Membrane Technology
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Lecture-29
PV Principle, Advantages, Mass Transfer and Applications, Hybrid Distillation

Good morning students today is lecture 29 under module 10 in today's lecture we will discuss basically the pervaporation its principal advantages membrane and modules, mass transfer in pervaporation, different replications of operations as well as hybrid distillation and pervaporation systems.

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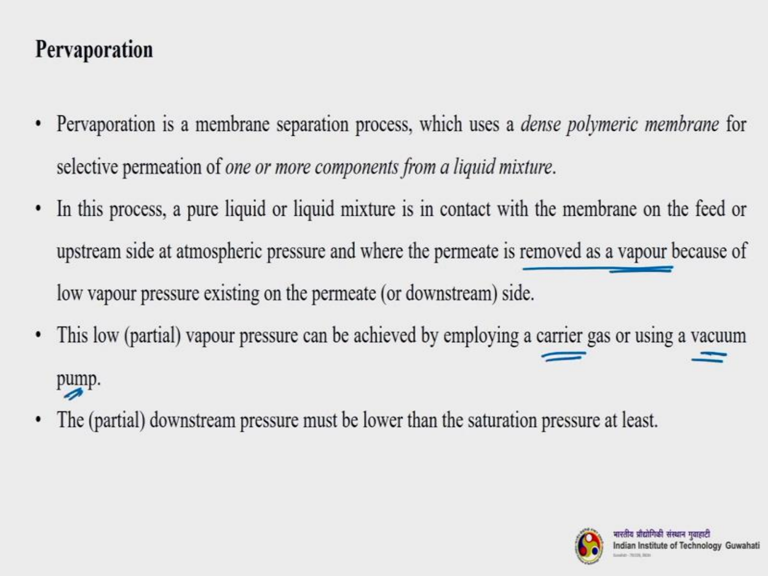

Pervaporation

- Pervaporation is a membrane separation process, which uses a *dense polymeric membrane* for selective permeation of *one or more components from a liquid mixture*.
- In this process, a pure liquid or liquid mixture is in contact with the membrane on the feed or upstream side at atmospheric pressure and where the permeate is removed as a vapour because of low vapour pressure existing on the permeate (or downstream) side.
- This low (partial) vapour pressure can be achieved by employing a carrier gas or using a vacuum pump.
- The (partial) downstream pressure must be lower than the saturation pressure at least.

Now let us start with so pervaporation actually means permit evaporation or permeate vaporization that means the permeate when it is coming down and the permeate side is getting vaporized by some means that will see of course. So, a little history about for pervaporation, so, pervaporation process can be traced back to 19th century but the word for pervaporation was first coined by Cobain in 1917. The process was systematically studied by Bining and co-workers at American oil in 1950s.

Membrane technology at that time could not produce high-performance membranes and modules are required for commercially competitive processes. The process was peaked in 1970s by Monsanto by Eli Perry and others interestingly between 1973 to 80s dozens of patents were assigned to Monsanto covering wide variety of pervaporation application. However none of these work led to commercialization.

By 1980s advances in number and technology made it possible to prepare economically viable for pervaporation system. So, pervaporation is a membrane separation process which uses a dense polymeric membrane for selective permeation of one or more components from liquid mixture. Now in this process a pure liquid or liquid mixture is in contact with the membrane on the feed side as well in for other for membrane systems and at atmospheric pressure and the permeate is removed as a vapor.

So, that is very important permeate is removed as a vapor because of low vapor present that is existing on the permeate or downstream side. Now this low vapor pressure can be achieved by employing a carrier gas or by using a vacuum pump so you can achieve it by two means so the partial downstream pressure must be lower than the saturation pressure at least so that the vaporization takes place.

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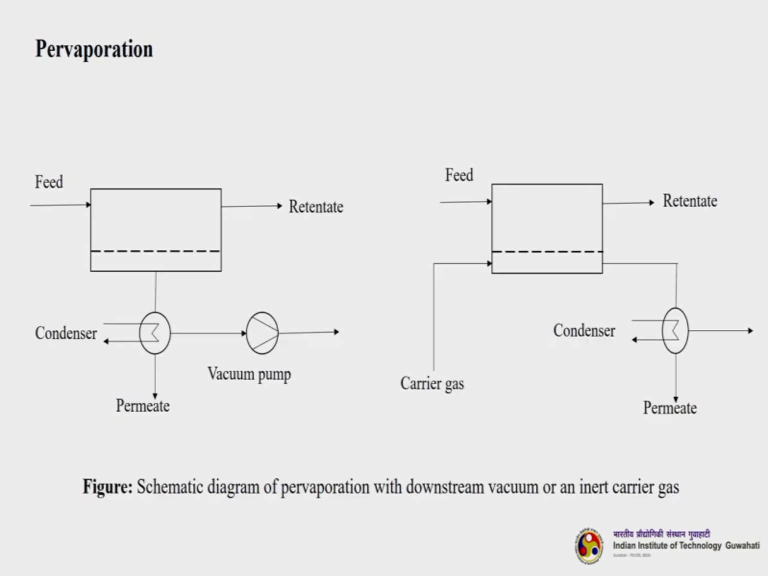

Pervaporation

Figure: Schematic diagram of pervaporation with downstream vacuum or an inert carrier gas

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Now let us see the schematic diagram you will understand it better. So, this is the pervaporation system here pervaporation membranes. So, you can see here in the first one the permeate vaporization is achieved using a vacuum pump. So, permeate is being drawn and its contents and it is it is done by a vacuum pump. So, here in this second case the low vapor pressure is being maintained by using a carrier gas. So, one carrier gas is being fed to the downstream side or to the permeate side so the lower vapor pressure maintains and then we have to condense at permeate and then finally draw it.

So these are two classic schemes of the pervaporation system by two means you can achieve the perforation one by vacuum pump another by a carrier gas.

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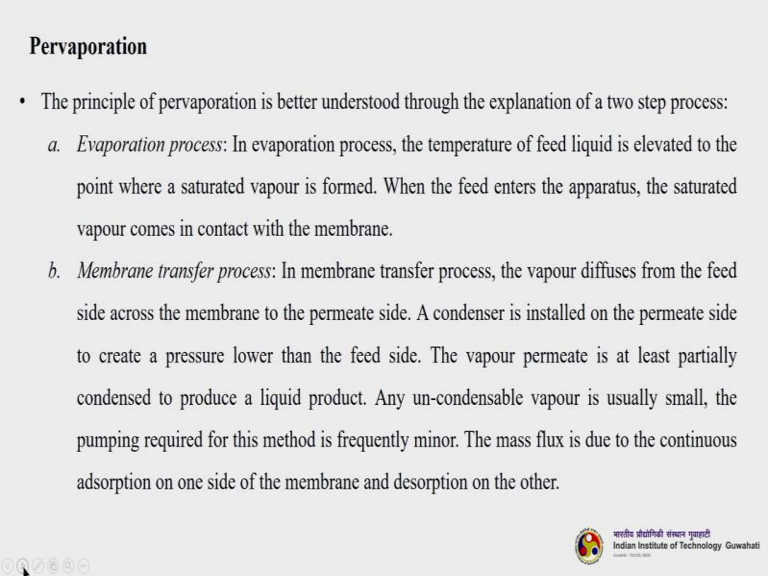

Pervaporation

- The principle of pervaporation is better understood through the explanation of a two step process:
  a. *Evaporation process*: In evaporation process, the temperature of feed liquid is elevated to the point where a saturated vapour is formed. When the feed enters the apparatus, the saturated vapour comes in contact with the membrane.
  b. *Membrane transfer process*: In membrane transfer process, the vapour diffuses from the feed side across the membrane to the permeate side. A condenser is installed on the permeate side to create a pressure lower than the feed side. The vapour permeate is at least partially condensed to produce a liquid product. Any un-condensable vapour is usually small, the pumping required for this method is frequently minor. The mass flux is due to the continuous adsorption on one side of the membrane and desorption on the other.

The principle we have put a pervaporation is better understood through the explanation of a two-step process the first is evaporation the second is membrane transport. So, in evaporation process the temperature of the feed liquid is elevated to the point where a saturated vapor is formed. So, basically you are heating the feed to a certain point where the vapor is getting formed. So, when that heated vapour enters the apparatus the saturated vapour comes in contact with that membrane.

Then in the second step it is membrane master transport. So, in the membrane transfer process the vapor diffuses from the feed side across the membrane to the permeate side. A condenser is installed on the permeate side to create a preserved lower than the feed side. The vapor permeate is at least partially condensed to produce a liquid product so you have just seen that in both the systems we have condensers. So, the job of the condenser is to condensate the vapor and produce a liquid.

Any uncontainable vapor is usually small the pumping required for this method is frequently minor. The mass flux is due to the continuous adsorption on one side of the membrane and desorption on the other side.

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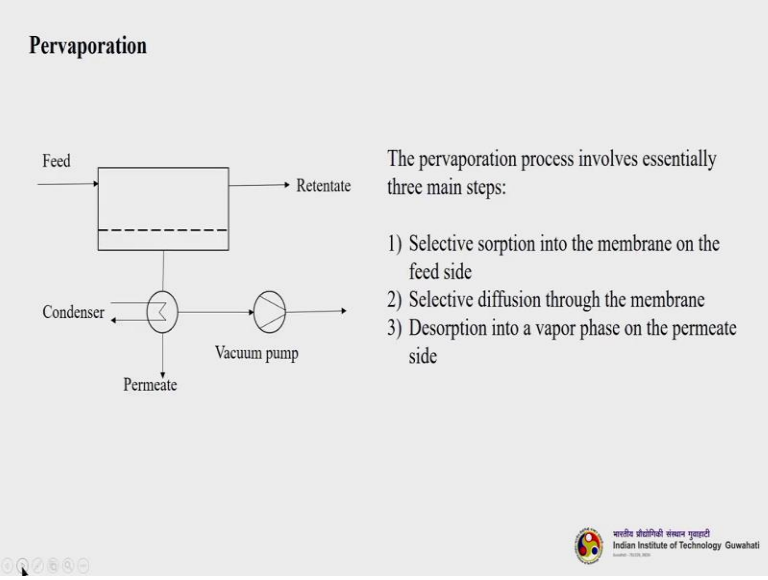

Pervaporation

The pervaporation process involves essentially three main steps:

1) Selective sorption into the membrane on the feed side
2) Selective diffusion through the membrane
3) Desorption into a vapor phase on the permeate side

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Pervaporation process essentially involves three main steps. First is selective sub some into the membrane on the feed side. Then second is selective diffusion through the membrane and third is desorption into a paper face on the permeate side. These are the three basic essential steps that is required for the pervaporation.

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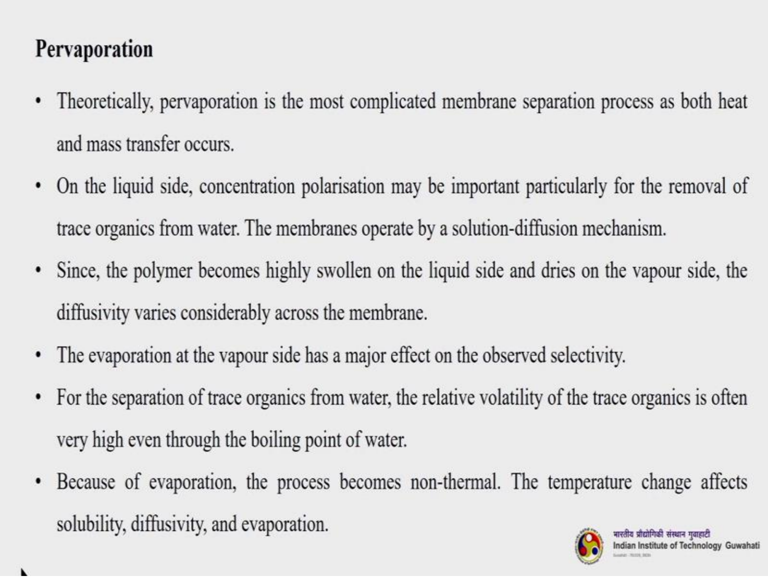

Pervaporation

- Theoretically, pervaporation is the most complicated membrane separation process as both heat and mass transfer occurs.
- On the liquid side, concentration polarisation may be important particularly for the removal of trace organics from water. The membranes operate by a solution-diffusion mechanism.
- Since, the polymer becomes highly swollen on the liquid side and dries on the vapour side, the diffusivity varies considerably across the membrane.
- The evaporation at the vapour side has a major effect on the observed selectivity.
- For the separation of trace organics from water, the relative volatility of the trace organics is often very high even through the boiling point of water.
- Because of evaporation, the process becomes non-thermal. The temperature change affects solubility, diffusivity, and evaporation.

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Theoretically pervaporation is the most complicated membrane separation process is both heat and mass transfer occurs. On the liquid side concentration polarization may be important particularly for the removal of trace organics from water the membranes operate by a solution diffusion mechanism. Since the polymer becomes highly swollen on the liquid side and dries in the vapor side the diffusivity varies considerably across the membrane.

The evaporation at the vapor side has a major effect on the object selectivity. Actually when the polymer gets swollen right so that is also not good and the diffusivity will vary if the polymer of the membrane gets swollen. So, that will affect the selectivity also. So, for the separation of trace organics from water the relative volatility of trace organics is often very high and even through the boiling point of the water.

So because of the pervaporation process becomes non-thermal and the temperature change affects solubility diffusivity and evaporation.

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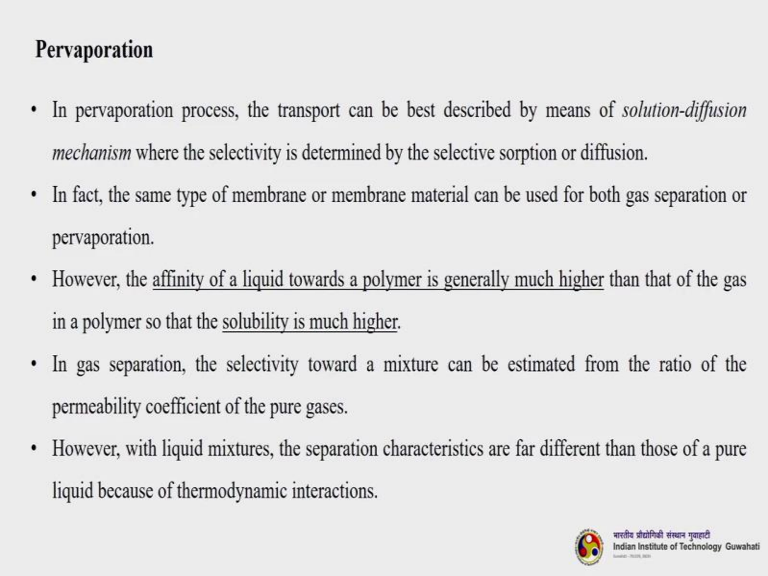

Pervaporation

- In pervaporation process, the transport can be best described by means of *solution-diffusion mechanism* where the selectivity is determined by the selective sorption or diffusion.
- In fact, the same type of membrane or membrane material can be used for both gas separation or pervaporation.
- However, the affinity of a liquid towards a polymer is generally much higher than that of the gas in a polymer so that the solubility is much higher.
- In gas separation, the selectivity toward a mixture can be estimated from the ratio of the permeability coefficient of the pure gases.
- However, with liquid mixtures, the separation characteristics are far different than those of a pure liquid because of thermodynamic interactions.

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In pervaporation process the transport can be best described by means of a solution diffusion mechanism. We have discussed solution deposit diffusion in detail earlier in our class. So, I am not going to tell you anything more on this just to remind you that solution diffusion is a system mechanism through which the transport happens in non porous membranes as well as in this case of pervaporation system where solubility and diffusivity both are very important or both play a vital role.

Infacts the same type of membrane or membrane material can be used for both gas separation and pervaporation that is what I was just telling non porous membranes. However the affinity of a liquid towards polymer is generally much higher than that of a gas in polymer so the solubility is much higher. So, when you talk about a liquid phase separation and a gas for separation the affinity of liquid all towards a polymer is obviously much more higher than that of the gas.

So that is why when the affinity is more the solubility is also more. So, in gas separation the selectivity toward a mixture can be estimated from the ratio of the permeability coefficient of the pure gases. However with liquid mixture the separation characteristics are far different than those of a pure liquid because of thermodynamic interactions.

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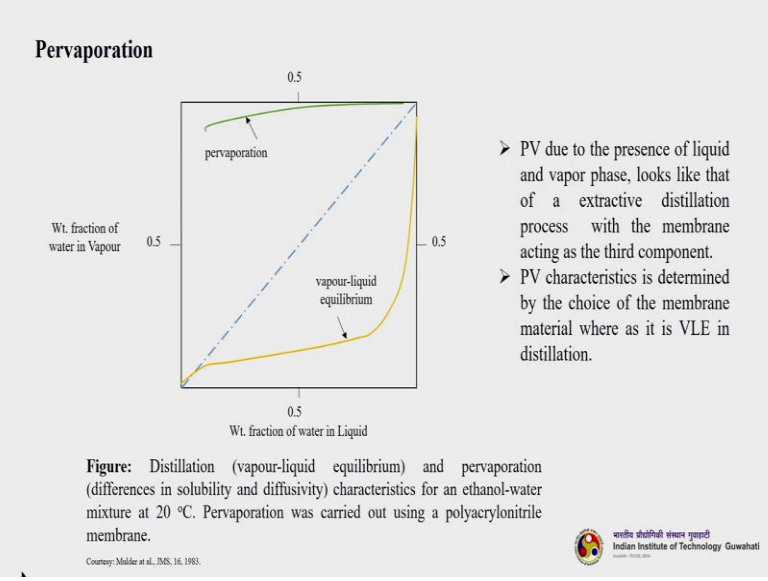

Pervaporation

- PV due to the presence of liquid and vapor phase, looks like that of a extractive distillation process with the membrane acting as the third component.
- PV characteristics is determined by the choice of the membrane material where as it is VLE in distillation.

Figure: Distillation (vapour-liquid equilibrium) and pervaporation (differences in solubility and diffusivity) characteristics for an ethanol-water mixture at 20 °C. Pervaporation was carried out using a polyacrylonitrile membrane.

Courtesy: Mulder at al., JMS, 16, 1983.

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Now let us try to understand the basic difference between distillation and pervaporation. Please look at this particular figure so this is a in distillation you know distillation the measure driving force easier vapour liquid equilibrium which is given by this particular this one a figure. And pervaporation is one in which the differences in differences in diffusivity and solubility plays a big role. So, you can see this in case of distillation there is no other the material is not playing a big role whereas in pervaporation the material of the membrane is playing a big role right.

So pervaporation due to the presence of liquid and vapour phase looks like that of a extractive distillation actually. So, wherein extracted is listen we are putting a third solvent or an internal so that and the phase masters what will happen to that particular entry done then you can selectively take it out. Whereas in case of pervaporation the third component that is nothing but the membrane itself here and the pervaporation characteristics is determined by the choice of the membrane material whereas it is exclusively vapour liquid equilibrium in case of the distillation.

So in this particular figure this is a classic example of distillation and pervaporation for an ethanol water mixture at 20 degree centigrade. Pervaporation was carried out using a poly acrylonitrile membrane.

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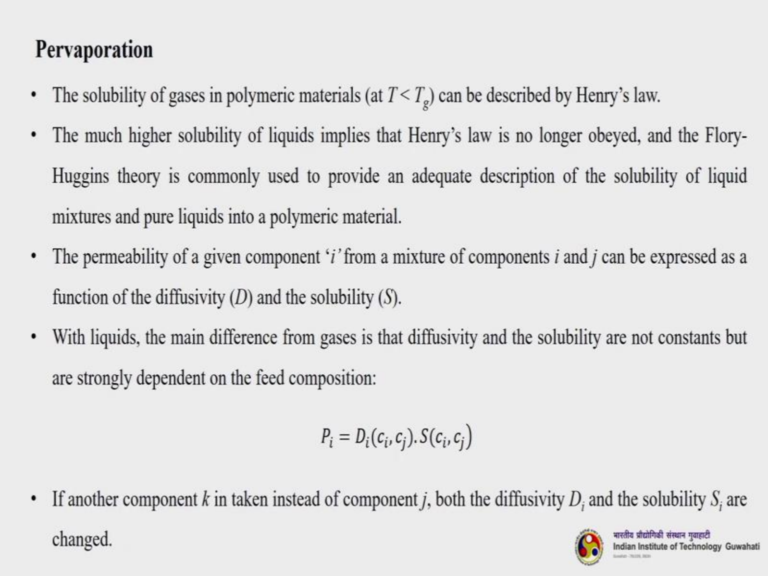

Pervaporation

- The solubility of gases in polymeric materials (at $T < T_g$) can be described by Henry's law.
- The much higher solubility of liquids implies that Henry's law is no longer obeyed, and the Flory-Huggins theory is commonly used to provide an adequate description of the solubility of liquid mixtures and pure liquids into a polymeric material.
- The permeability of a given component '*i*' from a mixture of components *i* and *j* can be expressed as a function of the diffusivity (*D*) and the solubility (*S*).
- With liquids, the main difference from gases is that diffusivity and the solubility are not constants but are strongly dependent on the feed composition:

$$P_i = D_i(c_i, c_j).S(c_i, c_j)$$

- If another component *k* in taken instead of component *j*, both the diffusivity D_i and the solubility S_i are changed.

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The solubility of gases in polymeric material can be described by Henry's law when T is less than T g, T g the gas transition temperature the much higher the solubility of liquids implies that Henry's law is no longer a bet. And the Flory-Huggins theory is commonly used to provide an adequate description of the solubility of liquid mixture in pure liquids into a polymeric material. So, when Henry's law is not applicable you can use the Flory-Huggins theory.

The permeability of a given component i from a mixture of components i and j can be expressed as a function of diffusivity and solubility. So, with liquids the main difference from gases is that a diffusivity and solubility are not constant but are strongly dependent on the feed composition. So, we can write Pi equals to D i c i c j into S c i c j. So, D i is your diffusivity and S is a solubility. If another component k is taken instead of a component j so both the diffusivity D i and the solubility S i are changed.

So if polyvinyl alcohol is used for the separation of methanol water mixture to compositions can be distinguished one is a low water concentration another is a low alcohol concentration. So, with this low alcohol concentration the membrane hardly swells and hardly any selectivity is obtained. So, the membrane is not getting swell that is fine but the selectivity that is what you are trying to achieve you will not get.

So with lower water concentration this same polymer may sauce high selectivity towards water and exhibits a reasonable flux. Now another important example is that of a mixture which consists of two components which are not miscible with each other about the whole composition range say for example trichloroethylene water. So, this is a system in which both this trichloroethylene and water are not completely miscible.

So, pervaporation can be used to remove a small amount of water from trichloroethylene or can remove small amount of trichloroethylene from water. So this is the beauty of evaporation system. In a mixture of two components either selectively you can remove any one of these two.

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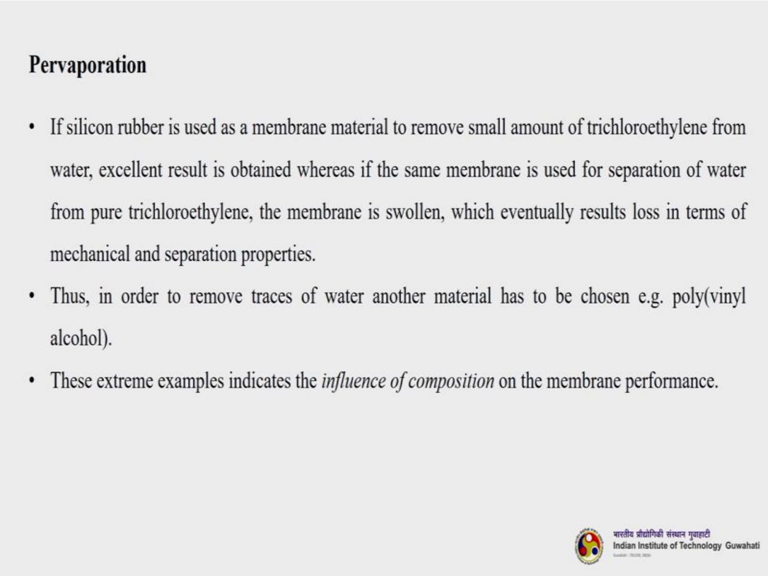

Pervaporation

- If silicon rubber is used as a membrane material to remove small amount of trichloroethylene from water, excellent result is obtained whereas if the same membrane is used for separation of water from pure trichloroethylene, the membrane is swollen, which eventually results loss in terms of mechanical and separation properties.
- Thus, in order to remove traces of water another material has to be chosen e.g. poly(vinyl alcohol).
- These extreme examples indicates the *influence of composition* on the membrane performance.

So, if silicon rubber is used as a membrane material to remove small amounts of trichloroethylene from water an excellent result is obtained, where achieve the same membrane is used for separation of water from pure trichloroethylene the membrane is swollen which eventually results loss in terms of mechanic separation properties. From this statement what is understood is that the membrane material plays a very big role.

When we are using a polyvinyl alcohol that time the membrane is getting swelled when I am using silicon rubber so membrane is not getting much swelled and I am getting a desirable flux and a very good separation properties. So, thus in order to remove traces of water another material has to be chosen as per example polyvinyl alcohol. So, these extreme examples indicate the influence of composition on the part of pervaporation performance.

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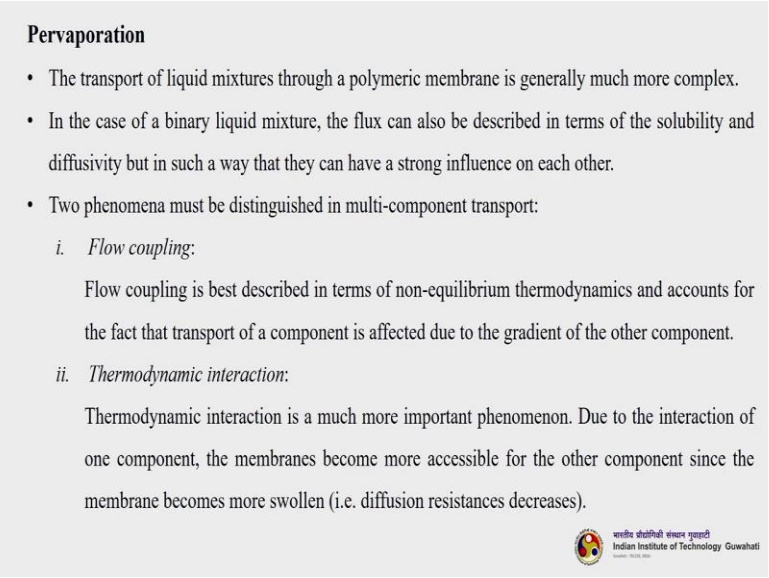

Pervaporation

- The transport of liquid mixtures through a polymeric membrane is generally much more complex.
- In the case of a binary liquid mixture, the flux can also be described in terms of the solubility and diffusivity but in such a way that they can have a strong influence on each other.
- Two phenomena must be distinguished in multi-component transport:
  - i. *Flow coupling*:
    Flow coupling is best described in terms of non-equilibrium thermodynamics and accounts for the fact that transport of a component is affected due to the gradient of the other component.
  - ii. *Thermodynamic interaction*:
    Thermodynamic interaction is a much more important phenomenon. Due to the interaction of one component, the membranes become more accessible for the other component since the membrane becomes more swollen (i.e. diffusion resistances decreases).

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The transport of liquid mixtures through a polymeric membrane is generally much more complex. In the case of a binary liquid mixture the flux can also be described in terms of the solubility and diffusivity but in such a way that they can have a strong on influence on each other. The two phenomena can be distinguished in a multi-component transfer one is flow coupling long back when you discuss thermodynamics.

So flow coupling is best described in terms of non-equilibrium thermodynamics and accounts for the fact that transport of a component is affected due to the gradient of other component. So, in a nutshell you try to remember flow coupling you just try to understand that in a multi-component system there are many components are trying to diffuse together or trying to get separated. So, one component will try to affect the gradient of another component.

So this is what is actually coupling or there can be positive coupling or negative coupling depending upon what type of components and what is their diffusivity and solubility and all these things. And in thermodynamic interaction is a much more important phenomena due to the interaction of one component the membranes become more accessible for the other component since the membrane becomes more swollen so the diffusional resistance decreases.

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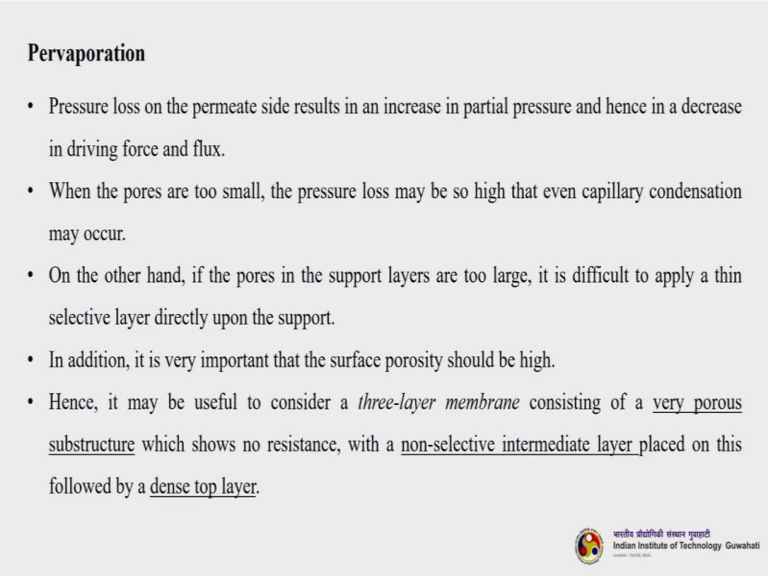

Pervaporation

- Pressure loss on the permeate side results in an increase in partial pressure and hence in a decrease in driving force and flux.
- When the pores are too small, the pressure loss may be so high that even capillary condensation may occur.
- On the other hand, if the pores in the support layers are too large, it is difficult to apply a thin selective layer directly upon the support.
- In addition, it is very important that the surface porosity should be high.
- Hence, it may be useful to consider a *three-layer membrane* consisting of a very porous substructure which shows no resistance, with a non-selective intermediate layer placed on this followed by a dense top layer.

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Pervaporation and gas separation non porous membranes are required preferably with an anisotropic morphology that means an asymmetric structure with a dense top layer and a porous sub layer as found in the asymmetric and composite membranes. The requirements for the sub structure are in fact the same is for gas separation membranes. So, an open sub structure to minimize resistance to vapor transport and to avoid capillary condensation and a high surface porosity with narrow pore size distribution.

Pressure loss on the permeate side results in an increase in partial pressure and hence in a decrease in driving force and flux. So, when the pores are too small the pressure loss may be so high that even capillary condensation may occur. Now please understand that capillary condensation phenomena also we have discussed by capillary condensation is not actually desired in case of pervaporation.

On the other hand if the pores in the support layers are too large it is difficult to apply a thin selective layer directly upon the support. So, you need some optimization actually basically what type of pores you need and how you will get it. In addition it is very important that the surface velocity should be high. And hence it may be useful to consider a three layer membrane this is what is telling us that we need a three layer membrane so consisting of a very porous of structure shows no resistance with a non-selective intermediate player placed on this followed by dense layer.

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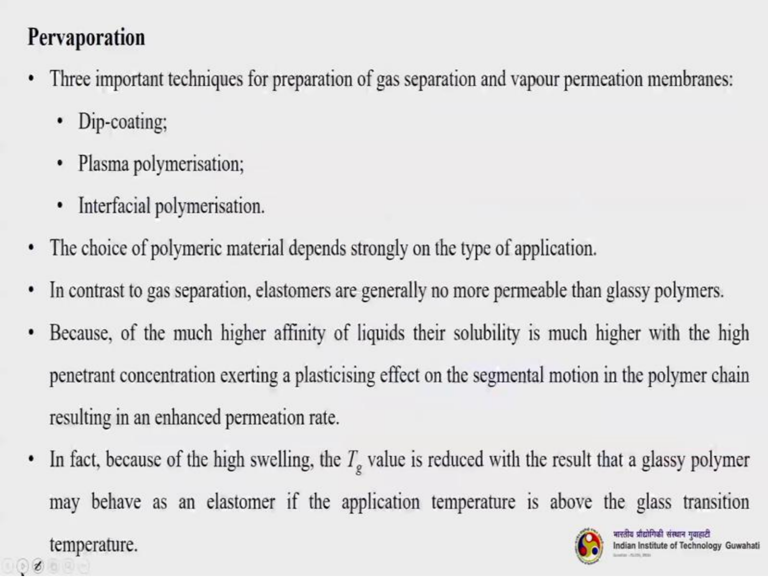

Pervaporation

- Three important techniques for preparation of gas separation and vapour permeation membranes:
  - Dip-coating;
  - Plasma polymerisation;
  - Interfacial polymerisation.
- The choice of polymeric material depends strongly on the type of application.
- In contrast to gas separation, elastomers are generally no more permeable than glassy polymers.
- Because, of the much higher affinity of liquids their solubility is much higher with the high penetrant concentration exerting a plasticising effect on the segmental motion in the polymer chain resulting in an enhanced permeation rate.
- In fact, because of the high swelling, the T_g value is reduced with the result that a glassy polymer may behave as an elastomer if the application temperature is above the glass transition temperature.

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So three important techniques for preparation of gas separation and vapour permeation membranes, so one is dip coating, another is plasma polymerization and then interfacial polymers and you know all these techniques we have discussed in detail. So, I am not going to discuss here in this particular pervaporation section. Now you can go back and read and refurbish here this one knowledge. So, the choice of polymeric material depends strongly on the type of application.

So what is the type of application actually when you are removing organic compounds then different type of polymer material has to be chosen. If we are doing a like other component separation which is not organic then maybe and the polymeric material that you will choose may be it will be different. So, and depending upon the type of application only we will decide which polymeric material has to be chosen.

So in contrast to gas separation elastomers are generally no more permeable than glassy polymers because of the much higher affinity of liquids their solubility is much higher with the high penetrate concentration exerting a plasticizing effect on the segmental motion in the polymer chain resulting in an enhanced formation rate. In fact because of the high swelling and the T g value is reduced with the result that a glassy polymer may behave as an elastomer if the application temperature is above the glass transition temperature.

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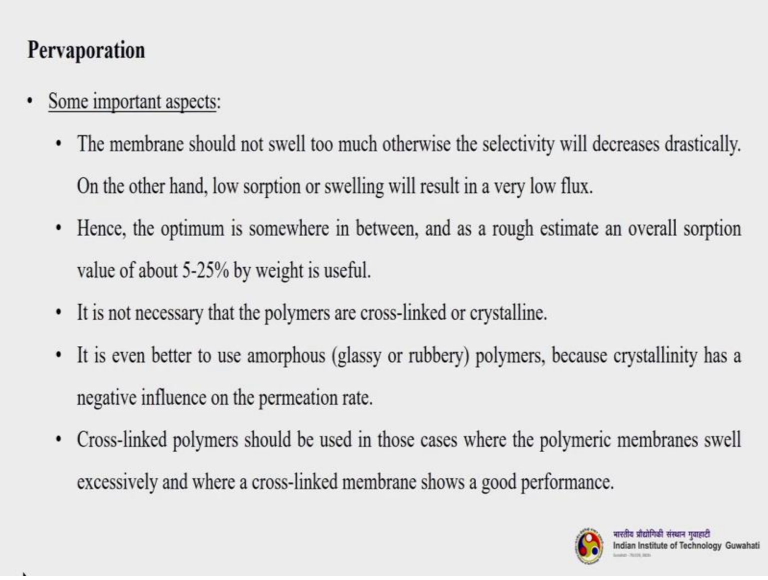

Pervaporation

- Some important aspects:
  - The membrane should not swell too much otherwise the selectivity will decreases drastically. On the other hand, low sorption or swelling will result in a very low flux.
  - Hence, the optimum is somewhere in between, and as a rough estimate an overall sorption value of about 5-25% by weight is useful.
  - It is not necessary that the polymers are cross-linked or crystalline.
  - It is even better to use amorphous (glassy or rubbery) polymers, because crystallinity has a negative influence on the permeation rate.
  - Cross-linked polymers should be used in those cases where the polymeric membranes swell excessively and where a cross-linked membrane shows a good performance.

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So, some important aspects of pervaporation the membranes should not swell too much otherwise the selectivity will decrease drastically. On the other hand low sorption or swelling would result in a very low plugs so you need to play with in this and you have to actually optimize the parameters and hence the optimum is somewhere in between and a rough estimate and overall sorption value of about 5 to 20% by weightage is useful.

Then it is not necessary that the polymers are cross-linked or crystalline it is even better to use the amorphous that is glacier rubbery polymers because crystallinity has a negative effect on influence on the permeation rate. The cross-linked polymers should be used in those cases where the polymeric membranes swell excessively and where a cross-linked membrane shows good performance otherwise we do not need actual cross linking.

We are fine with a glacier rubbery polymer because as I just told you crystallinity as such has a negative influence on the permeation rate.

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Advantages of Pervaporation

- Some major advantages of pervaporation involves:
  - With the low temperature and pressure involves in pervaporation, it often has cost and performance advantages for the separation of azeotrophic mixtures and mixtures of components with close boiling points.
  - The technology minimises the thermal degradation of heat sensitive compounds (such as flavour essence).
  - Significantly reduced energy consumption for hybrid systems (as in pervaporation combined with distillation).
  - No entrainer is required, thereby no contamination.

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Some major advantages are pervaporation involves so with the lower temperature and pressure involves in pervaporation it often is less cost and performance advantages for the separation of a azotrophic mixtures and mixtures of components with close boiling points. So, the PV is extremely good to separate a azotrophic as well as close boiling point mixtures. Now the technology minimizes the thermal degradation of heat sensitive compounds such as flavour essence.

Significantly we do not need a high temperature so that is why pervaporation is good for flavouring compounds or heat sensitive compounds. Significantly reduced energy consumption for hybrid system as in pervaporation combined with distillation this we will discuss a later in today's class only. So, entrainer is required thereby no contamination. So, I am not adding anything unlike your extractive distillation. So no extra additional component is added.

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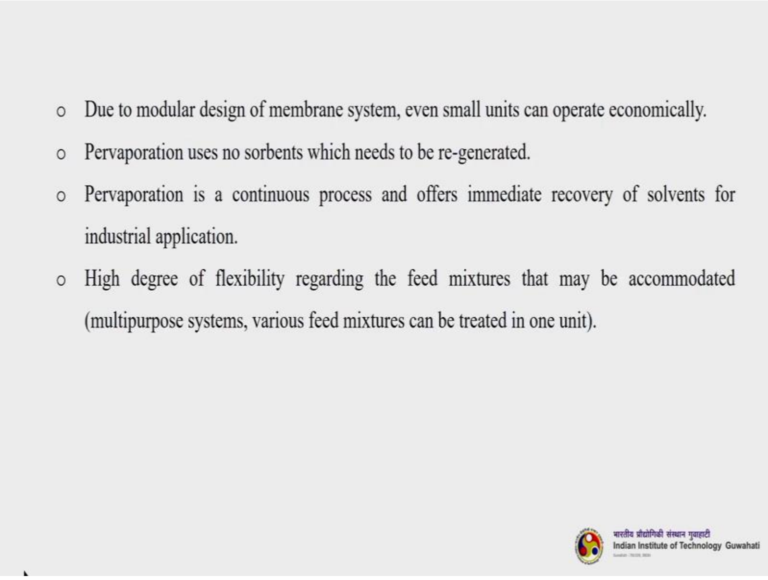

- Due to modular design of membrane system, even small units can operate economically.
- Pervaporation uses no sorbents which needs to be re-generated.
- Pervaporation is a continuous process and offers immediate recovery of solvents for industrial application.
- High degree of flexibility regarding the feed mixtures that may be accommodated (multipurpose systems, various feed mixtures can be treated in one unit).

Due to modular design of membrane system even small units can operate economically. Pervaporation uses no sorbents which needs to be regenerated. Pervaporation is a continuous process and offers immediate recovery of solvents per industrial application. High degree of flexibility regarding the feed mixtures that may be accommodated multi-purpose systems then various feed mixtures can be treated in single unit.

So, you can design a module smaller big or medium does not matter so in such a way that and modules design in the process and the entire PV system is not very complicated so that is why a small units also runs very successfully as well as large units.

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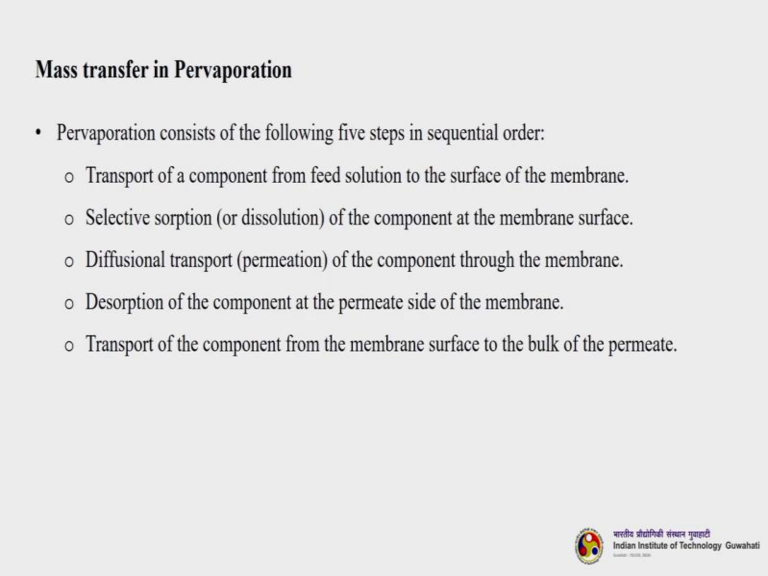

Mass transfer in Pervaporation

- Pervaporation consists of the following five steps in sequential order:
    - Transport of a component from feed solution to the surface of the membrane.
    - Selective sorption (or dissolution) of the component at the membrane surface.
    - Diffusional transport (permeation) of the component through the membrane.
    - Desorption of the component at the permeate side of the membrane.
    - Transport of the component from the membrane surface to the bulk of the permeate.

So, let us now try to understand the mass transfer in pervaporation. So, pervaporation consists of the following 5 test even sequential order. In the first step the transfer of component from feed solution to the surface of that membrane. So, if you consider this as the membrane surface and this is the bulk let us say this is the component, so the transfer of component from the bulk to the surface of the membrane then it is coming and sitting here.

Then selectively sorption ok or dissolution of the component and the membranes surface and since this has to be dissolved in the membrane surface so it will get dissolved in the membrane surface. So, once it get dissolved then it will try to diffuse. So, diffusional transport or permeation of the component through the membrane, so then once it reaches the permeate side then it will dissolve.

So it dissolve in the form of; so this is here this is liquid this is vapor phase so dissolve in the form of vapour. So, then this vapor when it goes to a condenser see it condenses and we get the liquid. So, transfer the component from the membrane surface to the bulk of that permeate. The 5 essential steps is how the must test for in permeation takes place.

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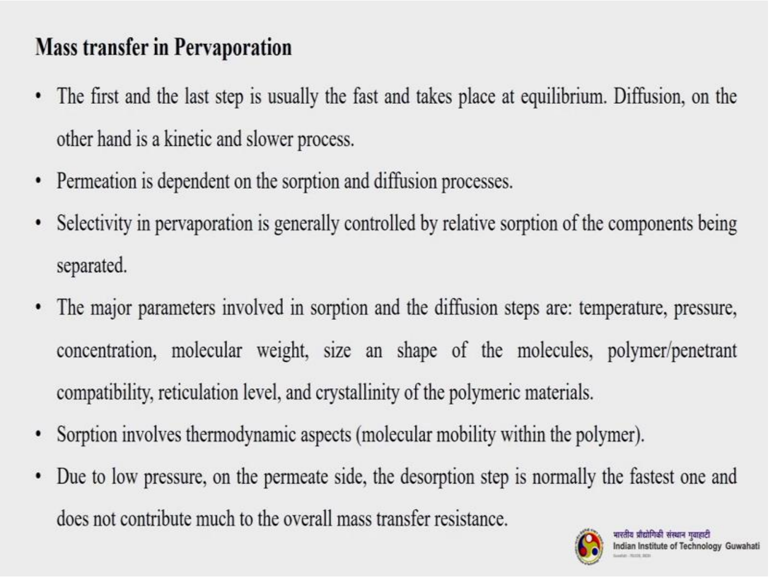

Mass transfer in Pervaporation

- The first and the last step is usually the fast and takes place at equilibrium. Diffusion, on the other hand is a kinetic and slower process.
- Permeation is dependent on the sorption and diffusion processes.
- Selectivity in pervaporation is generally controlled by relative sorption of the components being separated.
- The major parameters involved in sorption and the diffusion steps are: temperature, pressure, concentration, molecular weight, size an shape of the molecules, polymer/penetrant compatibility, reticulation level, and crystallinity of the polymeric materials.
- Sorption involves thermodynamic aspects (molecular mobility within the polymer).
- Due to low pressure, on the permeate side, the desorption step is normally the fastest one and does not contribute much to the overall mass transfer resistance.

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The first and the last step is usually the first and takes place at equilibrium and diffusion on the other hand is a kinetic and slower process. So, permeation is dependent on the sorption and diffusion processes. Selectivity in pervaporation is generally controlled by relative sorption of the component being separated. Now major parameter involved in sorption and diffusion steps are temperature, pressure, concentration, molecular weight, size and shape of the molecules polymers and penetrate and compatibility, reticulation level, crystallinity of the polymeric materials.

So all these you know there are big list of parameters they are trying to influence the process dynamics so you need to optimize all these things, so sorption involves thermodynamic aspects molecular mobility within the polymer due to low pressure on the permeate side and the desorption step is normally the fastest one and does not contribute much to the overall mass transfer resistance.

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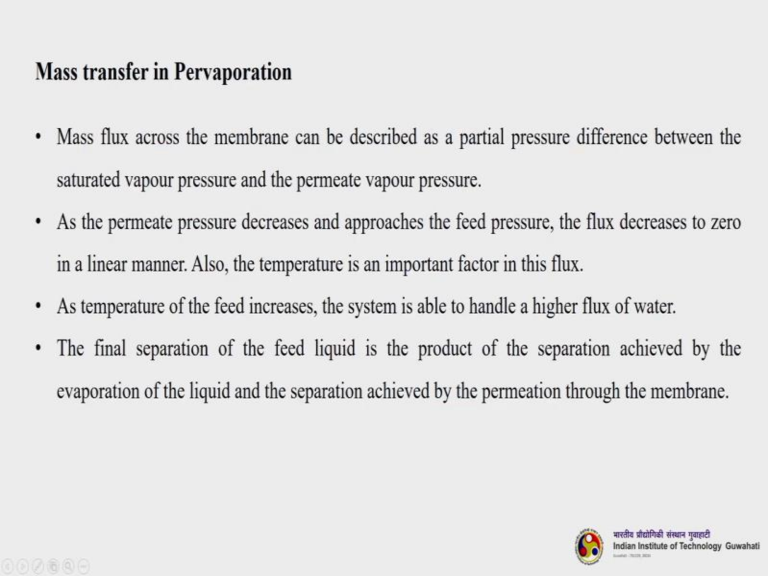

Mass transfer in Pervaporation

- Mass flux across the membrane can be described as a partial pressure difference between the saturated vapour pressure and the permeate vapour pressure.
- As the permeate pressure decreases and approaches the feed pressure, the flux decreases to zero in a linear manner. Also, the temperature is an important factor in this flux.
- As temperature of the feed increases, the system is able to handle a higher flux of water.
- The final separation of the feed liquid is the product of the separation achieved by the evaporation of the liquid and the separation achieved by the permeation through the membrane.

So your mass flux across the membrane can be described as a partial pressure difference between the saturated vapor pressure and the permeate vapor pressure. As the permeate such pressure decreases and approaches the feed pressure the flux increases to zero in a linear manner also the temperature is an important factor in this plus. As temperature of the feed increases the system is able to handle a higher flux of water.

The final separation of the feed liquid is the product of the separation achieved by the evaporation of the liquid and the separation is achieved by the permeation through the membrane.

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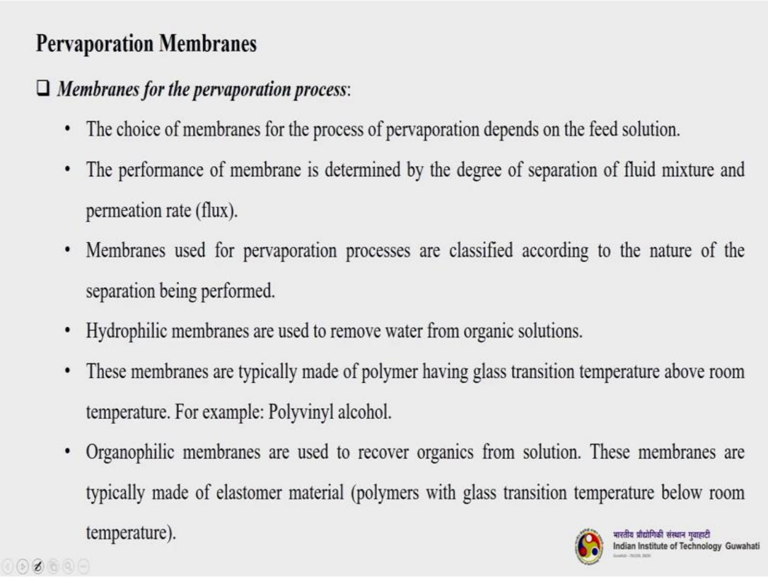

Pervaporation Membranes

☐ ***Membranes for the pervaporation process***:

- The choice of membranes for the process of pervaporation depends on the feed solution.
- The performance of membrane is determined by the degree of separation of fluid mixture and permeation rate (flux).
- Membranes used for pervaporation processes are classified according to the nature of the separation being performed.
- Hydrophilic membranes are used to remove water from organic solutions.
- These membranes are typically made of polymer having glass transition temperature above room temperature. For example: Polyvinyl alcohol.
- Organophilic membranes are used to recover organics from solution. These membranes are typically made of elastomer material (polymers with glass transition temperature below room temperature).

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So membranes for the pervaporation process the choice of permanent for the process of the pervaporation depends on the feed solution and of course as well as I forgot to mention as well is your intended application where you are going to apply. The performance of membrane is determined by the degree of separation of fluid mixture and the permeation rate that is flux. Membranes used for pervaporation processes are classified according to the nature of the separation being performed.

So hydrophilic membranes are used to remove water from organic solutions these membranes are typically made up of polymer have been gas transition temperature above room temperature. for example a polyvinyl alcohol. And then Organophilic membranes are used to remove organics organophilic membranes right. So, these membranes typically made up of elastomer polymer. So, for these polymers their gas transition temperature is always below room temperature.

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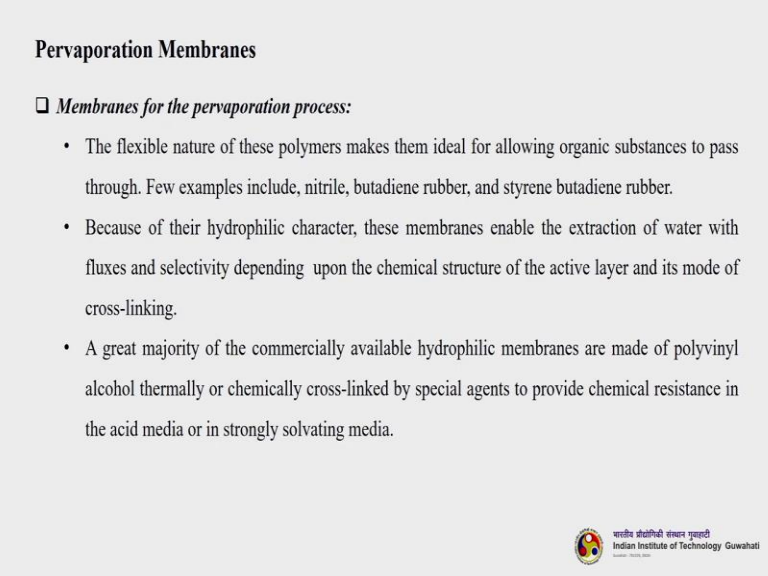

Pervaporation Membranes

❑ ***Membranes for the pervaporation process:***

- The flexible nature of these polymers makes them ideal for allowing organic substances to pass through. Few examples include, nitrile, butadiene rubber, and styrene butadiene rubber.
- Because of their hydrophilic character, these membranes enable the extraction of water with fluxes and selectivity depending upon the chemical structure of the active layer and its mode of cross-linking.
- A great majority of the commercially available hydrophilic membranes are made of polyvinyl alcohol thermally or chemically cross-linked by special agents to provide chemical resistance in the acid media or in strongly solvating media.

The flexible nature of these polymers makes them ideal for allowing organic substances to pass through for a few examples include nitrile then your butadiene rubber, styrene butadiene rubber that is SVR so because of their hydrophilic character these membranes enable the extraction of water with fluxes and selectivity depending upon the chemical structure of the active layer and its mode of cross-linking.

A great majority of the commercially available hydrophilic membranes are made of polyvinyl alcohol thermally are chemically cross-linked by special agents to provide chemical resistance in the acid media or in strongly solvating media.

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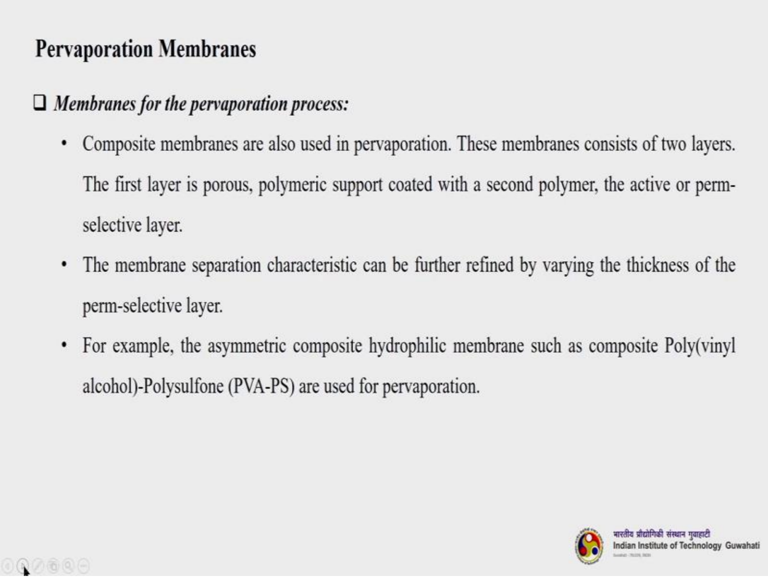

Pervaporation Membranes

❑ ***Membranes for the pervaporation process:***

- Composite membranes are also used in pervaporation. These membranes consists of two layers. The first layer is porous, polymeric support coated with a second polymer, the active or perm-selective layer.
- The membrane separation characteristic can be further refined by varying the thickness of the perm-selective layer.
- For example, the asymmetric composite hydrophilic membrane such as composite Poly(vinyl alcohol)-Polysulfone (PVA-PS) are used for pervaporation.

Composite membranes are now it is taking a lot of attention actually gaining a lot of attention these membranes consist of two layers the first layer is porous polymeric support coated with a second polymer the active or selectively layer. The membrane separation characteristic can be further defined by varying the thickness of the polymer selective layer for example the asymmetric composite hydrophilic membrane such as composite polyvinyl alcohol, polysulfone are used for pervaporation.

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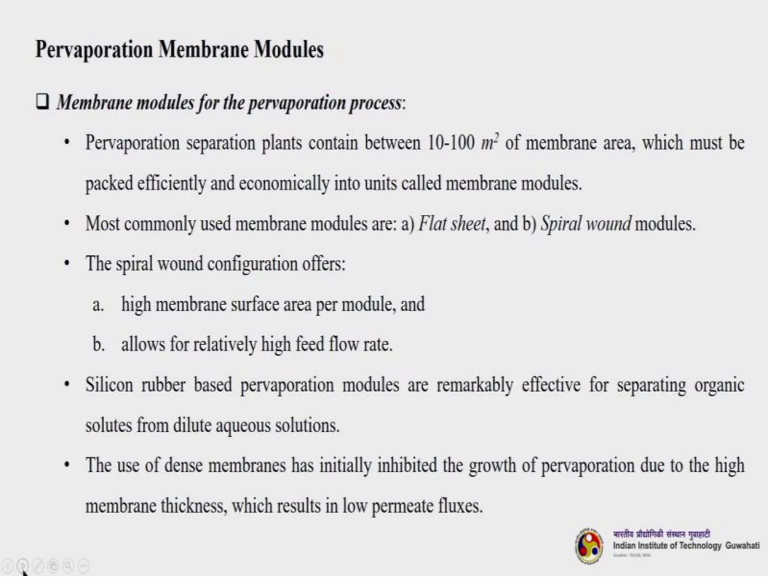

Pervaporation Membrane Modules

❑ ***Membrane modules for the pervaporation process***:

- Pervaporation separation plants contain between 10-100 m^2 of membrane area, which must be packed efficiently and economically into units called membrane modules.
- Most commonly used membrane modules are: a) *Flat sheet*, and b) *Spiral wound* modules.
- The spiral wound configuration offers:
    a. high membrane surface area per module, and
    b. allows for relatively high feed flow rate.
- Silicon rubber based pervaporation modules are remarkably effective for separating organic solutes from dilute aqueous solutions.
- The use of dense membranes has initially inhibited the growth of pervaporation due to the high membrane thickness, which results in low permeate fluxes.

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Than the modules the pervaporation separation plants contain between 10 to 100, meter square of membrane area which must be pegged efficient clean economically in two units called membrane modules. Now most commonly membrane modules are there are two types basically so either you can have a flat seat membrane material or you can have spiral membrane module. Now students you know we have discussed flat seat membrane module and spiral membrane module in detail when you discuss membrane modules.

And they are up there also we have discussed during our ultra filtration, micro filtration and Aero system about the flat seat and spiral wound membrane module. So, their advantages their characteristic features mostly there remains same right. So, the spiral is a better one why because it gives high membrane surface area per module and allows for relatively high feed flow rate. So, silicon rubber best pervaporation module are remarkably very effective for separating organic solutes from dilute aqueous solution because silicon rubber is not getting swelled so that is why it is very good its performance is good for organics removal.

The use of dense membrane has initially inhibited the growth of pervaporation due to the high membrane thickness which results in low permeate flux.

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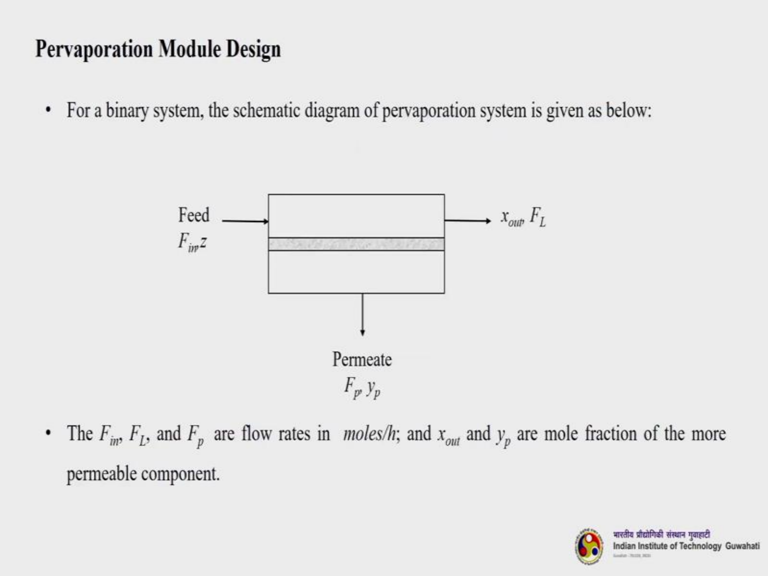

Pervaporation Module Design

- For a binary system, the schematic diagram of pervaporation system is given as below:

Feed
F_{in}, z

x_{out}, F_L

Permeate
F_p, y_p

- The F_{in}, F_L, and F_p are flow rates in *moles/h*; and x_{out} and y_p are mole fraction of the more permeable component.

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So, now let us discuss the perforation membrane module design so for a binary system the schematic diagram of pervaporation system is given below. So, this is you see feed then we have this is a product are tented out so a permeate here, so F in F L and F p are product in moles per hour and x out and y p at the more traction of the more permeable component please remember more permeable component.

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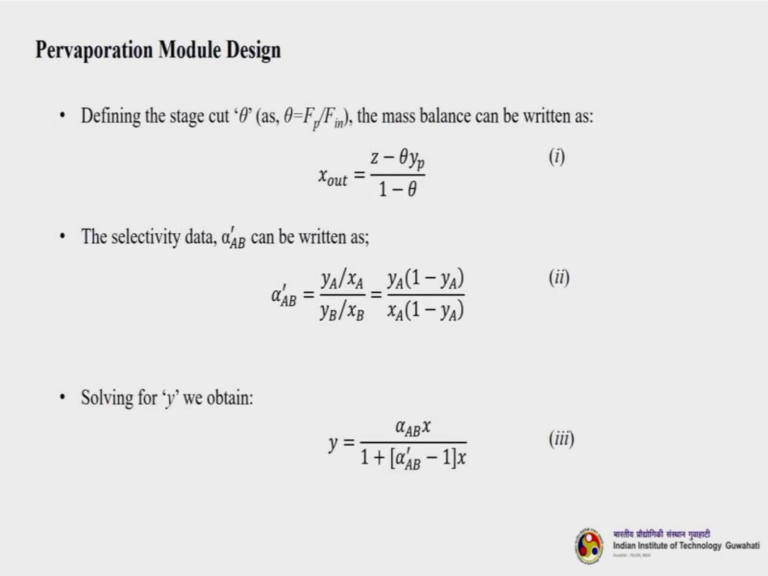

Pervaporation Module Design

- Defining the stage cut 'θ' (as, $\theta = F_p/F_{in}$), the mass balance can be written as:

$$x_{out} = \frac{z - \theta y_p}{1 - \theta} \qquad (i)$$

- The selectivity data, α'_{AB} can be written as;

$$\alpha'_{AB} = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A(1 - y_A)}{x_A(1 - y_A)} \qquad (ii)$$

- Solving for 'y' we obtain:

$$y = \frac{\alpha_{AB} x}{1 + [\alpha'_{AB} - 1]x} \qquad (iii)$$

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So, let us say a the equations so if you defining the stage cut theta so theta equal to F p by F in the mass balance can be written is x out equals to z - theta y p divided by 1 – theta. So, selectivity the data that is in terms of relative volatility we can write alpha a bit prime equals to y A by x A divided by y B by x B so we can rewrite it as y A into 1 - y A divided by x A into 1 -y A then solving for y we will get y equals to alpha AB into x divided by 1 + alpha AB prime - 1 into x.

Now you know for a complete mixing system here y p becomes y and here x out becomes x, so you can further substitute in these equations then the equation 3 becomes y p equals to alpha AB prime x out divided by 1 + alpha AB prime - 1 into x out now these equations 1 and 5 can be combined as and you will get z something like this it is a big equation I am just not reading it out. So, this equation you will be using to find out what is Z.

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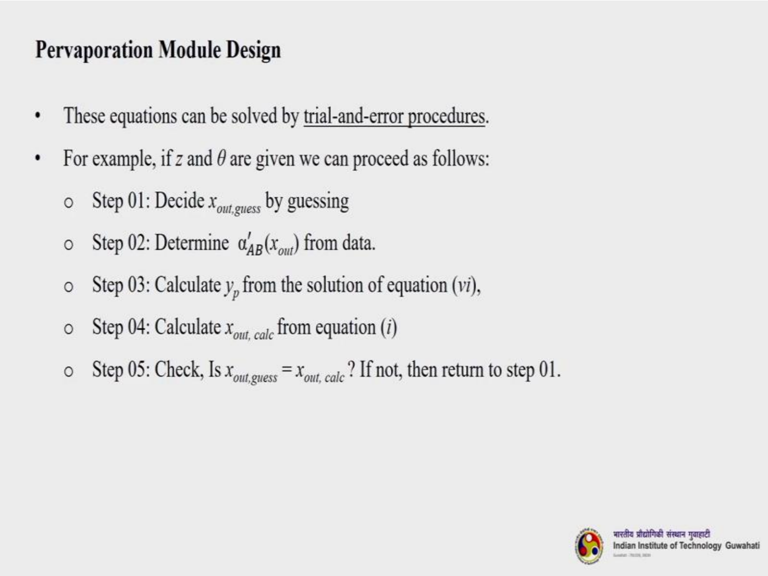

Pervaporation Module Design

- These equations can be solved by trial-and-error procedures.
- For example, if z and θ are given we can proceed as follows:
    - Step 01: Decide $x_{out,guess}$ by guessing
    - Step 02: Determine $\alpha'_{AB}(x_{out})$ from data.
    - Step 03: Calculate y_p from the solution of equation (*vi*),
    - Step 04: Calculate $x_{out,\ calc}$ from equation (*i*)
    - Step 05: Check, Is $x_{out,guess} = x_{out,\ calc}$? If not, then return to step 01.

So these equations can be solved by trial and error procedures. So, for example you can write a small code in any language and solve it let us say for example if Z and theta are given we can proceed as follows. So, step one decide x out guess by guessing you have to guess the x out value right. Determine alpha AB Prime and x out from the data calculate y p from the solution of equation six calculate x out calculator from Equation 1 and check if x out guess equals to x out calculator.

So, if your x out guess value is equals to x out calculated value and then it is fine if it is not then return to the step one. So, the cycle again repeats. This is how you can solve the equations.

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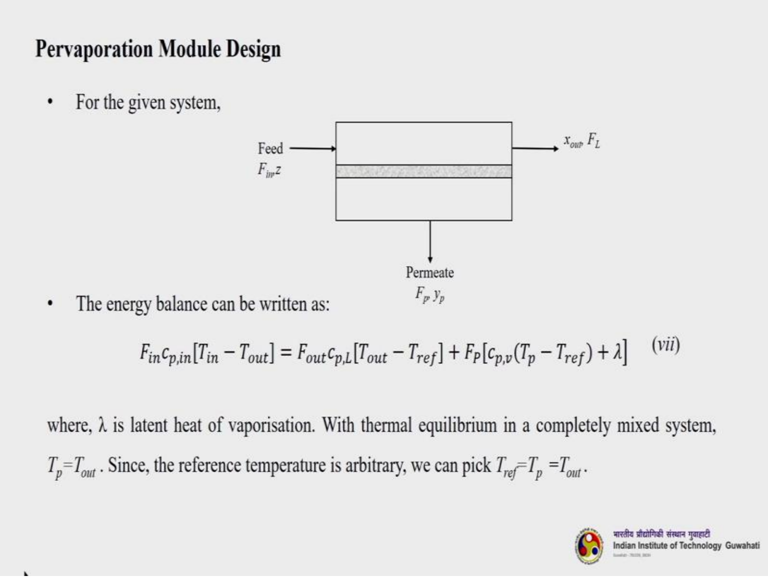

Pervaporation Module Design

- For the given system,

- The energy balance can be written as:

$$F_{in}c_{p,in}[T_{in} - T_{out}] = F_{out}c_{p,L}[T_{out} - T_{ref}] + F_P[c_{p,v}(T_p - T_{ref}) + \lambda] \quad (vii)$$

where, λ is latent heat of vaporisation. With thermal equilibrium in a completely mixed system, $T_p = T_{out}$. Since, the reference temperature is arbitrary, we can pick $T_{ref} = T_p = T_{out}$.

So, for the given system the energy balance can be written as F in C p in into T in - T out equals to Fout C p L T out - T reference + F p into C p v T p - T reference plus lambda. Now where is lambda is the latent heat of vaporization. So, in thermal equilibrium in a completely mixed system we are assuming completely mixed system T p equals to T out right. So, since that reference temperature is arbitrary we can write that T reference is equal to T P equals T out.

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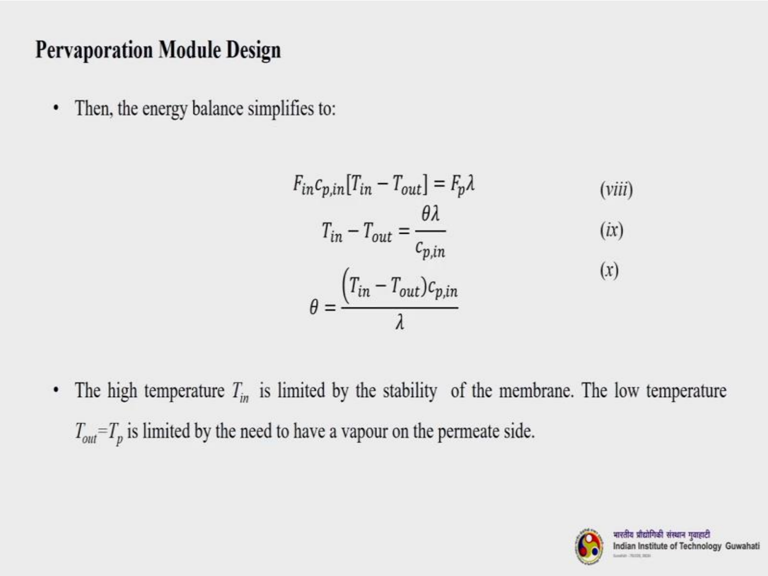

Pervaporation Module Design

- Then, the energy balance simplifies to:

$$F_{in}c_{p,in}[T_{in} - T_{out}] = F_p\lambda \qquad (viii)$$

$$T_{in} - T_{out} = \frac{\theta\lambda}{c_{p,in}} \qquad (ix)$$

$$\theta = \frac{\left(T_{in} - T_{out}\right)c_{p,in}}{\lambda} \qquad (x)$$

- The high temperature T_{in} is limited by the stability of the membrane. The low temperature T_{out}=T_p is limited by the need to have a vapour on the permeate side.

Then the energy balance simplifies to F in C p in T in - T out equals to F p into lambda, so you can get theta we can rewrite it by taking in and Cp in on that side. So, you can F in and F in actually get cancelled. So, it is theta T in - T out equals to theta lambda divided by C p in or from here we can calculate theta equals to T in - T out C p in by lambda. So, the high temperature T in is limited by the stability of the membrane the low temperature T out equals to T p is limited by the need to have a vapour on that perimeter side.

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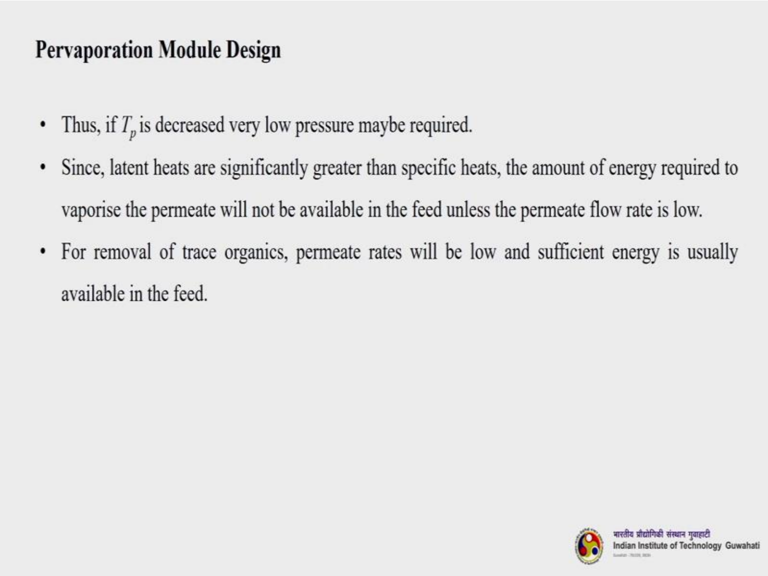

Pervaporation Module Design

- Thus, if T_p is decreased very low pressure maybe required.
- Since, latent heats are significantly greater than specific heats, the amount of energy required to vaporise the permeate will not be available in the feed unless the permeate flow rate is low.
- For removal of trace organics, permeate rates will be low and sufficient energy is usually available in the feed.

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So thus if T p is decreased very low pressure may be required since latent heat are significantly greater than specific heats the amount of energy required to vaporize the permeate will not be available in the feed unless the permeate flow rate is low. For removal of trace organics permeate rates will be low and sufficient energy is usually available in that field.

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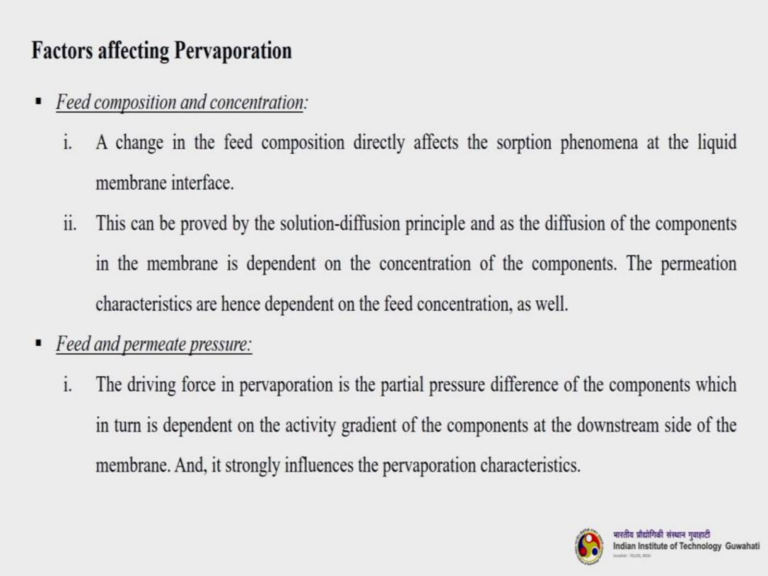

Factors affecting Pervaporation

- *Feed composition and concentration:*
  i. A change in the feed composition directly affects the sorption phenomena at the liquid membrane interface.
  ii. This can be proved by the solution-diffusion principle and as the diffusion of the components in the membrane is dependent on the concentration of the components. The permeation characteristics are hence dependent on the feed concentration, as well.
- *Feed and permeate pressure:*
  i. The driving force in pervaporation is the partial pressure difference of the components which in turn is dependent on the activity gradient of the components at the downstream side of the membrane. And, it strongly influences the pervaporation characteristics.

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Now let us understand what are the factors that affect the pervaporation system or process? So, we are discussing major factors. So feed composition and concentration. So, a change in the feed composition directly affects the sorption phenomena at the liquid membrane surface so this can be proved by the solution diffusion principle. And as the diffusion of the component in the membrane a diffusion of the diffusion of the components in the membrane is dependent on the concentration of the components. The permeation characteristics are hence depending on the feed concentration as well.

Then the second is feed and permeate pressure so you have the pressure it is not a pressure driven system. So, the pressure the driving force in pervaporation is the partial pressure difference of the components which in turn is dependent on the activity gradient of the components at the downstream side of the membrane. And it is strongly influences the pervaporation characteristics. So, it is not externally pressure driven basically.

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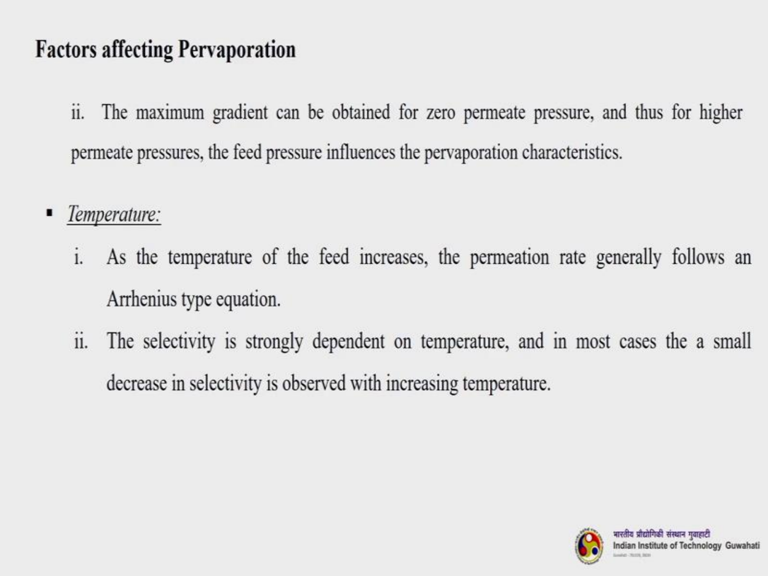

Factors affecting Pervaporation

ii. The maximum gradient can be obtained for zero permeate pressure, and thus for higher permeate pressures, the feed pressure influences the pervaporation characteristics.

- *Temperature:*
  i. As the temperature of the feed increases, the permeation rate generally follows an Arrhenius type equation.
  ii. The selectivity is strongly dependent on temperature, and in most cases the a small decrease in selectivity is observed with increasing temperature.

So, the maximum gradient can be obtained for zero permeate pressure and thus for higher permeate pressures. The feed pressure influences the pervaporation characteristics. Then temperature so as the temperature of the feed increases the permeation rate generally follows an Arrhenius type equation. The selectivity is strongly dependent on temperature and in most cases a small decrease in selectivity is observed with increasing temperature.

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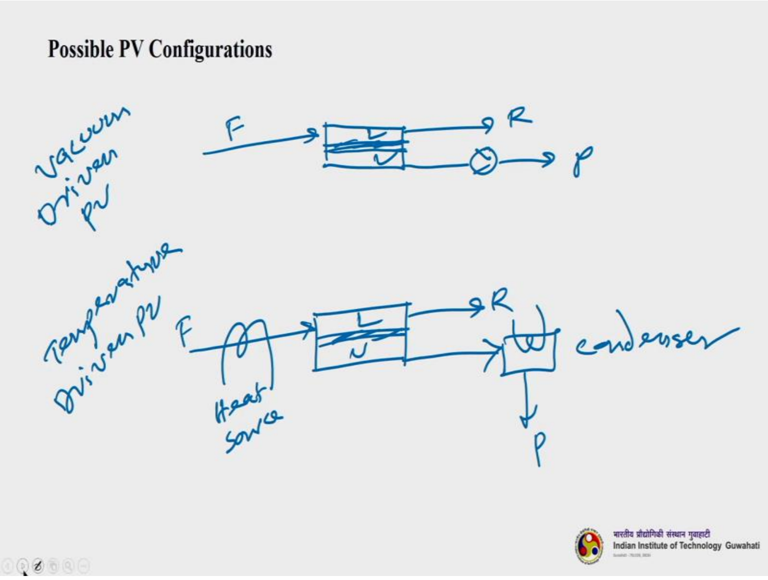
Possible PV Configurations

So, now let us try to see the different types of possible PV configuration I will try to draw it for you. So, we can we have actually six different types of configurations. So, the first one is this so let us say we have a membrane here, pervaporation membrane right. So, we have a feed here so we will get retantate here so we are getting permeate here. So, this is vacuum driven PV this is one type the usual general one basically. So, then we have temperature difference the second one is temperature driven PV.

So, here again we have a membrane pervaporation membrane then we have a feed now the feed is getting heated. So, this is your heat source right, so I forgot to write this is liquid here, liquid here we have vapour here so you get your retantate here and you have condenser and permeate. So, this is condenser all right, so this is another one where the feed is actually heated so this is temperature driven pervaporation.

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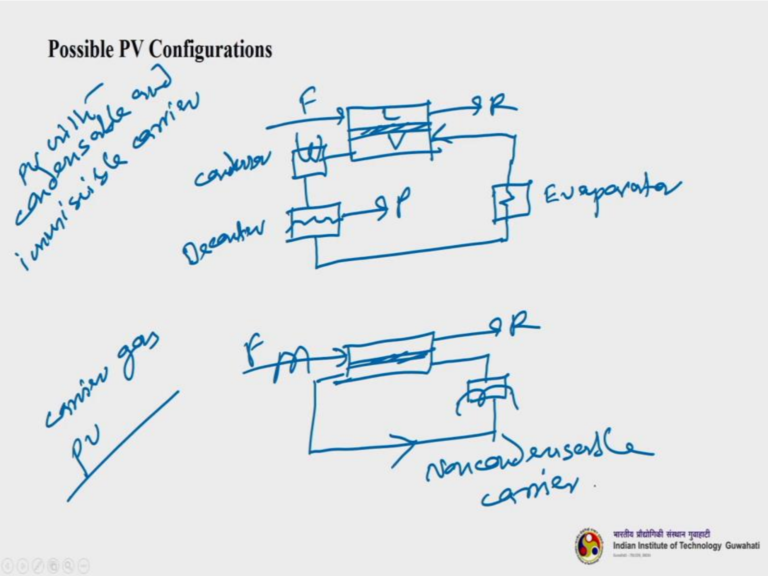

Possible PV Configurations

So the next type is pervaporation with condensable and immiscible carrier. So, PV with condensable and immiscible carrier, so let us see the pervaporation membrane feed, retantate so this is a evaporator this is a decanter and this is your condenser. So, what is extra you can see here, so here the condenser is actually convincing the liquid that it goes to decanter and then that liquid is being evaporated and again recycle back, so that is your carrier.

So it is a condensable and immiscible carrier. Now there is another one which is called pervaporation with carrier gas pervaporation only plane carrier gas. So, this the membrane, feed then we get a retentate, so this is your non condensable carrier. Now the basic difference between these two system is there here in this case so there is a immiscible but condensable carrier but in the second case which is usually more prefer or practice.

So this is a non condensable carrier gas so we do not need to condensate we can just remove the permeate liquid and then again recycle it back to the pervaporation system.

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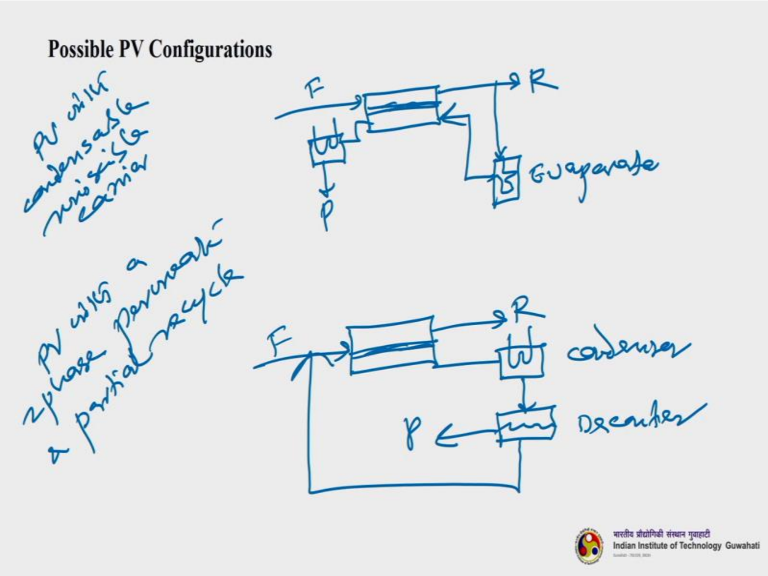

Possible PV Configurations

So, two more systems so that is called PV with condensable and miscible carrier it is condensable but now it is miscible. So, here your PV system right, feed is coming here retantate that you get here. So, what you have is a condenser then we get permeate here. So, this is a evaporator part of the retantate is bit fed back through the evaporator system and then send it back to the pervaporation system. So, then the next one is PV with a two phase permeate and partial recycle. So, let us see how this looks like feed here the retantate so then it goes to a condenser from condenser it comes to a decanter, just like the second one right.

So, you get a permeate liquid here and the rest is bring a recycle it is partial recycle that is why it is called partial recycle and it is pervaporation with a two phase permeate and a partial recycle system. So, you just saw six different types of configurations that is possible using pervaporation.

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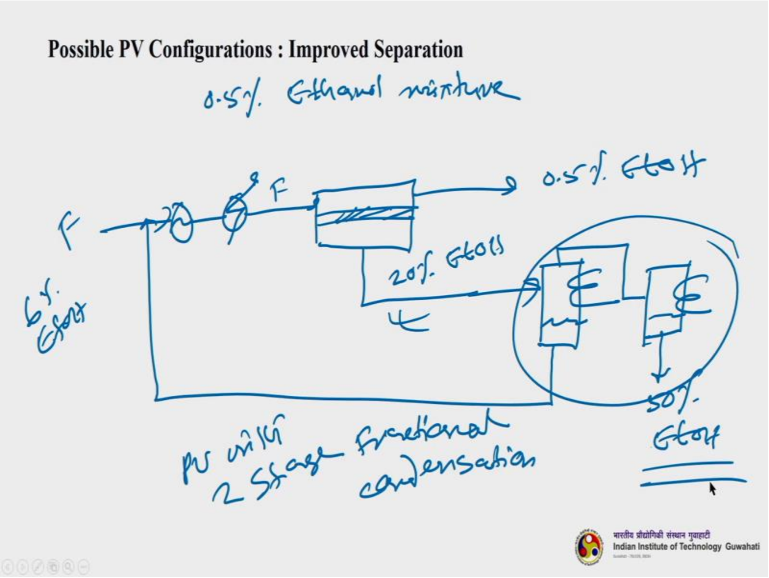

Possible PV Configurations : Improved Separation

So, the next one actually is a classic example of pervaporation configuration and how do you improve that is separation right. So, I put a 0.5% thonal mixture that we want to enrich actually so in a pervaporation system so you will have; so this is your feed then you get 0.5% ETOH. Then whatever it is getting, coming it is in these 20% ETOH ethanol so then it passes to fractional condensations. So, you get contents here so whatever it is coming is again passing through another stage of condensation then we get a 50% reach ETOH ethanol.

And whatever is remaining it again goes to the feed so this is 6% ETOH so you see that if you do not have these two only pervaporation so you get a 20% ethanol whereas if you are attaching fractional condensation so it is PV with two states fractional condensation. So, in 2 stress fractional condensation of course you are achieving a 50% ethanol. So, this is how you actually improve the performance.

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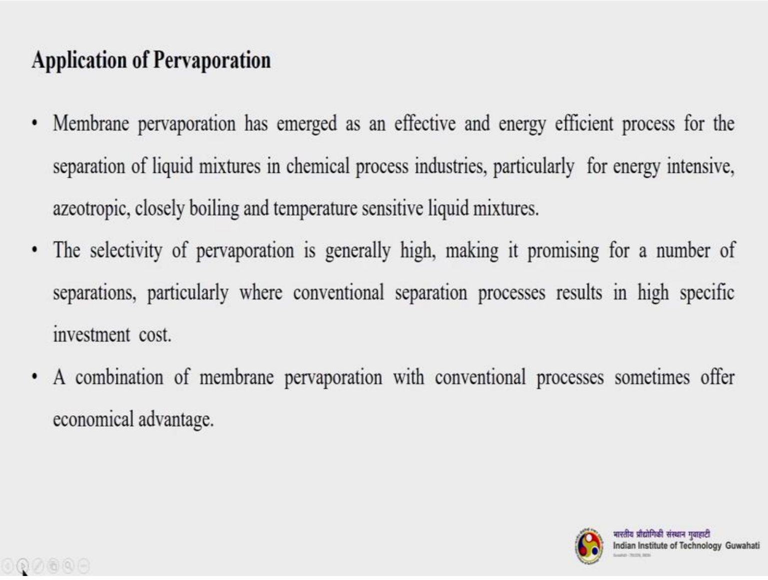

Application of Pervaporation

- Membrane pervaporation has emerged as an effective and energy efficient process for the separation of liquid mixtures in chemical process industries, particularly for energy intensive, azeotropic, closely boiling and temperature sensitive liquid mixtures.
- The selectivity of pervaporation is generally high, making it promising for a number of separations, particularly where conventional separation processes results in high specific investment cost.
- A combination of membrane pervaporation with conventional processes sometimes offer economical advantage.

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So, let us go ahead and discuss the applications of pervaporation. So, membrane pervaporation as has emerged as an effective and energy efficient process for the separation of liquid mixtures in chemical process industries particularly for energy intensive iazotrophic closely boiling and temperature sensitive liquid mixtures. So, the selectivity of pervaporation is generally high making it promising for a number of separations particularly where conventional separation processes results in high specific investment costs.

A combination of membrane pervaporation with conventional processes; sometimes offer economical advantage.

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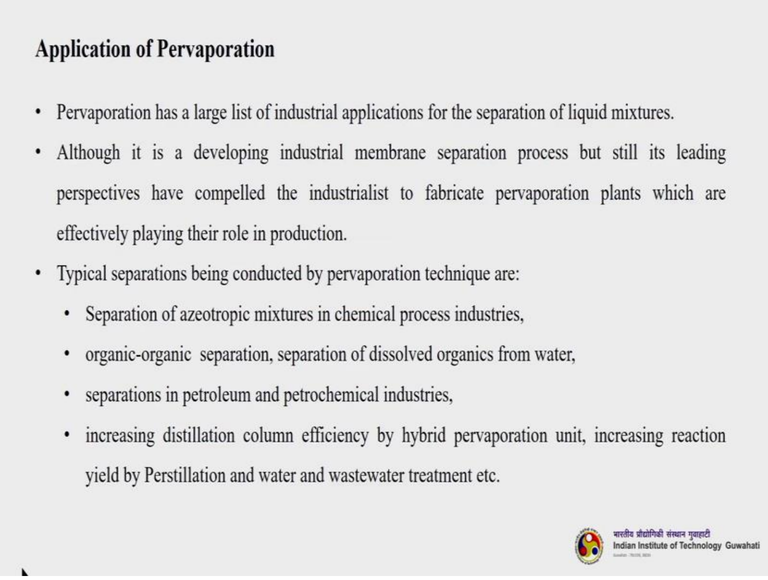

Application of Pervaporation

- Pervaporation has a large list of industrial applications for the separation of liquid mixtures.
- Although it is a developing industrial membrane separation process but still its leading perspectives have compelled the industrialist to fabricate pervaporation plants which are effectively playing their role in production.
- Typical separations being conducted by pervaporation technique are:
  - Separation of azeotropic mixtures in chemical process industries,
  - organic-organic separation, separation of dissolved organics from water,
  - separations in petroleum and petrochemical industries,
  - increasing distillation column efficiency by hybrid pervaporation unit, increasing reaction yield by Perstillation and water and wastewater treatment etc.

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Pervaporation has a large list of industrial applications for the separation of liquid mixtures although it is a developing industrial membrane separation process but still it's leading perspectives have compelled the industrialist to fabricate pervaporation plants which are effectively playing their role in production. So, typical separations are there is been conducted using pervaporation is the first and fore most is the separation azotropes.

In chemical process industries then organic-organic separation, separation of dissolve organics from water very important applications the separation that is being carried out downstream side in petroleum and petrochemical industries. Then increasing distillation column efficiency by hybrid for pervaporation unit this we will discuss. So increasing reaction yields by pervaporation and water and wastewater treatment etcetera.

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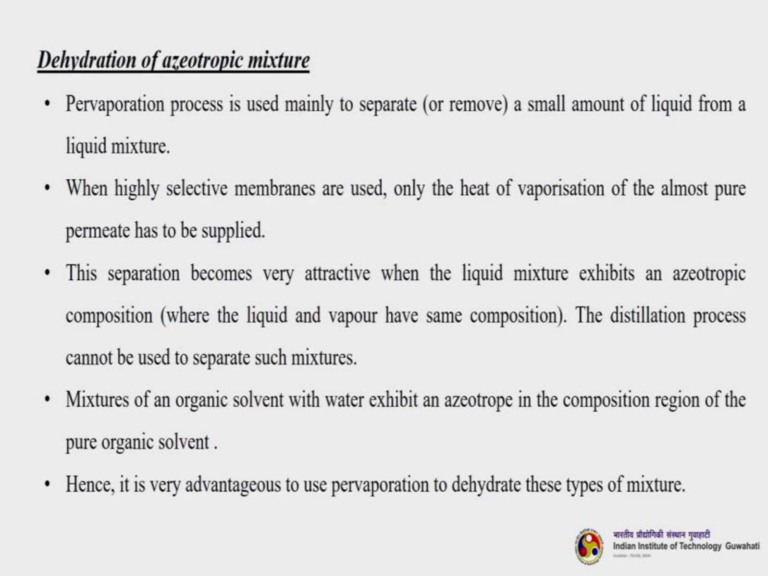

Dehydration of azeotropic mixture

- Pervaporation process is used mainly to separate (or remove) a small amount of liquid from a liquid mixture.
- When highly selective membranes are used, only the heat of vaporisation of the almost pure permeate has to be supplied.
- This separation becomes very attractive when the liquid mixture exhibits an azeotropic composition (where the liquid and vapour have same composition). The distillation process cannot be used to separate such mixtures.
- Mixtures of an organic solvent with water exhibit an azeotrope in the composition region of the pure organic solvent .
- Hence, it is very advantageous to use pervaporation to dehydrate these types of mixture.

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So, one example is dehydration azotropic mixture. The pervaporation process is used mainly to separate or remove small amount of liquid from a liquid mixture. When highly selective membranes are used only the heat of vaporization of the most almost pure permeate has to be supplied. Now this separation becomes very attractive when the liquid mixture exhibits azotropic composition where the liquid and vapor have same composition.

The distillation process cannot be used to separate such mixtures. Mixtures of an organic solvent with water exhibited azeotropic with water exhibit an azeotrope in the composition region of the pure organic solvent. Hence it is very advantageous to use pervaporation to dehydrate these types of mixtures.

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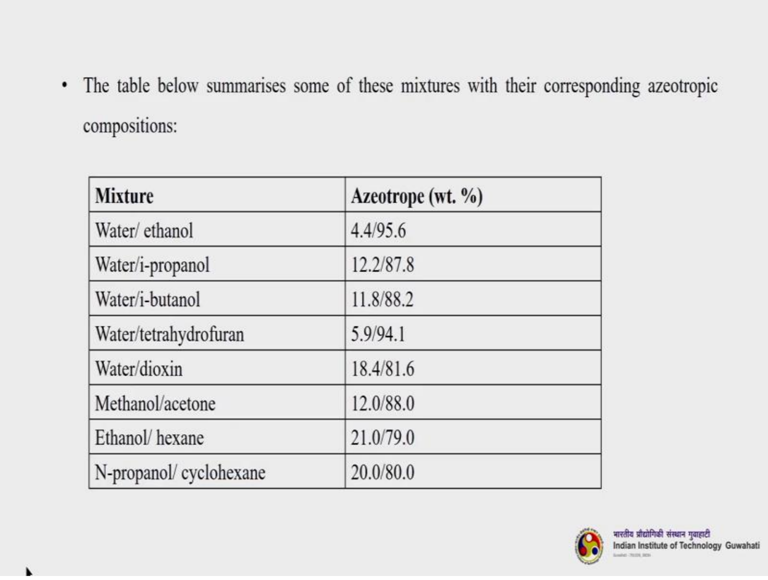

- The table below summarises some of these mixtures with their corresponding azeotropic compositions:

Mixture	Azeotrope (wt. %)
Water/ ethanol	4.4/95.6
Water/i-propanol	12.2/87.8
Water/i-butanol	11.8/88.2
Water/tetrahydrofuran	5.9/94.1
Water/dioxin	18.4/81.6
Methanol/acetone	12.0/88.0
Ethanol/ hexane	21.0/79.0
N-propanol/ cyclohexane	20.0/80.0

So, this table lists some of these mixtures with their corresponding azeotropic feed composition. So, water and ethanol the forms say azeotrope at 4.4 and 95.6 the similarly other it is given by water isopropanol, butanol and dioxin, acetone, hexane and all these things.

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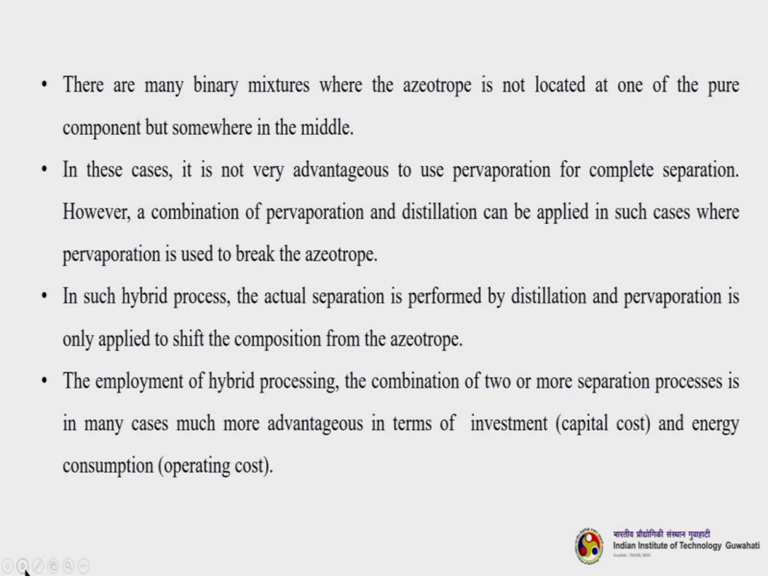

- There are many binary mixtures where the azeotrope is not located at one of the pure component but somewhere in the middle.
- In these cases, it is not very advantageous to use pervaporation for complete separation. However, a combination of pervaporation and distillation can be applied in such cases where pervaporation is used to break the azeotrope.
- In such hybrid process, the actual separation is performed by distillation and pervaporation is only applied to shift the composition from the azeotrope.
- The employment of hybrid processing, the combination of two or more separation processes is in many cases much more advantageous in terms of investment (capital cost) and energy consumption (operating cost).

So, there are many binary mixtures where the azotrope is not located at one of the pure component but somewhere in the middle. So, this is actually the problem in these cases it is not very advantageous to use pervaporation for complete separation. However a combination of pervaporation and distillation can be applied in such cases where pervaporation is used to break the azeotrope. So, then you can distill it off once the azeotrope is broken. So, in such hybrid processes the actual separation is performed by the distillation and pervaporation is only applied to shift the composition from the azeotrope.

The employment of hybrid processing the combination of two or more separation processes is mainly in many cases much more advantageous in terms of investment that is basically the capital investment and the energy consumption of course the operating cost.

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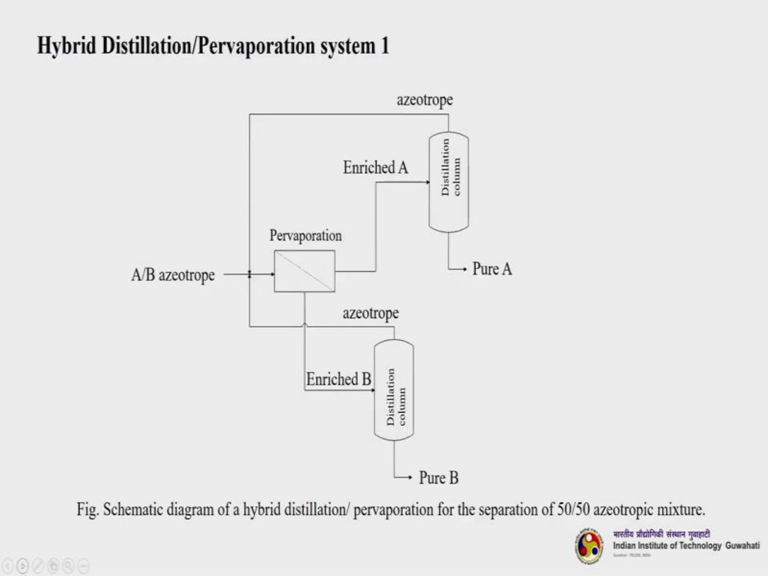

Hybrid Distillation/Pervaporation system 1

Fig. Schematic diagram of a hybrid distillation/ pervaporation for the separation of 50/50 azeotropic mixture.

So this is a classical example of separation affair 50-50 azeotropic mixtures so what is being done it is a hybrid on distillation and pervaporation system what is being done is AB azeotorpe is fed pervaporation. Now what this pervaporation system will do it will break the azeotrope and make a pure A or a pure B or you cannot do not say pure A, pure B. Let us say enrich A and enrich B one fraction goes to one distillation column another fraction goes to another distillation column so then in both the distillation columns we will get a pure fractions of A and pure fraction of B and whatever remains is being fed back to that original azeotropic mixtures to the AB.

So let us have a look so AB azeotropic is being separated in a pervaporation system so we get enriched A here and we get enriched B here. So, the enriched A is fed into the distillation column one so here we get a pure A and this enriched B this comes to the distillation column 2 we will get a pure B. So, whatever is left out as your drops is being pet and recycled back to the feed. So, this is a classic example of how you treat a 50-50 iazeotropic mixture. So, please remember here the job of pervaporation is shifting the azeotrope it is breaking the azeotrope it is not making pure A and pure B. The pure A and pure B are being made in the corresponding distillation column.

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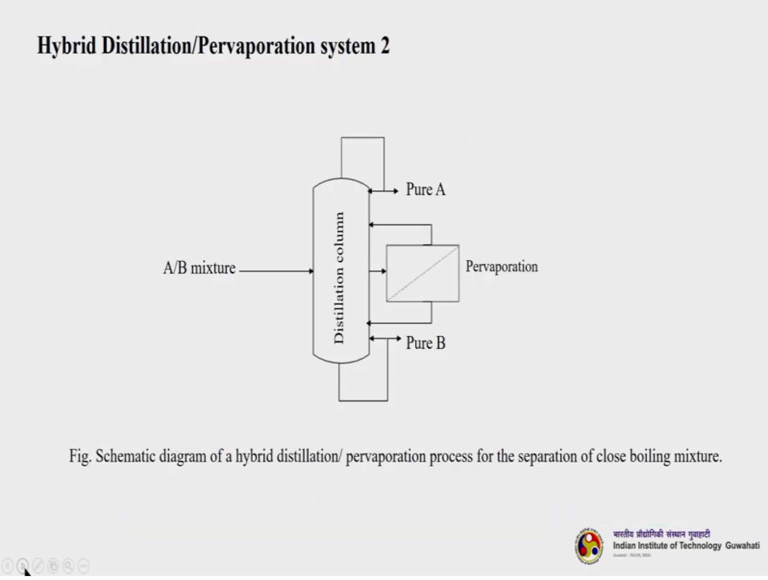

Hybrid Distillation/Pervaporation system 2

Fig. Schematic diagram of a hybrid distillation/ pervaporation process for the separation of close boiling mixture.

So, this is another classic example where this is pervaporation is coupled with a distillation system for the separation of close boiling point mixtures. So, you can see here we have one distillation column and pervaporation let us this is a more beautiful hybrid system here AB mixture is being fed to the mid of the column. Then this is being little heated here in the distillation column is a feed tray then it goes to the pervaporation where it is breaking this mixture into a enriched pure and enriched air.

So, this is actually enriched A and this is enriched B. So, enriched A and enriched B are being fed back to the distillation column a separate a trace. Now you will get a pure A from the top side and you get a pure B from the bottom side. So, you see here in this particular case we have a single distillation column and a single pervaporation system that is enough to separate that close boiling point mixtures to pure components. So these are actually being adapted in industries also commercially practice.

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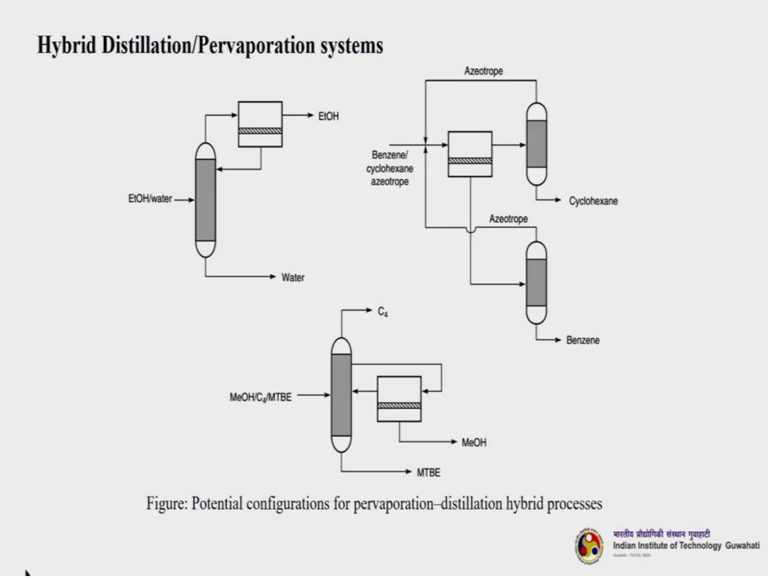

Hybrid Distillation/Pervaporation systems

Figure: Potential configurations for pervaporation–distillation hybrid processes

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So these are potential configurations of some pervaporation distillation hybrid process. So, you can see ethanol and water mixture. So, ethanol water is being fed to the distillation column from the top side on the that ratio of the feed that goes to the pervaporation system you get a pure ethanol here and whatever is left out is being recycled back so that is nothing but your water. So, in the second case here methanol and C4 MTB is being mixture is being treated.

So you get in the pervaporation what it is separating here with methanol and your C4 and MTB is being fed back it is not getting separated in pervaporation. So, the distillation column is separating your C4 and MTB into two different and distinct fractions. Similarly benzene and cyclohexane azeotrope is a classic example. The pervaporation is breaking this is the one the first one which we saw actually for 50-50 azeotrope.

So pervaporation is breaking the benzene and cyclohexane azeotrope. So, cyclohexane enriched component here is being fed to the distillation column here so you get a pure cycle oxygen and then a benzene reach fraction okay. So, this is benzene enrich fraction is being fed to this column so you get a pure benzene here and azeotripe is being recycled back. This is how we will have different configurations of hybrid distillation and pervaporation systems.

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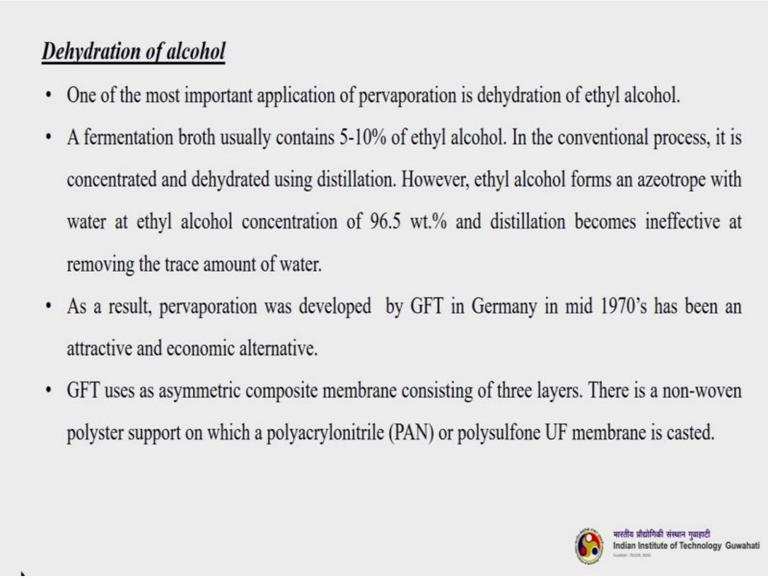

Dehydration of alcohol

- One of the most important application of pervaporation is dehydration of ethyl alcohol.
- A fermentation broth usually contains 5-10% of ethyl alcohol. In the conventional process, it is concentrated and dehydrated using distillation. However, ethyl alcohol forms an azeotrope with water at ethyl alcohol concentration of 96.5 wt.% and distillation becomes ineffective at removing the trace amount of water.
- As a result, pervaporation was developed by GFT in Germany in mid 1970's has been an attractive and economic alternative.
- GFT uses as asymmetric composite membrane consisting of three layers. There is a non-woven polyster support on which a polyacrylonitrile (PAN) or polysulfone UF membrane is casted.

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So then another example is dehydration of alcohols one of the most important application of pervaporation is dehydration of ethyl alcohol. So, fermentation broth usually contains 5 to 10% of ethyl alcohol in the conventional process it is concentrated and dehydrated using distillation. However ethyl alcohol forms an azeotrope with water at ethyl alcohol concentration of 96.58% and distillation becomes ineffective for removing the trace amount of water.

Now as a result pervaporation was developed by GFTin Germany in 1970s so this has been attractive and economic alternative. So, it uses an asymmetric composite membrane consisting of three layers. So, there is a non-movement polyester support on which a poly acrylonitrile or polysulfone ultra filtration membrane is casted.

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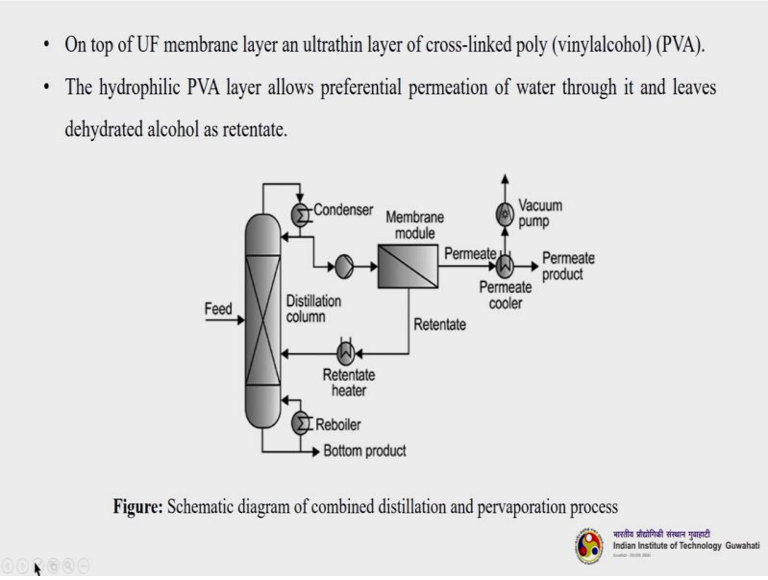

- On top of UF membrane layer an ultrathin layer of cross-linked poly (vinylalcohol) (PVA).
- The hydrophilic PVA layer allows preferential permeation of water through it and leaves dehydrated alcohol as retentate.

Figure: Schematic diagram of combined distillation and pervaporation process

So on top of ultra filtration membrane layer and ultra thin layer of cross-linked polyvinyl alcohol membrane is grafted so the hydrophilic PBA layer allows preferential permission of water through it and leaves dehydrated alcohol as retentate. So, this is the example how that combined distillation and pervaporation system is performing here separation here doing the dehydration of alcohol.

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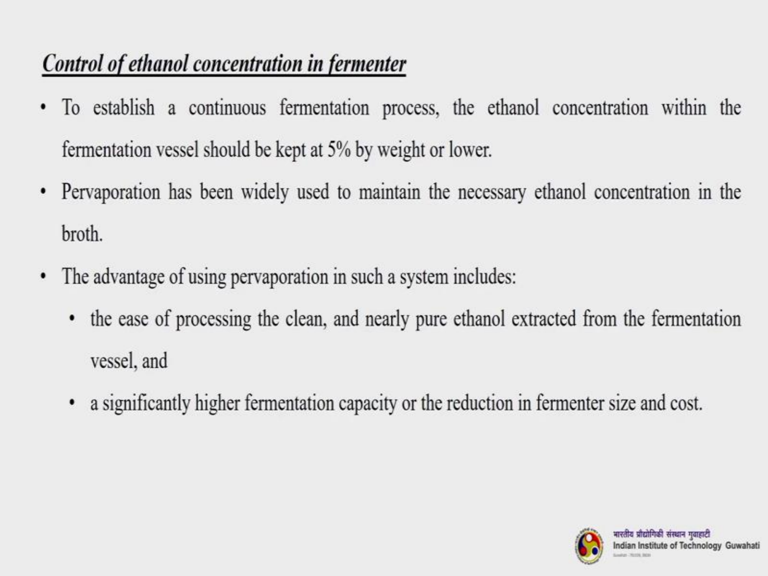

Control of ethanol concentration in fermenter

- To establish a continuous fermentation process, the ethanol concentration within the fermentation vessel should be kept at 5% by weight or lower.
- Pervaporation has been widely used to maintain the necessary ethanol concentration in the broth.
- The advantage of using pervaporation in such a system includes:
  - the ease of processing the clean, and nearly pure ethanol extracted from the fermentation vessel, and
  - a significantly higher fermentation capacity or the reduction in fermenter size and cost.

So, you know another classic example is control of ethanol concentration in fermenter. So, to establish a containers fermentation process the ethanol concentration within the fermentation vessel should be kept 5% by weight see ethanol is continuously being produced by the microorganisms inside the fermenter and if you are not it is a best process if you are not even in contrast process if you are not removing the ethanol that the ethanol concentration is increasing. Now that additional ethanol beyond 5% which is found out that up to 5% is fine will become toxic to the microorganism; thereby inhibiting the growth and their performance so there will be no more ethanol formation but this has to be removed.

The pervaporation has been widely used to maintain the necessary ethanol concentration in the broth. Advantage of using pervaporation in this type of system is that they ease of processing the clean and nearly pure ethanol extracted from fermentation result. So, you get extremely pure ethanol directly we are getting a very pure ethanol just by using a pervaporation system. And a significantly higher fermentation capacity or the reduction of fermentation fermenter size and cost.

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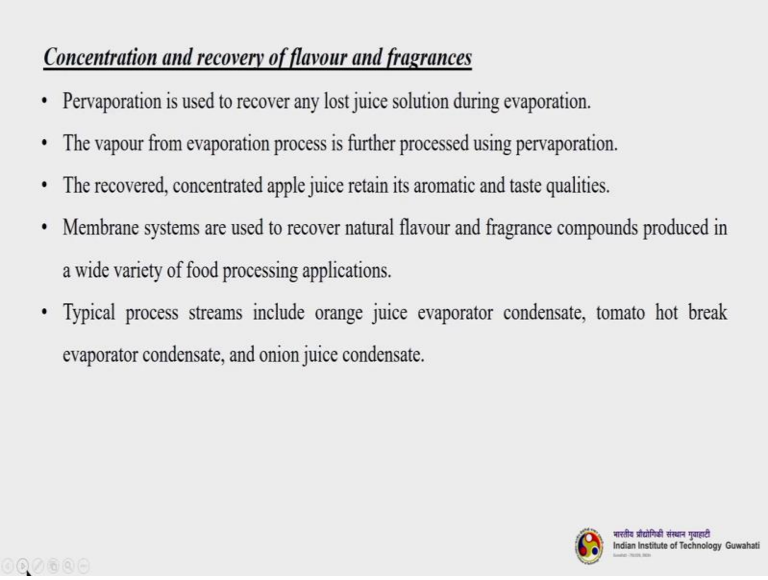

Concentration and recovery of flavour and fragrances

- Pervaporation is used to recover any lost juice solution during evaporation.
- The vapour from evaporation process is further processed using pervaporation.
- The recovered, concentrated apple juice retain its aromatic and taste qualities.
- Membrane systems are used to recover natural flavour and fragrance compounds produced in a wide variety of food processing applications.
- Typical process streams include orange juice evaporator condensate, tomato hot break evaporator condensate, and onion juice condensate.

Concentration and recovery of flavor and fragrances, pervaporation is used to recover any lost juice solution during the operation the vapor from evaporation process is further processed using pervaporation. The recover concentrated approaches retain its aromatic and test qualities membrane system are used to recover natural fiber and fragrance compounds produced in a wide variety of food processing applications.

Typical process streams include orange juice evaporator condensate, tomato hot break vaporator condensate and onion juice condensation.

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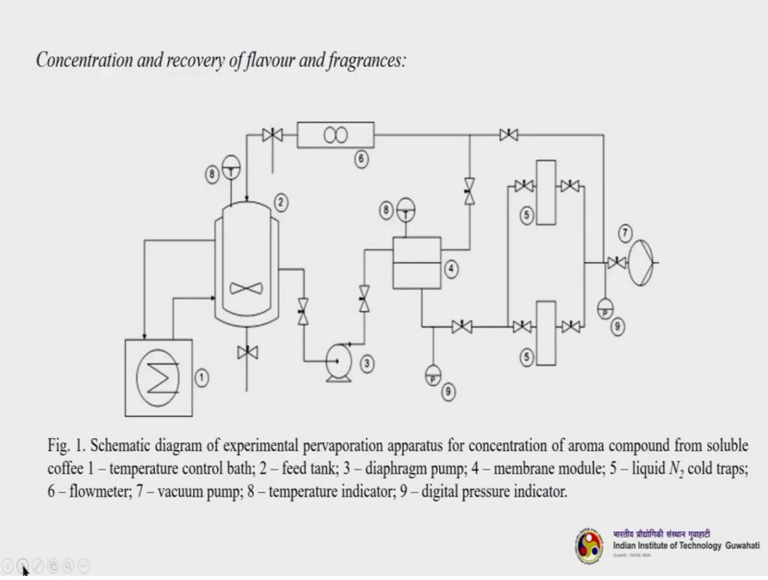

Concentration and recovery of flavour and fragrances:

Fig. 1. Schematic diagram of experimental pervaporation apparatus for concentration of aroma compound from soluble coffee 1 – temperature control bath; 2 – feed tank; 3 – diaphragm pump; 4 – membrane module; 5 – liquid N_2 cold traps; 6 – flowmeter; 7 – vacuum pump; 8 – temperature indicator; 9 – digital pressure indicator.

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So, this is a schematic diagram of experimental pervaporation apparatus for concentration of aroma compound from soluble coffee. So, from the coffee you are extracting the aroma compound so you can see that there are many components the one is the temperature control bath and this is the feed tank and then 3 is the diaphragm pump 4 is the membrane module so this is the pervaporation module.

Then 5 is the liquid nitrogen this is the liquid nitrogen coal trap, 6 is a flow meter 7 is a vacuum pump 8 is temperature indicator and 9 is digital pressure indicator. So, you can see that how in a particular integrated system the flavor or the aroma compound from the soluble copy is being extracted without compromising its properties.

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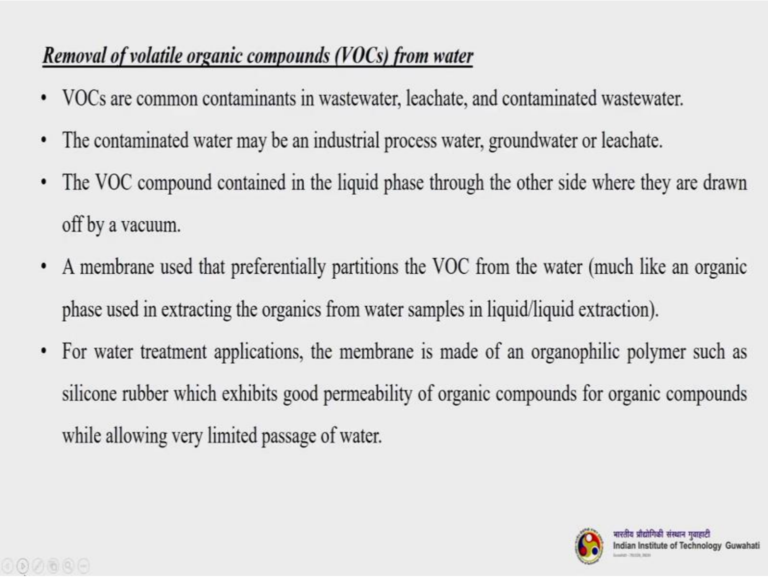

Removal of volatile organic compounds (VOCs) from water

- VOCs are common contaminants in wastewater, leachate, and contaminated wastewater.
- The contaminated water may be an industrial process water, groundwater or leachate.
- The VOC compound contained in the liquid phase through the other side where they are drawn off by a vacuum.
- A membrane used that preferentially partitions the VOC from the water (much like an organic phase used in extracting the organics from water samples in liquid/liquid extraction).
- For water treatment applications, the membrane is made of an organophilic polymer such as silicone rubber which exhibits good permeability of organic compounds for organic compounds while allowing very limited passage of water.

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Another example is removal of VOCs, VOCs are volatile organic compounds from water. So, their carbon contaminants in wastewater, leachate at contaminated wastewater. The contaminated water may be an industrial wastewater process water ground or leachate. VOC compound contained in the liquid phase through the other side when they had drawn up by a vacuum a membrane used that preferential partition of the VOC from the water much like an organic phase used in extracting the organics from water simple in liquid-liquid extraction.

So for water treatment application you can use either the membrane of a organophilic polymer such as a silicon rubber which exhibits good permeability for organic compounds. So, because it will not swell that is why silicon tube while allowing very limited passage of water.

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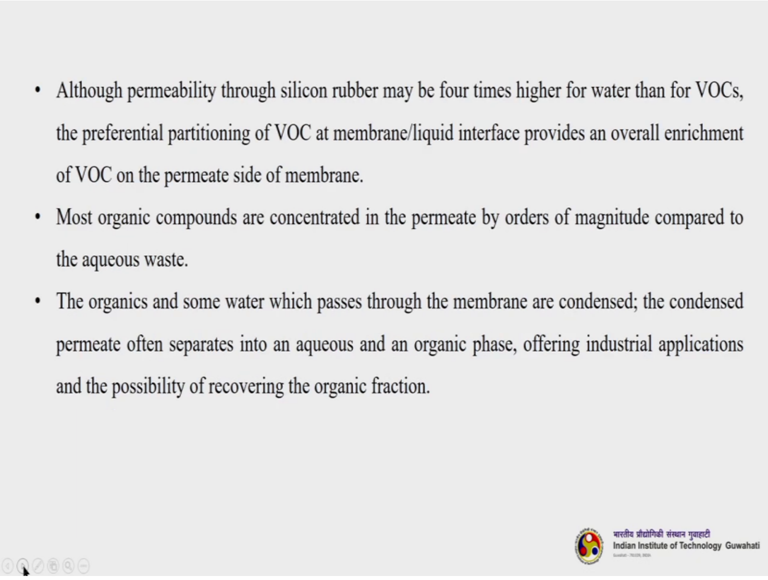

- Although permeability through silicon rubber may be four times higher for water than for VOCs, the preferential partitioning of VOC at membrane/liquid interface provides an overall enrichment of VOC on the permeate side of membrane.
- Most organic compounds are concentrated in the permeate by orders of magnitude compared to the aqueous waste.
- The organics and some water which passes through the membrane are condensed; the condensed permeate often separates into an aqueous and an organic phase, offering industrial applications and the possibility of recovering the organic fraction.

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All the permeability through silicon rubber maybe 4 times had for water than VOC's the preferential partitioning of uses at membrane liquid interface provides an overall enrichment of VOC on the permeate side of the membrane. So, most organic compounds are concentrated in the permeate by order of magnitude compared to an aquarist. The organics and some water which passes through the membrane are condense the contents permeate up and separates into an aqueous and organic path offering industrial applications and the possibility of recovering the organic fraction.

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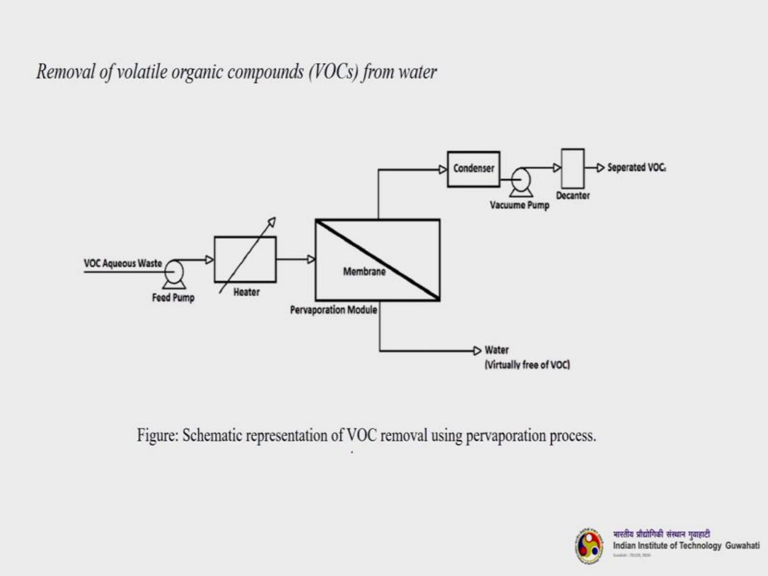

Removal of volatile organic compounds (VOCs) from water

Figure: Schematic representation of VOC removal using pervaporation process.

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So this is the schematic presentation of VOC removal using a pervaporation process. So, VOC aqueous waste being fed being pumped to a heater where it is being heated to a certain temperature then fed back to the pervaporation system where you will get a water which is virtually free of VOC here and you will through a condenser you can separate the VOC here.

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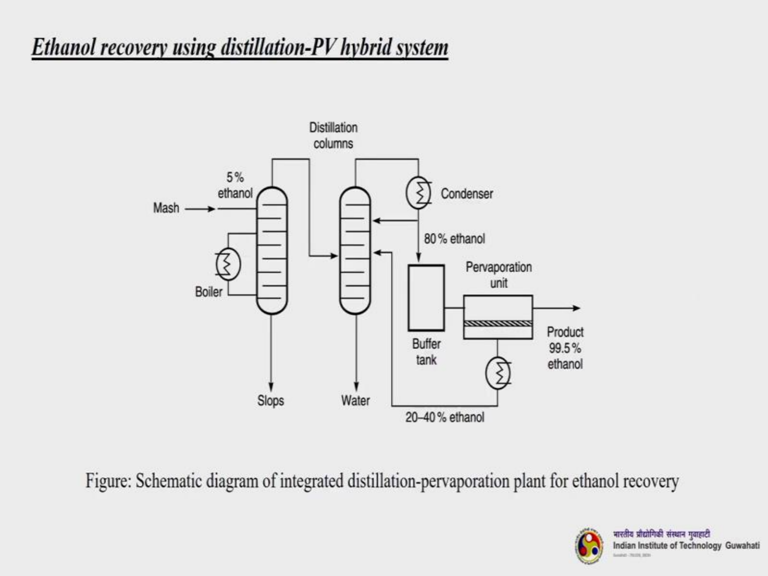

Ethanol recovery using distillation-PV hybrid system

Figure: Schematic diagram of integrated distillation-pervaporation plant for ethanol recovery

So, this is another classic example where ethanol is being recovered using a distillation PV hybrid system. So, this is an integrated system in which you have two distillation columns so you see you have a 5% ethanol is being prepared to here so by using a two-stage distillation column and then a final single pervaporation system we get 99.5% ethanol. So, this is a classic example in which two distillation columns and a single pervaporation system is enriching the 5% ethanol to 99.5%.

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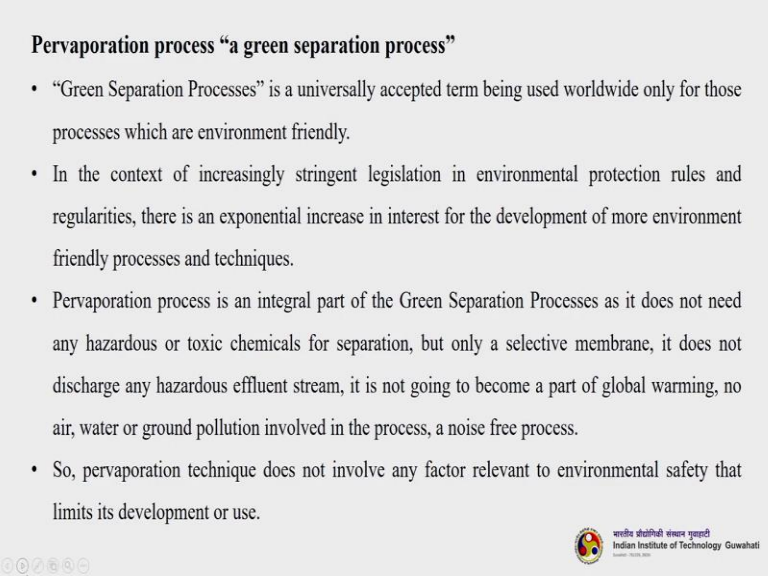

Pervaporation process “a green separation process”

- “Green Separation Processes” is a universally accepted term being used worldwide only for those processes which are environment friendly.
- In the context of increasingly stringent legislation in environmental protection rules and regularities, there is an exponential increase in interest for the development of more environment friendly processes and techniques.
- Pervaporation process is an integral part of the Green Separation Processes as it does not need any hazardous or toxic chemicals for separation, but only a selective membrane, it does not discharge any hazardous effluent stream, it is not going to become a part of global warming, no air, water or ground pollution involved in the process, a noise free process.
- So, pervaporation technique does not involve any factor relevant to environmental safety that limits its development or use.

So, pervaporation is a green separation process so it is a universally accepted term being used worldwide only for those processes which are environmentally friendly. So, those processes we called gain separation processes. In the context of increasingly stringent legislation in Environmental Protection rules and regularities there is an exceptional increase in interest for the development of more environment friendly processes and techniques.

Pervaporation is an integral part of the gain separation process as it does not need any hazardous or toxic chemicals for separation but only selective membrane he does not discharge any hazardous effluent stream, stream it is not going to become a part of the global warming. No air water or ground pollution is involved in the process a absolutely noise free process. So, pervaporation technique does not involve any factor relevant to environmental safety that limits his development or use.

So you can say without much thinking that pervaporation is a greener process, the greener separation process.

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Advantages of Pervaporation Process

- Capable of Breaking Azeotropes
- No Chance of Product Contamination
- No Need of Heavy Equipments
- Continuous Production System
- Involves Low Operational Pressure
- Multistage System can be Used
- Low Maintenance Cost
- Separation of Heat Sensitive Substances
- Involves Simple Process Schematics
- Energy Saving Process
- Involves Low Operational Temperature
- Flexibility in Operating System
- Low Operating Cost
- Low Capital Cost
- Results in High Purity Product.
- Environment Friendly and pollution free technique (Green Separation Technique)

Disadvantages of Pervaporation Process

- Pervaporation separation system requires purified feed
- Temperature reduction in pervaporation reduces the transmembrane flux

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So just before we wind up and just advantages of pervaporation process I am just listed out. So, capable of breaking azeotrope and no chance of product contamination, no need of heavy equipments, continuous production system, involves low operational pressure, multi-stage system can be used, low maintenance cost results in high purity product, environment friendly and pollution free technique.

A separation of heat sensitive substances involve simple process system schematics, energy-saving process involves low operational temperature, flexibility in operating system, low operating cost, low capital cost. But everything is not so Inuit so there are some disadvantages also. Pervaporation separation requires a purified feed. If you are supplying a feed with through so much of contamination then pervaporation might not work out.

And temperature reduction into an pervaporation reduced a step transmembrane flux. So, since there is a temperature effect inside the pervaporation system so, the flux gets reduced.

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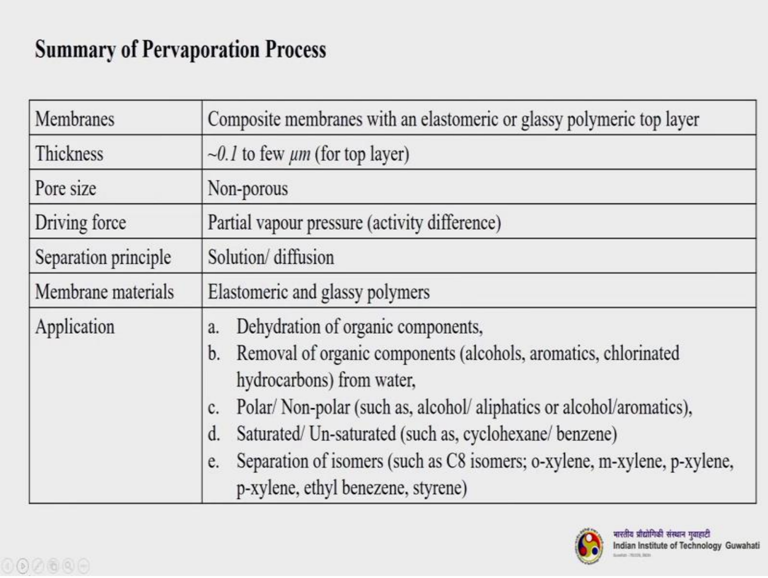

Summary of Pervaporation Process

Membranes	Composite membranes with an elastomeric or glassy polymeric top layer
Thickness	~*0.1* to few *μm* (for top layer)
Pore size	Non-porous
Driving force	Partial vapour pressure (activity difference)
Separation principle	Solution/ diffusion
Membrane materials	Elastomeric and glassy polymers
Application	a. Dehydration of organic components, b. Removal of organic components (alcohols, aromatics, chlorinated hydrocarbons) from water, c. Polar/ Non-polar (such as, alcohol/ aliphatics or alcohol/aromatics), d. Saturated/ Un-saturated (such as, cyclohexane/ benzene) e. Separation of isomers (such as C8 isomers; o-xylene, m-xylene, p-xylene, p-xylene, ethyl benezene, styrene)

So firm operation is a one system in which both heat and mass transfer were appearing simultaneously says the complex system. So, this is the summary of pervaporation, so you can go through later on. Some membranes its composite membranes the thickness is about 0.1 to few microns pore sizes it is a non porous membrane, driving force is partial vapor pressure, separation processes of course solution diffusion membrane materials are elastomeric and glassy polymers. And the application sees and there are so many applications we have just discussed.

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So, with this I conclude thank you very much. So, you can refer Mulder and Kenneth for today's lecture most of what is taken from Kenneth and if you have any doubt please feel free to write to me at kmohanty@iitg.in. In the next class so the module 10 lecture 30 will solve some problems based on electro dialysis and for pervaporation thank you very much.