beverage.

23.3.5 Condensed whey as animal feed

Ruminants can consume as much as 30% of their dry matter requirement in the form of liquid whey. But pigs are limited to an amount of whey equivalent to 20% if their dry matter intake. The hydrolysis of lactose reportedly improved the nutritional value of whey and deproteinated whey for pigs and other animals that are more or less lactose intolerant. Whey solids can also be fed to dairy cows and other ruminants if proper conditions are maintained.

23.3.6 Miscellaneous uses of whey powder

There are other suggested uses for whey powder, such as ingredients in crèmes, pastes, or tablets for cosmetic baths, stabilizers in agricultural foams against frost, pesticide carriers, and polyurethane foam additives to slow down concrete solidification.

***** 😊 *****

Lesson 24

WHEY BEVERAGES

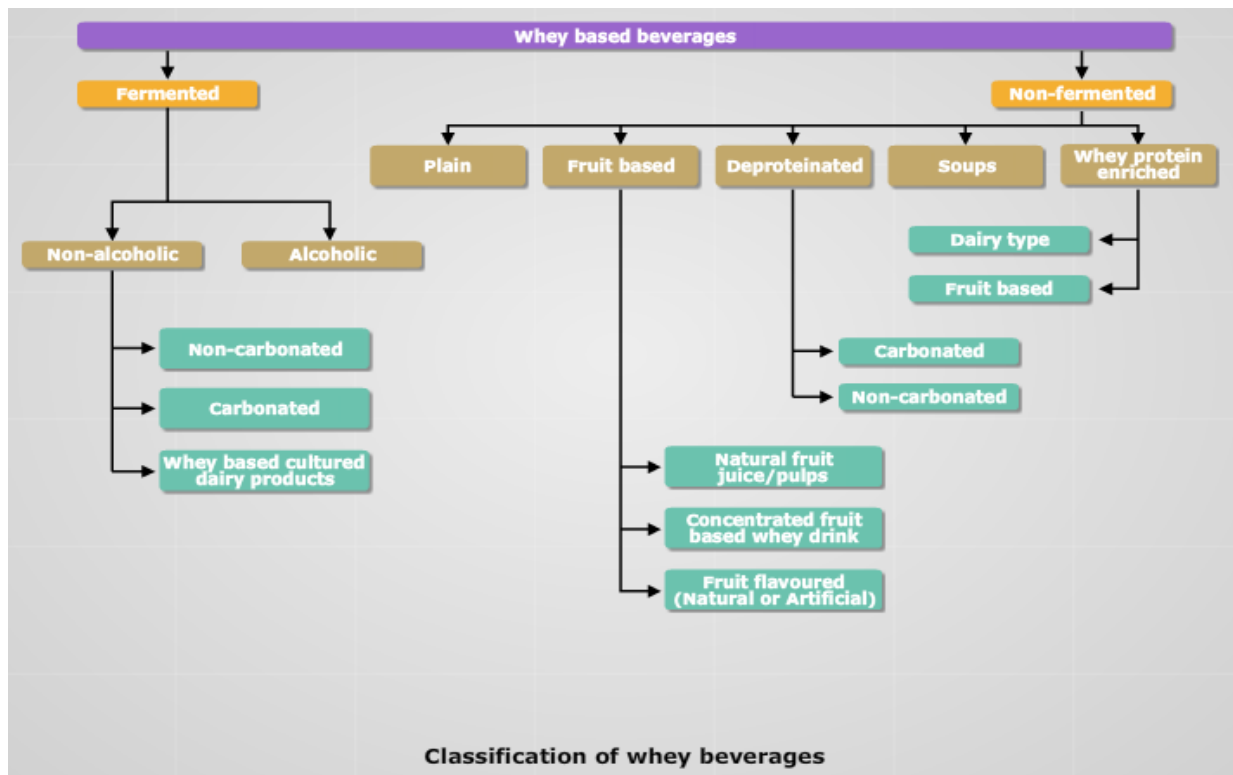
24.1 Introduction

Production of whey based beverages started in 1970's and until today a wide range of different whey beverages has been developed. Whey beverages include wide range of products obtained by mixing of native, sweet or acid whey, deproteinised whey and whey powder with different additives like tropical fruits (but also other fruits like apples, pears, strawberries, cranberries), crops and their products (mainly bran), isolates of vegetables proteins, CO₂, chocolates, cocoa, vanilla extracts and other aromatizing agents. Whey beverages also includes dietetic beverages, drinks with hydrolyzed lactose, milk like drinks and powder drinks. The prominent type of new whey drinks are based on blends of fruit juices and whey. The main advantages associated with such beverages are the healthful combination of the fruit base, vitamin containing components and the dairy based calcium and whey proteins. The manufacture of whey-fruit juice mixtures can be relatively simple and, therefore, many dairy processors have attempted to enter the beverage market with their, own *"variants of the common theme"*.

Other types of whey-containing beverages currently available in the market include whey proteins fortified whey beverages, deproteinated whey beverages, fermented dairy-type beverages containing whey, and flavoured milk-type products containing whey or whey components. Some of these products may be suitable for marketing in dry form as well. In view of increasing demand of beverage in the form of cold drinks and fruit juices, whey has a promising future in the beverage formulation. As a drink, it can replace much of the lost organic and inorganic salts to the extracellular fluid. It also possesses almost all the electrolytes of Oral Rehydration Solution (ORS), which is invariably used to control dehydration.

24.2 Classification of Whey Beverages

Figure 24.1 gives the classification of main type of commercial beverage product from whey. Whey based beverages are broadly classified into two categories: Fermented and Non fermented. In this lesson, non fermented whey beverages are discussed in detail.



24.2.1 Plain whey beverages

Plain whey beverages include the mixing of whole whey along with sugar, flavour (either synthetic or natural) and colour. These may or may not be carbonated.

24.2.2 Whey based fruit beverages

Different types of whey based fruit beverages have been prepared. Whey-fruit beverage products marketed in Europe is presented in Table 24.1. These whey based fruit beverages can be classified depending on the type of raw material used and different processing conditions. These are as follows:

24.2.2.1 Whey based natural fruit juice/pulp drink

Whey based fruit beverages are manufactured by mixing of appropriate fruit pulp/ juice or juice concentrate and processed whey (Fig.24.2). The more sophisticated technological approaches include the painstaking selection of proper flavour or flavour blends, complex whey treatment operations and often the inclusion of additional nutrients to increase the consumer appeal. The common operation for the manufacture of whey based beverage is to blend the whey and fruit juice components, followed by proper heat processing and packaging. The sedimentation problem can be removed by centrifugal clarification to remove all sedimentable casein fine particles (Jelen *et al*, 1987). The pH adjustment in the heat processed long shelf life beverage is important in order to minimize heat induced whey protein precipitation. A typical feature of these products is their low protein and high total carbohydrate content, often exceeding that of a carbonated soft drink or fruit juice product. This high carbohydrate content is a result of the high lactose content of the whey, which contributes little to product sweetness. The overall character of the successful products resembles fruit juices with a somewhat heavier body; the resulting image may be that of a nutritious, rather than a thirst-

quenching beverage. The tetra- pack paper based containers of 200 ml capacities predominate in India, while 250 or 500 ml plastic cups with aluminium foil are being used in western countries.

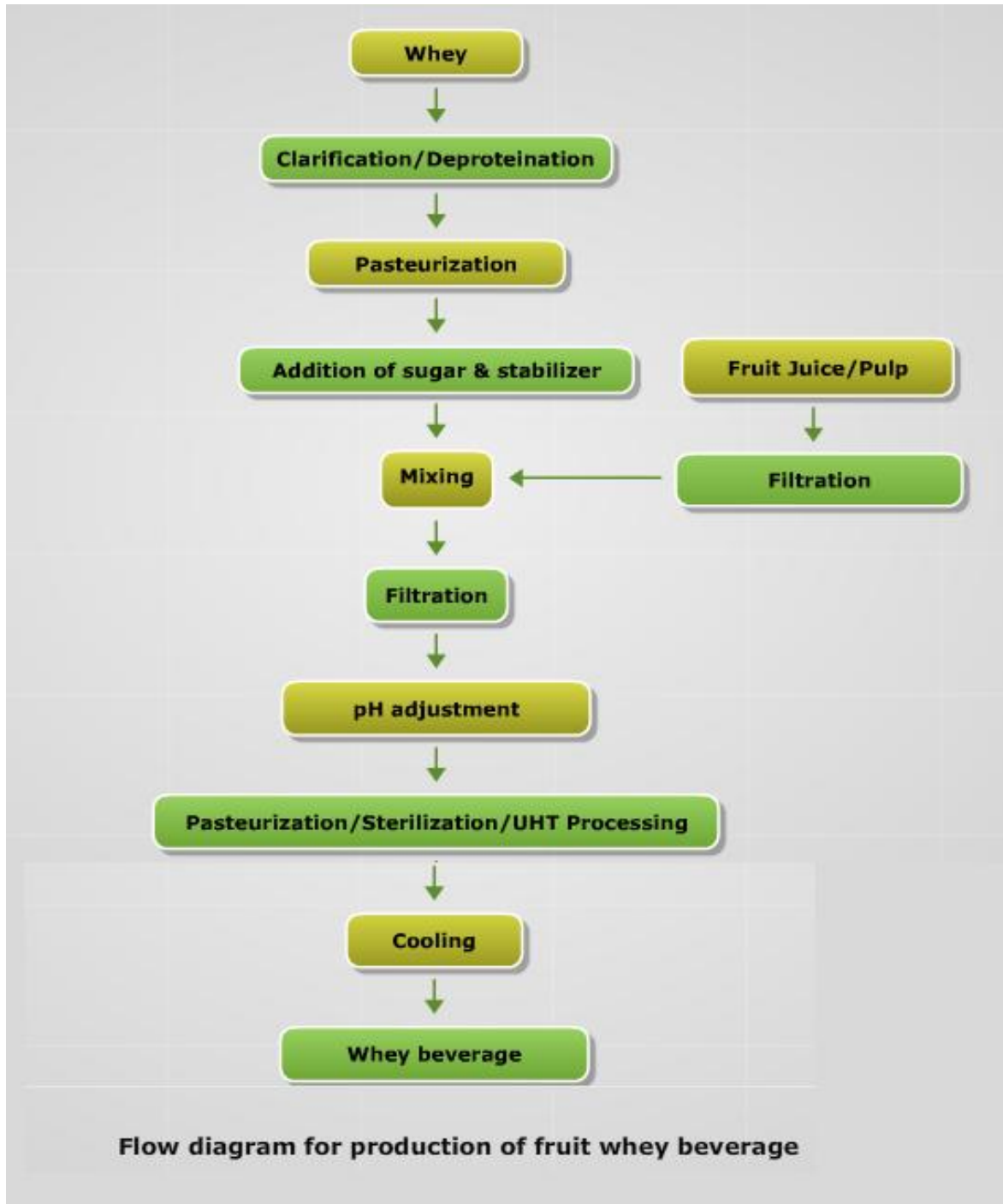


Table 24.1 Whey - fruit beverage products marketed in Europe

Product name	Type	Characteristics
Frusighurt	Fruit, artificial sweetener	Germany Whey + 10% apple/ lemon juice
Mango-molke-mix	Fruit	Whey and mango juice, Bifidobacterium culture
Frucht-molke (Heirler)	Fruit	Available in health food store, several varieties (peach, maracuya, passion fruit, apple)
Frucht-molke (Immensee)	Fruit	Whey + 15% blackcurrant (juice) or 25% fruit mix juice (orange, pineapple, apricot, apple, banana, grapefruit, mango, peach, papaya, lemon)
Kur-molke	Fruit, artificial sweetener	Apple or orange
Multivitamin-molke	Fruit, artificial sweetener	Whey with juice from 10 fruits and 10 vitamins added
Molke-frucht nektar	Fruit	Whey + 25% orange
Fit	Fruit	Switzerland Whey and grapefruit (15%) or mango juice
Latella	Fruit	Austria Whey with mango and grapefruit/ lime juices
Morea	Fruit	France Whey concentrates with 40% juice mix of mango, guava, kiwi, and passion fruit
Djoez	Fruit	Holland Whey (80%), fruit juice concentrate (12.8%), flavouring
Taksi	Fruit	Whey (85.3%), tropical fruit juice concentrate (6.3%), colouring
Hedelmatarha	Fruit	Finland Lactose-hydrolysed whey mixed with a mango or a tropical fruit juice mix

* Jelen. (1992)

24.2.2.2 Concentrated fruit based whey beverages

Concentrated fruit based whey beverages have been developed to deliver the product in more convenient form, minimize the transportation and packaging requirement and improve the protein content. For preparing such products whey is concentrated in vacuum pan or evaporators, mixed with fruit juice concentrate, sugar and other additives, heat treated and packaged.

24.2.2.3 Fruit flavored drinks

In this type of whey based fruit beverages, different types of fruit flavours are used which may be artificial and natural.

24.2.3 Deproteinated whey beverages

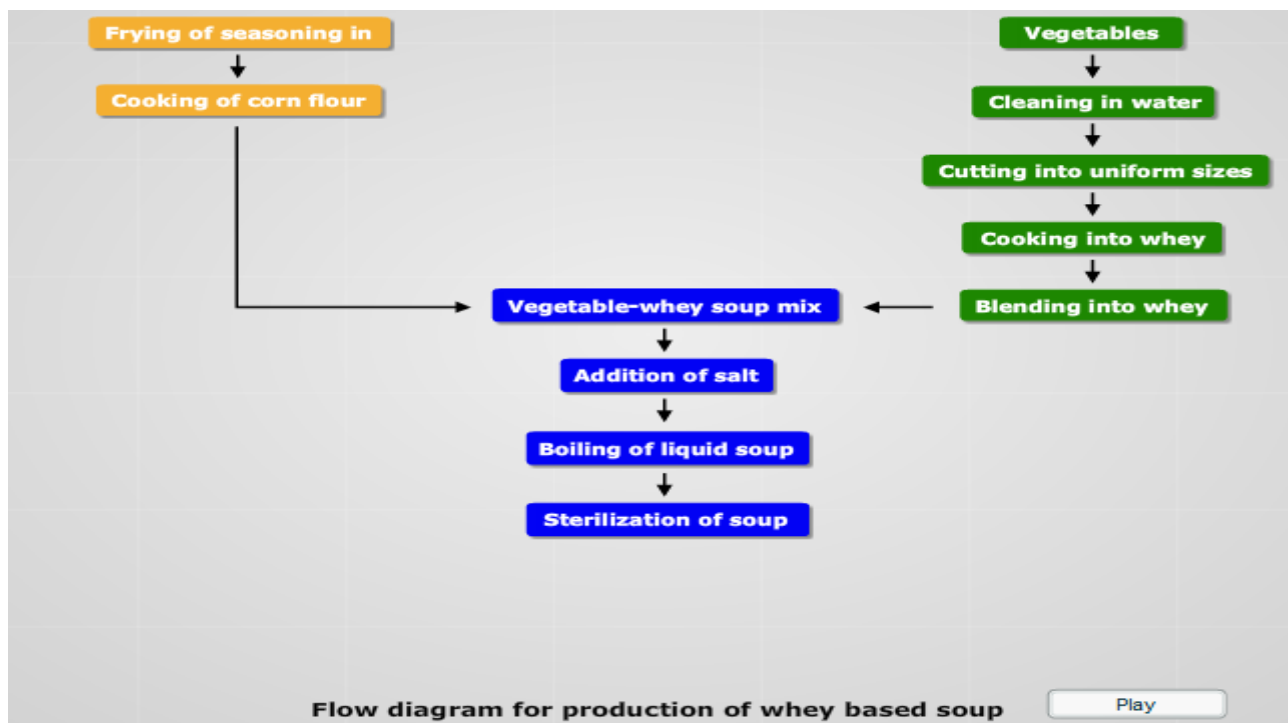
Whey permeate which is obtained during whey protein preparation using ultrafiltration process, can be an ideal starting material for the development of such products. These can be carbonated and non carbonated beverages. All beverages made with whey permeate are higher in electrolytes (Na, K, Zn, Mg, P) compared with commercially available sports beverage.

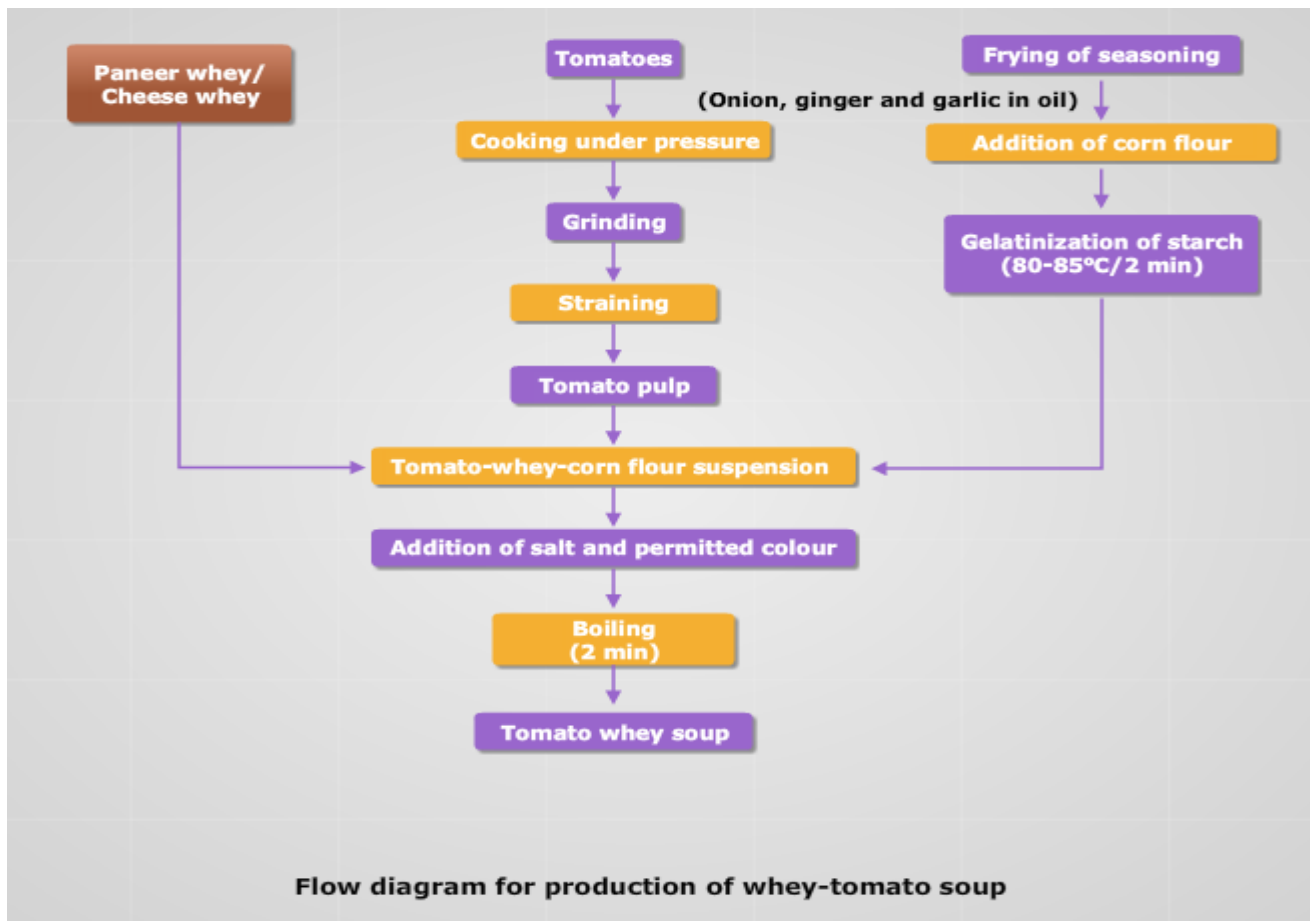
24.2.4 Whey protein enriched whey beverages

Whey protein is used to increase the protein content of whey based beverages. Swedish Dairy Cooperative developed and marketed a protein rich fruit drink called "Nature's Wonder". It was produced by mixing a high-grade whey protein, hydrolyzed lactose and pineapple, orange and passion fruit juices. Similarly whey in the form of high protein dry whey powder or concentrate is used for preparation of both dairy type or fruit based beverages.

24.2.5 Whey based soups

The common sequence of the operation in the development of whey based soup involves blending of vegetable in whey and cooking of corn flour followed by heat processing. The time-temperature combination for cooking of vegetables, corn flour and seasoning is important for proper dispersion of vegetables, gelatinization of starch and flavour perception of soups, respectively. The development of long shelf life soup involves proper sterilization of soup. Whey based soup powders can be manufactured by cooking of vegetables in concentrated whey, mixing of blended vegetables in whey, frying of seasonings, gelatinized starch followed by spray drying (Fig.24.3).





However, commercial soup powders are available as a result of blending of dried vegetables in gelatinized starch. Paneer and cheese whey were utilized for the potato-carrot-tomato and spinach soups (Fig.24.4). Cheese whey was preferred for the manufacture of vegetable soups than paneer whey (Singh *et al.*, 1994). The reason could be the low pH of paneer whey that resulted in acidic product not usually compatible with most vegetables. Whey based soups have been reported to be more viscous as compared to water based most probably gelation of whey proteins on heating.

24.3 Conclusion

Beverages and soups based on whey continue to receive a considerable amount of attention nowadays. These indicate the growing awareness among consumers and manufacturers alike for the enormous potential these offered for diversifying product profile. Technological packages are available for wide range of whey based such products and with better understanding regarding the functionality of different ingredients it would be possible to develop “functional” whey products for specific target groups.

***** 😊 *****

Lesson 25

FERMENTED WHEY BEVERAGES

25.1 Introduction

Fermentation is one of the oldest forms of food preservation and biological upgrading of dairy by-products into value added foods, which possesses nutritional properties in addition to their palatability. For whey fermentations, mainly starter and probiotic cultures of lactic acid bacteria are used, while in case of alcoholic fermentations mostly yeast species *Kluyveromyces* used. In this category of products big attention has been paid to development of probiotic whey beverages. The preparation of wide varieties of palatable beverages through microbial fermentation of whey by using selected strains of lactic acid bacteria, yeast, probiotic and prebiotic microorganisms has been reported. Whey is an excellent growth medium for lactic acid bacteria as it contains lactose in abundant amount, which is the basic medium for fermentation. On fermentation with lactic acid bacteria, it becomes a suitable drink for lactose-intolerant people. The lactic acid imparts fresh flavor, masks the effect of curdy flavour of whey and is known to suppress the growth of pathogenic spoilage organisms.

Broadly fermented whey beverages have been classified into two categories depending upon the starter culture used to carry out the fermentation process in whey. These are a) Lactic fermentation or non-alcoholic fermentation and b) Alcoholic fermentation. Different types of fermented whey beverages developed under these categories, have been described and some of the processes have been patented.

25.2 Preparation of Fermented Whey Beverages

A number of non alcoholic and alcoholic beverages have been prepared from the whey and market value of these beverages is increasing day by day. Some globally famous whey based fermented beverages are given in Table 25.1.

25.2.1 Non-alcoholic whey beverages

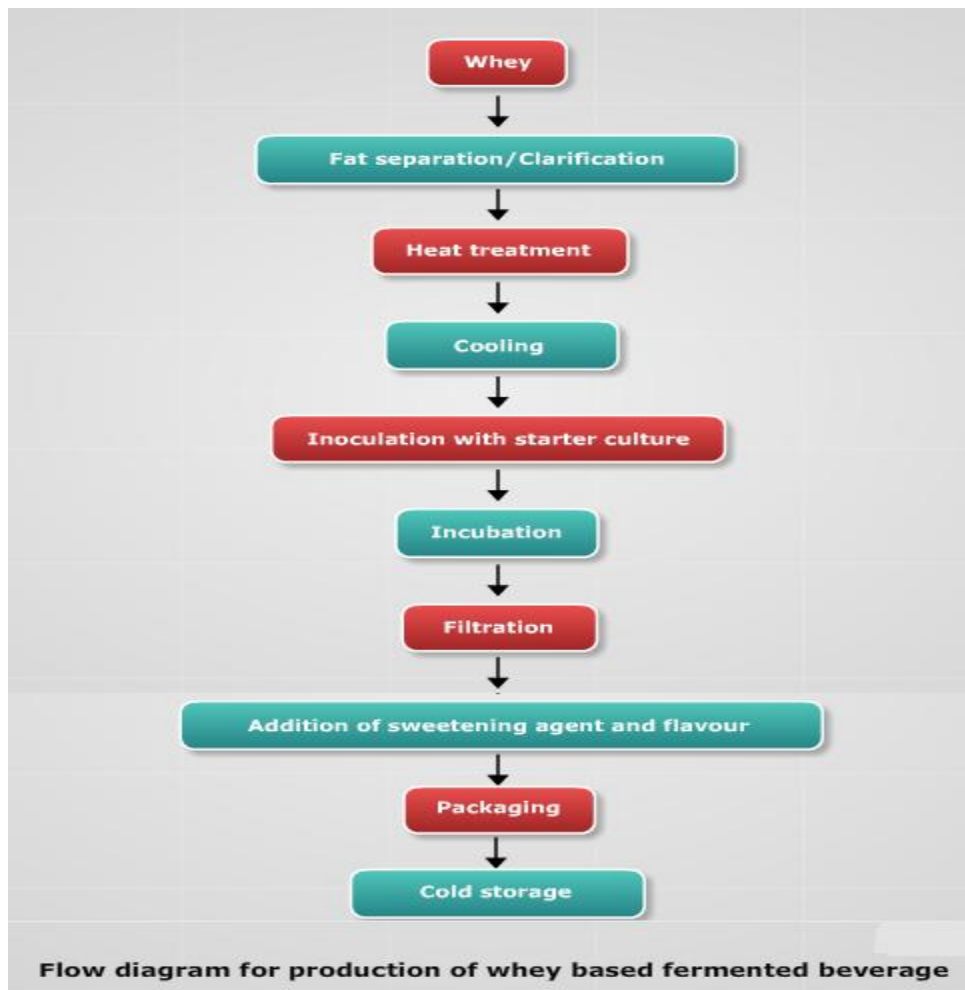
These beverages are obtained by fermenting lactose in whey to lactic acid by lactic acid bacteria (LAB) and can be mainly categorized into whey based fermented drink, whey based fermented carbonated drink and whey based cultured dairy products.

Table 25.1 Some famous whey based fermented beverage in the world

Product	Type	Characteristics
Rivella	Whey based fermented carbonated drink	35% deproteinated whey serum + water, sugar and flavor
Surelli	Whey based fermented carbonated drink	Almost same as rivella
Fauna-fit	Soft drink type	Approx. 85% sweet whey UF permeate fermented & after second UF mixed with fruit juice (mango, pineapple, strawberry)
Whey kwas	Alcoholic kefir like drink	Deproteinated whey inoculated with thermophilic starter and then treated with yeast
Servovit	Whey based cultured dairy products	Carbonated product based on whey and cultured buttermilk
Kumiss like beverage	Whey based fermented drink	Whey + buttermilk inoculated with culture comprised of kumiss yeast <i>L. bulgaricus</i> and <i>L. acidophilus</i>
Milone	Whey based fermented drink (mildly alcoholic and sweet sour in flavour)	Whey + 1% lactic acid + equal amount of tea, copper, remaining liquid is then incubated with lactose fermenting yeast (0.8% ethanol)
Alcoholic whey beer	Beer like beverage	Whey beer brewed with hops but without added malt
Malted whey beer	Beer like beverage	Malt and hops both were added to whey and fermented with bottom yeast
Whey malt beer	Beer like beverage	50% whey + malt, hop, sugar and coloring matter (produced with top fermentation)
Whey nutrient beer	-----	Whey + hops and nutrient salts (low alcoholic product)
Whey champagne	Alcoholic wine like	Deproteinated whey inoculated with 0.1% fresh baker's yeast + addition of coloring and flavouring substance
Whevit	Alcoholic soft drink	Whey is fermented with yeast culture (<i>Saccharomyces cerevisiae</i>), can be carbonated and non carbonated
Acidowhey	Non carbonated soft drink type	Whey fermented with lactic acid bacteria and free from preservative and synthetic color

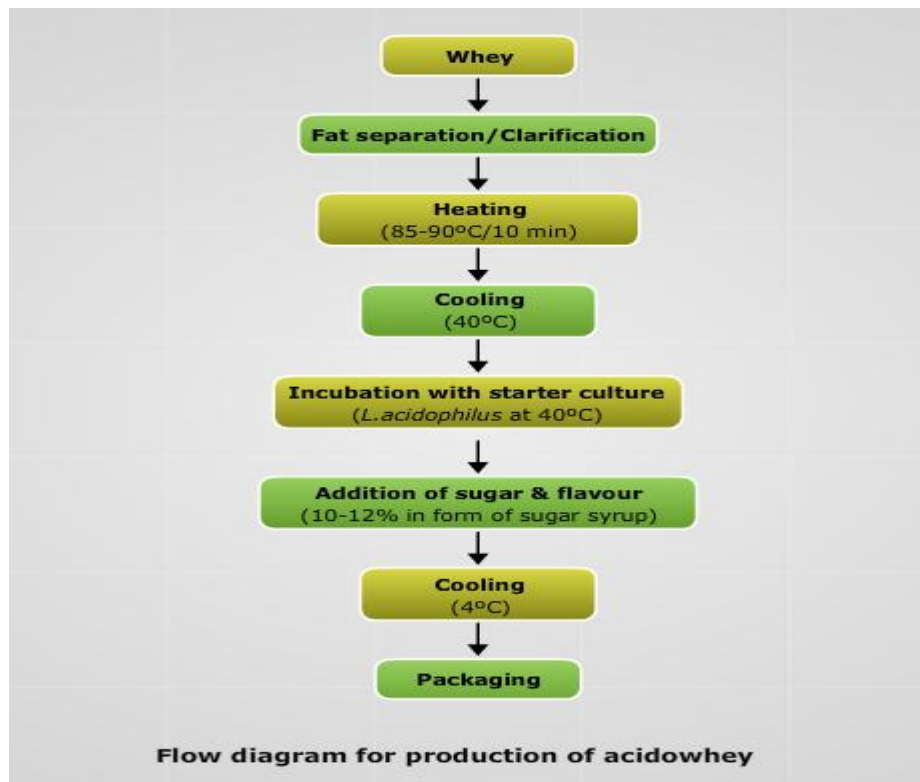
25.2.1.1 Whey based fermented & carbonated drinks

There are many fermented and carbonated whey beverages produced in different parts of the world and can be grouped accordingly to basal substrate and types of cultures used. A flow diagram for the preparation of fermented whey beverage by using lactic acid bacteria is given in Fig. 25.1.



25.2.1.2 Preparation of fermented whey drink 'Acidowhey'

A palatable soft drink "Acidowhey" from whey was developed at National Dairy Research Institute, Karnal. "Acidowhey" is a non-carbonated drink, fermented with selected strain of lactic acid bacteria and retaining all the nutrients of whey intact. For its preparation (Fig.25.2), whey from paneer, cheese, chhana or casein manufacturing is first separated to remove fat and traces curd particles. Clarified whey is heat treated to 85-90°C for 10 min. or its equivalent combination. Clarified whey after cooling to 40°C is inoculated with an active culture of *L. acidophilus* and incubated at 40°C temperature. After incubation, fermented whey is clarified to remove precipitated cellular mass, whey protein and minerals formed during the process. Sugar is then added to the product at the rate of 10-12% in the form of 50% sugar syrup, which had been earlier pasteurized. Then desirable amount of pineapple flavor or any compatible citrus flavor is added and the beverage is chilled to 4°C and packaged. Beverage should be pasteurized before packing or alternatively pasteurized in the container. Additional studies demonstrated antibacterial properties of 'Acidowhey' against certain gram positive and gram negative organisms such as *Micrococcus flavus*, *Staphylococcus aureus*, *Escherichia coli* and *Bacillus subtilis*.



25.2.1.3 Whey-based cultured dairy products

Current world-wide popularity of fruit-flavoured drinkable yoghurt offers an excellent opportunity for the incorporation of whey into these products. The compatibility of whey - especially of acid whey and/ or further fermented sweet whey-with the character of cultured dairy beverages makes such an approach particularly attractive for traditional dairy processors. In addition to whey based yoghurt drink for example yor and interlac 'thin buttermilk' products, prepared by culturing a mixture of regular milk and an ultrafiltration whey protein retentate containing the same protein content as milk are another example of whey-containing cultured dairy beverages.

25.2.2 Alcoholic whey beverage

Alcoholic whey beverages include drinks with small amount of alcohol (to 1.5%), whey beer, whey wine and whey champagne. Some of these beverages have been well accepted by the consumers and are being produced commercially. Patents have been granted on the processes of production of alcoholic beverages.

25.2.2.1 Whey wine

Whey is used for production of various types of whey based wines that contains relatively low alcohol amount (10-11%) and mostly flavored with fruit aromas. These have been made from demineralised UF permeate or reconstituted acid whey powder. In reconstituted acid whey powder, protein is removed by UF and permeate had a total solids concentration of 26-28% before demineralizing to a mineral level of 1% or less. Any residual whey taints after fermentation are removed with bentonite and charcoal. In one process for the preparation of sweet whey wine, whey is deproteinized, heated at 82°C for 5 min and approximately 22% dextrose added depending upon the

amount of alcohol desired in the wine. Fermentation is completed in seven days at room temperature using the yeast *Saccharomyces cerevisiae* spp. *ellipsoides*. As the whey itself contains sufficient nutrients for yeast growth, no additional nutrients are added. Similarly different type of whey based wines like pop wine, whey champagne, sweet wine etc can be prepared by using different strains of yeast and processing conditions.

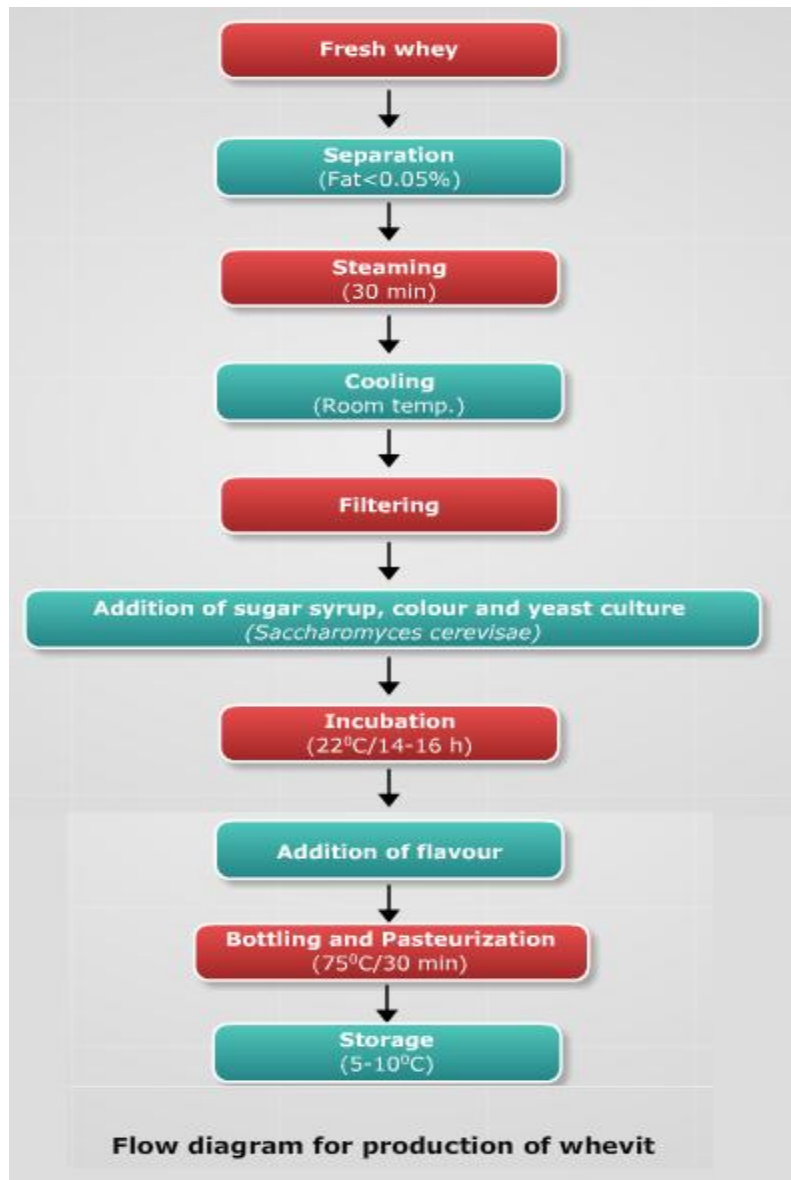
25.2.2.2 Beer like whey beverage

Like wine, whey is also used for preparation of different types of whey based beer type beverages. Whole whey or whey concentrate can be used as suitable substitute ingredient of cereals in the manufacturing of beer and beer like products. Whey has been reported to have certain materials similar to the colloids of beer wort and has great capacity for binding carbonic acid. On prolong heating under pressure, it develops caramel like flavor, which is similar to the taste and odour of the cured malt. Dietrich (1988) developed a beer substitute by making 5.4% malt wort with 2.5% deproteinized whey. The malt whey mixture was fermented by *Saccharomyces lactis*. After 5-7 days, the product had developed a true beer flavor and characteristics.

25.2.2.3 Whevit- A nourishing soft drink

National Dairy Research Institute, Karnal, have developed a soft drink out of whey known as "Whevit". The manufacturing process of whevit is: fresh whey obtained from *chhana* (or *paneer*) making is passed through a cream separator, and the separated whey is steamed for 30 min in a double jacketed vat. It is cooled to room temperature and kept overnight to allow the precipitated proteins to settle down, and then filtered through a muslin cloth. Now 50% sugar syrup @ 22-23% of whey, 10% citric acid @ 2-2.1% of whey and sugar mixture, selected colour and flavours in requisite amounts are added (Fig.25.3). This mixture is inoculated with a culture of *Saccharomyces cerevisiae* @ 1% of yeast whey broth (whey broth is prepared by adding 1% sugar in filtered whey and sterilizing it at 15 lb pressure for 15 min; the inoculum is prepared by inoculating it with the yeast culture and incubating it for 48 h at 25°C). After mixing the inoculum in the whey, it is incubated at 22°C for 14-16 h. The product is then filled in bottles leaving about 5% air space. The bottles are then crown corked to retain CO₂ and pasteurized at 75°C for 30 min in hot water, cooled and stored at low temperature (5-10°C).

In the above process of manufacture, the carbonation is achieved by the fermentation of sugar by the yeast culture. With a view to meet situation where cultivation of the yeast and fermentation of whey is not practicable, the process has been modified to incorporate CO₂ through a carbonated plant.



***** 😊 *****

Lesson 26 FERMENTED PRODUCTS FROM WHEY-1

26.1 Introduction

Fermentation for the large-scale utilization of whey was first investigated in 1930s and 1940s. The industrialization of these technologies has been slow. Whey contains lactose as a major component of whey solids in addition to proteins, minerals and water soluble vitamins, which make it excellent growth medium for various microorganisms. Numerous microbial processes have been developed recently to utilize whey for the production of some useful products of industrial importance such as single cell protein, baker's yeast, ethyl alcohol, methane (biogas), organic acids, vitamins etc. (Fig.26.1 and Table 26.1). In this lesson, production of single cell protein, baker's yeast, enzyme (β -galactosidase), ethyl alcohol and methane is discussed.

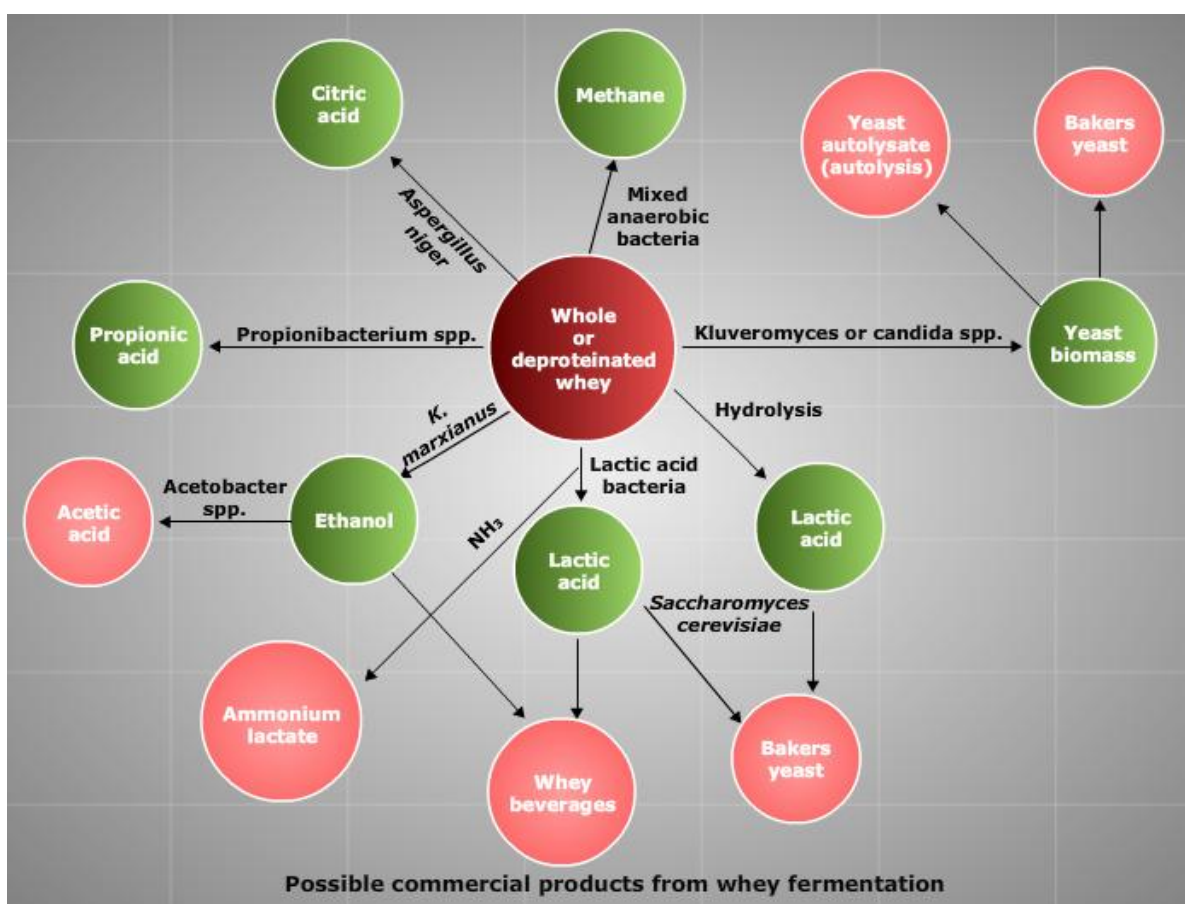


Table 26.1 Fermented products from whey

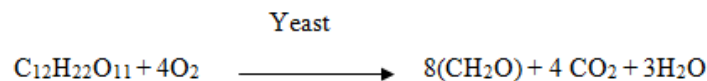
Products	Organism	Comment
<u>Yeast</u>		
Single cell protein	<i>Kluyveromyces fragilis</i> <i>Saccharomyces fragilis</i> <i>Saccharomyces cerevisiae</i> Candida spp.	Commercial process
Bakers yeast	<i>Saccharomyces cerevisiae</i>	via lactic acid or hydrolysed lactose
<u>Solvents</u>		
Ethanol	Various yeasts, commonly <i>Kluyveromyces fragilis</i>	Commercial process
Butanol/Acetone	Clostridium spp.	Commercial process
<u>Biogas</u>		
Methane	Mixed population of anaerobic bacteria	Commercial process
<u>Organic acids</u>		
Lactic acids	<i>Lactic acid bacteria</i>	Commercial process
Citric acids	<i>Aspergillus niger</i>	Commercial process
Acetic acids	Acetobacter spp. <i>Clostridium thermoaceticum</i>	Commercial process
Lactobionic acids	Pseudomonas spp.	Commercial process
Itaconic acids	<i>Aspergillus terreus</i>	
<u>Enzymes</u>		
Lactase	Various <i>Saccharomyces fragilis</i>	Commercial
<u>Polysaccharides</u>		
Xanthan	<i>Xanthomonas campestris</i>	
Pullulan	<i>Aureobasidium pullulans</i>	
Alginic acid	<i>Azobacter vinelandii</i>	
Indican	<i>Beijerincka indica</i>	
<u>Vitamins</u>		
Riboflavin	<i>Ashyba gossypii</i> <i>Clostridium acetobutylicum</i>	
Vitamin B ₁₂	<i>Propioni-bacterium shermanii</i>	
2-keto-L-gluconic acid	<i>Erwinia spp.</i>	
<u>Antibiotics/penicillin</u>		
	<i>Penicillium spp.</i>	
<u>Other biochemicals</u>		
D(-)-3-hydroxy butyric acid	<i>Alcaligenes autrophus</i>	
Gibberellic acid	<i>Fusarium moniliforme</i>	
2,3 butane-diol	<i>Bacillus polymyxa</i>	
Hydrogen	<i>Citrobacter intermedius</i>	
Diacetyl	<i>Streptococcus diacetylactis</i>	
Calcium gluconate	<i>Aspergillus niger</i>	
Propionic acid	<i>Propionibacterium spp.</i>	
Pyruvic acid	<i>Escherichia coli</i>	
Galactose	<i>Kluyveromyces fragilis</i>	
<u>Oil</u>	Candida spp.	

26.2 Food Yeast Production

26.2.1 Single-cell-protein (SCP)

Many scientists believe that single-cell protein production is possible solution to meet out the shortage of protein. Many yeasts such as *Candida spp.*, *Saccharomyces fragilis*, *Torula spp.*, *Rhodotorula spp.* use whey, ethyl alcohol, starches, n-paraffins, sulphite waste, etc. as raw material for production of SCP.

Yeast biomass has been produced commercially by aerobic fermentation of lactose from whey or whey permeates by *Kluyveromyces fragilis*, strains of *K. marxianus* var. *lactis* or var. *marxianus*. This transformation is presented as:



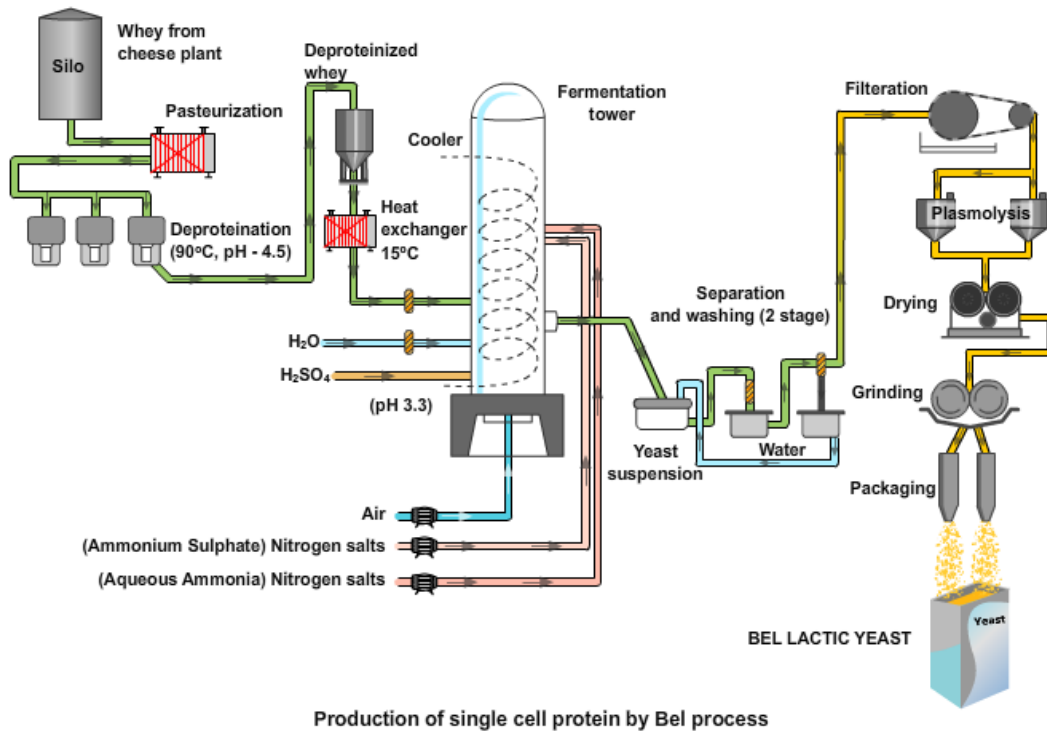
The resulting product, acetaldehyde, participates in the krebs cycle in protein synthesis. For its growth and development, this yeast requires lactose, oxygen, and presence of particular nutritive salts and other component, which are added to the medium.

In some cases, ethanol is also produced as a by-product by varying the aeration rate during the fermentation. The requirements of a suitable culture strains are as follows:

- High specific growth rate and biomass yield to ensure a high productivity
- The strains must not be affected by whey proteins if they are present.
- The strain must be suited to continuous culture.
- The strains must be acid resistant. To control contamination it is necessary to operate at a low pH or to wash the yeast at frequent intervals with acid to remove contaminants.
- Large cell size and uniform morphology to aid cell separation and concentration.
- Adequate protein content and acceptability in feeding trials.

The 'Bel' process (Fig.26.2), developed in France in 1950s, is a frequently cited example of this fermentation. Here, strains of *K. marxianus* var. *lactic* or var. *marxianus* are those most commonly grown for the production of SCP. Sweet cheese whey is first deproteinated and diluted to a lactose concentration of 20-24 kgm⁻³. Whey is limiting in nitrogen sources for yeast growth, so ammonium salts are added to maintain high nitrogen content and growth rate and trace metals (Fe, Cu, Mn, and Zn) may also be added. The continuous fermentation is operated at a dilution rate of 0.33 h⁻¹ and a temperature of 39°C. There is continuous mixing and aeration of the culture. For a fermenter of 23 m³ capacity, about 1800 m³ air is pumped per hour. The fermentation period is 4 hours and the substrate addition of deproteinated fresh whey constitutes 5,600-6,000 l/h. The residual sugar level is about 1 kgm⁻³, the biomass yield is 0.55-0.6 kg yeast (dry basis) per kg lactose metabolized and the biomass productivity is approximately 4.5 kgm⁻³ h⁻¹. The yeast is separated and concentrated in two-stage washing and centrifugation process, plasmolyzed to render the yeast protein more accessible and dried.

The composition and uses of biomass produced from whey are similar to those of other food yeasts. The crude protein content is about 50% on dry basis and the only significant limitation is of the sulphur-containing amino acids. The protein value is similar to casein. "Protibel" the yeast-protein compound obtained by the Bel process is made up of about 50% protein, 30% carbohydrates, 6% lipids and 8% minerals. This can be very well used in foodstuffs.



26.2.2 Baker's yeast

Baker's yeast or a yeast autolysate can also be obtained by whey fermentation. The yeast autolysate may be used to replace yeast extract in microbiological media. Two processes have been developed for the production of baker's yeast to overcome the limitation of *S. cerevisiae* not being able to utilize lactose. In the first, the lactose is hydrolyzed using β -galactosidase, and the glucose and galactose are consumed simultaneously by the yeast in continuous culture. The second process utilizes a two-stage fermentation system. In the initial stage, lactic acid bacteria convert lactose to lactate which is used in subsequent fermentation by the yeast. Although the baker's yeast so produced appears comparable in quality to that from the conventional process, only very limited quantities are manufactured by those methods.

26.3 β -Galactosidase

Lactase is an enzyme which catalyses hydrolysis of the galactosidic linkage of lactose. Lactase occurs naturally in some plants and in intestine of various animals. Additionally it is prepared by a wide variety of molds, yeast and bacteria. The production of enzyme β -galactosidase or lactase has been, of

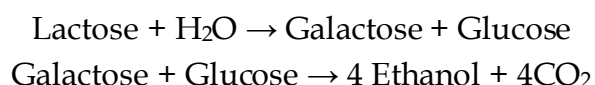
late, the subject of considerable interest. Whey seems to provide the best medium for the production of this enzyme. The enzyme β -galactosidase or lactase can be produced from selected strains of *Kluyveromyces spp.* following growth on diluted whey.

The production of enzyme using permeate as substrate was suggested by a group of workers. *Candida pseudotropicalis* was grown at 30°C on 2% whey solution supplemented with 0.5-0.1% yeast extract, 0.1-0.2% ammonium sulphate at a pH of 3.5. The enzyme was extracted with chloroform. β -galactosidase is used to hydrolyse lactose to overcome intolerance, and to generate syrups which are sweeter than lactose and which do not crystallize as readily.

26.4 Ethanol Production

The conversion of lactose in whey to bio-ethanol has long been considered as a possible solution for whey bioremediation. Acid whey from the production of lactic and sulphuric casein is used to ferment the lactose to ethanol. In New Zealand, acid casein whey is processed to produce ethanol, which is used in pharmaceuticals, perfumes and inks as well as beverages. The technology to process deproteinated whey into ethyl alcohol was developed in Europe about 20 years ago and was purchased from Ireland by the Anchor Ethanol Company in the late 1970s. Since that time, two plants have been established, at Tirau (using a continuous fermentation process) and Reporoa (using a batch fermentation process). The combined annual production of these two plants is 11,000,000 litres of ethanol. Two further independent distilleries based on whey have subsequently been built in New Zealand, producing an additional 6,000,000 litres. The production of ethanol from whey involves total lactose fermentation and a reduction of BOD value. Various lactose fermenting yeasts are capable of forming ethanol, and strains from *K. marxianus*, *C. Kefyr* and *Torula cremoris* as well as a mixed culture of *K. marxianus* and *Zymomonas mobilis*, are particularly efficient in this respect. High ethanol yields (about 80%) can be reached from adapted *Kluyveromyces fragilis* strains. Ethanol can then be further used as an energy source or to produce vinegar or acetic acid. Ethyl alcohol is produced by the conversion of lactose present in whey.

The yeast is added to ferment the lactose in two reactions: firstly splitting the lactose into the two sugars of which it is composed and secondly fermenting these sugars to ethanol.



The yeast is then removed from the liquid and the ethanol separated out by distillation to produce eight different grades of ethanol for a variety of industrial uses.

Cheese whey generally contains carbon and nitrogen substrate required for microorganism growth. Lactose is first hydrolyzed by β -galactosidase and the resulting mixture of glucose and galactose is then used as the carbon source by *Saccharomyces cerevisiae*. Different processes based on continuous fermentation with cell immobilization or cell recycling have been explored for production of ethanol. A recent alternative is to use recombinant yeast grown directly on cheese whey, allowing high yield

of ethanol.

In a typical process of ethanol production, deproteinated cheese or acid casein, whey are used as the substrate, and may be concentrated by reverse osmosis or supplemented by other lactose-rich streams to increase the lactose concentration to a maximum of 10-13%. The fermentation employs strains of the yeast *Kluyveromyces marxianus* var. *marxianus*. The process may be operated under aseptic conditions using pasteurized serum. Fermentation temperatures are in the range 24-34°C. Typically the fermenter vessels are of 120-150 m³ total volume and some mixing is required to prevent supersaturation of CO₂ in the vessel. Almost complete utilization of the lactose can be achieved and ethanol yield is in the range of 75-85% of the theoretical value of 0.538 kg ethanol per kg lactose metabolized. A maximum ethanol concentration of about 5.5% is achieved by fermentation of concentrated whey streams.

26.5 Methane (Biogas)

The production of methane or biogas via fermentation of whey is a process composed of three successive steps: lactose (and protein) hydrolysis, fermentation and methanogenesis. This complex process involves several mixed bacterial species. According to Fig.26.3, the methanogenic process converts around 90% of hydrolyzed organic matter to biogas: CH₄ and CO₂. The microbial production of methane from whey offers the major benefits of an efficient waste treatment process coupled with the production of convenient energy source. The methane fermentations, or anaerobic digestion, requires a limited input of energy or nutrients and produces very little sludge for ultimate disposal in comparison with conventional aerobic treatment processes.

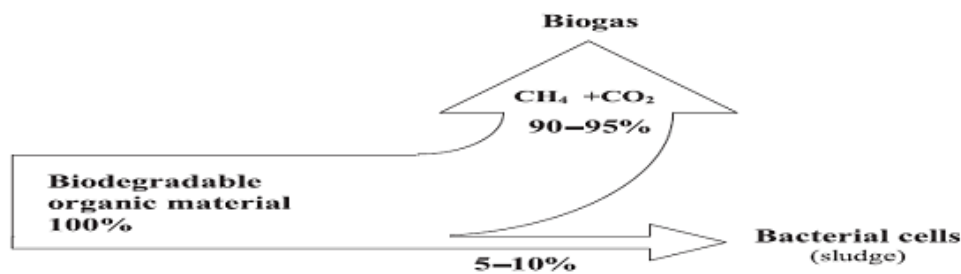


Fig. 26.3 Anaerobic production of Biogas

***** 😊 *****

Lesson 27

FERMENTED PRODUCTS FROM WHEY-2

27.1 Introduction

Various fermented products such as organic acids, vitamins, exopolysaccharides and many other products like antibiotics, glycerol etc. can be produced from whey.

27.2 Production of Organic Acids

27.2.1 Lactic acid

Lactic acid is formed by the fermentation of milk sugar (lactose) by *Streptococcus lactis* and is commercially produced under controlled fermentation of hexose sugar from molasses, corn sulphite waste or whey. Whey has been considered more economical for the commercial production of lactic acid. The starter culture *Lactobacillus delbrueckii* spp. *bulgaricus* grows rapidly at 45°C or 50°C and can ferment all the lactose in whey to lactic acid in about 40 h. The use of high temperature is not only favourable to the more rapid growth of the culture, but it is also effective in controlling the development of many contaminants that could grow at lower temperature and reduce the yield of lactic acid.

Whey has been a traditional feedstock for the production of lactic acid and lactate by fermentation. This is typically conducted in batch mode using homofermentative strains of *Lactobacillus* such as *L. bulgaricus*, corn-steep liquor and/or other complex nutrients such as malt sprouts, and malt or yeast extracts may be supplemented. The pH is controlled in the range 5.5-6.5 by addition of $\text{Ca}(\text{OH})_2$ or CaCO_3 and the optimum temperature is about 43°C. The medium is usually pasteurized, but the combination of the relatively high temperature with the high acid concentration and large inoculum (5-10% of the fermenter volume) mean that contamination is not a serious problem. For natural-strength whey, the fermentation will be complete in less than 24 hours with a yield of 90-95%.

27.2.2 Ammonium lactate

Whey is used for production of ammonium lactate by the addition of liquid ammonia to the fermentation broth during lactic acid production by *L. bulgaricus*. After the completion of the fermentation, the broth is evaporated, neutralized by the addition of further ammonia and processed to a range of liquid or solid products. These are used as an animal feed and are especially suitable for ruminants. Ammonium lactate is superior to urea and similar to soya bean meal in its nutritive value and digestibility.

27.2.3 Citric acid

Production of citric acid using whey permeates as one of the substrates has been reported. Maximum yield of citric acid has been obtained usually from sucrose and fructose and in general high concentration of sugar is required to produce high yield of citric acid. However, using a mutant strains of *Aspergillus niger* during fermentation, citric acid concentration of 8-3g/l representing a yield of 19% (w/s) based on lactose utilized has been observed. Supplementation of permeate with lactose

(final concentration of 40 g/l) increased the production to 14.8 g/l (yield 23%); An addition of methanol (concentration 3% v/w) to the fermentation increased the citric acid production to 25 g/l (yield 33% based on lactose utilized).

27.2.4 Propionic acid

Propionic acid is added as a fungistatic agent to bread and bakery products and can be produced by the whey fermentation using strains of *Propionibacterium shermanii* or *P. acidipropionici*. Whole whey is typically used and the fermentation must proceed under sterile conditions at around 30°C and pH 6.5-7.5. Nutritional supplements such as yeast extract considerably enhance propionate production and a typical yield of about 40% of the lactose fermented is achieved after 60-70 h. The culture fluid is spray-dried to obtain a powder containing both the acid and whey proteins.

27.3 Production of Vitamins

Whey has been used to produce vitamins, mainly riboflavin and vitamin B12. Riboflavin is synthesized by many microorganisms including bacteria, yeasts, and fungi. The first microorganism reported to be capable of producing riboflavin was *Clostridium acetobutylicum* and subsequently two other microorganisms, ascomycetes, namely, *Eremothecium ashbyii* and *Ashbya gossypii* have been reported. The fungus *A. gossypii* produces a huge amount of this vitamin and is, therefore, used for most of the microbial production processes. Commercial fermentation processes for the production of riboflavin or riboflavin concentrates have been developed. About 30% of the world industrial riboflavin output is produced by direct fermentation with *A. gossypii* and up to 15 g/l is reported to be the maximum yield.

The pattern of growth and vitamin B₁₂ production by *Propionibacterium shermanii* has been established in several types of substrates including cheese whey. This organism grows anaerobically and produces propionic acid, which accumulates in the medium. Most industrial processes for the production of vitamin B₁₂ by *P. shermanii* require neutralization of the accumulated propionic acid to keep the culture growing logarithmically. The formation of vitamin takes place during the later part of the fermentation after the organism approaches maximum growth.

27.4 Exopolysaccharides

Whey lactose has been widely used for the production of a large number of exopolysaccharides: dextrans (*Leuconostoc mesenteroides*), phosphomannans (*Hansenula sp.*), gellans (*Pseudomonas elodea*) and several heteropolysaccharides (*Streptococcus thermophilus*, *S. cremoris*, *S. lactis*, *Lactobacillus bulgaricus* and *L. Pastorianus*), but lactose needs to be first hydrolysed before being fermented by commercial bacterial strains. Only *Lactobacillus delbrueckii ssp. bulgaricus* has been used for production of exopolysaccharide in sweet whey and simulated whey permeate supplemented with combinations of lactose, KH₂PO₄, NH₄Cl, casamino acids, and mineral salts.

27.5 Miscellaneous

Whey is also used as a raw material for production of various other miscellaneous fermented

products. Pediocin has been produced from whey by using different microbial strains. *Pediococcus acidilactici* NRRL B-5627 is used to produce bacteriocin on whey by batch fermentation. *Kluyveromyces marxianus* NRRL-665 is commonly used to produce glycerol from whey due to their high growth rate and glycerol yield. Succinate-rich animal feed supplement has also been produced from raw whey with *Anaerobiospirillum succiniciproducens* by anaerobic fermentation.

***** 😊 *****

Lesson 28

ELECTRODIALYSIS PROCESS FOR DEMINERALISATION

28.1 Introduction

Electrodialysis is a membrane process based on electrochemical laws governing the migration of ions under the effect of direct current at a given potential through an ion-selective semipermeable membrane. This process removes ionic (electrically charged) species from non-ionic species. In dairy industry, it is used to demineralise whey and other milk derivative solution.

28.2 Electrodialysis Membrane

The key to the electrodialysis process is the use of ion-selective membranes. Electrodialysis membranes are thin sheets of cation or anion exchange resins, usually reinforced with synthetic fibres necessary to give mechanical strength. Ion selective membranes that allow passage of positively charged cations (Na^+ , K^+) are called cation membranes. Membranes that allow passage of negatively charged ion (Cl^- , PO_4^{3-}) are called anion membranes. An example of a cation membrane is styrene-divinyl benzene copolymer with sulfonic acid groups as active sites. The corresponding anion-selective membrane has the same copolymer with quaternary ammonium groups or tertiary amine compounds as anion exchanging active sites. Most commercially available membranes are having effective pore sizes of 10-20 A° , which are slightly greater than atomic dimensions and therefore, impermeable to flow of liquids and to diffusion of large molecules. General properties of electrodialysis membranes is given in Table 28.1. Desirable characteristics & properties of electrodialysis membranes are as follows:

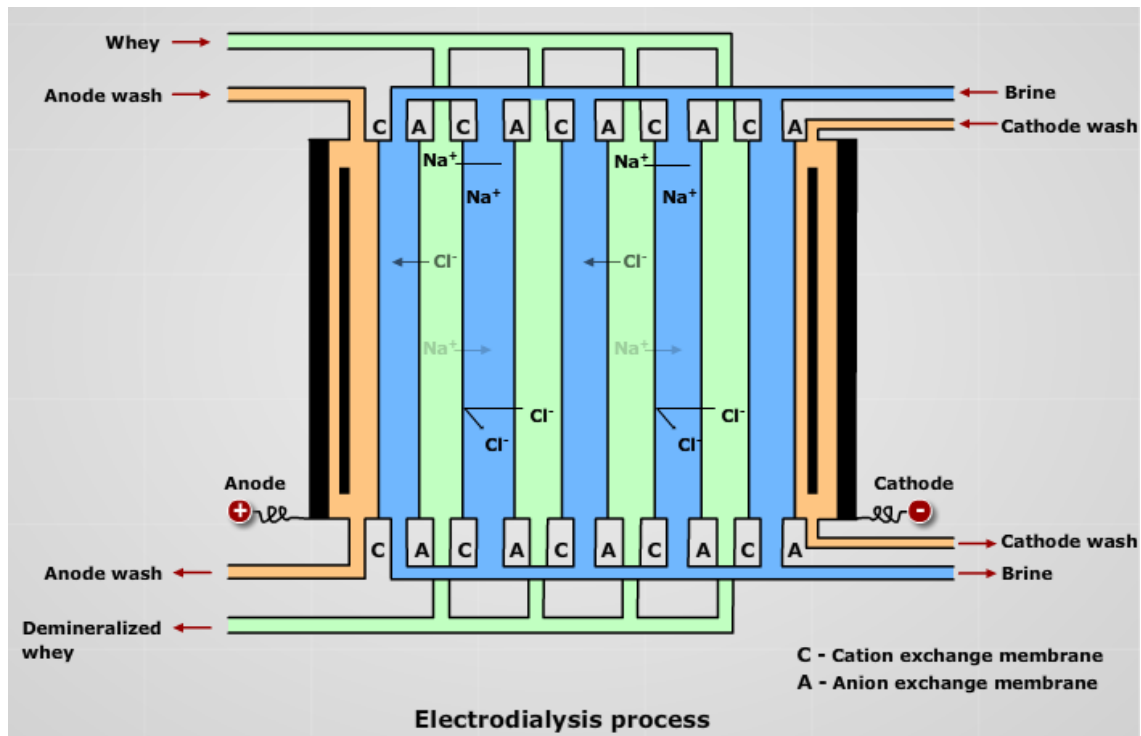
- It should have high ion selectivity, low water transfer & low electrical resistance.
- It should have strength to withstand pressure difference across the channels, as the membranes are very thin.
- It should have dimensional stability.
- It should have chemical resistance mainly to oxidising and basic solutions used during cleaning.

Table 28.1 Properties of electro dialysis membranes

Properties	Range
Electrical resistance	2-20 Ohm/cm ²
Strength, Mullen burst	200-1400 kPa
Tensile strength	150-300 kPa
Dimensional change on wetting & drying	2-20%
Membrane thickness	0.15-1.00 mm
Temperature to which membrane is stable:	
Cation exchange membrane	90°C
Anion exchange membrane	60°C

28.3 Electro dialysis Module

To achieve separation by electro dialysis, cation and anion membranes are altered with plastic spaces in a stack or module configuration with positive electrode (anode) at one end and cathode at other end. The spacers, whilst creating the flow channel, also support the membranes and include turbulence promoters. There are two main types of spacers: i) sheet flow spacers ii) tortuous flow spacers with linear flow velocities, 5-10 cm/sec and 30-50 cm/sec, respectively. It would be expected that the use of higher flow rate should alter advantages through increased turbulence and reduced boundary layer problem. Alternate cation and anion membranes are called 'cell pairs', which form a 'stack' or module. Electro dialysis module accommodates between 5 and 500 cell pairs. At the end of the stack are two electrodes that create the driving force over the whole stack. The electrodes are rinsed with their own rinse solution to avoid the possibility of scale formation. The preferred solution for rinsing of electrodes is sulphuric acid, rather than hydrochloric acid, which can lead to chlorine production. The stack may operate either in vertical or in horizontal positions. The typical batchwise layout consists of several stacks or modules, each consisting of 200 pairs of cells in parallel connection. The line is completed with pumps, tanks, valves and instrumentation for controlling and recording flow and pressure in the stack, as well as pH, temperature, and conductivity of whey and brine. A typical layout is shown in Fig.28.1.



28.4 Principle of Electrodeialysis Process

When a DC voltage is applied across the electrodes, electrical potential created causes anions to move in the direction of anode and cations towards cathode. The ion-selective membranes form barrier to ions of opposite charge. The result is: anions attempting to migrate to anode will pass through anion membranes and are stopped by cation membranes: cations trying to migrate to cathode pass through cation membranes but are stopped by anion membranes. Hence, membranes form alternate compartments of ion-diluting cells and ion-concentrating cells. The ion removal medium is generally a brine solution prepared from hydrochloric acid. This solution is continuously replaced to prevent high concentrations of ions being accumulated, leading to high osmotic pressure. By circulating whey through diluting cells and brine solution through concentrating cells, free mineral ions leave the whey and collect in brine stream. The flow is generally co-current to prevent the development of large pressure differences.

28.4.1 Electrodeialysis process

The driving force to operate electrodeialysis unit is generally provided by a high direct current voltage of up to 4 V per cell. For currents of up to 100 A, current density is generally in the range of 10-200 A/m². In the safe design of equipment, possible hazards through the existence of such currents may be taken into account. In general, increasing voltages result in increased rates of demineralisation.

The maximum operating voltages and currents are, however, restricted by the phenomenon of concentration polarization. Concentration polarization occurs when the current-carrying capacity of a particular solution of ions is exceeded. The limiting current density is reached when ions from the ionization of water are being transported through the membranes, and is higher at higher ion

concentrations in the feedstock. The limiting current and hence limiting current density, therefore, influences the membrane area required for ion transfer under any given set of conditions. High voltages are limited by practical heat generation considerations. Thus, overall, in the early stages of operation, a stack is voltage limited owing to the high conductivity and high allowable current density. In the later stages, the stack is current limited because of the low conductivity of solutions.

28.4.1.1 Processing modes

i) Within the module

A process option, which is available on some plants is current reversal during operation. Since ion movement is reversed, the flow between the chambers must also be switched. The effect of current reversal is to prevent and remove embedded deposits on or within the membranes, thus extending their life. This process option has been available for some time, but has not been utilized by all manufacturers. Both “Corning” and “Ionics” now include this technology as standard for their whey processing plants.

ii) Overall

Three modes of operation are commonly used:

a) Batch

A batch system, which is often used for demineralization rates above 70%, can consist of one membrane stack. An initial feed charge is recirculated through demineralization module until required level of demineralisation is achieved. High velocity of feed through the stacks is required to avoid fouling and polarization results in a low residence time and thus a low degree of demineralisation per pass. This leads to the need for recycling of the feed to achieve useful level of demineralisation. Batch processing allows for simple control of process, with operating times determined by batch size, membrane area and extent of demineralisation.

b) Continuous

In continuous operation, feed is passed once through a series of modules to achieve the required demineralisation. The continuous electro dialysis method is advantageous when products with lower levels of demineralization (often limited to 60-70%) are desired. The brine cells as well as the line for electrode rinsing are connected in parallel. Variation in flow and feed quality require more complicated controls than batch operation to achieve a constant product. Voltage and current programmes for individual stacks are controlled by the various stream sensors. There is independent hydraulic control for each stack. An electro dialysis plant can easily be made automatic and supplied with a CIP system. Cleaning sequence include water rinse, alkaline solution cleaning (pH 9), water rinse, cleaning with HCl (pH 1) and final water rinse.

c) Feed and bleed

This is a combination of batch and continuous modes and involves recycling of feed stock with continuous small removal of product, compensated by equivalent feed rate. Again, greater capacity can be achieved by the use of parallel lines and multiple stages within a line. Residence times are, in general, 10-30 min.

28.5 Membrane Fouling

Membrane fouling is a major problem in electro dialysis of whey. Such fouling can involve both inorganic and organic molecules.

28.5.1 Inorganic fouling

Fouling by inorganic molecules results in general from operating too close to or above the limiting current. Under these circumstances, hydrogen ions and hydroxyl ions are transferred, causing a change in pH which will in turn result in precipitation of calcium salts such as calcium carbonate, calcium sulphate and calcium phosphate. Precipitation of these salts can occur on either the anionic or cationic membranes, but is more generally found on the brine side of the cationic membranes. These precipitates cause scaling on the surface of the membranes, which may be removed by normal acid cleaning conditions. Colloidal silicates are also well recognized inorganic foulants.

28.5.2 Organic fouling

Organic fouling of anionic membranes is more difficult to overcome. Many organic molecules, such as protein and protein fractions, amino acids, humic substances, are partially charged and are attracted to the anionic membranes during processing. Although many are deposited on the surface of membrane, some become embedded within the membrane itself. This results in increased electrical resistance within the system leading to a loss of performance. At a current density of 20-25 mA/cm², and with continuous operation, there is a danger of irreversible protein deposition. Effective cleaning of the anionic membranes can only be achieved by washing with alkaline solutions. As a consequence, however, of the alkaline effect, the lifespan of the anionic membranes is shorter than that of the cationic.

28.6 Some Developments

In order to avoid membrane fouling, a new commercial electro dialysis process, called transport depletion, has been developed. This method involves the substitution of selective anion membranes by non-ionic membranes of regenerated cellulose. In this way, no concentration polarization of the whey constituents occurs on the membrane surface. Higher current densities can be applied, the lifespan of the membranes is longer and the cleaning process is simpler.

Another modification of electro dialysis is ion substitution. When applying this method, a third liquid stream, containing an ion selected for substitution, passes through the apparatus in addition to the usual whey and brine stream. A particular feature of this method is the structure of the ion

membranes as compared to those used for conventional electro dialysis. The whey runs between two cation-selective membranes and the sodium is separated, into the brine, on the cathode side of the apparatus. At the same time, another cation, e.g., potassium travels through the membrane into the whey stream. The anions remain in the whey and form new salts.

A further modification of electro dialysis is electro-osmosis, which has been industrially applied in the USA, Japan and Norway since 1967.

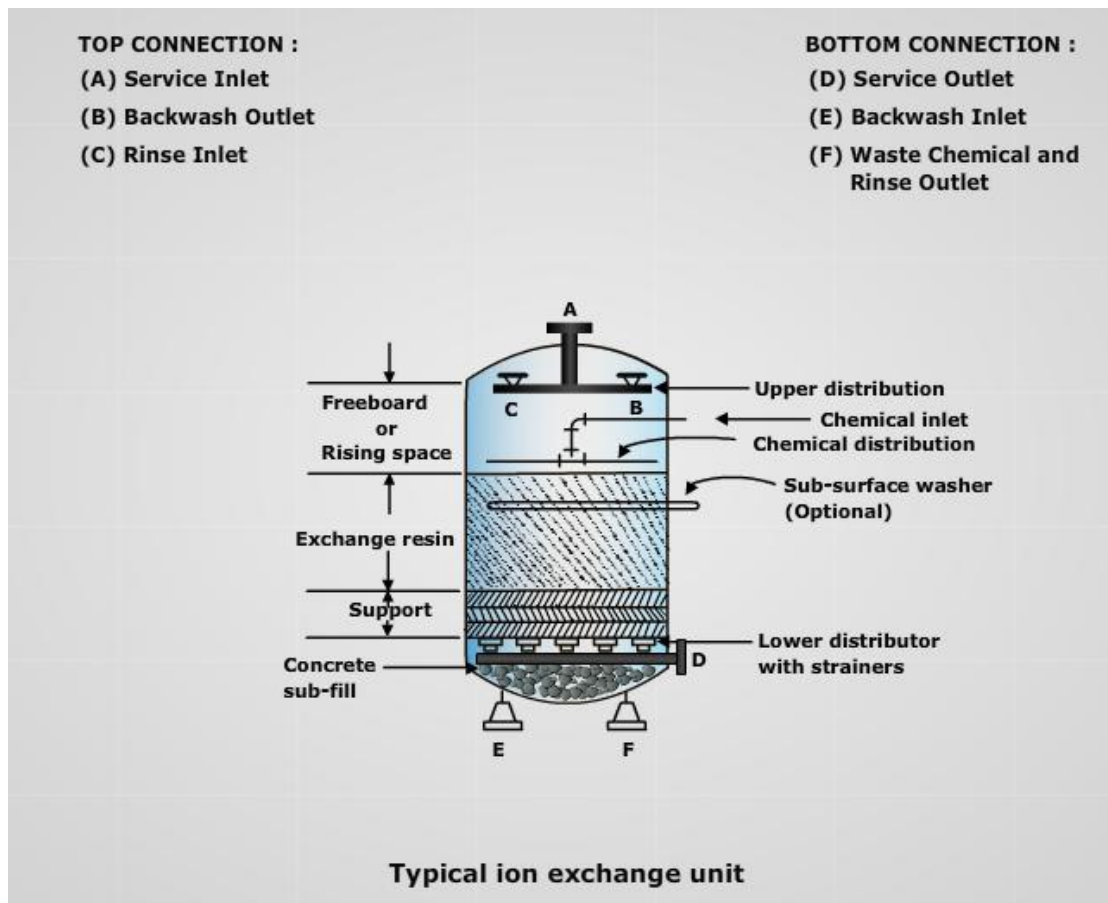
***** 😊 *****

Lesson 29

ION EXCHANGE PROCESS FOR DEMINERALISATION

29.1 Introduction

Ion exchange is now the most mature of the demineralisation technologies. It is a fixed-bed technique involving use of resins which have a discrete capacity for absorption of minerals. When this capacity is used up, the absorbed minerals have to be removed from the resin and the resin regenerated, before it can be used again. It is quite widely used for whey demineralisation. However, the process has a number of disadvantages, including potential denaturation of protein due to low pH in the cation column and loss of protein in the anion column that makes the product less widely accepted for use in infant formula than electro dialysis whey. A typical ion exchange unit is shown in Fig.29.1.



29.2 Ion Exchange Resin

Modern ion exchange resins are macro-molecular porous plastic materials formed into beads with diameter in the range of 0.4-0.8 mm having a large number of attached bonds on their surface which can absorb (reversibly) one specific type of ions. Chemically they act as insoluble acids or bases, which when converted into salts, remain insoluble. A wide range of base polymers may be used in ion exchange resins (Table 29.1) depending on the specific physical and chemical requirements of the

system. The average pore size within the polymer is normally less than 40A°. Macro porous resins are prepared by re-dissolving of part of the matrix of the polymer to controlled pore sizes up to 1000A°.

Table 29.1 Resin matrix materials

Silicates - inorganic cellulose base	Cross-linking agent, e.g.
Phenol formaldehyde	divinyl benzene (DVB)
Polystyrene	
Polyacrylate	

The matrix of the resin contains the charged sites involved in the ion exchange process. These sites may be occupied by anionic or cationic groups (Table 29.2). Table 29.3 shows the affinity of each group of resins for the removal of various ions.

Table 29.2 Classification of ion exchange resins

Charge type	Affinity level	Functional group
Cation exchange resin	Strong acid	SO ₃ ⁻ sulphonate
	Weak acid	COO ⁻ carboxyl
Anion exchange resin	Strong base	NR ₃ ⁺ quaternary ammonium
	Weak base	NH ₂ , HNR, NR ₂ substituted amino groups

Table 29.3 Ion affinities for different exchange resin group

Resin group	Affinity series
Strong acid cation	Fe ³⁺ > Al ³⁺ >Ca ²⁺ >Mg ²⁺ >K ⁺ >Na ⁺ >H ⁺
Weak acid cation	H ⁺ >Fe ³⁺ >Ca ²⁺ >K ⁺ >Na ⁺
Strong base anion	SO ₂ ⁻ >Cl ⁻ >CH ₃ COO ⁻ >OH ⁻ >HSO ₃ ⁻
Weak base anion	OH ⁻ >SO ₄ ²⁻ >CH ₃ COO ⁻ >HCO ₃ ⁻

A major factor determining the effectiveness of an ion exchange resin is the size, valency and concentration of the ionic species to be exchanged. These factors influence the capacity and selectivity of the resin. Lower porosity (higher degree of cross linking) resins are more selective towards smaller ions, which can more easily diffuse to the reactive sites. Lower porosity resins also have a higher exchange capacity per unit. Exchange capacities of resins typically range between 1 and 4 equivalents per litre of resin. When the capacity of an ion exchange resin is exhausted, the resins may be regenerated with regenerant solutions.

29.3 Processing Variables

Both the degree of demineralisation and the feed condition and type of whey and permeate must be considered during the demineralisation of whey and ultrafiltration permeates.

29.3.1 Degree of demineralisation

Levels of up to 95% demineralisation of whey-based fluids can be achieved by ion exchange. In general, the required level of demineralisation is achieved by operating the ion exchange plant at constant flow rate and a high degree of demineralisation, and by using varying amounts of bypass to achieve the desired level of demineralisation in the end product. Ion exchange is generally non-selective with respect to the ions removed. Bypassing is a particularly useful technique since it does not result in a significant change in the distribution of the various minerals present in the end-product. Bypassing can also reduce the losses of protein and lactose.

29.3.2 Feed condition and type

The physical condition of the whey feedstock is an important factor determining the efficiency and effectiveness of ion exchange processes. Most problems are caused by the inadequate removal of agglomerates prior to ion exchange. These agglomerates may be casein or cheese curd fines, or may be produced by pretreatments of the feedstock such as heat treatment or pasteurization. In general, the manufacturers of ion exchange equipment set specific criteria for the presence of fines in the feedstock.

There are often benefits by increasing the concentration of the feedstock prior to ion exchange. Whilst concentration reduces the volume to be processed, it does not reduce the demineralisation load. As the concentration of the solution increases, the selectivity of ion exchange system generally moves towards monovalents. Furthermore, the increased concentration of the non-ash components may also lead to increased losses of these components through, for example, increased protein absorption by the resin.

In general, the source of whey (sweet or acid) does not influence the mineral profile of the dematerialized product, although the demineralisation load is of course higher for acid whey. Some differences do occur amongst those ions present in a multitude of forms (calcium and phosphate). A major factor in the level of demineralisation of these ions is the pH of the feedstock. Losses of the non-mineral components are mainly non-protein nitrogen components.

29.3.3 Temperature of operation

The temperature at which demineralisation is carried out is often dictated by matters not related to the actual demineralisation process. However, care must be taken, because the use of excessively high temperatures of operation can lead to resin degradation. Maximum temperatures of operation for resins vary from 35-50°C for strong base resins, 60-100°C for weak base, to 120 and 150°C for weak and strong acid resins, respectively. The use of lower temperatures will reduce the extent of losses of protein and lactose by resin absorption, and assist in the prevention of microbial growth in the system during the long loading phase. Temperatures of 10°C are often employed for these reasons. The extent of protein losses, and thus reduced yield, can be very significant as temperature rises.

29.4 Operating Problems

Some of the drawbacks of the ion exchange process outlined above have been overcome by the SMR process, through development of a system for reuse of regenerant. Physical and chemical hindrances in the operation of ion exchange systems are outlined below.

29.4.1 Physical

Resin beads are physically fragile, but often are subjected to considerable stress in operation. Bead fracture and attrition is common, and can be caused by the effects of changing of the processing parameters during the various cycles of loading, backwashing, regeneration and rinsing. The change in type of solutions to which the resins are exposed during these cycles also subjects them to osmotic shocks. In addition, resin may be subjected to stress owing to pumping operation and temperature changes. All of these factors can lead to loss of performance of the bead, and unwanted particulate matter in the final product.

29.4.2 Chemical

Chemical fouling of resins is the most common problem encountered in ion exchange processing. The feedstock, whey or permeate contains many organic substances in low concentrations. These may enter the feedstock through the milk, or from sanitizers used on the farm and in plant operations such as cheese- or casein-making. Foulants can also enter the system from the regenerants, and via the wash or rinse waters. Such foulants include tannic, humic and fulvic acids. Foulants can be either organic or inorganic.

Fouling by organic compounds occurs mostly on anionic resins; fouling by inorganic compounds occurs most commonly on cationic resins. Fouling by organic molecules can be the result of their very slow diffusion through the resin matrix, because of their large size. Irreversible bonding can also occur if there is a high selectivity for sites. Strongly basic anion exchange resins cross-linked with acrylic derivatives rather than divinyl-benzene have been reported to be less susceptible to fouling.

Fouling by inorganic ions cationic resins is generally caused by minor elements such as iron, manganese and copper. Precipitates, such as calcium sulphate, can cause surface fouling and scaling of the resins. Inorganic silica fouling can also occur with anionic resins.

29.4.3 Non-mineral losses

Protein losses, owing to factors other than temperature and pre-treatment history, have been reported to occur on demineralisation by ion exchange. Significant losses of non-protein nitrogen (NPN) can also occur. Losses of 50-70% of NPN have been reported on demineralisation of cheddar cheese whey with strong acidic and weak basic resins.

29.4.4 Structural leakages

The possibility of slow leakage of organic material from the resin structure during its life of operation is a cause for concern. Styrene monomer, which may be present in the bead from incomplete polymerization, will slowly leave the bead during its service life. To address this concern, manufacturers make a range of special grades of ion exchange resins designed for food applications.

In such products, particular attention has been paid to the control of the polymerization reaction.

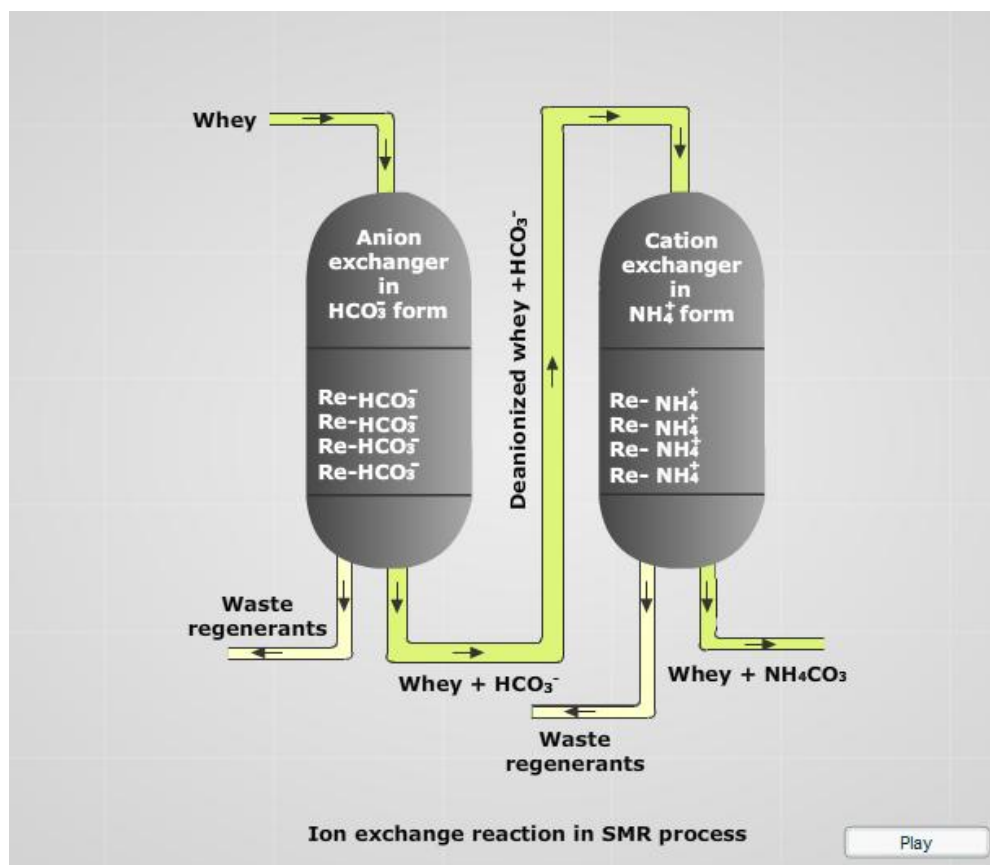
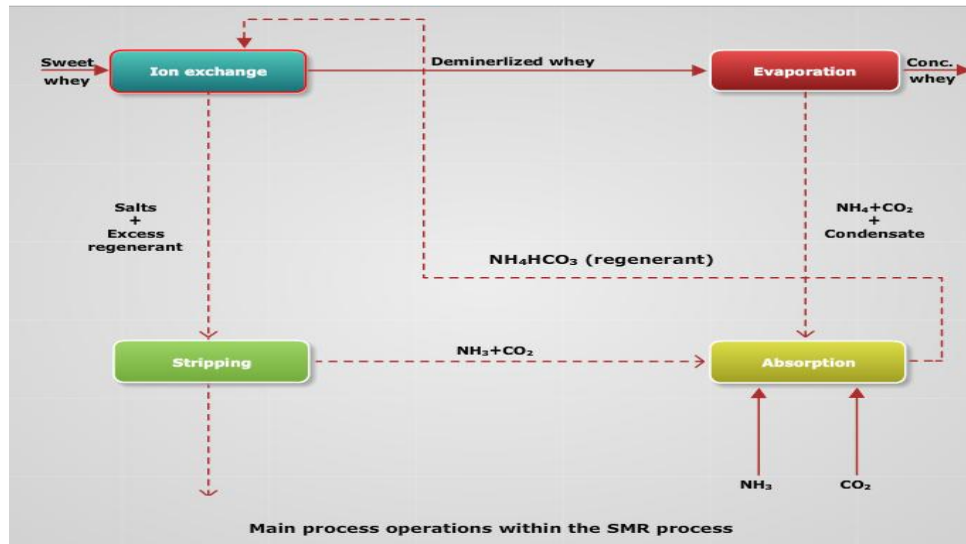
29.5 Process Variations

29.5.1 SMR process

A variant of the traditional ion exchange process is the Swedish SMR (Svenska Mejeriernas Riksförning or Swedish Dairy Association) process. It is designed primarily to reduce the consumption of regeneration chemicals, which apart from saving money, also leads to a better waste (reduced salt load) situation from demineralisation plant. Instead of using cation resin of H^+ form and anion resin on OH^- form, this process uses a cation resin on NH_4^+ form and an anion resin on HCO_3^- form. The system has two major innovations; first the order in which ions are exchanged is reversed from that commonly employed - anions are exchanged first, and cations second; secondly, the separate regenerants are replaced by a solution of one salt. Thus, both ions in this single regenerant solution are used, one for each of the anion and cation exchange columns.

Using the weak anion exchange resins for treatment in the first stage means that the feedstock to the first column is acidic, as required. The resultant basic product can then be fed to a weak cation resin exchanger for the second step. This allows the use of bicarbonate and ammonium ions - thus, a solution of ammonium bicarbonate is used as the single regenerant. Ammonium carbonate being a thermolytic salt, it may be removed from the demineralised whey by heat, by passing the whey/ammonium bicarbonate mixture through an evaporator. The ammonia and carbon dioxide so produced are then recombined in an absorption column to effectively regenerate the ion exchange regenerant. The main operations of SMR process are shown in Fig.29.2.

The SMR process is claimed to reduce the high consumption of chemicals and water normally associated with ion exchange processes during regeneration. It is also claimed to reduce associated water disposal problems and their cost. The process does not result in such wide changes in the pH of the feedstock during demineralisation as in the case of normal ion exchange. During normal ion exchange, decationised whey reaches at pH of 1.5 and on deionisation, the pH of the product may increase to 9 or 10. For sweet whey, the SMR process restricts the pH variation between 6.5 and 8.2. This has the very beneficial effect on reducing protein losses.



29.5.2 Thermal regeneration

The use of thermal processing for the regeneration of resins can reduce both chemical and effluent processing costs. A range of such products, known as Sirotherm resins, are now commercially available. Mild heat treatment results in regeneration of these resins.

***** 😊 *****

Lesson 30

DEMINERALISATION OF WHEY AND ITS UTILIZATION

30.1 Introduction

The high level of minerals (0.7-0.8%) present in whey restricts their commercial utilization in many applications. A major problem with many whey based products is their salty flavour owing to their high mineral content. Whey is demineralised to produce dry demineralised whey for specialised uses. Processes that have been utilized for the demineralisation of whey include electro dialysis, ion exchange, and loose reverse osmosis. These processes do not denature proteins, thereby preserving protein solubility in demineralised whey. The exact process used will determine the mineral profile of the final product. Demineralised whey often will have a less salty flavor because of the removal of minerals.

30.2 Electrodialysis Process

Gap between ED membrane is very small (0.4-1 mm), so whey is clarified before processing otherwise deposits will be formed varying the level of demineralisation. Other whey pretreatments such as pre-concentration, acidification and decalcification can also affects demineralisation considerably. Manufacture of demineralized whey by electro dialysis begins with the pasteurization of whey and concentration to around 28% TS. The concentrated whey is clarified to remove any insoluble protein and fines and then passed through the ED stack. The size of an electro dialysis apparatus is a function of the applied membrane surface. A typical structure with 100 pairs of cells represents a space of 50 μm and can remove 60% of salts from a 25% whey concentrate at a flow rate of 500 l/h. Each membrane has an effective area of about 0.5 m^2 , giving a total of about 50 m^2 /ED stack. Production capacities of about 50 kg of whey cheese solids/ m^2 of membrane area per day for a 75% demineralization level are typical.

The ions which are removed by electro dialysis are Na^+ and K^+ . Calcium, magnesium phosphate and citrates are not transported as they are probably present, at the pH value of the electro dialysis, in the form of soluble complexes. Ions of different charges and sizes have quite different mobilities, and hence the removal of ions from whey by electro dialysis is not uniform, depending in particular on the ionic composition, mode of operation and contact time. In general, multivalent ions are only removed after monovalents are essentially removed. Thus the mineral profile of the product is significantly different from the feed stock. The level of demineralisation is determined by initial ash content, whey viscosity, current density and residence time. The cost of demineralisation increases very rapidly as the conductivity of feed decreases with increasing level of demineralisation. Electro dialysis is generally used for applications where low levels of demineralisation are sufficient, since power consumption at high level of demineralisation is excessive. In practice, levels of demineralisation of about 50% are viable.

Batch operation is quite convenient when a high and uniform level of demineralisation is required (i.e. 90% whey demineralisation for infant formulations). For batch operation, process times of 3.5 to 6 hours are typical, depending on operating temperature i.e. usually 35-45°C, that provides maximal electric conductivity, degree of demineralisation etc. Sometimes, operating temperature of less than 10°C is preferred for getting good microbial count. For 90% demineralisation, holding in batch system can be as long as 5-6 hours at 30-40°C. Pre-concentration of whey to 20-30% DM is desirable for better capacity utilization and lower electrical power consumption. However, lower temperatures (20°C) and feed concentrations (even 12% TS) may be used, but a higher voltage is then required to provide the corresponding current density.

In continuous operation, the whey flows through a number of electro dialysis stacks in series with partial flow recirculation through individual stacks. Operation temperature is relatively low (as low as 20°C) and the pH remains constant (about 4.7) during processing. Whey at 6% TS can also be processed, with no pre-concentration. Continuous electro dialysis has a longer period of uninterrupted operation (10-12 h) than batchwise processing, which is convenient for large-scale production. Conductivity, pH and temperature of the whey and brine streams are monitored continuously.

Losses of non mineral components occur in electro dialysis. This is obviously a loss in product yield. Loss of lactose and proteins is undesirable. These losses usually occur at higher level of demineralisation. Overall, NPN losses are about 25% and lactose losses of about 6% occur on 90% demineralisation. Protein losses of 2-3% of total protein can be expected during electro dialysis, with overall yield of 90-75% expected for 50-90% demineralisation, respectively. Physical losses may also occur due to leakage at gaskets.

After demineralisation, whey is usually further concentrated by evaporation to about 55% solids and spray dried.

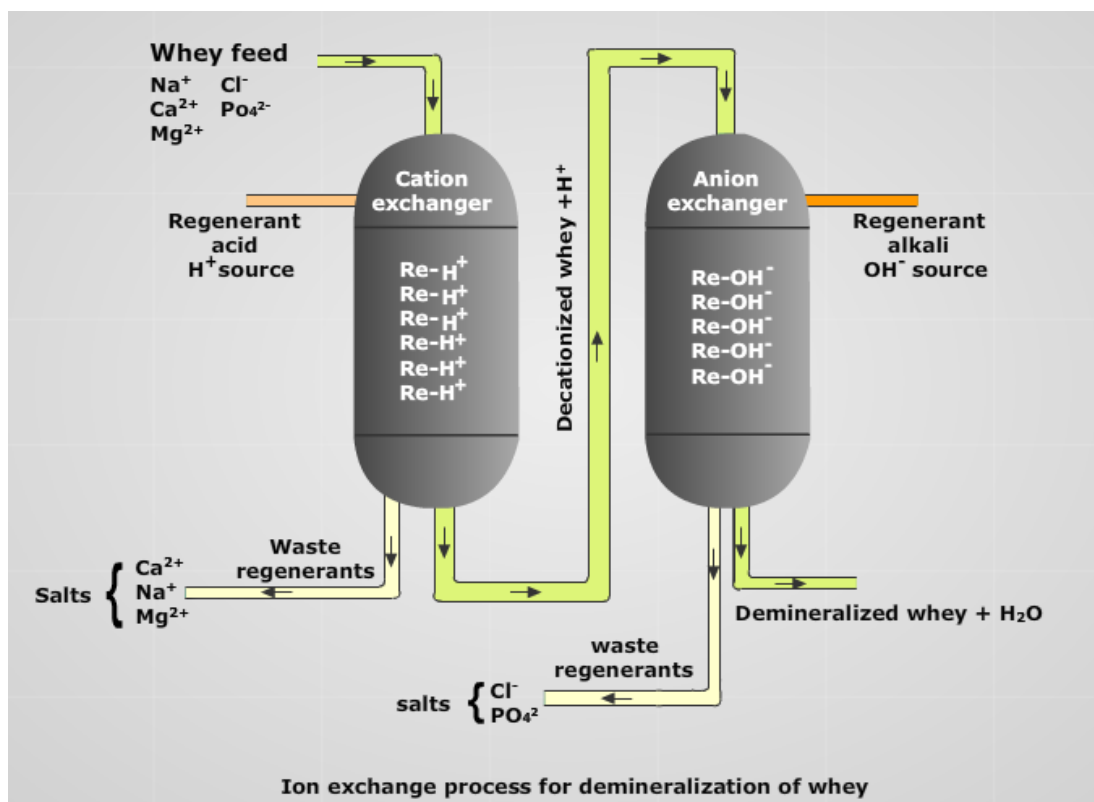
30.3 Ion Exchange

Ion exchange processing of whey is based on the ability of macromolecular resins to exchange their surface-bound ions for mobile ions of the same charge from the treated whey. As the result of experience over many years, it has been found that whey processing is best carried out using strong acid cation and medium to weak base anion resins.

There are only a few options available for the application of ion-exchange resins for the practical demineralisation of whey. Column systems are the most widely employed. In such systems, either each resin is packed into its own column, or alternatively, sometimes, the resins are used in a 'mixed bed' column. The simplest system is a continuously-stirred reactor tank. Before demineralisation, whey has to be pasteurized, clarified and separated, because contamination of the resin with fat, and/or fine cheese curd, results in a shortening of the production life of the resins. Whey pasteurization should be as mild as possible (65°C, 15 sec), since any contact with fresh ion-exchange

resins will shift the pH and may cause protein destabilization. Whey is first introduced into a cation exchanger, where all the positively charged ions (Na^+ , Ca^{2+} etc.) are replaced with H^+ . The whey is then pumped in an anion exchanger where all the negatively charged ions (Cl^- , PO_4^{3-} , SO_4^{2-} , etc.) are replaced with OH^- . The process illustrated diagrammatically in Fig.30.1. The ion exchange of whey can be carried out at higher temperatures ($> 50^\circ\text{C}$), if it has previously been deproteinized. However, if the whey is not deproteinized, protein destabilization and loss during ion exchange can be avoided by using lower temperatures such as $5\text{-}12^\circ\text{C}$.

Ion exchange is actually a batch process. The transfer of whey through the resin beds continues, until the resins are saturated with cations and anions. This point is controlled by means of a conductivity meter, after which the resin beds are purged of whey, washed with water and regenerated by means of acid and alkali solutions. These solutions should be sufficiently concentrated to remove the absorbed cations and anions and replace them by H^+ and OH^- bringing them back to their previous state. After the regeneration, the resins are washed with clean water, preferably condensate from an evaporator. After this, the process can start again. The production line consists of ion-exchange vessels, storage tanks for chemicals, feed and product storage, pumps, valves and dosing systems, a water supply, and a refrigeration system. If continuous production is required, it is necessary to erect 2 demineralisation plants. Putting one plant into operation allows the regeneration of the other. Each regeneration can process 10-15 bed volumes of whey; a figure which is based on the volume of the cation exchanger.



With a one-line configuration consisting of typical 2 hours of production and 4 hours of regeneration, four cycles can be performed per day, i.e., 8 hours of productive work. Two parallel lines provide 16

hours of production, and three parallel lines provide 24 hours of production. Usually, one or two lines are installed.

After its passage through both exchanger columns, the whey is demineralised, depending on its type, from 90 to 98%. The processing/holding time is 20 min. The processing temperature is $< 10^{\circ}\text{C}$ and therefore no bacteriological growth is experienced. Whey that has been demineralised up to 90% can be directly concentrated and dried. The obtained powder is non-hygroscopic. This advantageous phenomenon has as its probable cause the partial hydrolysis of the lactose at the cation exchanger. For some applications, though, a degree of demineralisation of only 50-60% is desirable. In such a case the demineralised whey is automatically mixed, in appropriate proportions with the untreated whey (pH control).

After completion of the operation or on exhaustion of the resin, the residual whey is flushed out. The flushing normally uses 2 bed volumes. Back washing may be employed, which results in expansion of the bed as a result of reverse flow and allows easier removal of physically entrapped material. After washing, the resins are regenerated through introduction of the regenerate solutions (generally 3 to 10 bed volumes for cation exchangers and 3 to 5 bed volumes for anion exchangers). The regenerant solution is then finally resumed. This takes place automatically and, for the cation exchanger, uses HCl. The deionized water used for the final rinse is derived from the condensation water supply of the evaporator (up to 10 bed volume). Na_2CO_3 and NH_4OH are used as regeneration solution for anion exchangers. Sanitization is possible after the regeneration stage using sodium isocyanurate solution. Counter current re-generation minimises the amount of the regenerating agent.

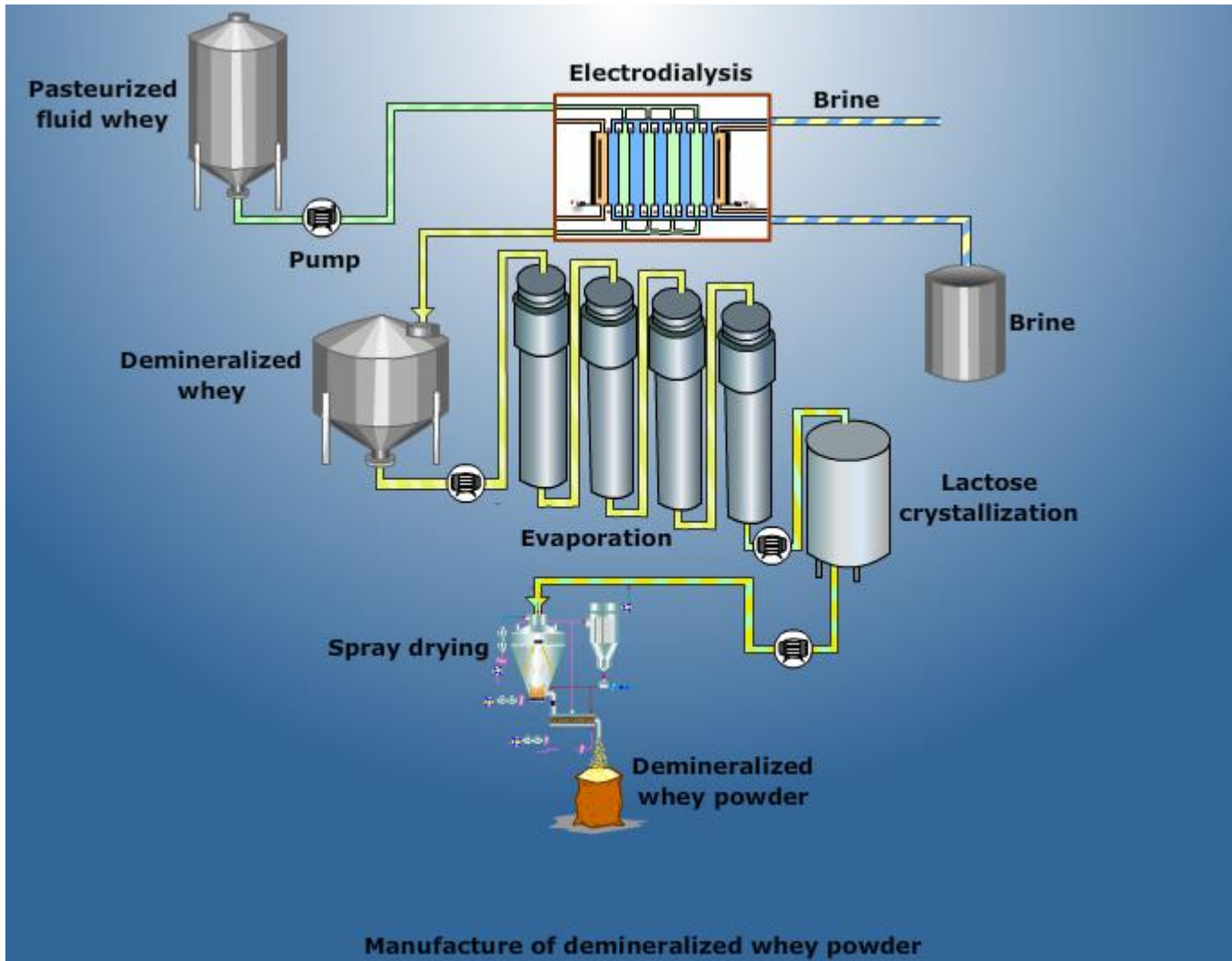
30.4 SMR Process

In SMR process, whey first enters anion column, where whey anions are exchanged for HCO_3^- ions. After this, the whey enters cation column, where cations of whey are exchanged for NH_4^+ ions. After the process, whey salts are thus exchanged for ammonium bicarbonate. Ammonium bicarbonate is thermolytic salt which decomposes to recoverable NH_3 , CO_2 and water, when heated during subsequent evaporation of whey. A plant using the SMR system at Arjang, Sweden, has achieved 70% recovery of NH_3 and 90% recovery of CO_2 , with a plant yield of 85%. Of the 15% yield loss of more than two thirds is due to demineralization. The other losses are less than 5% and protein losses were less than 1%. The choice of resins is very important- some results in much higher protein losses. The details of the process have been described by Batchelder (1987) and Hoppe and Higgins (1992).

30.5 Electrodialysis vs. Ion Exchange Process

Electrodialysis is very capital intensive, whereas ion exchange has high operating cost. Based on economic studies, the recent trend is towards installation of combined electrodialysis/ion exchange plants for high level demineralisation of whey. The cost for electrodialysis demineralization is greatly dependant on conductivity and, therefore, increases with reduced ash content. Realistic cost effective demineralization figures are 50% with electrodialysis. A consumption of 10 to 28 KWH of electrical

energy must be considered for each kg of demineral-ised whey powder. The process of manufacture of demineralized whey powder is given in Fig.30.2.



The costs for ion exchange demineralisation are essentially linear with ash removal. Lower the ash content, lower is the cost of ion exchange demineralisation. In Industrial practice, electro dialysis demineralisation of 50% is followed by further 50-95% demineralisation by ion exchange process. The typical composition of demineralised whey powder is given in Table. 30.1.

Table 30.1 Composition of two different demineralised whey powders

Composition	Whey Powder	
	50% Demineralised	90% Demineralised
Fat	0.6 - 0.9%	0.6 - 0.9%
Protein	12.0 - 14.5%	13.0 - 15.5%
Lactose	75 - 80%	80 - 85%
Mineral Salts	4.0 - 5.0%	0.7 - 1.0%
Sodium	0.4 - 0.5%	0.06 - 0.12%
Potassium	0.6 - 1.0%	0.25 - 0.3%
Chloride	0.1%	0.05%
Calcium	0.6%	0.15%
Phosphorus	0.4%	0.14%
pH in 5% Sol.	6.4 - 6.9	6.4 - 6.9
Solubility Index	< 0.1 ml	< 0.1 ml
Total counts	< 3000/g	< 3000/g
Yeasts of Moulds	< 10/g	< 10/g
<i>B. cereus</i>	< 200/g	< 200/g
Faecal streptococci	< 100/g	< 100/g
Coagulose +ve staphylococci	Nil in 1 g	Nil in 1 g
<i>E. Coli</i>	Nil in 10 g	Nil in 10g
<i>Coli aerogenes</i>	Nil in 0.1 g	Nil 0.1g
<i>Salmonella, shigella</i>	Nil in 50 g	Nil in 50 g

30.6 Nanofiltration (Loose Reverse Osmosis)

Electrodialysis and ion-exchange processes are effective, but are limited by high capital cost, high running cost and high level of effluents. Ion exchange is relatively non selective and removes both monovalent and polyvalent ions, whereas electrodialysis is more dependent on ionic mobility and tends preferentially to remove monovalent ions. Nanofiltration (also known as loose reverse osmosis or ultra-osmosis) is a membrane separation process which allows selective passage of water, salts and very low molecular weight organic molecules. The membrane pore size used is 10-50Å and the operating pressure used is about 300 psi. First installation of this process in the United States was in 1986, for the reduction of the salt content of whey. Today, there are many plants utilizing this technology for the partial demineralisation of sweet whey, hydrochloric acid casein whey and ultrafiltration permeates. About 50% demineralisation is economically feasible with this technology. An added advantage of the process is that water is also removed from the product during operation, and thus a significant degree of concentration (>20% solids) is also achieved. Diafiltration in conjunction with loose RO further increases the effectiveness and degree of demineralisation.

30.7 Utilization of Demineralised Whey

There is a high demand for demineralised whey for many applications in human and cattle feed: these include instant formula (baby food; min. 90% demin.), confectionary, baking, meats, etc.

- A most important application of demineralised whey-based products is as ingredients in infant formulae, which more closely resemble human milk. Approximately 65% of total reduced minerals whey is used to manufacture infant-formulae.
- Europe utilizes 25,000 tonnes of electrolysed whey solids annually in the production of demineralised calf milk replacers.
- Ultrafiltration permeate may also be demineralised by electrolysis to increase lactose yield in crystallization.
- Demineralised sweet whey (25-65% demineralisation) used in dietetic food, coffee whi-tener, soft serve icecream, milk shakes, whey drinks and caramel, citrus drinks, salad dressing, animal feeds, baker goods, confectionary coating and dry mixes.
- Although usage of reduced mineral whey in food processing products is small in com-parison to usage of whole whey powder, there are a number of applications for which the lower overall ash content or the lower level of a specific ion such as sodium is desirable.
- Demineralisation may also be used as a pretreatment of whey or permeates prior to lac-tose hydrolysis.
- Demineralised whey products have also been used in a range of beverages.
- Reduced mineral whey is used as a less expensive substitute for non fat dry milk.
- In USA, cottage cheese whey is demineralised to reduce effluent costs.

***** 😊 *****

Lesson 31

METHOD OF WHEY PROTEIN RECOVERY FROM WHEY

31.1 Introduction

Whey proteins are recovered from whey either in the form of whey protein concentrates (WPC) or whey protein isolates (WPI). WPC are mostly available with 35, 55, or 75–80% protein on dry matter basis, while WPI contain >90% protein on dry matter basis. The principal manufacturing processes of whey protein products are based on known behaviour of whey components under defined conditions. Properties that have been exploited commercially include: molecular size differences (ultrafiltration, gel filtration), insolubility of protein at high temperature, charge characteristics (demineralization, protein removal by ion exchange), aggregation by polyphosphates and crystallization of lactose. Capital cost for most of these processes are high and product yields are characteristically low.

31.2 Heat Precipitation Process

Whey proteins may be precipitated (and thereby rendered insoluble in water) by heating whey at acid or near-neutral pH. Acid whey must be heated to at least 90°C and maintained at such temperature for at least 10 min to achieve maximum yields. For sweet wheys, good yields can be obtained by heating at pH between 6.0 and 6.5, although products so derived have higher mineral concentrations than those of acid whey unless pH is adjusted to 4.6 prior to protein removal. The precipitate so formed is firmer and more readily separated than that formed in unacidified whey. Precipitated proteins are removed by settling (static or accelerated), washed, re-separated, and dried. In modern plants, high speed centrifuges such as clarifiers and decanters are used to affect both primary and secondary (after washing) separations. Ring, fluid bed, roller, and spray driers have been used to obtain the finished dried product. Typical yields are 4.2 to 5.2 kg/m³.

Process refinements include demineralisation prior to heating, pre-concentration by reverse osmosis and ultrafiltration, and continuous, high temperature reaction (120°C for 8 min at pH 6). Most processes result in an insoluble product, but through heating whey to 95°C at pH 2.5 to 3.5, then adjusting to pH 4.5 prior to separation, it has been claimed that a product soluble at pH 5 can be produced.

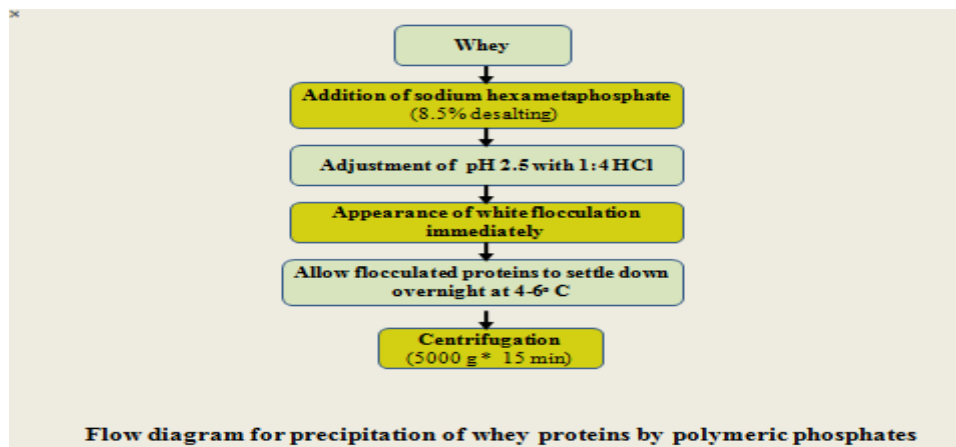
31.3 Precipitation By Complexing Agents

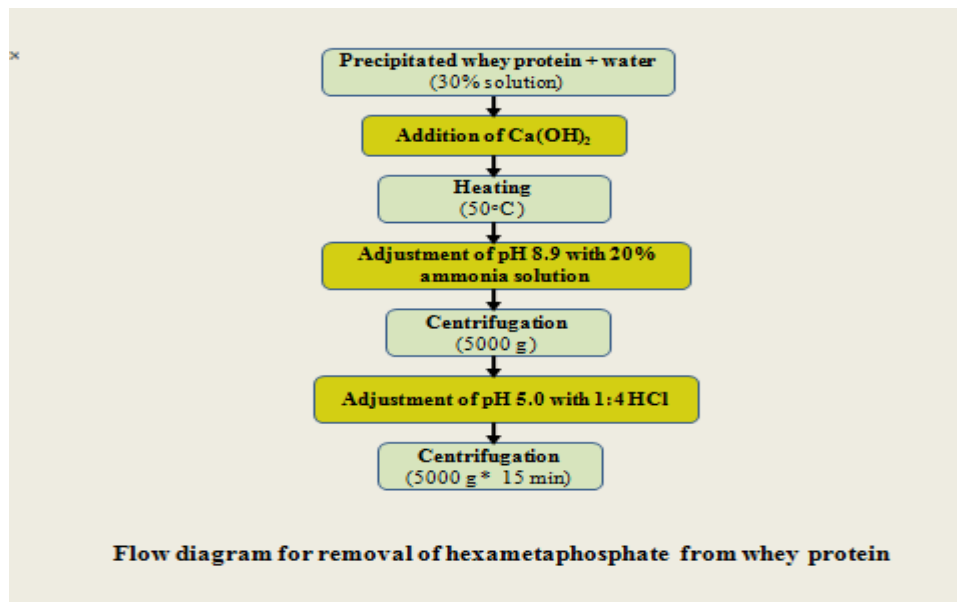
Salts of heavy metals have long been used to precipitate proteins from solutions. This process is also called the “cold precipitation process”. Numerous complexing agents can be used to recover proteins from whey; of these, only polyphosphates appear to be used commercially for this purpose.

31.3.1 Polymeric phosphates

Long-chain polyphosphates precipitate protein from whey at low pH e.g., 2.5. Typically, potassium polymetaphosphate and sodium hexametaphosphate are used. Use of hexametaphosphate (up to 0.07 molar concentration of phosphorus) was found to be quite effective for the precipitation of nearly 75% of the proteins. A group of workers adjusted the pH of cheese whey to about 2.5 followed by addition of 0.5% sodium hexametaphosphate. The whey was not heated. The precipitates so formed are removed by centrifugation, and washed. The precipitated proteins gave electrophoretic patterns similar to the native whey proteins. Further processing by ion exchange or gel filtration was required to increase the protein content by removing the polyphosphate and lactose. The protein phosphate complex can be resolubilized by raising the pH to > 6 and metaphosphate can then separated by large scale sephadex column, dialysis or precipitation with added calcium ions. A treatment with $\text{Ca}(\text{OH})_2$ at pH 8.9 was found to remove some of the complex hexametaphosphate from WPI. The typical process is given in Fig.31.1.

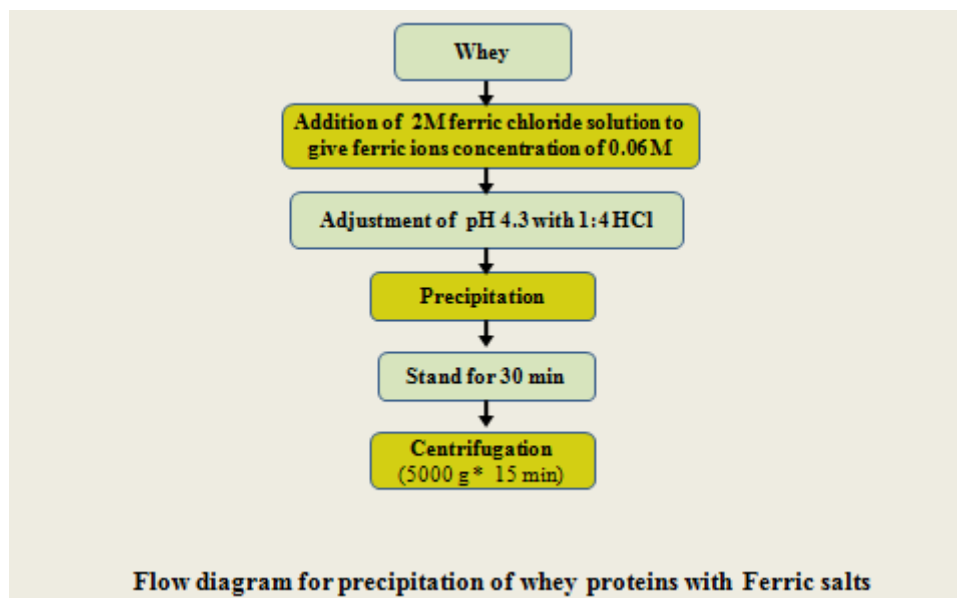
Dialysis could reduce the ash content of WPC by only about 12%. Column hydrolysis treatment of hexametaphosphate WPC in conjunction with dialysis or desalting reduced the ash content by 35-91%. This latter process is costly and, therefore, not commonly used. As a result most metaphosphate complex WPC retain their metaphosphate and thus exhibit greatly impaired solubility at pH < 6. Removal of calcium prior to phosphate addition reduces the amount of phosphate required and results in recovery of up to 90% of the original whey proteins at pH 3. On dry basis, the products contained 70-85% protein, 10-20% sodium hexametaphosphate and 10-15% lactose. Further modification of this process is also possible. The dried protein concentrate contained upto 80% undenatured whey proteins.





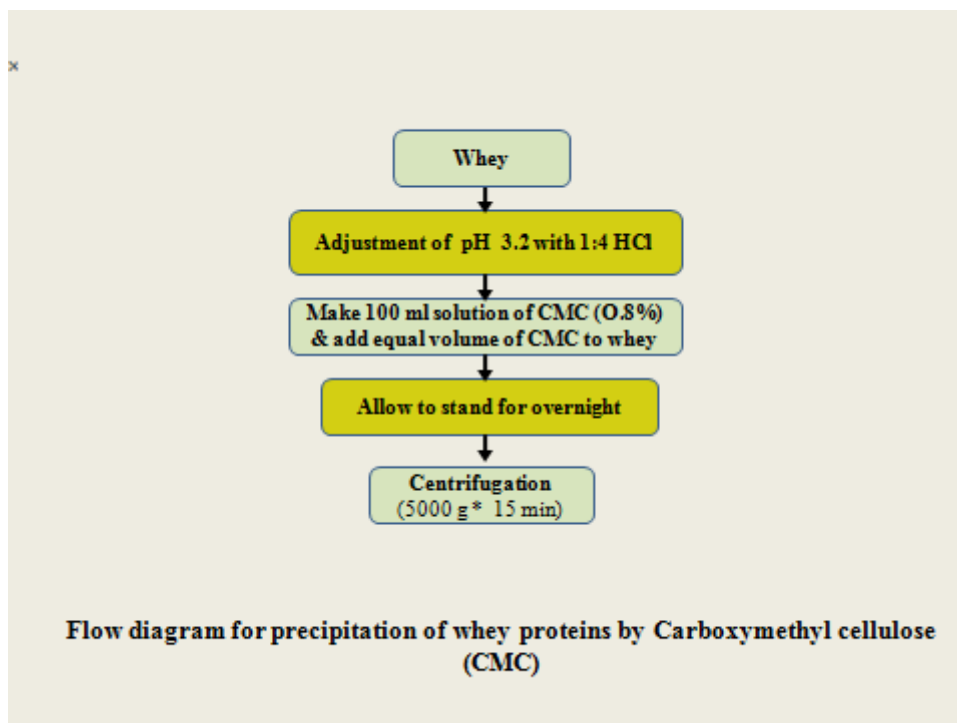
31.3.2 Ferric salt precipitation

In this procedure, a chelated protein complex is prepared from whey by adding to it a dilute solution of a ferric salt. The ferric ion may be later removed from the product by treating with SO_2 . Sodium thionite treatment of ferric precipitated WPC in conjunction with dialysis or desalting reduced the ash content by 35-91%. The use of ferric chloride for precipitation of whey proteins has been described in a process patented. In this process, use of FeCl_3 at the rate of 0.93 g Fe per litre of sweet whey and 1.35 g Fe per litre of sour whey is recommended for maximum yields. A group of workers showed that ferric chloride could be effectively used for the precipitation of whey proteins at pH 4.5. The product prepared by them was soluble at neutral pH and free from the metal ion (dialyzable fraction). Nutritional studies carried out by them showed that the iron present with such protein isolates was readily available for regeneration of haemoglobin in rats and protein had PER value of 3.30 (casein 3.11).



31.3.3 Carboxy methyl cellulose (CMC) precipitation

A group of workers described the use of carboxymethyl cellulose (CMC) for the reclamation of whey proteins. At pH 3.2, more than 90% of the protein was recovered; the product contained 60% protein and 30% CMC. The product was solubilized by adjustment of the pH in the range 7-7.5. The interaction between whey protein and CMC is only at low ionic concentrations (maximum at ionic strength less than 0.1). Therefore, necessary dilution is attained by diluting the whey system with equal volume of water, in which CMC at 0.8% level has been dissolved at 60°C with rapid agitation (Fig. 31.3). After cooling, the pH is adjusted to 3.2 with (1:4) HCl. Then this mixture is left undisturbed overnight. Precipitated protein is recovered by centrifugation, and washed.



31.3.4 Polyacrylic acid precipitation

In one procedure, a group of workers adjusted pH of cottage or cheddar cheese whey to 4.0 with 2.5 M H_3PO_4 at a temperature of 18°C, mixed with 1.5 g of filter aid and 3 ml of a 25% polyacrylic acid solution. After 10 min stirring, the precipitate was allowed to settle for 1 h and the supernatant siphoned off. Solids were separated by vacuum filtration suspended in 100 ml water and mixed for 1 h with 0.6 g of magnesium carbonate, which increased the pH to 6.5. After filtration, the solution containing the protein was concentrated in vacuum at 40°C up to 20% total solids and freeze dried.

31.4 Adsorption Process

Adsorption techniques, based on the ion exchange properties of whey protein, are used for the recovery of whey proteins. Whey proteins being amphoteric, solid phase charged adsorption media can be used to remove them from whey under appropriate conditions. At pH values lower than their isoelectric point, whey proteins have a net positive charge and behave as cations, which can be

adsorbed on the cation exchangers. Conversely, at pH values above their isoelectric point, the proteins can be adsorbed on anion exchanger. Media suitable for this purpose include regenerated cellulose, titania plus alumina, and silica with pore sizes and surface characteristics specially designed for the recovery of proteins from whey. Of these, cellulose and silica-based systems have progressed to semi-commercial operation. Two major ion exchange fractionation processes have been introduced for the preparation of whey protein concentrates based on modified cellulose and silica.

31.4.1 Vistec process

Regenerated cellulose is used in the "Vistec" (BioIsolates) process. The development of sulfopropyl cellulose resins of high charge density (1.1 meq/g) for use in Vistec process has enhanced its commercial prospects. The pH of the whey is adjusted to < 4.5 and pumped into the stirred tank reactor and mixed with resin to allow protein adsorption onto the ion exchanger (resin). Lactose and non protein materials are eluted with water. The desorption of bound proteins is accomplished by changing the pH to 9. The dilute eluate containing the protein is separated from the resin by filtration in the tank reactor. Ultrafiltration is used to concentrate by vacuum evaporation (and demineralize) the protein solution, which is then spray dried. Protein yield is 85%, and the dried WPC may contain as much as 95% protein. Because lipid molecules are not adsorbed by the media, such products have low fat concentrations. For better efficiency, a newer process has designed using resin packed in a column in place of stirred tank reactors.

31.4.2 Spherosil processes

Silica-based adsorbents are used in the "Spherosil" process. The "Spherosil" processes use their cationic spherosil S or anionic spherosil QMA ion exchangers, and the adsorption is accomplished in fixed bed column reactors.

31.4.2.1 For acid whey

For acid whey, an adsorbent with strong cation exchange properties is used. Acid whey ($\text{pH} \leq 4.5$) is adsorbed to the spherosil S reactor and after lactose and other solutes are eluted with water, the pH is raised by the addition of alkali (generally 0.1 N ammonium hydroxide) and adsorbed proteins are eluted from the reactor.

31.4.2.2 For sweet whey

For sweet whey, an anion exchange properties is used. Sweet whey ($\text{pH} \geq 5.5$) is passed through a spherosil QMA reactor to permit negatively charged protein molecules to adsorb on to the ion exchanger. After the elution of non protein materials with water, the proteins are eluted with an acidic solution, such as 0.1 N Hydrochloric acid. As with the Vistec process, ultrafiltration and spray drying are then necessary. Protein yield is 90%.

Several following major problems are associated with the ion exchanger processes:

- i. Production of large volumes of rinse, chemical solutions and deprotenized whey that must be processed or disposed.

- ii. The need to concentrate and purify the dilute protein fraction by ultrafiltration, evaporation and drying.
- iii. An excessive time required to conduct each fractionation cycle.
- iv. Control of microbiological contamination of the reactor.

31.5 Removal of Lactose and Minerals

Composition of whey can be modified by removal of lactose and minerals to give whey protein products of 15 to 40% protein on dry matter bases. For many years, the lactose industry has produced a protein concentrate in the form of mother liquor, the material that remains after lactose has been crystallized and separated from concentrated whey. The product, known as delactosed whey powder, contains about 25% protein. It has been used as a stock food because of the extensive protein denaturation in the process. In more modern plants, with lower temperature-shorter residence time evaporators, the product is more functional and, therefore, of greater value. Delactosed whey powder has a high mineral concentration (up to 25%). Processes have been described whereby pre-concentrated whey (up to 30% TS) is subjected to electrodialysis, the whey is concentrated to 60% TS, lactose is crystallized and removed, and the remaining liquid is concentrated and spray dried. The resultant product may contain up to 35% protein.

***** 😊 *****

Lesson 32

MANUFACTURE OF WHEY PROTEIN CONCENTRATES BY MOLECULAR SEPARATION PROCESS

32.1 Introduction

The aim of manufacture of whey protein products is to separate proteins from whey in such a form that they remain, as far as possible, fully undenatured and thus retain their functionality.

Ultrafiltration is a molecule separation process where components of a liquid are separated based on their difference in size. It is low energy consuming process and is being widely used in the dairy industry to recover whey proteins. The dairy industry typically uses membranes with a molecular weight cut off of 10,000 daltons. Thus, any component smaller than 10,000 daltons will be part of the permeate fraction. Ultrafiltration retains (in the liquid product termed retentate) any insoluble material or solutes larger than about 20,000 Da molecular weight. The rest of the whey stream passes through the membrane, driven by the applied pressure and is called permeate. Ultrafiltration of whey enables the whey protein to be separated from the lactose, mineral and other water-soluble low-molecular-weight species. By 1981, Ultrafiltration (UF) had become the most widely used process for recovery of soluble whey protein concentrates (WPC). It is now a major means of WPC production throughout most of the dairy countries of the world. With this process, 90-95% of the proteins in the whey is recovered. WPC is commonly characterised by its protein content on dry basis (e.g. WPC-80 has 80% protein on dry basis). The development of robust, synthetic and cleanable membranes and the refinement of continuous operation using multi-stage recycle loops, and diafiltration have been significant factors contributing to the success of this process. Another procedure for the separation of whey proteins from whey is by gel filtration.

32.2 Ultrafiltration Process

Membrane configurations designed to date have included tubular, plate and frame, spiral wound, hollow fiber, and flat leaf. Examples of each type are in commercial operation. The hollow fiber membranes, manufactured from synthetic polymers such as polysulphone or polyamide, are normally used in the dairy industry. Although UF is currently the method of choice for the commercial production of whey protein concentrates of varying protein concentration, several major problems limits its operational performance including: high capital cost and operating cost; membrane fouling and concomitant loss of permeate flux rate; incomplete removal of low molecular solutes unless diafiltration is used; cleaning, sanitation and related microbial problems; disposal of large volumes of permeate. The permeation behaviour and the characteristic of WPC obtained by ultrafiltration, widely vary with the type of feed stream, pH, ionic strength and various other constitutional make up of the system. It is low energy consuming process. The economy of the process and the characteristics of the resultant WPCs are dependent on the permeation behaviour of

the constituents during ultrafiltration. The upper limit to fractionation will be set by the design of the plant, but commercially dried WPC products produced by UF may contain 30 to 80% protein. In order to achieve higher protein values (up to 90% of dry matter), one or more diafiltration steps may follow. Diafiltration means that water is added to the retentate, thereby the viscosity is reduced, and the concentration of lactose, ash, and NPN is decreased by further UF. Both sweet and acid whey may be used in the production of WPC. The protein content of product is achievable with a given UF plant without diafiltration is tied to the hydrodynamics of the special system design. In essence the higher the total solids level attainable in the concentrate, the higher the protein purity achievable without diafiltration. The range of various suppliers is 50-65% purity without diafiltration.

32.2.1 Pre-treatment of whey to increase the permeate flux rate

During ultrafiltration process, fouling of membranes is normally observed. This can be caused by concentration polarization and by progressive accumulation of materials, such as calcium phosphate, on UF membranes during processing. The design of modern UF plants is directed toward better control of concentration polarization, primarily through maximizing shear at the membrane surface. To minimize progressive fouling in continuous plants (e.g., at constant concentration factor), pre-treatment techniques can be sequestration of calcium, demineralization, heating plus calcium precipitation or pH adjustment, replacement of calcium with sodium, clarification and filtration. Other pretreatments include protein interaction, which aids in larger aggregates or precipitates formation, which are non fouling. There is an increase in flux by 50% when cheese whey is heated to 80°C/15 sec instead of pasteurization temperature. Whey, regardless of type, usually must be filtered or centrifuged to remove suspended cheese or casein particles and for cheese whey, to remove fat also.

A method, which claims to provide complete removal of lipoproteins, lipids, and colloidal calcium phosphate, is based on cooling cheese whey to 0-5°C, adding calcium chloride, adjusting to pH 7.3, warming to 50°C, and removing the insoluble precipitate that is formed by centrifugations or decantation. UF permeate flux rate of pretreated whey was about double than that for control whey; pretreated whey was essentially turbidity-free, contained 85% less milk fat, 37% more calcium and 40% less phosphorus than whey.

32.2.2 Manufacture of whey protein concentrates

The whey produced during cheese production is separated for fat and fines, pasteurized, cooled to 55°C and transferred to balance tank (Fig.32.1). The balance tank should have residence time of 30-60 min that will serve not only to balance flow, but also to preconditioning the whey to maximize capacity of UF plant. The preconditioning is quite complex and consists at least of modification of the form of the calcium complexes and deaeration. Whey is then pumped into UF plant, from which WPC is produced. Also a protein depleted permeate (the stream which passes through the semi permeable membrane) is produced, from which a variety of different products can be produced profitably. The protein content of the retentate stream will depend on the volume of permeate removed from the whey. This can be regulated readily.

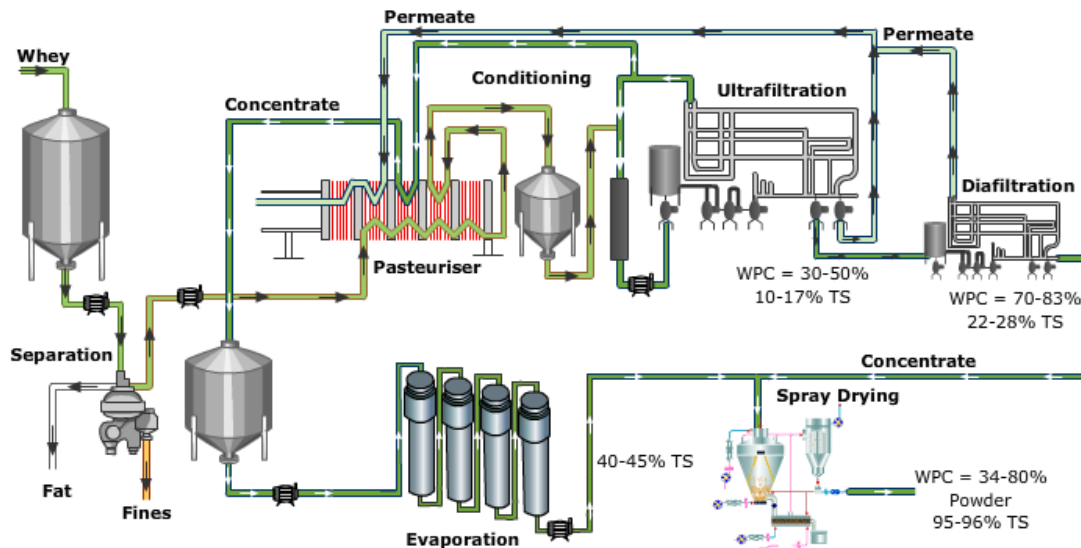
Gupta and Reuter (1987) investigated the manufacture of WPC from sweet cheese whey. Clarification of cheese whey, prior to Ultrafiltration (UF), was found essential for the effective operation of an UF plant. UF permeation rates were greater with higher UF temperature and with pre-holding of the whey for 30-40 min at temperatures (68-72°C), higher than the UF temperature (50°C). Probably, holding of whey at a temperature higher than the UF temperature causes the main precipitation of calcium phosphate to take place in the balance tank itself. Therefore, there is much less tendency for the precipitation of calcium phosphate in the membrane system. The increase in total solids concentration in the retentate was slow during early UF stages, but improved considerable in advanced stages. 15, 20 and 25% TS WPC were obtained at about 92.5, 95.35 and 96.8% whey volume reduction (WVR), respectively, irrespective of the preheating and UF temperatures used. In diafiltered concentrates, 15, 20, and 23% TS were achieved at greater WVR, i.e. 95.2, 96.7 and 97.35%, respectively. Preheating and UF temperatures treatment affects the constituents of concentrates. The effect was most distinguished on calcium content. The preheating treatment of 68-72°C for 30-40 min, before ultrafiltration of whey at 50°C, increased calcium/TS of concentrates considerably higher with increased UF concentration compared to lower preheating temperatures (equivalent to UF temperatures).

In addition, concentrates produced at higher UF temperatures had higher calcium/TS. Ash/TS of concentrates decreased during ultrafiltration and further with diafiltration. The decrease was more rapid in cases, where lesser calcium was retained. During both UF and diafiltration, lactose/TS of concentrates reduced drastically. Protein purity of whey protein concentrates improved greatly with increased UF concentration, but at a diminishing rate during later UF stages. 50, 60, 70 and 75% protein/TS in concentrates were obtained at about 12, 15.5, 21 and 25.5% TS concentration, respectively. As the protein content increases, the fat content increases and lactose, moisture, and ash contents decrease. The membranes not only retain the protein, but also the fat. On the other hand, in this process lactose and minerals are lost in the permeate resulting in their proportional decrease in the remaining solids. With diafiltration, the protein purity of the product improves significantly. Thus, by manipulating the UF conditions, it is possible to produce WPC with different protein: lactose: calcium ratios. The acidity/TS of concentrates showed a slight decrease during UF. The diafiltration, however, reduced acidity/TS of concentrates significantly.

32.2.3 Manufacture of spray dried WPC

If the UF plant has a constant feed and concentration capacity, WPC can be evaporated and dried directly. UF plant concentrate is evaporated to 25 to 40 percent solids, depending on the concentrate composition. To achieve acceptable powder densities (0.35 to 0.5 g/cm³), it is normally necessary to concentrate in evaporators the WPCs 35-50% prior to spray drying. WPCs 50-80% often has 27-30% TS and can be pumped directly to spray drying. WPC is evaporated to 25-40% solid concentration depending upon the concentrate composition. Concentration for 35% protein powders is typically evaporated to 40% solids. Concentration for 75% protein powders is evaporated to 25% or less TS. Evaporated WPC is then spray dried (typically to 4% moisture or less). The spray drying process for this product is conventional. Nozzle atomisation is preferably used. The typical inlet drying air temperature is 175-190°C. Between 90 and 95% of the protein in the whey is recovered. The resulting powder may be blended to ensure good product uniformity, and then bagged. Low-temperature

processing is necessary because of the heat sensitivity of the product, but suitable equipment is readily available.



Manufacture of whey protein concentrates (WPC) by ultrafiltration process

32.3 Gel Filtration Process

This useful technique for separation of whey components is essentially a batch process. Gel filtration separates molecules on the basis of size. The solid support used in gel filtration is called media or matrix that consists of spherical gel beads, whose size and porosity are carefully controlled by swelling in an appropriate buffer. The gel filtration matrix in the name of Sephadex G-10, Sephadex G-25, Sephadex G-50, Sephadex G-75 etc are used for separating different range of molecular size constituents. G-25 has the molecular sieving ability of 1KDa - 5KDa and is suitably used after packing in a column for separation of whey proteins from other constituents of whey.

Generally whey is pretreated to remove lipids and fine particles, concentrated by RO or evaporators to about 20% total solids, centrifuged and filtered to remove precipitated solids and applied to the gel. When the whey is passed through a column or bed of porous Sephadex G-25 beads, various whey constituent molecules diffuse into the beads to varying degrees. Smaller molecules of lactose, minerals etc. diffuse further into the pores of the beads and are forced to follow a circuitous path before later exiting the beads, resulting in their movement through the bed more slowly. By contrast, large molecules of whey proteins flow around the resin beads, taking a relatively direct path through the column resulting in their movement through the bed more quickly (Fig.32.2). This causes the larger molecules of whey proteins to elute earlier than the other smaller molecules of lactose, minerals etc. The difference in the flow rates of large and small molecules allows the faster-flowing

macromolecules of whey proteins to get recovered separately from the slower small molecules of other whey constituents as the whey travels the distance of the sephadex porous beads packed in the column.

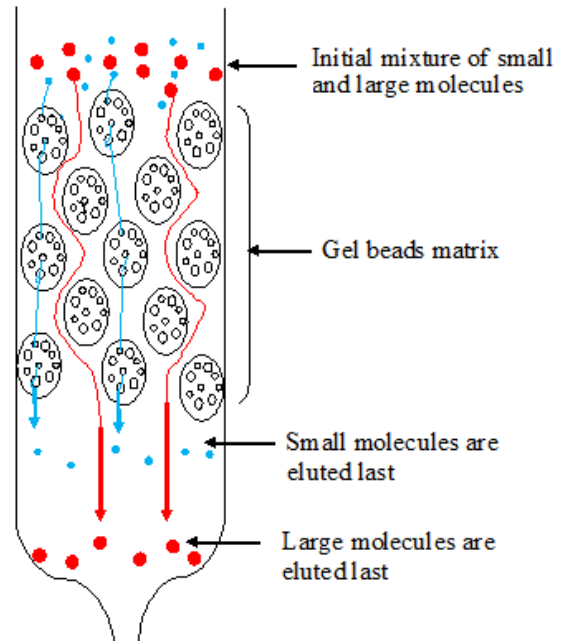


Fig. 32.2 Gel Filtration Process

The high molecular weight fractions is further concentrated by evaporation and spray dried. Products of 30 to 80% protein can be manufactured. The process is expensive to install and operate, and the yield, at 65% of the protein in whey, is low. It is subjected to fouling and microbial contamination also. It appears that it is no longer in commercial operation after the development of UF process.

***** 😊 *****

Lesson 33

PHYSICO-CHEMICAL PROPERTIES OF WHEY PROTEIN CONCENTRATES

33.1 Introduction

Chemical, physical and functional characteristics of WPC vary according to method of their manufacture. WPC contain, on average, 4% moisture. Whey proteins concentrate powder recovered by ion exchange adsorption is characterized by high protein (> 85%) and low (< 0.5%) lactose, low ash and low lipid contents. The product prepared through heat precipitation process is in denatured form with no innate property. The product prepared by ferric salt precipitation is reported to be light yellow to brown in colour. The product prepared by molecular separation processes contains whey proteins in their native form and possess exceptional functional properties including high solubility of considerable value to the food industry. WPC produced by UF process have a protein content typically ranging from 34 to 80% and spray dried WPC has bulk density of 0.35 to 0.5 g/cm³. As the protein levels increase, the percentage of lactose and minerals decreases.

33.2. Protein content

Commercially available WPC contain from 35 to 85% protein. If they are added to food on a solid basis, there will be large differences in functionality owing to the differences in protein content. Most food formulations call for certain protein content and thus WPC are generally utilized on a constant protein basis. In this case the differences due to protein content as such should be eliminated. As the protein content increases, the composition of other components in the WPC must also change (Table 33.1.) and these changes in composition might be expected to have an effect on functionality.

33.2.2 Lipid content

WPC contain residual lipid despite attempts by producers to remove as much lipid as is possible from the whey. The lipid found in WPC does not have the same composition as the bulk lipid of milk, but is greatly enriched in phospholipids and milk fat globule membrane material. Removal of residual lipid from whey has been shown to increase ultrafiltration flux and to improve WPC functionality. The lipid content of WPC tends to increase as the protein content increases. Typical changes in WPC composition that occur as the protein content of the product is altered is shown in Table 33.1. Residual lipid has long been recognized as being detrimental to the quality of WPC with particular attention to the foaming and flavour qualities of the product. Small amounts of fat in whey protein solutions cause the rapid collapse of foams that are otherwise stable. It has been demonstrated that the removal of residual lipids from whey protein solutions by ultracentrifugation resulted in a three-fold increase in overrun. Further, the residual lipid is detrimental to the foaming properties and also inhibits the gel-forming properties of WPC.

Table 33.1 Typical composition of whey protein concentrate powders

Composition (%)	Percent protein			
	35	50	65	80
Moisture	4.6	4.3	4.2	4.0
Crude protein	36.2	52.1	63.0	81.0
True protein	29.7	40.9	59.4	75.0
Lactose	46.5	30.9	21.1	3.5
Fat	2.1	3.7	5.6	7.2
Ash	7.8	6.4	3.9	3.1

33.2.3 Mineral content

The mineral content of whey is altered as the whey is concentrated to form WPC. The method of processing can have a large effect on both the total ash content and the mineral present. Ash contents for commercially available WPC produced by ultrafiltration, electro dialysis and metaphosphate complex formation range from 0.5 to 15%. Calcium content ranges from 13.9 to 2180 mg/100 g sample, while the phosphorous content ranges from 0.26 to 3.53%. The samples precipitated as metaphosphate complexes, as expected, contain the largest amount of phosphate. High ash content may inhibit the emulsion and foaming characteristics of WPC. WPC have been shown to function better in a number of applications, where minerals have either been removed or their content modified. Such applications include uses in ice cream, infant formulas, bakery products and dietetic foods. The mineral that has received most attention regarding its effect on functionality is calcium. The solubility of WPC was improved by calcium replacement, with the largest improvement occurring at the isoelectric point. The textural parameters of heat-induced gels also increased as sodium replaced calcium, as did the time to form a coagulum at 70°C. Overrun was decreased by calcium replacement while foam stability and solution viscosity were affected in a non-linear manner.

It has long been known that calcium concentration has a large effect on the heat stability of both β -lactoglobulin and α -lactalbumin. The dependence of heat denaturation on calcium content is probably responsible for the effects of heat denaturation on gel strength. At very low concentrations, the addition of calcium increases gel strength. As the calcium concentration increases past a certain maximum, further increases cause decreases in gel strength. At low concentrations, calcium can increase gel strength by aiding in the formation of crosslinks that are necessary for proper gel formation. At higher concentrations of calcium, protein precipitation occurs at a faster rate than does crosslink formation and gel strength is weakened.

33.2.4 Lactose content

As the concentration of protein in WPC increases, the lactose concentration decreases. Values for the lactose content of commercially available WPC range from 0.1 to 46%. Values below 5% are derived from products produced by an ion exchange procedure, while the value of 46% was for a 35% protein WPC. Generally, lactose is considered filler that has little effect on protein functionality. Lactose is a reducing sugar and can react with proteins via non-enzymatic browning to produce less nutritious and lower functional products. This should not be a problem for WPC stored at reasonable moisture levels. Lactose can increase the heat stability of proteins and lactose concentration has been related to the solubility of whey proteins following heat treatment. This should not, however, be a significant

factor in the solubility characteristics of most WPC. Care is certainly warranted in the processing of products that contain very low concentrations of residual lactose and this may explain the observation that WPC produced by ion exchange are difficult to manufacture with high solubility.

Table 33.2 Protein yields^a and concentrations of principal classes of dried whey protein products

	Basis of recovery									
	Heat Precipitation	Molecular size ^b		Adsorption ^c		Phosphate Complex	Removal of ^d			
		-----		Cell.	Sil.		Lac	Min.	Lac+	Min
		UF	GF							
Yield %	70-80	90	50-90	50-90	70-85	90	90	90	90	
Concentration %	65	30-80	30-80	30-80		30-85	40	20	45	
Product name ^e	WPC	WPC	WPC	WPC	WPC	WPC	DLW	DMW	DLDMW	

^a Expressed as percentage of (total-nonprotein N) X 6.38 in original whey.

^b Ultrafiltration, UF; gel filtration, GF

^c Regenerated cellulose, cell; silica, sil. Pilot-scale data only.

^d Lactose, Lac; Minerals, Min.

^e Whey protein concentrate, WPC; delactosed whey, DLW; demineralized whey, DMW; delactosed, demineralized whey, DLDMW.

Table 33.3 Percentage composition of whey protein concentrates

Method of Isolation	Composition/Source of Whey														
	Protein			Carbohydrate			Fat			Ash			Moisture		
	CW	AW	PW	CW	AW	PW	CW	AW	PW	CW	AW	PW	CW	AW	PW
Gel filtration	83.1	86.2	65.6	1.4	1.3	4.1	2.4	1.6	6.2	0.04	0.04	2.48	8.2	7.1	11.4
Ion Exchange	77.4	85.4	46.6	0.4	0.4	1.9	0.3	0.1	4.1	13.2	13.0	28.8	7.5	5.3	14.3
Hexmetaphosphate complex	62.3	59.4	33.9	9.7	12.8	14.5	6.8	1.5	35.0	17.8	19.6	19.1	3.1	4.5	6.1
Carboxy methyl Cellulose complex	60.99	69.63	28.0	17.8	18.0	32.8	15.6	4.5	19.0	1.9	1.2	3.6	2.2	5.1	2.1

CW= Cheese whey; AW= Acid whey; PW= Paneer whey

***** 😊 *****

Lesson 34

MANUFACTURE OF CRUDE LACTOSE

34.1 Introduction

Lactose is a characteristic carbohydrate of milk and is the only sugar of animal origin. It is white, water soluble crystalline powder in its pure form and moderately sweet in taste. Crystalline lactose occurs in two forms: α -hydrate and β -anhydride lactose or a mixture of both forms. The most common form of commercial lactose is α -hydrate, very little lactose is in the form of β -anhydride. Lactose crystallises as α -hydrate from saturated solution at temperature below 93.5°C. The crystals contain one molecule of water per molecule of lactose. The β -anhydride which contains no crystalline water is formed when the crystallisation takes place at temperature higher than 93.5°C. The crystallisation of lactose from saturated solution is the α -form which is less soluble.

Lactose can be manufactured both from sweet whey and acid whey. Generally, unfermented whey is preferred because of its high lactose and low ash content. Acid whey if neutralised, changes the whey characteristics and increases the cost of manufacture. Lactose can be isolated on a commercial scale from whole whey or from deproteinized whey.

The deproteinized whey at the same total solid concentration contains more lactose and is thus more supersaturated than concentrated whey. Moreover, due to the decreased viscosity, a higher concentration can be obtained in evaporator equipped with a suitable finisher. If the whey were not to be deproteinized then due to the greatly increased viscosity of concentrated whey, the separation of the crystallized lactose would be exceedingly difficult or in extreme cases the lactose may not crystallize out at all. On the other hand, adding processing steps of material to clarify the whey has limitations. It may result in loss of lactose through occlusion with the extraneous matter being removed, add to the cost of materials used and yield less useful mother liquor because of the materials added. Thus, purity may be improved at the expense of reduced yield of lactose and less desirable mother liquor for food or feed use. Lactose yields varying from 65 to 76 % have been reported. However both methods, after the recovery of the crystallized lactose, result in a by-product, the mother liquor. This may be either dried, as a fodder product, or can be improved either by demineralization or by protein enrichment with a cheap vegetable protein.

34.2 Manufacturing Process

The conventional process for lactose manufacture consists of following steps:

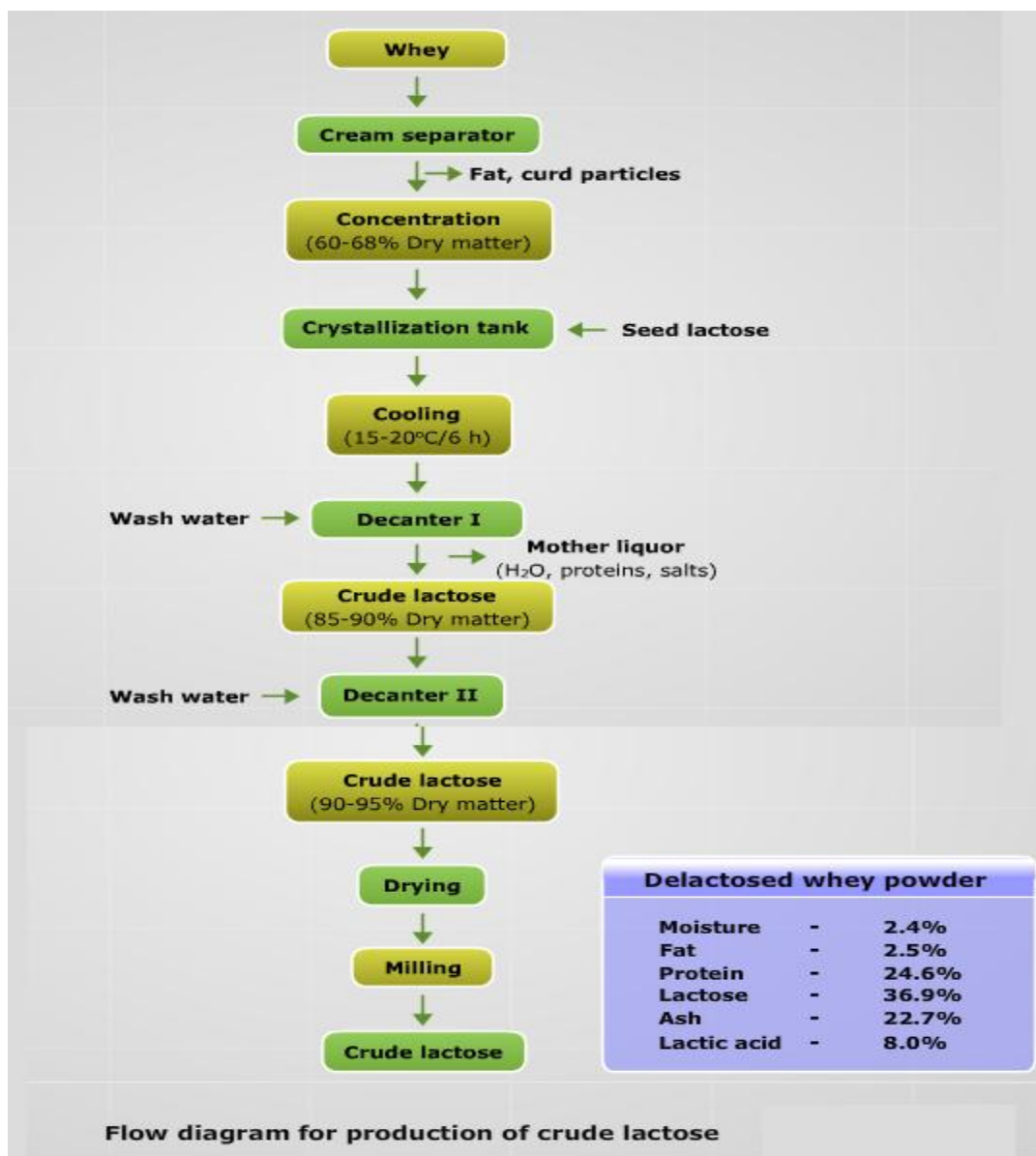
34.2.1 Clarification of whey

Clarification is necessary to remove fat, suspended curd particles and other impurities (dust, dirt, microbes) from whey (Fig. 34.1). Microfiltration is a pressure-driven membrane separation process using porous membranes with cut off pore size in the region of 10^{-6} m allowing passage of proteins. Microfiltration is done at 55°C and can be used to remove large particles, casein fines, micro-

organisms or microbial spores, fat globules, somatic cells, phospholipoproteins etc. from whey.

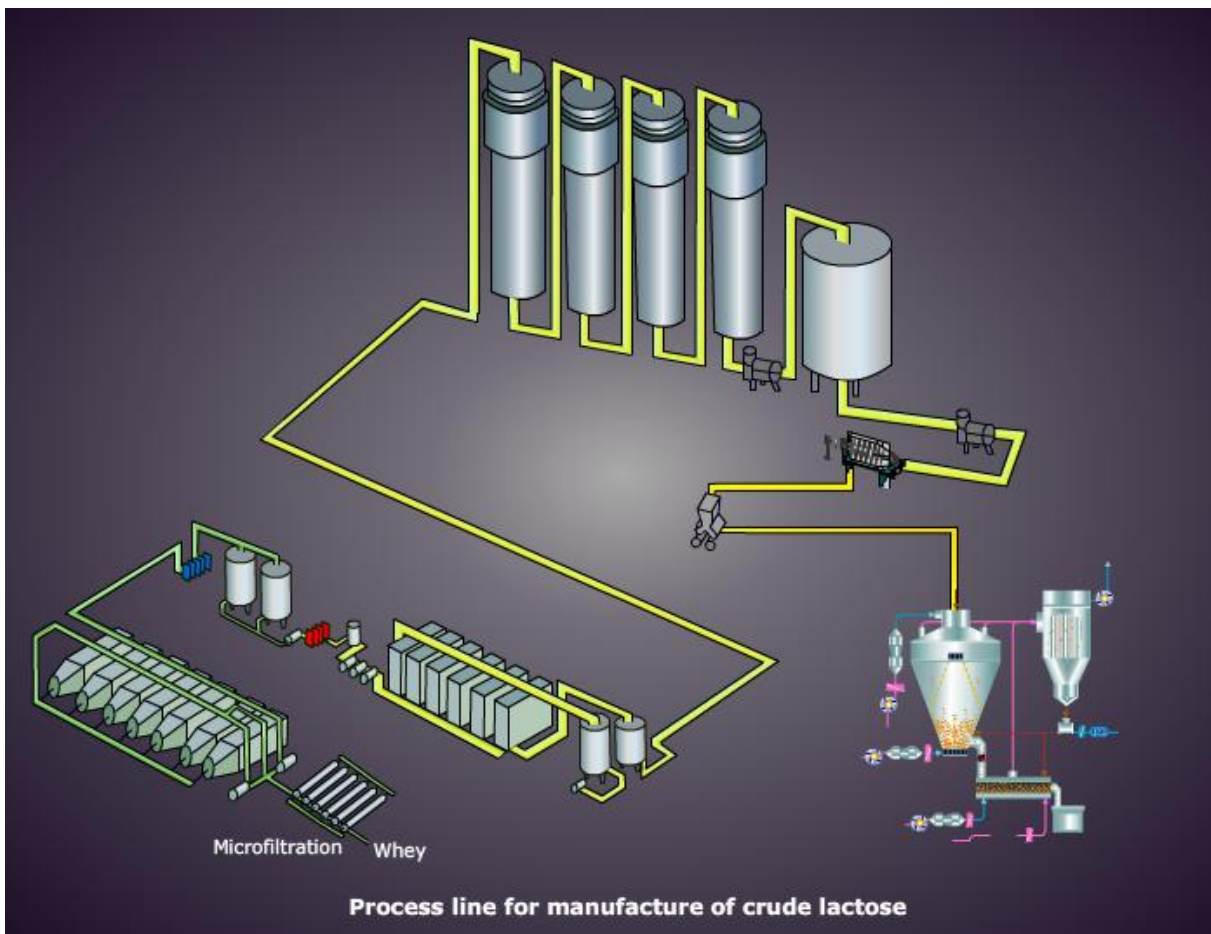
34.2.2 Deproteinisation and demineralisation of whey

The main drawbacks of the traditional process of lactose manufacture are with respect to low yield and purity of recovered lactose and the high cost of manufacture and energy consumption. Whey contains about 20% of the total protein of milk. Degree to which the proteins and salts are removed from whey prior to concentration and crystallisation, determines the purity of lactose. The presence of protein and salts in whey increases the viscosity of concentrated whey and hinder the lactose crystal separation, and in extreme case even prevent the crystallisation. Lower amounts of whey protein denaturation have been found to improve the lactose quality mainly due to lesser inclusion of protein and minerals in the crystallised lactose. Some processing steps have to be included so as to increase the purity but these lead to increased loss of lactose and add to the cost. Subsequently, it yields mother liquor, which is less useful for food or feed. Thus a compromise has to be made between the yield and purity aspects in the process to be adopted for lactose manufacture.



Cheese whey on heat treatment to 85-87°C at pH 4.8, is reported to remove maximum whey proteins cum salts on filtration, while in case of paneer whey, higher deproteinization could only be obtained by heating to 90 to 92°C for 10 min at pH 6.6. In another study, heating whey to 95°C, addition of different coagulants, holding for 15 to 20 minutes, centrifuging at 1500 RPM for 5 minutes has been suggested for maximum deproteinisation.

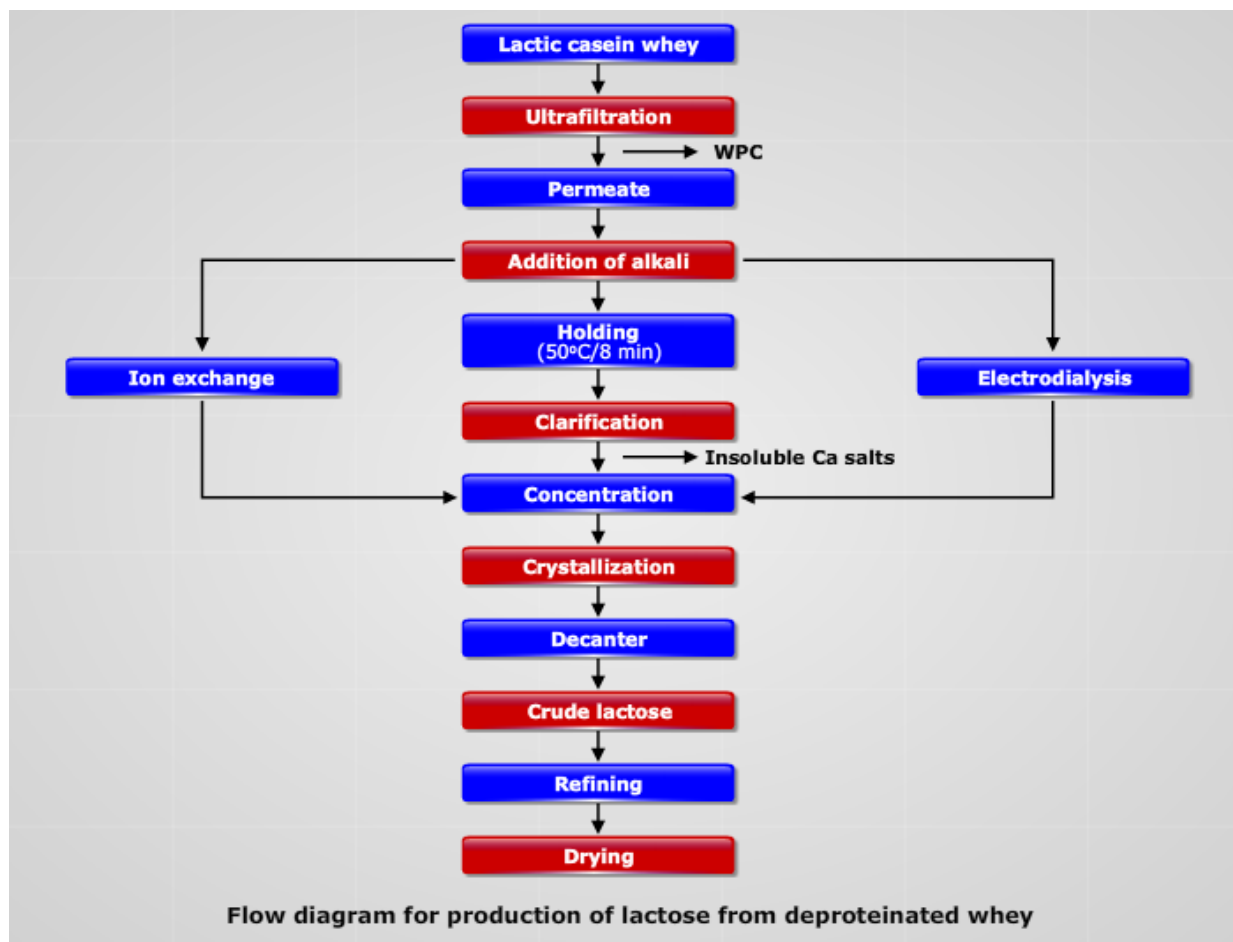
Lately, ultrafiltration has also successfully been applied industrially for the deproteinisation of whey (Fig. 34.2). The membrane technology has an edge over the conventional technology because of improved product yield, improved product consistency, continuous processing operation, minimum man power and energy requirement, greater efficiency due to decreased processing time and over and above, the whey proteins can be recovered in their natural form. Using UF permeate as the starting material would have the associated advantage of shorter crystallisation time. At present, nearly 12% of the total whey utilised is processed by ultrafiltration. The protein free lactose solution is ideal for producing lactose syrup except for its high mineral content.



The UF permeate, particularly the acid whey permeate has a very high calcium content. During lactose crystallisation, the insoluble calcium salts may contaminate the lactose crystals, and because of their low solubility, they are not readily removed by washing with water. Concentration by evaporation causes precipitation of calcium salts and can result in rapid fouling or scaling of heat exchanger surfaces. Therefore, UF permeate must be pre-treated prior to or during evaporation.

Removal of approximately 50 % calcium is sufficient to avoid difficulties during evaporation.

Demineralisation by ion-exchange and electro dialysis and by using an ammonium bicarbonate process has been recommended (Fig. 34.3). The main limitations of these processes are, high capital cost, high running cost and the problem of effluents, although, the ash content is reduced to less than 0.5%. Other suggested pre-treatment include reducing pH to eliminate the formation of insoluble salts and addition of food grade calcium chelating agents (e.g., sodium hexametaphosphate) to form insoluble complexes that may be removed prior to crystallisation. Hobman (1984) reported a process to reduce calcium salt levels by upto 80% by treating with alkali and heat. To improve the purity of lactose, it is necessary to reduce the mineral load.



Partial demineralisation can also be achieved by nanofiltration (NF). NF performs two functions simultaneously. It partially demineralises a solution while concentrating lactose component. It can be used for the concentration and partial demineralisation of whole whey upto 28% of dry matter and also for concentration of the UF permeate. NF removes 75% of the water when operated at a typical 4 fold concentration. Demineralisation of cheese whey by NF shows 20-45 % overall demineralisation while more than 90-95 % of non-ionic species such as lactose. A 2-5 % loss of lactose can be expected in a typical whey demineralisation process (Jelen, 1991).

Table 34.1 Chemical composition of UF permeate stream from cheese and casein whey

Constituents	Cheddar cheese	Casein
Total solids (%)	6.40	5.9
Lactose (%)	5.80	4.6
Total N (%)	0.05	0.06
NPN (%)	0.04	0.04
Ash (%)	0.54	0.74

34.2.3 Concentration

The concentration of whey to particular total solids is very critical because, a high total solids concentrate will be too viscous to pump, while a lower total solids concentrate will result in insufficient lactose crystallisation. The permeate is concentrated to a solid content of 60% or more (upto 70%). This is performed either by a pre-concentration through reverse osmosis, followed by evaporation or merely by evaporation. Reverse osmosis, when employed as a pre-concentration step, has the potential for removing a major portion of the water from whey or permeate more economically and in more energy efficient way than the evaporator process. Evaporation is carried out in falling film multi effect evaporators for economic reasons. The basic limitations of the these systems are: high cost of operation, problem of foaming, fouling, increase in viscosity and browning due to high residence time. For a higher level of concentration of whey, a combination of reverse osmosis and evaporation is the most energetically favourable way. The concentration process must be conducted in such a way that no lactose crystallisation takes place in evaporator and piping. This is done by keeping the temperature and concentration within metastable area.

34.2.4 Crystallization

The purpose of crystallisation is to secure the formation of crystals that can be separated from the mother liquor. The crystallisation rate depends on available crystal surface for growth, purity of the solution, degree of supersaturation, temperature, viscosity and agitation. Crystallisation is initiated in the hot concentrated whey or UF permeate. The nucleation process is initiated by seeding and agitating the supersaturated solution. Cooling of lactose syrup to a temperature below saturation temperature is necessary for crystallisation of lactose. During crystallisation, β -lactose is converted into α -lactose which is crystallised out. For easy recovery of lactose crystals, their size must be sufficiently large to ensure quick settling of crystals. Easy recovery is obtained with an average size of 0.2 mm. The number of crystals and their average size can be controlled by seeding the concentrate with a known number of very fine lactose crystals. The seed crystals must be added in the form of fine particles of α -lactose monohydrate (200 mesh) at the rate of 0.1% of concentrate. The cooling of the concentrate should be slow. The entire crystallisation process lasts between 15-24 h under constant slow agitation. Automatic systems in lactose crystallisation tanks are available to regulate temperature within 0.5°C. The system can be supplied pre-programmed since random access memory has a battery buffer to prevent loss of data in case of power failure. Different cooling rates

have been employed by different workers for crystallisation of lactose. Slow cooling to 10°C in 20 h and further holding for 15 h has been suggested. Cooling rate of 5°F/h and cooling from 78°C to 10-15°C in 50-60 h with intensive stirring have been recommended. Intermediate cooling temperature of 60°C with a final cooling temperature of 30°C over a 12 h period has also been recommended for effective lactose crystallisation.

34.2.5 Recovery of crude lactose

34.2.5.1 Harvesting of lactose crystals

The lactose crystals can be harvested either in a basket centrifuge batchwise or in a continuous decanter attached with a screw conveyor. Continuous decanters with a screw conveyor for crystal discharge are more commonly used on a commercial scale. The liquid phase overflows and consequently a liquid level is formed. The solid outlet ports are situated higher and crystal mass is discharged with relatively low moisture content. The crystals from decanter are fed into a second decanter in order to improve washing and removal of mother liquor. It is important that the choice of the decanter should not only be decided on the basis of the size of initial investment but also on parameters like loss of lactose and free moisture.

34.2.5.2 Washing of lactose crystals

Wash water is introduced into the centrifuge during the separation of lactose crystals to assist in the removal of the remaining impurities. The use of 10 % wash water can reduce the ash level of the lactose by more than 66 %. Washing with demineralised water or possibly, RO permeate which can be injected into the decanter to wash out as many impurities as possible has also been suggested. A specially designed centrifuge gives a high degree of separation of lactose crystals from condensed cheese whey. Crystals of 40 µm can be recovered with final moisture content of 1.5-2.5%. Another designed centrifuge proved capable of continuously separating crystalline lactose with 2.5-2.9% moisture from concentrated whey at the rate of 250-300 kg/h.

***** 😊 *****

Lesson 35 REFINING OF LACTOSE

35.1 Introduction

Crude lactose is refined for high degree of purity, such as in the manufacture of pharmaceutical grades. Different grades of lactose are produced varying in lactose purity as per their specific requirements. In general, the process for the manufacture of edible- grade lactose produces a product that does not meet the ash, protein and light absorption standards for pharmaceutical- grade lactose. The impurities usually consist of riboflavin, a variety of proteins, lactose phosphate and lactic acid. Durham *et al.* (2007) claimed to produce USP lactose directly from whey permeates by using ion exchange, nanofiltration, chromatography, evaporation and crystallisation, without the need for a second crystallization step, with a yield approaching 95%.

35.2 Grades and Specification of Lactose

The international trade recognises several commercial forms of lactose as shown in Table 35.1. BIS standard for commercial lactose is given in Table 35.2.

Table 35.1 Grades of lactose

S. No.	Grade	Lactose (%)
1	Technical lactose	90-92
2	Crude Lactose	95-99
3	Food grade lactose	98-99
4	Pharmaceutical lactose	99.5-99.9

Pharmaceutical-Grade Lactose must meet the standards for contaminants described by Anonymous (1993) and USP-25 (2001). These two standards are almost identical and the test procedures that must be followed are prescribed. As a general guideline, heavy metals must be below 5µg per g, the microbial count must be less than 100 per g, with no *Escherichia coli* present and with a combined mould and yeast count below 50 per g. There are also ash, clarity and light-absorbing tests which must be passed.

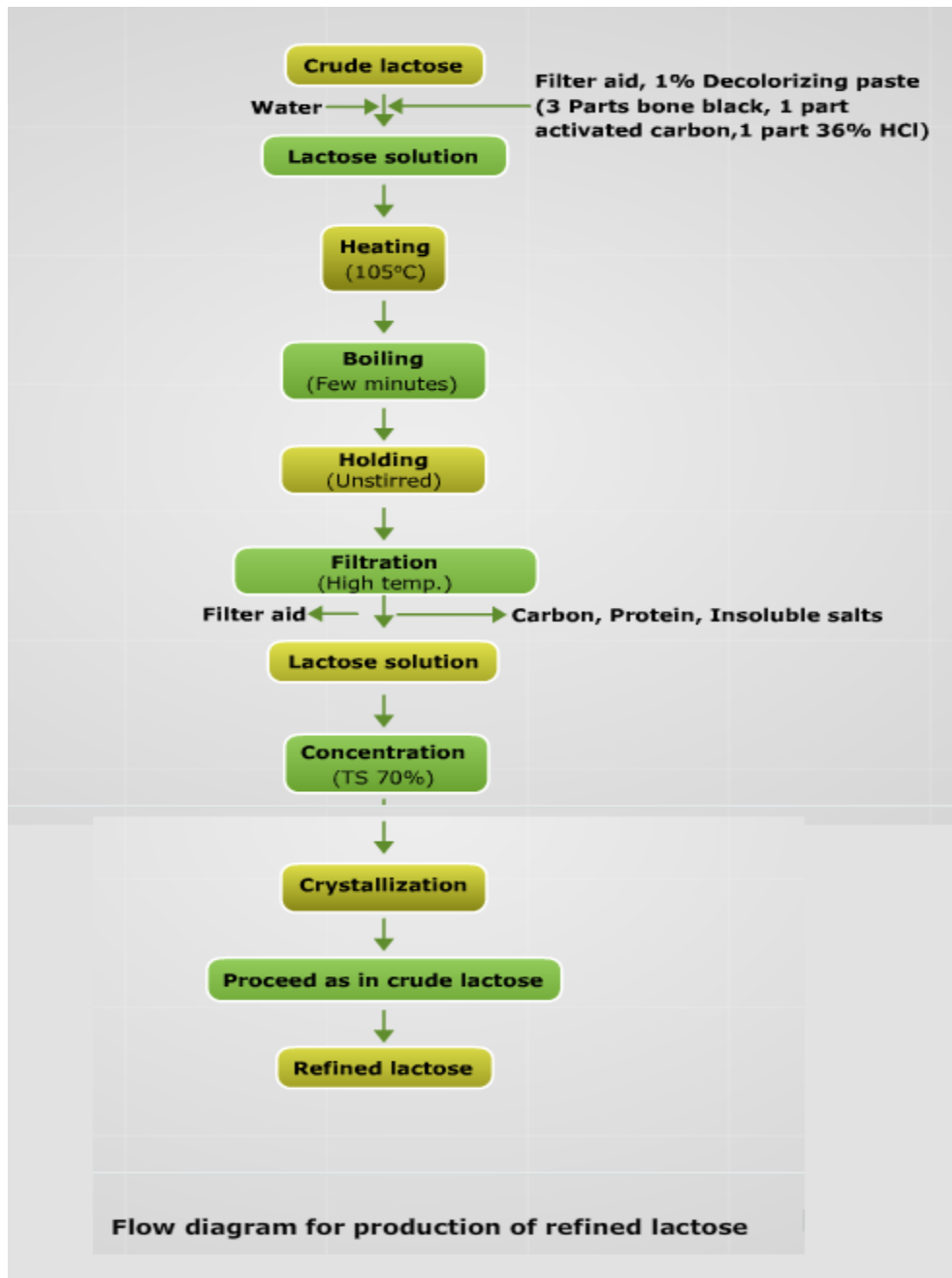
Table 35.2 Lactose Commercial - Specifications (IS 1000:1989)

S. No.	Specifications	Requirement
1.	Lactose (on dry basis), % by mass, min.	99
2.	Moisture % by mass, max. a) for lactose monohydrate b) for lactose anhydrous	5.5
3.	Sulphated Ash (on dry basis), % by mass, max.	0.2
4.	pH (of 10% solution)	4.0-6.5
5.	Sp. rotation	52.0-52.6
6.	Nitrogen, % by mass, max.	0.05
7.	Arsenic, mg/kg, max.	1
8.	Lead, mg/kg, max.	2
9.	<i>E. coli</i> , per 0.1 g	Absent
10.	<i>Salmonella</i> , per 0.1 g	Absent

35.3 Refining Process

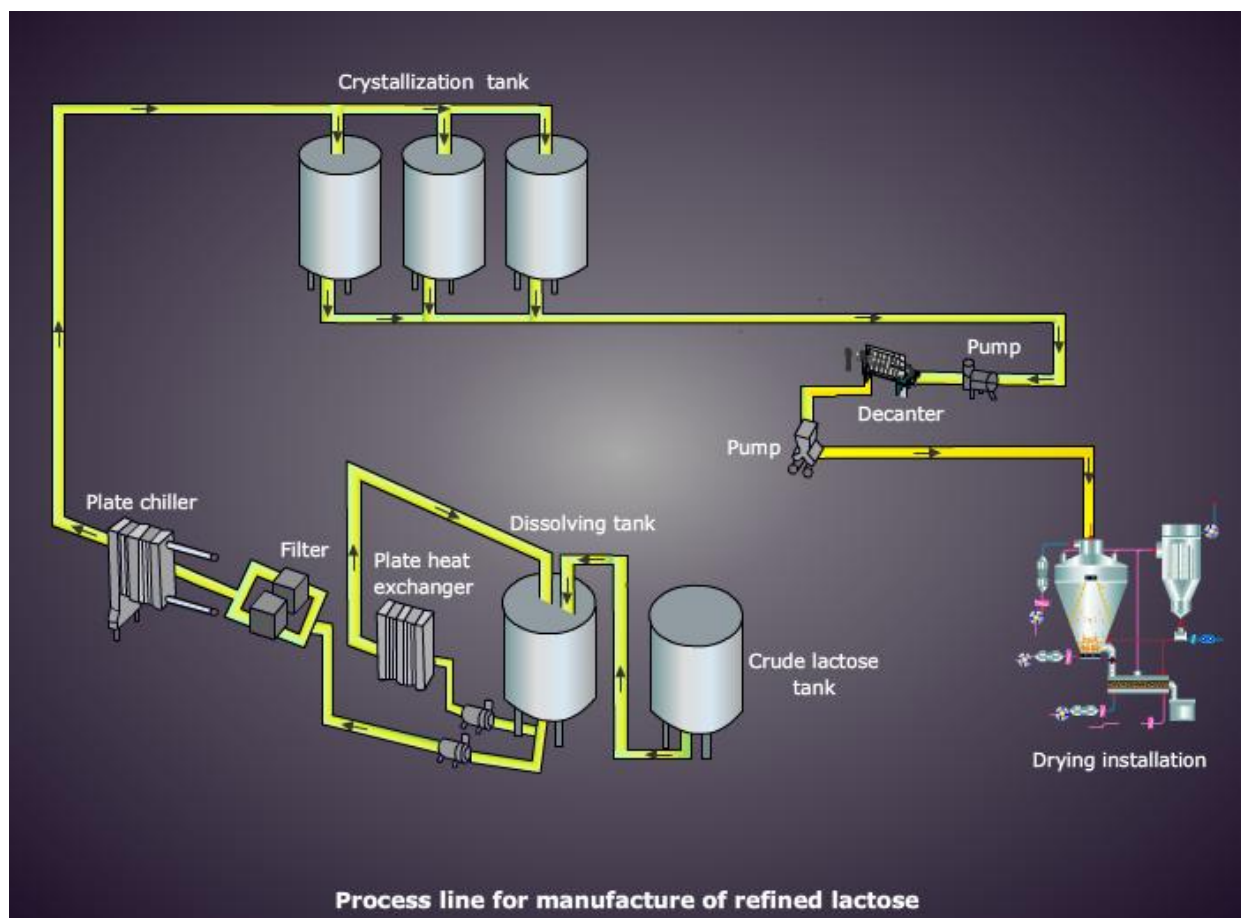
In the refining process, decolourising carbon is used to adsorb colour and probably removes other impurities to some degree. Hydrochloric acid is added to assist the action of the carbon, to solubilise salts and to aid in removal of protein. Lime is used to adjust the reaction to that most favourable for the precipitation of protein and probably aids by combining with the protein to some extent. The carbon and the precipitated impurities are removed by filtration, and the soluble impurities stay with the mother liquor and in the washings from the centrifuged crystals.

The process of producing up to pharmaceutical grade lactose is to re-dissolve the crude lactose in clean water and then to remove the impurities by a combination of adsorption and filtration processes, followed by re-crystallization. A typical refining process of lactose consists of subjecting crude lactose to treatment for removing colour, residual protein and salts followed by re-crystallisation (Fig. 35.1). Less refining is required for lactose prepared from permeate than that made from whey. Crude lactose is dissolved in hot water to a 50-60% concentration depending on its purity. About 1% of decolorizing paste consisting of 3 parts bone black, 1 part activated carbon and 1 part 35% HCl is added. Quick dissolution requires heating to 105°C. The slurry is passed through self cleaning filter at a high temperature and is introduced into crystallising tanks. The crystals are cooled to approximately 20°C in about 6 h. After cooling, crystals are separated and dried. This process is shown in Fig.35.2.



35.4 Drying

Edible lactose is normally dried to 0.5% moisture content and pharmaceutical lactose to 0.1% moisture content. The drying process is limited to a product temperature of 93°C, otherwise lactose will be crystallised into β -lactose anhydride at temperature above 93.5°C. Another important factor is the drying time. If the lactose solution is dried rapidly, crystals do not have an opportunity to form, and the result is the non crystalline glass, which contains the equilibrium mixture of the alpha- and beta-lactose. Flash drying can easily result in the formation of a thin layer of amorphous lactose on α -hydrate crystals, resulting in the risk of lumps formation in the bagged lactose afterwards. A fluidized bed drier with a maximum product temperature of 92°C/15-20 min would give good results. Pneumatic transport of lactose from the drier must be carried out by means of dry air at about 30°C. It gives gentle product cooling.



35.5 Milling and Bagging of Lactose

Dried lactose is milled and sifted through 100-200 mesh sieves and hermetically sealed in moisture proof bags. Pharmaceutical-grade lactose is generally sold by mesh size, the different products being milled to different degrees, possibly in conjunction with air or sieve classification. As well as the traditional α -lactose monohydrate, two other forms are sold to the pharmaceutical industry, i.e. anhydrous lactose (β -lactose) and spray-dried lactose.

35.6 Other Forms of Pharmaceutical Grade Lactose

35.6.1 Anhydrous lactose

This has the same heavy metal, microbial and colour specifications as USP-grade α -lactose monohydrate. Anhydrous lactose is usually made by roller drying, a solution of USP-grade lactose at a temperature greater than 93°C which produces a flaked-type product consisting of very fine crystals of β -lactose caked together. The flaked cake is then milled to the required size distribution.

35.6.2 Spray-dried lactose

Fine pharmaceutical-grade α -lactose monohydrate crystals are partially dissolved in clean water and the slurry is then spray dried. This produces a product that has crystals of monohydrate lactose joined together by amorphous lactose into roughly spherical agglomerates. Because most of the

amorphous lactose is in the centre of the agglomerates, the resultant powder is free flowing without becoming too sticky. The amount of amorphous lactose present can be controlled by adjusting the temperature of the water or lactose solution in which the α -lactose monohydrate crystals are suspended.

***** 😊 *****

Lesson 36 USES OF LACTOSE

36.1 Introduction

Lactose, a milk carbohydrate, has high nutritional value and is mainly used as constituent of foods and medicinal products. Lactose has various applications in food and pharmaceutical industries due to its multifunctional properties. In countries, such as New Zealand, where the lactation of the national herd is largely synchronized to match seasonal grass availability, the protein content of milk powder fluctuates markedly throughout the year. The addition of lactose to standardize protein level is now permitted, provided that the adjustment does not alter the whey protein to casein ratio of the milk being adjusted. Standardization of milk for protein as well as fat levels is being introduced within Europe also. This, at times, has resulted in a great demand for lactose causing a worldwide shortage. This effectively means that lactose has an inherent value approaching that of skim milk powder.

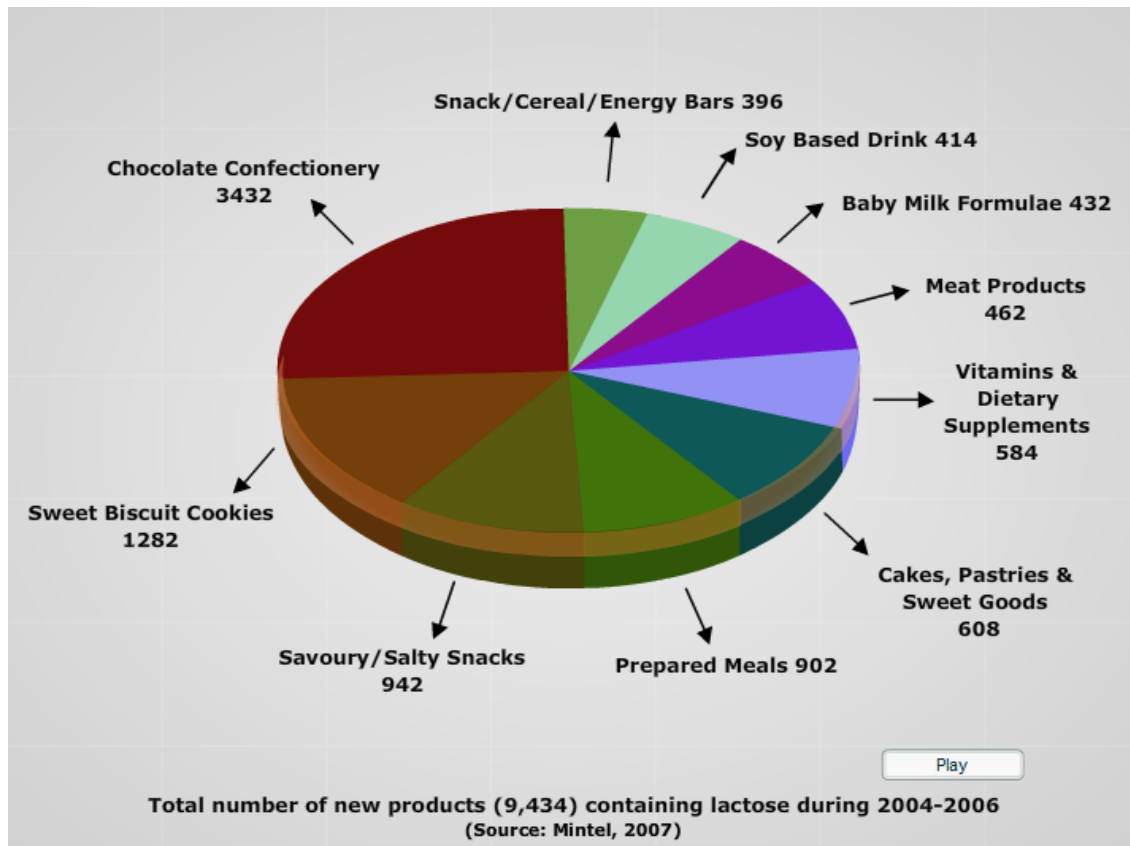
A significant part of the supply of lactose (approximately 80%) goes into food applications such as infant formula, meat products, confectionery and bakery products, and the remaining lactose primarily goes into different pharmaceutical products. Lactitol production is showing interesting new application opportunities and significant annual growth rates. In the last decade, a number of consumer products have been launched containing lactose ingredients, the new products during 2004-06 are illustrated in Fig.36.1. The market for lactose ingredients is likely to be strengthened as the dairy industry focuses more on healthy and nutritional products. Much current research is being carried out in the area of lactose derivatives, with the aim of producing high-value nutraceuticals. This is area in which more commercial activity is likely to be seen and if it works, then it will be another driver in increasing the price of lactose. Lactulose, a derivative of lactose is used in the treatment of tumors.

36.2 Properties of Lactose Providing Basis for Its End Uses

Lactose has various applications in food and pharmaceutical industries due to its multifunctional properties:

36.2.1 Relative sweetness and solubility

Lactose is less sweet than sucrose, it can be used in foods such as icing, toppings and fruit pie added to filling to increase the total solids without excessive sweetness.



36.2.2 Reducing properties

Lactose is a reducing sugar and can react with proteins, peptides and amino acids to form brown pigments. Hence, it is used for controlled browning in the food industry, especially in baked goods.

36.2.3 Protein stabilizing properties

Lactose protects the solubility of the caseinate complex in milk during spray drying. In absence of lactose, the caseinate complex loses approximately half of its capacity to redisperse.

36.2.4 Influence on crystallization habits

The crystallization of lactose in ice cream and sweetened condensed milk constituted a defect if the crystals are large enough to provide a sandy or gritty texture. This can be avoided by seeding with fine lactose powder or rapid agitation of the mix to alter the crystallization habit of lactose.

36.2.5 Absorptive properties

Lactose absorbs flavors, aroma and coloring materials. The absorptive capacity of anhydrous lactose offers a great potential for foods, whereas, retention of volatiles is desirable, such as in coffee. It is also useful in trapping and removing undesirable volatile flavour through filtration.

36.2.6 Dispersing properties

The non hygroscopic and free flowing nature of μ -lactose offers wide potential in the food and pharmaceutical industry as a dispersing agent.

36.3 Applications and Uses of Lactose

Sweetness reduction, consistency improvement in confectionary & bakery goods, as carrier & anti caking agent in powder foods, carrier for tablets, controlled browning in bakery goods, flavor enhancer in sauces & dressings, nutritional importance in infant formulas etc, are some of the desirable functional properties and application of crystalline lactose powder.

36.3.1 Pharmaceutical products

Pharmaceutical grade lactose is widely used as diluents, filler, bulking agent and excipient in tablets, drugs, capsules, pills, powders and other oral forms, of which tablets are most important in its purified form. Lactose is best carrier for tablet making. In capsules, it is filled along with the active materials and used as a coating agent for pills and tablets. Many of the properties of crystallized lactose make it suitable for tableting. It is a known fact that most active ingredients can't be used in the form in which they have been obtained by the isolation of chemical synthesis. A drug can only be effective if it is released under proper conditions. A drug may be distributed uniformly in powdered lactose, which is then moulded or compressed into tablets. Other tablets may be given a lactose shell by first wetting the tablet surface with a small amount of coating syrup, and then tumbling the wetted pill in lactose powder. The coating seals in the contents, but is easily handled and readily dispersible. A series of different lactose products are available to provide a range of granular distribution, free flowability, bulk density and avoiding segregation of mixtures to meet the growing demands of the pharmaceutical industry. These products include those that offer directly compressible properties, eliminating the need for tablet producers to use the costly wet granulation process. In homeopathic medicines, lactose is used in making bio-chemic tablets and mixtures.

36.3.2 Confectionery products

The confectionery industry uses lactose in certain types of candies because it changes the crystallization behaviour of other sugars present and improves body, texture, chewiness and shelf-life. It can be added to fondants at 20% level to reduce sweetness without affecting other product characteristics.

Reduced sweetness, fortification of aroma, improved colour binding, better mouth feel and improved shelf life are the major reasons for using lactose (along with sucrose, dextrose and fructose) in confectionery products. In chocolate and sugar confections especially, lactose is a well established ingredient. The delayed crystallization brought about by the addition of lactose to concentrated sucrose solutions is useful in the coatings of various candies. It is particularly beneficial in caramels and fudges to improve body, texture, chewiness or shelf life.

36.3.3 Bakery products

In the baking industry, lactose can enhance the creaming properties of shortenings to improve product quality, facilitate baking operations, gives increased loaf volume and external appearance score and extend shelf-life, apparently by minimizing starch retrogradation. It can provide better elasticity to the gluten during heating, resulting in better crumb development, crumb stability and pastry volume. In addition, advantage is taken of the ability of lactose to participate in the Maillard reaction which improves browning and flavour of many baked products. The reducing and unfermentable nature of lactose offers unique characteristics to the baking industry. The addition of lactose increases the browning of the crust, which is often highly desirable. Since lactose is not fermented, the functional properties provided by the addition of lactose are not lost during manufacture (Zadow, 1984). The improvement provided by lactose in the emulsifying properties of shortenings result in uniform cell structure and desirable texture, thus promoting good distribution of shortening with minimal mixture. This is of particular value in making pie crusts, which are more tender and shorter, sheet out better and shrink less (Webb and Whittier, 1970). Cake batter containing 10-15% lactose on a replacement basis creamed better and yielded better volume, grain and texture.

Cookie and doughnut doughs made with lactose can be machined rapidly, are easily released from the moulds and retain their shape better in baking. Also, batters show more tolerance to variations in mixing and processing. The chemical reducing power of lactose is less than that of glucose. Therefore lactose can replace glucose in foods in warmer climates.

36.3.4 Meat and sausage products

In the meat and sausage industry, lactose may be added to raw sausage formulation as a carbohydrate source for fermentation by selected starter cultures to produce lactic acid for preservation in dry sausage types, such as salami. Lactose also contributes to controlled browning of these products due to maillard reactions and acids in masking off-flavours and after-tastes caused by emulsifying salts, phosphates and other bitter compounds.

36.3.5 Health foods

The most recent application for lactose and its derivatives is in the formulation of 'nutraceutical' health foods, believed by many to enhance health and well-being if not actually preventing the development of certain diseases, especially in Japan. Due to its slower rate of hydrolysis and absorption, lactose has little influence on the blood-glucose level and therefore is less burdening for diabetics than sucrose. Also for sportsmen this is a positive item. Lactose is a long lasting source of carbohydrate, independent of the insulin system. Long-endurance foods reformulated with high protein and lactose contents.

36.3.6 Baby/Infant foods

Bovine milk differs from human milk in several aspects. Human milk contains higher concentration of lactose than bovine while mineral load is less. For humanization of infant formulations lactose is to be adjusted to meet the intestinal requirement of the infants. A major use of lactose is in humanized infant formulae, where it is used to correct the balance between carbohydrate and protein in human

milk replacers based on cow's milk. Due to its relatively slow digestion, energy is provided to the infant over a period of several hours. Because of its bifidogenic activity, it is viewed as being necessary for the establishment of a healthy intestinal flora. Finally, lactose impacts on mineral absorption, enhancing absorption of calcium, magnesium and possibly zinc, perhaps by increasing the permeability of the villus membrane of the intestine. Lactose is also used for fortification of baby foods.

36.3.7 Instant powdered foods

Lactose is used as an additive to improve the free-flow properties of powdered foods. Lactose glass is used in the instantizing process to increase the dispersibility of such foods as instantized spray dried milk powder by crystallizing to form agglomerates. These products are free flowing and capable of dispersing rapidly, similar to instant milk powders. The hygroscopicity of lactose has been used for adsorbing the free moisture in low moisture foods and fixing it as water of crystallization. One example is the coating of food particles with a liquid flavouring and colouring material and tumbling the product in powdered lactose glass, which absorbs surface moisture and forms a capsule around the food particles.

36.3.8 Instant soups and sauces

Lactose is added to salad dressing, mayonnaise, soups and sauces to enhance flavour and confer added stability to various proteins in the formulations against flocculation at acid pH and pasteurization. Because of its properties as a free-flow agent, lactose may be added to instant powdered soups and sauces.

36.3.9 Beverages

Lactose can be used to increase viscosity, improve mouth-feel and flavor without making the product too sweet. The acceptability of milk as a beverage, especially skimmed milk, may be attributed in part to lactose. As a supplement in skimmed milk, butter milk or chocolate drink, it improves smoothness and mouth-feel, adds richness and enhances acceptance. Further, the addition of 1% lactose of milk chocolate drinks allowed the reduction of butter fat from 2 to 1%, while retaining the same richness in flavour. It has also been used in beer manufacture because it is not fermented by the yeast and remains in the finished product to increase viscosity and improve mouth-feel and flavor. It has similar uses in other beverages.

36.3.10 Other uses

Lactose acts as a stabilizer for proteins in acid fermented products, in frozen milk and in high protein milk powders and milk based coffee whiteners. Addition of lactose can improve the mouthfeel of low fat foods and impart a full flavor. Lactose is also a carrier for artificial sweeteners such as aspartame and saccharine. In freeze dried solutions, lactose increase plug size and aid caking. In sugar coating solutions, it is used in combination with sucrose. Lactose also Improves flavor of raw fish.

Lower solubility of lactose than that of sucrose can be very helpful in special applications. For example hard boiled sweets often have a tough structure if glucose syrup is used as a crystallization

retarder, replacing tartaric acid. In these products the original brittleness can be regained by the addition of finely ground lactose.

Other uses of lactose include its use as a substrate in the production of materials such as penicillin and other fermentation products. The use of lactose in fermentation broths offers advantages owing to the delayed decomposition of the lactose. Further, supersaturated lactose has been used as a binder in making salt-lick blocks for cattle.

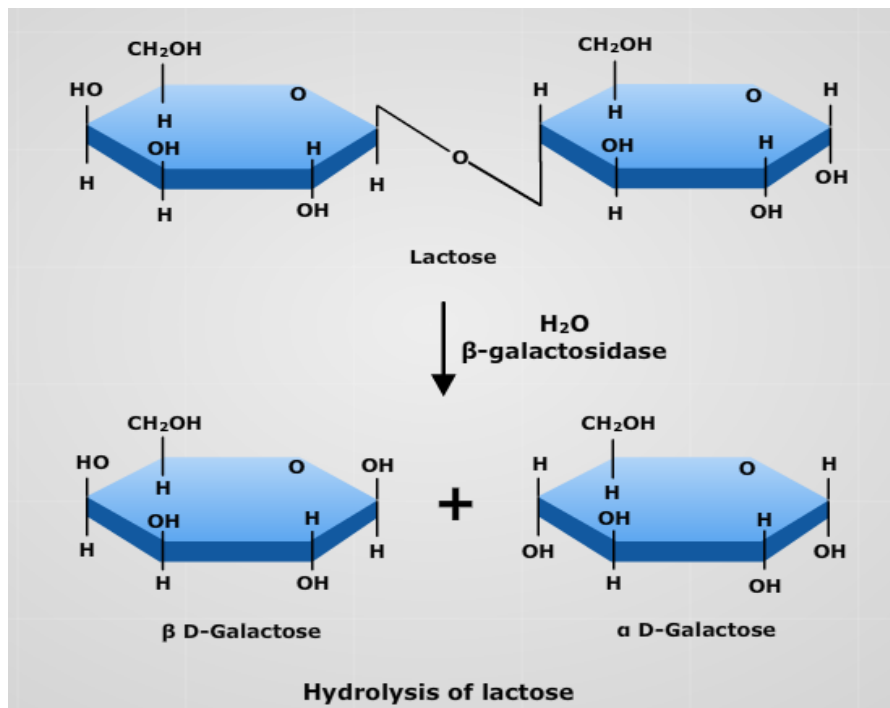
***** 😊 *****

Lesson 37

LACTOSE HYDROLYSIS

37.1 Introduction

Lactose is a reducing sugar and disaccharide composed of a molecule each of glucose and galactose. Hydrolysis of lactose yields 1 equivalent of D-glucose and 1 equivalent of D-galactose. In other words, 100 g of lactose will produce 50 g each of galactose and glucose. This is shown schematically in Fig. 37.1. Lactose hydrolysis by acid and hydrogenation process are also discussed.



37.2 Advantages of Lactose Hydrolysis

Lactose hydrolysis is a promising process with the following advantages:

- i. *Increased solubility*: Glucose and galactose have a higher solubility than lactose (Table 37.1).

Table 37.1 Solubility data for various sugars at room temperature

Carbohydrate	Solubility %
Sucrose	67.9
Glucose	45.4
Galactose	40.6
Lactose	18.0

- ii. A certain proportion of the world's population is lactose intolerant. Hydrolysis would make it possible for them to consume dairy products and foods containing dairy products, which would not have been possible previously.
- iii. A microbiologically stable syrup which does not crystallize may be produced, so that the expense of drying may be avoided
- iv. This process could help to overcome problems associated with lactose crystallization in ice cream and other refrigerated dairy products.

37.3 Methods of Hydrolysis

There are a number of different methods available for hydrolysis, which may be categorized as follows:

37.3.1 Enzyme

- a. Free or single-use
- b. Immobilized
- c. Reactor

37.3.2 Acid

- a. Direct
- b. Ion Exchange

37.3.3 Hydrogenation

In this chapter, enzymic hydrolysis of lactose is discussed in detail.

37.3.1 Enzyme process

The hydrolysis of lactose into glucose and galactose could be achieved by the application of lactose β -galactosidase enzyme. The enzymic hydrolysis of lactose may be catalysed by utilizing free enzyme or by immobilized enzyme, which permits the reuse of enzyme and Enzymic process allows use of milder conditions of temperature and pH. The immobilized and reactor enzymic processes are designed to allow effective reuse of the lactase, making the process continuous and cost effective. To date, only the single-use system and the immobilized system have been used commercially. The relative costs and benefits of these three processes depend very much on the processor's circumstances. Single-use systems are more likely to be economic in smaller operations, particularly when hydrolyzed products are not manufactured daily. Larger operations, manufacturing more regularly, would gain cost advantages by the use of an immobilized system. However, the cost of single-use enzymes is continuing to decrease, and this coupled with the comparative complexity and high costs of immobilized systems, is likely to make single-use systems even more attractive.

All the enzymic methods can be used to hydrolyse lactose solutions or permeate, but if there are

significant quantities of protein present as in whey, then only enzyme methods a and b may be employed. The enzyme reactor which is used to retain the enzyme would also retain proteins limiting its use to deproteinised solutions.

37.3.1.1 Free or single use enzyme

β -galactosidase is produced commercially from yeast, fungi and bacteria, *Aspergillus* and *Kluyveromyces spp.* being most common, as shown in Table 37.2. The source of the enzyme gives it its own unique properties and optimum growth conditions. In general, enzymes are only effective over a limited range of pH. Whilst it is possible to adjust the pH of whey or permeate to that of particular maximum activity of a given enzyme, this is costly and generally results in an increase in the ash content of end-product. Of the microorganisms listed in Table 37.2, lactase from only *Aspergillus oryzae* has sufficient activity to allow economic hydrolysis of whey and permeate at their normal pH values.

The source of enzyme affects its characteristics. Fungal enzymes, with acid pH and relatively high temperature optima, are especially suitable for hydrolysis of lactose in acid whey. Compared to bacterial and yeast enzymes, they do not require metal ions for their stability or activity. However, they are more strongly inhibited by D-galactose, thereby slowing the rate of conversion that can be achieved under practical conditions.

The yeast enzymes have neutral pH optima making them suitable for the hydrolysis of lactose in sweet whey. They are less stable than the fungal enzymes and can only be used at moderate temperatures. However, they are also less inhibited by the reaction products. It is likely that the bacterial enzyme from *E.coli* would not be permitted in food products due to possible toxicity factors associated with coliforms, unless it were available in a highly purified form.

Table 37.2 Properties of microbial lactases

Source	pH Optimum	pH stability	Temperature optimum (°C)	Co-factors needed
<i>Aspergillus niger</i>	3.0-4.0	2.5-8.0	55-60	None
<i>Aspergillus oryzae</i>	5.0	3.5-8.0	50-55	None
<i>Kluyveromyces fragilis</i>	6.6	6.5-7.5	37	Mn ²⁺ , K ⁺
<i>Kluyveromyces lactis</i>	6.9-7.3	7.0-7.5	35	Mn ²⁺ , Na ⁺
<i>Escherichia coli</i>	7.2	6.0-8.0	40	Na ⁺ , K ⁺
<i>Lactobacillus thermophilus</i>	6.2	-	55	-
<i>Leuconostoc citrovorum</i>	6.5	-	60	None

The attraction of using free enzyme is its simplicity of operation and that a suitable enzyme may be found to process any lactose containing stream, whether it be whey or permeate. The main drawback is that the enzyme is lost into the product, which firstly means that it could affect the properties of the product and secondly it has to be replaced, so resulting in a high running cost.

In practice, the enzyme is added directly to the reactor in such an amount as to obtain the required degree of hydrolysis within the given holding period. When a longer time is allowed for hydrolysis, the operating temperature will have to be kept low to prevent other undesirable reactions taking place, whereas when using a shorter time for hydrolysis, a higher operating temperature could be used. Since the activity of the enzyme will increase with temperature, there may not be a significant saving in enzymes by carrying out the hydrolysis over a long period. Also as the hydrolysis time is increased, the volume of the reactors will also have to be made larger, although in practice the reactor may be nothing more complex than an agitated silo. Since the reaction is inhibited by the D-galactose formed, attempts to reduce the reactor size by processing concentrated whey are restricted by the increased running costs due to higher quantity of enzyme required to overcome the inhibition.

An alternative approach is to use a continuous stirred reactor, in which feed and enzyme are continuously added to the reactor, and the hydrolysed product (containing some of the enzyme) is continuously removed. Such a system has the advantage of allowing reductions in reactor size, but is less cost effective in enzyme use than a batch reactor. Batch processing of hydrolysis is widely used in the dairy industry for the production of hydrolysed milk, whey and permeate. A number of factories regularly utilize this technology for the manufacture of syrups from whey or permeate, or for in-house use in products such as yoghurt or ice cream. However, such applications may be limited by the ash content of the product.

The commercial attraction of the single-use process lies in its simplicity and flexibility, both in enzyme selection and in operating conditions. The major drawbacks are the cost, and the fact that the enzyme is lost in the product. Although the activity of the enzyme is normally destroyed by pasteurization of the product, its presence, even in a denatured form, may create functional, legal and marketing problems.

37.3.1.2 Immobilized enzyme

In order to overcome the problem described with the use of free enzymes, immobilization techniques have been employed to fix the enzyme to an inert support. The immobilization procedures employed include adsorption, entrapment and covalent linkage.

Some of the enzyme/support systems proposed in the literature for immobilization of lactase are shown in the Table 37.3. In general, supports which are likely to be useful in commercial operations should be of a significantly higher or lower density than the substrate, should have a very even particle size, and should be resistant to degradation by operating temperatures, pH values and cleaning regimes. They should not support microbial growth, and should be safe for use in food processing operations. Particle size in particular is important, in fixed bed operation; a too small particle size may lead to the development of high back pressures, and severe packing of the bed, resulting in inefficient contact of enzyme with substrate. In fluidized bed systems, a too small particle size reduces the terminal velocity of the particles in the system, and, therefore, limits the average upward velocity in the reactor. This in turn limits the minimum holding time possible with particular

designs of fluidized bed. Clearly, the selection of support particle size and its density are key factors if a system is to be commercially successful. It should be noted that the activity/pH profile of lactases is usually modified as a result of immobilization.

Table 37.3 Supports employed for the immobilization of lactose

Supports	Source of lactase			
	<i>A.niger</i>	<i>E.coli</i>	<i>K.lactis</i>	<i>K.fragilis</i>
Agar gel		×		
Alumina	×			
Carbon	×			
Cellulose	×	×	×	
Chitin	×			
Chitosan	×			
Collagen	×		×	
Feather Protein	×			
Glass Beads	×	×	×	×
Ion Exchange Resin	×			×
Iron Oxide		×		
Nickel	×			
Nylon	×	×		
Phenol Formaldehyde Resin	×			
Polyacrylamide	×	×	×	
Polyacrylate		×		
Polyisocyanate		×		
Polyvinylpyrrolidene	×			
Sephadex		×	×	
Silk Fibroin				
Stainless Steel	×			

A number of immobilized enzyme systems are now commercially available e.g. Valio systems, Corning glass works and Amerace in USA, Rhone Poulenc in France, Sumitomo Chemical Co Ltd in Japan etc. Corning Glass works are exploiting their technology through the formation of joint companies with producers of whey, e.g. Specialist Dairy Ingredients with the Milk Marketing Board of England and Wales, Thames Ditton, Surrey, England; Nutrisearch with Kroger Foods; Corvire with U.L.N.

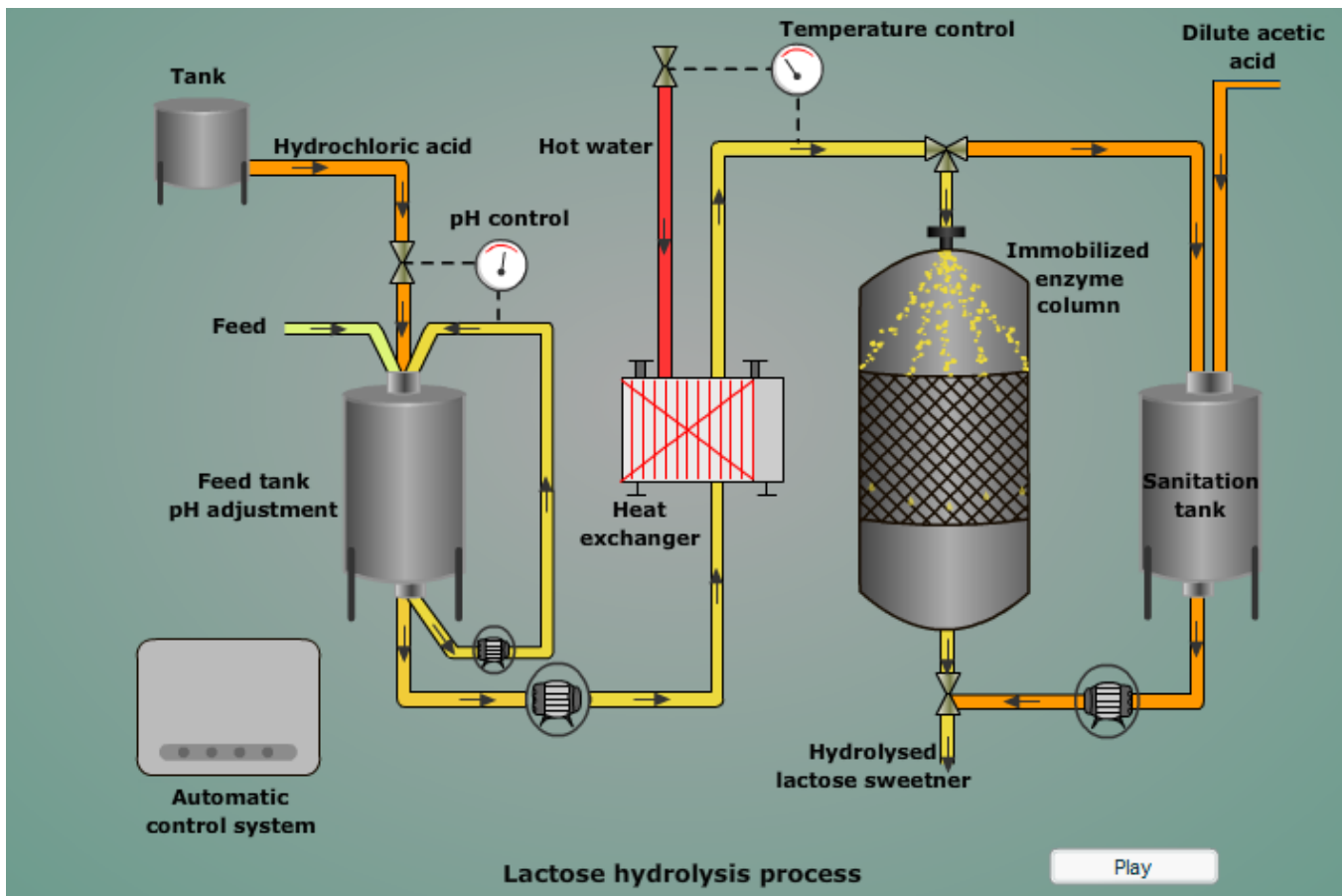
a) Valio system

The historical development of the Valio Hydrolysis Process for hydrolysing lactose in whey using enzyme from *Aspergillus niger* has been described by Heikonen *et al.* (1985). The system operates at a pH of about 4, and a temperature of 40°C. It cannot be used for the treatment of products of neutral pH such as milk or sweet whey (without pH adjustment). The concentrated hydrolysed product can be used in fruit yoghurts, ice cream, whey drinks and confectionery.

b) Corning system

The Corning system employs lactase from *Aspergillus oryzae*, which is covalently bonded to glass beads using a silane-glutaraldehyde coupling. Details of the Corning scheme are shown in Fig. 37.2. The pH of the raw whey is adjusted to the operating level of 4.5. The whey is pasteurized and then clarified to remove any fines which could block the column. The operating temperature of the column is gradually increased as the activity of the enzyme declines so that a constant degree of hydrolysis may be achieved. In order to prevent any bacteriological problems, the column is cleared once in every 24 hours. The cleaning procedure is designed to take 4 hours and includes a cleaning and sanitation procedure.

The hydrolysis is carried out in a column filled with graphite granules upon which the lactose enzyme has been immobilized. Control of column pH as well as the enzyme activity is achieved by means of an electric charge across the column. Thus, not only is the necessity of adding chemicals to adjust the pH of the medium eliminated but also any loss in enzyme activity may be countered by adjusting the electric current flowing.



37.3.1.3 Reactor systems

Most reactor systems operate at or near the optimum temperature of the enzyme, generally in the range 30-40°C. The use of such temperatures for hydrolysis in a commercial operation, where running times of at least 6 h are desirable, means that considerable care must be taken in reactor

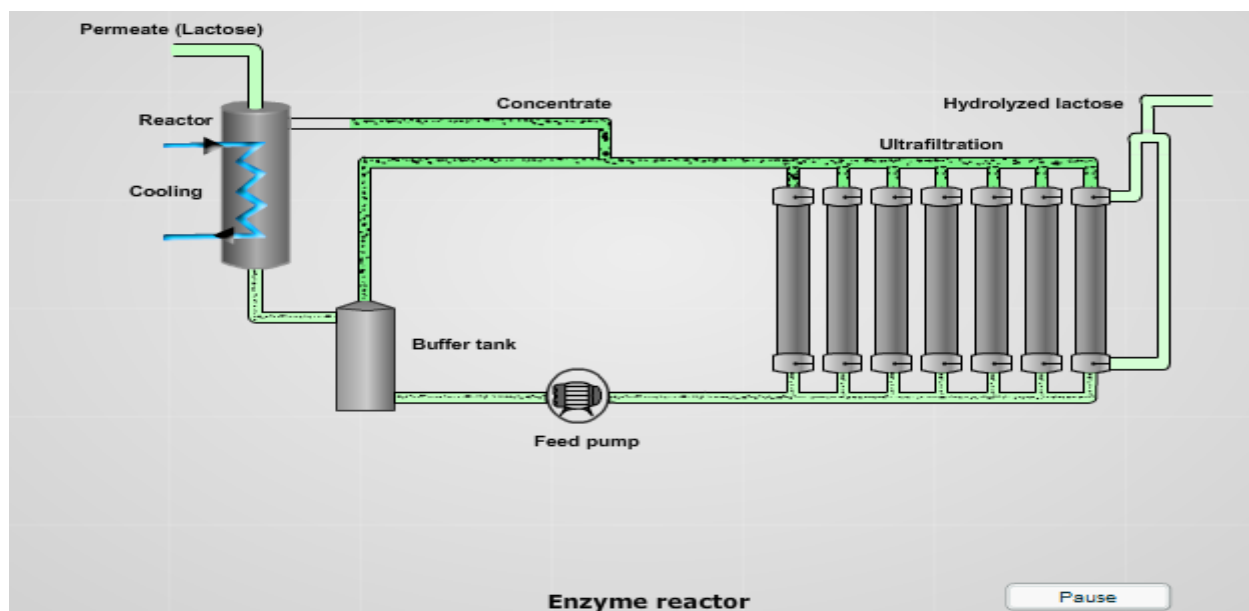
design to minimize opportunities for microbial growth. A second area of concern is sanitation of the system after hydrolysis. The enzyme systems currently employed are highly sensitive to the commonly used high temperature and acid/alkali cleaning treatments.

a) *Reactor for immobilized enzyme systems*

In general, two types of reactor may be used for immobilized enzyme systems, either fixed bed or fluidized bed. In addition to these, a system where the enzyme is 'immobilized' or entrapped by the pressure difference between the lumen and the cartridge of a UF system has been suggested.

b) *Reactor for enzyme recovery*

The comparatively high costs of single-use enzymes and their presence albeit inactivated in the end-product have led to interest in the development of a reactor system utilizing membrane processing for enzyme recovery and reuse. These systems utilize ultrafiltration membranes to allow the low molecular weight lactose, and the reaction products, glucose and galactose, to pass through the membrane, whilst retaining the comparatively high molecular weight enzyme. Such system can then be utilized in a feed/bleed mode, so that, in a steady state operation, there is no change in the composition of the permeate. It could either be operated continuously or batchwise. The Process is shown in Fig.37.3. The product, hydrolysed lactose, passes through the membrane whilst the enzyme is retained. Unlike the two other enzyme systems previously described, the use of an ultrafiltration plant to retain the enzyme means that the system is only applicable to deproteinized streams.

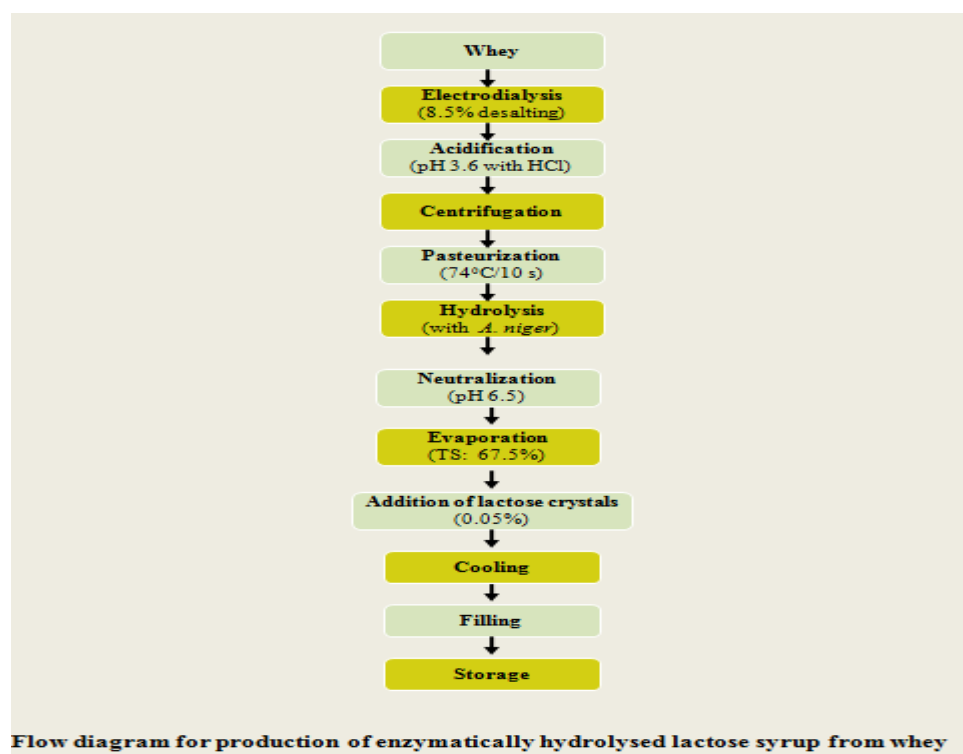


Whilst in principle it would be possible to utilize this technology for treatment of whey and milk, by ultrafiltration (UF) of the substrate, hydrolysis of resulting permeate in the reactor and addition of the hydrolysed stream back to the retentate from the initial ultrafiltration (Norman *et al.*, 1978), the complexity and cost of such operations are likely to make them commercially uneconomical.

It is difficult to imagine that the recovery of the expensive enzyme using a relatively expensive extraction system will make economic sense, although one study shows that it would be feasible. Norman *et al.* (1978) also describe a system using two ultrafiltration plants to produce low lactose milk. The first U.F. plant removes the milk proteins, the permeate is hydrolysed in the UF. enzyme reactor and then the hydrolysed permeate is recombined with the milk protein concentrate.

37.3.1.4 Hydrolysis of Lactose in Milk, Whey and Whey Permeate

A report from the USA (Anon 1982) describes a process for the hydrolysis of cheese whey, using immobilized enzymes of fungal origin (β -galactosidase) producing products combining the functional and nutritional properties of whey proteins with the sweetening power of glucose/galactose syrup. The β -galactosidase can be used to hydrolyze lactose in milk, whey and whey permeate. The selection of process technology depends upon the type and nature of substrate, characteristics of enzyme and economics of production, storage and marketing. β -galactosidases can be used as free or single use enzyme or immobilized enzyme. An enzymatic process scheme for the manufacture of hydrolysed lactose syrup from whey has been presented in Fig.37.4. Normally the whey obtained from cheese/*paneer*/casein making is desalted by employing electro dialysis technique and then the pH is brought down to normally 3.6 with hydrochloric acid. The acidified whey is centrifuged and pasteurized. Whey hydrolysis of lactose is performed by application of β -galactosidase enzymes obtained from any microbial source. The content is partially concentrated (about 67.5% TS) after neutralization to pH 6.5. After lactose seeding, the content is cooled and packaged which is ready for marketing.



37.3.2 Acid process

Lactose hydrolysis can be carried out very effectively and economically under conditions of low pH and high temperatures. Clearly, this procedure is of value for protein-free streams such as permeates or deproteinized whey. The adjustment of pH can be made either by direct addition of acid to the system, or by treatment of the product with a cation exchange resin.

Homogenous or single-phase hydrolysis uses hydrogen ions in solution, with a defined heat treatment (ranging from about 60°C for 24 h to 140°C for 11 min at a pH of about 1.2). These hydrogen ions can be provided either by addition of mineral acids, or by treatment of the stream with a cation exchange resin. *Heterogeneous or two-phase hydrolysis* utilizes hydrogen ions bound to a cation exchange resin to catalyse the reaction. In such processes the demineralized product is passed at 90-98°C through a bed of cation exchange resin in the hydrogen form with a residence time of about 80 min. Significant cost benefits are claimed by this process. The products typically are brown, and may require neutralization, demineralization and decolourisation before use.

37.3.2.1 Direct acidification

In this process, significant lactose hydrolysis occurs at a temperature less than 100°C, the pH of the solution must be less than 1.0. Therefore, it would be necessary to use mineral acid such as hydrochloric acid in order to acidify the solution.

37.3.2.2 Ion exchange hydrolysis

Boer & Robbertson (1981) have described in detail a homogeneous system for hydrolysis of permeate in 3 schemes when an ion exchange system has been used to catalyse the hydrolysis reaction.

Scheme 1: Cation → Cation Hydrolysis → Decolorizer → Anion

Scheme 2: Cation → Anion → Cation Hydrolysis → Decolorizer

Scheme 3: Cation → Heat Exchanger → Decolorizer → Anion

In scheme 1, the pH of concentrated ultrafiltration (UF) permeate of about 10% total solids was brought to 1.2 by use of a strong acid cation exchange resin.

In Scheme 2, since the solution is already at a low pH as a result of the cation column, the hydrolysis column operates more efficiently than the same column in Scheme 2. However, in Scheme 2 because the anion column has removed the nitrogen compounds the degree of coloration is much lower so that there is less colour to remove in the decolorizing column.

In Scheme 3, the heat exchanger raises the temperature of the liquor to 150°C in order for hydrolysis to occur. 80% degree of hydrolysis was reached on treatment of the liquid at 150°C for 3 min. As a result of this high operating temperature, some 50-60°C higher than that employed in Schemes 1 and

2, the necessary decolorizing is much more difficult. A brown colour was formed in the product, the level of which depended in part on the non-protein nitrogen content of the permeate. Purification of the product took place in a weak anion resin, followed by a second pass through both resins. Best results were obtained when adsorbing anion resins were used, which not only removed salts, but also the colour. Final purification took place with 0.1% activated charcoal, after concentration to 62% total solids. The final syrup contained, besides carbohydrates, 0.1% ash and 0.024% nitrogen.

Whilst both homogeneous and heterogeneous systems have been studied on a semi-commercial scale, there appears to have been no commercial adoption of these processes. Commercialization of these processes must have been inhibited by the fact they are restricted to be used with permeate, and the comparative higher cost of the product compared to its main competitors, sucrose and corn syrup product.

37.3.3 Hydrogenation

The possibility of using hydrogen gas in the presence of a nickel catalyst for hydrolysis has been mentioned in U.S. patent No. 2,642,462, but it is likely that control of product composition would be difficult. Furthermore, processing conditions may well be in excess of 100°C, restricting the substrate to permeate or lactose solutions.

***** 😊 *****

Lesson 38
APPLICATIONS OF HYDROLYSED LACTOSE

38.1 Introduction

To be commercially viable, lactose-hydrolysed products must offer the food manufacturer commercial advantages over competitive products. These advantages must either provide direct benefits to the consumer (such as the ability to be tolerated by lactose malabsorbers) or commercial benefits to the manufacturer (with functional or economic advantages bestowed on the product through the incorporation of lactose-hydrolysed products). Clearly the major benefits of hydrolysed whey and permeate relate to their ability to replace costly sucrose.

38.2 Applications of Lactose Hydrolysed Whey

Lactose hydrolysed whey can be utilized in various products including ice cream.

38.2.1 Confectionery

Partially demineralized lactose hydrolysed whey syrup can easily replace skimmed sweetened condensed milk (well known ingredient in the manufacture of caramels) because of their very similar composition, when compared (Table 38.1). Lactose hydrolysed whey syrups can replace 100% of the condensed milk in an enrobed fudges and caramel and is deposited soft caramel in chocolate shells (for toffee and hard caramel modification of the recipe is done). The benefits of hydrolysed lactose for the replacement of sweetened condensed milk in caramels are: an increase in chewiness due to the presence of whey proteins, reduced crystallization of lactose due to the inhibiting effect of the glucose and galactose, and a darker colour and improved flavour.

Hydrolysed permeate (or lactose) syrups may be regarded as equivalent to a 63 D.E. glucose syrup and as such may be substituted in recipes employing glucose syrup. e.g.

Pectin jellies: 100% replacement of glucose syrup entirely satisfactory.

Fudge: 50% replacement of glucose syrup entirely satisfactory

Fondant creams: 50% replacement of glucose syrup satisfactory but off flavour development occurred with prolonged storage.

Boiled sweets: 50% replacement of glucose syrup unsatisfactory because of rapid coloration during boiling.

Table 38.1 Comparison of Partially demineralised hydrolysed whey syrup with skimmed sweetened condensed milk

Analysis	50% Demineralized and hydrolysed whey syrup (80%) (%)	Skimmed sweetened condensed milk (%)
T.S	72.0	72.0
Protein	11.0	10.0
Lactose	11.5	14.3
Glucose	23.0	-
Galactose	23.0	-
Sucrose	-	46.1
Ash	3.0	2.3
Fat	1.0	0.3

Lactose hydrolysed whey, without or with partial demineralization or in a dried form, is used in chewing gum to at least partially replace the soluble sweetener, emulsifier and plasticizer components of conventional formulations. The inclusion of hydrolysed whey results in a softer gum which is not sticky. It is also advantageous in an athlete's gum which promotes salivation. There are also cost benefits.

38.2.2 Ice cream and mousse

The incorporation of hydrolysed lactose into ice cream would replace the di- and polysaccharides in the mix by monosaccharides which will result in an ice cream which has a lower freezing point and produce a somewhat softer texture, which may be considered as a market advantage for certain application. It is possible to produce a "soft scoop" ice cream without the use of a freezing point depressant such as glycerol. The mix that scored the highest in creaminess, smoothness and fullness of flavor contained 15% SNF, supplied by a 1:1 blend of skim milk and whey protein concentrate, and 75% hydrolyzed lactose syrup.

The potential for incorporation of hydrolysed products into ice creams will depends to some extent on the particular legislation controlling minimum ice cream composition within a particular country. When using hydrolysed whey, it will also be necessary to re-balance the sugar composition in order to maintain a similar sweetness level as the original. In general, the use of hydrolysed milks to replace added sucrose results in decreasing the total solids of the product. In some cases the reduced level of solids may be below that required by legislation, thereby negating the benefits of using hydrolysed products.

38.2.3 Whey drinks

In whey beverages, hydrolysis of lactose avoids problems of proteins precipitation as well as lactose intolerance. Whey drinks as a mixture of tropical fruit juices, hydrolysed lactose and whey protein concentrate have been prepared. These drinks use the sweetening power of the glucose and galactose but at the same time gain the advantage of having the presence of whey proteins, which have a high nutritional value. A range of similar products may be produced using different fruit juices such as orange, lemon, apple, etc.

38.2.4 Bakery

Hydrolysed whey syrup can be used to replace up to 30% of the egg (on solids basis) in Sponge cake and Madeira cake according to recipes published by Specialist Dairy Ingredients. Hydrolysed whey syrup could also be used to replace a part of the milk powder in the recipes. It is suggested that up to 50% replacement could be achieved.

Lactose hydrolysed whey can lead to faster dough development and higher loaf volume, porosity and crumb compressibility, all due to more readily fermentable sugar. Browning in baked products is also enhanced due to presence of the highly reactive galactose. Use of hydrolyzed lactose syrup (50, 75, 95%) from whey permeate as sugar substitute in milk bread formulation with or without demineralization were decolorized and concentrated to 50 per cent solids to give hydrolyzed lactose syrup (HLS). These were added to bread mix at 6% of the flour content. Bread made from 95% HLS (demineralized) was comparable with control bread pH, volume, texture and flavour.

The high content of sugars which are readily fermentable by yeast and can take part in melanoidin reactions makes the syrup suitable for use as sweetener in the bakery industry. Addition of 3.9-4.1 percent lactose syrup significantly improved the physio-chemical and organoleptic properties of wheat bread. They yielded even better results in thin and thick dough sponges. Hydrolysed lactose whey is also used in the manufacture of biscuits.

38.2.5 Jams

Hydrolysed permeate syrups has been used to replace up to 50% of the glucose syrup in jam manufacture. The products were satisfactory but whilst full decoloration of the syrup was not required, it was necessary to minimize the mineral level in the syrup.

38.2.6 Meat products

Extenders for fermented sausage products incorporating lactose-hydrolysed whey or permeate have been described. As extenders, lactose-hydrolysed products are equivalent to, but less expensive than products such as skim milk powder. The suggested level of incorporation is 3.5% of the mix, with 70% of the lactose hydrolysed. The use of hydrolysed whey products in comminuted meats has also described.

38.2.7 Animal feeds

Both hydrolysed permeate and hydrolysed whey have been employed in animal feeds. Work carried out in Finland on pig feeding indicated a higher efficiency of utilization in comparison to ordinary whey.

39.2.8 Other Uses

A wide variety of different other products have been suggested when hydrolysed whey or permeate could be used. Some of these are given in Table 38.2.

Table 38.2 Other uses for hydrolysed whey and lactose (or permeate)

S.No	Hydrolysed Whey	Hydrolysed Lactose
1.	Imitation Maple Syrup	Beer
2.	Honey Substitute	Tinned Fruit
3.	Biscuit Fillings	Yogurts
4.	Chocolate Nut Spread	Puddings
5.	Salami	Wine making
6.	Liver Sausage	Fermentation Feedstock

***** 😊 *****

Lesson 39

FUNCTIONAL PROPERTIES OF WHEY PROTEINS

39.1 Introduction

The general behavior of whey proteins indicate that they are highly soluble over a wide range of pH, especially acid pH, able to produce firm gels on heating, exhibit good fat and water binding properties, especially on denaturation and good aerating agents. Whey proteins play an important role in controlling the texture of many food products. In this respect, the rheological and gelling behaviour of whey protein are important. A brief overview of some of the important functional characteristics of whey proteins is included here.

39.2 Solubility

Whey proteins are unique among the milk proteins used in food applications since in their native conformation they are soluble at low ionic strength over the entire pH range required for food applications. Solubility is an important functional property of WPCs; complete solubility of the proteins is a requisite for optimum functionality in foams, emulsions, beverages, and similar applications. Macromolecules are not soluble in the same manner as small molecules are. However, the amino acid side chains in the proteins can interact with water and proteins can be suspended in water. This property is often used as an indicator of whey denaturation. Protein solubility is a function of temperature, pH, presence of other ions, and the values obtained for solubility are highly dependent on the methods used to achieve the solubility. Proteins are least soluble at the isoelectric point but whey proteins are soluble over a wide range of pH values. This property of whey proteins makes it desirable for use in beverages.

In some cases, whey proteins may be soluble in a non-aggregated state, so that they can thoroughly mix with the other ingredients of formulation or orient at the interface of emulsions or foams. In order to accomplish this in food systems throughout the pH range of 3 to 8 and in the presence of calcium ions, it is essential that proteins be in undenatured state, otherwise they will aggregate and precipitate when incorporated into such food systems and fail to provide adequate functionality. However, being globular proteins, their solubility decreases at high salt concentrations due to salting out and they are susceptible to thermal denaturation at temperature $> 70^{\circ}\text{C}$. Solubility at pH 4.6 is widely used as an index of the extent of denaturation caused by processing and storage of protein-rich whey products. The level of denaturation and subsequent insolubility at pH 4.6 depends on heating temperature and time, whey pH and ionic calcium concentration. Whey ingredients have good dispersibility, Instantized forms of WPC and WPI are available for applications that require whey ingredients to dissolve quickly and without an excessive amount of agitation.

39.3 Hydration/Water Binding Properties

Bound water is defined as the water retained by protein containing slurries following filtration or application of either mild pressure or centrifugal force. Water binding or hydration is defined as the g of water associated with or occluded by 1 g dry protein. Hydration values determined for individual native whey proteins range from 0.32 to 0.60 g H₂O/g, depending on the assay method used. Water binding is especially important when whey proteins are used in viscous food products viz. beverages soups, sausages and custards. Moreover, the water binding and associated properties (i. e. swelling, gelation and viscosity) of proteins are the major determinants of texture in a number of food products. However, when whey protein solutions of sufficient protein content and suitable solution conditions (pH, ions, etc.) are heated, gels are formed and the water holding capacity of such gels make significant contributions to the texture and rheology of a number of processed foods. Heat denatured whey protein (lactalbumin) absorbs more water than undenatured whey protein. Practical uses of whey protein concentrates, in which water-protein interactions are utilized include yoghurt drinks, hard pack ice cream, low fat ice cream, non fat ice cream, and soft serve ice cream, yoghurt, sour cream, and coffee whiteners. In cheese sauces, low fat cream soups, creamy salad dressings, refrigerated pasta and orange marmalade, viscosity and the ability of whey proteins to bind water are useful.

39.4 Viscosity

Viscosity which results from water-protein interactions have been discussed extensively by de Wit (1989). The relative viscosity of whey decreases between 30 and 65°C. Above 65°C, this relatively viscosity increases as a result of protein denaturation and above 85°C a further increase is observed as a consequence of protein aggregation. The viscosity of whey protein concentrates (WPC) in the range 25-39% TS depends strongly on the composition and pre-heat treatment of the whey due to the rate of crystallization of the lactose in the concentrate.

Due to their compact globular shapes, solutions of undenatured whey proteins are much less viscous than caseinate solutions. They exhibit minimum viscosity around the isoelectric point (pH 4.5) and relative to water, their viscosity decreases between 30 and 65°C, but increases thereafter owing to protein denaturation. Solutions of WPC containing 4-12% (w/v) protein were reported to exhibit Newtonian flow while at higher concentrations flow became more pseudoplastic.

39.5 Heat Gelation

Gelation is formation of three dimensional structures capable of entrapping sufficient water to produce gel. One worker defined gelation as a protein aggregation phenomenon in which polymer-polymer and polymer solvent interactions are so balanced that a tertiary network or matrix is formed. Whey proteins, in undenatured soluble form, as in WPC prepared by UF process, have ability to form heat induced irreversible gels at appropriate protein concentration, pH and ionic conditions. At about 5% concentration and above, whey proteins are able to produce firm gels on heating, Optimum gel strengths are formed between 10-15% protein concentration. Gel characteristics depend on the protein concentration, the pH of the solution, and the calcium and sodium ion concentration. The

process of gelation is a two-stage one involving: an initial denaturation or unfolding of a protein molecule followed by subsequent aggregation. Whey proteins form thermo-irreversible gels. Whey proteins form irreversible gels by restructuring into extended three-dimensional networks that have the capability to entrap fat and water. A strong gel network helps hold this water and prevents moisture loss, which assists in controlling syneresis. The gelation characteristics of whey protein systems can be improved by dialysis to remove interfering components and adding calcium salt just before heat. Heating whey proteins to temperatures above 70°C can cause denaturation and polymerization, resulting in gel formation. Heating skim milk with 0.5% added WPC's produce gelation.

39.6 Emulsification and Foaming Properties

Whey proteins have both hydrophilic and hydrophobic groups, which allow the proteins to adsorb and unfold rapidly at the oil-water interface and form a layer that stabilizes the oil droplets and prevents flocculation and/or coalescence. The hydrophilic sites of the whey protein molecule bind water while the hydrophobic sites encapsulate the fat, resulting in stabilization of the system. Whey protein adsorb at the interfaces at a slower rate than other proteins like β -casein. Factors affecting whey protein emulsions include pH and ionic strength. Around their isoelectric point whey protein form poor unstable emulsions. If the milk used for cheese making is pasteurized or if the whey resulting from the cheese making is pasteurized the emulsification properties of the whey proteins are not adversely affected. Pasteurization of the retentate greatly diminished the emulsion capacity of the proteins.

Whey proteins do help in emulsification in infant formula, meal replacement beverages, soups and gravies and coffee whiteners. They are used in conjunction with low molecular weight emulsifier. Whey protein-enriched products are widely used in foaming applications in foods and factors such as protein concentration, level of denaturation, ionic environment, pre-heat treatment and the presence of lipids all influence whipping properties. Whey proteins have low emulsion capacities than casein. A number of compositional and processing conditions such as pH, redox potential, heat denaturation, enzymic hydrolysis, polyphosphate, residual lipids, phospholipids, sodium lauryl sulphate affect foaming properties. This is may be due to the inherent hydrophobic-hydrophilic nature of the amino acid side chains, which the whey protein molecules orient to the air liquid interface. Heating increases the foaming properties because heat unfolds protein molecules, to expose buried and alter their effective hydrophobic-hydrophilic balance.

***** 😊 *****

Lesson 40

FUNCTIONAL PROPERTIES OF CASEIN PRODUCTS

40.1 Introduction

The term functionality as applied to food ingredients, is defined as any property, other than nutritional attributes, that influences ingredients usefulness in food. The functional properties of proteins are those physico-chemical properties that enable proteins to contribute to the desirable characteristic of food. Besides providing nutritional value, casein preparations are used in food system due to their various functional properties. (Table 40.1) The hydrophobicity (due to aliphatic and aromatic side chains) and open, amphipathic structure (due to high content of proline) of the caseins are very significant in deciding the functional properties like viscosity, gelation, swelling, foaming and emulsification and are of great technological significance. Caseins are good film-formers and find use in whipping and foaming applications, and in emulsions of fats or oils. Sodium caseinate is more effective as an emulsifier, thickener and foaming agent than calcium caseinate and absorbs water more effectively in wheat flour system. Important functional properties of casein and casein products are discussed in detail in this lesson.

40.2 Water Absorption/Moisture Binding Properties

Casein micelles bind large amount of (2-4 g/g protein) water as compared to globular protein (50 g/100 g of protein). This is due to the mechanical entrapment of water in the micellar matrix (*via* colloidal calcium phosphate). The *k*-casein 'hairs' (having carbohydrate moiety) that protrude from the surface of the micelles also contribute to the large amount of water associated with the micelles. So casein 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. Ability of caseinates to bind moisture through hydrogen bonding and entrapment has also been advantageous in meats and sausages. This property can be modified by heat treatment and by ionic environment. For example, syneresis of yoghurt is prevented by a high heat treatment. Replacing calcium ions by sodium, increases moisture binding properties of caseins.

Table 40.1 Functional role of food proteins in food system

FUNCTION	MECHANISM	FOOD SYSTEM
Solubility	Hydrophilicity	Beverages
Water binding	H-bonding, ion hydration	Meat sausages, cakes, breads
Viscosity	Water binding, hydrodynamic size, shape, thickening	Soups, gravies and salad dressing, desserts
Gelation	Water entrapment and immobilization, network formation, protein matrix formation & setting	Meats, gels, cakes, bakeries, cheese
Cohesion/adhesion	Hydrophobic, ionic and H-bonding	Meal, sausages, pasta, baked goods
Elasticity	Hydrophobic bonding, disulfide cross-links	Meats, bakery
Emulsification	Adsorption and film formation at interfaces	Sausages, bologna, soup, cakes, dressings
Foaming	Interfacial adsorption and film formation	Whipped toppings, ice cream, cakes, desserts
Fat & flavour binding	Hydrophobic bonding, entrapment	Simulated meats, bakery, low fat bakery products, doughnuts

Source: J.E. Kinsella, S. Damodaran, and J.B. German (1985)

40.3 Solubility

Solubility is an important functional property and is a pre-requisite for most other functionalities. A typical solubility-pH profile of casein shows that close to its isoelectric pH, i.e. pH 4.0-5.0, the acid casein is completely insoluble, while at pH values >5.5, it is converted to cationic salt (Na, K, and NH₃) and is solubilized. Caseinate solutions (10-15%) can be readily prepared at pH 6.6-7.0. Sodium and ammonium caseinates show better solubility and viscosity than calcium caseinates which is perhaps due to higher ionisation of the former caseinates. Calcium caseinate in water exists as large aggregates that are stable at pH more than 5.5. Casein is also soluble at <~pH 3.5 but the viscosity coefficient is higher at acid than at neutral pH values and gel like system is formed. Virtually all applications of casein products require them to be dissolved first.

Acid soluble caseins may be produced by enzymatic or chemical modification. High calcium co-precipitates and rennet caseins are very insoluble in water because of their high calcium content, and it is necessary to use calcium sequestering agents (citrate or polyphosphate) to solubilize them. Higher pH above 9.0 also increases the solubility of rennet casein.

40.4 Viscosity

High solution viscosity of casein is a result of the very open, nearly random structures of casein molecules. Sodium caseinate finds application in products where high viscosity is required. Caseinates from highly viscous solution at concentration greater than 15% and even at high temperatures containing greater than 20% protein is so high as to make them difficult to process. The viscosity of sodium caseinate is logarithmically related to concentration, while there is a linear relationship between log viscosity and the reciprocal of absolute temperature. The viscosities of casein solutions differ, not only with different caseins, but with the concentration, cation present, pH value, temperature and the age of the solutions. The viscosity of sodium caseinate is strongly dependent on pH, with a minimum at about pH 7.0. The viscosity of casein is much higher at low pH (2.5-3.5) than at neutral pH, gel-like structures are formed at >5% protein at temperatures <40°C. For many food applications, high viscosity is advantageous. Sodium caseinate finds application in products where high viscosity is required. High solution viscosity of casein is a result of the very open, nearly random structures of casein molecules. The lack of solubility in the presence of calcium changes the behaviour of casein. As calcium is added to a solution of sodium caseinate, a number of changes are evident. The calcium causes aggregation of casein into structures that resemble micelles. As these aggregates increase in size and number, the viscosity of the solution decreases. The solution also becomes turbid as the particles become large enough to scatter light. Calcium caseinate is selected when a solution of relatively low viscosity and high turbidity (milky appearance) is desired.

Limited proteolysis by indigenous milk proteinase reduces the viscosity of caseinate solutions and may explain the low viscosity of caseinates produced from late lactation milk, which has a high level of indigenous proteinase. The viscosity of caseinates can also be reduced by treatment with disulphide-reducing and/ or sulphhydryl blocking agents.

40.5 Gelation and Coagulation

Gels are systems in which a small proportion of solid is dispersed in a relatively large proportion of liquid but which have the property of mechanical rigidity or the ability to support shearing stress at rest properties of solids. Gelation or coagulation occurs when milk is subjected to limited proteolysis by acid proteinases, e.g. rennets, which hydrolyse the micelle-stabilizing κ -casein, producing para- κ -casein-containing micelles, which coagulate at the concentration of Ca^{2+} in the milk serum. This phenomenon forms the basis for the manufacture of rennet casein and most cheese varieties. Gel-like structures are formed at > 5% protein at temperatures < 40°C, which may be exploited in the preparation of milk protein-containing fruit gels.

Concentrated Ca-caseinate dispersions (> 15% protein) gel on heating to 50-60°C. Gelation temperature increases with protein concentration from 15 to 20% and with pH in the range 5.2-6.0. The gel liquefies slowly on cooling but reforms on heating; calcium caseinate is the only milk protein system reported to exhibit reversible thermal gelation properties.

40.6 Melting Properties

Casein also exhibits melting properties that are unique among proteins. Following limited proteolysis, casein will become thermoplastic and will flow upon heating. A similar effect can be achieved by chelating of some of the calcium ions present. These phenomena are the basis for the melting of natural cheeses and the production of process or imitation process cheese. Structure must exist before a substance can be said to melt. With caseins, this structure may be obtained by precipitation with calcium, acid or the addition of rennin. Casein does not form thermal gels and has little functionality in applications that require temperature set. High heat stability and the ability to melt are the two properties of caseinates that make them difficult to replace in many food applications. The demand for casein for products like cheese analogues (Processed cheese, Mozzarella cheese) depends on the formation of a protein matrix from calcium caseinate which will undergo thermo melting similar to its processed cheese counterpart.

40.7 Surface Active Properties

The surface activity of proteins is important in number of functional applications (film-formation, foaming and emulsification). These applications require the formation of continuous cohesive films at surface interphase. This event of film formation (diffusion, adsorption, spreading and partial unfolding) is influenced by the inherent structural characteristics of protein e.g. composition, conformation, molecular flexibility and extrinsic factor e.g. pH, temperature, protein concentration, type of ion species etc. The caseins due to their small size migrate quickly to air/water or oil/water interfaces and their open conformations allow them to spread readily at interfaces. The amphipathic structure of caseins facilitates orientation of the hydrophobic residues into the air or oil phases with the hydrophilic residues in the aqueous phase, thus exhibiting their surfactant properties. Sodium caseinate is a more effective interfacial tension depressor than whey protein, blood plasma, gelatin or soy protein; it diffuses more quickly to an interface and on reaching the interface adsorbs more quickly than the other proteins, probably because of direct and rapid anchoring of freely-available hydrophobic segments.

The surface activity of whole and individual caseins may be modified enzymatically.

Dephosphorylation or treatment of sodium caseinate with plasmin (to produce γ -caseins and proteose peptones) greatly increases its surface activity.

40.8 Whipping/Foaming Ability

Caseinates generally give higher foam overruns, but produce less stable foams than egg white or whey protein concentrates. The excellent surfactant property of the amphiphilic casein is also responsible for its use in whipped toppings, cake mixes, and ice-cream.

40.9 Emulsion Properties

The emulsifying power of a protein is its capacity to stabilise oil-water or water-oil emulsion with minimum concentration under specified conditions. This power is mainly due to numerous surface hydrophobic (due to polar amino acids) sites which promote a greater affinity of protein for the oil

phase. Casein forms complexes with milk fats and other lipids and acts as emulsifier by forming a stable coating around fat globules. Due to emulsifying properties, casein is also used in paint industry. In general, milk protein products, especially caseinates, are very good fat emulsifiers and are widely used in emulsifying applications in foods. Na-caseinate containing emulsions are resistant to heat shock of pasteurization, have an increased freeze-thaw tolerance, and remain unharmed during spray drying treatment.

***** 😊 *****



AGRIMOON.COM

All About Agriculture...

Lesson 41

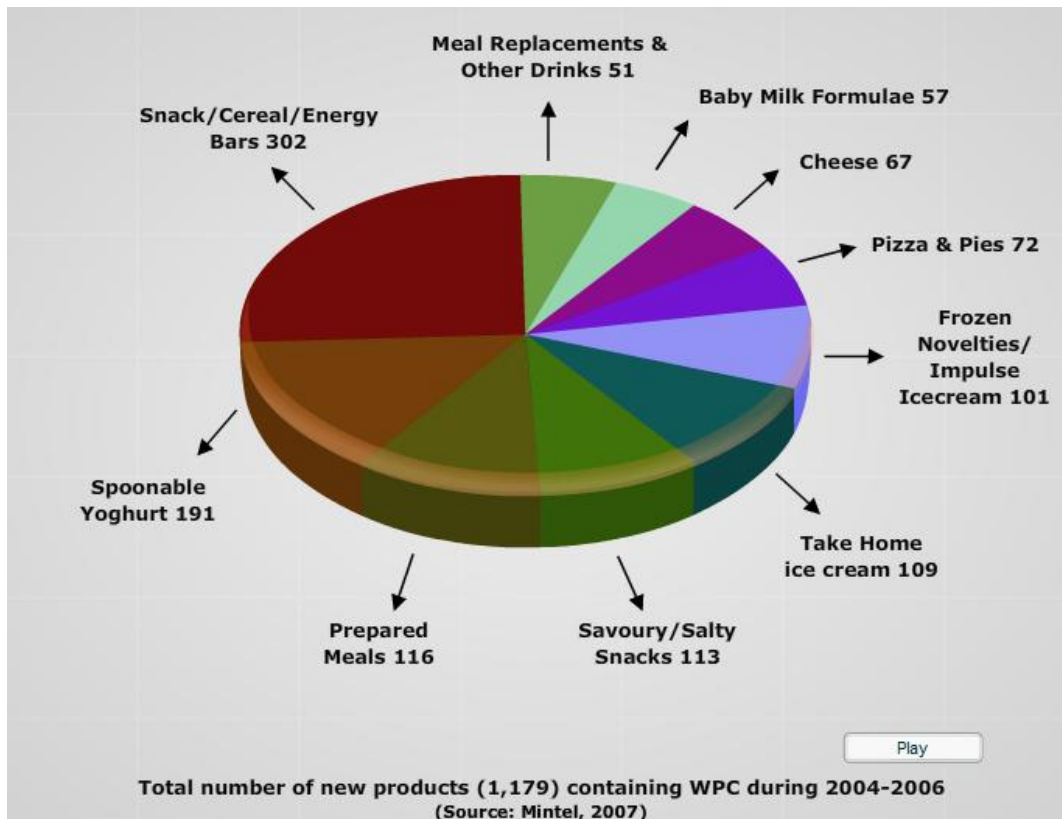
FOOD APPLICATION OF MILK PROTEIN PRODUCTS-1

41.1 Introduction

The utilization of milk protein products as food ingredients is dependent on their physico-chemical and functional properties. Milk protein products are used for food application because of their unique properties that 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. Sodium caseinate has very good water binding and whipping properties and is announced by FAO and WHO as unrestricted food additive. The two main reasons for using sodium caseinate as an ingredient in foods are its functional properties and nutritive value. Industries of meat processing, baking and modified dairy products are the largest consumer of sodium caseinate. Other casein products, used in a descending order in the food industry are calcium caseinate, potassium caseinate, other caseinates and finally pure casein. One another form of casein that is commonly used in the food and pharmaceutical industry is its hydrolysates. Protein hydrolysates can be used in products depending upon the functional properties which are influenced by the raw material used; process employed; extension of hydrolysis and conditions of hydrolysis. Accordingly, protein hydrolysates can be used in foodstuffs, noodles, cheeses, bacterial assay media and as a food for persons who are allergic to milk proteins. Milk protein hydrolysates also have pharmaceutical applications.

Soluble whey protein concentrates have been found to be technically suited to a wide range of products, but its use is not cost effective in all cases. Presently, whey protein concentrates constitutes a very small proportion (10%) of protein utilization in food industry. The largest potential use of whey protein concentrates is as a replacement for non-fat dry milk (NFDM) in the food industry. Whey protein concentrates with 35% protein is perceived to be a universal substitute for NFDM, because of the similarity in gross composition and its dairy character. Superiority of whey protein concentrate over NFDM is also due to cost advantage. Whey protein concentrates of 34% protein is commonly used as a stabilizer in yogurt, bakery mixes, dietetic foods, infant foods, and confections because of its water binding, fat-like mouth-feel and gelation property. Whey protein concentrates of 50% or 80% protein offers distinct functional attributes. It is especially suited for use in nutritional drinks, soups, bakery, meat, dietary foods, and protein fortified beverages. It gives clear suspensions over a wide pH range and has a bland flavor. Some applications require undenatured ingredients to maximize water-binding capacity during food processing. It is also available in gel-forming version. During 2004-2006, number of new products produced from WPC is shown in Fig.41.1.

Milk protein products are used in different food products including bakery, confectionery, dairy, beverages, dietary, and meat, textured, pharmaceutical and medical application. In this lesson food applications of milk protein products in dairy, bakery, confectionery and pasta are discussed in detail.



41.2 Application in Dairy Products

Milk protein products are widely used to supplement the protein content and therefore, enhance sensory characteristics of conventionally processed dairy products and are also used in the production of a range of imitation, low fat and non fat dairy products (Table 41.1).

Table 41.1 Applications of milk protein products in dairy-type products

A. Caseins/Caseinates/Co-precipitates	
<i>Used in</i>	<i>Effects</i>
Imitation cheeses (vegetable oil, caseins/caseinates, salts and water)	Fat and water binding, texture enhancing, melting properties, stringiness and shredding properties
Coffee creamers (vegetable fat, carbohydrate, sodium caseinate, stabilizers and emulsifiers)	Emulsifiers, whitener, gives body and texture, promotes resistance to feathering, sensory properties
Cultured milk products, e.g. , yoghurt	Increase gel firmness, reduces syneresis
Milk beverages, imitation milk, liquid milk fortification, milk shakes	Nutritional, emulsifier, foaming properties
High fat powders, shortening, whipped toppings and butter-like spread	Emulsifier, texture enhancing, sensory properties
B. Whey Proteins	
<i>Used in</i>	<i>Effects</i>
Yoghurt, Quarg, Ricotta cheese	Yield, nutritional, consistency, curd cohesiveness.
Cream cheeses, cream cheese spreads, sliceable/squeezable cheeses, cheese filling and dips	Emulsifier, gelling, sensory properties
C. Microparticulated Milk Proteins	
<i>Used in</i>	<i>Effects</i>
Low fat and/or non-fat milks, yoghurts, dairy spreads, natural and processed cheeses	Fat replacements, sensory properties

41.2.1 Use of casein products

Casein and co-precipitates are used in the preparation of imitation cheeses (cheese analogues), which are used in pizza, sauces, burgers, grilled sandwiches, macaroni and other dishes with a significant cost-saving compared to the use of natural cheese. The functional properties of caseins that favour their use in imitation cheese include fat and water binding, texture enhancing, melting properties, stringiness and shredding ability. Most of the edible rennet casein is used in the production of processed cheese and cheese analogues because it can significantly contribute to the structure and the functional properties of these products. In these processes, rennet casein is partially solubilised by the use of melting salts (calcium sequestering compounds) and its properties are tuned to the specific application.

Sodium caseinate is valued for its ability to emulsify fat in the production of modified dairy products such as coffee whiteners, high-fat powders, whipped cream and ice cream. Sodium caseinate is used in powdered coffee creamers, which also contain vegetable fat, a carbohydrate source and added emulsifier and stabilizers. These creamers are cheaper, have a longer shelf life and are more convenient to use than fresh coffee creams. In these products, sodium caseinate acts as an emulsifier/fat encapsulator and whitener, imparts body and flavour and promotes resistance to feathering. The use of sodium caseinate in dairy industry and in the manufacture of modified milk products has increased all around the world. The addition of 1% sodium caseinate into UHT low-fat

milk fortifies this dietetic drink with protein. Soluble and dispersed high calcium co-precipitates can replace skim milk solids satisfactorily in the preparation of sterilized, flavoured low fat milk beverages. Milk products like cultured milk and UHT milk may be enriched with co-precipitates.

The addition of sodium caseinate to cultured milk products simultaneously increases the nutritive value and improves the technological quality by products. Sodium caseinate is used to increase gel firmness and reduce syneresis in yoghurts, and is added to milk shakes for its emulsifying and foaming properties. In the manufacture of yoghurt, the skim milk solids may be replaced partly with the addition of soluble co-precipitates. But when the replacement is more than 30% an apparent coarseness in texture is observed in the finished yoghurt. Incorporation of hydrolysates at 5% level in cheese like foods give best results for flavor and texture.

41.2.2 Use of whey protein products

Whey protein concentrates (WPC) have been used in many different types of dairy products including various types of cheese, yogurt, ice cream, frozen yogurt, dairy spreads such as butter and low-fat butter, infant formula, cream liqueurs, creamy chocolate dairy desserts, *peda* and *gulabjamun* (Indian dairy products derived from *khoa*), and *kulfi* (a traditional frozen dairy product). Greater amount of WPC produces bigger grains in *khoa*, which is a desirable property for preparing *kalakand* - a popular *khoa*-based sweet. Addition of 5% WPC solids to cow milk improves the flavour, body and texture and colour of *khoa*. In yoghurt the viscosity and stability are improved by fortification with WPC to replace skim milk solids. Based on the emulsifying and gelling properties of whey proteins, sliceable and squeezable cheese-type products have been produced by heat treatment of skim milk and WPC solids dispersed in an emulsion of milk fat in WPC. WPC are also used in cheese filling and dips as they tend to complement cheese flavour and produce a soft end product. Whey protein hydrolysates can be used in accelerating the ripening of Domaiti cheese.

41.3 Application in Bakery Products

Milk proteins do not have properties close enough to those of wheat gluten to enable them to replace the latter protein to any great extent in bakery products; however, their use as a nutritional supplement and for functional effects in cereal-based products has considerable potential. An important functional characteristic of milk protein products in bakery applications is water binding which affects dough consistency. Bread, with milk proteins added in one form or another, shows a good crumb structure, bread yield, flavour and keeping quality. In the manufacturing of high protein biscuits, milk proteins play an important role as they increase the nutritive value and also the texture. Milk proteins are often incorporated into the base flour for pasta manufacture for the purpose of enhancing nutritional quality and to improve texture.

41.3.1 Use of casein products

One of the most important functional characteristics of casein products in bakery products is its water binding capacity. A satisfactory loaf volume can be obtained by the use of casein products. Acid and rennet casein, sodium caseinate and calcium caseinate can be used in bread making and are added at a level of 15-20% of the wheat flour. Products fortified by addition of sodium or calcium caseinate prior to extrusion include macaroni and pasta. Casein and casein derivatives are mainly used in bakery products like frozen baked cakes and cookies as an emulsifier and to improve texture, in breakfast cereals, milk biscuits and protein-enriched bread to enhance flavour and other sensory properties and also for nutritional fortification of the wheat flour (Table 41.2). The limiting amino acid in most cereal proteins is lysine and since caseins are particularly rich in lysine, they make excellent supplements for cereals. Only about 4% casein in a casein-wheat flour mixture is required to increase the lysine content by 60%. The protein efficiency ratio (PER) of wheat flour is only 1.1, compared with 2.5 for casein. By supplementing the wheat flour with casein, it is possible to increase considerably the PER of the mixture. For instance, for a 50:50 mixture of casein and wheat protein, the PER can be raised to 2.2 - 2.3. Similarly co-precipitates are also used in different bakery products.

Table 41.2 Applications of milk protein products in bakery products

Food product	Milk protein products	% in food product	Purpose/effect
Pastry glaze	Soluble high-calcium co-precipitate	63.4	Colour, shine (with lactose)
Breakfast cereal	Casein	1.5-10	Nutrition
Milk biscuits	Calcium caseinate or high-calcium co-precipitates	16-20	Nutrition
Protein-enriched bread	Calcium caseinate	5-10	Nutrition
Cake mix for diabetics	High calcium co-precipitates	6.5	Nutrition and cake volume
Frozen baked cake	Sodium caseinate	0.5-5	Texture, emulsifier
Protein-enriched milk biscuits	Sodium caseinate	12.5	Nutrition
Biscuits	Calcium caseinate	20	Nutrition
High-protein bread	Casein	2-6	Nutrition
Fortified bread	Co-precipitate	3-10	Dough consistency and sensory properties
Cookies	Casein and co-precipitate	6.5	Nutrition and texture
Bread, cake, muffins & croissants	Whey proteins	-----	Nutritional, emulsifier, egg replacer

41.4 Application in Confectionery and Pasta Products

Milk protein products are often incorporated into the flour base for pasta manufacture to enhance nutritional quality and also to improve texture. Products fortified by the addition of sodium or calcium caseinate, low calcium co-precipitate or WPC prior to extrusion include macaroni and pasta. Milk protein products are also used in confectionery products because of their water binding, emulsifying, whipping and browning properties.

41.4.1 Use of casein products

Caseins are used in toffee, caramel, fudge and other confections as they form a firm, resilient, chewy matrix on heating and they contribute water binding and aid emulsification. Casein hydrolysates are used as foaming agents in place of egg albumen in marshmallow and nougat as they confer stability to high cooking temperatures and good flavour and browning properties.

Casein and casein products are used in macaroni, pasta and imitation pasta products to improve texture and nutritional properties (Table 41.3). Sodium caseinate hydrolysates can be used in the preparation of noodles. Use of hydrolysates in chocolate manufacturing for increasing the protein content has also been suggested.

41.4.2 Use of whey protein products

WPCs have limited use in these products as they result in a softer coagulum and the high lactose content tends to cause crystallization during storage. However, whey proteins are very suitable for use in aerated candy mixtures and are incorporated as a frappe, which is a highly aerated sugar syrup containing the whipping protein. Replacement of egg white by WPC in the manufacture of meringues results in acceptable products only when defatted WPCs are used, while the manufacture of acceptable sponge cakes requires fat-containing rather than defatted WPCs.

Whey solids are used as an ingredient for the formulation of confectionery and pasta products to enhance the texture, flavour and colour characteristics of the finished products. It also preserves the freshness of the product in year round usage. Enrichment of pasta flours with undenatured whey protein products produces firmer cooked noodles which are also more freeze-thaw stable and suitable for microwave cooking. 'Imitation' or 'synthetic' pasta-type products containing a substantial proportion of milk protein have also been manufactured.

Table 41.3 Applications of milk protein products in confectionery and pasta products

A. Caseins/ Caseinates/Co-precipitates	
<i>Used in</i>	<i>Effects</i>
Toffee, caramel, fudges	Confers firm, resilient, chewy texture; water binding, emulsifier
Marshmallow and nougat	Foaming, high temperature stability, improves flavor and brown colour
Macaroni, pasta, imitation pasta	Nutritional, texture
B. Whey Proteins	
<i>Used in</i>	<i>Effects</i>
Aerated candy mixes, meringues, sponge cakes, pasta	Whipping properties, emulsifier, freeze-thaw stability, microwaveable

***** 😊 *****

Lesson 42
FOOD APPLICATION OF MILK PROTEIN PRODUCTS-2

42.1 Introduction

Milk protein products have application in beverages, desserts-type products, meat products, convenience foods, textured products and dietary, pharmaceutical and medical products.

42.2 Application in Beverages

Milk protein products are widely used in different types of beverage because of their whipping, foaming and emulsifying and nutritional properties (Table 42.1).

Table 42.1 Applications of milk protein products in beverages

A. <u>Caseins/ Caseinates/Co-precipitates</u>	
<i>Used in</i>	<i>Effects</i>
Drinking chocolate, carbonated drinks and fruit beverages	Stabilizer, whipping and foaming properties
Cream liqueurs, wine aperitifs	Emulsifier
Wine and beer industry	Fines removal, clarification, reduce colour and astringency
B. <u>Whey Proteins</u>	
<i>Used in</i>	<i>Effects</i>
Soft drinks, fruit juices, powdered or frozen orange beverages	Nutritional
Milk-based flavoured beverages	Viscosity, colloidal stability

42.2.1 Use of casein products

Casein products are used as stabilizers or for their whipping and foaming properties in drinking chocolate, fizzy drinks and fruit beverages. There is also a large market for sodium caseinate as an emulsifier in cream liqueurs and to a lesser extent in wine aperitifs. Cream liqueurs typically contain 16% (w/w) milk fat, 3.3% sodium caseinate, 19% added sugar and 14 % ethanol. Casein products have also been used in the wine and beer industries as fining agent, to reduce colour and astringency and to aid in clarification.

42.2.2 Use of whey protein products

Having solubility over a broad range of pH (3-8), even at their iso-electric pH, whey proteins find applications in both dairy type as well as fruit based acidic drinks. Fruit juices, soft drinks or milk-based beverages supplemented with whey protein concentrates are highly nutritious products. For use in soft drinks, defatted WPC with a low ash content, good solubility at pH 3.0 and a bland flavour

is required. The WPC must also be resistant to physical deterioration or flavour changes on storage of the product and it must not mask the typical flavour of the soft drink *via* protein-flavour component interactions. WPCs are added to milk-like flavoured drinks to impart viscosity, body and colloidal stability and they have been included as protein supplements in powdered orange beverages and in frozen orange juice concentrates.

42.3 Application in Desserts-Type Products

Milk proteins present in dessert type products are mainly foam formers; they accelerate foaming and homogenous bubble distribution of the gaseous phase and its fixation in the liquid phase.

Table 42.2 Applications of milk protein products in dessert-type products

A. <u>Caseins/ Caseinates/Co-precipitates</u>	
<i>Used in</i>	<i>Effects</i>
Ice cream, frozen desserts	Whipping properties, body and texture
Mousses, instant pudding, whipped topping	Whipping properties, film former, emulsifier, imparts body and flavour
Ice cream, frozen juice bars, frozen dessert coatings	Skim milk solid replacement, whipping properties, emulsifying, body/texture
B. <u>Whey Proteins</u>	
<i>Used in</i>	<i>Effects</i>
Ice cream, frozen juice bars, frozen dessert coatings	Skim milk solid replacement, whipping properties, emulsifying, body/texture

42.3.1 Use of casein products

Sodium caseinate is used in ice cream substitutes and frozen desserts to improve whipping properties, body and texture and to act as a stabilizer (Table 42.2). It is also used extensively in mousses, instant puddings and whipped toppings for similar reasons and also because it acts as an emulsifier and film-former.

42.3.2 Use of whey protein products

WPC has also been used in frozen juice bars and in compound coatings, especially in chocolate coatings and for frozen desserts etc.

42.4 Application in Meat Products

In the meat industry, milk proteins are used mainly in comminuted meat products rather than prime cuts; however, they are also used in injection brines for non-comminuted products like cooked hams (Table 42.3). Milk proteins have been utilized as fillers, binders and extenders in cooked comminuted meat products to reduce cook shrink and formulation cost, as well as to improve emulsifying capacity, emulsion stability, water binding, potential nutritive value and slicing characteristics. The dairy proteins can also improve or alter the consumer acceptance (flavour, mouth-feel, colour, appearance etc.) of the finished product. These proteins significantly increase the gel strength of meat

proteins and it has been shown that there is a synergistic effect between milk proteins and salt soluble meat proteins, through covalent cross-linkages.

Table 42.3 Applications of milk protein products in meat products

A. <u>Caseins/Caseinate/Co-precipitates</u>	
<i>Used in</i>	<i>Effects</i>
Comminuted meat products	Emulsifier, water binding, improves consistency, releases meat proteins for gel formation and water binding
B. <u>Whey Proteins</u>	
<i>Used in</i>	<i>Effects</i>
Frankfurters, luncheon rolls	Pre-emulsion, gelation
Injection brine for fortification of whole meat products	Gelation, yield

42.4.1 Use of casein products

The main reason for growth in the use of casein in meat products lies in its functionality. Solubilised rennet caseins with high calcium levels are used in some meat products. The commonest form in which casein is incorporated in meat products is as sodium caseinate. Besides nutritional value, they are mainly used due to their excellent water binding and emulsifying properties. In comminuted meat products, a considerable amount of free fat is released during the manufacture of these products, which must be stabilized. The ability of caseinates to bind and entrap moisture through H-bonding and thereby enhancing the yield of end products has been used beneficially in various meat and sausage preparations. In addition, their salt tolerance and high protein content attract many meat traders. Caseinate thickens the gravy during frying and prevents its running out, but too much caseinate would dry up the sausage. Amongst many other functional properties, the bland flavour and neutral colour of caseinates deserve a special mention. They show no heat gelation or denaturation and have a high viscosity in solution.

Casein hydrolysates obtained by acid hydrolysis has a meat-like flavor. These are, therefore, used to accentuate the meat flavor in heat-treated canned and dried meat products such as soups. Incorporation of 3.5% protein hydrolysate gives better binding, emulsification and flavor development in fermented sausages and comminuted meat products.

Co-precipitates enhance water binding property and may prove superior to caseinate in chopped meats. The co-precipitates have good potential in various meat products such as frankfurters, sausage batter and luncheon meats as meat replacers or extenders. Sausages act as a good medium for the use of co-precipitates. The finally dispersed dairy protein matrix in sausages also can acts as a moisture binding agent, thus, developing the desirable chewy texture besides controlling shrinkage during storage and deformation while slicing. It has been found that both low and high co-precipitates improved the emulsifying capacity, emulsion stability and water holding capacity of the meat emulsion in fresh sausages at 20% replacement level.

42.4.2 Use of whey protein products

Use of denatured WPC as a meat extender in processed meat products has been found to have promising results. In frankfurters and luncheon rolls, meat protein may be replaced by whey proteins. In these systems, whey proteins are used to prepare pre-emulsions of part of the fat and to support network formation, *via* gelation, during subsequent cooking. Soluble, low viscosity whey protein concentrates are suitable for use in injection brines for fortification of whole meat products. Injection of fresh and cured meats with whey protein solution may increase the yield substantially.

42.5 Application in Textured Products

Milk protein-enriched products have been used in the production of textured foods (Table 42.4). Rewetted acid caseins or acidified rennet casein or co-precipitate have been mixed with carbonates or bicarbonates of alkali metals or alkali earth metals and extruded to produce puffed snack foods while caseinates have been co-extruded with wheat flour to produce protein-enriched snack-type food products.

Table 42.4 Applications of milk protein products in textured products

<u>Caseins/Caseinate/Co-precipitates/Whey Proteins</u>	
<i>Used in</i>	<i>Effects</i>
Puffed snack foods, protein-enriched snack-type products, meat extenders, surimi, restructured fish	Structuring, texturing, nutritional

42.6 Application in Dietary, Pharmaceutical and Medical

Milk protein products are used extensively in dietary preparations for people, who are ill or convalescing, for malnourished children in developing countries on a therapeutic diet and for people on weight-reducing diets (Table 42.5). Milk protein hydrolysates are used for intravenous nutrition for patients suffering from intestinal disorders, protein metabolism disorders and for post-operative patients.

42.6.1 Use of casein products

Caseins are used in special preparations to enhance athletic performance and have been incorporated into formula diets for astronauts while in space. While casein products are not generally used in infant formulae, they are used extensively in specialized preparations for infants with specific nutritional problems. Caseinates, co-precipitates and milk protein concentrates are used in low-lactose formulae for lactose-intolerant infants while various types of caseinates have been used in infant foods with a specific mineral balance, e.g., low-sodium infant formulae for children with specific renal problems. Casein hydrolysates are used in specialized foods for premature infants, in formulae for infant suffering from diarrhea, gastroenteritis, galactosaemia and malabsorption. A special casein hydrolysate, low in phenylalanine, has been prepared for use in formulae for feeding infants with phenylketonuria. Casein products are also added to various foods for children and infants and to drinks as a nutritional supplement.

Table 42.5 Applications of milk protein products in dietary, pharmaceutical and medical products

Used in	
Special Dietary Preparations	<ul style="list-style-type: none"> • Ill or convalescent patients
	<ul style="list-style-type: none"> • Dieting patients/ people
	<ul style="list-style-type: none"> • Athletes
	<ul style="list-style-type: none"> • Astronauts
Infant Foods	<ul style="list-style-type: none"> • Nutritional fortification
	<ul style="list-style-type: none"> • “Humanized” infant formulae
	<ul style="list-style-type: none"> • Low-lactose infant formulae
	<ul style="list-style-type: none"> • Specific mineral balance infant foods
	<ul style="list-style-type: none"> • Casein hydrolysates: used for infants suffering from diarrhoea, gastroenteritis, galactosemia, malabsorption, phenylketonuria
	<ul style="list-style-type: none"> • Whey protein hydrolysates used in hypoallergic formulae preparation
	<ul style="list-style-type: none"> • Nutritional fortification
Intravenous Feeds	<ul style="list-style-type: none"> • Patients suffering from metabolic disorders, intestinal disorders or for post-operative patients
Special Food Preparations	<ul style="list-style-type: none"> • Patients suffering from cancer, pancreatic disorders or anaemia
Healthcare Preparations	<ul style="list-style-type: none"> • β-casomorphins used in sleep or hunger regulation or insulin secretion
	<ul style="list-style-type: none"> • Immuno-enhancing diets for HIV patients
	<ul style="list-style-type: none"> • Anti-tumor diets for cancer patients
Miscellaneous Products	<ul style="list-style-type: none"> • Toothpastes
	<ul style="list-style-type: none"> • Cosmetics
	<ul style="list-style-type: none"> • Therapeutic creams

Diets that are suitable for geriatrics, high-energy supplements, weight-control diets, hypoallergenic infant formulas and therapeutic or enteric diets are some of the areas in which casein hydrolysates are most useful. Casein hydrolysates are boon to people who are suffering from protein allergy or stomach disorders and to those who require easily digestible foods. The production of hydrolysed protein provides an opportunity for the dietary management of patients with various digestive disorders as a result of pancreatic malfunction, pre- and post-operative abdominal surgical patients, patients on geriatric and convalescent feeding and others who for various reasons are not able to ingest a normal diet.

Casein hydrolysates also have pharmaceutical applications in intensive care foods, anemia treatment, and prevention of blood cholesterol, treatment of dental diseases and in administration of amino acid mixture intravenously.

Specific drugs have been produced from casein; β -casein is used as raw material for production of β -casomorphins, tetra- to hepta peptides, which can regulate sleep, hunger or insulin secretion.

Sulphonated glycopeptides prepared from casein have been used for the treatment of gastric ulcers. It is claimed that the use of casein in toothpaste prevents dental caries, in cosmetics it conceals facial wrinkles and in special therapeutic creams it heals wounds.

42.6.2 Use of whey protein products

Whey proteins are the wonder proteins for nutritional, clinical, dietetic, sports, infant foods because of their high nutritive value.

42.7 Application in Convenience Foods

Milk protein products are widely used in convenience foods, i.e. foods, which require a minimum of preparation by the consumer (Table 42.6). Milk protein products have been proposed as texture, stability and flavour enhancers in microwaveable foods.

42.7.1 Use of casein products

Whey/ caseinate blends are used as whitening agents in gravy mixes. Whey solids are used in dehydrated soup mixes and sauces to impart a milky or dairy flavour, as flavour enhancers and to provide emulsifying and stabilizing effects. Caseinates are used as emulsifying agents and viscosity controllers in canned cream soups and sauces and for the preparation of dry emulsions for use in dehydrated cream soups and sauces. In some convenience foods, caseinate-whey protein blends are used as cheap replacements for skim milk powders.

Table 42.6 Applications of milk protein products in convenience foods

<u>Caseins/Caseinate/Co-precipitates/Whey Proteins</u>	
<i>Used in</i>	<i>Effects</i>
Gravy mixes, soup mixes, sauces, canned cream soups and sauces, dehydrated cream soups and sauces, salad dressings, microwaveable foods, low-fat convenience foods	Whitening agents, dairy flavour, flavour enhancer, emulsifier, stabilizer, viscosity controller, freeze-thaw stability, egg yolk replacement, fat replacement

42.7.2 Use of whey protein products

Whey protein products have potential as replacements for egg yolk in salad dressing. Modified whey protein-based products, with potential to replace lipids in a variety of convenience foods, have been developed.

Lesson 43

PHYSICO-CHEMICAL CHARACTERISTICS OF BUTTERMILK AND ITS PRESERVATION

43.1 Introduction

Buttermilk is an important by-product obtained during manufacture of butter. In addition, a substantial amount of *lassi* (sour buttermilk) is also produced during the manufacture of *makkhan* directly from fermented milk (curd). Sweet cream buttermilk (SCBM) is almost similar in composition to skim milk except for their high amount of phospholipids and milk fat globular membrane proteins.

43.2 Types of Buttermilk

- a) Sweet cream buttermilk obtained by churning of fresh/ pasteurized cream with little or no developed acidity
- b) Sour buttermilk obtained by churning naturally sour milk or cream
- c) Desi buttermilk (*lassi*) obtained by churning of curd (*dahi*) during the manufacture of *makkhan*.

43.3 Chemical Composition of Buttermilk

The chemical composition of buttermilk varies to a great extent, depending on the amount of water added to cream. Some of the butter manufacturers standardize cream with water, thereby decreasing the total solids level of buttermilk. The chemical composition of buttermilk produced under ideal conditions is almost similar to that of skim milk (Table 43.1).

Sour buttermilk differs from sweet cream buttermilk in respect of titratable acidity. The acidity in sweet cream buttermilk varies from 0.10 to 0.14%, whereas in sour buttermilk it is more than 0.15% and even as high as 1%. However, there is not much difference in the chemical composition of two types of buttermilk. Desi buttermilk has wide range of composition depending on the quality of milk used for making curd and levels of addition of water during churning. Desi buttermilk on an average contains 4% total solids comprising of 0.8% fat, 1.29% protein and 1.2% lactic acidity. The colour of desi buttermilk is brownish due to prolonged heating of milk before culturing. When kept undisturbed for sometimes, curdy material deposits at the bottom of desi buttermilk.

Table 43.1 Average gross composition and physico-chemical properties of sweet cream buttermilk and skim milk (obtained from buffalo milk)

Characteristic	Skim Milk	Sweet cream Buttermilk
T.S. (%)	10.38	9.88
Fat (%)	0.09	0.59
Total proteins (%)	4.27	3.73
Lactose (%)	5.20	4.81
Ash (%)	0.82	0.75
Total phospholipids (mg %)	8.65	78.56
Titrateable acidity (% LA)	0.16	0.12
pH	6.69	6.86
Curd tension (g)	66.85	18.84
Relative viscosity (cP at 30°C)	1.64	1.80

Source: Pal & Mulay (1983)

43.3.1 Difference between sweet cream buttermilk and skim milk

Buttermilk contains higher fat content than skim milk, which can be reduced to some extent by subjecting it to centrifugal separation. Buttermilk contains a larger proportion of protein mixture sloughed from the fat globule-milk-serum interface by churning process. The amount of fat globule membrane protein (FGMP) is, however, not as large in comparison with total buttermilk proteins. The FGMP are hydrophilic and hydrophobic in nature and their physical properties, nitrogen content and amino acid composition do not correspond with any other milk proteins. These proteins exert emulsion in milk and milk products during manufacture and storage. The FGMP also contributes a complex mixture of glycerophospholipids to buttermilk. Sweet cream buttermilk contains about nine times higher phospholipids than skim milk (Table 43.1). It has been noticed that phospholipids in buttermilk do not have short chain fatty acids. The principal fatty acids are C₁₆ (palmitic) and higher acids. Of the total phospholipid fatty acids, about 40% by wt. are saturated acids and the rest are non-conjugated di- to penta-unsaturated acids. Phospholipids of buttermilk include more or less equal proportions of lecithin, sphingomyelin and cephalin together with a small proportion of cerebrosides.

Various physico-chemical properties of buttermilk also differ from that of skim milk (Table 43.1). These differences in physico-chemical properties of buttermilk and skim milk provide many choices for their selective applications in dairy products manufacture. Buttermilk solids have also been demonstrated to possess antioxidant activity and have been suggested for use in stabilizing food matrixes against lipid peroxidation reactions.

43.4 Buttermilk Powder

Buttermilk can be preserved by converting it in powder form. Production of buttermilk powder from buttermilk follows essentially the same process as the production of skim milk powder from skim milk. The buttermilk is first pasteurized, then concentrated in an evaporator and finally dried (spray or roller dried) to produce buttermilk powder. It shall contain not less than 4.5% milk fat and not more than 5% moisture. It shall have a protein content of not less than 30% and the label should specify the minimum protein content. The phospholipids and total lipid content of dried buttermilk is higher than NFDM. It may not contain or be derived from, skim milk powder, dry whey or products other than buttermilk, and contain no added preservative, neutralizing agent or other chemicals. Heat stability of sweet cream buttermilk is considered to be better than skim milk, thereby making it

more suitable for processing to very high heat treatments. The gross composition and physico-chemical properties of spray dried sweet cream buttermilk and skim milk are given in Table 43.2.

Table 43.2 Typical physicochemical characteristics of spray powders

Characteristics	Skim milk powder	Sweet cream buttermilk powder
Moisture (%)	2.75	2.59
Fat (%)	1.05	6.38
Total protein (%)	40.29	37.09
Lactose (%)	48.15	47.00
Ash (%)	7.76	6.94
Total phospholipids (mg %)	97.1	625.25
Titralable acidity (% L.A.)	1.39	1.17
Solubility index (ml)	0.30	0.15
Bulk density (g/ml)	0.543	0.345

Source: Pal & Mulay (1983)

Buttermilk powder is a cream colored powder with a clean, dairy flavor. The solubility of spray dried buttermilk powder is excellent, while the solubility of the roller dried product is not quite as good.

The protein composition of buttermilk powder is essentially the same as skim milk powder with the addition of some protein material originating on the fat globule surface. Sweet cream buttermilk powder has high total lipids including phospholipids than skim milk powder as some small fat droplets are lost to the buttermilk during butter making. Spray dried buttermilk powder has lower bulk density and is less free flowing and dusty because of high fat content in comparison with skim milk powder.

The shelf life of buttermilk powder is 6-9 months and is limited by the potential oxidation of the fat in the powder, which produces an off flavor. Oxidation can be discouraged by maintaining a low moisture content and avoiding exposure of the powder to elements that promote oxidation including light and metals such as copper and iron.

***** 😊 *****

Lesson 44 UTILIZATION OF BUTTERMILK

44.1 Introduction

The uses of sweet cream buttermilk are somewhat similar to those of skim milk. It is valued in the food industry because of its emulsifying capacity and its positive impact on flavor. Commercially produced buttermilk is mostly sweet cream buttermilk. It is a desirable component of bakery products to improve their flavor and texture, the condensed and dried forms being the most convenient ones. High phospholipids content in dried buttermilk makes it a good functional ingredient in food formulations. Casein made from buttermilk is different in many respects from skim-milk casein. For most purposes, it is less desirable than casein from skim milk. But for casein paints, it is especially suitable if used in paste form without being dried. Buttermilk as such and in condensed form is also used as animal feed and dried buttermilk is added in the formulation of their mixed feeds.

44.2 Utilization of Sweet Cream Buttermilk

Sweet cream buttermilk, because of its resemblance in gross chemical composition with skim milk, is usually admixed with bulk of skim milk for further spray drying or even products manufacture in dairy plants. Sweet cream buttermilk can be used in beverage form and in the fluid milk industry as a milk extender with specific benefits over skim milk. The other potential uses of buttermilk solids are in manufacture of soft varieties of cheese, paneer, fermented milks and traditional milk products. Judicious use of buttermilk solids in the development of functional foods is another promising area.

44.2.1 Market milk

The undiluted sweet cream buttermilk can be admixed with the whole milk for fluid milk supply. The use of sweet cream buttermilk in the market milk for toning of buffalo milk, improves its palatability, viscosity and heat-stability and reduces the curd tension without adversely affecting the keeping quality. In addition to plain fluid milk, it can also be used for the preparation of flavoured milks and milk beverages. The powder made from the mixture of skim milk and sweet cream buttermilk is treated as a skim milk powder and used for reconstitution purposes.

44.2.2 Fermented dairy products

44.2.2.1 Dahi

Curd prepared by incorporating sweet cream buttermilk into whole milk has soft-body, which is probably due to i) the change in the electric charge on the casein during churning, ii) the presence of phospholipids and other MFGM materials, and iii) the free fat in the buttermilk. Addition of 1-2%

skim milk powder is recommended for improving the body of *dahi* made from buttermilk. As an alternative to curd making, sweet cream buttermilk can be successfully utilized in the manufacture of cultured buttermilk and *lassi*, in which the firmness is not of much consideration.

44.2.2.2 Yoghurt

Increasing the total solids in yoghurt milk to around 14-16% is one of the essential steps in the process of yoghurt making. Traditionally, the fortification of the total solids in the yoghurt mix is achieved by boiling to reduce the volume of the milk to two-thirds of its original or by the addition of skimmed milk powder (SMP). Replacement of SMP with buttermilk powder up to 50% in the manufacture of low-fat yoghurt was found to be acceptable and similar to the control product. Buttermilk powder when added to low-fat yoghurts up to 4.8%, yielded a soft and smooth product. Among the various dairy ingredients used in the manufacture of yoghurt, dried buttermilk was found to reduce its susceptibility to syneresis.

44.2.2.3 Cheeses

Mixture of buttermilk and skim milk can be utilized for the production of low fat cheeses. Addition of buttermilk in the manufacture of low-fat Cheddar cheese can improve the texture of the cheese because of the high water-holding capacity of phospholipids. The preparation of hard varieties of cheese like Cheddar and Gouda involves the adjustment of casein and fat ratio with the help of skim milk. The replacement of skim milk with sweet cream buttermilk results into softer body due to the presence of higher amount of fat globule membrane materials in buttermilk. Joshi and Thakar (1996a) however, were successful in improving the firmness and producing acceptable quality of Cheddar cheese from blends of buffalo milk and sweet cream buttermilk. They maintained the setting temperature at 33°C, added starter @ 2% and rennet @ 4.5 g/100 kg milk. The cheddar cheese so prepared was also used for making processed cheese of satisfactory quality. Several benefits of utilizing buttermilk solids in the manufacture of soft varieties of cheeses are: decreased waste disposal problems, reduction in cost, increased cheese yield and improved flavour, texture, biological value and hypocholesterolaemic effects of cheese.

44.2.3 Indian traditional dairy products

44.2.3.1 Channa

Channa produced from buffalo milk is reported to be hard and greasy because of inherent differences in qualitative and quantitative aspects of buffalo milk than cow milk. Recently, it has been reported that good quality *channa* can be produced by admixing SCBM to buffalo milk. Good quality rasogolla and sandesh could also be prepared from this *channa*.

44.2.3.2 Paneer

Buffalo milk has to be standardized to a fat and SNF ratio of about 1:1.65 to meet the FSSAI requirements for the manufacture of *paneer*. The replacement of skim milk with sweet cream buttermilk for the standardization of buffalo milk has been found to increase the yield of *paneer* by about one per cent without altering the organoleptic and textural properties. It is also possible to prepare good quality *paneer* from low fat milk by incorporating buttermilk solids to buffalo milk.

44.2.3.3 Basundi

Basundi, a partially desiccated sweetened milk product, is prepared traditionally from buffalo milk. Attempts were made by Patel and Upadhyay (2004) to replace buffalo milk solids by SCBM solids in *basundi* making and reported that 100% replacement of buffalo milk solids resulted in a significant decrease in the lactose and ash contents and adversely affected the physico-chemical properties such as free fatty acids (FFA) and hydroxyl methyl furfural (HMF) contents. However, it was recommended by the workers that replacement up to 25% would check such adverse effects on the product.

44.2.3.4 Chakka and shrikhand

Chakka, a semi-solid mass obtained after draining whey from *dahi*, is an intermediate product for *shrikhand* manufacture. Karthikeyan *et al*, (2000) studied the effect of replacement of buffalo skim milk by SCBM on various technological parameters and reported that *chakka* made from 50% replacement of skim milk by SCBM had improved flavour and with smoother body and texture, and no adverse effect on chemical composition. Karthikeyan *et al*, (1999) attempted to prepare *shrikhand* from SCBM with varying total solids content and reported that *shrikhand* prepared from SCBM with 15% total solids was similar to that of control product prepared from buffalo skim milk.

44.2.4 Frozen dairy products

The buttermilk powder has been extensively used in preparation of ice cream and other frozen desserts. The 100% replacement of skim milk solids in the form of a blend of spray dried whey protein concentrate (WPC) and dried SCBM (50:50) in ice cream resulted in better quality product than the control.

44.2.5 Beverages

The most economical use of buttermilk is in the manufacture of beverages that is highly used as a refreshing drink in summer season. Besides providing valuable nutrients and freshness to consumers at cheaper cost, it offers variety to the consumers. As beverage, buttermilk is consumed in plain and spiced forms throughout the year. Salted spiced buttermilk (SSBM) is prepared by addition of

common salts, sugar, roasted jeera, chilli powder in plain buttermilk. After preparation of SSBM, the fruit flavours in form of syrup *viz.* Cashew and Kokum are added and mixed properly to obtain uniform consistency. The prepared buttermilk is cooled to 7-10°C for 3 to 5 h.

Fresh buttermilk beverages prepared by the addition of flavor concentrates and sugar results in a product having smooth texture and rich tangy fruity flavor. Addition of fruit juices or fruit pulps is an attractive avenue for the utilization of buttermilk. With the availability of a variety of region-specific and season/climate-specific fruits country wide, a large variety of beverages can be formulated and marketed as ready-to-serve drinks. Fruits like pineapple, cherry or raspberry and orange or strawberry have been tried for fortification and enhancement of flavor of buttermilk. Addition of fruit pulp/syrup to buttermilk not only enriches its taste, but also enhances its quality. Shukla *et al.* (2004) studied the suitability of blending apple, banana, guava, litchi and mango juice/pulp with buttermilk at different levels and reported that apple juice, litchi juice, banana pulp, guava pulp and mango pulp could be added up to 30%, 30%, 20%, 10% and 20% levels, respectively in buttermilk to make refreshing drinks.

Shrivasta *et al.* (1985) reported the utilization of buttermilk in the preparation of drink using culture of *Streptococcus thermophilus* or mixed culture of *S. thermophilus* and *Lactobacillus acidophilus* and added sugar and pineapple flavorings. Buttermilk acidified by starter culture containing lactic streptococci, is widely used as a beverage in Europe.

44.2.6 Probiotic drinks

The growing interest worldwide in probiotic foods led the researchers to find all possible ways of developing health foods and buttermilk is no exception. Various workers have developed buttermilk-based probiotic drinks with different probiotic bacteria. Rodas *et al.* (2002) developed probiotic buttermilk by adding the probiotic strain of *Lactobacillus reuteri* at a rate of 1%.

44.3 Utilization of Sour Buttermilk

During the manufacture of butter, a considerable amount of sour buttermilk is obtained either from natural souring of milk/cream or by controlled fermentation. Sour buttermilk obtained from first category is not preferred for human consumption. This may, however, be converted into casein by adopting modified processing conditions for other uses. A process has been standardized for the manufacture of *paneer* from the mixture of buffalo milk and sour buttermilk. The *paneer* prepared by this method gave higher yield by retaining more moisture in comparison with control *paneer*. The organoleptic quality and shelf life of the buttermilk extended *paneer* were comparable to control *paneer*.

44.4 Utilization of Desi Buttermilk

Desi buttermilk also known as *chhach* makes an excellent drink, especially in warm weather. *Chhach* is an important domestic beverage in India. It can be flavored in various ways with salt, mint, cumin, and even spicy additions such as ground chilies, fresh ginger or garlic. It is considered to be an excellent thirst quenching and nourishing beverage, particularly during summer months. It is also

used for making some popular traditional preparations e.g. *karhi*, *rabri* (fermented) etc. The industrial utilization of *chhach* cannot be exploited due to lack of proper collection system and day-to-day variations in the composition and quality of desi buttermilk.

44.5 Utilization of Buttermilk Powder

Buttermilk powder can replace partly skim milk powder for incorporation into baked goods, ice cream, Pudding, sauces, beverages and chocolates. In baked goods it provides desirable flavor, help to incorporate air into product, aid in the development of browning as the product is baked and preserve freshness by binding water. In pudding, sauces and beverages, buttermilk powder is used to absorb water and increase their viscosity. In chocolate it provides the beneficial emulsifying ability.

Great scope lies in the effective use of buttermilk or buttermilk solids in the manufacture of some of our popular indigenous Indian dairy products, e.g., *khoa*, *kheer*, *rabri* and *gulabjamun*. The dried buttermilk can replace the SMP in the manufacture of *gulabjamun* mix powder. Because of high lecithin content in buttermilk, it may improve the textural properties of *rasogolla*.

***** 😊 *****

Lesson 45
GHEE-RESIDUE AND ITS CHARACTERISTICS

45.1 Introduction

Ghee-residue is the by-product of ghee manufacturing industry. It is partially charred (burnt) light to dark brown and moist residue that is obtained on the cloth strainer after the ghee is filtered. During the manufacture of ghee, the solids not fat (SNF) present in cream or butter appears in the form of small particles known as ghee-residue. It is obtained after molten ghee has been either strained out with bag filters or muslin cloth or separated by continuous centrifugal clarifiers. The yield of ghee-residue varies with the method of preparation of ghee. This is due to the variation in the non-fatty serum constituents of the different raw materials used for the preparation of ghee. The average yield of ghee-residue is maximum in direct creamery (DC) method (12%) followed by about 3.7% yield in creamery butter (CB) and desi butter (DB) method. Ghee-residue, particularly one obtained from creamery-butter, has higher content of phospholipids 17.39% of its total fat. Higher phospholipids (a good emulsifier) content of ghee-residue is beneficial in developing certain products where emulsification of fat and aqueous phase is desired. Keeping quality of all types of GR clarified at 120°C is 3 months. Its shelf life can further be increased to more than 4 months by pressing it in cake form.

45.2 Physico-chemical and Functional Properties of Ghee-Residue

Depending on the intensity of the heat treatment used during the ghee manufacture, colour of ghee-residue (GR) may vary from light to dark brown. It has smooth to granular texture with glossy exterior due to the presence of excessive free fat. The average particle diameter of ghee-residue is about 105 microns and average density is 1.14 g/cm³.

45.2.1 Chemical composition

There are considerable variations in the chemical composition of ghee-residue (Table 45.1) depending upon the method of preparation of ghee. The approximate composition (%) of ghee-residue varies as fat (32-70), protein (12-39), moisture (8-30), lactose (2-14) and ash (1-8). Moisture, protein and ash contents are more in CB and DB ghee-residue than in DC ghee-residues. Fat content is higher in DC residues than in butter ghee-residue. Lactose content is highest in DB followed by DC and CB ghee-residues. Thus ghee-residue is a rich source of lipids, proteins and carbohydrates.

Table 45.1 Chemical composition and yield of ghee-residue (Hand pressed)

Source of ghee-residue	Average % fat of source	Chemical composition (%)					Yield (Kg/100 Kg source)
		Moisture	Fat	Protein	Lactose	Ash	
<i>From buffalo milk</i>							
Desi butter	77.0	13.4	33.4	32.8	15.4	5.2	1.6
Creamery butter (unsalted)	85.0	5.7	65.0	25.5	Trace	3.8	1.2
Sweet cream	67.0	4.1	63.2	18.0	12.3	2.4	7.7
Sour cream	67.0	8.0	38.8	41.6	7.3	4.3	5.1
Washed sweet cream	71.0	1.7	80.8	16.2	Trace	1.3	3.5

45.2.1.1 Lipids in ghee-residue

The lipids of ghee-residue have lower Reichert Meissl value and Polenske value (24.4, 1.3) but higher iodine value (43.4) in comparison to those of corresponding ghee (30.1, 1.6, and 33.9 respectively). The lipids of ghee-residue have lesser lower chain fatty acids C₄ to C₁₂ (5.3%) and total saturated fatty acids (58.7%) and more of unsaturated fatty acids (41.3%) in comparison to those of ghee (10.1, 66.8, 33.2%, respectively). Irrespective of the method of preparation, PUFA content of ghee-residue lipids (4.4%) is higher than those of corresponding ghee (2.8%). The fatty acid composition of phospholipids shows that it has no fatty acids lower than 12 carbon atoms.

Ghee-residue is rich in phospholipids (1-9%). The phospholipid content of ghee-residue is dependent upon the method of preparation. It is highest in CB ghee-residue lipids (17.39%) followed by DB ghee-residue lipids (4.95%) and the least in DC ghee-residue lipids (1.57%). These levels are much higher than those in ghee (0.004-0.08%). Phospholipid acts synergistically with reducing substances in ghee-residue and protects it from oxidative defect. The phospholipid content of ghee-residue decreases as the period of heating increases due to the transfer of phospholipids from ghee-residue to ghee. While heating cream/butter, only a small fraction of the phospholipids get transferred to ghee, most of the phospholipids remain with the residue because of their polar character. The differences observed in the physico-chemical constant, fatty acids and PUFA contents between lipids of ghee-residue and ghee are due to the high phospholipid content of ghee-residue.

45.2.1.2 Proteins in ghee-residue

Soluble nitrogen content of ghee-residue prepared from cream or creamery butter decreases with heating time. This decrease is due to the denaturation of almost all the proteins. The total reducing capacity expressed as mg of cysteine hydrochloride/g of CB ghee-residue (26.0) and free sulphhydryl content ($\mu\text{m/g}$) of ghee-residue (2.90) are much higher than those in ghee (0.075 and 0.02, respectively). These substances are liberated from protein during heat treatment and because of their polar nature are mostly retained in the ghee-residue. Whey proteins, especially β -lactoglobulin are the main source for these sulphhydryl compounds.

45.2.1.3 Milk sugars in ghee-residue

Main sugars (wt %) in ghee-residue prepared at 120°C are lactose (76.6), galactose (14.1), glucose (5.3), and two more unidentified spots, one at the origin (4.0) and second of faster mobility. As the period of heating is increased, the lactose content of ghee-residue decreases with a corresponding increase in galactose and glucose content. The unidentified spots are also found to increase as the period of heating is increased. The unidentified spots might be due to some of the breakdown products or sugar fragments formed during browning or caramelization reactions.

45.2.2 Flavouring properties

Ghee residue is also a rich and natural source of flavour compounds *viz.* FFA, carbonyls and lactones. The level of FFA, carbonyls and lactones in ghee-residue are respectively 11, 10 and 132 times those in ghee as shown in Table 45.2.

Ghee flavour can be induced in vanaspati and butter oil etc. by adding 10% ghee-residue and clarification at 120°C/flash (10%). This treatment also enhances their keeping quality because of the antioxidant property of ghee-residue. Further, ghee, especially prepared from fresh creamery-butter (without ripening) has mild flavour. GR can be used to enhance flavour in such ghee. Creamery butter is mixed thoroughly with ghee-residue (10%) and clarified at 120°C, filtered through 4-fold of muslin cloth and subsequently centrifuged to get ghee with enhanced flavour.

Table 45.2 Flavour potential of ghee and ghee-residue

FFA ($\mu\text{m/g}$)		Carbonyls ($\mu\text{m/g}$)		Lactones ($\mu\text{g/g}$)	
GR	Ghee	GR	Ghee	GR	Ghee
627.5	53.6	43.7	4.3	3992.9	30.3

45.2.3 Antioxidant properties

Ghee-residue is a rich source of natural antioxidants. It is rich in phospholipids and nitrogenous compounds, which contribute towards its antioxidant properties. Other constituents discharging the same function include free amino acid and reducing substances like free sulphhydryls from denatured proteins and free sugars from lactose. The antioxidant properties of ghee-residue are affected by method of preparation. CB ghee-residue has the maximum antioxidant properties followed by DB and DC ghee-residues. The overall antioxidant properties are due to both lipid and non-lipid constituents. In lipid constituent of ghee-residue, phospholipids show the maximum antioxidant activity followed by α -tocopherol and vitamin A. Among the various phospholipid fractions, cephalin shows the greatest antioxidant activity. The oxidative stability of ghee can be increased by increasing its phospholipid content to 0.1% either through heat treatment process or through solvent extraction process. It has been observed that heating ghee-residue with ghee in the ratio of 1:4 at 130°C have maximum transfer of phospholipids from ghee-residue to ghee. These antioxidant concentrates can be added to ghee to give about 0.1% phospholipids so as to increase the keeping quality of ghee.

Among the non-lipid constituents, the amino acids, proline, lysine, cysteine hydrochloride and tryptophan show the antioxidant properties. Further, the addition of lactose, glucose, galactose and their interaction products with protein and phospholipids to ghee also increase the oxidative stability of ghee. As ghee-residue contains large amount of reducing substances including free sulphhydryls, such compounds may also contribute to the antioxidant properties of ghee-residue.

***** 😊 *****

Lesson 46

GHEE-RESIDUE: PROCESSING AND UTILIZATION

46.1 Introduction

Ghee-residue is a nutritious by-product. This by-product has been studied for its physico-chemical characteristics and its utilization in a number of food products like chocolate burfi, samosa filling, chapatis etc. Ghee-residue, by virtue of its chemical composition, bulk of production, physical characteristics, long shelf life permitting its collection and centralized handling, has great potential and is more amenable to exploit its utilization in food industry. Further, the flavour potential of ghee-residue is much greater than that of ghee. Hence it can be utilised for flavouring bland fats and also enhancing their keeping quality.

46.2 Recovery of Ghee from Ghee-Residue

In dairy plants, attempt is made to recover as much ghee as possible from ghee-residue. Two methods of recovery of ghee from ghee-residue are adopted.

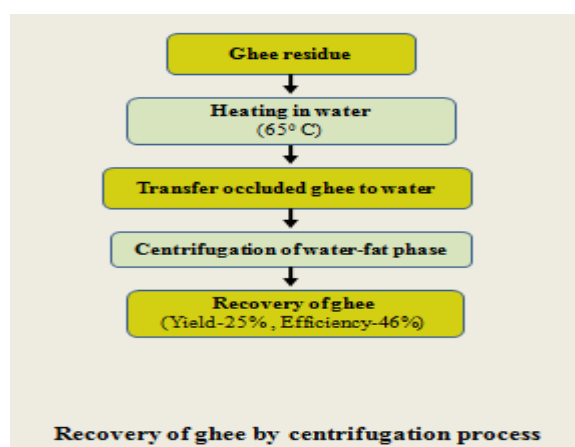
46.2.1 Pressure technique

This consists of subjecting the heated ghee-residue (65-70°C) to a limited pressure in hand screw or hydraulic press. This method gives a yield of about 45% (extraction efficiency of about 67%). This method is simple, efficient, more practical, economical and requires no electricity or sophisticated equipment.

46.2.2 Centrifugation process

This consists of heating ghee-residue in water (65°C) due to which fat entrapped within the residue matrix melts and oozes out, and collects as the top layer above soak water. Ghee is subsequently recovered by centrifuging the water-fat phase. The method yields 25% ghee (46% efficiency). The process is shown in Fig. 46.1.

Alternatively the released fat at the surface of water is recovered by solidification by cooling either by adding ice/cold water or leaving it in a cold store (5-10°C) over night.



46.3 Treatment and Processing of Ghee-Residue

Ghee-residue has soft and smooth body, but gets progressively hardened during storage. The change in the textural characteristics is much faster particularly during the first 15 days and by the end of a month it becomes hard and gritty. In order to eliminate the undesirable characteristics it is necessary to process it so as to yield a soft and smooth texture essential for edible preparations. Before subjecting the residue to any-treatment, lumps are broken and then pulverized by passing through 40 mesh sieve. A number of processing treatments are possible for ghee-residue (Table 46.1). All the treatments make the processed residue soft and smooth. It was reported that the changes brought about in the constituents of the residue remained same. Residues absorb considerable amount of moisture, its acidity reduces; in case of treatments II, IV and VI acidity reduced to nil. Fat and lactose contents of the residue also reduced considerably. Washing of residue with 50% alcohol followed by cooking in baking soda, i.e., treatment IV was reported to be the best as far as removal of excess fat from the residue was concerned. Autoclaving of this residue after incorporating 2% vinegar lowered the moisture content and improved the texture of the product. Keeping quality of all types of GR clarified at 120°C is 3 months. Its shelf life can be further extended to more than 4 months by pressing it in cake form.

Table 46.1 Comparison of chemical composition of ghee-residue subjected to various processing treatments

Particulars	Treatment I		Treatment II		Treatment III		Treatment IV	Treatment V		Treatment VI
	Before	After	Before	After	Before	After	After	Before	After	After
Acidity (ml N/10 NaOH/g)	18.8	9.2	20.6	---	18.1	10.3	---	20.6	5.0	---
Moisture	13.3	49.7	13.8	65.0	15.3	61.5	70.7	13.8	49.0	68.0
Fat	52.2	26.7	49.8	18.5	46.8	18.2	15.0	49.8	22.0	15.4
Protein	19.7	17.6	19.9	10.8	19.9	16	10.1	19.9	23.6	12.0
Lactose	11.5	3.8	12.5	2.5	13.1	1.1	1.6	12.5	1.2	1.4
Ash	3.3	2.2	4.0	3.2	4.3	2.3	2.6	4.0	3.2	3.2

Treatment I Loosely tying the residue in the form of bundle and cooking in boiling water for 30 min.

Treatment II Cooking the residue in boiling 1.0% sodium bicarbonate for 30 min.

Treatment III Washing the residue with 50% alcohol and then cooking in boiling water for 30 min.

Treatment IV Washing the residue with 50% alcohol followed by boiling in 1% sodium bicarbonate.

Treatment V Autoclaving the residue (15 PSI/10 min) obtained from III after incorporating 2% vinegar

Treatment VI Autoclaving the residue obtained from IV after incorporating 2% vinegar.

Sripad *et al*, (1996) reported that addition of ethanol extracts of browning compounds (1%) from defatted GR to cow and buffalo ghee clarified at 100°C and stored at 37°C extended the shelf life by about 1.5 and 2 months respectively.

46.4 Applications of Ghee-Residue

46.4.1 Preparation of confections

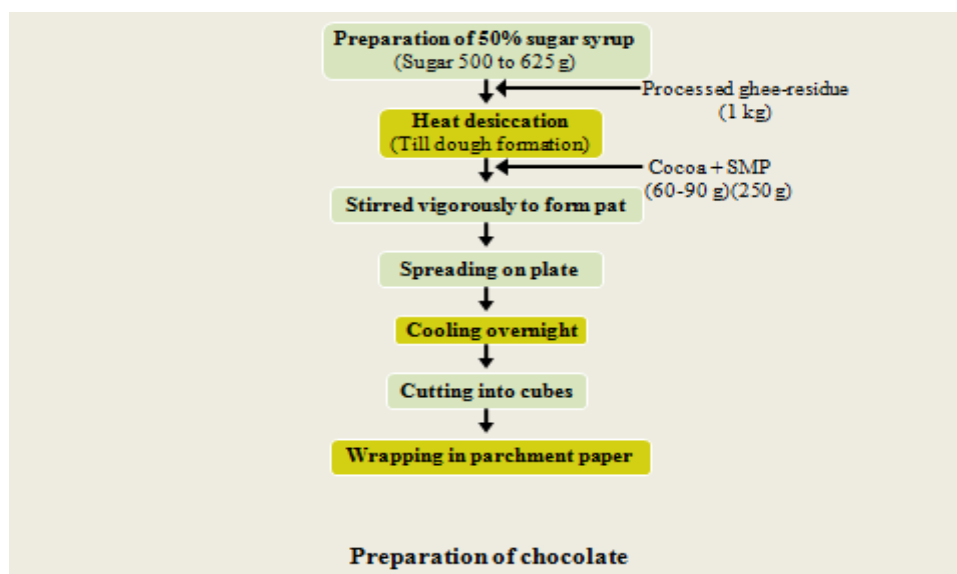
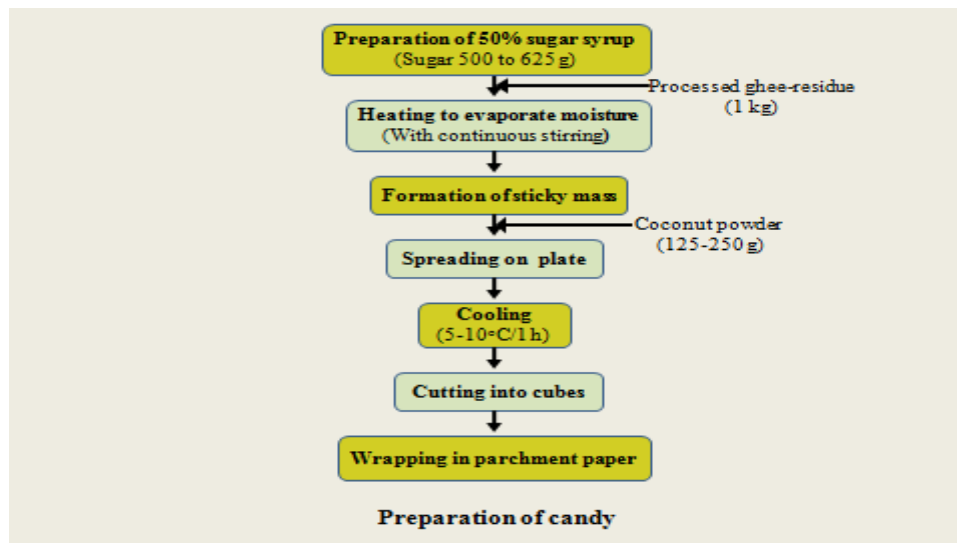
The physico-chemical properties of processed GR make it suitable for preparation of confections. It contains the major constituents in suitable proportion and possesses fine texture that imparts requisite body to such products. Further the treatment during processing of these confections involves heating to such an extent that it completely arrests enzymatic activity and flavour deterioration in the final product. The higher fat content in the residue quite often obviate the need for addition of oils and fats in its preparation.

46.4.1.1 Preparation of candy

The recipe for candy preparation consists of 1 kg processed ghee-residue, 500 to 625 g sugar and 125 to 250 g dry coconut powder. 50% sugar syrup is prepared and processed ghee residue is thoroughly mixed in it with the help of suitable ladle (Fig.46.2). The mixture is heated on low fire with continuous stirring to evaporate moisture. When the mass becomes sufficiently sticky, coconut powder is added. The candy is evenly spread on a plate and cooled (5-10°C) for about an hour and cut into small cubes and wrapped in parchment paper.

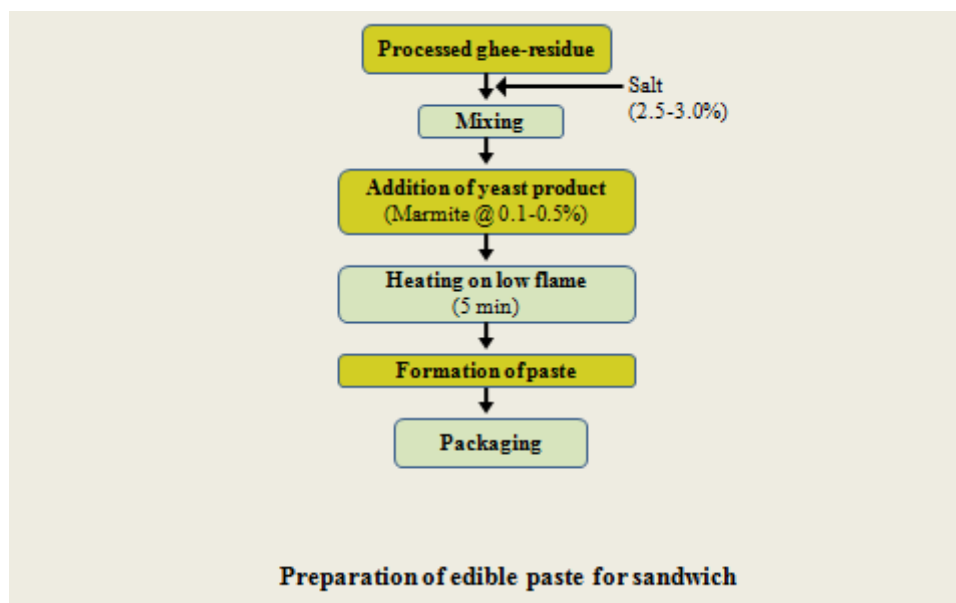
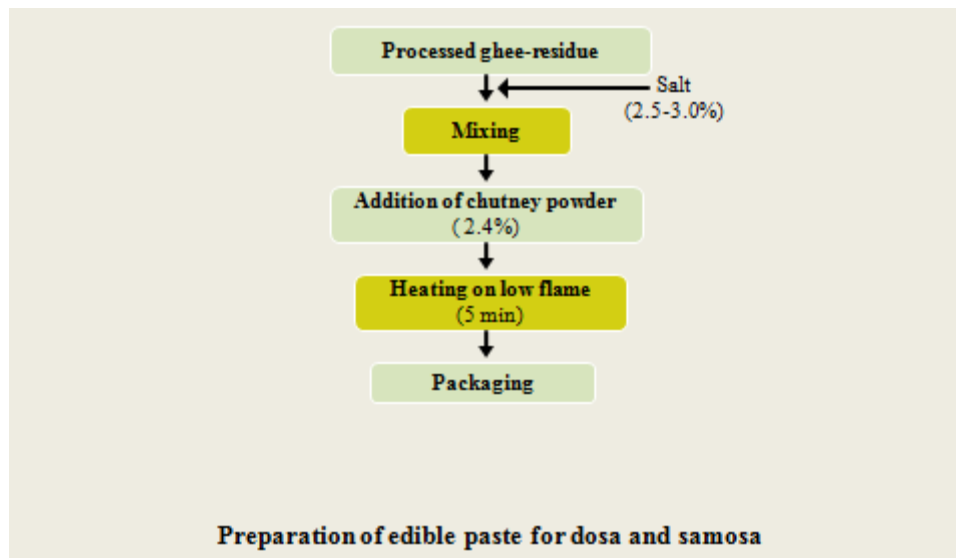
46.4.1.2 Preparation of chocolate

The recipe for preparation of chocolate consists of 1 kg processed ghee-residue, 500 to 625 g sugar, 60 to 90 g cocoa powder and 250 g skim milk powder. 50% sugar syrup is prepared and processed ghee-residue is thoroughly mixed in it with the help of suitable ladle (Fig.46.3). The contents are desiccated on a low flame till dough is formed. At this stage cocoa and skim milk powder are added and stirred vigorously till pat is formed. Finished product is spread on a plate and cooled overnight in refrigerator and cut into slabs or cubes and wrapped in parchment paper. The product has a shelf life of more than 3 months.



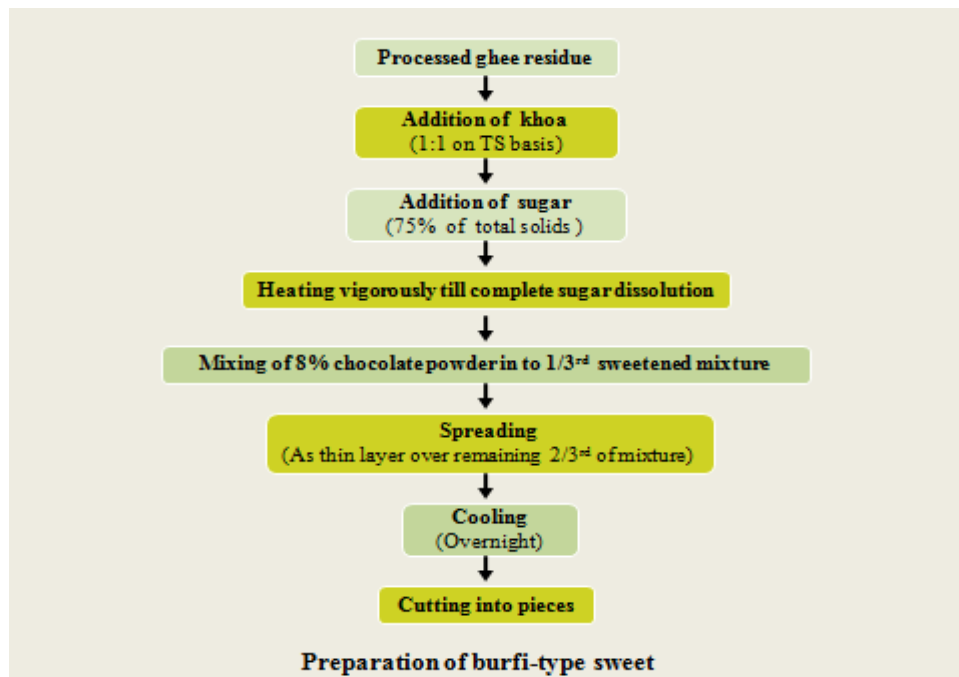
46.4.2 Preparation of edible pastes

For preparation of edible paste for sandwich, processed ghee-residue is first mixed with 2.5-3% salt and then 0.1-0.5% marmite (a yeast product). The whole mass is heated on a low fire for about 5 min till a paste is formed (Fig.46.4). An edible paste for 'dosa' and 'samosa' can be prepared if 2-4% chutney powder is used instead of marmite. Both these preparations, if properly packaged, can remain marketable for 2 months.



46.4.3 Preparation of burfi-type sweet

Processed ghee-residue is mixed with khoa in the proportion of 1:1, on total solids basis. Sugar is added @75% of the total solids (khoa + ghee-residue). The whole mass is heated and worked rigorously for 10-15 minutes so as to dissolve the added sugar completely. At this stage about one-third of the sweetened mass is separated and 8% chocolate powder (Fig.46.5), on total solids basis, is added to processed ghee residue and khoa and thoroughly mixed. This portion containing the dissolved chocolate is applied as a thin layer over the remaining two-third of the mixture, which has already been spread-out as a thick layer on a well-greased tray. The mass is cooled and when set, cut into pieces of uniform size and shape.



[Click for PPT \(Fig. 46.5 Preparation of burfi-type sweet\)](#)

46.4.4 Preparation of bakery products

Nankatai type cookies and sponge cake can be prepared from processed ghee-residue obtained from ripened cream. 30 and 20% part of vanaspati fat used in preparation of cookies and sponge cake, respectively is replaced by ghee-residue fat. Use of ghee-residue enriches both the bakery products in protein content.

46.4.5 Broiler/animal feeds

Ghee-residue because of its nutritional value is used as broiler feeds up to 20% in broilers diet. It can also be served as feed to animals with combination with other feeds.

***** 😊 *****

Lesson 47

**NUTRITIONAL CHARACTERISTICS OF SKIM MILK AND ITS BY-PRODUCTS,
BUTTERMILK AND GHEE-RESIDUE**

47.1 Introduction

Skim milk, buttermilk, ghee-residue and further derived by-products from them contain valuable milk nutrients. Each and every component of milk that is passed on to these by-products has its unique nutritional value. Skim milk and buttermilk are rich in solid-not-fat portion of milk, while ghee-residue is rich in all the milk components, but in modified forms.

47.2 Nutritional Characteristics of Skim Milk & Its By-products

Skim milk lacks the fat and the accompanying vitamin A of whole milk, but is rich in protein, lactose, calcium, phosphorus, and riboflavin. It is nutritionally important for those people, who are suffering from heart diseases. It is valued largely for its high quality proteins, which make up 41% and 37% of total solid content in buffalo and cow milk, respectively. Casein is the major protein in skim milk. With a content of 0.7-0.9% phosphorus, covalently bound to the casein by a serine ester linkage, casein as a phosphoprotein is a member of a relatively rare class of proteins. The phosphate groups bind bivalent minerals such as Ca^{2+} . Skim milk is an important source of calcium in readily available form. It provides up to 75% of total calcium intake in western countries. Increased calcium intake results in significant reduction in blood pressure by (i) increasing the urinary excretion of sodium, (ii) preventing the rise in vitamin D hormone, which increases blood vessel resistance, (iii) relaxing smooth muscle cells that line the blood vessels, (iv) suppressing the renin-angiotensin system and (v) increasing production of endothelial relaxing factors. The nutrition provided by skim milk accounts for 55% of the total energy of whole milk. Various by-products are prepared from skim milk.

47.2.1 Casein

Casein is nutritionally an excellent protein due to its high proportions of essential amino acids. Essential amino acid composition of various casein products is given in Table 47.1. Casein contains 45% essential amino acids. The Biological Value (BV), Net Protein Utilization (NPU) and Protein Efficiency Ratio (PER) for casein are 77, 76 and 2.5, respectively, which are mostly unaffected by the processing conditions usually employed during the dairy operations. PER value of lactic and rennet casein is 2.51 and 2.45, respectively. Casein has the primary function in the nutrition of the new born, supplying not only amino acids, but also minerals mainly calcium and phosphorus. Casein also has been demonstrated to be possessing anticarcinogenic properties. Casein inhibits fecal β -glucuronidase, an enzyme produced by intestinal bacteria, which deconjugates procarcinogenic glucuronides to carcinogens. Casein derived peptides isolated from the microbial fermentation of milk inhibit colon cancer by altering cell kinetics. Several peptides with opium like (sleep inducing) activity have been extracted from the casein include β -casomorphins (from β -casein) and exorphin

(from α_{S1} casein). These opium-like peptides have been shown to prolong gastrointestinal transit time exerting anti-diarrhoeal effect. These also stimulate secretion of insulin and somatostatin.

Table 47.1 Essential amino acid composition (in mg amino acid/g N) of FAO reference protein and various casein products

Essential amino acid	FAO reference point	Casein	Sodium caseinate	Calcium caseinate	Co-precipitate
Isoleucine	250	345	325	328	338
Leucine	440	607	613	589	612
Lysine	340	518	494	480	503
Methionine+ ½ cystine	220	201	202	199	230
Phenylalanine+ tyrosine	380	705	661	665	674
Threonine	250	297	253	265	272
Tryptophan	60	ND	77	75	ND
Valine	310	430	414	412	406
Total essential amino acids	2250	3103	3039	3013	3035

47.2.2 Caseinates

Nutritional characteristics of casein remain similar when it is prepared in its solubilized form e.g. sodium and calcium caseinates. In addition to provide casein, calcium caseinate also provides the valuable and highly bioavailable mineral calcium. Calcium is important to bone, tendon as well as muscle growth. The protein efficiency ratio (PER) of sodium and calcium caseinates is reported to be 2.57 and 2.59, respectively.

47.2.3 Casein hydrolysates

Casein hydrolysates are partly to fully digested casein. Nutritionally, protein hydrolysates are particularly useful to people suffering from protein allergy and for the management of patients with various digestive disorders as a result of pancreatic malfunction, pre-and post-operative abdominal surgical patients, patients on geriatrics and convalescent feeding and other who for various reason are not able to ingest a normal diet. Absorption of short-chain peptides (mainly, di- and tripeptides) is considered a more efficient compared to an equivalent amount of free amino acids. Hydrolysates containing peptides with a high ratio of branched-chain amino acids (BCAA) to aromatic amino acids (AAA), referred to as Fischer's ratio, are used in specific medical diets.

47.2.4 Co-precipitates

Co-precipitates of milk proteins contain not only casein, but also whey proteins, which contain a relatively high concentration of sulphur-containing amino acids, cysteine and cystine, contributing to the higher biological value of co-precipitates. Calcium concentration is in the range of 0.1-3.0% and depends on the thermal treatment, the added quantity of CaCl_2 , and the pH value of the medium. A high calcium co-precipitate is nutritionally much superior to casein.

47.3 Nutritional Characteristics of Buttermilk

Buttermilk is luscious, low-fat and loaded with health benefits. It contains all the non-fat components present in milk like casein, whey protein, lactose, minerals, vitamin A, α -tocopherols and cholesterol. It is a good source of valuable milk proteins, lactose and larger proportion of milk fat globule membrane (MFGM) proteins; Phospholipids component of MFGM is considered beneficial for its various health-related properties. The nutritive value of buttermilk is as high as fermented milk and favours the opinion of diet conscious people, since it contains very less quantity of fat but has high content of phospholipids that perform a wide range of biological functions and are significant in human nutrition. Phospholipids have anti-ulceral properties, work as anti-tumor-promoters and aid in the cure of intestinal illness. The phospholipids of buttermilk have more or less equal proportion of lecithin, sphingomyelin, and cephalin together with small proportion of cerebrosides. Lecithin is widely used to stabilize the fat components of the products and has health benefits such as prevention and curing of memory loss, high blood cholesterol and nervous disorder (Brown, 1990). Sphingomyelin prevents water loss through skin and genetic disease and lowers blood cholesterol level. Successful attempts were made by Corredig *et al.* (2003) to isolate the phospholipids rich MFGM material. Such isolates can be used as functional ingredients in the development of nutraceuticals.

The consumption of buttermilk has been found to lower blood pressure and reduce the serum cholesterol level. Buttermilk is sometimes, recommended for the prevention and treatment of diarrhea in infants. The famous classified Ayurvedic medicine "Takrarishta", in which buttermilk is the chief ingredient, is helpful in many diseases such as gastrointestinal upsets, acute and chronic condition and first-degree piles with bleeding or non-bleeding. In jaundice and alcoholic liver diseases, regular use of buttermilk immensely helps the patients to regain appetite (Anon, 2003). In addition, buttermilk has recently gained attention as a potential source of functional ingredients.

Desi buttermilk (*lassi*) has therapeutic value in addition to being nutritive. In addition to normal milk constituents, *lassi* is also a rich source of vitamins. Buttermilk's active cultures fight undesirable bacteria and help to stimulate the immune system. Many people, who are lactose-intolerant, can use desi buttermilk because the cultures convert lactose partially into more digestible lactic acid. *Lassi* has a similar place in the diet as other cultured milk products, but over and above, it has beneficial effects in the treatment of patients suffering from acute hepatitis and from a sepsis of the mucous lining of the stomach. Irish folklore claims- a glass of buttermilk will cure a hangover, and when heated with cloves and garlic, it was sure to cure any variety of ailments.

Buttermilk powder is low in fat and provides an excellent source of all nutrients of buttermilk in concentrating form.

47.4 Ghee-Residue

Ghee-residue contains good quantities of milk fat, protein and minerals. Therefore, it can be used as human dietary supplement. But it has poor quality of protein because of its lower lysine content. When it is treated at high temperature (105-110°C), some of lysine and other essential amino acids are lost. The lack of lysine in ghee residue is the most dominant factor in depressing the PER of ghee-residue and damage of some essential amino acids is responsible for low protein nutritional value of ghee residue. Relwani (1978) reported that supplementation of ghee residue with some good quality protein such as skim milk powder (SMP) sharply increased its protein efficiency ratio (PER) from 0.66 to 2.4. Supplementation with 8% lysine, 2.5% methionine and 1.4% tryptophane strikingly improved its nutritive value which was even slightly higher than SMP (Table 47.2).

Table 47.2 Nutritive value of ghee-residue

Diet	Protein Efficiency Ratio	Digestibility Coefficient	Biological Value (%)	Net Protein Utilization (%)
Skim Milk Powder	3.92	93.61	91.99	86.12
Ghee-residue	0.75	62.65	65.07	40.77
Ghee-residue + 8% lysine	3.24	82.48	77.87	64.23
Ghee-residue + 8% lysine + 2.5% Methionine + 1.4% Tryptophane	4.11	86.24	93.84	80.64

***** 😊 *****

Lesson 48

NUTRITIONAL CHARACTERISTICS OF WHEY AND ITS BY-PRODUCTS

48.1 Introduction

The composition of whey and whey by-products varies considerably, depending on milk source and the manufacturing processes involved. Approximately 54% of the nutrients from milk are found in the fluid sweet whey of Cheddar cheese, while about 73% of the nutrients of the non-fat milk used for Cottage cheese show up in fluid acid whey. Being a rich source of lactose, whey is a good fermentation medium for a number of fermented products. In many applications, lactose in whole or deproteinised whey is hydrolysed to glucose and galactose. In the future, one of the most dynamic uses of whey by-products will continue to be as nutritional ingredients.

48.2 Nutritional Characteristics of Whey

In general, whey is rich in lactose, proteins, minerals and vitamins. Lactose acts as a major source of energy with high calorific value. Numerous studies have demonstrated that lactose increases calcium absorption and retention. It may also improve the absorption of magnesium and zinc. In animal studies, lactose extended life expectancy and reduced the accumulation of body fat. The proteins in whey are complete and of exceptional quality. They contain, in varying amounts and in the right proportion, all the amino acids required by humans, among which sulfur amino acids are particularly valuable owing to their anticancer activities. They are also readily digestible and completely bio-available. Clearly, whey proteins are among the most valuable component of whey. Whey proteins, though present in small quantities, have high protein efficiency ratio (3.6), biological value (104) and net protein utilisation (95), and are next only to egg protein in terms of nutritive value.

Whey is also rich source of Ca, P and water soluble vitamins. As the pH of milk decreases, more of the salts dissociate. This results in higher concentrations of soluble calcium, magnesium, zinc and phosphorous in acid whey. The concentration of calcium and other minerals may be altered during whey processing. The ratio of Ca:P is about 0.8 in whey (Modler, 2000); this is a high Ca:P ratio compared with other food products. Whey minerals are involved in the regulation of the water flow by osmosis between different regions of the body. Further, the composition of whey salts reveals a low ratio of sodium/potassium, which is important for preventing elevated blood pressures (hypertension). It also contains copper, zinc and iron as minor constituents. Zinc performs many functions, like the stimulation of the insulin activity for the absorption of glucose from blood. Iron is part of several metalloproteins such haemoglobin, lactoferrin, lactoperoxidase, catalase and supports several important functions as a carrier of oxygen.

Glycomacropeptide (GMP) derived from *k*-casein induces production of cholecystokinin, a hormone associated with satiety. GMP inhibits the adhesion of oral actinomycetes and streptococci to erythrocytes, and binding of cholera toxins to its receptor. GMP is free from aromatic amino acids, and therefore a suitable protein substitute for those suffering from hereditary disorder of aromatic amino acid metabolism, such as phenylketonuria.

48.3 Nutritional Characteristics of Whey By-products

48.3.1 Condensed whey

Condensed whey contains whey constituents in more concentrated form. Whey solids in the form of condensed whey is a cheap source of high-quality proteins and carbohydrate and the fat is generally removed by centrifugation. Sweetened condensed whey contains sugar equal to the weight of solids in whey which is a source of energy.

48.3.2 Whey powder

Whey powder is the dried form of whey that contains relatively high concentration of all whey constituents including lactose and protein. In the presence of moisture, lactose and protein readily participate in the maillard reaction. This interaction may result in a decrease in protein quality, which is accompanied or followed by undesirable colour changes. During drying, high heat denatures whey proteins, destroying some bioactive compounds, such as the amino acid cystine. Acid whey powder from Cottage cheese and related products contains approx. 65 percent lactose, 12 percent protein, 6 percent lactic acid, 2.5 percent moisture and large quantities of calcium; in fact, all of the calcium that originally existed in the milk. Furthermore, acid whey powder contains the vitamin B complex, vitamin C, and the natural milk fermentation flavour compounds, like diacetyl. Essential mineral content in acid and sweet whey powder is given in Table 48.1.

Because of low concentrations of sodium, potassium and chloride, but high lactose and high-quality whey proteins contents, demineralised whey powder at 90% demineralization level is eminently appropriate for the preparation of infant formulae for meeting the nutritional requirements of infants.

Table 48.1 Essential mineral content in acid and sweet whey powder

Minerals	WHO recommended Daily intake* Adult male	Acid whey powder content/100g**	Sweet whey powder content/100g**
Calcium	500 mg	2,054 mg	796 mg
Zinc	22 mg	6.31 mg	1.97 mg
Magnesium	300 mg	199 mg	176 mg
Phosphorus	-----	1,348 mg	932 mg

*World Health Organization, 1974.

**Potosi and Orr, 1976.

48.3.3 Whey based beverages

Whey based soups and fruit beverages possess low protein and high carbohydrate content. The high carbohydrate content is mainly due to the high lactose content of the whey, which contributes little to the product sweetness. Fruits are good source of ascorbic acid and fruits and vegetables contain flavonoids. These flavonoids influence the blood circulation, increasing the permeability and

elasticity of capillary vessels and have a protective action against infections of the respiratory system. Soups are served as appetizers before meals as they stimulate the secretion of gastric enzymes that leads to feeling of hunger. Some lactic acid bacteria particularly *L. acidophilus* enhances nutritional properties and adds certain therapeutic attributes to beverages. Further, antibacterial substances produced during fermentation have curative properties in controlling several gastro-intestinal disorders. Fermented whey beverages can also be enriched with probiotic and prebiotic substances. Probiotics are the live microbes which when administered in adequate amounts confer a health benefit on the host. They reduce blood cholesterol, maintain intestinal health, alleviate intestinal bowel diseases, modulate immune system, reduce incidence of gastrointestinal (GI) infections, reduce incidence of urinary and vaginal infections, alleviate lactose intolerance, anti-cancerogenic and anti-tumorogenic, reduce incidence and severity of diarrheal diseases while prebiotics like fructooligosaccharide and galactooligosaccharide are the non-digestible food ingredients that beneficially affects the host by selectively stimulating the growth and/or activity of one or a limited number of bacteria in the colon, and then improve host health.

48.3.4 Fermented whey products

Whey being rich source of lactose, there is a good potential for production of fermented products like microbial biomass, alcohol, galactose, lactic acid, other organic acids, flavour concentrates, vitamins etc. Fermented whey products like food yeasts are highly nutritious nontoxic source of proteins and vitamins and under right circumstances, can find application in human and animal nutrition. Calcium lactate, being an easily re-absorbed calcium salt, offers an attractive way to improve the calcium intake potential in products for mineral deficient consumers.

48.3.5 Whey protein products

Whey protein concentrates (WPC), whey protein isolates (WPI) and whey protein hydrolysates are the whey protein products. Whey protein concentrates (WPC) contain 30-85% protein by weight and are indeed very rich in high quality whey proteins. Besides having functional properties, WPC improves the nutritional attributes of the product. The PER value of whey protein concentrates is similar to that of egg protein, i.e. it is higher than that of milk powder and of other milk protein products (caseinates, co-precipitates). The high protein and low fat content of whey protein concentrates makes them particularly suitable for incorporation into special diets which are thereby enriched with high quality protein. These products have been recommended for slimming diets, diets for patients suffering from hyperlipoproteinaemia and generally for feeding patients, particularly those suffering from liver and gall bladder diseases and from diabetes. They are especially suitable for addition to baby foods as well as to the diets of sportsmen, children and elderly people who also have benefits from a product rich in high quality protein.

Whey protein isolates in its purest form contains 90-98% protein, but no fat, lactose or cholesterol. It is packed with loads of essential and non-essential amino acids. Whey proteins are an excellent protein choice for individuals of all ages. They contain higher levels of bioactive compounds. Their content of essential amino acids is always greater than that of the FAO reference protein. This applies also to methionine and cystine. Whey proteins also have the highest levels of BCAAs (Branched

Chain Amino Acids), which results in building and retaining muscle tissue of any natural food source and have been shown to boost immune system functioning and also helpful in blood sugar control. The quality of proteins in whey is incomparable. They provide a number of benefits in areas including sports nutrition, weight management, immune support, bone health, and general wellness. Whey proteins have recently been shown to have potential positive impact in other areas including appetite suppression, cholesterol reduction, and the inhibition of dental plaque and dental caries. It enhances the production of glutathione, one of the body's most powerful natural antioxidants. Therefore, whey proteins aid in improving the body's immune system, by acting as an antioxidant.

Whey protein hydrolysates find uses in high value specialist nutritional applications such as tube-feeding preparations or special dietary supplements. In a hydrolysate, we might seek to get all the protein into peptides of two to five amino acids, with few free amino acids and no larger peptides. Interestingly, some peptides released from milk proteins can be biologically active. Some can transport calcium from the gut into the blood during digestion, some can inhibit enzymes in the human body involved in excessive blood pressure and some can induce sleepy feelings. Hydrolyzed whey proteins can significantly increase glutathione level within the prostate epithelium. This represents a potential mechanism by which whey protein isolate can provide protection against the development of prostate cancer. Hydrolyzed Whey Proteins assist in reducing the blood pressure of hypertensive individuals by inhibiting ACE (Angiotensin Converting Enzyme). Without ACE, the changes in the body that result in hypertension cannot occur.

48.3.6 Lactose and its hydrolysed products

From the nutritional point of view, lactose is very important. Compared to other sugars such as sucrose, lactose produce minimal tooth decay. Several investigations have shown that lactose promotes the utilization of calcium, magnesium and phosphorus. The acidic condition created due to fermentation of lactose by intestinal bacteria may increase the solubilisation and absorption of calcium. Part of the effect may also be due to the ability of lactose to form soluble complex with calcium. Lactose promotes the diffusion of calcium across the intestinal wall, which is the only route of calcium transport in human infant, since the active transport system is not developed at the time of birth. The slow hydrolysis of lactose by the body during digestion generates a prolonged energy supply. Lactose stimulates the growth of acid forming lactobacilli in the intestinal tract. Recent nutritional studies suggest that lactobacilli helps to fight intestinal disorders and that lactose could be used in dietary therapy for ailing infants. In the gut, it is usually hydrolysed by β -galactosidase to glucose and galactose along with some oligosaccharides, commonly known as galactosyloligosaccharide (GOS). GOS are an interesting class of nutraceuticals having prebiotic properties. Lactose has relatively low glycemic index and low carcinogenicity, and is a precursor for other bioactives such as lactulose and lactobionic acid. Lactulose, a disaccharide, originally not present in milk, is produced from lactose during heating or long storage. It is not hydrolysed by intestinal lactase, and hence passes almost completely into large intestine where it is fermented by *Bifidobacterium bifidus* and *L. acidophilus* to produce lactic acid. Microbial flora in the intestine of infant fed on mother's milk consists almost entirely of anaerobic lactobacilli, e.g., *B. bifidus*. Glycoproteins and oligosaccharides, present in mother's milk in high concentration, promote the

growth of *bifidus* bacteria and thus provide baby resistance against intestinal infection.

ANNEXURE - I

FSSAI (2011) Microbiological parameters of edible casein, caseinates and whey powder

S. No.	Requirements	Sampling plan	Edible casein, caseinates, whey powder
1.	Total Plate Count ¹	m M	40,000/g 50,000/g
2.	Coliform Count ²	m M	10/g 50/g
3.	<i>E.coli</i> ³	M	Absent/g
4.	<i>Salmonella</i> ⁴	M	Absent /25g
5.	<i>S. aureus</i> ⁵ (coagulase positive)	M	Less than 10/g
6.	Spore Count: (a) Aerobic ^{6a} (<i>B. cereus</i>) (b) Anaerobic ^{6b} (<i>Clostridium perfringens</i>)	m M m M	100/g 1000/g 10/g 100/g
7.	<i>Listeria monocytogenes</i> ⁷	M	Absent/g
8.	Sampling Guidelines	n 1-7 c Storage & transport Sample size	5 2 ^{1,2,6a,b} 0 ^{3,4,5,7} Ambient, max. 30°C 100g

Hydrolysed lactose is nutritionally beneficial for lactose intolerant peoples. Galactose is important for the development of cerebrosides.

48.3.7 Milk mineral product

Milk mineral products rich in natural milk calcium and phosphate are valuable nutritional supplements in today osteoporosis-sensitive world. Milk minerals are used as a natural calcium supplement in health foods. Calcium and phosphate support the growth of bones and teeth, and also perform a variety of other functions in the body. Calcium from milk is readily absorbed in the intestinal tract, which is facilitated by the presence of lactose. The presence of phosphate reduces the excretion of calcium in urine.

Sampling plan and interpretation:

The following terms, as used by the International Commission on Microbiological Specifications of Foods (ICMSF) are defined and used in this standards:

n = The number of sample units which must be examined from the batch/lot of food to satisfy the requirements of a particular sampling plan.

c = the maximum allowable number of defective sample units. This is the number of sample units, which may exceed the microbiological limit specified by m . These are considered marginally acceptable results provided they did not exceed the limit specified by M . When more than this number is found; the lot is rejected by the sampling plan.

m = Represents an acceptable level and values above it are marginally acceptable in terms of the sampling plan.

M = A microbiological criterion which separates marginally acceptable quality from unsatisfactory/potentially hazardous quality. Values above M are unacceptable in terms of the sampling plan and detection of one or more samples exceeding this level would be cause for rejection of the lot.

When 5 or more units of the same variety from a lot or consignment are analyzed ($n=5$), no more than 2 units ($c=2$) should exceed the maximum tolerance (m) for microbiological levels stated in the reference criteria and no 1 unit should exceed the stated level for the maximum tolerance (M).

Microbiological criteria and their interpretation:

1. Satisfactory: if a maximum of c/n value are between m and M , and the rest of the values observed are $< m$ --- means the results are within limits of acceptable microbiological quality and no action is required.
2. Unsatisfactory: If one or more of the values observed are $>M$ or more than c/n values are between m and M --- means the results are outside acceptable microbiological limits linked with hygiene indicators (Total plate count, Coliform count and Yeast and mold count) and are indicative of poor hygiene or poor handling practices.
3. Potentially hazardous: If one or more of the values observed are $>M$ or more than c/n values are between m and M --- means the results are outside acceptable microbiological limits linked with pathogenic bacteria (*E. coli*, *Salmonella*, coagulase positive *Staph aureus*, *B. cereus*, *Cl. Perfringens*, *L. monocytogenes*) and are indicative of serious food safety concern and immediate remedial action should be initiated. Such results will attract enforcement/prosecution by the concerned food safety authorities.

***** 😊 *****

This Book Download From e-course of ICAR

VISIT FOR OTHER AGRICULTURE BOOKS, NEWS,
RECRUITMENT, INFORMATION, AND EVENTS AT

WWW.AGRIMOON.COM

Give FeedBack & Suggestion at info@agrmoon.com

DISCLAIMER:

The information on this website does not warrant or assume any legal liability or responsibility for the accuracy, completeness or usefulness of the courseware contents.

The contents are provided free for noncommercial purpose such as teaching, training, research, extension and self learning.

***** 😊 *****