

**Post-Harvest Operations and Processing of Fruits, Vegetables, Spices and Plantation
Crop Products**
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Lecture No: 27
Concentrates and Pastes

Concepts Covered

- Concentration process
- Methods of concentration
 - ✓ Evaporation
 - ✓ Cryo concentration
 - ✓ Membrane concentration
- Tomato paste, Fig paste & Mango paste



IIT Kharagpur

The topics covered in this lecture are the concentration process, methods of concentration such as evaporation, cryo concentration, membrane concentration, and lastly some common concentration paste like tomato paste fig paste and mango paste with their manufacturing process.

Concentration

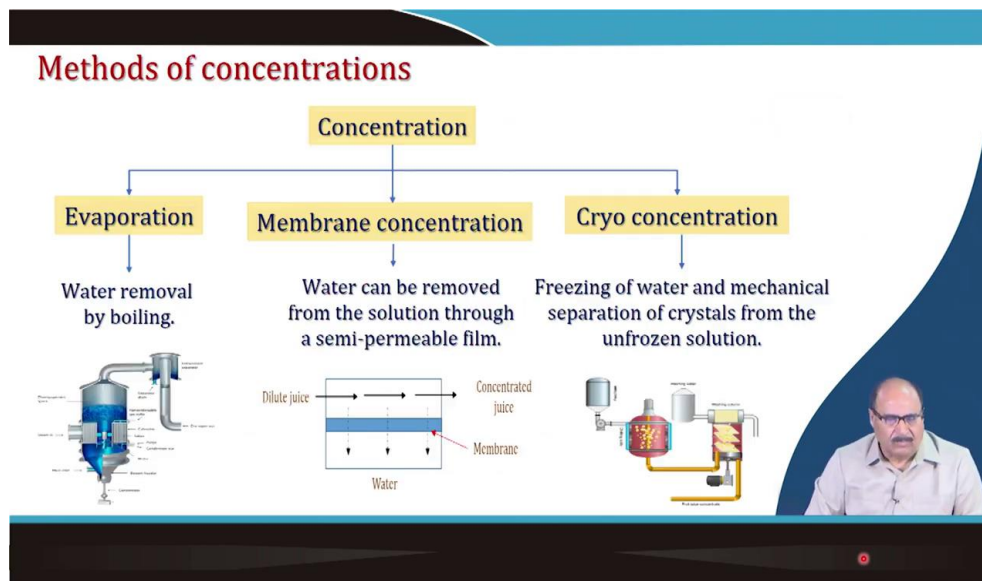
- Juice concentration is aimed at removing water and increasing the soluble solids (SS °Brix) content.
- **Increasing SS concentration in juice offers advantages in preservation of its quality, longer shelf life, storage and shipping.**
- Juice concentration is mainly accomplished to
 - ✓ Reduce water activity (a_w) of the juice product which lengthens its shelf life.
 - ✓ Minimize packaging, storage, and transport cost.
 - ✓ Stabilize or simplify the handling of the final juice product.



Concentration

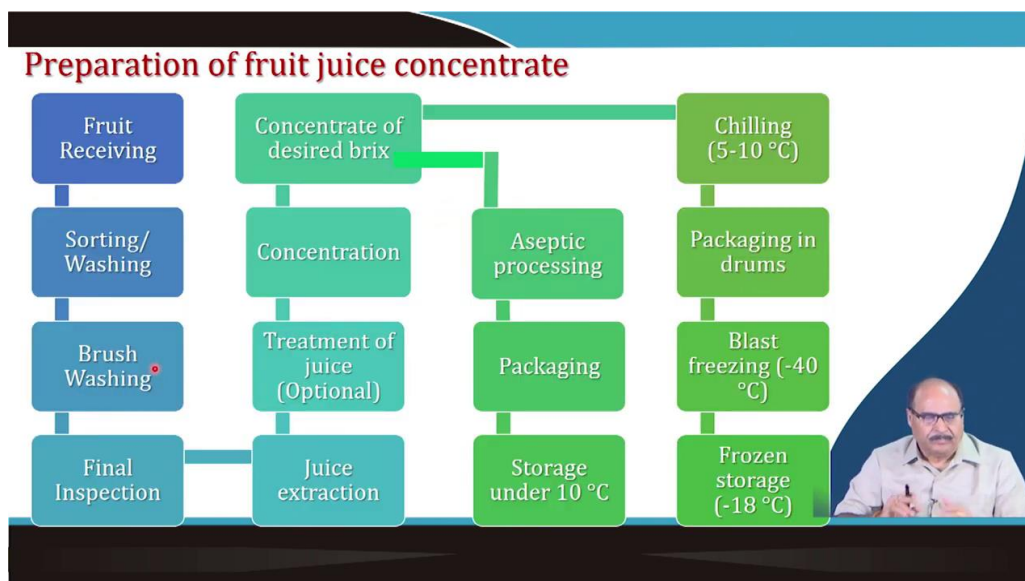
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longer shelf life, storage and shipping. Juice concentration is mainly accomplished to reduce water activity (a_w) of the juice product which lengthens its shelf life, minimize packaging, storage, and transport cost, and stabilize or simplify the handling of the final juice product.



Method of concentrations

The concentration processes may be three types, such as evaporation, membrane concentration or cryogenic concentration or low temperature concentration. Evaporation is the removal of water by boiling. Whereas, in the membrane concentration, the juice is passed through a semi permeable membrane and the membrane selectively retains certain components and solids and allows the water to work, for example reverse osmosis and microfiltration are commonly used. In the cryo concentration, the freezing of water and then mechanical separation of the ice crystals from the unfrozen solution.



Preparation of fruit juice concentrate


It involves receiving of fruits, sorting/washing, brush washing, final inspection, concentrate of desired brix, concentration, juice extraction, aseptic processing, packaging, storage under 10 °C, chilling at 5-10 °C, packaging in drums, blast freezing at -40 °C, and frozen storage at -18 °C.

Evaporation

- Evaporation is the process that separates water from the juices by means of heat energy.
- It may be executed in batch or continuous mode to produce desired pumpable concentrated liquids.

Types of evaporators

Single effect evaporators	Multi-effect evaporators
<ul style="list-style-type: none"> Heating medium is steam/ water vapors. Inefficient use of thermal energy. Evaporation of 1 kg/h of water would require 1 kg/h of live steam). 	<ul style="list-style-type: none"> Heating medium is vapors from the previous stage/effect. More efficient use of thermal energy. Evaporation of water from juice at a lower temperature.



Evaporation

Evaporation is the process that separates water from the juices by means of heat energy. It may be executed in batch or continuous mode to produce desired pumpable concentrated liquids. In single effect evaporator, heating medium is steam or water vapours and involves inefficient use of thermal energy and for evaporating 1 kg of water about 1 kg per hour live steam is required. In multi-effect evaporator, heating medium is vapors from the previous stage/effect, and is more efficient use of thermal energy. Evaporation of water from juice occurs at a lower temperature.

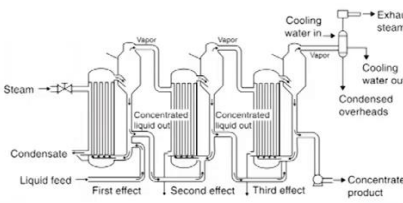

Evaporation (Contd...)

Multi-effect evaporator

- In multi-effect evaporator (MEE), the single effect evaporators are connected in series.
- The vapours produced in first and second effects (or evaporation chambers) are used again as the heating medium in second and third effects, respectively.
- In MEE, steam is used only in the first effect. The reuse of vapours results higher energy-use efficiency from the system
- The partially concentrated product leaving the first effect is introduced as feed into the second effect and so on.

$$\text{Steam economy} = \frac{\dot{m}_{v1} + \dot{m}_{v2} + \dot{m}_{v3}}{\dot{m}_f}$$

Where, \dot{m}_{v1} , \dot{m}_{v2} and \dot{m}_{v3} are the vapours produced in 1st, 2nd, and 3rd effects, respectively (kg/h) and \dot{m}_f is steam supplied (kg/h).

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- **Mass balance on flow streams**

$$\dot{m}_f = \dot{m}_{v1} + \dot{m}_{v2} + \dot{m}_{v3} + \dot{m}_p$$
- **Mass balance on solid fractions**

$$x_f \dot{m}_f = x_p \dot{m}_{v1}$$

Where x_f & x_p are the solid fraction in the feed stream at first effect and the product stream from the third effect.
- **Enthalpy balances around each effect**

$$\dot{m}_f H_f + \dot{m}_s H_{vs} = \dot{m}_{v1} H_{v1} + \dot{m}_{f1} H_{f1} + \dot{m}_s H_{cs}$$

$$\dot{m}_{f1} H_{f1} + \dot{m}_{v1} H_{v1} = \dot{m}_{v2} H_{v2} + \dot{m}_{f2} H_{f2} + \dot{m}_{v1} H_{c1}$$

$$\dot{m}_{f2} H_{f2} + \dot{m}_{v2} H_{v2} = \dot{m}_{v3} H_{v3} + \dot{m}_p H_{p3} + \dot{m}_{v2} H_{c2}$$

Where, the subscripts 1, 2, 3, s and c refer to the first, second, and third effect, steam and condensate, respectively; H represent enthalpy of the stream (kJ/kg).

Mass balance on flow streams

$$\dot{m}_f = \dot{m}_{v1} + \dot{m}_{v2} + \dot{m}_{v3} + \dot{m}_p$$

Mass balance on solid fractions

$$x_f \dot{m}_f = x_p \dot{m}_{v1}$$

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Enthalpy balances around each effect

$$\dot{m}_f H_f + \dot{m}_s H_{vs} = \dot{m}_{v1} H_{v1} + \dot{m}_{f1} H_{f1} + \dot{m}_s H_{cs}$$

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Where, the subscripts 1, 2, 3, s and c refer to the first, second, and third effect, steam and condensate, respectively; H represent enthalpy of the stream (kJ/kg).

$H_f = C_{pf}(T_f - T_{ref})$
 $H_p = C_{pp}(T_3 - T_{ref})$

Where, C_{pf} and C_{pp} are the specific heat content of feed and product ($\text{kJkg}^{-1}\text{°C}^{-1}$)
 T_f, T_3 , and T_{ref} are the feed, product and reference temperature (°C)

Heat transfer across the heat exchanger

$q_1 = U_1A_1(T_s - T_1)$
 $q_2 = U_2A_2(T_1 - T_2)$
 $q_3 = U_3A_3(T_2 - T_3)$

Where, q is heat transfer rate (W)
 U is overall heat transfer coefficient ($\text{Wm}^{-2}\text{K}^{-1}$)
 A is area of heat exchanger (m^2)
 T is temperature (°C)
Subscript 1, 2, 3 and s are the first, second, third effects and steam, respectively.


Pressure and temperature in each effect

- Pressure (P) in each subsequent stage
 $P_1 > P_2 > P_3 > \dots > P_N$
- Boiling temperature (T_b) of water decreases as pressure decreases
 $T_1 > T_2 > T_3 > \dots > T_N$

Where, P is pressure (Pa)

Advantages

- Juice boiling at lower pressure is achieved at lower temperatures.
- Heat-labile vitamins and flavonoids are better retained.



$$H_f = C_{pf}(T_f - T_{ref})$$

$$H_p = C_{pp}(T_3 - T_{ref})$$

Where, C_{pf} and C_{pp} are the specific heat content of feed and product ($\text{kJkg}^{-1}\text{°C}^{-1}$); T_f, T_3 , and T_{ref} are the feed, product and reference temperature (°C).

Heat transfer across the heat exchanger

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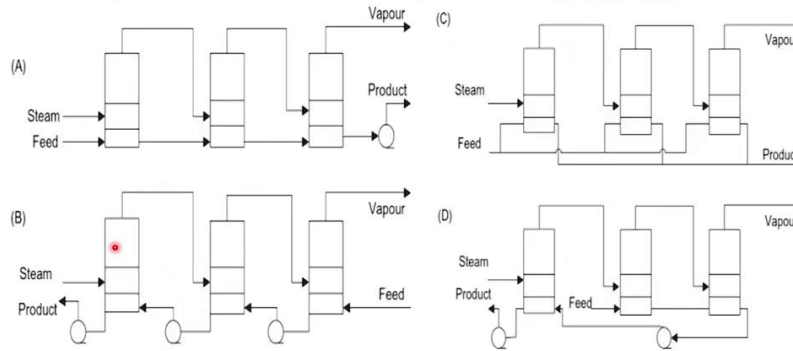
$$q_3 = U_3A_3(T_2 - T_3)$$

Where, q is heat transfer rate (W); U is overall heat transfer coefficient ($\text{Wm}^{-2}\text{K}^{-1}$); A is area of heat exchanger (m^2); T is temperature (°C); Subscript 1, 2, 3 and s are the first, second, third effects and steam, respectively.

Pressure and temperature in each effect

Pressure (P) in each subsequent stage: $P_1 > P_2 > P_3 > \dots > P_N$, Boiling temperature (T_b) of water decreases as pressure decreases: $T_1 > T_2 > T_3 > \dots > T_N$, Where, P is pressure (Pa).

Arrangement of effects in multiple effect evaporation



(A) Concurrent (B) Countercurrent (C) Parallel (D) Mixed

Arrangement of effects in multiple effect evaporation

In the co-current type, the steam and feed both are passing in the same direction. Similarly, in the parallel also the almost similar arrangement is there, where in the counter current there is the steam and feed is entering in the opposite direction.

Evaporators

Pan or kettle evaporator

- They are simplest and oldest types of evaporators.
- Used for the concentration of *juices, sauces, jams, and confection products*.

Construction

- ✓ Hemispherical shells (pans) made of SS.
- ✓ Heating by steam circulating in coils or by heating coils made of copper (high thermal conductivity).
- ✓ Shell can be mounted permanently in vertical position for product exit at the bottom of the pan.

Working

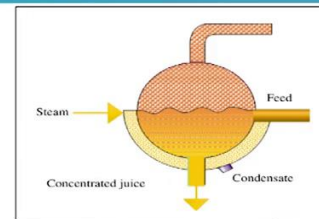
- ✓ Heat conduction to the solution raises temperature of fruit juice causing evaporation of water.

Advantages

- ✓ Easy installation
- ✓ Easy scalability
- ✓ Easy maintenance
- ✓ Smaller capital costs

Disadvantages

- ✓ Not suitable for evaporation of thermally labile products.



Pan or kettle evaporator

They are simplest and oldest types of evaporators, which are used for the concentration of juices, sauces, jams, and confection products. It consists of a hemispherical shells (pans) made of SS. Heating may be by steam circulating in coils or by heating coils made of copper (high thermal conductivity). Shell can be mounted permanently in vertical position for product exit at the bottom of the pan. Heat conduction to the solution raises temperature of fruit juice causing evaporation of water. So, the advantages of this is that easy installation, easy scalability, easy maintenance, and smaller capital cost. However, it is not suitable for evaporation of thermally labile heat products.

Evaporators (Contd...)

❑ Vacuum pan evaporators

- Concentration of juices by boiling under vacuum is the only practicable method for the commercial production of fruit juice concentrates.
- Vacuum pan evaporators (VPEs) are similar to pan or kettle evaporators in all ways except that they are connected to high-power vacuum pumps.
- VPEs are suitable for the concentration of fruit juice/pulp to prepare concentrate/paste.
- VPEs are composed of stainless steel pan, anchor- and paddle-like stirring assemblies, steam jacket, and condenser.
- VPEs operate at around 70 °C and are often capable of concentrating up to 200 kg of fruit juice per hour, with an average evaporation rate of 3000 kg/h.



Vacuum pan evaporators

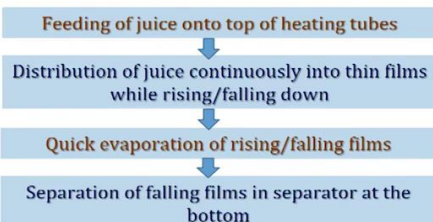
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Evaporators (Contd...)

❑ Rising/falling film evaporators

- In these evaporators, thin films of juice are passed over rising or falling plates.
- This allows the evaporation process to occur more quickly at lower temperatures.

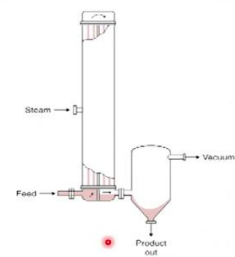
Principle : Heat conduction → Temperature rise of juice → Evaporation



Construction

These evaporators consist of

- ✓ A tubular heat exchanger
 - ✓ Lateral/concentric centrifugal separator
- ❑ They are mainly used where juice cannot endure prolonged exposure to elevated temperatures.



Rising/falling film evaporators

In these evaporators, thin films of juice are passed over rising or falling plates. This allows the evaporation process to occur more quickly at lower temperatures. Due to conduction, temperature of juice rises, and finally the water evaporates from the juice. These evaporators generally consist of a number of heat exchangers and lateral concentric centrifugal separators.

These are mainly used where the juice cannot endure prolonged exposure at elevated temperature. The juice is fed into the top of the heating tubes and this is distributed continuously into the thin film while rising or falling the films that facilitates the quick evaporation of rising and falling films and there is separation of falling films in the separator at the bottom.

Evaporators (Contd...)

❑ Thermally accelerated short-time evaporator (TASTE)

- TASTE is a continuous HTST evaporator which comprises a long vertical tube of falling film.
- TASTE is also known as seven-effect evaporator as steam is reused 7 times to evaporate the water.
- TASTEs operate on the principle of
 - ✓ High temperature, short-time exposure
 - ✓ Thermally accelerated descending flow (longer falling film tubes)
 - ✓ Low steam consumption
- This type of evaporator is most suitable for
 - ✓ Orange juice concentration
 - ✓ Other low-pulp or clear fruit juices
 - ✓ Pre-concentration of products containing higher fiber



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Effects of evaporative concentration process on quality attributes

- Changes in the organoleptic quality or nutritional value of the concentrate is reduced when volatile recovery is used.
- Without volatile recovery, losses of aroma compounds, including esters, aldehydes and terpenes, reduce the flavour of concentrated juices.
- Darkens the colour of foods, partly because of the increase in concentration of solids.
- Reduction in water activity promotes chemical changes (e.g. Maillard browning) and causes changes to anthocyanins and other pigments in fruit products.
- Improperly selected concentration method may
 - ✓ be detrimental to product's sensory and nutritional profile
 - ✓ increase production costs.
- Selection of concentration approach depends on
 - ✓ Nature and state of juice
 - ✓ Extent of concentration



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Membrane technology

- Membrane technology is a non-thermal processing technology having advantages of
 - ✓ Lesser energy consumption, and
 - ✓ Lesser loss of nutritional profile especially thermolabile vitamins and phytonutrients.
- **One of the promising alternatives of thermal-based technology is reverse osmosis, but it cannot satisfy the concentrations normally higher than 25-30 °Bx.**
- Recent developments in membrane engineering to overcome this limitation include
 - ✓ Membrane distillation (MD)
 - ✓ Osmotic evaporation
 - ✓ Integrated membrane processes

Driving force
(Pressure)

Membrane Separation

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Membrane technology (Contd...)

❑ Membrane distillation

- Membrane distillation (MD) uses a microporous hydrophobic membrane to separate two aqueous solutions maintained at different temperatures.
- A net flux of pure water occurs from solution at higher temperature to that at low temperature.
- The driving force is due to difference in vapor pressure at solution-membrane interface.
- MD occurs at ordinary pressure and temperature (much lower than conventional evaporation).
- It is used to concentrate juices sensitive to high temperature and high osmotic pressure.

Typical membrane characteristics

- ✓ 0.1-0.2 μm in diameter
- ✓ 80-250 μm thick
- ✓ porosity range: 0.60-0.80

Membrane materials

- ✓ Polytetrafluoroethylene
- ✓ Polyvinyl difluoride
- ✓ Polypropylene

Process flow chart

Formation of a vapor pressure gap at solution-membrane interface.

Passage of vapors through microporous membrane system.

Condensation of vapor phase at the cold side of membrane.



Membrane distillation

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Membrane technology (Contd...)

❑ Direct osmosis concentration

- Direct osmosis concentration (DOC) operates at low temperature and pressure.
- In DOC, the osmotic pressure gradient between fruit juice and solution of osmotic agent is maintained across a semipermeable membrane.
- Therefore, water flows from single-strength juice (low osmotic pressure) to a hygroscopic, nontoxic, inert osmotic agent (high osmotic pressure) that does not affect the taste, color, or odor of the juice product.
- Generally, the solids of smaller molecular weight, when present in higher concentrations, offer higher osmotic pressure.
- It is capable of retaining the original flavor and sensory characteristics of fruit juices.



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Representation of DOC process

(A) DOC process

(B) DOC membrane module

(C) Mechanism of direct osmosis

(Water transports from the solution of low osmotic pressure to the solution of high osmotic pressure).
 π_1 and π_2 are osmotic pressures of feed and osmotic agent solution; P_1 and P_2 indicate feed side and osmotic agent side hydraulic pressures.

Representation of DOC process

The DOC process contains direct osmosis flat module, ball valve, peristaltic pump, feed reservoir, osmotic agent reservoir, and balance. The DOC membrane module is shown in this figure and its mechanism of direct osmosis. Basically, water transports from the solution of low osmotic pressure to the solution of high osmotic pressure. π_1 and π_2 are osmotic pressures of feed and osmotic agent solution, P_1 and P_2 indicate feed side and osmotic agent side hydraulic pressures.

Membrane technology (Contd...)

❑ **Reverse osmosis**

- If pressure exerted on high-brix solution (juice) exceeds osmotic pressure, solvent (water) moves in opposite direction through the membrane.
- RO has been used for concentrating juices of peach, pear, apple, and mandarin.
- Soluble solids increased from 12.2 to 30.5 and 21.52 °Bx under 4 and 2 MPa transmembrane pressure.

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Membrane technology (Contd...)

❑ **Reverse osmosis (Contd...)**

Theories for solute and water transport

Preferential sorption theory
Solute and solvent pass through the membrane by diffusion


Solution diffusion theory
Solute and solvent are first absorbed at membrane surface before passing through the membrane

Factors leading to reduced flux

- ✓ Accumulation of solute at membrane surface
- ✓ Increase in osmotic pressure
- ✓ Concentration polarization impact

Solutions

- ✓ Altering operating conditions such as feed pressure, concentration, temperature, crossflow velocity.
- ✓ Promoting turbulence
- ✓ Back flushing/ Washing
- ✓ Pulsed flow




The theories involved for solute and water transport are preferential sorption theory (solute and solvent pass through the membrane by diffusion), and solution diffusion theory (solute and solvent are first absorbed at membrane surface before passing through the membrane). Factors leading to reduced flux are accumulation of solute at membrane surface, increase in osmotic pressure, and concentration polarization impact. The possible solutions are altering operating conditions such as feed pressure, concentration, temperature, crossflow velocity, promoting turbulence, back flushing/washing, pulsed flow.

Membrane technology (Contd...)

❑ **Osmotic evaporation**

- In osmotic evaporation/osmotic distillation, a hydrophobic microporous membrane is used to detach two liquid phases that differ greatly in terms of solute concentration.
- **The microporous membranes work as physical supports at the vapor-liquid interface.**
- The evaporation process accompanied by simultaneous heat and mass transfer and the overall permeation rate is decided by membrane properties, operating conditions (mass or heat transfer).
- **In particular, this technique best fits the situation encountering thermally labile and volatile coloring and flavoring agents such as fruit juices.**

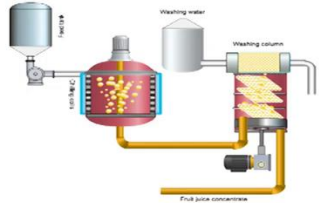


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Cryo concentration (Freeze concentration)


- Cryo concentration is an effective way to concentrate biological materials without harming their integrity.
- It involves removal of pure water in form of ice crystals at subzero temperature.
- It is particularly suitable for the concentration/separation of thermosensitive biological compounds.



Freeze concentration

Components of single-stage cryo-concentration unit

- Crystallizer**: Ice crystallizes in scrapped surface heat exchangers (SSHE) and encapsulated with cooling coils/circulating refrigerants.
- Washing column**: Concentrated liquid is separated efficiently from ice crystals.



Cryo concentration (Freeze concentration)

Cryo concentration is an effective way to concentrate biological materials without harming their integrity. It involves removal of pure water in form of ice crystals at subzero temperature. It is particularly suitable for the concentration/separation of thermosensitive biological compounds. The components of single-stage cryo-concentration unit are crystallizer, where ice crystallizes in scrapped surface heat exchangers (SSHE) and encapsulated with cooling coils/circulating refrigerants, and washing column, where concentrated liquid is separated efficiently from ice crystals.

Freeze concentration (Contd...)

Advantages

- ✓ Maximum retention of original product characteristics
- ✓ No or little effect on taste, aroma, color, or nutrients
- ✓ Higher concentration level achievable than reverse osmosis

Disadvantages

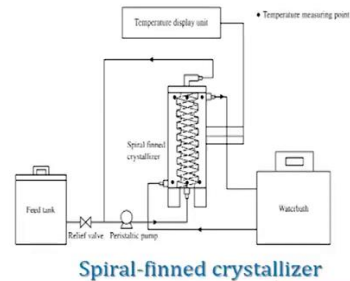
- ✓ Lower concentration level achievable than boiling under vacuum
- ✓ Very high capital costs
- ✓ Difficult control of ice crystal growth for a longer time (capacity constraint)
- ✓ Large energy consumption (due to nonstop rotation of the scraping blades)
- ✓ Solids loss due to juice entrapped in ice crystals
- ✓ Sometimes phase changes can be detrimental to nutritional and sensory characteristics



The advantages are maximum retention of original product characteristics, no or little effect on taste, aroma, color, or nutrients, and higher concentration level achievable than reverse osmosis. The disadvantages includes lower concentration level achievable than boiling under vacuum, very high capital costs, difficult control of ice crystal growth for a longer time (capacity constraint), large energy consumption (due to nonstop rotation of the scraping blades), solids loss due to juice entrapped in ice crystals, and sometimes phase changes can be detrimental to nutritional and sensory characteristics.

Progressive freeze concentration (PFC)

- PFC is an exceptional modification in conventional process.
- It avoids capacity constraint and nutritional losses.
- In PFC, SSHE are replaced with more efficient spiral exchangers.
- In PFCs, crystals are deposited in the form of layers over one another on the cooled surface of the larger surface area (spiral fin) which exceptionally reduces the capital costs and undesirable changes.



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Pressure-shift nucleation cryo-concentration (PSN)

- In PSN, ice nucleation is avoided while cooling the liquid to subzero temperature at high pressure.
- A sudden pressure release would induce a uniform supercooled liquid that would crystallize thoroughly rather than on the surface of the liquid as happens during conventional freezing.

Problems with conventional freeze concentration process

- ✓ Ice crystals formed at the cold surface of SSHE's are dendritic and too small.
- ✓ Their efficient separation in the washing column is difficult.
- ✓ The ice crystals may have pockets and scoops which might be occupied by concentrated juice.

Advantages of PSN

- ✓ It is easier to set temperature of a high-pressure vessel than for a SSHE.
- ✓ There is no need for complex scraping devices, thus energy is saved.
- ✓ Crystallization takes place in whole vessel; no need to recirculate juice to increase size/volume of ice formed.
- ✓ Ice crystals grown during expansion are round and free of pockets and scoops.
- ✓ Retains and stabilizes thermolabile food products.
- ✓ Use of high pressure can inactivate microbial or enzymatic loads.



Pressure-shift nucleation cryo-concentration (PSN)

In PSN, ice nucleation is avoided while cooling the liquid to subzero temperature at high pressure. A sudden pressure release would induce a uniform supercooled liquid that would crystallize thoroughly rather than on the surface of the liquid as happens during conventional freezing. Problems with conventional freeze concentration process are ice crystals formed at the cold surface of SSHE's are dendritic and too small, their efficient separation in the washing column is difficult, and the ice crystals may have pockets and scoops which might be occupied by concentrated juice. The advantages of PSN are that it is easier to set temperature of a high-pressure vessel than for a SSHE, there is no need for complex scraping devices, thus energy is saved, crystallization takes place in whole vessel; no need to recirculate juice to increase size/volume of ice formed, ice crystals grown during expansion are round and free of pockets and scoops, retains and stabilizes thermolabile food products, and use of high pressure can inactivate microbial or enzymatic loads.

Tomato paste

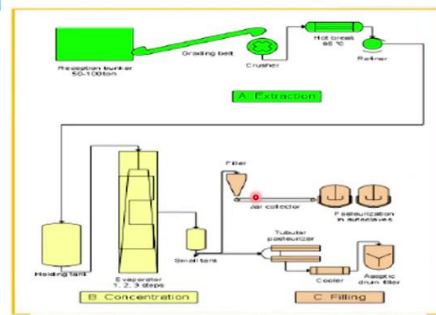
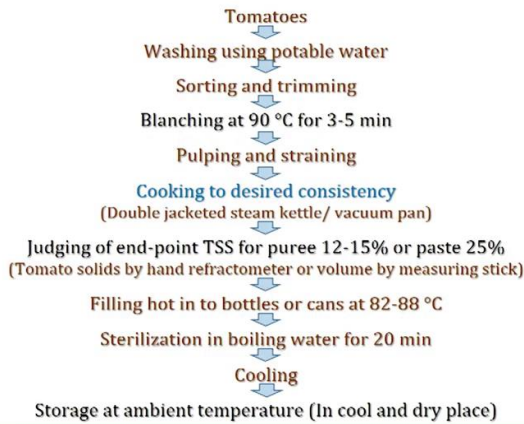
According to Codex Alimentarius, tomato paste must contain at least 24% tomato solids on a salt-free basis. Tomato paste is made by de-seeding and de-skinning the tomatoes and cooking/concentrating them for several hours. The production of a paste can be performed with the following processes such as thermal evaporation, freeze concentration, membrane separation (Ultrafiltration or reversed osmosis), and application of thickening agents to improve the consistency of the product.

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Tomato paste (Contd...)



The process for preparation of tomato paste includes selection of tomatoes, washing using potable water, sorting and trimming, blanching at 90 °C for 3-5 min, pulping and straining, cooking to desired consistency (double jacketed steam kettle/vacuum pan), judging end-point TSS for puree 12-15%, or paste 25% (tomato solids by hand refractometer or volume by measuring stick), filling hot into bottles or cans at 82-88 °C, sterilization in boiling water for 20 min, cooling, and storage at ambient temperature (in cool and dry place).

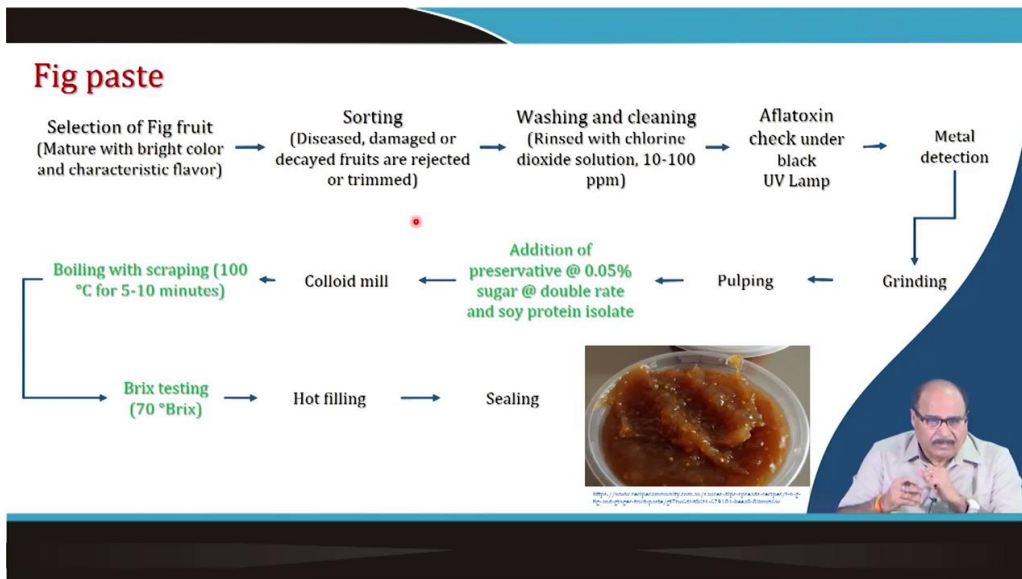
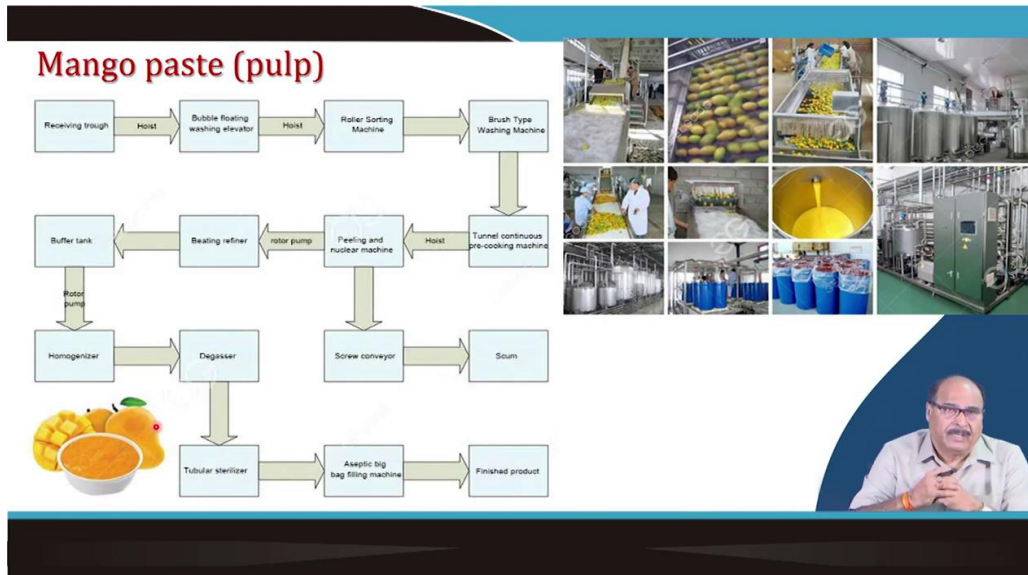


Fig paste

The process manufacture of fig paste consists of selection of fig fruit (mature with bright color and characteristic flavour), sorting (in which diseased, damaged or decayed fruits are rejected or trimmed), washing and cleaning (rinsed with chlorine dioxide solution, 10-100 ppm), checking of aflatoxin under black UV lamp, detection of metal, grinding, pulping, addition of preservatives @ 0.05%, sugar @ double rate and soy protein isolate, colloidal milling, boiling with scraping (100 °C for 5-10 min, brix testing (70 °Brix), hot filling, and sealing.



Mango paste (pulp)

The process includes series of machineries such as receiving trough, bubble floating washing elevator, roller sorting machine, brush type washing machine, tunnel continuous pre-cooking machine, peeling and nuclear machine, screw conveyor, beating refiner, buffer tank, homogenizer, degasser, tubular sterilizer, aseptic bag filling machine.

Summary

- Juice concentration is an important processing technique to increase shelf-life of juice products.
- A wide array of fruit juice concentration methods mainly based on evaporation, cryoconcentration, and membrane filtration techniques.
- Evaporation may be executed in batches or in a continuous manner to produce the desired pumpable concentrated liquids.
- Freeze or cryoconcentration has been believed to be an effective way of concentrating the materials without harming their integrity.



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In summary, Juice concentration is an important processing technique to increase shelf-life of juice products. A wide array of fruit juice concentration methods mainly based on evaporation, cryoconcentration, and membrane filtration techniques. Evaporation may be executed in batches or in a continuous manner to produce the desired pumpable concentrated liquids. Freeze or cryoconcentration has been believed to be an effective way of concentrating the materials without harming their integrity.

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These are the references for further study. Thank you.