Introduction to Process Modeling in Membrane Separation Process

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Lecture – 01

Fundamentals of Separation Processes and Introduction of Membrane System

Good morning everyone, so we will be beginning the course on fundamental applications and modelling of membrane separation processes are initially in these lecture what we will be covering will be defining the separation processes and then we will be looking into fundamentals and various definitions of introduction of the membrane separation system.

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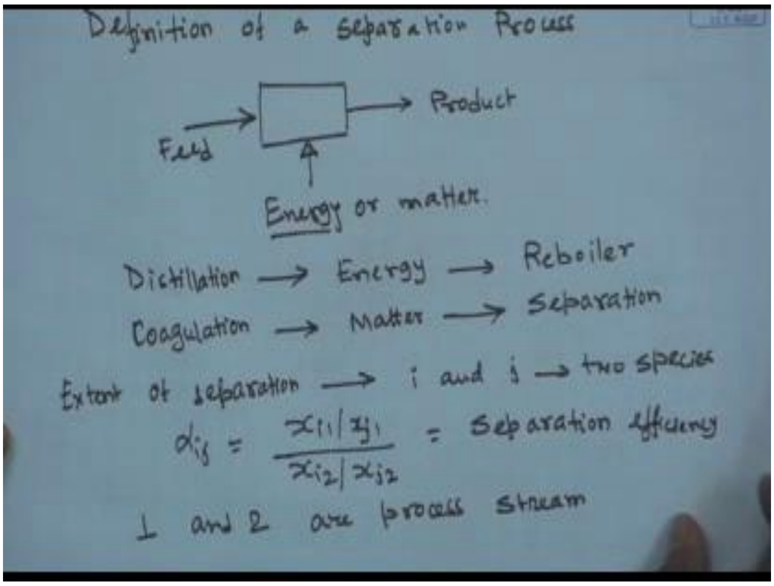

Definition of a separation Process

$$\text{Feed} \longrightarrow \boxed{} \longrightarrow \text{Product}$$

Energy or matter.

Dictillation ⟶ Energy ⟶ Reboiler

Coagulation ⟶ Matter ⟶ Separation

Extent of separation ⟶ i and j ⟶ two species

$$\alpha_{ij} = \frac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}} = \text{Separation efficiency}$$

1 and 2 are process stream

So, we start with what is separation processes let us look into definition of a separation process. In a separation process, there should be a feed stream then there will be some agent will be giving input to the system between feed stream and the product stream and the external agent can be either energy or matter. So, one example of energy is distillation where energy is given into in the form of heat energy supplied by a re boiler.

So, re boiler supplied the energy and the feed stream are divided in to the various product streams. So, in case of let say coagulation or absorption, it is the external agent is matter. We add an external agent to effect the separation. So, input of energy or matter is essential for effecting a separation processes. Now let us look into the extent of separation how we define extent of separation between two species i and j; i and j are two species. Alpha i j is defined as x i 1 divided by x j 1 divided by x i 2 x j 2 where one and two are two process streams these also known as the separation efficiency.

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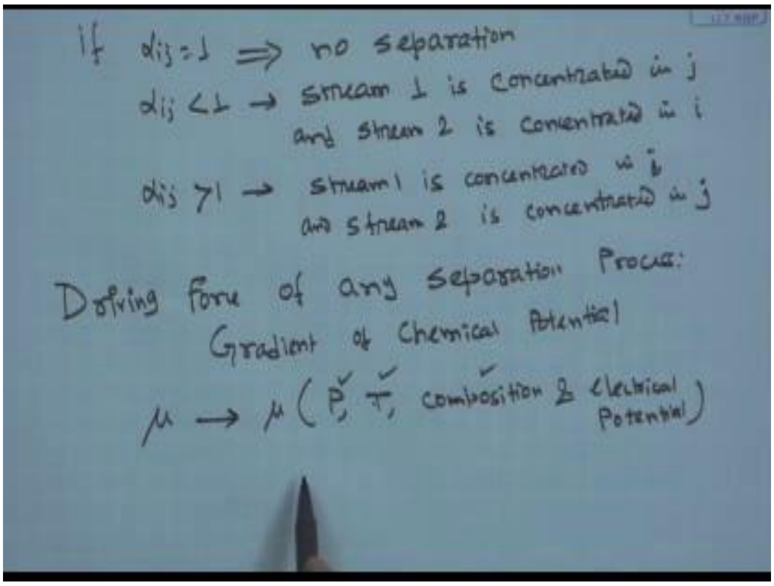

if $\alpha_{ij} = 1 \Rightarrow$ no separation

$\alpha_{ij} < 1 \rightarrow$ stream 1 is concentrated in j
and stream 2 is concentrated in i

$\alpha_{ij} > 1 \rightarrow$ stream 1 is concentrated in i
and stream 2 is concentrated in j

Driving force of any separation Process:
Gradient of Chemical Potential

$\mu \rightarrow \mu(\overset{\checkmark}{P}, \overset{\checkmark}{T}, \overset{\checkmark}{\text{composition}}$ & electrical potential$)$

So, if so i and j are two species one and two are the two process streams. So, if alpha i j is equal to 1, then there is no separation occurs; if alpha i j is less than 1, then stream one is concentrated in j, and stream two is concentrated in i. If alpha i j is greater than 1, then stream one is concentrated in j and stream two is concentrated in stream; stream one is concentrated in i and stream two is concentrated in j. So, by looking into the value of alpha i j and the composition of the product stream and the feed stream, one can identify which stream will be reached in which species and which stream will be lean in the other species.

Now, let us look into the driving force of any separation process is gradient of chemical potential. Now, all of you must know about the chemical potential if you forgot just brush up your idea of basic thermodynamics, chemical potential will be a function of if you a remember pressure, temperature, composition and electric potential of the system. Typically, in an (Refer Time: 06:09) system, we will be having only these three independent thermodynamic properties which will be influencing chemical potential. Now, chemical potential is not a directly measurable property, only pressure temperature composition etcetera are the directly measurable thermodynamic properties and there exist relations like Gibbs to a relationship by which this independent properties will be related to chemical potential.

So, therefore, if there is a change in pressure, temperature, composition of the system that will lead to a gradient of chemical potential and that will be finally, leading to separation of species. So, basically there may be a combined effect of this any of this thermodynamic properties or if any one of them, any two of them, if any all of them will be changing that will be effecting the gradient of the chemical potential leading to separation of the species.

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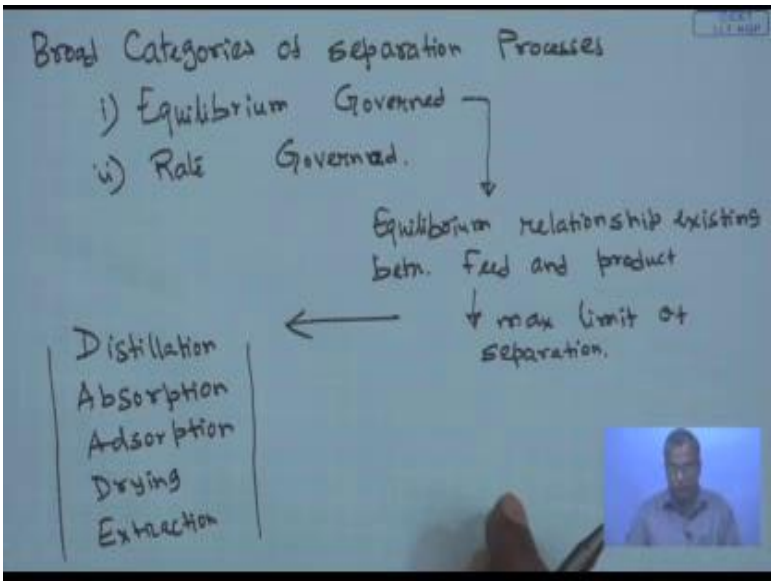

Broad Categories of separation Processes

i) Equilibrium Governed

ii) Rate Governed.

Equilibrium relationship existing betn. Feed and product

↓ max limit of separation.

Distillation
Absorption
Adsorption
Drying
Extraction

Once that is identified, let us go to the definition of separation processes. There are basically two broad categories of separation processes; one is equilibrium governed separation processes; another is rate governed separation processes. In equilibrium governed separation processes, the equilibrium relationship equilibrium existing between feed and product stream will govern the extent of separation. So, therefore, there will be a maximum limit at a particular temperature, there will be a maximum limit of separation that is that can be attend or exist in equilibrium governed separation processes, because the composition of a particular species will be following at equilibrium relationship in the feed and the product stream.

So, one cannot go beyond that a maximum composition. So, there is a limit existing between in case of equilibrium relationship equilibrium based separation processes and all the basic separation processes that we have studied in third year and forth year, they are falling under this category equilibrium governed separation processes. So, what are the examples distillation, absorption, adsorption, drying extraction, there are many others. So, basically these are some of the examples of equilibrium governed separation processes.

And in any process engineering of came a typically appearing in chemical engineering the separation is in integral part. So, one has to go for the product separation even if you if you have a reactive system there will be product of separate several species that will be coming out after the reaction and some of the products will be desirable some of the products will be undesirable. One we have an aim to maximise a particular product out of various other products existing in this room. So, therefore, one has to go for a separation process in the downstream and based on the system performance or based on the you know your objective one as to take recourse to the either equilibrium governed separation processes or rate governed separation process.

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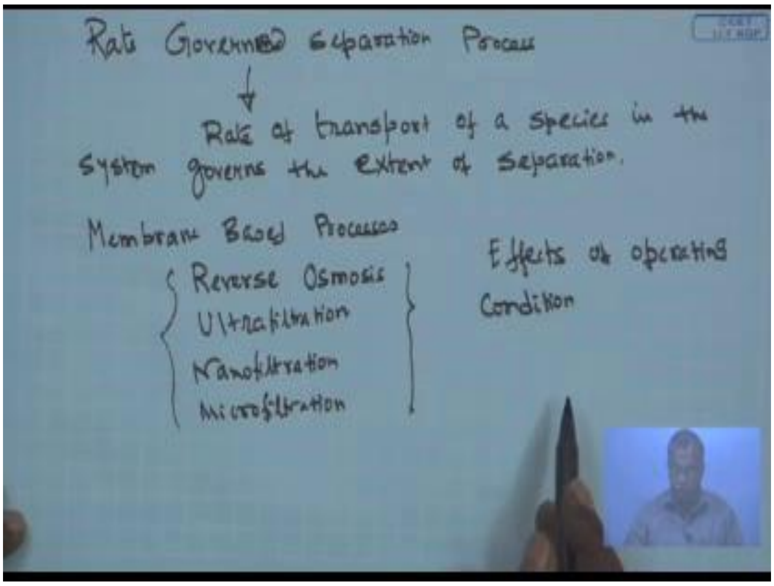

Rate Governed Separation Process

↓

Rate of transport of a species in the system governs the extent of separation.

Membrane Based Processes

- Reverse Osmosis
- Ultrafiltration
- Nanofiltration
- Microfiltration

Effects of operating Condition

Now, let us see what are the rates governed separation processes; the rate governed separation processes are basically those processes where rate of transport of a species in the system governs the separation - extent of separation. For example, most of the membrane separation processes they fall under rate governed separation processes membrane based processes; for example, reverse osmosis, ultra filtration, nano filtration, micro filtration, all pressure given separation processes the membrane separation processes they fall under the rate governed separation processes.

Now, so that is the difference between equilibrium governed separation processes and rate governed separation processes. So, effects of operating conditions are quite crucial in rate governed separation processes. For example, if you can maintain all these separation processes that I have given example they are basically the pressure driven separation processes. So, if we increase the major driving force or is that pressure drop across the membrane. If you increase these driving forces then the rate of the species will be altered. So, one can go for a higher through (Refer Time: 12:48) or higher extent of separation by controlling the operating conditions or is by controlling the rate of transport of the species through in the process or in the system. So, that is the difference between the equilibrium governed separation processes and rate governed separation processes. Now, I think we should directly get into the membrane based separation processes.

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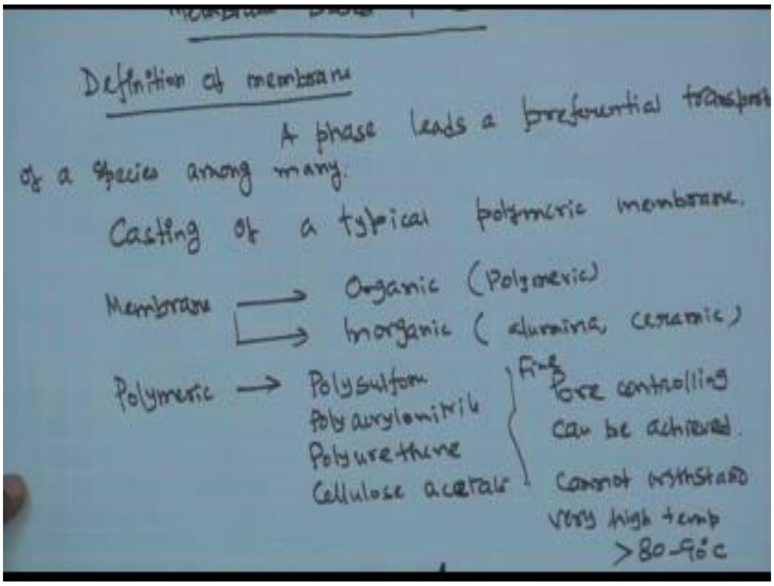

Definition of membrane

A phase leads a preferential transport of a species among many.

Casting of a typical polymeric membrane.

Membrane → Organic (Polymeric)
→ Inorganic (alumina, ceramic)

Polymeric → Polysulfone
Polyacrylonitrile
Polyurethane
Cellulose acetate

Fine pore controlling can be achieved.

Cannot withstand very high temp
> 80-90°C

So, in membrane based processes, first we will be look into what is the definition of a membrane. Membrane is defined by a phase that gives a preferential transport leads a preferential transport of a species among many. So, if there are number of species present in the feed stream then a particular species will be preferred to be transport to the through the membrane, therefore the product stream will be enriched in the particular species and in terms of other species it will be of having lower concentration, so that is a definition of membrane. Before going into the fundamental transport mechanisms of the membrane and categorization of the various processes, first look into what is the typical casting process of a membrane casting of a typical polymeric membrane. I will mostly concerned under concentrated on polymeric membrane, because these membranes can be of two types; either they can be polymeric, they can be inorganic; it can be organic like polymeric; they can be inorganic like alumina, ceramic, etcetera.

Now, there are advantages and disadvantages of both types of membranes for example, the polymeric membranes, the basic polymer the base polymer by whose the membrane is from either polysulfone, poly acrylonitrile, polyurethane, pvc - polyvinyl chloride - their blends, cellulose acetate that is the starting material of membrane polymeric membrane their combination blames so and so forth.

Now, the major advantage of the polymeric membrane is that one can really control the four size of polymeric membrane to a fine extent; one can control the procedure up to the range of angstrom which will be used for separation of monovalent salts. On the other hand these polymeric, so there is major advantage; that means, pore controlling can be achieved; fine pore controlling can be achieved. On the other hand, these polymeric membranes they cannot with stand high temperature. And what is the very high temperature typically beyond 80 to 90 degree centigrade. So, therefore, if you have a process stream of high temperature you cannot directly get into the polymeric membrane system one as to go through a heat exchanger bring the temperature down and then you know directed into the membrane based in the process having the polymeric membranes.

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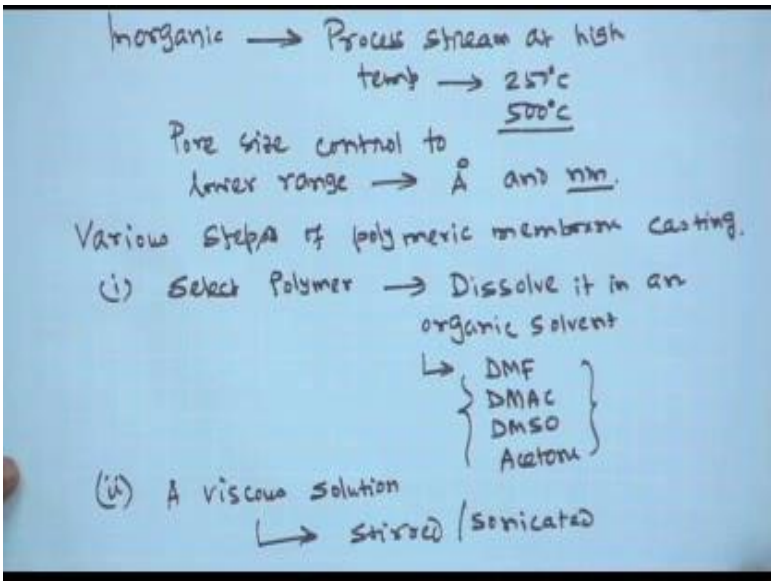

Inorganic → Process stream at high
temp → 250°c
500°c

Pore size control to
lower range → Å and nm.

Various steps of polymeric membrane casting.

(i) Select Polymer → Dissolve it in an
organic solvent
↳ DMF
DMAC
DMSO
Acetone

(ii) A viscous solution
↳ stirred / sonicated

On the other hand, in case of inorganic membrane the problem is not that much. In case of inorganic membrane, one can really go to you know a process one can handle a process stream at very high temperature. And what is the typical high temperature so in any anything 250 degree centigrade, 500 degree centigrade, it should not be have a problem it has a thermal stability high thermal stability, but the major problem of the inorganic membrane is that the pore size control; at lower pore like way in less than micron is very difficult to obtain. So, pore size control to lower range, what is a lower range in the range of angstrom and nanometer is not possible. So, therefore, for the inorganic membranes cannot go below the micron sized force, for example, for the micro filtration. So, these are the difference between the organic and inorganic membranes, and then we will be looking into the membrane casting, various steps of membrane polymeric membrane casting.

First, we select polymer polymer dissolve it in an organic solvent. In an organic solvent and what is that typical organic solvent typical organic solvent is DMF that is dimethyl fluoride, DMAC, DMSO - dimethyl sulfoxide and then acetone, so these are various typical organic solvents by which polymer is dissolved. Once we select the polymer polymer composition and the solvent then it will be dissolve in the solvent what will be resulting, resultant will be a viscous solution. And these solution will be continuously stirred or sonicated, so that there will be no agglomeration of the polymeric material into the (Refer Time: 20:02) it will be producing a homogeneous solution.

So, once the homogeneous solution is done, actually the homogenization of the solution is kept one should be continued so that there will be no deserved air bubble present into the solution. Otherwise, if you would like to cast it then there will be defects that will be appearing in the polymer film and which is not desirable at all because that will be you know destructing the continuity of the polymer film and it will deteriorate the performance of the membrane.

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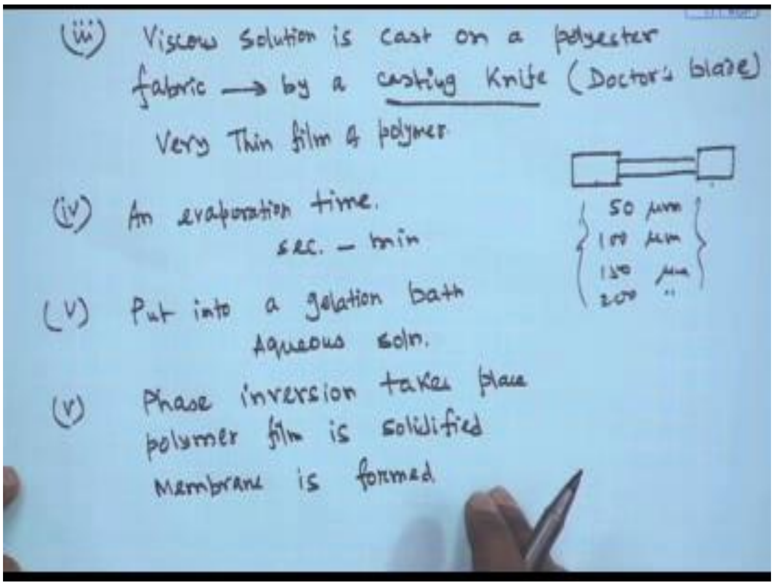

(iii) Viscous Solution is cast on a polyester fabric → by a casting Knife (Doctor's blade)
Very Thin film of polymer

(iv) An evaporation time.
sec. – min

(v) Put into a gelation bath
Aqueous soln.

(v) Phase inversion takes place
polymer film is solidified
Membrane is formed

So, once the viscous solution is done then it is cast on a third step is the viscous film viscous solution is cast on a polyester fabric, (Refer Time: 20:59) polyester fabric by a casting knife which is also known as the doctors blare. So, once it is cast then it will create a very thin film thin film of polymer. Now, what is a typical casting knife a typical casting knife is a mirror polished cylindrical solid cylindrical object having the square or rectangular cross section at the end and the typical cross section looks like this.

So, when you place this cross section on a surface and all this surfaces are calibrated properly that if you just turn it then it will be creating a gap let say 50 micron between the surface and the polymer film solution. And if you just turn it once again, so there one can realise let say 100 micron. So, since there are four surfaces of this square or rectangular cross section of the end one can realise you know at least four thickness of the casting film let say 50, 100, 150 and 200 micron in the same doctors blare. So, therefore, using the doctors blare same doctors blare, one can realise four thickness of polymer on the polyester fabric.

Then there will be given an evaporation time. What is evaporation does during this evaporation the solvents will be evaporated to the polymer film during their evaporation the fine pores are form into the polymer matrix. And typically this evaporation time may be in order of second two minute one or two minute. Once that is done then it will be immediately put into a gelation bath. What is the typical gelation bath typical gelation bath is basically an aqueous solution, let us say water. Water being an anti solvent, it is a bath of anti solvent to the polymer once the anti solvent comes in contact with the polymer film the immediately the phase inversion takes place, so this is also known as the phase inversion technique.

And the polymer film gets solidified and transfer from the liquid stream. And the membrane is formed polymer film is solidified, membrane is formed. There will be exchange of solvent and non-solvent from the non-solvent from the polymer matrix and solvent from the polymer matrix and non-solvent from the aqueous stream because of the concentration gradient there will be immediately exchanging. The non-solvent, solvent will be coming out from the polymer matrix into the gelation bath and the non-solvent will be going into the polymer matrix from the gelation bath.

So, therefore, whenever the non-solvent will be getting into the polymer matrix immediately they will be forming bigger post and the force will be formed. So, these will be creating the pores into the membrane matrix and these solvent, non-solvent exchanges are known as the demixing. These demixing can be two types it can be a quick demixing. So, in case of quick demixing the exchange of solve, non-solvent will be very, very quick and it will be leading to de very dense matrix polymer matrix. On the other hand, if the solvent and in the demixing is delayed delayed demixing then there will be it will forming a larger pores into the membrane matrix. So, by controlling the extent of mixing and demixing, one can really control the pore size distribution.

So, what is the what are the basically the various controlling controlling factors of pores once the membrane is kept in the gelation bath and the formed the it is formed then it is taken out then it is taken out from the from the solution and it is its dried. And once it is dried then it is stored either in distilled water or into you know vapours preservative solution so that there will no microwave attack on the polymer film on the membrane film.

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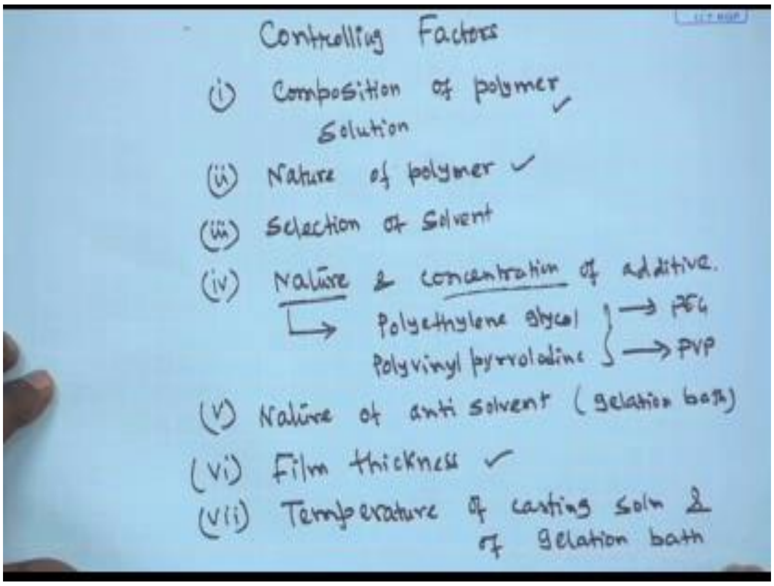

Controlling Factors

(i) Composition of polymer solution ✓

(ii) Nature of polymer ✓

(iii) Selection of Solvent

(iv) Nature & concentration of additive.

↳ Polyethylene glycol → PEG

Polyvinyl pyrroladine → PVP

(v) Nature of anti solvent (gelation bath)

(vi) Film thickness ✓

(vii) Temperature of casting soln & of gelation bath

So, once by by controlling the solvent demixing quick demixing or delayed demixing, one can really control the pore size of the membrane. Hence, the various let us let us just tabulate various effecting factors controlling factors which can be essentially the control the membrane pore size. First factor is composition of polymer. If you take a 10 percent polymer solution then it will be you will be landing up with a particular membrane it would take a 20 percent, it will land up probably a denser polymer matrix. So, composition of polymer solution so basically I am talking about the composition of the casting solution. Second is nature of the polymer of course, selection of polymer is very very important if you select a poly acrylonitrile membrane we will be getting more porous membrane for example, micro filtration membrane. If you select a polysulfone membrane then one will land up into an ultra filtration membrane like that, so nature of the polymers is very important composition of the casting solution is very important.

Third one is the selection of solvent. Now, depending on whether you will be selecting DMF, DMSA, DMSC or acetone, the pore size distribution of the membrane will be altered. Fourth one will be the nature of additive and their concentration nature and concentration of additives. One can use various pore forming agency they are also known as the porogenes these pore forming agents are polyethylene glycol, polyvinyl pyrrolidine and there are various molecular of polyethylene glycols are available there are various molecular of molecular of polyvinyl pyrrolidone are available. So, one can you one can alter the concentration of this additives the molecular rate of the additives and these pore forming agents the forming pores into the membrane surfaces and can alter the pore size distribution.

Then the nature of the anti solvent is also important that means nature of gelation bath whether you are using water, whether you are using water pg solution, whether you are using water solvent mixture so that will very important. So, if you use pure water the transform demixing will be more; on the other hand if you use a solvent anti solvent mixture then the concentration gradient of the concentration gradient at will be driving anti solvent into the polymer matrix will be less. So, by that way one can control the pore size distribution also.

Another important point is the film thickness because if you have a film of shorter thickness then the resistance the hydrolic resistance offered by the membrane. Again the solvent flux will be less and one can expect a higher through put of the process if you one if one goes for a largest film thickness from the resistance against the solvent flux will be more and what the resultant through put will be less. So, film thickness is also an important factor then next one is the temperature of casting solution of casting solution as well as temperature of gelation bath. As you have already discussed earlier that temperature is one of the controlling factor to alter the gradient of chemical potential.

So, if you alter the temperature of the casting film or the gelation bath that will be really controlling the demixing process of solvent and non-solvent resulting into a particular pore size of the membrane, so that will complete the membrane casting process and the basic fundamentals of the behind any separation process. So, we will be taking the next class on different factors of different properties of the membrane which will be very, very important and we will categorise the various membrane with separation processes.

Thank you.