Unit I - Topic 6

Freeze and Membrane Concentration

FREEZE CONCENTRATION

23.1 Introduction

Freeze concentration is an excellent alternative to evaporation and reverse osmosis for concentration of many liquid foods. Product quality is generally high since low temperatures are used and no vapor-liquid interface occurs. However, current commercial freeze concentration technology is not economically competitive with the more established alternatives. Freeze concentration is applied where focus is on aroma retention and high quality products. It is specially suited for heat sensitive products. Freeze concentration is used for coffee extracts, fruit juices, vinegar, beer, wine and practically any other aqueous solution .

23.2 Process

- Freeze concentration has been practiced for centuries. In its earliest form it was as simple as leaving a barrel of liquid outside in the cold winter night. Water would crystallize and grow as a thick layer of ice along the inside walls of the barrel. The next day they would simply cut a hole through the ice shell and drain the now concentrated product. The water (now ice) was simply discarded.
- Understanding the principles by which ice crystals grow in fluid foods would aid in furthering freeze concentration technology. In particular, if optimal heat balance conditions can be maintained throughout the freeze concentration process, large, easily separated crystals can be grown in short times. Modern freeze concentration processes consist of a crystallization section, where part of the water is converted into solid ice crystals using a refrigeration system. The ice crystals are then separated by filters, centrifuges or using the wash columns.
- Now, through a process of innovative engineering, process simplification and component standardization, the patented technology has reduced both equipment costs and energy usage significantly making Freeze Concentration a practical option for the constantly growing number of applications throughout the food and drink sector.

23.3 Freeze Drying

Freeze-drying (also known as lyophilization or cryodesiccation) is a dehydration process typically used to preserve a perishable material or make the material more convenient for transport. Freeze-drying works by freezing the material and then reducing the surrounding pressure and adding enough heat to allow the frozen water in the material to sublime directly from the solid phase to gas. Freeze drying is a superior preservation method for a variety of food products and food ingredients. The plant sizes available ranges from pilot scale to large industrial batches and continuous plants. During the freeze drying process deep-frozen products are dried at temperatures below -18°C in freeze dryer. No thawing of the product takes place, which ensures a high quality product.

23.4 Advantages of Freeze drying

The modern plants provide high-quality products for customers as well as unrivalled financial and operational advantages for the company by eliminating product loss, reduced energy costs and maximizing plant reliability and ease of use. Other benefits are:

- The plants offer an advanced technology and efficient design to ensure the preservation of excellent quality in a wide range of food products, such as vegetables, temperate and tropical fruits, fish, meat, TV-dinners, coffee, flavour essences and several other products.
- The original flavour, proteins and vitamins are preserved.The products will retain their original shape, colour and texture.
- Re-hydration is rapid and complete.
- The process results in stable products with long shelf life.
- The products are durable at a wide range of temperatures, eliminating the need for complicated cold chain distribution systems.
- The low weight and easy handling of freeze dried products reduce shipping costs dramatically.

23.5 Applications of freeze-drying

Freeze-drying is a relatively expensive process. The equipment is about three times as expensive as the equipment used for other separation processes, and the high energy demands lead to high energy costs. Furthermore, freeze-drying also has a long process time, because the addition of too much heat to the material can cause melting or structural deformations.

- Therefore, freeze-drying is often reserved for materials that are heat-sensitive, such as proteins , enzymes , microorganisms , and blood plasma . The low operating temperature of the process leads to minimal damage of these heat-sensitive products.
- Freeze-drying is used to preserve food and make it very lightweight.
- The process has been popularized in the forms of freeze-dried ice cream, an example of astronaut food.
- It is also popular and convenient for hikers because the reduced weight allows them to carry more food and reconstitute it with available water.
- Instant coffee is sometimes freeze-dried, despite high costs of freeze-dryers. The coffee is often dried by vaporization in a hot air flow, or by projection on hot metallic plates.
- Freeze-dried fruit is used in some breakfast cereal.

- However, the freeze-drying process is used more commonly in the pharmaceutical industry.
- In bacteriology freeze-drying is used to conserve special strain.

23.6 Freezing

- The freezing process consists of freezing the material.
- In a lab, this is often done by placing the material in a freeze-drying flask and rotating the flask in a bath, called a shell freezer, which is cooled by mechanical refrigeration, dry ice and methanol, or liquid nitrogen.
- On a larger-scale, freezing is usually done using a freeze-drying machine. In this step, it is important to cool the material to the lowest temperature at which the solid and liquid phases of the material can coexist. This ensures that sublimation rather than melting will occur in the following steps
  - Larger crystals are easier to freeze-dry.
  - To produce larger crystals, the product should be frozen slowly or can be cycled up and down in temperature.
  - This cycling process is called annealing.
  - However, in the case of food, or objects with formerly-living cells, large ice crystals will break the cell walls.
  - Usually, the freezing temperatures are between −50°C and −80°C.
  - The freezing phase is the most critical in the whole freeze-drying process, because the product can be spoiled if badly done.
  - Amorphous (glassy) materials do not have a eutectic point, but do have a critical point, below which the product must be maintained to prevent melt-back or collapse during primary and secondary drying.
  - Large objects take a few months to freeze-dry.

23.7 Primary Drying

1. During the primary drying phase, the pressure is lowered (to the range of a few millibars), and enough heat is supplied to the material for the water to sublimate.

2. The amount of heat necessary can be calculated using the sublimating molecules' latent heat of sublimation.

3. In this initial drying phase, about 95% of the water in the material is sublimated.

4. This phase may be slow (can be several days in the industry), because, if too much heat is added, the material's structure could be altered.

5. In this phase, pressure is controlled through the application of partial vacuum.

6. The vacuum speeds sublimation, making it useful as a deliberate drying process.

7. Furthermore, a cold condenser chamber and/or condenser plates provide a surface(s) for the water vapour to re-solidify on.

8. This condenser plays no role in keeping the material frozen; rather, it prevents water vapor from reaching the vacuum pump, which could degrade the pump's performance. Condenser temperatures are typically below −50°C.

9. In this range of pressure, the heat is brought mainly by conduction or radiation; the convection effect can be considered as insignificant.

23.8 Secondary Drying

1. The secondary drying phase aims to remove unfrozen water molecules, since the ice is removed in the primary drying phase.

2. This part of the freeze-drying process is governed by the material’s adsorption isotherms.

3. In this phase, the temperature is raised higher than in the primary drying phase, and can even be above 0°C, to break any physico-chemical interactions that have formed between the water molecules and the frozen material.

4. Usually the pressure is also lowered in this stage to encourage desorption (typically in the range of microbars, or fractions of a pascal). However, there are products that benefit from increased pressure as well.

5. After the freeze-drying process is complete, the vacuum is usually broken with an inert gas, such as nitrogen, before the material is sealed.

6. At the end of the operation, the final residual water content in the product is around 1 to 4%, which is extremely low.

23.9 Properties of Freeze-Dried Products

- If a freeze-dried substance is sealed to prevent the re-absorption of moisture, the substance may be stored at room temperature without refrigeration, and be protected against spoilage for many years. Preservation is possible because the greatly reduced water content inhibits the action of microorganisms and enzymes that would normally spoil or degrade the substance.
- Freeze-drying also causes less damage to the substance than other dehydration methods using higher temperatures.
- Freeze-drying does not usually cause shrinkage or toughening of the material.
- In addition, flavours and smells generally remain unchanged, making the process popular for preserving food. However, water is not the only chemical capable of

sublimation, and the loss of other volatile compounds such as acetic acid (vinegar) and alcohols can yield undesirable results.

Freeze-dried products can be re-hydrated (reconstituted) much more quickly and easily because the process leaves microscopic pores. The pores are created by the ice crystals that sublimate, leaving gaps or pores in their place.

MEMBRANE CONCENTRATION

24.1 Introduction

Industrial membrane filtration plants were introduced in the dairy industry in the beginning of the 70's. The basis for using membrane filtration in the dairy industry is that the dry matter components in milk and whey particles consist of different sizes as shown in Table 24.1. By selecting filters/membranes of different pore sizes and applying pressure on the product to be filtered, it is possible to divide the milk and whey in different fractions. What passes the filter/membrane is permeate and what does not pass is retentate as shown in.

24.2 Membrane Types

- **Spiral Membrane:** Due to their compact layout and large amount of membrane area per element, spirals are typically used for high-flow applications with minimal or no suspended solids. Their advantage is low hardware and operating costs.
- **Ceramic Membrane:** Ideally suited for value-added or sanitary products, as well as applications requiring selective separations from fluid streams containing aggressive components such as solvents.
- **Stainless Steel Membrane:** Rugged design, especially effective for demanding applications with extreme process conditions or feed streams with elevated particulate solids and/or high viscosity.
- **Tubular Membrane:** Highly resistant to plugging when processing streams with large amounts of suspended solids or fibrous compounds.
- **Hollow Fiber Membrane:** Extremely high packing density and open channel design; offers the possibility of backwashing from the permeate side, particularly suited for low solids liquid streams.
- **Plate and frame:** Open channel design allows it to be used for products with very high viscosity, particularly suited for high solids pharmaceutical and food applications.

24.3 Filtration Types

24.3.1 Reverse osmosis

Reverse Osmosis is used to remove water from a product to increase the solids content; evaporator condensate is often 'polished' by reverse osmosis, so that it can be used elsewhere in the dairy. Reverse osmosis is a high-efficient technique for dewatering process streams, concentrating/separating low-molecular-weight substances in solution, or cleaning wastewater. It has the ability to concentrate all dissolved and suspended solids. The permeate contains a very low concentration of dissolved solids. Reverse Osmosis is typically used for the desalination of seawater.

In order to describe Reverse Osmosis, it is first necessary to explain the phenomenon of osmosis. Osmosis may be described as the physical movement of a solvent through a semi-permeable membrane based on a difference in chemical potential between two solutions separated by that semi-permeable membrane.

The example given in the Figure 24.2 serves to demonstrate and clarify this point. A beaker of water as shown inis divided through the center by a semi-permeable membrane. The black dotted line represents the semi-permeable membrane. We will define this semi-permeable membrane as lacking the capacity to diffuse anything other than the solvent, in this case water molecules.

Now, when a little common table salt (NaCl) is added to the solution on one side of the membrane (Fig. 24.2) the salt water solution has a lower chemical potential than the water solution on the other side of the membrane. In an effort to equilibrate the difference in chemical potential, water begins to diffuse through the membrane from the water side to the salt water side. This movement is osmosis. The pressure exerted by this mass transfer is known as osmotic pressure.
The diffusion of water will continue until one of two constraints is met. One constraint would be that the solutions essentially equilibrate, at least to the extent that the remaining difference in chemical potential is offset by the resistance or pressure loss of diffusion through the membrane. The other constraint is that the rising column of salt water exerts sufficient hydrostatic pressure to limit further diffusion. By observation then, we can measure the osmotic pressure of a solution by noting the point at which the head pressure impedes further diffusion.

Reverse Osmosis : By exerting a hydraulic pressure greater than the sum of the osmotic pressure difference and the pressure loss of diffusion through the membrane, we can cause water to diffuse in the opposite direction (Fig. 24.2), into the less concentrated solution. This is reverse osmosis. The greater the pressure applied, the more rapid the diffusion. Using reverse osmosis we are able to concentrate various solutes, either dissolved or dispersed, in a solution.

24.3.2 Nanofiltration

Nanofiltration is used to remove mainly the monovalent ions from whey. A partly demineralization and water removal is obtained. Nanofiltration is selected when Reverse Osmosis and Ultrafiltration are not the correct choice for separation. Nanofiltration can perform separation applications such as demineralization, color removal, and desalination. In concentration of organic solutes, suspended solids, and polyvalent ions, the permeate contains monovalent ions and low-molecular-weight organic solutions like alcohol.

Like Reverse Osmosis, the mass transfer mechanism in Nanofiltration is diffusion. Though generally quite similar in terms of membrane chemistry, the Nanofiltration membrane allows the diffusion of certain ionic solutes (such as sodium and chloride), predominantly monovalent ions, as well as water. Larger ionic species, including divalent and multivalent ions and more complex molecules are highly retained.

Since monovalent ions are diffusing through the Nanofiltration membrane along with the water, the osmotic pressure difference between the solutions on each side of the membrane is not as great and this typically results in somewhat lower operating pressure with Nanofiltration compared with Reverse Osmosis.

Some typical applications for Nanofiltration are:

- Desalination of food, dairy and beverage products or byproducts
- Partial Desalination of whey, UF permeate or retentate as required
- Desalination of dyes and optical brighteners
- Purification of spent clean-in-place (CIP) chemicals
- Color reduction or manipulation of food products
- Concentration of food, dairy and beverage products or byproducts
- Fermentation byproduct concentration.

24.3.3 Ultrafiltration

Ultrafiltration is a selective fractionation process using pressures up to 145 psi (10 bars). Ultrafiltration is widely used in the fractionation of milk and whey, and in protein fractionation. The whey proteins are separated to form a product with 35, 60 or 80% Whey Protein Concentrate. If ultra filtration is applied to skim milk, then Milk Protein Concentrate is obtained. It concentrates suspended solids and solutes of molecular weight greater than 1,000. The permeate has low-molecular-weight organic solutes and salts. The protein fractions are typically evaporated in multi-effect evaporators with either TVR or MVR recompression to save steam, before spray drying.

24.3.4 Microfiltration

Microfiltration is a low-pressure cross-flow membrane process for separating colloidal and suspended particles in the range of 0.05-10 microns and as such used for bacteria removal, fermentation broth clarification and biomass clarification and recovery.

24.4 Application

Membrane filtration is today used in the Food & Dairy industry and likewise in other process plants. Membrane filtration can be used to meet very distinct liquid separations.

Table 24.1 Milk constituents and their sizes

Cross-flow membrane filtration has opened the doors to a variety of new and innovative dairy products. Nowadays, the mechanical separator is not the only means of harvesting a component of milk. Today, not only the cream can be separated but virtually every major component of milk through membrane filtration can be separated. Membrane filtration technology has rapidly gained prominence in the processing of dairy ingredients. Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis, is making it possible to produce products with very unique properties and functionalities.