Carbohydrates & Fermentation Industries

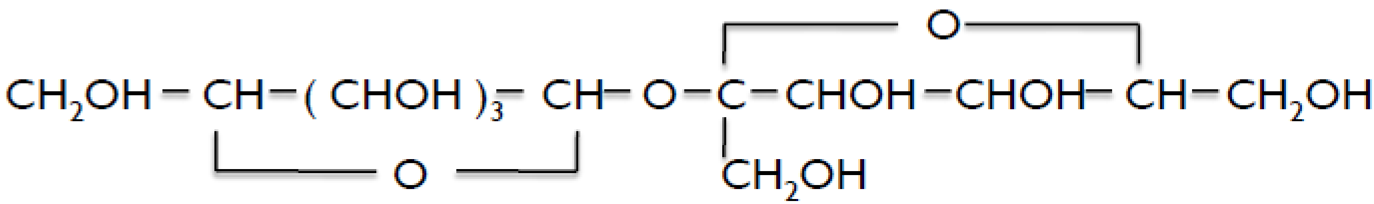
Carbohydrates

- Naturally occurring combinations of C, H and O
  - With H and O in 2:1 ratio (Hydrates of Carbon)
- The most common types
  - Sucrose (ordinary sugar)
  - Starch
  - Dextrose
  - Cellulose
- Fermentation Industries
  - Use carbohydrates as a substrate for production of various chemicals & biologicals.

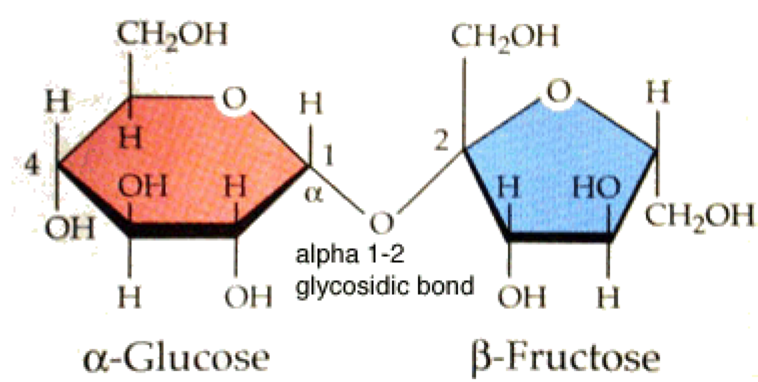
Sucrose

- Chemical formula : $C_{12}H_{22}O_{11}$ (disaccharide)
- Naturally in most fruits and vegetables. Sugar occurs in greatest quantities in sugarcane and sugar beets from which sugar is separated economically and commercially.

- Structural formula : (Glucose + Fructose)



- Molecular weight – 342
- Density = 1.58 kg/m^3
- Sucrose is soluble in water but slightly soluble in methyl alcohol and ethyl alcohol.

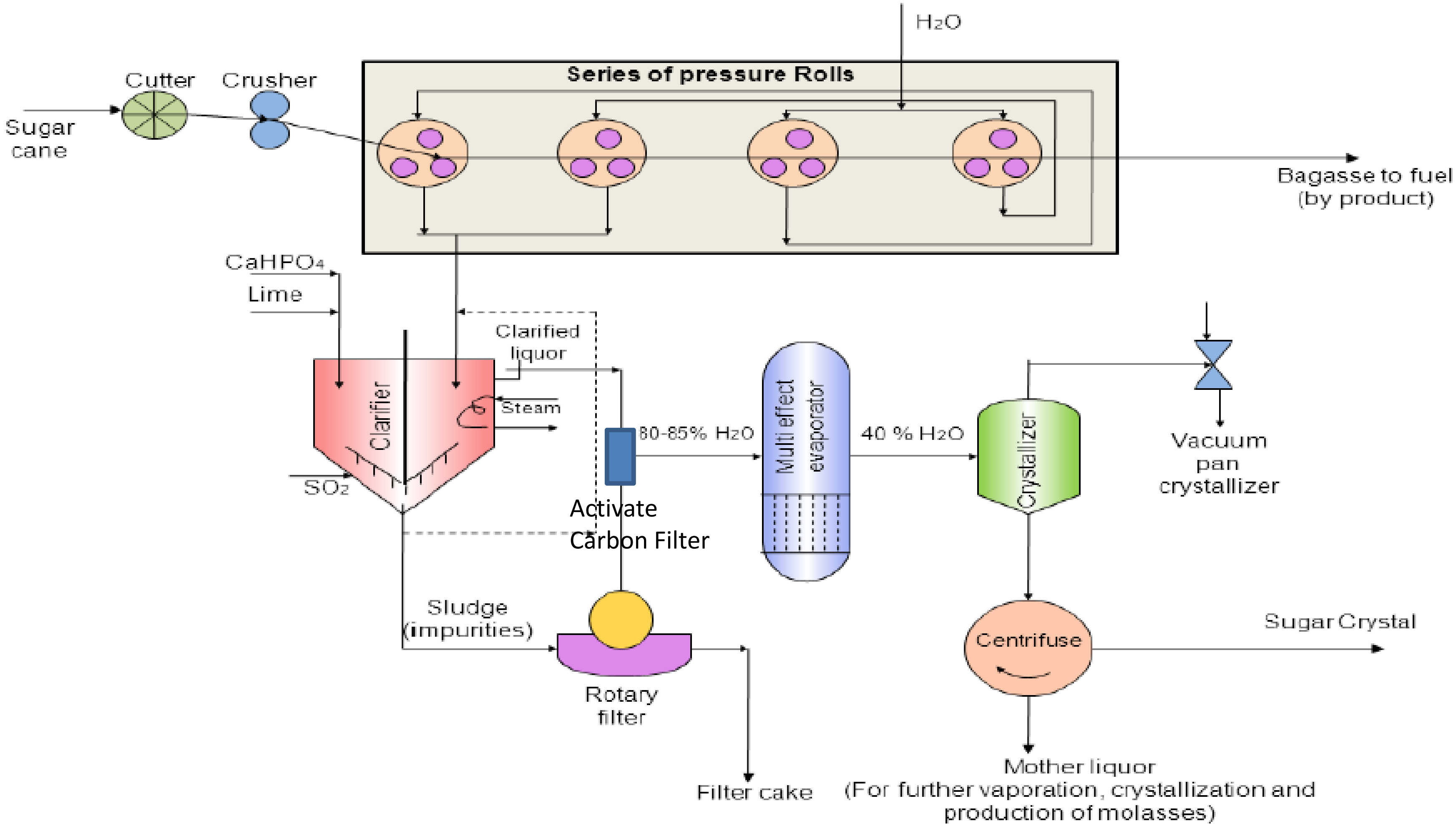


Sucrose

Production Process

- India is the homeland of sugarcane and sugar.
- Process : Extraction of sugarcane
  - Crystalline white sugar
  - Gur, a dark brown sugar concentrate
- Raw Material : Sugarcane
  - composition of sugarcane juice differences between varieties and location. It is a solution, containing soluble and insoluble impurities (i.e non sucrose species).
  - It's is also slightly acid with the pH between 4.5- 5.5, TSS 15-25 and sucrose 10 – 20 % w/w.

Process Flowsheet



Juice extraction pressing →Purification of juice →Clarification → evaporation → Crystallization → Centrifugation → Drying and screening

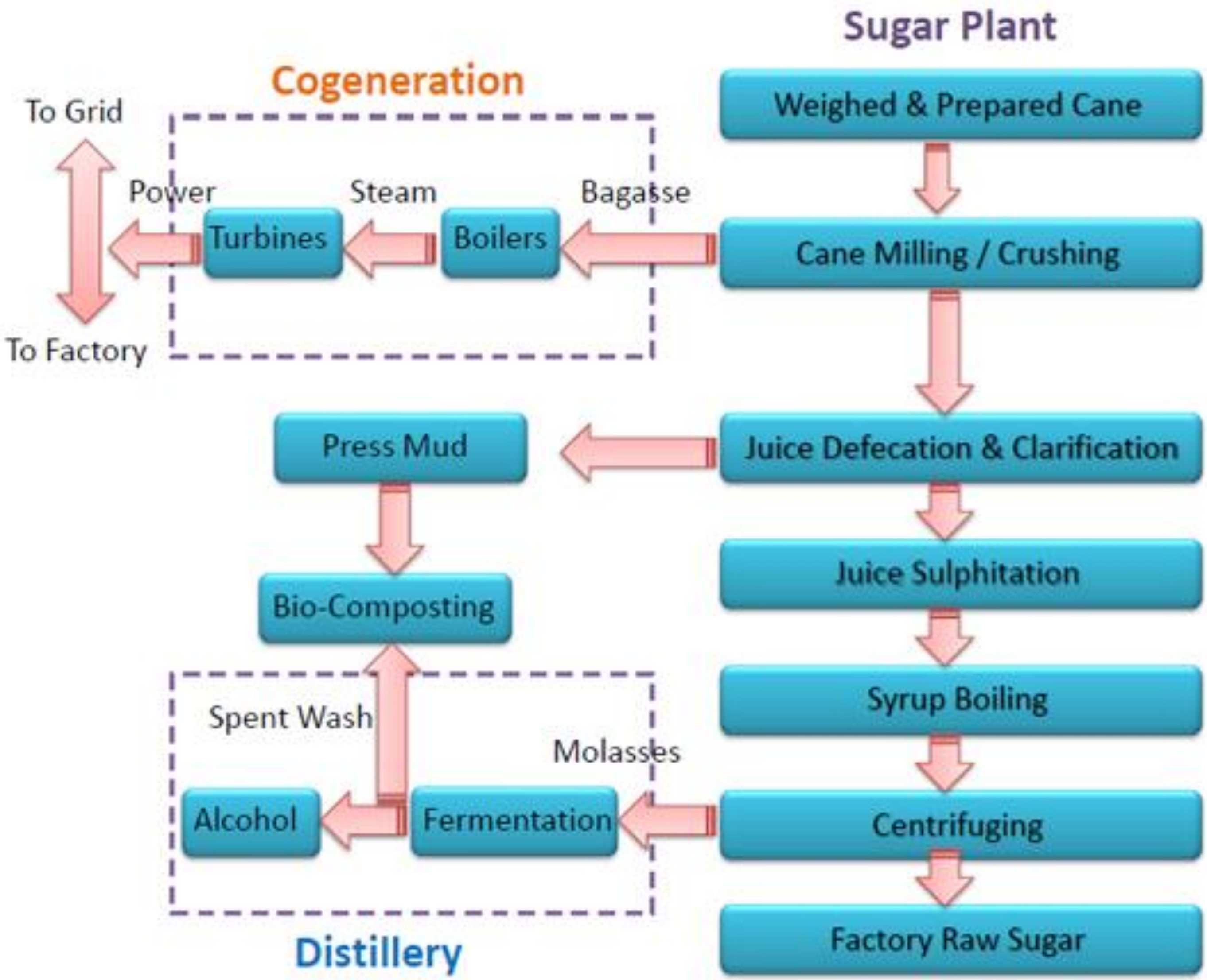
Process Description

- ***Juice extraction pressing***
  - Two or three heavily grooved crusher rollers break the cane and extract a large part of the juice. Revolving knives cutting the stalks into chips are supplementary to the crushers.
  - As the cane is crushed, hot water (or a combination of hot water and recovered impure juice) is sprayed onto the crushed cane counter currently.
- ***Clarification***
  - The juice from the mills, a dark green color, is acid and turbid.
  - The clarification (or defecation) process is designed to remove both soluble and insoluble impurities (such as sand, soil, and ground rock)
  - The process employs lime and heat as the clarifying agents. Milk of lime neutralizes the natural acidity of the juice, forming insoluble lime salts.
  - Heating the lime juice to boiling coagulates the albumin and some of the fats, waxes, and gums, and the precipitate formed entraps suspended solids as well as the minute particles.
  - The muds separate from the clear juice through sedimentation. The non-sugar impurities are removed by continuous filtration. The final clarified juice contains about 85 percent water and has the same composition as the raw extracted juice except for the removed impurities.

- ***Evaporation***
  - To concentrate this clarified juice, about two-thirds of the water is removed through vacuum evaporation.
  - Generally, four vacuum-boiling cells or bodies are arranged in series so that each succeeding body has a higher vacuum (and therefore boils at a lower temperature). The vapors from one body can thus boil the juice in the next one—the steam introduced into the first cell does what is called *multiple-effect evaporation.* The vapor from the last cell goes to a condenser. The syrup leaves the last body continuously with about 65 percent solids and 35 percent water.
- ***Crystallization***
  - Crystallization is the next step that takes place in a single-stage vacuum pan. The syrup is evaporated until saturated with sugar. As soon as the saturation point has been exceeded, small grains of sugar are added to the pan. These small grains, called *seed,* serve as nuclei for the formation of sugar crystals. Additional syrup is added and evaporated so that the original crystals that were formed are allowed to grow in size.
  - The growth of the crystals continues until the pan is full. When sucrose concentration reaches the desired level, the dense mixture of syrup and sugar crystals, called *massecuite*, is discharged into large containers known as crystallizers. Crystallization continues in the crystallizers as the massecuite is slowly stirred and cooled.

- ***Centrifugation***
  - Massecuite from the mixers is allowed to flow into centrifugals, where the thick syrup, or molasses, is separated from the raw sugar by centrifugal force.
  - The high-speed centrifugal action used to separate the massecuite into raw sugar crystals and molasses. A centrifugal machine has a cylindrical basket suspended on a spindle, with perforated sides lined with wire cloth, inside which are metal sheets containing 400 to 600 perforations per square inch.
  - The basket revolves at speeds from 1,000 to 1,800 RPM. The raw sugar is retained in the centrifuge basket because the perforated lining retains the sugar crystals. The mother liquor, or molasses, passes through the lining (due to the centrifugal force exerted). The final molasses *(blackstrap molasses)* containing sucrose, reducing sugars, organic non-sugars, ash, and water, is sent to large storage tanks.
- ***Drying and packaging***
  - Damp sugar crystals are dried by being tumbled through heated air in a granulator. The dry sugar crystals are then sorted by size through vibrating screens and placed into storage bins. Sugar is then sent to be packed in the familiar packaging we see in grocery stores, in bulk packaging, or in liquid form for industrial use.

Plant Economy



Major engineering problems

- Extraction of juice from cane
  - Optimization : design of rolls, temperature, time of operation
  - Use of ultrasonic vibration
- Choice of flocculation agents
  - High magnesia lime is old but best choice
  - CO_2 in carbonation step : reduce alkalinity ; improved filterability and decolorization
- Evaporation & Crystallization
  - Difficult crystallization, Calendria type evaporators are used
  - Crystallization : batch-wise in 4th or last effect
  - Measurement of supersaturation : boiling point rise, vacuum measurement and control

- **Critical zone of supersaturation**
  - Transition region- pulverized sugar seeds are added and new nuclei are produced at highest point of saturation (graining)
  - Metastable region- degree of supersaturation is reduced by decreasing vacuum and crystal will grow
    - Simultaneous feed liquor addition and evaporation can raise the total quantity of crystal.
- **Separation of crystal from syrup**
  - Improved centrifugal machine design (high speed 1800-2400 rpm)
  - Control of viscosity and surface tension of syrup give clean and rapid separation

- **Inversion of sugar**
  - Acid hydrolysis of sugar in glucose and fructose

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

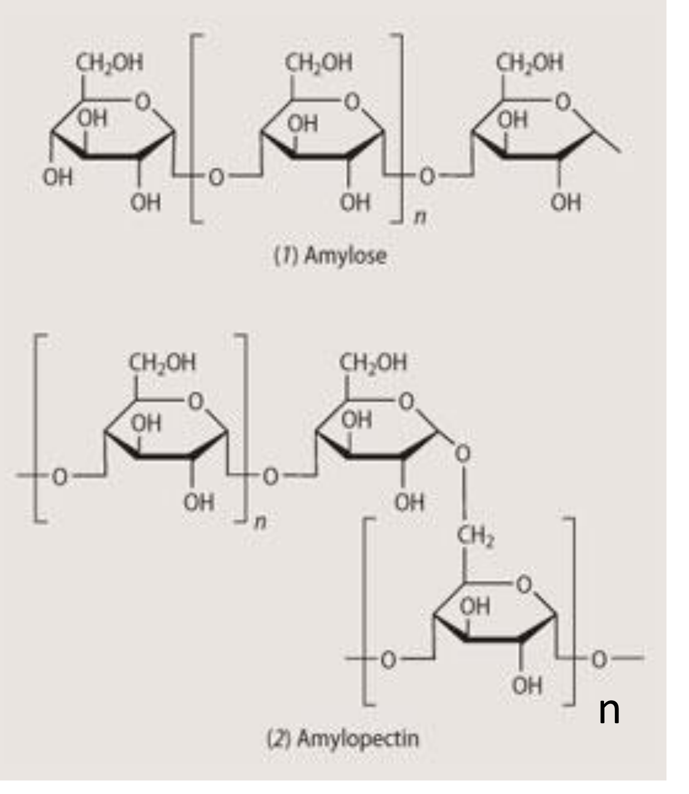
  - The extent of inversion is measured by polarimeter. The non inverted sugar has +97° polarization and completely inverted sugar has -20° polarization.
  - Minimized by : making quick delivery to the sugarcane presses less than 2 days
  - Low temperature – short time conditions : to reduce inversion

Extraction from sugarcane for Gur production

- Low cost product made by simple evaporation process.
- Cane juice extraction → Clarification
- Concentration
  - Occurs in open pan evaporators until (80-85% solidification).
  - The product run out of the bottom of pan.
  - The product is dark brown solidifies paste at room temperature and invert partially to mono-saccarides on storage.
  - It contains neutritionally desirable minerals, particularly iron.

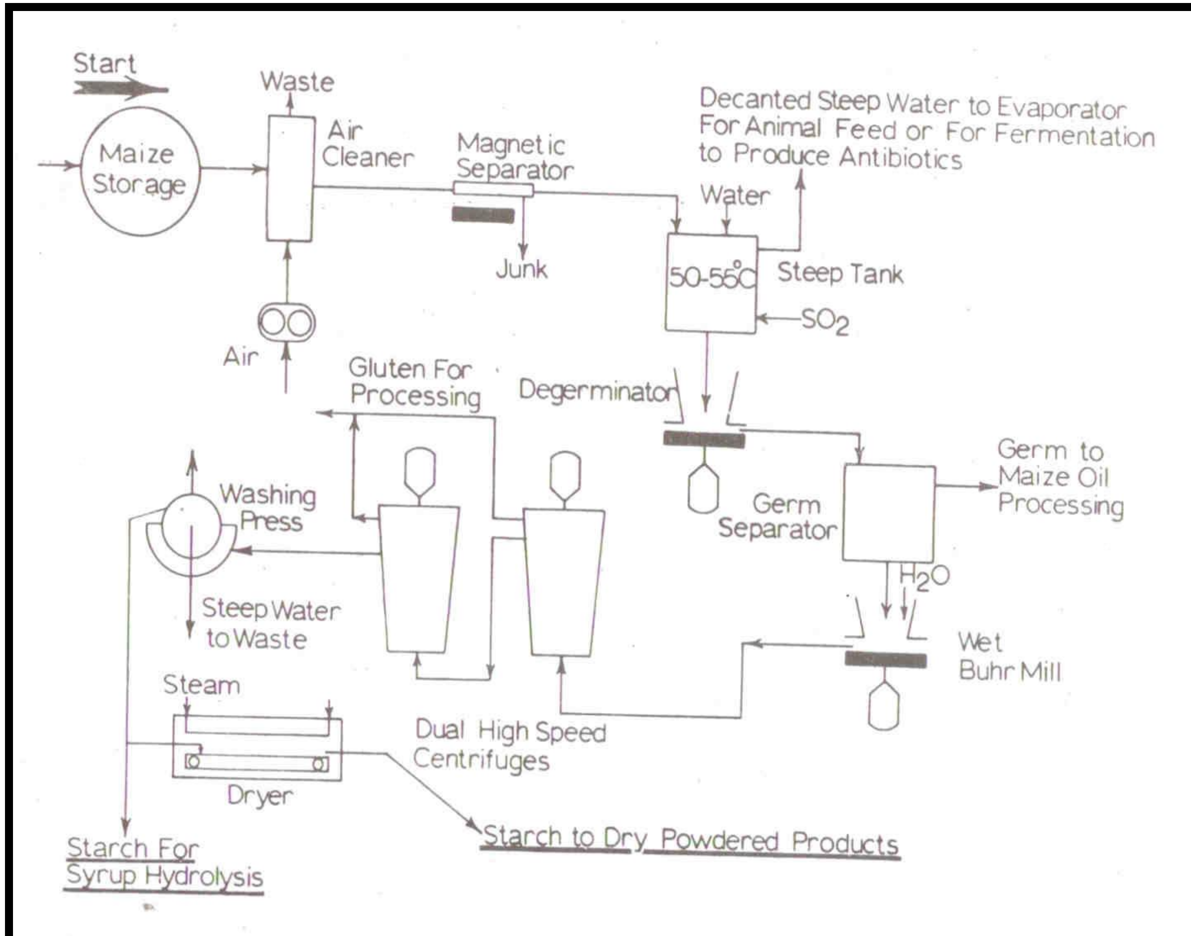
Starch

- High polymer carbohydrate
- Occur in grains and roots in form of granules (3-100 μ)
- Chemical formula : $C_6H_{10}O_5$
- n varies 200-500
- Major source : Maize kernel



Process Description

- Cleaning & screening
- Steeping
- Coarse grinding & degermination
- Fine grinding & extraction
- Gluten separation
- Starch refining
- Dehydration & drying



Manufacture of Ethanol from Molasses

- Ethanol is a volatile, flammable, clear, colorless liquid.
- A good solvent. It is also used as a germicide, beverage, antifreeze, fuel, depressant and chemical intermediate.
  - Molecular formula- C_2H_5OH
  - Molecular weight- 46.07
  - Density- 0.791 at 20˚C
  - Boiling Point- 78.3˚C
- It can be made by the fermentation process of material that contains sugar or from the compound which can be converted to sugar.

Methods of Production

- Fermentation
  - From sucrose substrate
    - Yeast enzyme readily ferment sucrose to ethanol.
  - From waste sulfite substrate of paper mills
  - From starch substrate
- Petroleum Processing
  - Catalytic hydration of ethylene
  - Esterification and hydrolysis of ethylene
  - Oxidation of petroleum

Fermentation

- Fermentation applies to both the aerobic and anaerobic metabolic activities of micro-organisms in which specific chemical changes are brought about in an organic substrate due to the enzymes produced by those microbes.
- Fermentation is the core part of distillery which is carried out in large cylindrical vessel generally made of stainless steel is called as fermenter.
- The media which has been prepared is introduced in the prefermenter and after 7 - 8 hours it is transferred into fermenter where fermentation is carried out.
- Here batch fermentation is carried out without maintenance of complete sterility of equipment. However, this pre supposes a rapid start of the yeast fermentation. This fermentation inhibits the growth of other microbes by depleting the available nutrients, by lowering the pH and most importantly by the formation of ethanol. To reduce the pH H_2SO_4 is usually added.
- As we know molasses contain approximately 50% invert sugar i.e. sucrose. It is converted into glucose and fructose in the presence of yeast and invertase enzyme.

- Ethyl alcohol by fermentation

(a) Main Reaction

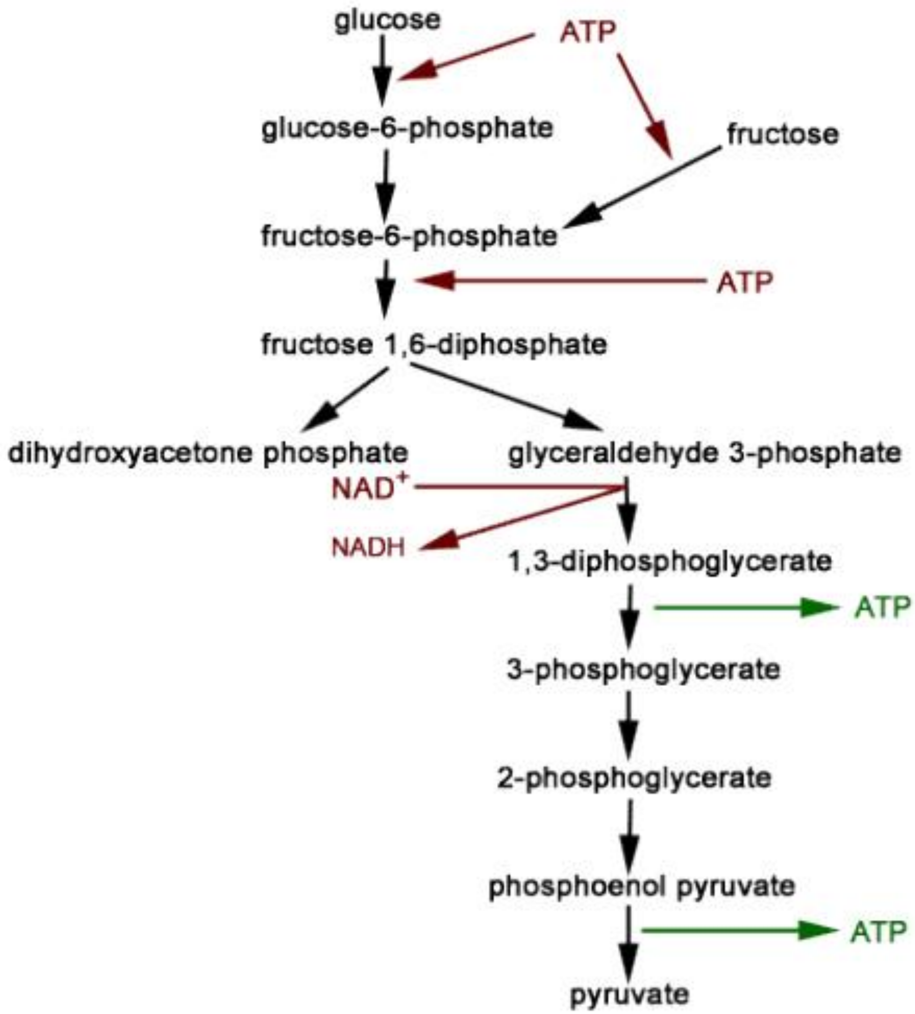
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} 2C_6H_{12}O_6$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2 \qquad \Delta H= -31.2 \text{ kcal}$$

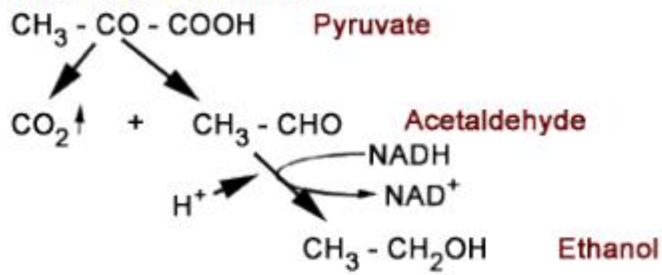
(b)Side reaction

$$2\ C_6H_{12}O_6 + H_2O \rightarrow \underbrace{ROH + R'CHO}_{\text{Fusel oil}}$$

- Enzymatic reactions
  - Enzymes (bio-catalyst)are produced by living organism (bacteria)
  - Mild Condition : pH 4 -9 and T 30 to 70 ˚C.
- Raw material requirements: Molasses (50-55% total sugar); Sulfuric acid; Ammonium sulfate.



Ethanol Formation



Effect of various factors on ethanol conversion

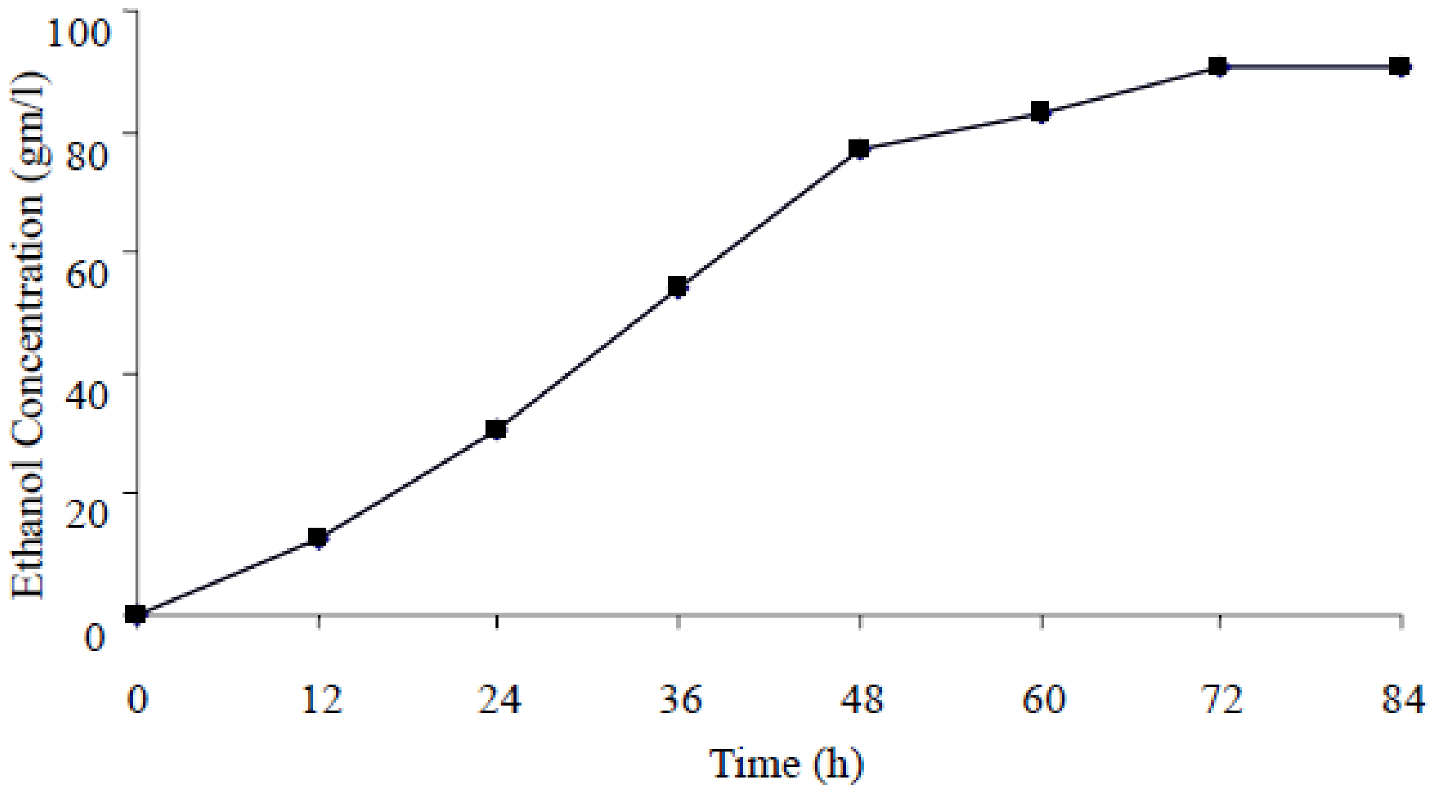
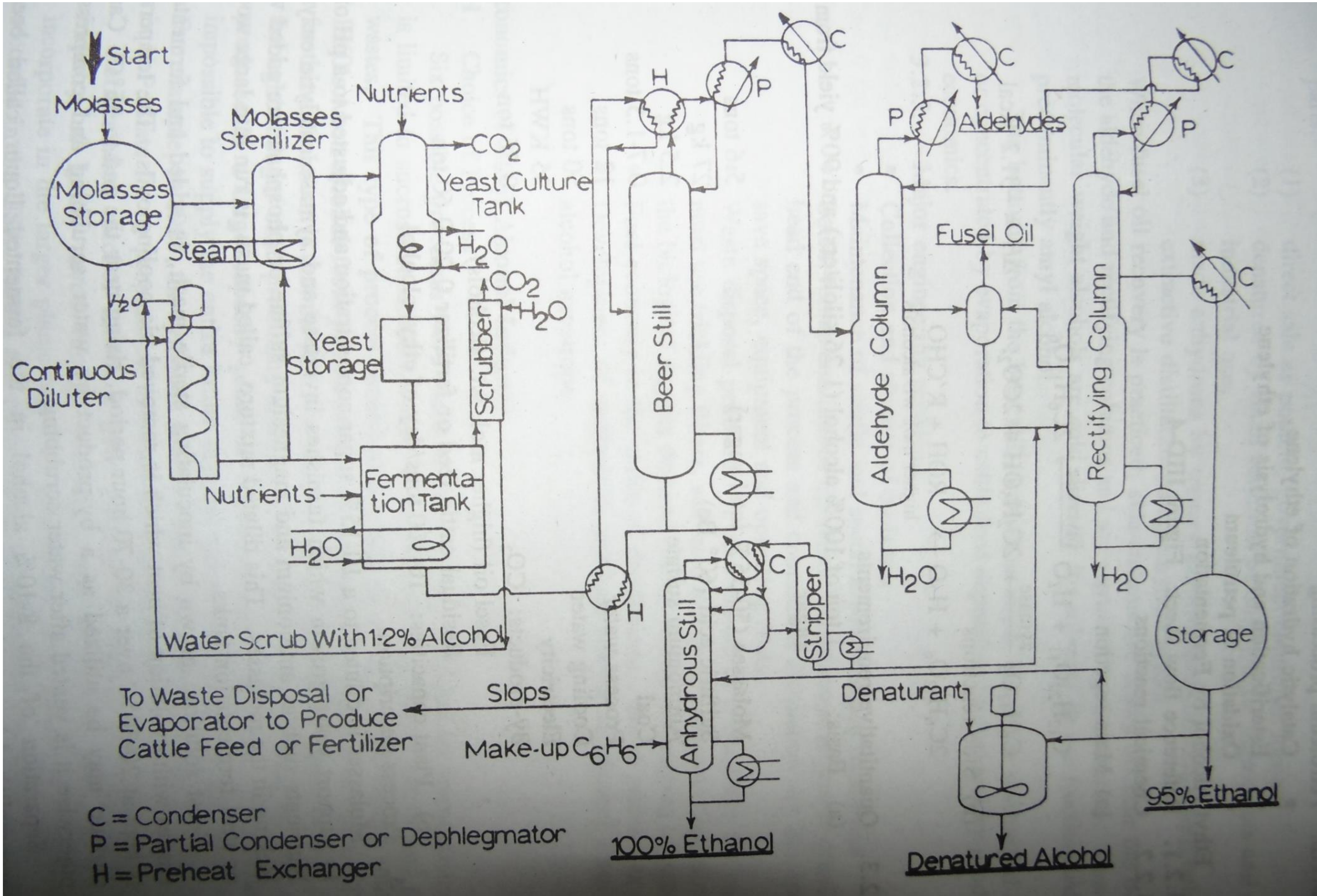


Figure 5. Productivity of bio-ethanol

Process Description



Functional role of various units

(a) Molasses storage tank: Molasses (liquor obtained as by product of sugar industries) is a heavy viscous material, which contains sucrose, fructose and glucose (invert sugar) at a concentration of 50-60(wt%).

(b) Sterlization tank: Yeast is sterilized under pressure and then cooled.

(c) Yeast cultivation tank: Yeast grows in the presence of oxygen by budding. Yeast is cultivated in advance.

(d) Yeast storage tank: Yeast are unicellular, oval and 0.004 to 0.010mm in diameter. PH is adjusted to <u>4.8 to 5</u> and temperature up to <u>32˚C</u>.

(e) Fermentation tank: Chemical changes are brought by the action of enzymes invertase and zymase secreted by yeast in molasses. Fermentation is anaerobic. Heat is evolved which is removed by cooling coils. Residence time is 30-70 hours and temperature is maintained at <u>20-30˚C</u>. 8 -10%alcohol by volume(beer) is produced by fermentation process. HCl or sulfuric acid is added to obtain <u>pH 4.5</u>

(f)Diluter: Here molasses is diluted to <u>10 to 15% </u>sugar solution.

(g)Scrubber: Carbondioxide is released and utilized as by product. By-product CO_2 contains some ethanol due to Vapor liquid evaporation and can be recovered by water scrubbing. Water is sent back to continuous diluter stream.

(h)Beer still: 50-60% concentration alcohol and aldehyde is produced. Slops are removed as bottom product. Slop is concentrated by evaporation for cattle feed or discharged as waste. Slop contains proteins, sugar and vitamins.

(i)Aldehyde still: Undesirable volatile liquid; aldehyde is taken off from the top of the still. From the side stream alcohol is feed to the decanter.

(j)Decanter : Fusel oil which is high molecular weight alcohol is recovered by decantation. The principle behind extraction of fusel oil from ethanol is that higher alcohols are more volatile than ethanol in solution containing a high concentration of water.

(k)Rectifying column: In the column, azeotropic alcohol- water mixture of 95% ethanol is withdrawn as side product. This 95% ethanol is condensed in condenser and stored in storage tank. Side stream is withdrawn and sent to decanter. At the bottom, water is discharged. Here, alcohol – water mixtures are rectified to increase the strength of alcohol.

(l)Storage tank: From storage tank, three streams are evolved:

- Direct sale as potable alcohol
- Denatured by small addition of mildly toxic agent for industrial use.
- To anhydrous still to produce 100% ethanol.

(m)Mix tank: For producing denatured alcohol, denaturant is mixed with the 95% ethanol produced from rectifying column. Denaturant is normally methanol/naphtha (10vol%)

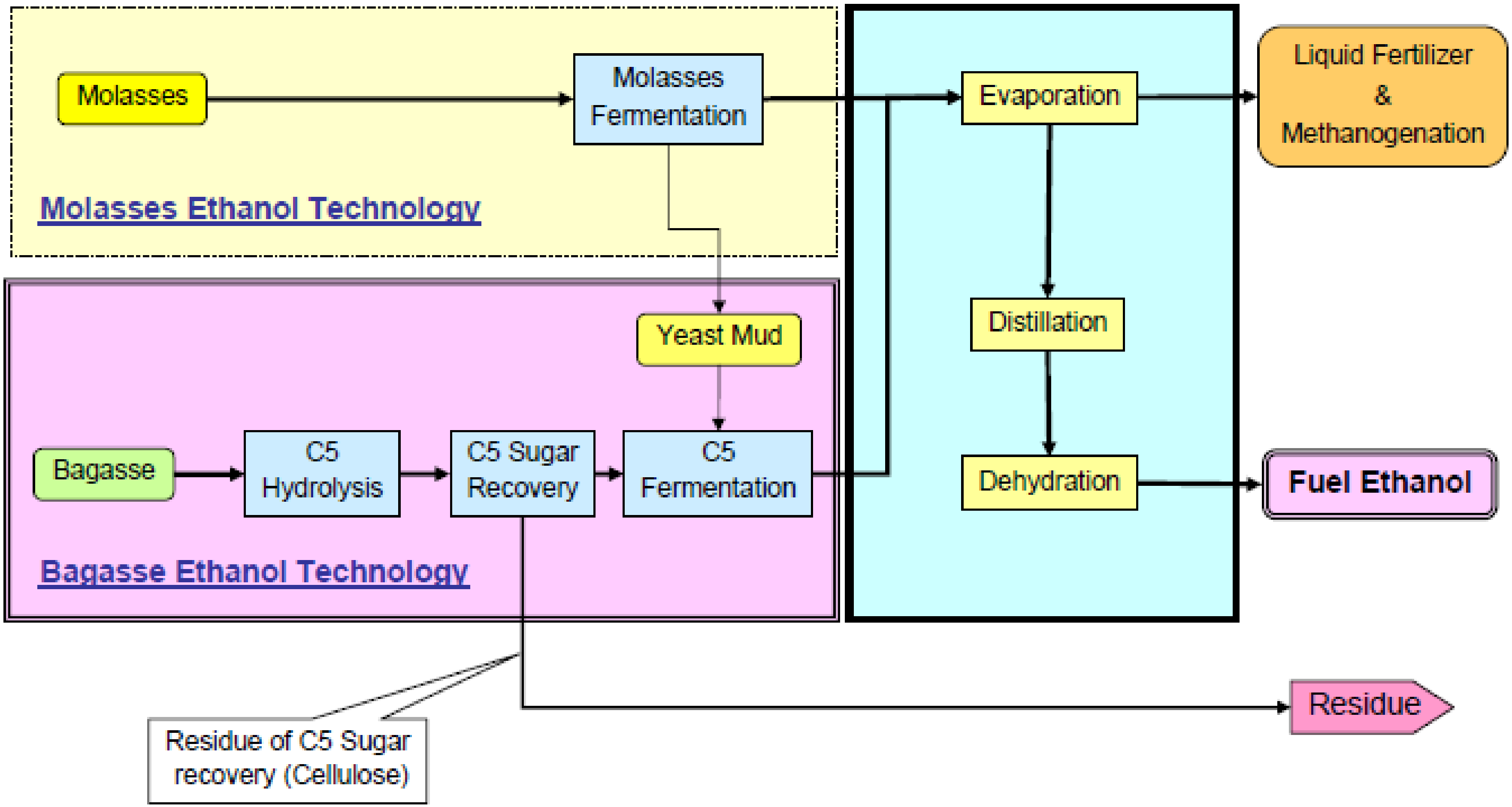
(n)Ternary Azeotropic distillation: The product from rectifying column is a ternary minimum boiling azeotrope of ethanol, water and benzene. Benzene is an azeotropic agent.

- Main units present are: anhydrous still, decanter, stripper and few heat exchangers.
- Anhydrous motor fuel grade ethanol (100% ethanol) is produced as product.
- Heat integration and energy recovery plays a vital role in reducing energy requirements.

Engineering Problems

- Collection and storage of molasses
- Maintenance of sterile and specific yeast culture conditions.
- Batch versus continuation operation
- Waste disposal problem
- Development of methods to produce anhydrous alcohol from the 95% alcohol azeotrope

Second generation ethanol production technology



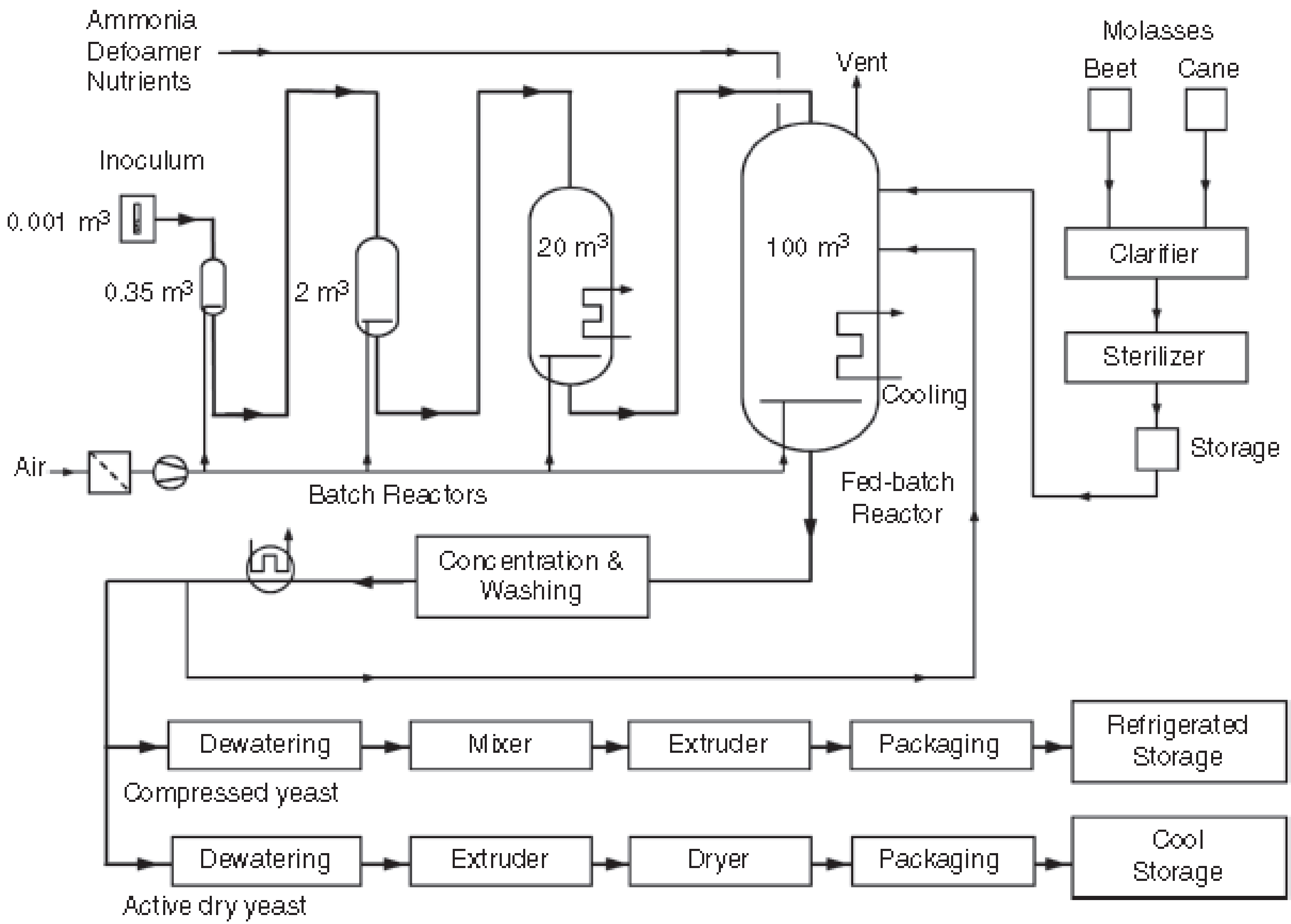


Figure 13.5 *Process steps in the production of bakers' yeast.*