

Lecture 26: Preparation of wood pulp by sulfate (kraft) process

26.1 What is pulp?

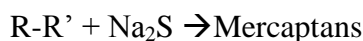
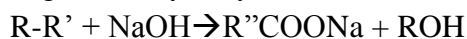
- Pulp is a commercial fibrous material obtained from bamboo, wood, bagasse (waste material) etc. by mechanical and chemical means.
- Pulping means disintegration of bulky fibrous material to small fibres.
- There are mainly three modes of production of pulp:
 - (a) Mechanical
 - (b) Chemical
 - (c) Semi chemical

26.2 Sulfate (Kraft) Pulping Process (Figure 26.1)

- Most popularly used process.
- This is an alkaline process.
- Na_2SO_4 is added to the cooking liquor. So its common name is sulfate process.
- The presence of sodium sulfide makes bleaching of pulp easier and the paper produced has better strength.

Chemical reactions involved

- (i) Digestion (hydrolysis and solubilization of lignin)

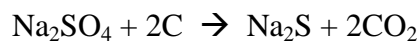


- (ii) Chemical recovery from black liquor

- (a) Smelting

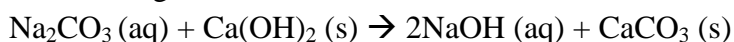


(lignin)



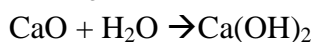
(from R) (white liquor)

- (b) Causticizing



(green liquor)

(white liquor)



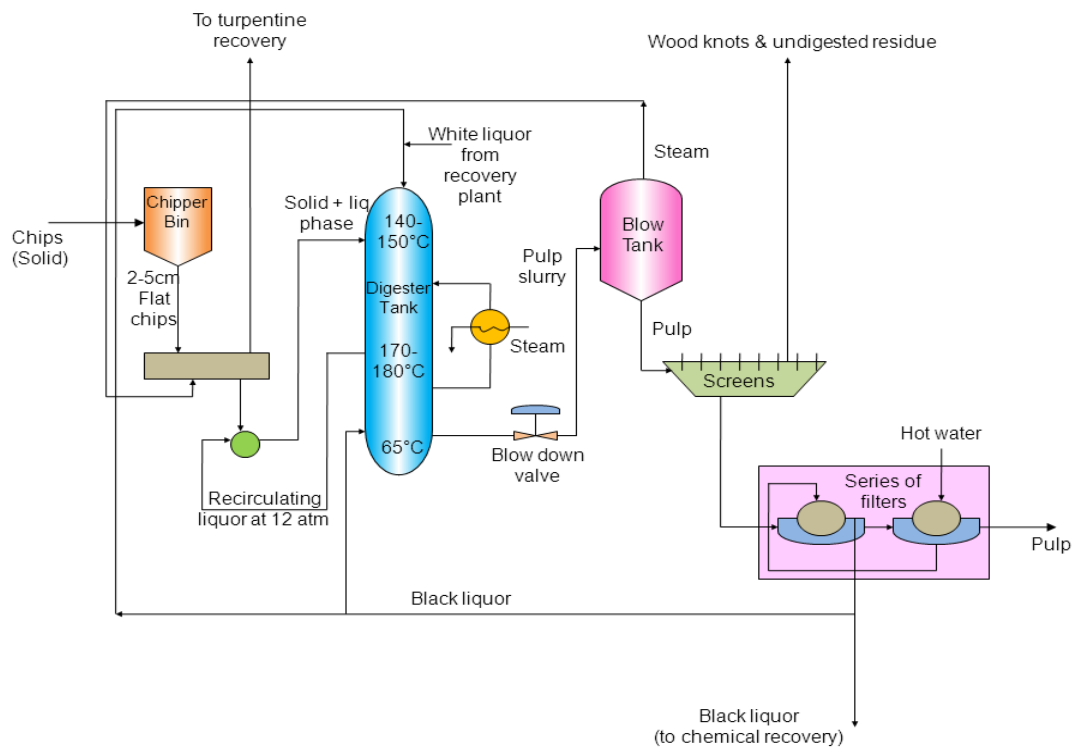


Figure 26.1 Flow sheet of manufacture of pulp manufacture

26.3 Functional role of various processes

(a) Chipper bin:-

- Chips are fed in this device.
- Cut logs are conveyed to the chipper where rotary disks with heavy knives reduce the wood to size 2-5cm flat chips.
- Size reduction is done to maximize penetration of process chemicals.

(b) Digester tower:-

- Continuous digester tower is 25 – 30m tall.
- Chips are preheated with volatilizing turpentine and non-condensable gases.
- For controlling digestion temperature, cooking liquor is withdrawn as side streams and circulated through heat exchanger.
- Digestion is done to free lignin and other non-cellulosic content.
- Cooking time is about one and a half hours at 170°C.
- To avoid mechanical weakening of fibres, digested chips are cooled with recycled black liquor.
- Temperature is maintained at 140-180°C and pressure at about 10 atm.
- Bottom temperature is maintained at 65°C

(c) Blow down valve:-

- This valve reduces the pressure of the stream from 80atm to 1atm before entering blow tank.

(d) Blow tank:-

- When hot pulp slurry is passed to the blow tank, heat is recovered in the form of steam.
- The chips are preheated with this recovered steam.
- The blow tank has high concentration of pulp and low concentration of water.

(e) Screens:-

- Pulp is screened so as to remove wood knots and undigested residues.

(f) Series of filters

- Pulp is filtered to separate black liquor for chemical recovery plant.
- Black liquor is also recycled back to digester for cooling the digested chips.
- Hot water is added to second filter for better filtration.

Bleaching of pulp

To produce white paper, the pulp is bleached. The chemicals used to bleach pulp must be environment friendly. Bleaching with chlorine produces dioxins and other undesirable products. So, nowadays pulp is bleached with hydrogen peroxide, ozone, chlorine dioxide, oxygen etc. The objective of bleaching is to remove small fractions of lignin that remains after digestion.

26.4 Technical Questions

1. Why is blow down valve introduced in the flow process?

Ans: It reduces the pressure of pulp slurry from 80atm to 1atm before entering the blow tank.

2. Why is hot water added to the second filter and then the spent water is circulated to the first filter?

Ans: Hot water has maximum efficiency to remove dissolved chemicals from leached pulp. Therefore, hot water is used in the second filter which eventually becomes spent water. The spent water can remove maximum solids from the pulp. The operation is counter-current in effect.

3. What is the technical difference between Sulfate(Kraft) Process and Sulfite Process?

Ans: i) Sulfate process is an alkaline process whereas the Sulfite process is an acidic process.

- ii) The pulp has to be bleached more in the Sulfate Process as compared to the Sulfite process.
- iii) For Sulfate process, digestion time is 2-5hrs at temperature 170-176°C and pressure 660-925kPa whereas for Sulfite process, time required is 6-12hrs at temperature 125-160°C and pressure 620-755kPa.
- iv) Raw materials are less significant and fibers have better strength properties in Sulfate process.

4. Why does the black liquor enter at various sections of the digester ?

Ans:

- Black liquor is recycled to the base of digester tower for cooling digested chips so as to avoid mechanical weakening of fibres.
- It is withdrawn as side stream from digester and circulated through heat exchanger to reheat and control the digester temperature.
- It is also used along with white liquor to adjust solid -liquid ratio in the digester entry section. Thereby, desired operating conditions of the digester are met.

5. How is turpentine recovered in the pulp manufacturing process ?

Ans: Turpentine is obtained by the distillation of the resin obtained in the pulp manufacturing process.

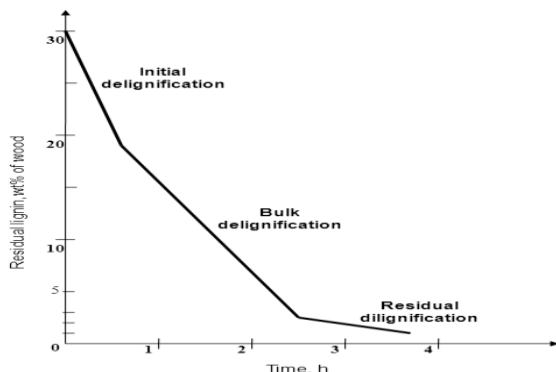
6. What are the other by-products of the pulp and paper industries ?

Ans: Main byproducts of the Kraft process are turpentine, rosin and tall oil soap.

7. What is sulfidity?

Ans: The mass ratio of sodium sulfide to caustic soda plus sodium sulfide, (where all masses are expressed on Na₂O basis) is known as sulfidity. The presence of sodium sulfide makes the bleachability of pulp easier and paper produced has better strength properties.

8. From literature survey, obtain digester kinetics for lignin removal along with relevant technical information that will be useful for its design as well as operation.



Delignification Kraft pulping rate for softwoods at 160 °C (Kleppe (1970)).

Kinetic expression:

At constant sulfidity and alkali charge, the delignification rate is regarded as a homogeneous first order reaction with respect to Lignin concentration (wt %) in the wood using the expression (Vroom (1957)):

$-dL/dt = kL$ where ‘k’ is the rate constant.

The temperature dependency of ‘k’ is provided as

$\ln k = (43.2 - 16.113/T)$.

where T is the temperature of the digester.

Q. 9. What is solvent pulping ?

Ans. In solvent pulping, lignocellulosic feedstock is contacted with organic solvents such as acetone, methanol, ethanol, butanol, ethylene glycol, formic acid or acetic acid at 140 – 220 ° C in an aqueous solution consisting of 20 – 60 % water. Subsequent separation and recovery of the solvent is carried out using distillation. Ethanol is the preferred solvent for solvent pulping. Solvent pulping provides 4 – 5 % higher yield than cracked pulping.

References :

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 27: Chemical recovery from black liquor and production of paper

27.1 Introduction

The black liquor (lignin-rich) produced from the Sulfate pulp production contains 95-98% of digested chemicals. To reduce air and water pollution and to balance economy of operation, these chemicals should be removed before disposal.

In chemical recovery process, black liquor is concentrated, burned and limed.

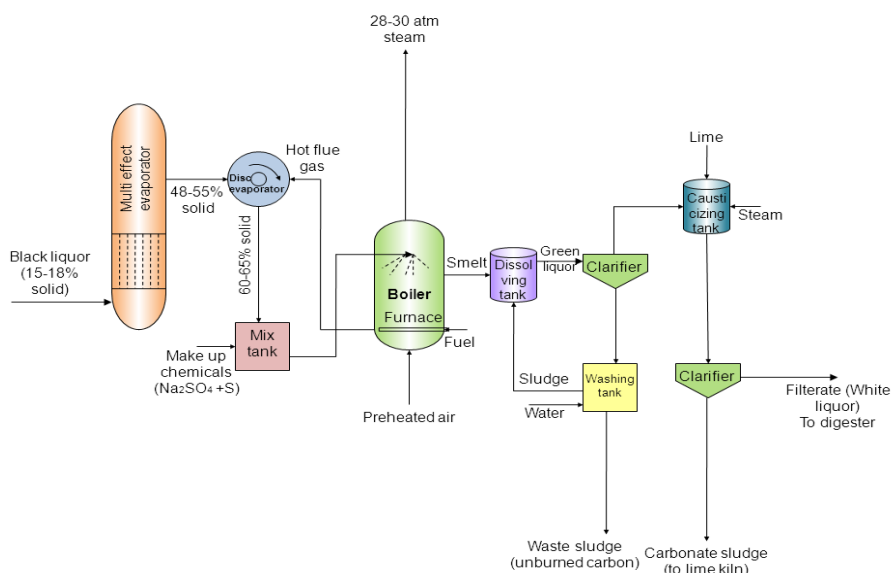


Figure 27.1 Flow sheet of chemical recovery from black liquor

27.2 Functional role of various units (Figure 27.1)

(a) Multi effect evaporator

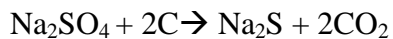
- It is a series of single effect evaporators.
- Multi-effect evaporator and disc evaporator concentrate the black liquor from 15-18% solid to 60-65% solid.

(b) Mix tank

- It is designed with two agitators to mix the product.
- Make up chemicals ($\text{Na}_2\text{SO}_4 + \text{S}$) are added.

(c) Boiler

- It produces molten slag.
- Here organic carbon present in black liquor is burned.
- High pressure 28 atm to 30atm steam is produced.
- The reaction that takes place inside furnace is



(d) Dissolving tank

- The molten chemical smelt dissolve immediately with cold water and yield green liquor (aqueous Na_2CO_3).

(e) Clarifier

- It is used for filtering.
- It separates calcium carbonate sludge and white liquor.
- Filtering medium is monel metal.

(f) Washing tank

- Impurities are washed away in this tank after clarifying.

(g) Causticizing tank

- It precipitates lime mud.
- Carbonate is causticized by adding $\text{Ca}(\text{OH})_2$

27.3 Production of Paper (Figure 27.2)

Paper is a sheet material made of fibers which are held together by hydrogen bonds. In wet process, fiber suspension in water is made and it is then made into sheet and dried. Paper making process is generally done on Fourdrinier machine.

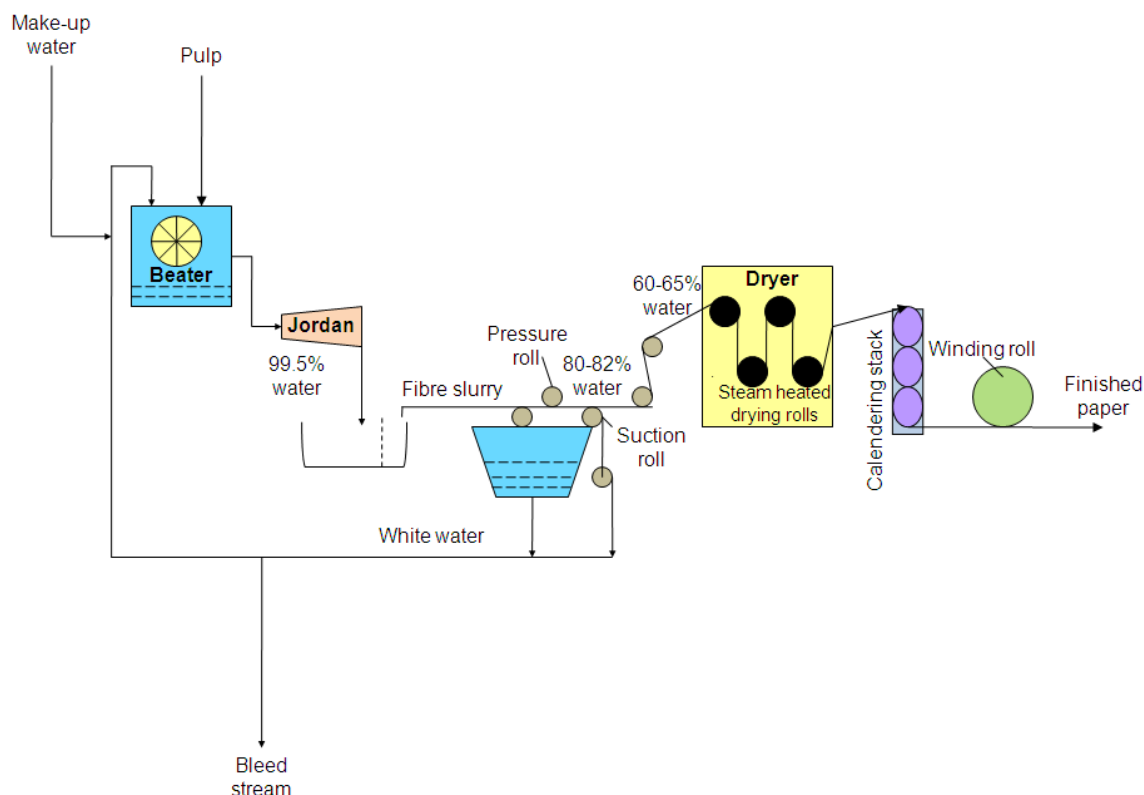


Figure 27.2 Flow sheet of production of paper

27.4 Functional role of various units

(a) Beater

- Beater mechanically disintegrates the pulp fibers to make paper stronger, uniform, dense, opaque etc.
- It consists of metal blades attached with rotating drum.
- Finely ground fillers (to increase brightness, flexibility, softness and weight) and coloring agents are also added.

(b) Jordan

- It is a conical refiner or Jordan engine.
- Metal bars and stones are set inside.
- Here, pulp is deformed, defibered and dispersed.

(c) Web forming

- 99.5% water fiber slurry are made to run on an endless belt at a speed of 50m/min to 500m/min.
- Pulp fibers are arranged into web.
- Water is drained out by gravity.
- Shaking motion is provided for better interlocking of fibers on mat.
- White water is collected and it is reused to conserve water and additives and to avoid pollution.

(d) Pressing

- Free water is removed by pressing with pressure roll, water mark roll and suction roll.
- Water content is reduced to 60-65% water.

(e) Drying

- Additional water is removed by smoothing rolls and series of steam-heated metal drying rolls.
- Water is reduced from 60-65% to 5-6%.

(f) Finishing

- Here paper is passed through a series of calendaring rolls for producing smooth paper.
- It is wounded on a large winding roll.

27.5 Technical Questions

1 Why are make-up chemicals added to the mix tank before the smelter?

Ans: White liquor chemicals ($\text{Na}_2\text{S} + \text{NaOH}$) are lost in the pulp manufacturing process in various ways. These include loss along with pulp, waste sludge, wood knots and undigested residue. Though significant portion of the make-up chemicals are recovered from the recovery plant, the make-up chemicals are still required to add up for the loss. These chemicals are added to the mix tank for smelting reaction. This is because Na_2SO_4 is not desired in the digester and Na_2S is desired which is generated from the smelting reactions.

2 Discuss energy economy in the paper and pulp manufacturing process

Ans:

- Chip dust is burnt in the paper mill boiler to reduce the consumption of purchased fuel.
- Half of total fuel and electricity used is self-generated from biomass (primarily from spent pulping liquors, wood residues, and bark) and thus reduces energy costs.

- By products of paper industries such as tall oil, rosin, turpentine, gums, resins are well utilized.
- Steam produced in the boiler is used in various processes (causticizing and heat exchangers associated to the digester for temperature control).
- Flue gas produced in the furnace is used in the disc evaporator.

3 The smelt produced by boiler is in solid, liquid or gaseous phase?

Ans: Smelt is a molten salt mixture.

4 How are environmental issues taken care in pulp and paper production?

Ans:

- Chip dust is burnt in the boiler to eliminate environmental problems associated with chip dust disposal.
- Bleaching of pulp with chlorine produce dioxins and other undesirable products. So chlorine is replaced by hydrogen peroxide.
- White water is collected and is reused to conserve water & additives and to avoid massive pollution.
- In pulp production process, hot water which is added in second filter is reused in first filter to conserve water.
- Waste-water treatment involving incineration is usually associated with the paper and pulp manufacturing plant. This solves both environmental and energy issues of the pulp and paper plant.

5 What is white water?

Ans: White water consists of flour (minute fibers) that drains from the wire part of the paper manufacturing machines. It consists of about 0.5 % of pulp.

6 Why is bleed stream taken out?

Ans: White water contributes to the slurry viscosity and blending issues of the pulp + water mixture. Since beyond a desired viscosity the pulp + water mixture would not provide good quality paper for fixed choice of other operating parameters of the paper manufacturing process, white water needs to be bleed out. Also, usually, white water from the machinery where web forming is carried out is usually recycled and white water emanating from the pressing machines is sent for wastewater treatment and appropriate disposal.

7 Explain how dryer performance can be controlled to obtain good paper quality in quantity.

Ans:The dryer needs to operate in such a way that the temperatures of different rolls and their speeds be optimized. This is due to the fact that paper with about 60 % water enters the dryer and leaves with about 5 % moisture in the paper. Therefore, the drying rolls need to be efficient to quickly remove the moisture using steam heated rolls. A variation in the steam heated rolls temperature is also expected, as progressively variant temperatures along the rolls will provide maximum removal efficiency of the paper. In summary, there exists trade-offs with respect to the roller speed and roller temperature. Subsequently, the roller temperature is controlled using steam flow rate. In other words, both steam flow rate and roller speed contribute towards the dryer efficiency and providing required quality control for the manufactured paper.

8. Why is web forming process supported by the endless belt ?

Ans:Aslurry of 99.5 % cannot withstand its own weight and disperses away. Therefore, the endless belt would act as a support system to gradually form the web as the solution progresses ahead.

References :

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 28. Manufacture of sugar from sugarcane

28.1 Introduction

Sucrose is a disaccharide that occurs naturally in most fruits and vegetables.

Sugar occurs in greatest quantities in sugarcane and sugar beets from which sugar is separated economically and commercially.

Chemical formula – $C_{12}H_{22}O_{11}$

Molecular weight – 342

Density = 1.58 kg/m^3

Sucrose is soluble in water but slightly soluble in methyl alcohol and ethyl alcohol.

Process flow sheet: Illustrated in Figure.

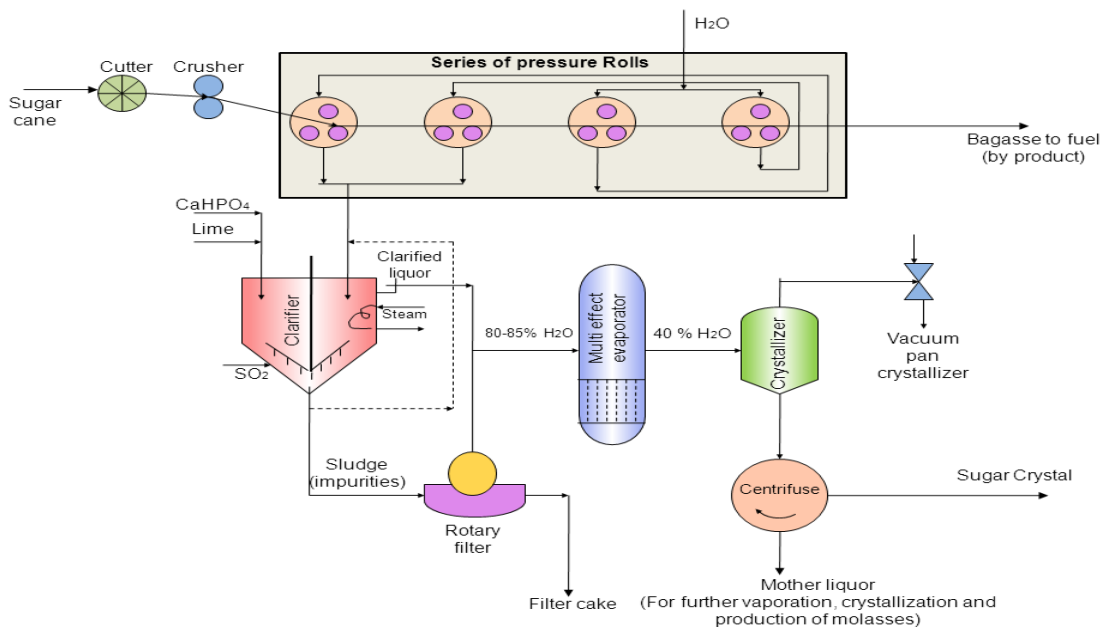


Figure 28.1 Flow sheet of manufacture of sugar from sugarcane

Raw material: Sugar cane

28.2 Functional role of various processes (Figure 28.1)

(g) Cutter

- The cutter consists of knives on a cylindrical shaft which rotate at a velocity of 400 to 500 rpm.
- The knives cut the canes into small pieces.

(h) Crusher

- Canes are shredded here.
- It consists of two rollers rotating in opposite direction.

(i) Series of Pressure mills

- Crushed canes are passed through four pressure mills to extract juice.
- Each pressure mill is made up of cast iron rolls.
- Rolls are grooved and the width decreases from first roll to the last.
- Make up water added in the third and fourth mill is recycled back to the first two mills.
- About 85-90% of juice present in cane is extracted.
- Bagasses are produced as byproduct.

(j) Clarifier

- In general two methods of clarification are available for the manufacture of white sugar, namely, Sulfitation process and Carbonation process.
- The juice now comes to thickener.
- To precipitate the colloids, calcium phosphate(CaHPO_4) is added followed by milk of lime.
- The milk of lime used has 9 to 10% strength and about 400mg CaO/litre alkalinity.
- Apart from maintaining p^{H} about 7, SO_2 gas also acts as a bleaching agent.
- Phosphoric acid or CO_2 can also be substituted as acidifying agent depending upon the type of extracted juice.
- At the bottom of clarifier, mud (impurities) are settled and drained.
- Steam is used to slightly heat the juice.

(k) Rotary filter

- The underflow mud from the bottom of thickener is passed to a continuous rotary filter press to recover sugar solution.
- This sugar solution if it is clear, is passed to multieffect evaporator or otherwise recycled back to clarifier.
- The filter cake produced is used for fertilizer.

(l) Multieffect evaporator

- The clarified liquor overflows to the 3-4 forward feed multieffect evaporator.
- Here juice is concentrated from 80-85% H₂O to 40% H₂O to make juice ready for crystallization.
- A vacuum of 63cm is maintained in the last effect.

(m)Crystallizer

- The clarified concentrated sugar solution comes to crystallizer.
- The sugar solution is further boiled in vacuum pans at vapor temperature of 57°C until fine cloud of crystals is seen.
- Crystallization is completed in vacuum pan unit.

(n) Centrifuge

- The mixture of crystals and syrup is called masscuite.
- The masscuite from crystallizer is centrifuged in basket type centrifuged to basket type to centrifuge remove mother liquor (molasses) which is a byproduct.
- The high grade sugar crystals are obtained here.
- The centrifuge speed is maintained at 800 to 1000 rpm.

28.3 Technical Questions

1. What is special about the sugar production process from sugarcane

Ans:

Sugarcane is a biological resource for sugar. If sugar is used for the production of alcohols which can be in turn used as fuels in modern cars, then the original source for obtaining these fuels is the agricultural industry. In other words, a biological source for fuels is an interesting technological concept for energy requirements of the modern society. On the other hand, over consumption of sugars for fuel requirements could enhance sugar demand for food usage and could spiral up the prices of the sugarcane. Therefore, a careful policy needs to be adopted for the utilization of sugar towards various process routes and technologies.

2. Why last effect evaporator is maintained at 63cm vacuum?

Ans:

- To allow the flow of juice from first effect to other due to pressure drop.
- To increase temperature gradient for better heat transfer.

3. What is the technical difference between sulfitation and carbonation clarification process?

Ans: Sulfitation process is based on large quantities of sulfurous acid with proportional quantity of lime. Calcium sulfite formed prevents oxidation and darkening of juice. It also precipitates gums and albuminous matter thereby it helps in filtration.

In this process at about 65°C, SO₂ gas is bubbled to juice to slightly increase acidity. The juice is then heated to boiling point for 2 hours. After sulfitation process, P^H becomes 7 and concentration becomes 12 to 13 Brix.

In carbonation process, 1 to 1.5% of lime by weight at 50 to 55°C is added to the juice. CO₂ gas is bubbled to remove alkalinity. The temperature is raised to the boiling point to remove excess carbonic acid.

4. What are the byproducts of sugar industries?

Ans: Bagasse, filtercake and molasses.

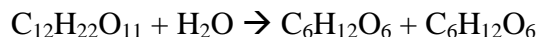
5. Discuss energy economy in the sugar manufacturing process?

Ans:

- Bagasse can be used to generate steam. Steam can be used for electricity generation which can be used to run machinery in the plant. Additional power can be exported to household usage and thus save consumption of fuel.
- Bagasse is also used as raw material for paper industries as fertilizer and cattle feed.
- The final mother liquor; molasses is sent for the production of ethyl alcohol by fermentation process.
- Press mud is used as phosphatic fertilizer in farms.

6. What is the problem in storage of sugarcane?

Ans: There should be no delay in transporting freshly cut sugarcane to sugarmill because after 24 hours of cutting causes loss of sucrose by inversion to glucose and fructose (monosaccharides).



Sugar glucose fructose

The extent of inversion is measured by polarimeter. The non inverted sugar has $+97^\circ$ polarization and completely inverted sugar has -20° polarization.

This inversion of sucrose is maintained by quick delivery of freshly cut sugarcane to sugar mills.

7. Why vacuum pan crystallizer is used?

Ans: With the use of vacuum pan crystallizer, the pressure is reduced so as to super saturate the sugar solution. After supersaturation the formation of crystals starts. When the volume of massecuite (sugar solution + crystals) exceeds certain limit, then it is transferred to centrifuge for separation.

8. What are the environmental problems faced by sugar industries.

Ans:

- Flue gas(fly ash) produced by combustion of bagasse.
- The untreated effluent from sugar mills have BOD of 1.7 to 6.6 g/lit, COD of 2.3 to 8g/lit, TSS up to 5g/lit and high ammonium content.
- Mill generates lot of dust and odor.
- Sometimes pesticides are also present in sugar cane juice.

Lecture 28.4 Starch

28.4.1 Introduction

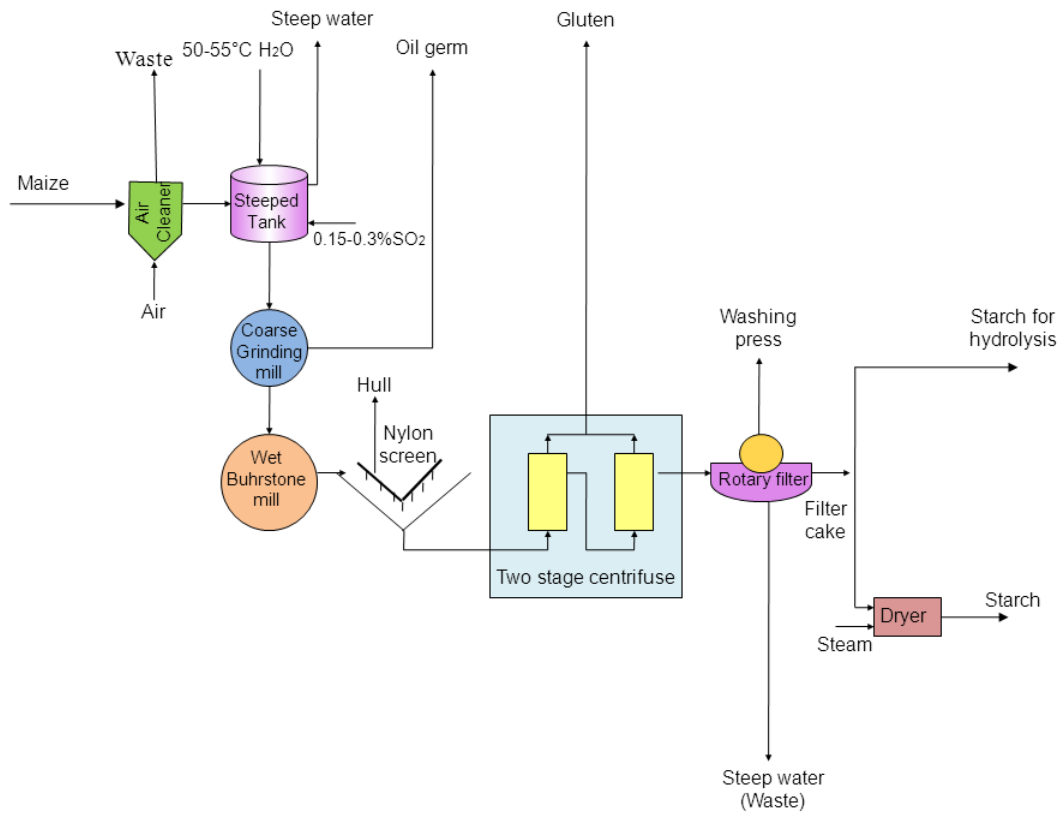
Starch consists of a chain of D-glucopyranosyl units. It is used in the manufacture of textiles, paper, adhesives, insecticides, paints, soaps, explosives, and derivatives as dextrins, nitro starch and corn sugar.

Chemical formula- $C_6H_{10}O_5$

Starch gets hydrolysed by acids, alkalis and enzymes giving dextrin, dextrose. Starch forms gels with water within several minutes at 60-80°C.

The major source of starch is maize kernels.

Process flow sheet: Illustrated in Figure.



28.4.2 Functional role of various processes

(a) Air cleaner:-

- At first, maize kernel containing 60-65% starch is introduced in air cleaner.
- Air is passed through the bottom of cleaner.

(b) Steeped tank:-

- Air cleaned maize kernel is passed to steeped tank to make it soft.
- 50-55°C water and 0.15-0.3% SO₂ is added.
- Here SO₂ acts as a bacteriostatic.
- Steeping is done to yield high production and quality of starch.
- The residence time is 40-50 hours.

(c) Grinding mill:-

- The soft grains are passed through coarse grinding mill to rupture the cells.
- The floating germ oil from the tank is removed.

(d) Buhrstone mill:-

- The kernel is then wet ground in buhrstone mill.
- This mill completely disrupts the cells of endosperm and release starch granules.

(e) Nylon screen:

- The wet ground kernel is then passed through nylon cloth.
- Water washes the starch through the screens.
- The fibre and hulls is left over on the nylon screen.

(f) Two stage centrifuge:

- The gluten is water insoluble protein.
- Gluten is a light fraction which is separated in two-stage centrifuge.

(g) Rotary filter:

- Water starch mixture is then passed then passed to continuous rotary filter.
- Starch is separated as filter cake which is of yellow colored and contains high amounts of protein.
- Other products can also be made by hydrolysis of starch.

(h) Dryer:

- Starch as filter cake is dried and powdered in dryer with the introduction of steam in dryer and produced as pearl starch.

28.4.3 Technical Questions

1.How is degermination carried out?

Ans: To free germs the maize kernels are coarsely ground in mill with cane to avoid oil leakage from germs otherwise oil will get soaked up with starch granules, which reduce starch quality. Lighter germs are separated by hydrocyclones.

For complete degermination, grinding and degeneration steps are performed twice. Then the germs are washed, dried and sold for corn oil production.

2.What is the use of steep water?

Ans: Concentrated steep water is consumed in the growth of penicillin and streptomycin. Steep water softens the kernels and release solubles.

3.How is gluten removed?

Ans: Gluten is starch milk, which contains water insoluble proteins. It is mostly separated by two successive nozzle type continuous centrifugal separators. The separation occurs due to density difference between starch and protein.

References :

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 29. Manufacture of Ethanol from Molasses

29.1 Introduction

Ethanol is a volatile, flammable, clear, colourless liquid. Ethanol is a good solvent. It is also used as a germicide, beverage, antifreeze, fuel, depressant and chemical intermediate. It can be made by the fermentation process of material that contains sugar or from the compound which can be converted to sugar. Yeast enzyme readily ferment sucrose to ethanol.

Molecular formula- C_2H_5OH

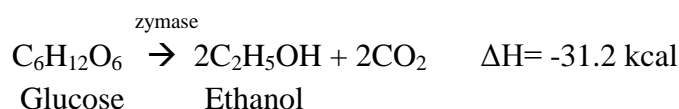
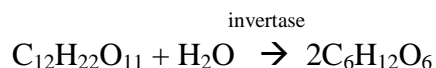
Molecular weight- 46.07

Density- 0.791 at 20°C

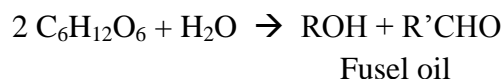
Boiling Point- 78.3°C

Chemical Reactions:

(a) Main Reaction

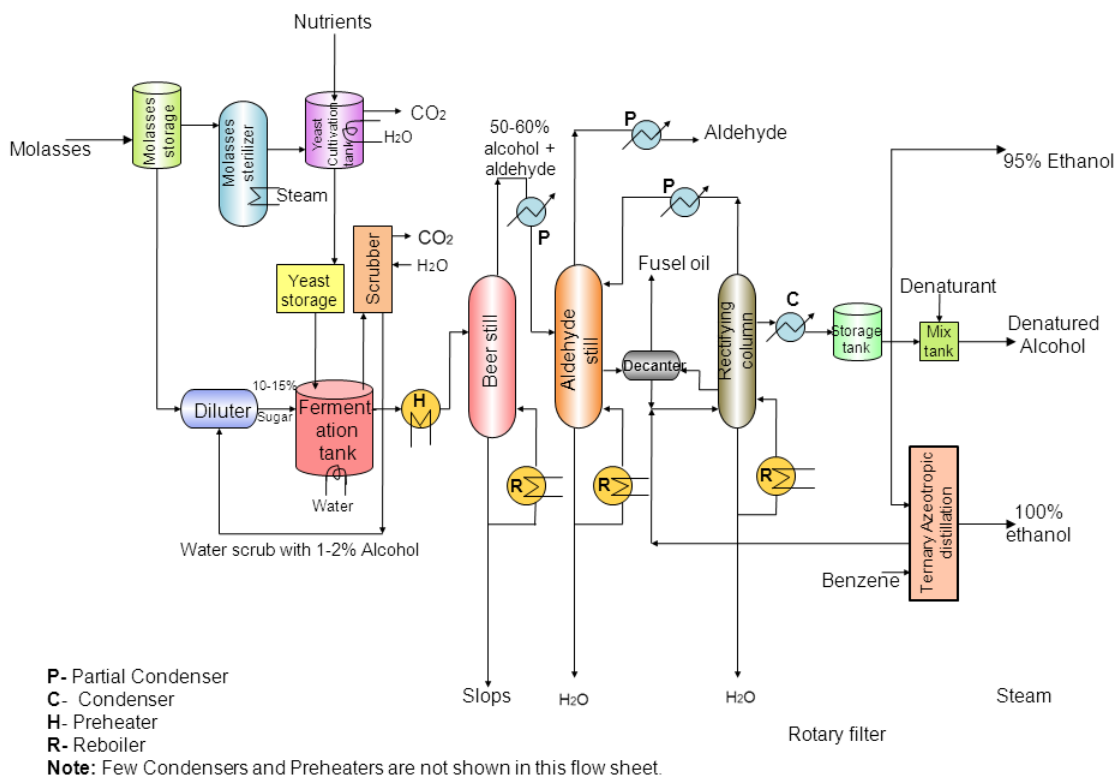


(b) Side reaction



Ethanol is raw material for many downstream organic chemical industries in India.

Raw Material: Molasses



29.2 Functional role of various units

(a) Molasses storage tank:

Molasses is liquor obtained as by product of sugar industries.

Molasses is a heavy viscous material, which contains sucrose, fructose and glucose (invert sugar) at a concentration of 50-60(wt/vol).

(b) Sterilization 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 4.8 to 5 and temperature up to 32°C

(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 20-30°C

8-10% alcohol by volume (beer) is produced by fermentation process.

HCl or sulfuric acid is added to obtain 4.5 P^H.

(f) Diluter:

Here molasses is diluted to 10 to 15% sugar solution.

(g) Scrubber:

Carbondioxide is released and utilized as by product.

By-product CO₂ 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.

It is extractive distillation column, and operates at a pressure of around 0.6-0.7 MPa.

(j) Decanter :

Fusel oil which is high molecular weight alcohol is recovered by decantation.

Fusel oil is fractionated to produce amyl alcohol or are sold directly.

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 portable.

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 (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.

Here mainly two units are present; 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.

29.3 Technical Questions

1. Explain Azeotropic distillation process for manufacturing 100% ethanol?

Ans1: The separation process of ethanol and water is energy intensive. Complete separation of ethanol and water is not possible by simple distillation. This is due to the fact that ethanol forms a minimum boiling azeotrope with water at 89 mole % (96.4 vol%) ethanol concentration at atmospheric pressure and 351 K. Therefore, a third component benzene is added as azeotropic agent. With addition of benzene, unfortunately, a ternary azeotrope containing benzene (53.9 mol%), water (23.3mol%) and ethanol (22.8mol%) is formed with a boiling point of 338K which is lower than the boiling point of ethanol. Eventually, the anhydrous still produces 100% pure ethanol as bottom product and ternary azeotrope at the top. The ternary azeotrope on cooling separates into two phases in the decantation unit in which two phases are formed:

(a) Benzene rich organic phase.

(b)Aqueous phase of benzene and ethanol.

While the benzene rich organic phase is recycled as reflux to the anhydrous still, the aqueous phase of benzene and ethanol is sent to a second column (stripper) which separates the ethanol/water from benzene. It is interesting to

note here that cooling enabled the phase separation of the azeotrope which eventually was further separated using stripping.

2. Why yeast storage is required?

Ans2: In due course of the fermentation process, it is possible that due to variations in the addition of nutrients, flow rates and conditions of the fermenter, there could be a possibility in the variation of solution concentration of microorganisms. In addition, prolonged biological activity could also encourage genetic modification. Therefore, yeast is always stored after the yeast culture tank so that always a reference stock is available and can be used for further growth of the microorganisms as a base cell culture.

3. What is the function of scrubber?

Ans3: In natural mass transfer processes, it is inevitable that 100 % separative distribution of compounds such as ethanol is not possible. Ethanol having a boiling point of 78.3 °C at atmospheric pressure due to existing vapor pressure circumstances enters the air leaving the fermentation tank. Therefore, the ethanol produced could get lost if left to the atmosphere as a vent stream. Henceforth,

4. Why molasses is sterilized?

Ans4: The molasses consist of other types of microorganisms which contribute to the production of other types of alcohols other than ethanol. Therefore, to allow the larger production of ethanol in comparison to other alcohols and ketones, the molasses is sterilized for the removal of other types of microorganisms.

5. What is denatured alcohol?

Ans5: Denatured Alcohol is ethanol which has been rendered toxic or otherwise undrinkable, and in some cases dyed. It is used for purposes such as fuel for spirit burners and camping stoves, and as a solvent. Some agents such as denatonium benzoate, methanol, naphtha, pridine are added to the ethanol.

6. Why alcohol obtained from rectifying column can't be more than 95% strength?

Ans6: Water form a binary constant boiling mixture which has higher boiling point than alcohol, anhydrous and absolute alcohol.

7. Why are partial condensers used in the process

Ans.7: A partial condenser is typically used in a distillation column when the product desired is send for further processing and the vapors are only cooled to obtain the desired reflux stream flow rates. In this way, in a sequence of distillation columns, it will lead to energy savings. The ethanol process flow

sheet consists of complex column stream interactions in terms of reflux streams. For instance, for the reflux for aldehyde column is supplied from both distillate vapors emanating from aldehyde and rectifying columns. It is also further interesting to note that the pressures of these two distillation columns are bound to be different. On the other hand, heat integration using the concept of pre-heat exchangers is encouraged for maximizing energy savings. All these have been factually encouraged by the presence of partial condensers. The development of better processes from base case scenarios is of course based on rigorous process design studies followed by pilot plant studies of the most encouraging options. Therefore, the utility of partial condensers is in fact a rigorous process design and systems engineering exercise.

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Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 30: Soaps and Detergents

30.1 Introduction

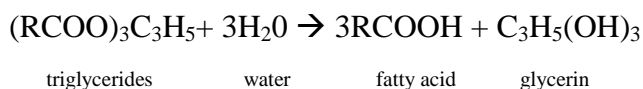
Soaps are sodium or potassium salts of fatty acid. Common fatty acids used are oleic acid, stearic acid, palmitic acid, lauric acid and myristic acid . Soaps are used for human comfort, cleanliness and for industrial use.

Soap is a surface active agent or surfactant. The soap molecules contain both hydrophilic part and hydrophobic part. The hydrophilic part of soap is carboxylate head group and hydrophobic part is aliphatic chain. The dirt or grease is cleaned by key mechanism.

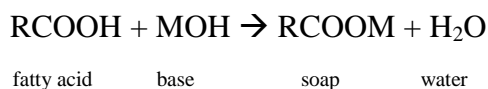
Most marketed bar soaps contains TiO_2 as an opacifier or as a whitener. A variety of dyes are also used to produce colour soaps.

Chemical Reactions:

Fat splitting reaction:



Saponification Reaction:



Process flow sheet: Illustrated in Figure.

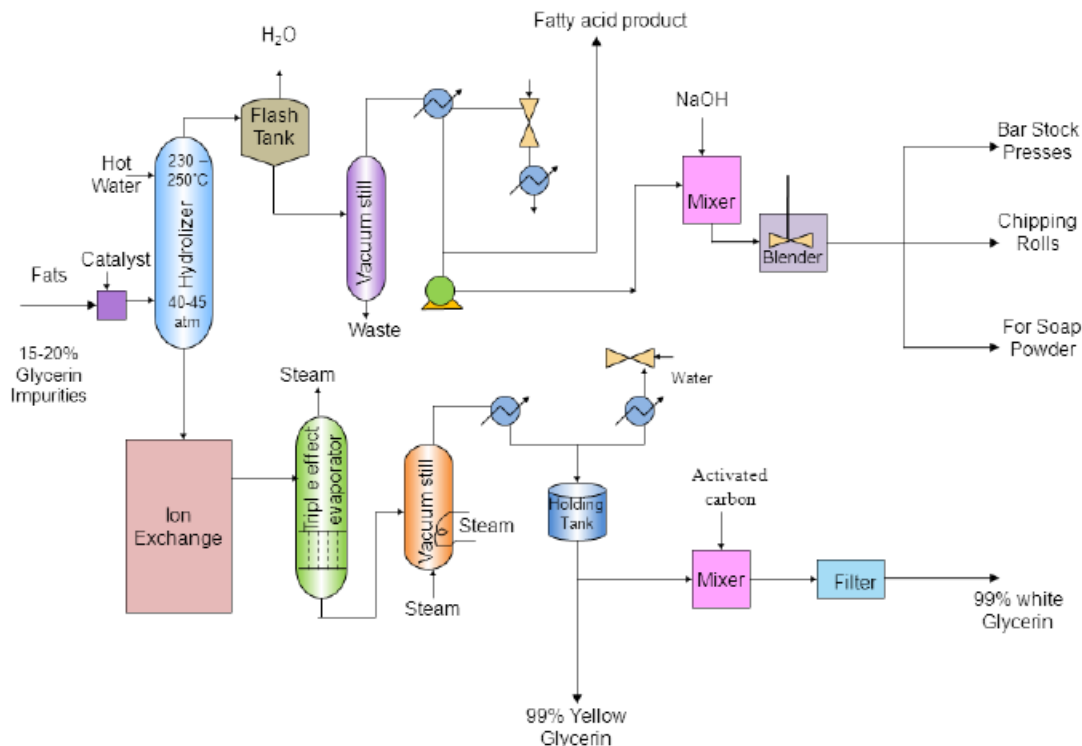


Figure 30.1 Flow sheet of manufacture of soaps, fatty acids and glycerin

30.2 Functional role of various processes (Figure 30.1)

(o) Hydrolyser

- The fat and catalyst are mixed together and enter the hydrolyser.
- Hot water is added here.
- Intimate mixing is required for the water oil immiscible phase.
- Water has 10 – 15% solubility in oil and fats.
- Temperature is maintained at 230°C - 250°C and pressure at 40 – 45 atm for reaction between water and organic compound.
- The fatty acids stream is produced as top product while glycerin stream is produced as bottom product.

Fatty acid stream block

(p) Flash tank:

- Fatty acids from the hydrolyser enters the steam flash tank to remove water & concentrate the fatty acids.

(q) Vacuum still:

- The concentrated fatty acids enter a high vacuum still.
- Jet ejector is used to generate vacuum in the still.
- Wastes are separated from the bottom.
- Fatty acid is also taken out as a marketable product.

(r) Mixer:

- Fatty acid produced from vacuum still is now pumped to mixer.
- Base such as NaOH or KOH is mixed in appropriate proportions and mixed thoroughly.
- After mixing a viscous mass is produced.

(s) Blender:

- The viscous mass from the mixer is sent to the blender.
- Ingredients like scents, anti fungal & anti bacterial chemicals etc. is mixed in the blender.
- The blender removes the solid mass which is then sent to:

1. Chipping rolls: to manufacture soap strips.
2. Spray dryer: To get soap powder (used in manufacture of liquid soaps).
3. Bar Press Stock: To press and cut the viscous mass into bars of soap.

Glycerin stream block

(t) Ion Exchange:

- 15 – 20% glycerin along with impurities from the hydrolyser goes for ion exchange.
- Here salt and colour is removed from glycerin.

(u) Triple effect evaporator:

- The product stream from ion exchanger is sent to triple effect evaporator.
- The glycerin solution is concentrated in evaporator.

(v) Vacuum still:

- The glycerin obtained from vacuum still is called yellow glycerin. It is used for industrial use.
- The steam produced from evaporator is used in vacuum still to further concentrate the glycerin.

(w) Mixer:

- For removing color, yellow glycerin is treated with activated carbon in mixer.

(x) Filter:

- Activated carbon is separated from the solution.
- 99% white glycerin is produced. The yield is 30 – 35kg per ton of soap produced.

30.3 Detergents

Detergents have better surface tension lowering action than soaps. Due to excessive foaming, it is unable to reduce organic content of sewage effluent. Biodegradation of detergent is an important environmental factor. Detergents react with hard water ions. Detergents are of four types - anionic, cationic, non-ionic and amphoteric. Most common type is anionic which is generally made up of sodium salts of an organic sulfate or sulfonate.

General method to make synthetic detergents:

Alkylbenzene + oleum \rightarrow alkylbenzene sulfonate

Tallow fatty alcohol + oleum \rightarrow fatty alcohol sulfate

Sulfonate + sulfate + NaOH \rightarrow sodium salts

Sodium salts + builders \rightarrow Detergents

30.4 Technical Questions

1. Discuss about raw material of soap.

Ans:

- Fatty constituents from refined tallow, coconut and palm oil, refined grease, byproducts of vegetable oil refining etc.
- In India, for the source of fatty acids mostly depends on imported tallow and palm oil.
- Coconut oil is the primary vegetable oil used for the manufacture of soaps.

2. Discuss the economy in soap manufacturing process.

Ans:

- The vacuum still uses the steam from triple effect evaporator thus reducing the make up steam in the still.
- Good amount of glycerin is produced as a byproduct which is sold in market.
- Fatty acid is also taken out as a marketable product. These fatty acids find use in manufacturing cosmetics, beauty products etc.

3. Why is ion exchanger used?

Ans: 15 – 20% glycerin (sweet water) along with impurities from the hydrolyser is put to the successive beds of anion and cation exchange resin. The glycerin reacts with salts. Ion exchange removes the colour and dissolved salts.

4. What is the difference between soft soaps and hard soaps?

Ans:

- Sodium salts are called hard soap where as potassium salts are soft soaps.
- A hard soap is moderately soluble in water and does not lather easily whereas soft soap dissolve faster and lather readily.
- Soft soap performs better than hard soaps in cleansing action.
- Tallow, animal fats and coconut oils are the main sources of hard soaps, while linseed oil, castor oil etc produces soft soaps. Mahua and ground nut oil produce intermediate consistency soaps.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984

Lecture 31: Edible and Essential Oils

31a.1 Introduction

Oils are organic molecule of carbon, hydrogen, oxygen and sometimes nitrogen and sulfur. It is composed of long chain fatty acids and esters (glyceride ester) as well as derivative of glycerine, long chain fatty alcohol, sulfate and sulfonates. Oils like castor oil, linseed oil are non edible and oils like ground nut oil, coconut oil are edible .

Oil is used in producing vanaspati ghee, soaps and detergents, cosmetics, medicines, polymers, paints and varnishes and in many other applications.

31a.2 Vegetable oil extraction

Raw material: Seeds of oilseed plant

Process flow sheet: Illustrated in Figure.

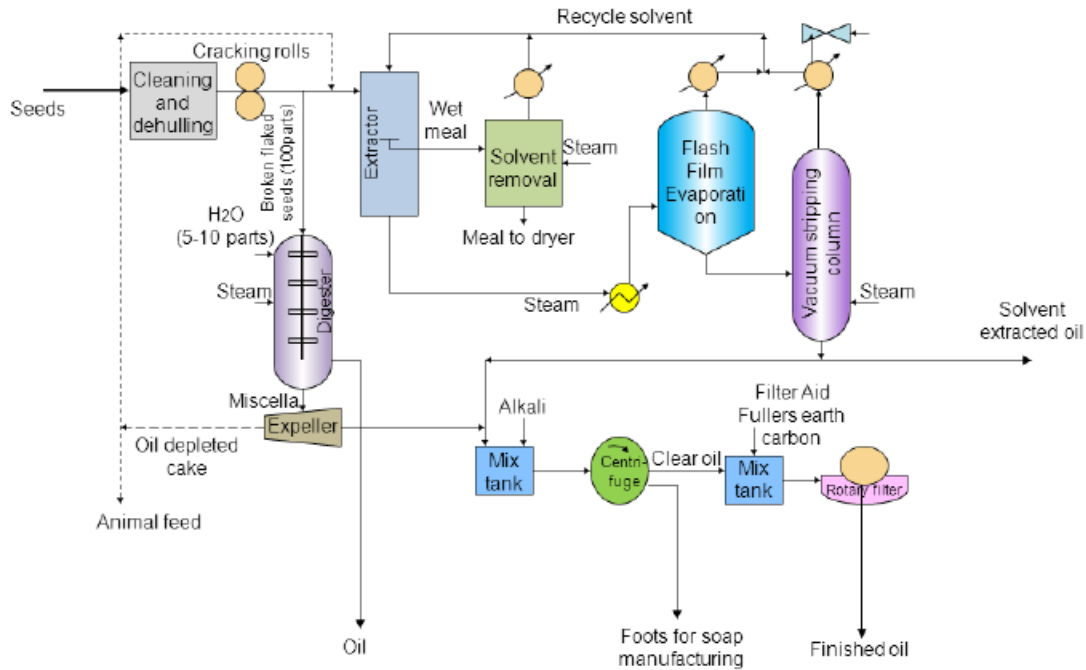


Figure 31.1 Flow sheet of vegetable oil extraction

31a.3 Functional role of various processes (Figure 31.1):

(a) Cleaner and dehulling:

- Mechanical cleaning is done to remove stones and other undesirable material.
- Dehulling remove hulls, dry outer covering of seed.

(b) Cracking rolls:

- Crushing rolls crush the oil seeds and gets flaked seeds.

(c) Digester:

- 100 parts of flaked seeds are thoroughly mixed with 5-10 parts of water by rotating blades.
- Softening by means of heat and moisture is done here.
- Steam is added for heating purpose.
- Acid is formed by hydrolysis of ester.
- The seeds get swollen up.

(d) Expeller:

- The swollen seeds are crushed under great pressure.
- Cells of seeds get ruptured and oil is released.
- The tapering shape ensures more application of pressure on the seeds
- The oil depleted cake is either sent for solvent extraction or used as animal feed.
- Oil is sent for purification.

(e) Mix tank:

- The extracted oil is treated with alkali like NaOH or Na₂CO₃ to remove fatty acids.
- It also removes heavy metals, which can start oxidation of oil.

(f) Centrifuge:

- Acids are separated in centrifuge separator.
- These separated acids are used as foots for soap manufacturing.

(g) Rotary filter:

- The clear oil is treated with some bleaching agent like "Fullers Earth Carbon" in filter aid before rotary filter.
- Rotary drum filter is used for removal of seed particles which may be present.
- This finished oil is produced.
- From this process around 1-2% oil content remains in the meal.

(h) Extractor:

- The flaked seeds or oil extracted seeds from crushing rolls are fed on a moving bed.
- Oil depleted cake is also added in extractor.
- The solvent extracts oil from the seeds.
- The wet meal (the left seed part) is collected in the middle and is sent for solvent removal.

(i) Solvent removal:

- Steam is used to extract solvent carried by the oil seeds.
- The rotating blades ensure better exposure to steam.
- The solvent free meal is sent to dryer and then used as animal feed.
- Solvent is collected from top and is recycled after cooling it in heat exchanger.

(j) Flash film evaporator:

- The solvent is preheated by steam.
- Oil is concentrated here by evaporating the more volatile component (hexane).
- The hexane is recycled back to extractor after heat recovery.
- The use of flash evaporator reduces the cost of vacuum stripping column.

(k) Vacuum stripping column:

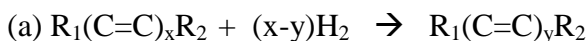
- The oil from flash evaporator is fed here.
- The stripping is done by steam i.e. steam carries away the hexane.
- And it is under vacuum for the reason that the boiling point of hexane and oil are close to each other.
- Jet ejector is used here to generate vacuum.
- The hexane is recycled again.
- Oil produced here is either directly used or sent for purification.

31b.1 Hydrogenation of oil

Hydrogenation process is used to remove double bonds and to make fats and oil saturated. Hydrogenation also raises its melting point and improves its resistance to rancid oxidation. The most common end product of hydrogenation is Vanaspati ghee. Other products include vegetable ghee, hardened industrial oils and partially hydrogenated liquid oil.

Chemical Reactions: (* indicates activated catalytic state)

Ni* catalyst



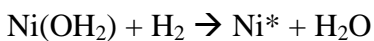
(b) Nickel catalyst preparation:

190°C



This produces a finely divided catalyst which is preferred for well-stirred hydrogenation reactors.

(c) Nickel catalyst preparation (reduced Ni on inert catalyst support)



Nickel salts are precipitated on inert porous carrier such as kieselguhr or diatomaceous earth and reduced at high temperature in a hydrogen atmosphere.

(d) Nickel catalyst preparation



Alloy

Raney nickel

Produces spongy, high-surface area catalyst when the sodium aluminate is washed with water.

Raw material: Oils which is to be saturated and pure hydrogen.

Process flow sheet: Illustrated in Figure.

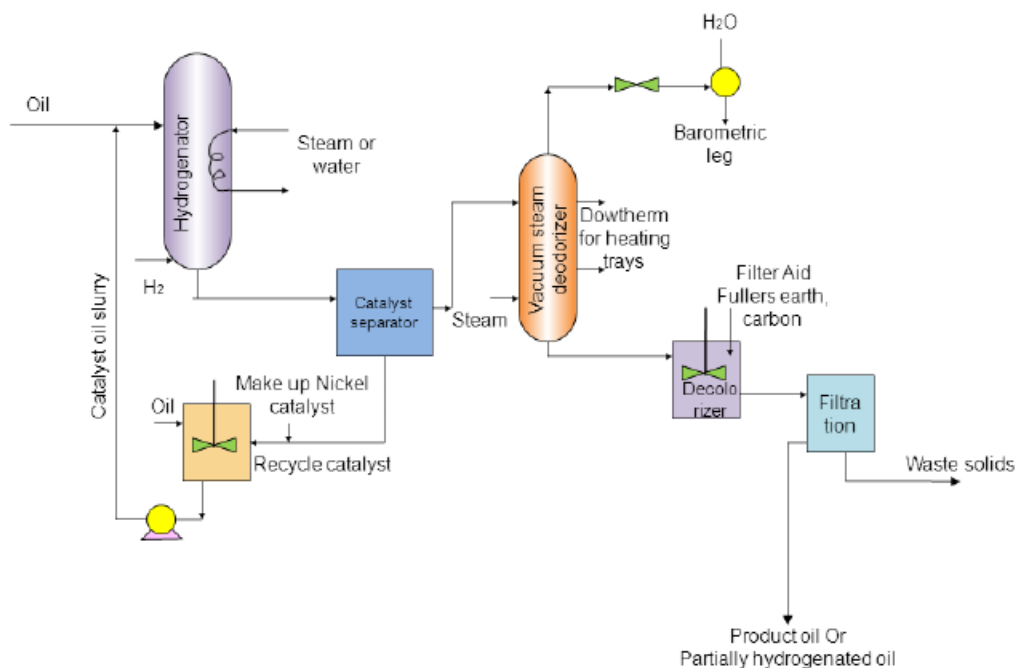


Figure 31.2 Flow sheet of hydrogenation of vegetable oils

31b.2 Functional role of main units (Figure 31.2):

(a) Hydrogenator:

- Oil is fed to the hydrogenator.
- Hydrogen, and steam is introduced in it.
- The catalyst oil slurry of concentration 5 to 15 kg per ton of oil is also put.
- The reaction is slightly exothermic so steam is sometimes turned off.

(b) Deodorizer:

- The hydrogenated oil is now fed to vacuum steam deodorizer.
- It operates in continuous basis.

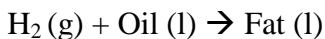
(c) Finishing

- Oil colour is removed by treating with fuller's earth or carbon.
- It is then filtered, mixed with some vitamins.
- Now the finished oil is sent for packaging and storage.

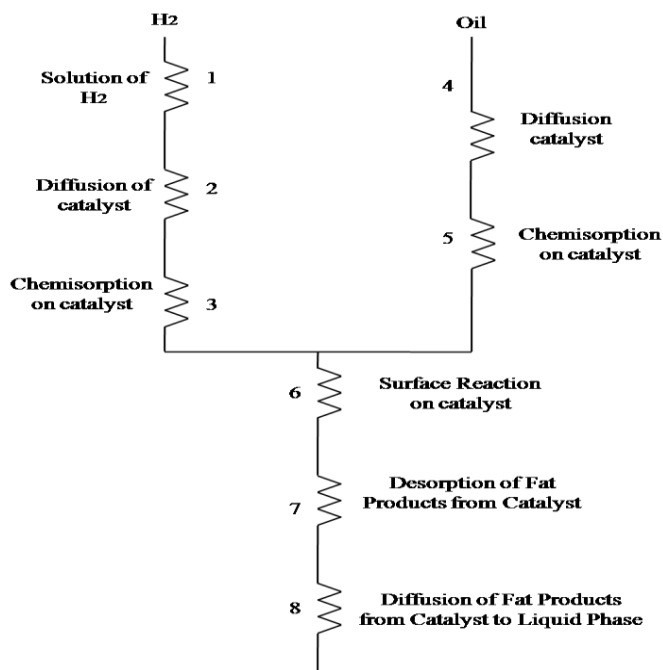
31b.3 Technical Questions

1. Discuss the detailed process related to the gas liquid hydrogenation reaction?

Ans: For gas liquid reaction in hydrogenation



A series of rate process and 8 kinetic reaction exist as shown in fig below:



For many heterogeneous catalytic reactions, the rate behavior is characterized by:

- Surface reaction and adsorption controls the reaction rate at 100°C.
- Rates increase as H₂ pressure increases (at the max 7 atm gage)
- At 180°C, mass transfer for solution of H₂ and diffusion to and from catalyst are rate controlling steps.

2. What is Rancidity?

Ans: The moisture and oxygen cause deterioration of fats. The combined action of both moisture and oxygen causes rancidity which is characterized by bad smell, development of red colour, increase in acidity and increase in viscosity. During frying, cooking, baking etc, oil undergoes hydrolytic and polymerization reactions. These reactions are undesirable in edible oils. Prolonged exposure to air yields undesirable resinous products causing rancidity.

3. What is winterising?

Ans: When oils are cooled slowly to a lower temperature, then less soluble glycerides rich in fatty acid crystallize out. These crystals can be separated by centrifuge or by filter. This separation of solid fats by chilling is called winterising.

4. What is saponification value?

Ans: Alkaline hydrolysis of fats and oils is known as saponification. This forms the basis of soap making.

Saponification value indicates the average molecular weight of a fat or oil. This may also be defined as number of mg of caustic potash required to neutralize the fatty acid obtained by complete hydrolysis of 1 gm of oil or fats.

5. What is acid value?

Ans: It indicates the proportion of free fatty acid present in oil or fats. Acid value is defined as number of mg of caustic potash required to neutralize the acid in 1gm of the sample. Generally acid value for most of samples lies within 0.5.

6. What is Iodine value?

Ans: Iodine value is a measure of extent of unsaturated fatty acid present in fats. It is defined as number of grams of iodine that combines with 100gms of oil and fats.

The iodine value of non-drying oil is less than 90, of semi-drying oil is between 90 to 140.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984