Plant Design and Economics

Prof. Debasis Sarkar
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture No -44
Azeotropic Distillation: Residue Curve Maps

Welcome to lecture 44 of plant design and economics. In this lecture, we will start talking about Azeotropic distillation.

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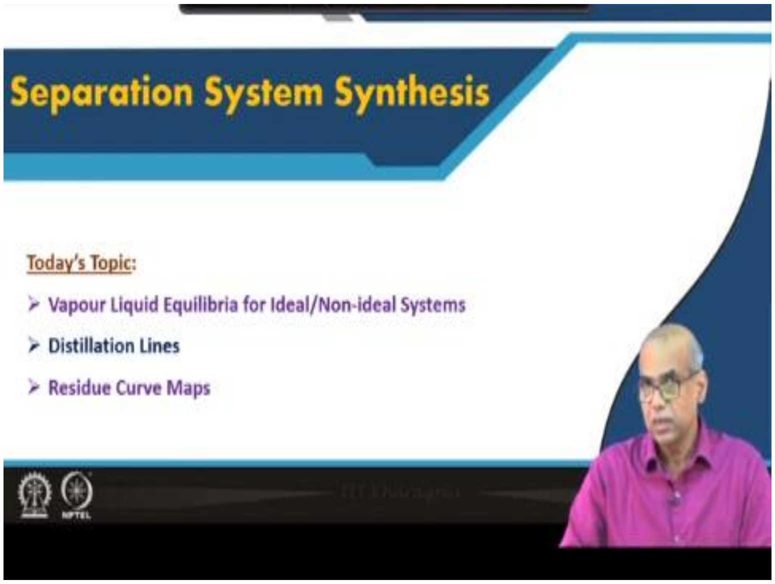

Separation System Synthesis

Today's Topic:

- Vapour Liquid Equilibria for Ideal/Non-ideal Systems
- Distillation Lines
- Residue Curve Maps

So today we will first start with a brief description of vapour liquid equilibria for ideal as well known ideal systems and then we will introduce to important concepts known as distillation lines and residue curve maps that are very useful to assess the performance of separation of ternary mixtures.

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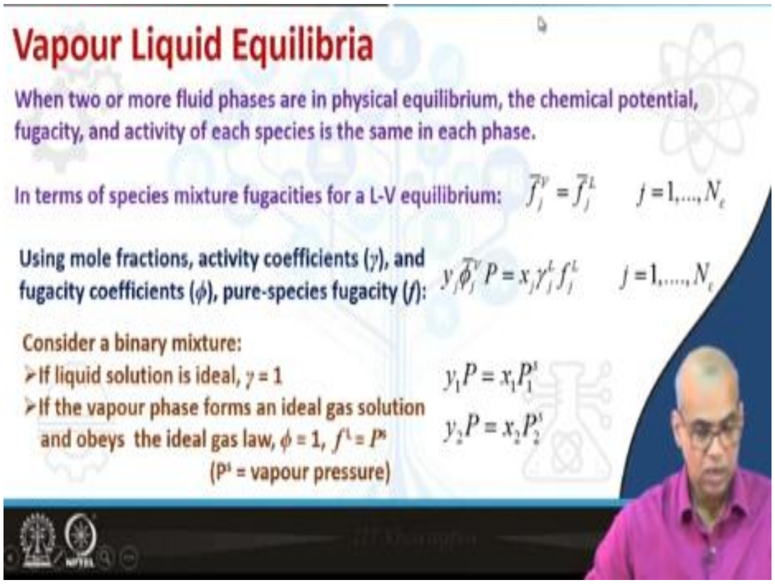

Vapour Liquid Equilibria

When two or more fluid phases are in physical equilibrium, the chemical potential, fugacity, and activity of each species is the same in each phase.

In terms of species mixture fugacities for a L-V equilibrium: $\bar{f}_j^V = \bar{f}_j^L \quad j = 1,\ldots,N_c$

Using mole fractions, activity coefficients (γ), and fugacity coefficients (ϕ), pure-species fugacity (f): $y_j \bar{\phi}_j^V P = x_j \gamma_j^L f_j^L \quad j = 1,\ldots,N_c$

Consider a binary mixture:

- If liquid solution is ideal, $\gamma = 1$
- If the vapour phase forms an ideal gas solution and obeys the ideal gas law, $\phi = 1$, $f^L = P^s$

(P^s = vapour pressure)

$$y_1 P = x_1 P_1^s$$

$$y_2 P = x_2 P_2^s$$

So let us start with a brief introduction to vapour liquid equilibria. When two or more fluid phases are in physical equilibrium, the chemical potential, fugacity, and activity of each species is the same in each phase. So in terms of species mixture fugacities for a liquid vapour equilibrium, where a vapour phase is an equilibrium with a single liquid phase we can write, equality of this species mixture fugacity for all the components present in the mixture.

Now with this vapour phase fugacity we can replace it as a product of mole fraction, the fugacity coefficient and the pressure. On the other hand we can equate this liquid phase fugacity as a product of mole fraction, activity coefficient and pure species fugacity. So this relation will also hold for all the components present in the mixture. Now if you consider a binary mixture and we consider an ideal binary mixture, where the liquid solution is ideal and the vapour phase forms an ideal gas solution and obeys the ideal gas law, then activity coefficient will be equal to 1.

The fugacity coefficient will also be equal to 1 and the pure phase fugacity in the liquid phase will be equal to the vapour pressure. So we can write for two components in a binary mixture, y1 into p is equal to x1 into vapour pressure, same can be written for component 2 as well.

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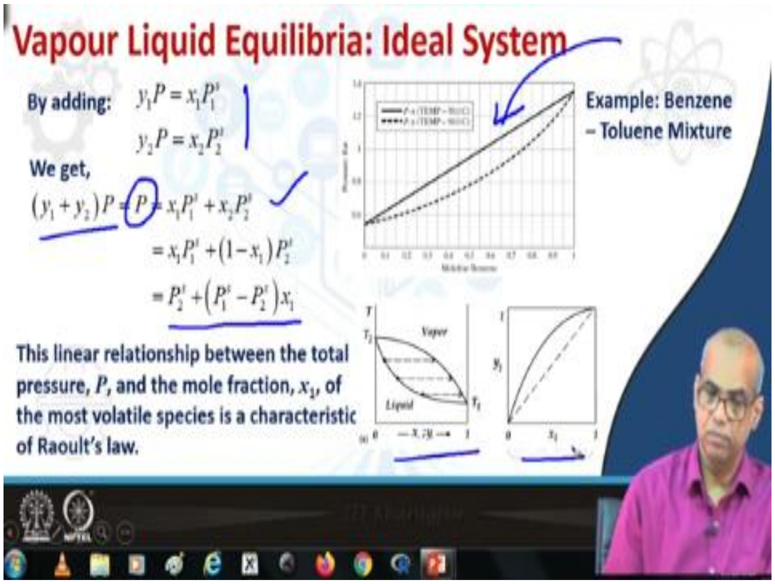

Vapour Liquid Equilibria: Ideal System

By adding: $y_1P = x_1P_1^s$

$y_2P = x_2P_2^s$

We get,

$$\underline{(y_1 + y_2)P} = \boxed{P} = x_1P_1^s + x_2P_2^s$$

$$= x_1P_1^s + (1 - x_1)P_2^s$$

$$= \underline{P_2^s + (P_1^s - P_2^s)x_1}$$

This linear relationship between the total pressure, P, and the mole fraction, x_1, of the most volatile species is a characteristic of Raoult's law.

Example: Benzene – Toluene Mixture

Now if I add these two I will obtain x1 into vapour pressure of component 1 + x2 into vapour pressure of component 2. Now y1 + y2 = 1, so y1 + y2 into P will give me P, the total pressure, so I get a relation between total pressure and the mole fraction of the more volatile component. Now, this is a linear relationship between the total pressure and the mole fraction x1 of the more volatile species and this relationship is characteristic of Raoult's law.

For example, you can see the linear relationship between P and x, where the total pressure is plotted against the mole fraction of benzene in a benzene toluene mixture, which is assumed to behave as an ideal or near ideal mixture. So for an ideal mixture, you also get this familiar T x y diagram or x y diagram.

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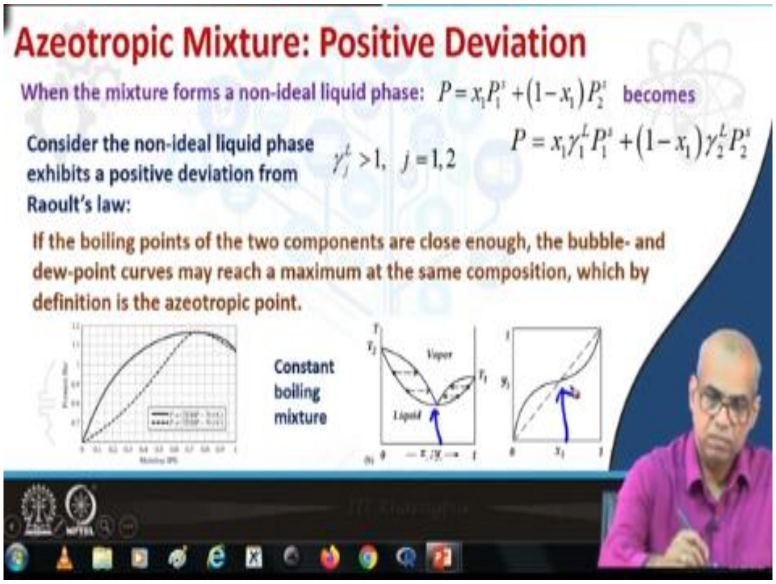

Azeotropic Mixture: Positive Deviation

When the mixture forms a non-ideal liquid phase: $P = x_1 P_1^s + (1 - x_1) P_2^s$ becomes

Consider the non-ideal liquid phase exhibits a positive deviation from Raoult's law: $\gamma_j^L > 1, \; j = 1, 2$ $\quad P = x_1 \gamma_1^L P_1^s + (1 - x_1) \gamma_2^L P_2^s$

If the boiling points of the two components are close enough, the bubble- and dew-point curves may reach a maximum at the same composition, which by definition is the azeotropic point.

Constant boiling mixture

Now all mixtures do not form or all mixtures do not form an ideal liquid mixture. So when a mixture forms a non ideal liquid phase, the previous relationship between the pressure and the mole fraction will not hold true. That equation is to be corrected by introduction of liquid phase activity coefficients, and you will get the equation as shown here. Now if we consider a non-ideal liquid phase which exhibits a positive deviation from Raoult's law.

In other words when the activity coefficient in the liquid phase is greater than 1 for both the components 1 and 2, then we can get a relationship between pressure and the mole fraction of the more volatile component in the liquid phase as shown here. So both the bubble point curve and the dew point curve that is p x diagram and p y diagram will run above the straight line that represents the ideal situation. If the boiling points of the two components are close enough, then the bubble point and the dew point curves may reach a maximum at the same composition.

And this is by definition is the azeotropic point which indicates a constant boiling mixture where the compositions in the liquid phase and the vapour phase will be the same. So this becomes obvious from the T x y diagram or the x y diagram where you have the same composition for the liquid phase and vapour phase and what we obtain here for systems showing positive deviation from Raoult's law is a minimum boiling mixture.

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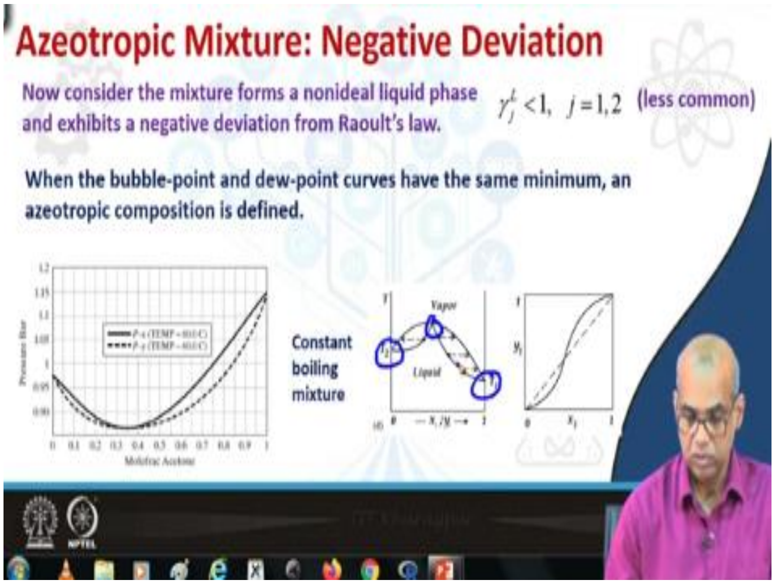

Azeotropic Mixture: Negative Deviation

Now consider the mixture forms a nonideal liquid phase and exhibits a negative deviation from Raoult's law. $\gamma_j^L < 1, \quad j = 1,2$ (less common)

When the bubble-point and dew-point curves have the same minimum, an azeotropic composition is defined.

Constant boiling mixture

Similarly although less common but some systems will show negative deviation from Raoult's law and in that case both the bubble point curve and the dew point curve will run below the straight line representing Raoult's law behavior. And in this case when the bubble point curve and the dew point curve have the same minimum will get an azeotropic composition which is known as maximum boiling isotropia.

Note in the T x y diagram that azeotropic composition has the highest temperature here compared to other two temperatures corresponding to two pure components. So we can have a minimum boiling azeotrope or a maximum boiling azeotrope.

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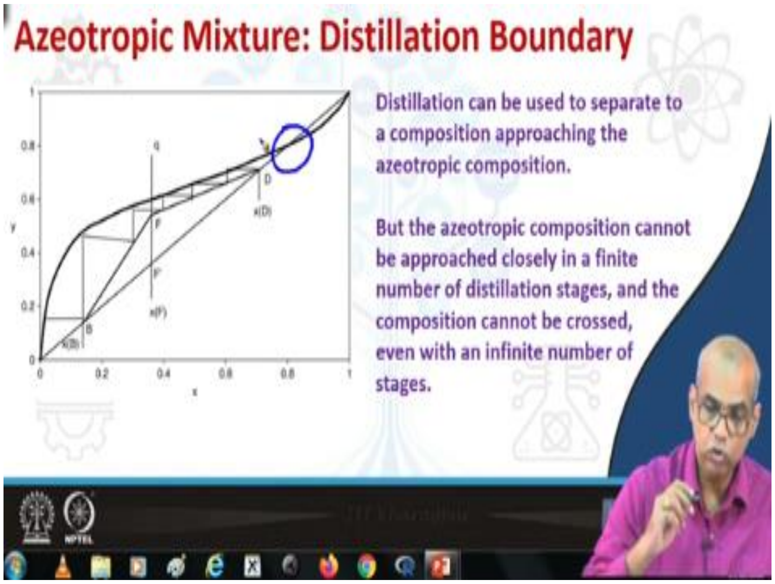

Azeotropic Mixture: Distillation Boundary

Distillation can be used to separate to a composition approaching the azeotropic composition.

But the azeotropic composition cannot be approached closely in a finite number of distillation stages, and the composition cannot be crossed, even with an infinite number of stages.

Now when you have an azeotropic mixture the distillation becomes problematic. Distillation can be used to separate a composition approaching the azeotropic composition. But the azeotropic composition cannot be approached closely in a finite number of distillation stages and the composition cannot be crossed, even with an infinite number of stages. So you cannot cross this azeotropic point, so this represents a boundary to the distillation.

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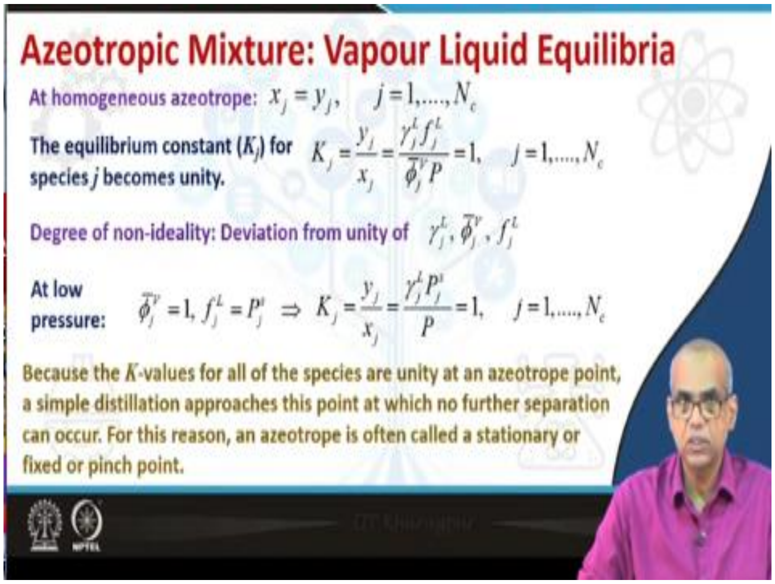

Azeotropic Mixture: Vapour Liquid Equilibria

At homogeneous azeotrope: $x_j = y_j, \quad j = 1, \ldots, N_c$

The equilibrium constant (K_j) for species j becomes unity. $K_j = \frac{y_j}{x_j} = \frac{\gamma_j^L f_j^L}{\bar{\phi}_j^V P} = 1, \quad j = 1, \ldots, N_c$

Degree of non-ideality: Deviation from unity of $\gamma_j^L, \bar{\phi}_j^V, f_j^L$

At low pressure: $\bar{\phi}_j^V = 1, f_j^L = P_j^s \Rightarrow K_j = \frac{y_j}{x_j} = \frac{\gamma_j^L P_j^s}{P} = 1, \quad j = 1, \ldots, N_c$

Because the K-values for all of the species are unity at an azeotrope point, a simple distillation approaches this point at which no further separation can occur. For this reason, an azeotrope is often called a stationary or fixed or pinch point.

When azeotropic composition is formed, your liquid phase composition and the vapour phase composition will be the same. So x j will be equal to y j for all the components and that will give you the value of the equilibrium constant K equal to 1 for all the species. Because the K values for all the species are unity at an azeotropic point, a simple distillation approaches this point at which no further separation can occur. For this reason, an azeotrope is often called a stationary or a fixed point or a pinch point.

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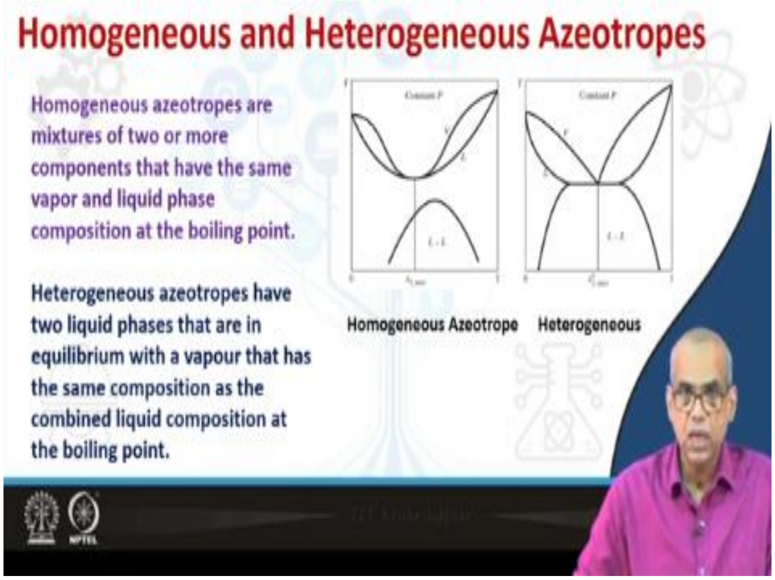

Homogeneous and Heterogeneous Azeotropes

Homogeneous azeotropes are mixtures of two or more components that have the same vapor and liquid phase composition at the boiling point.

Heterogeneous azeotropes have two liquid phases that are in equilibrium with a vapour that has the same composition as the combined liquid composition at the boiling point.

Now let us define two terms homogeneous azeotropes and heterogeneous azeotropes. Homogeneous azeotropes are mixtures of two or more components that have the same vapour and liquid phase composition at the boiling point. Heterogeneous have two liquid phases that are in equilibrium with a vapour that has the same composition as the combined liquid compositions at the boiling point.

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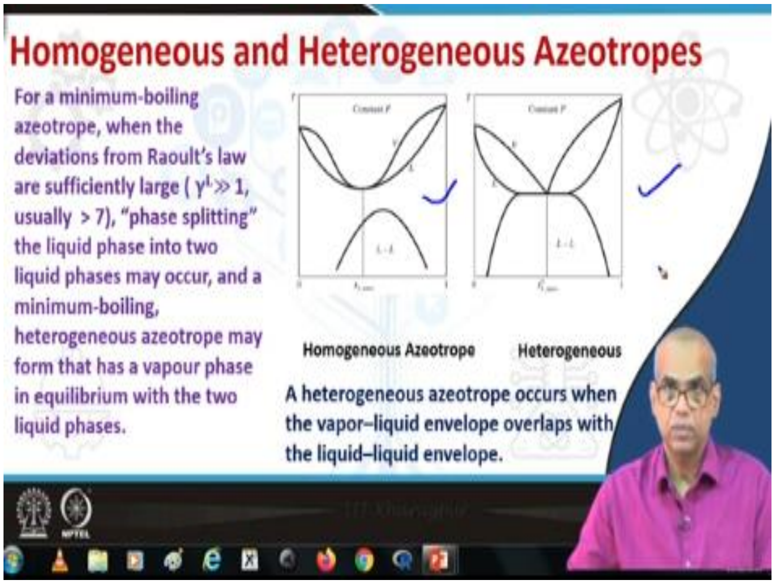

Homogeneous and Heterogeneous Azeotropes

For a minimum-boiling azeotrope, when the deviations from Raoult's law are sufficiently large ($\gamma^L \gg 1$, usually > 7), "phase splitting" the liquid phase into two liquid phases may occur, and a minimum-boiling, heterogeneous azeotrope may form that has a vapour phase in equilibrium with the two liquid phases.

A heterogeneous azeotrope occurs when the vapor–liquid envelope overlaps with the liquid–liquid envelope.

For a minimum boiling azeotrope, when the deviation from Raoult's law are sufficiently large, the phase splitting the liquid phase into two liquid phases may occur and a minimum boiling heterogeneous azeotrope may form that has a vapour phase in equilibrium with two liquid phases. Now the deviation from this Raoult's law must be sufficiently large and typically the liquid phase activity coefficient value which should be greater than 7 or so.

If you look at this figure, this represents a homogeneous azeotrope, where this represents a heterogeneous azeotrope. Heterogeneous azeotrope occurs when the vapour-liquid envelope overlaps with the liquid-liquid envelope.

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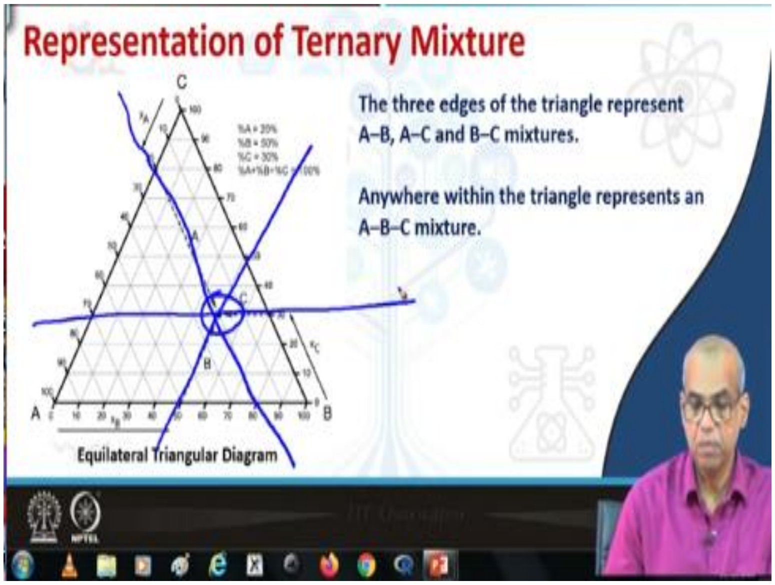

Representation of Ternary Mixture

The three edges of the triangle represent A–B, A–C and B–C mixtures.

Anywhere within the triangle represents an A–B–C mixture.

Now, let us discuss the representation of ternary mixture and you know that we can conveniently represent the composition of a ternary mixture using a triangular diagram. We can use equilateral triangular diagrams or you can also use right angle diagrams. For example, what you see is an equilateral triangular diagram, where the vertices A, B and C represent pure components. The sides A B, A C and B C represent binary mixtures and anywhere within the triangle will represent a mixture of A, B and C.

Look at the parallel lines, for example; this vertex represents a pure component A, 100% A and this side represents mixture A C, so this represents pure component C. If I go in this direction the value of A increases. Now look at the parallel lines, like these parallel lines represent a constant percentage of A. For example, this line belongs to 20% A, similarly this line represents constant percentage B. So, this line will represent 50% B, similarly for C, which are these lines.

So now focus your attention on this point, this point represents 20% A, because this is the line representing 20% A. This represents 50% B, because this is the line which represents 50% B and this line represents 30% C. So the composition is 20% A, 50% B and 30% C.

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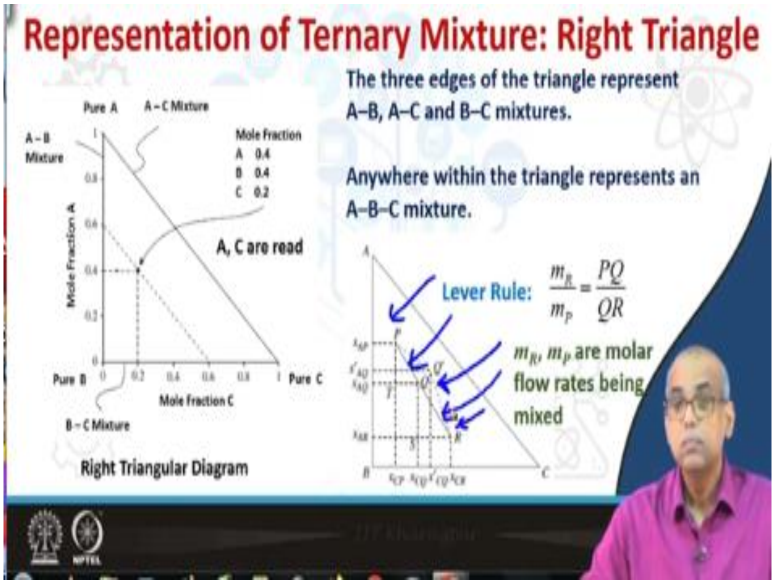

Representation of Ternary Mixture: Right Triangle

The three edges of the triangle represent A–B, A–C and B–C mixtures.

Anywhere within the triangle represents an A–B–C mixture.

Lever Rule: $\frac{m_R}{m_P} = \frac{PQ}{QR}$

m_R, m_P are molar flow rates being mixed

It is also possible to make use of right angle diagram and you do not need to know all the percentages to be computed from the or to be rate from the triangular diagram, because you can find out the same mole fractions of A and B of any two components and can find out the other, because the sum of the mole fractions will be equal to 1. For example, in this right angle diagram, we will read A and C, we read A as 0.4 and we read C as 0.2, so obviously B is 1 - 0.6, which is 0.4.

So here also the vertices represent pure components and the sides represents binary mixtures and we just saw that to anywhere within the triangle represents ABC mixture and you can find out the mole fractions or the compositions of A and C and by subtraction you can find out the composition of B or the mole fraction of B. The lever rule applies on this diagram, let point R and point P, they represent molar flows with mR and mP.

Now if these two are mixed will get say point Q, which will be following, mR by mP equal to P Q by Q R, so the regular liver rule will apply.

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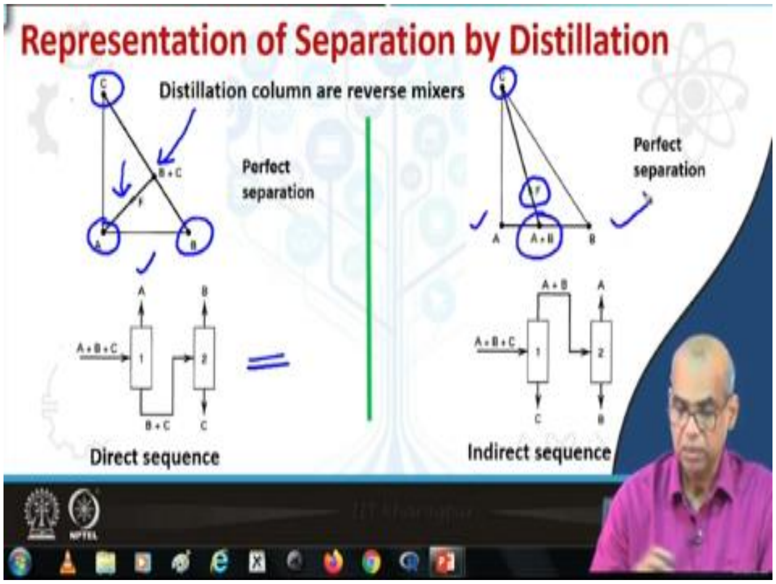

Representation of Separation by Distillation

Distillation column are reverse mixers

Perfect separation

Direct sequence

Perfect separation

Indirect sequence

We can use the triangular diagram to represent separation by distillation. To start with, let us consider perfect separation, so 100% separations of components A, B and C. So in case of direct sequence we take out pure components A from the first column and B and C from the second column. So the distillation column we can consider it as a reverse mixer, so the mixture F which is a ternary mixture of A B C in the first column is splitted into pure components A, that is why it sits on the vertex A and a mixture of B and C, so it sits on the side B C.

In the second column, the mixture B C splitted into pure component B and pure component C. The same way you can infer the indirect sequence, where the ternary mixture is splitted in the first column into pure component C and mixture of A B, which is in the second column splitted as A and B.

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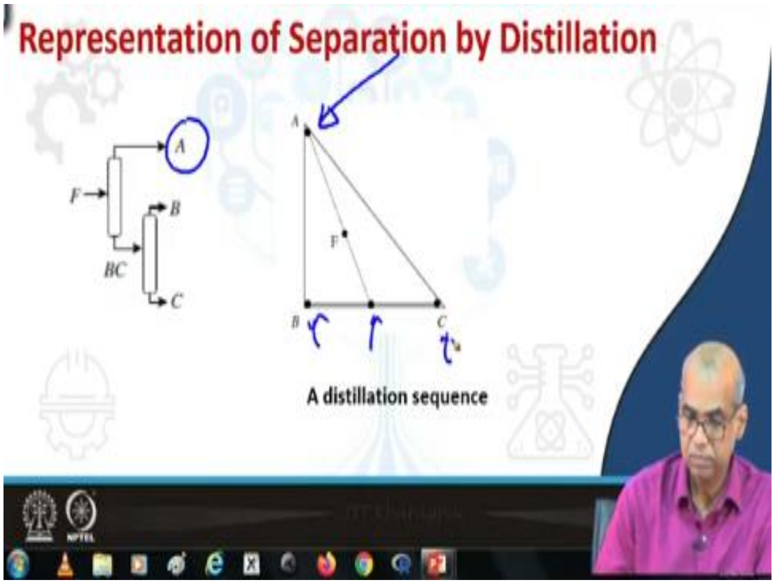

Representation of Separation by Distillation

A distillation sequence

However if the 100% separation is not possible, then this stream A instead of containing pure A will also have some little amount of B and C. So the point will not sit exactly on the vertex but it will be very close to that, but within the triangle so that it represents a ternary mixture but which is mostly pure A and a very little amount of B and C, the same holds true for the mixture B C as well as component B and C.

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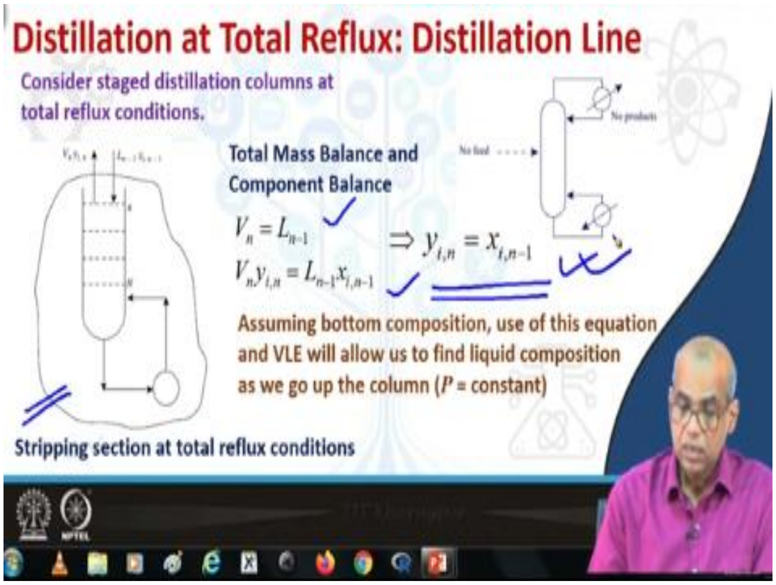

Distillation at Total Reflux: Distillation Line

Consider staged distillation columns at total reflux conditions.

Total Mass Balance and Component Balance

$$V_n = L_{n-1}$$

$$V_n y_{i,n} = L_{n-1} x_{i,n-1} \Rightarrow y_{i,n} = x_{i,n-1}$$

Assuming bottom composition, use of this equation and VLE will allow us to find liquid composition as we go up the column (P = constant)

Stripping section at total reflux conditions

Now, let us talk about distillation lines. We first considered distillation at total reflux, so let us consider an envelope around the stripping section of a distillation column at total reflux conditions. So if we write down the mass balance and component balance equations, we can see that y i, n will be equal to xi, n - 1. So, the mole fraction of the ith component in the vapour phase coming out of the nth distillation column is equal to the mole fraction in the liquid phase of yth component that is coming out from the n - 1th column.

Now if we assume some bottom compositions, then use of this equation and the vapour liquid equilibria will allow us to find liquid composition in the trace as we go up from the bottom with an assumption of constant pressure.

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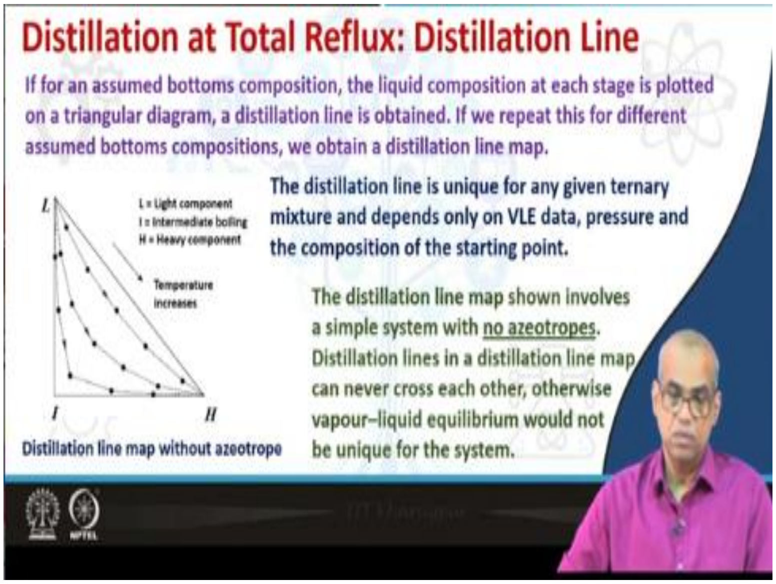

Distillation at Total Reflux: Distillation Line

If for an assumed bottoms composition, the liquid composition at each stage is plotted on a triangular diagram, a distillation line is obtained. If we repeat this for different assumed bottoms compositions, we obtain a distillation line map.

The distillation line is unique for any given ternary mixture and depends only on VLE data, pressure and the composition of the starting point.

The distillation line map shown involves a simple system with no azeotropes. Distillation lines in a distillation line map can never cross each other, otherwise vapour–liquid equilibrium would not be unique for the system.

Distillation line map without azeotrope

If for an assumed bottom composition, the liquid composition at each stage is plotted on a triangular diagram, what you obtain is known as a distillation line. If we repeat this for different assumed bottom compositions, we obtain a family of such distillation lines and together they constitute a distillation line map. The distillation line is unique for any given ternary mixture and depends only on vapour liquid equilibria data, pressure and the composition of the starting point. In the figure you see a distillation line map without any azeotrope.

So the system here does not show any azeotrope. We will see later what happens when the mixture has azeotrope. Now these 3 vertices represent 3 pure components, so L for light component or the low boiling component, I for intermediate boiling component and H for heavy component or highest boiling component. Note that the distillation lines in a distillation line map can never cross each other because if they cross each other then the vapour liquid equilibrium will not be unique for the system.

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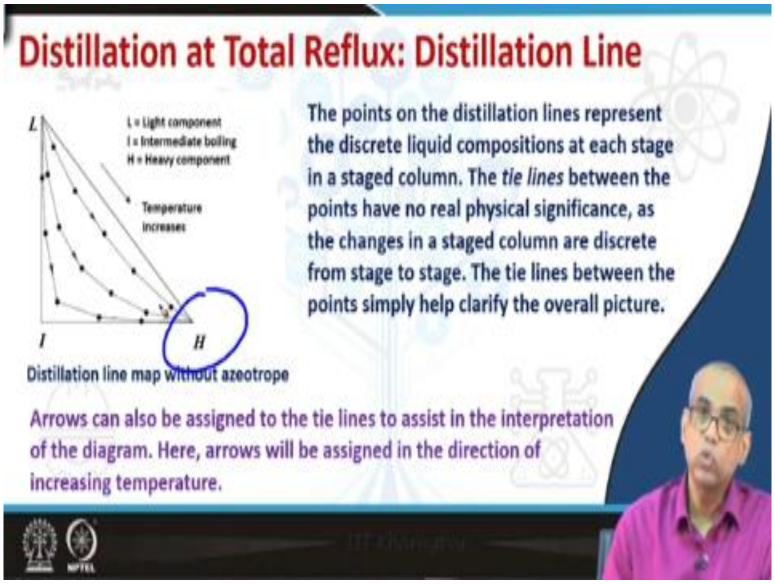

Distillation at Total Reflux: Distillation Line

The points on the distillation lines represent the discrete liquid compositions at each stage in a staged column. The *tie lines* between the points have no real physical significance, as the changes in a staged column are discrete from stage to stage. The tie lines between the points simply help clarify the overall picture.

Distillation line map without azeotrope

Arrows can also be assigned to the tie lines to assist in the interpretation of the diagram. Here, arrows will be assigned in the direction of increasing temperature.

So the points on the distillation line represent the discrete liquid composition at each stage in a stage column. Note that we are talking about a stage distillation column and we are applying that equation yi, n = xi, n - 1 in each stage. So we get these points as discrete liquid composition and each stage. The tie lines between the points have no real physical significance as the changes in a stage column are discrete from stage to stage. The tie lines between the points simply help clarify the overall picture.

Note that arrows had been placed these are assigned to the tie lines to assist in the interpretation of the diagram. Here arrows will be assigned in the direction of increasing temperature. So as you see that all the arrows are directed towards vertex H here which represent heavy components, it is the highest boiling component, this represents the highest temperature, so all the temperatures are directed to this high boiling temperature. So arrows will be directed from lower temperature to higher temperature.

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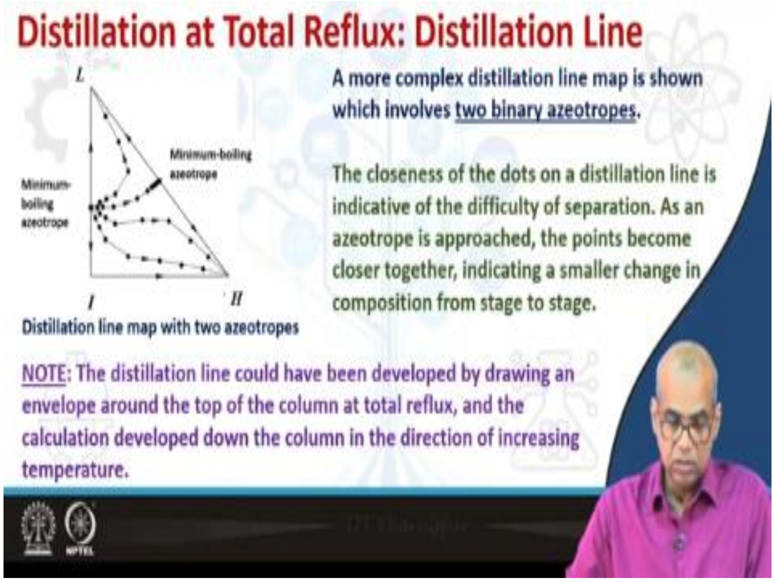

Distillation at Total Reflux: Distillation Line

A more complex distillation line map is shown which involves two binary azeotropes.

The closeness of the dots on a distillation line is indicative of the difficulty of separation. As an azeotrope is approached, the points become closer together, indicating a smaller change in composition from stage to stage.

Distillation line map with two azeotropes

NOTE: The distillation line could have been developed by drawing an envelope around the top of the column at total reflux, and the calculation developed down the column in the direction of increasing temperature.

Now, here we saw a more complex distillation map, which involves two binary azeotropes. Look at the dots on the distillation line that are very closely spaced as we approach the azeotrope. As an azeotropic is approached, the points become closer together, indicating a smaller change in the composition from stage to stage. In this case we derived the distillation lines by taking an envelope around the bottom of the distillation column at total reflux condition. We could have also used the envelope around top of the distillation column and we will get the identical results.

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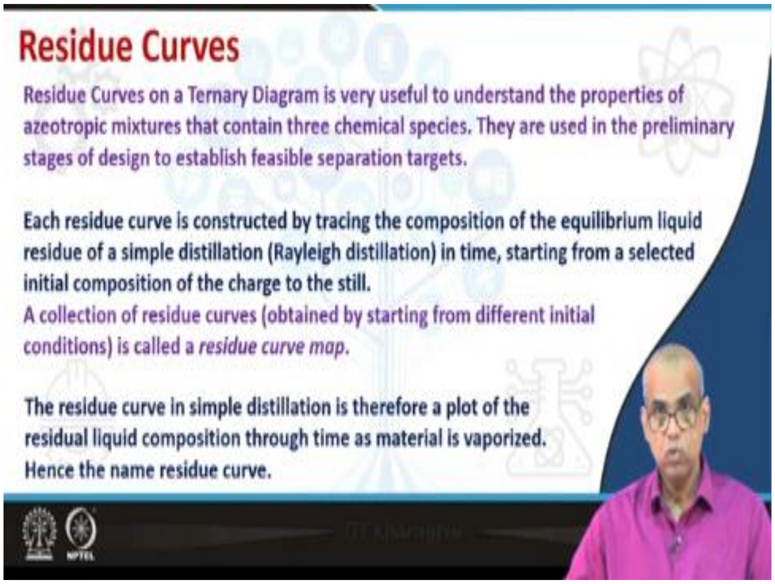

Residue Curves

Residue Curves on a Ternary Diagram is very useful to understand the properties of azeotropic mixtures that contain three chemical species. They are used in the preliminary stages of design to establish feasible separation targets.

Each residue curve is constructed by tracing the composition of the equilibrium liquid residue of a simple distillation (Rayleigh distillation) in time, starting from a selected initial composition of the charge to the still.
A collection of residue curves (obtained by starting from different initial conditions) is called a *residue curve map.*

The residue curve in simple distillation is therefore a plot of the residual liquid composition through time as material is vaporized. Hence the name residue curve.

Now let us move on to residue curves and residue curve maps. Residue curves on a ternary diagram are very useful to understand the properties of azeotropic mixtures that contain three chemical species. They are used in the preliminary stages of design of azeotropic distillation column to establish feasible separation targets. Each residue curve is constructed by tracing the composition of the equilibrium liquid residue of a simple distillation also known as Rayleigh distillation in time, starting from a selected initial composition of the charge to the still.

A collection of residue curves, which you can obtain by starting from different initial conditions, is called a residue curve map. Note that both the distillation line and the residue curve will indicate the feasibility of separation in a distillation column. The residue curve in simple distillation is therefore a plot of the residual liquid composition through time as material is vaporized and hence it gets the name residue curve.

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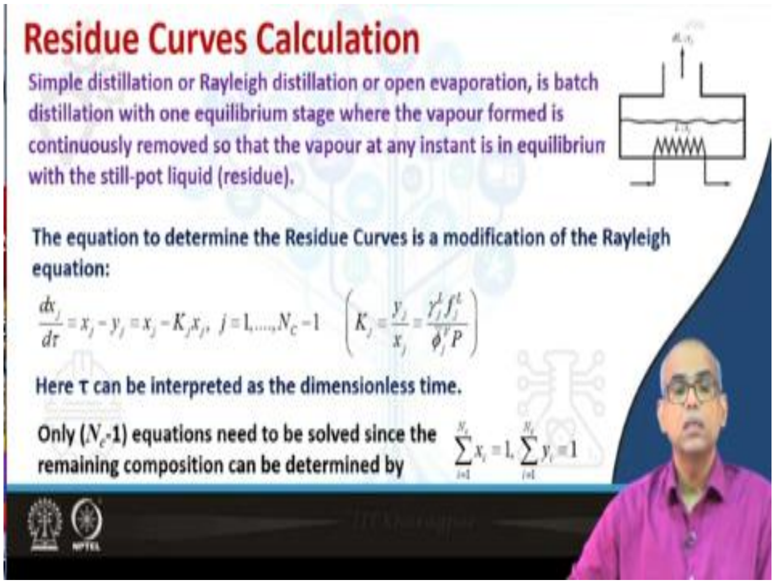

Residue Curves Calculation

Simple distillation or Rayleigh distillation or open evaporation, is batch distillation with one equilibrium stage where the vapour formed is continuously removed so that the vapour at any instant is in equilibrium with the still-pot liquid (residue).

The equation to determine the Residue Curves is a modification of the Rayleigh equation:

$$\frac{dx_j}{d\tau} = x_j - y_j = x_j - K_j x_j, \ j = 1, \ldots, N_C - 1 \qquad \left(K_j = \frac{y_j}{x_j} = \frac{\gamma_j^L f_j^L}{\phi_j^V P} \right)$$

Here τ can be interpreted as the dimensionless time.

Only (N_c-1) equations need to be solved since the remaining composition can be determined by $\sum_{i=1}^{N_c} x_i = 1, \sum_{i=1}^{N_c} y_i = 1$

Simple distillation or Rayleigh distillation or open evaporation, is batch distillation with one equilibrium stage where the vapour formed is continuously removed so that the vapour at any instant is in equilibrium with the still-pot liquid or residue. Now the equation to determine the residue curve is basically a modified form of the Rayleigh equations that we can establish for such simple distillation or Rayleigh distillation. And the equation to determine the residue curve is d x j by d tau equal to x j - y j for all j = 1 to the number of components - 1.

Note that x j and y j can be related through the equilibrium constant K. Here the parameter tau can be interpreted as a dimensionless time. Note that this differential equation d x j by d tau equals x j - y j should be written only for Nc - 1 number of components because for the remaining composition that can be determined using the sum of mole fraction equal to 1 relationship.

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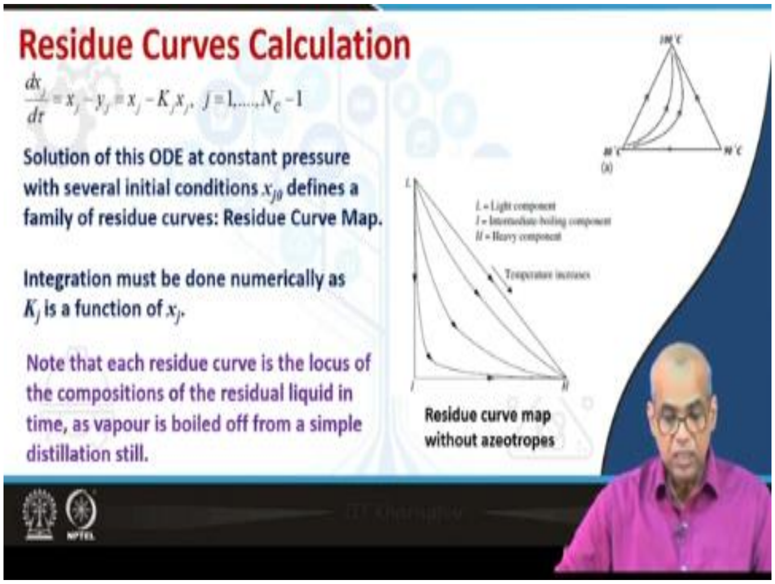

Residue Curves Calculation

$$\frac{dx_j}{d\tau} = x_j - y_j = x_j - K_j x_j, \; j = 1, \ldots, N_C - 1$$

Solution of this ODE at constant pressure with several initial conditions x_{j0} defines a family of residue curves: Residue Curve Map.

Integration must be done numerically as K_j is a function of x_j.

Note that each residue curve is the locus of the compositions of the residual liquid in time, as vapour is boiled off from a simple distillation still.

Residue curve map without azeotropes

So to establish the residue curves, we need to solve the ordinary differential equation that represents the residue curves; the solution of this ODE at constant pressure with several initial conditions will define a family of residue curves and they will constitute what is known as residue curve map. Note that when you integrate these differential equations, the integration has to be done numerically because the system is non-linear, because the K j is a function of x j.

So the residue curve is basically the locus of the compositions of the residual liquid in time, as vapour is boiled off from a simple distillation still. I repeat each residue curve is the locus of the composition of the residual liquid in time as vapour is boiled off from a simple distillation still.

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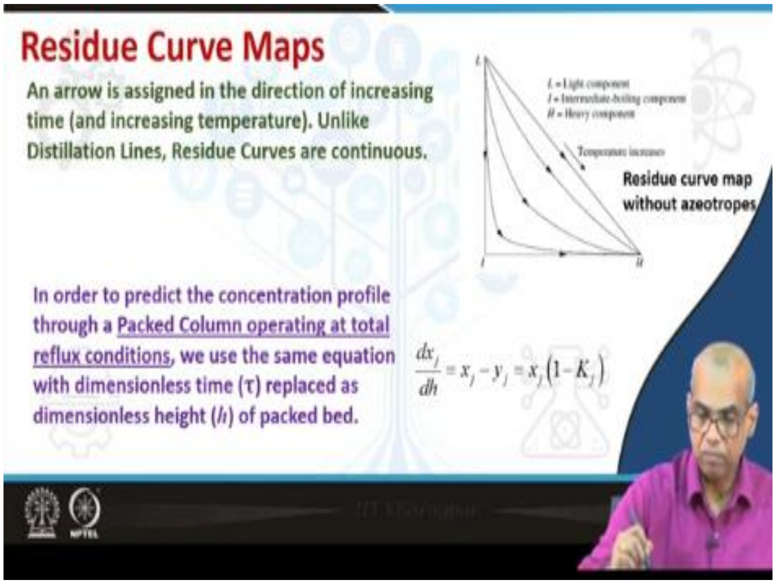

Residue Curve Maps

An arrow is assigned in the direction of increasing time (and increasing temperature). Unlike Distillation Lines, Residue Curves are continuous.

Residue curve map without azeotropes

In order to predict the concentration profile through a Packed Column operating at total reflux conditions, we use the same equation with dimensionless time (τ) replaced as dimensionless height (*h*) of packed bed.

$$\frac{dx_j}{dh} = x_j - y_j = x_j\left(1 - K_j\right)$$

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Here again arrow is assigned in the direction of increasing time and increasing temperature unlike the distillation lines residue curves are continuous. In order to predict the concentration profile through a packed column operating at total difference conditions we use the same equation. But we replace the dimensionless time as dimensionless height and the equation can be written as d x j d h = x j – y j where h represents dimensionless time.

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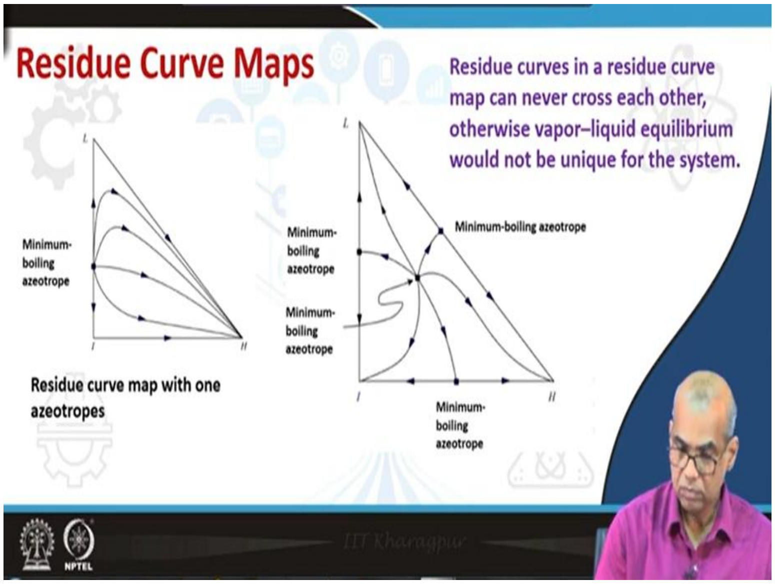

Residue Curve Maps

Residue curves in a residue curve map can never cross each other, otherwise vapor–liquid equilibrium would not be unique for the system.

Residue curve map with one azeotropes

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Residue curves in a residue curve map can never cross each other similar to distillation line otherwise vapour-liquid equilibrium will not be unique for the system. What you see in figure is a residue curve map with one azeotrope. This one is more complex, you will have 4 azeotropes here. Note that 3 azeotropes are binary and 1 azeotrope is ternary.

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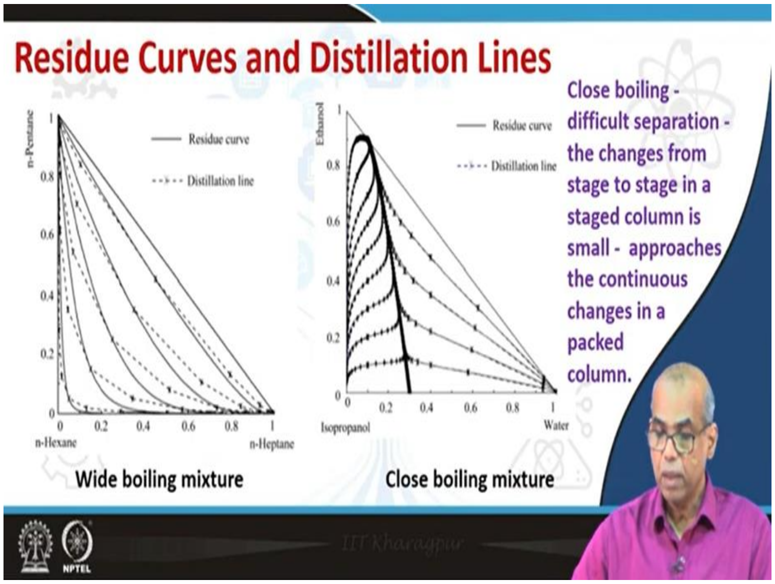

Residue Curves and Distillation Lines

Close boiling - difficult separation - the changes from stage to stage in a staged column is small - approaches the continuous changes in a packed column.

Wide boiling mixture

Close boiling mixture

Let us make a comparison between residue curves and distillation lines. If you look at these two figures for wide boiling mixtures there is substantial difference between residual curves and distillation line whereas for close burning mixtures the difference is quite less. Because for close boiling mixtures the separation is difficult so there is very less change from one stage to another in a staged column.

So the compositions will approach the compositions that you get in a continuous operation such as impact column.

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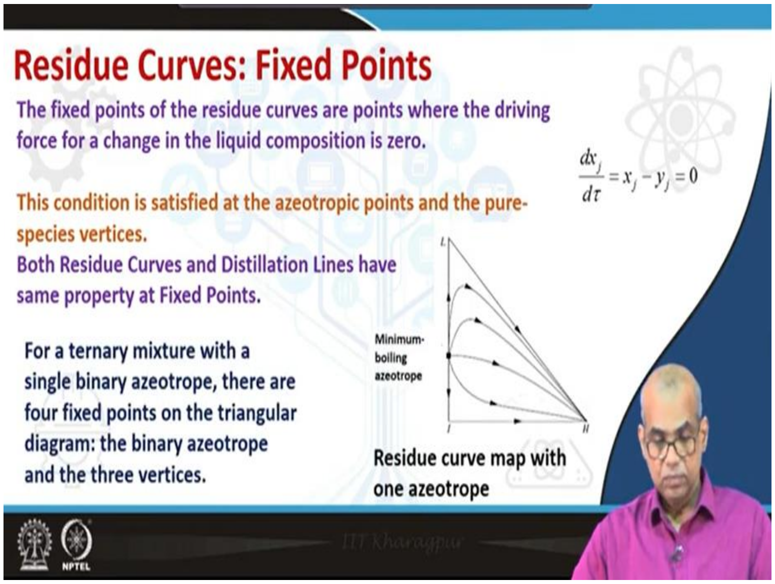

Residue Curves: Fixed Points

The fixed points of the residue curves are points where the driving force for a change in the liquid composition is zero.

$$\frac{dx_j}{d\tau} = x_j - y_j = 0$$

This condition is satisfied at the azeotropic points and the pure-species vertices.

Both Residue Curves and Distillation Lines have same property at Fixed Points.

For a ternary mixture with a single binary azeotrope, there are four fixed points on the triangular diagram: the binary azeotrope and the three vertices.

Residue curve map with one azeotrope

Let us define fixed points of residue curves. The fixed points of the residue curves are points where the driving force for a change in the liquid composition is 0. So this can be obtained by setting d x j d tau = 0. This condition is satisfied at the azeotropic points as well as at the pure species vertices. Both residue curves and displacement lines have some proper same property at fixed points.

So the example that you see has one minimum boiling azeotrope. So there are four fixed points here. Three fixed points for the three vertices and one more fixed point for the minimum boiling binary azeotrope.

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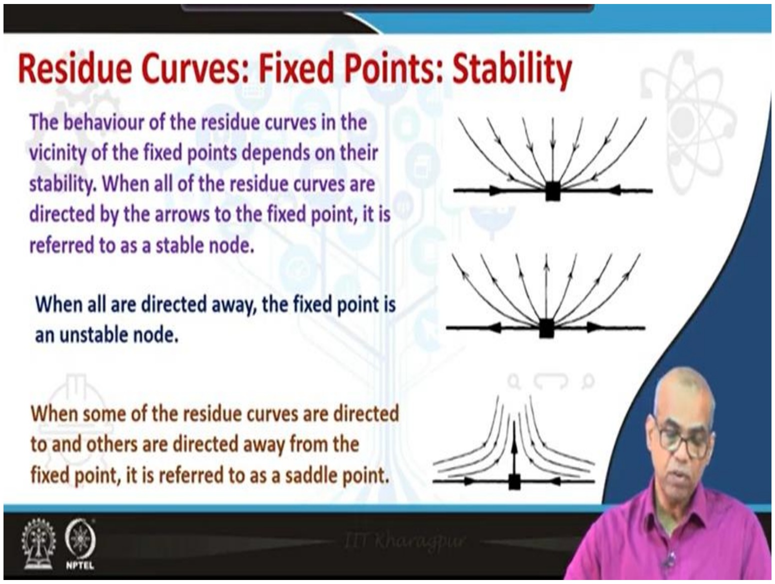

Residue Curves: Fixed Points: Stability

The behaviour of the residue curves in the vicinity of the fixed points depends on their stability. When all of the residue curves are directed by the arrows to the fixed point, it is referred to as a stable node.

When all are directed away, the fixed point is an unstable node.

When some of the residue curves are directed to and others are directed away from the fixed point, it is referred to as a saddle point.

We can determine the stability of the fixed points by looking at the direction of the residue curves. When all the residue curves are directed to a particular fixed point that fixed point is stable node. When all the residue curve are directed away from that particular fixed point that will be called unstable node. And when some residue curves are directed to the fixed point and some residue curves are directed away from the fixed point this will be referred to as saddle point.

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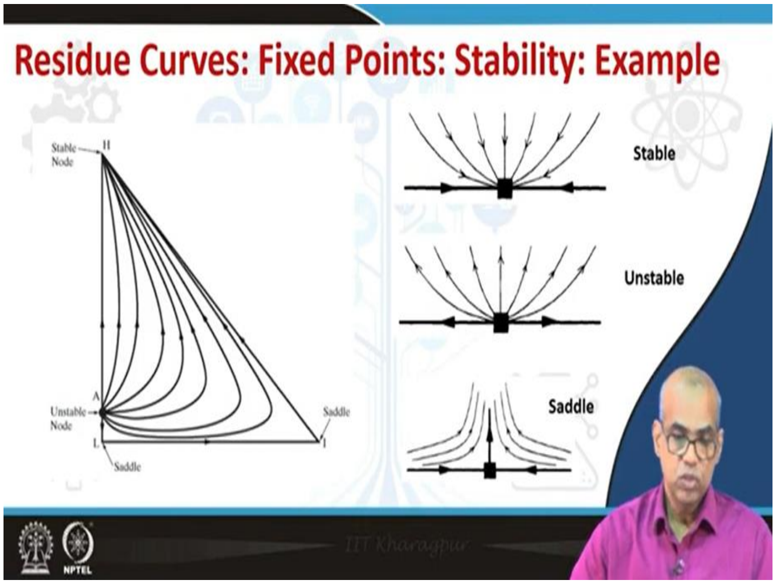

Residue Curves: Fixed Points: Stability: Example

So if you look at this figure point the vertex H is the stable node because all the residue curves are directed towards it. Whereas this binary azeotrope is unstable because all the residue curves are directed away from it, whereas the vertex I and H are saddle because some residue curves are directed towards it and some are directed away from it.

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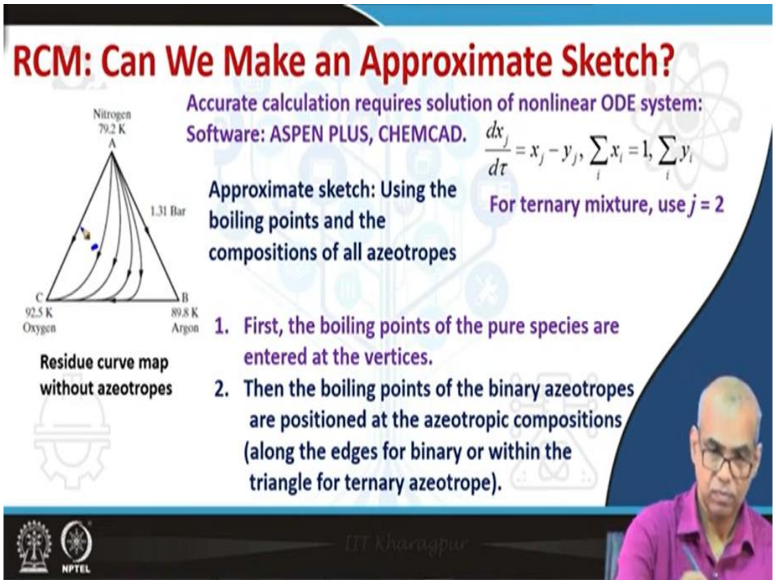

RCM: Can We Make an Approximate Sketch?

Accurate calculation requires solution of nonlinear ODE system:

Software: ASPEN PLUS, CHEMCAD. $\frac{dx_j}{d\tau} = x_j - y_j, \sum_i x_i = 1, \sum_i y_i$

Approximate sketch: Using the boiling points and the compositions of all azeotropes

For ternary mixture, use $j = 2$

1. First, the boiling points of the pure species are entered at the vertices.
2. Then the boiling points of the binary azeotropes are positioned at the azeotropic compositions (along the edges for binary or within the triangle for ternary azeotrope).

Residue curve map without azeotropes

Residue curve map is a very useful tool will now see some examples to demonstrate how residue curve map can be used to study the feasibility of separations. It can also tell us what are the attainable product compositions from distillation of ternary mixture? Now for that of course we first have to establish the residue curve map. Now, there are several softwares which you can use for generation of such residue curve map.

Note that the accurate calculation or the establishment of residue curve map will require the solution of these differential equations. Note that this is a non-linear ordinary differential equations. The liquid vapor relationship may be non-linear. It is not necessary that you will always be working with ideal systems. So you have to take care of non ideality. Now, if you have a ternary mixture then you have three components.

But it is enough to solve two such OD because the third one composition can be used by making use of the sum of mole fractions equal to unity relationship. Now, can we make an approximate sketch for a residue curve map. Look like it is possible to have some idea about the residue curve map only from the knowledge of boiling points of the pure components and the boiling point and composition of the azeotropes.

So what we do is we first consider the boiling points of the pure species and enter those at the three vertices then the boiling points of the binary azeotropes will be positioned at the azeotropic compositions. The binary azeotropes will be positioned at the sides or the edges of the triangle. And if it is a ternary azeotrope it will be anywhere within the triangle depending on its composition.

Now the informations of the boiling points of pure components are available in various handbooks also information about various azeotropes are also available in literature.

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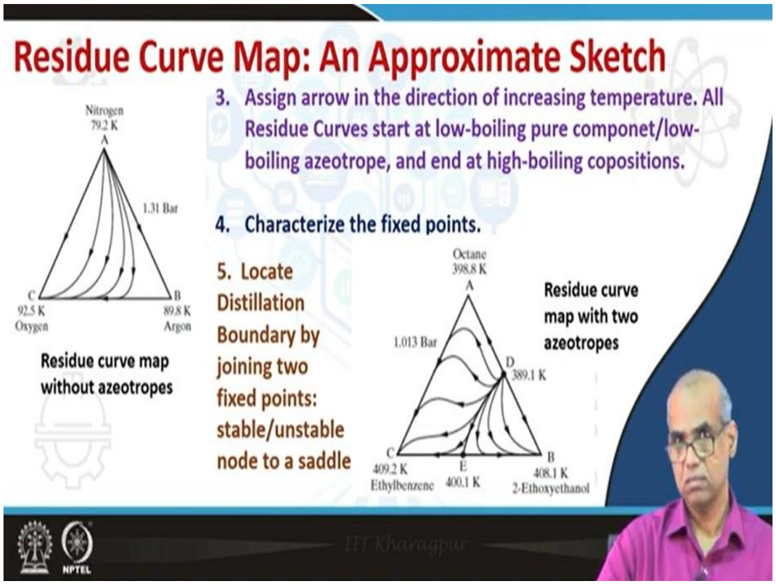

Residue Curve Map: An Approximate Sketch

3. Assign arrow in the direction of increasing temperature. All Residue Curves start at low-boiling pure componet/low-boiling azeotrope, and end at high-boiling copositions.

4. Characterize the fixed points.

5. Locate Distillation Boundary by joining two fixed points: stable/unstable node to a saddle

Residue curve map without azeotropes

Residue curve map with two azeotropes

Now after you have located the pure components boiling points and azeotropes boiling points and compositions we assign arrows in the direction of increasing temperature. Note that all residue curve will start at a low boiling pure component or low boiling azeotropes and aimed at high boiling compositions. We have seen that residue curve map was established based on the compositions of the liquid of the residue in a simple distillation column.

So as time progresses in the residue more and more of less volatile component will be accumulating. So the temperature will increase. So the temperature increases as the time increases. So the residue curve map will arrow will assign arrows in the direction of increasing temperature. For example, we have seen use can see that arrows are placed on the residue curves which are originating from nitrogen.

Which is the lowest temperature among these ABC; three components nitrogen, oxygen, nitrogen argon and oxygen and all are terminating at the highest boiling component oxygen. Then you characterize the fixed points. The fixed points can be stable or unstable. We call these nodes either stable node or unstable node or the fixed point can also be saddled. And you know that the fixed points are the pure components or the azeotropic points.

Now this is an example of ternary system where we have obtained ethylbenzene and two ethoxyethanol. So here you have two binary azeotropes. Arrows have been placed. You can note that this particular azeotrope is unstable as all arrows are going away from this. Whereas this one point E is basically a saddle because one arrow is coming towards it other two arrows are going away from it.

Now we can locate the distillation boundary by joining these two azeotopic points, note that distillation boundary is obtained by joining two fixed points. One of the fixed point is either a stable or unstable node and other fixed point is saddle. So here you have one unstable node and you have a saddle. So the line D is the distillation boundary that divides the entire region or the triangle into two distinct regions will talk more about distillation boundary soon.

So this is how you can have a rough sketch but of course a computer generated residue curve map based on the accurate solutions of the ordinary differential equation will be more advantageous.

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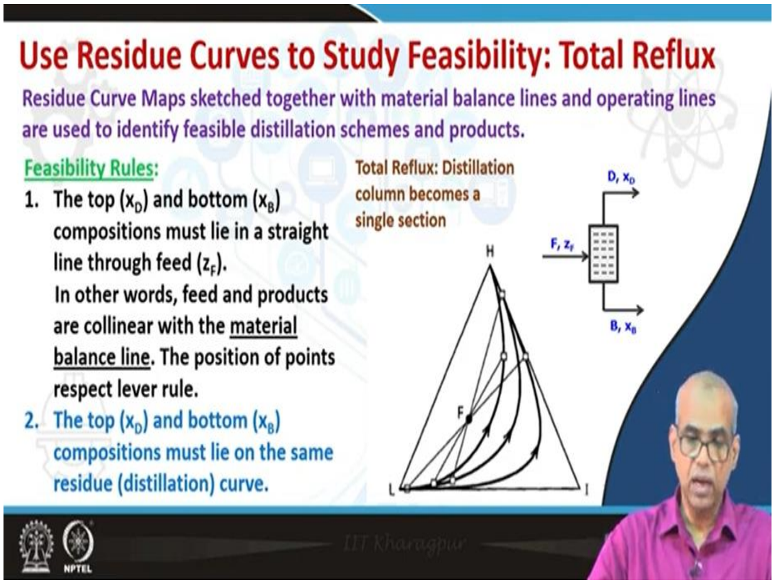

Use Residue Curves to Study Feasibility: Total Reflux

Residue Curve Maps sketched together with material balance lines and operating lines are used to identify feasible distillation schemes and products.

Feasibility Rules:

1. The top (x_D) and bottom (x_B) compositions must lie in a straight line through feed (z_F). In other words, feed and products are collinear with the material balance line. The position of points respect lever rule.
2. The top (x_D) and bottom (x_B) compositions must lie on the same residue (distillation) curve.

Total Reflux: Distillation column becomes a single section

Now let us take the case where we will use a residue come back to study the feasibility of separations under total reflex conditions note that when a distillation column is operating under total reflux the streams are not getting affected by the feed stream the dot because there is no feed stream entering into the distillation column. So the internal streams are not getting affected by the feed streams.

In other words when the distillation column is operating under total reflux condition the entire distillation column is working as a single section. So the residue curve map generated on the basis of liquid phase compositions in a simple distillation or lid distillation can be used to study the feasibility of the separations under total difference conditions in a trade distillation column as well as in a bag bed distillation column.

Now, there are two feasibility rules the top product the bottom product compositions must lie in a straight line through the feed. In other words feed and products are collinear with their material balance line. The position of the points respects the lever rule. And also the top and the bottom compositions must lie on the same residue curve. For example, you consider this particular residue curve.

And let us say the tetradynamic mixture is represented by this point f. So note these two compositions. Sorry these two compositions are lying on the same residue curve as well as on the same material balance line. So this separation is feasible. So separation will be feasible when the display composition bottom composition are lying on the same residue curve and this xd and xb the bottom composition and the distillation composition follows the lever rule. So, they are co linear on the material balance line.

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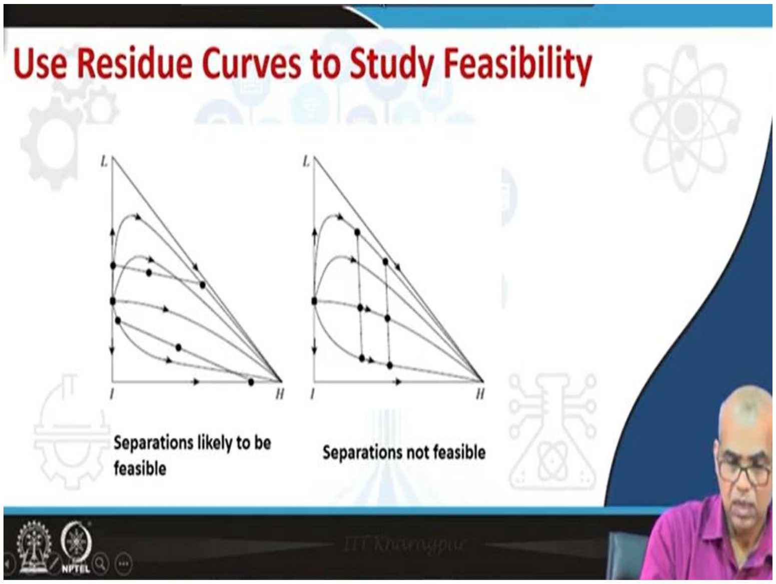

Use Residue Curves to Study Feasibility

Separations likely to be feasible

Separations not feasible

Say, for example if we consider this residue curve map. Note that we can present the residue curve map both in equilateral triangular diagram as well as right angular diagram. If this is my feed now these two compositions representing top product and bottom product lying on the same residue curve map and also lying on the same material balance line, so this is the feasible separation.

But note if this is the feed point. Now these two points lying on two different residue curves and this separation is not feasible.

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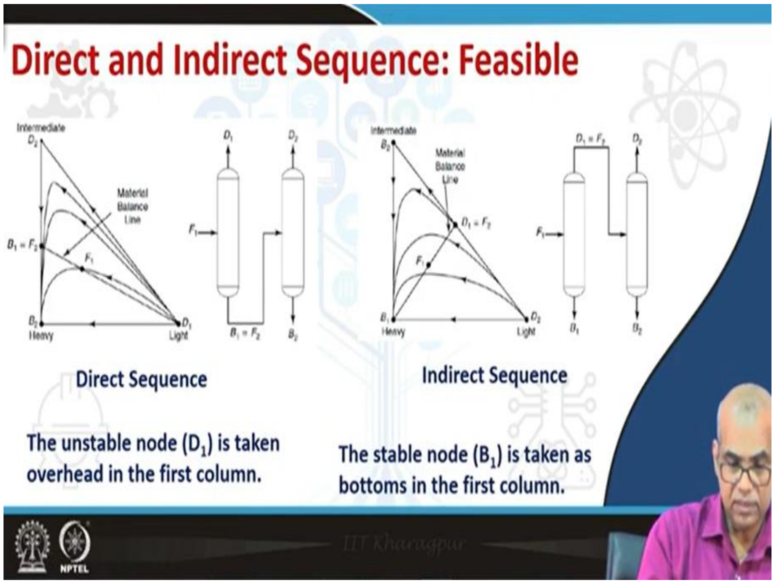

Direct and Indirect Sequence: Feasible

Direct Sequence

The unstable node (D_1) is taken overhead in the first column.

Indirect Sequence

The stable node (B_1) is taken as bottoms in the first column.

Similarly you can analyze, that the direct and indirect sequence for separation of a ternary mixture is the feasible sequence using residue curve map consider first the direct sequence the light component represents an unstable node here. Note that all the arrows are pointing away from it. Now this mixture through this mixture if we draw a material balance line connecting point D1.

It essentially means that the D1 is being taken out from the top of the first distillation column. So the bottom will be determined by this material balance line from the point which is lying on the heavy and intermediate joining side which is a mixture of intermediate and heavy component. This bottom product goes to the second distillation column which is splitted into your heavy and intermediate component.

Exactly the same way you can analyze that indirect sequence is also possible. Note that this line which represents the separation in the column one the points satisfying the rules for the feasibility lying on the same residue curve map, lying on the same residue curve and collinear with the material balance line. The same holds for the indirect sequence. But indirect sequence we take out these heavy as the bottom in the first column.

So we get a mixture of light and intermediate as top product from the first column which goes at which goes to second column as feed where it is separated. So, this is a feasible sequence.

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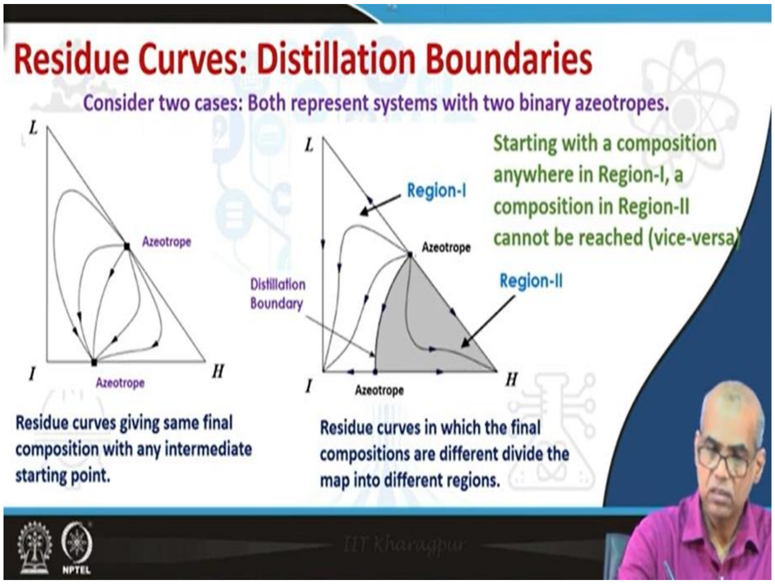

Residue Curves: Distillation Boundaries

Consider two cases: Both represent systems with two binary azeotropes.

Starting with a composition anywhere in Region-I, a composition in Region-II cannot be reached (vice-versa)

Residue curves giving same final composition with any intermediate starting point.

Residue curves in which the final compositions are different divide the map into different regions.

Now consider the case shown here. All the residue curves terminates here. So residue curves gives same final composition with any intermediate starting point. But about what about this? Note that this particular residue curve separates the entire triangle into two regions region 1 and region 2. So the residue curves originating here terminate at the intermediate node which is a stable node. And the residue curves originating here in the region two is terminating at heavy component node which is also us stable node.

So it is difficult to obtain a composition in region two starting from region one and vice versa. Because it is difficult to cross the distillation bounded.

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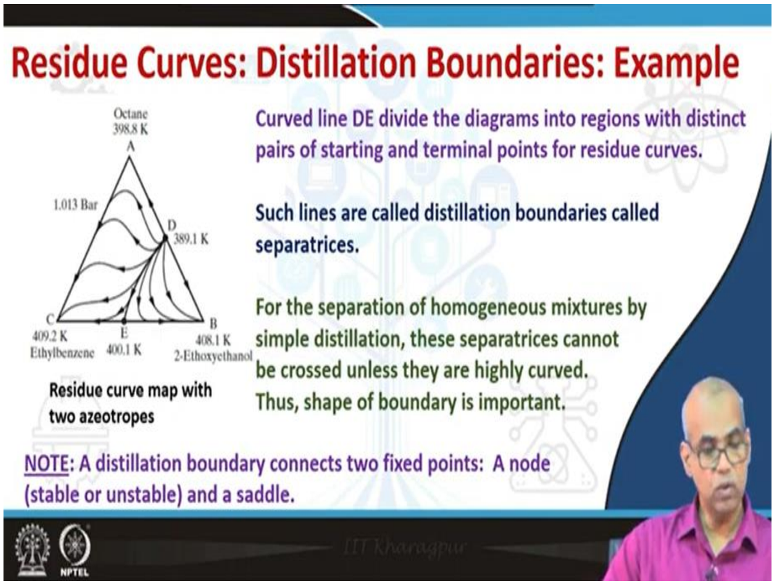

Residue Curves: Distillation Boundaries: Example

Residue curve map with two azeotropes

Curved line DE divide the diagrams into regions with distinct pairs of starting and terminal points for residue curves.

Such lines are called distillation boundaries called separatrices.

For the separation of homogeneous mixtures by simple distillation, these separatrices cannot be crossed unless they are highly curved. Thus, shape of boundary is important.

NOTE: A distillation boundary connects two fixed points: A node (stable or unstable) and a saddle.

Again, take an example of octane, ethylbenzene and 2-ethoxyethanol. The curve line D represents the distillation boundary which divides the triangular region into two distinct zones such lines are called distillation boundaries or separatrices. For the separation of homogeneous mixtures by simple distillation these separatrices cannot be crossed unless they are highly curved we will see an example.

The shape of the distillation boundary is very important. If it is not highly curved we will not be able to cross this distillation boundary. So starting with composition in one region we will not be able to obtain the composition in the other region.

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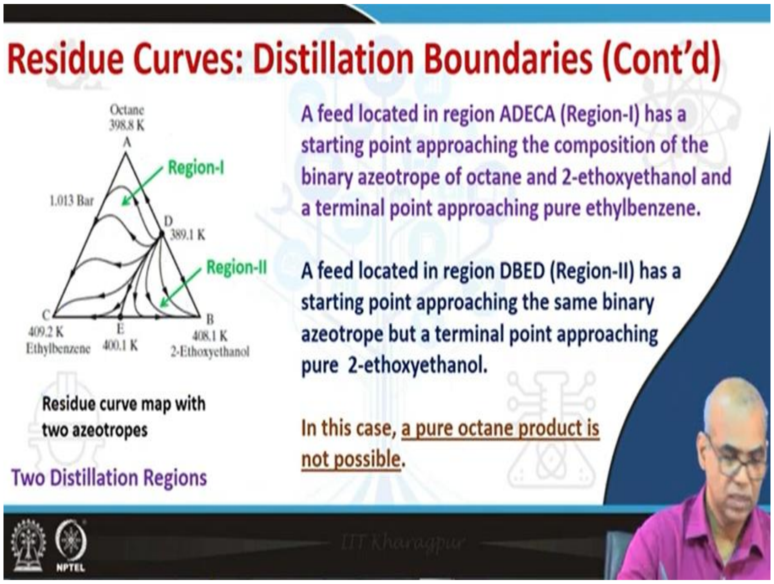

Residue Curves: Distillation Boundaries (Cont'd)

Residue curve map with two azeotropes

Two Distillation Regions

A feed located in region ADECA (Region-I) has a starting point approaching the composition of the binary azeotrope of octane and 2-ethoxyethanol and a terminal point approaching pure ethylbenzene.

A feed located in region DBED (Region-II) has a starting point approaching the same binary azeotrope but a terminal point approaching pure 2-ethoxyethanol.

In this case, a pure octane product is not possible.

For example in the same example of octane, ethyl benzene and ethoxyethanol if we start with the composition in the region 1 will get pure ethylbenzene. Similarly if we start in the region 2, we will get pure 2-ethoxyethanol. So from this residue curve map, we can also conclude that pure octane product cannot be obtained by this distillation skip. So in this example, we had distinct 2 distillation bounded 2 distillation regions obtained by the distillation boundary D.

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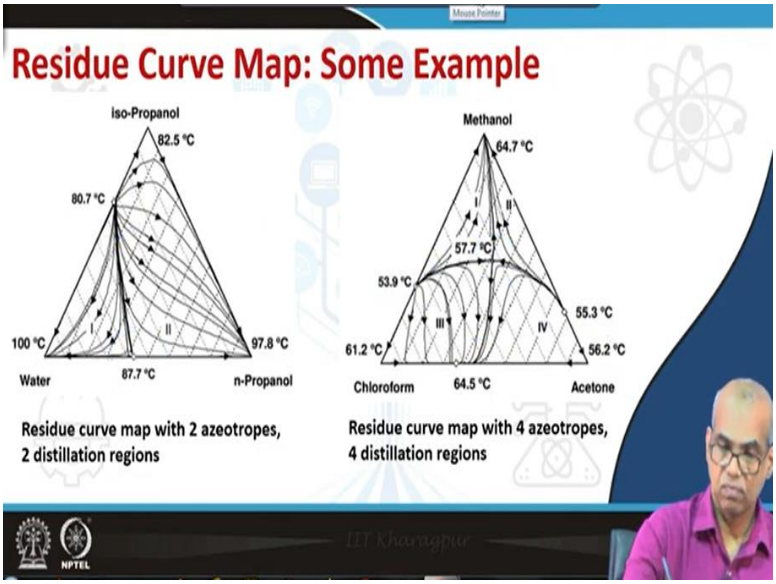

Residue Curve Map: Some Example

Residue curve map with 2 azeotropes, 2 distillation regions

Residue curve map with 4 azeotropes, 4 distillation regions

Let us see some of some more examples. So here you see our residue curve map with one azeotrope. But one distillation region on your left the other one we have residue curve map with one azeotrope, but two distillation regions, region 1 and region 2. So the components are also indicated. We have here residue curve map with two azeotropes and two distillation regions. Here is an example where we have 4 azeotropes, 3 binary azeotropes and 1 ternary azeotropes. So together they give us four distillation regions.

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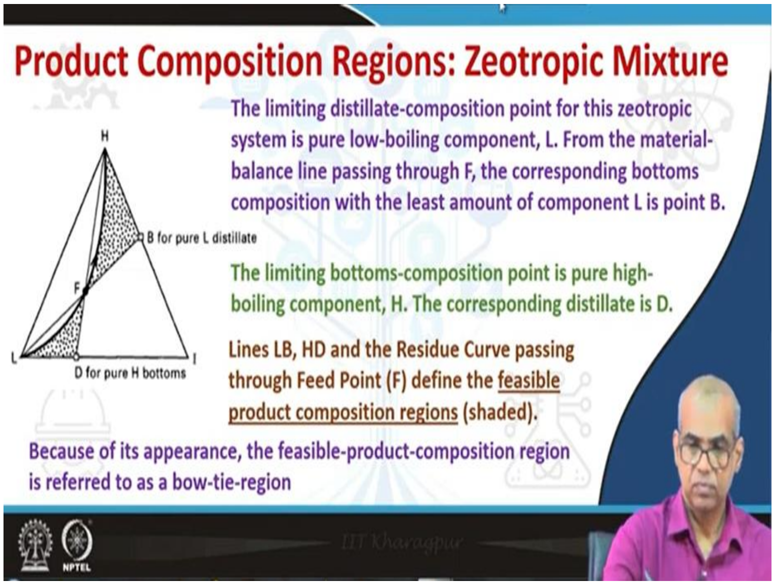

Product Composition Regions: Zeotropic Mixture

The limiting distillate-composition point for this zeotropic system is pure low-boiling component, L. From the material-balance line passing through F, the corresponding bottoms composition with the least amount of component L is point B.

The limiting bottoms-composition point is pure high-boiling component, H. The corresponding distillate is D.

Lines LB, HD and the Residue Curve passing through Feed Point (F) define the feasible product composition regions (shaded).

Because of its appearance, the feasible-product-composition region is referred to as a bow-tie-region

Now let us consider how residue curve map can be used to determine what are the feasible product compositions, that means what are the attainable product compositions. So consider a ternary mixture. Consider the residue curve map we have low boiling component, high boiling component and intermediate boiling component. In the distillation the limiting distillate composition will be the pure low boiling component L.

So now if I draw the material balance line from point L through the feed point F which is the ternary mixture so lying within the triangle. So draw a material balance line connecting low boiling component L and F and extend then I will get the point B on the side H I, which represents the corresponding bottom composition, which will have minimum amount of the lowering component L.

Similarly we can also find that the limiting bottom composition will be pure H and the corresponding distillate will be obtained by joining the material balance line from H to F and then extend to line L I. So this D will represent the corresponding distillate, so these two are limiting cases. One is the limiting distillate composition and other is the limiting bottom compositions.

Now these two lines that means the L B and the line L B and the line H D together with the residue curve maps that passes through the feed point F will constitute the region which will tell us the feasible product compositions. The region is shaded here so the shaded region indicates the feasible product composition region or attainable product composition region, so any composition within the shaded region is possible to be attained.

So because of it is appearance the feasible product composition region is referred to as bow-tie-region. Now this is was about zeotropic mixture where there was no azeotrope. Now what will happen if we have azeotrope.

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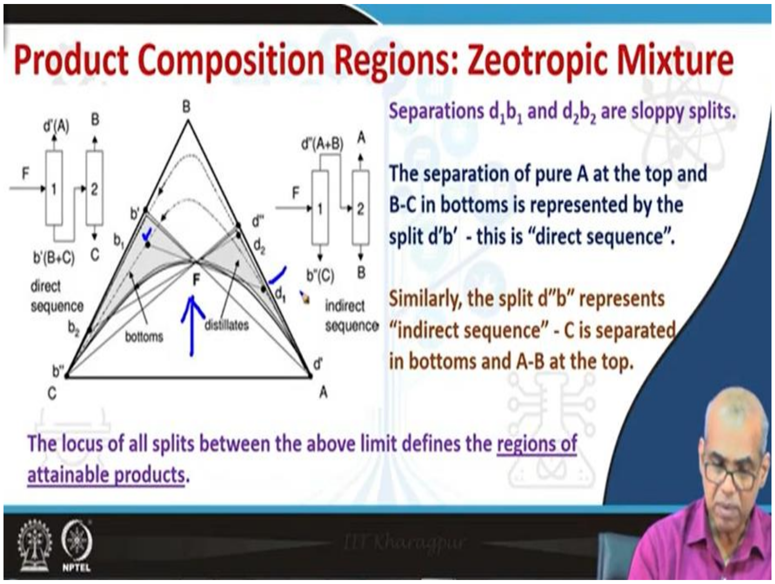

Product Composition Regions: Zeotropic Mixture

Separations d_1b_1 and d_2b_2 are sloppy splits.

The separation of pure A at the top and B-C in bottoms is represented by the split d'b' - this is "direct sequence".

Similarly, the split d"b" represents "indirect sequence" - C is separated in bottoms and A-B at the top.

The locus of all splits between the above limit defines the regions of attainable products.

So if I have an azeotropic mixture or before that let us consider the same zeotropic mixture further. So the bow-tie-region is shown the cellar region is the feasible region attainable region. F is the feed point feed mixture. Now the material line passing through say B 1 D 1, so B 1 F D 1 is a feasible split. But note that this is not a sharp split this is sloppy split. You do not get pure A pure B.

Similarly d 2 b 2 is also sloppy split. Now if you want to obtain pure A so I must join A with F and consider that material balance line. So d prime b prime passing through point F will tell us that a separation of pure A at the top and mixture of B and C at the bottom is possible by this split and this is an example of direct sequence because you are getting A as the low boiling component as the top product.

Similarly the d double prime b double prime this material balance line now this split will represent an indirect sequence where you are obtaining pure C as bottom and AB mixture as top product. So note that this split and this split there the two limiting splits. Corresponding to direct sequence and indirect sequence where in the first case we get pure A as top in the first column in the second case we get pure C as bottom in the second column. The locus of all splits between these two limiting cases defines the regions of all attainable product composition.

So this curve tells you immediately; what are the product compositions that are possible to be obtained by separation through distillation.

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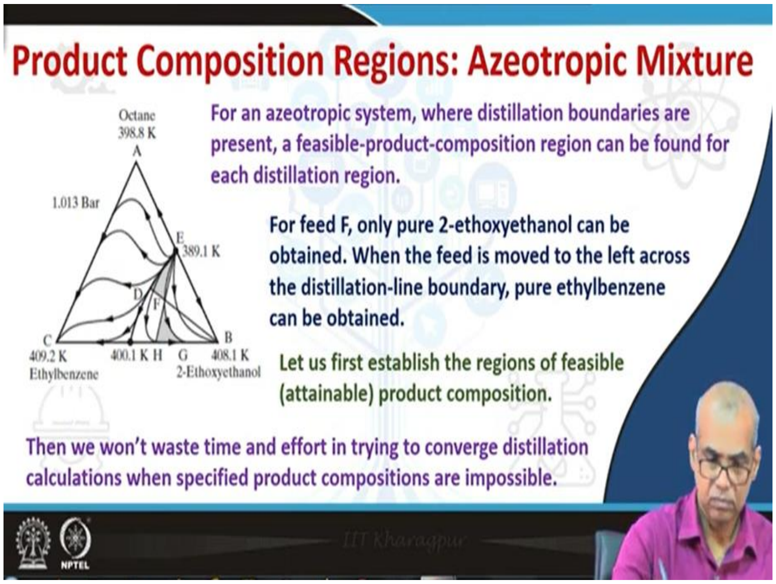

Product Composition Regions: Azeotropic Mixture

For an azeotropic system, where distillation boundaries are present, a feasible-product-composition region can be found for each distillation region.

For feed F, only pure 2-ethoxyethanol can be obtained. When the feed is moved to the left across the distillation-line boundary, pure ethylbenzene can be obtained.

Let us first establish the regions of feasible (attainable) product composition.

Then we won't waste time and effort in trying to converge distillation calculations when specified product compositions are impossible.

Now if you have an azeotropic mixture where distillation boundaries are present a feasible product composition region can be found for each distillation region separately. For example in the example of octane ethylbenzene and 2-ethoxyethanol you consider pure feed you consider feed point F. You consider feed point A only pure 2-ethoxyethanol can be obtained. So the shaded region obtained by the material balance line joining B F D and E F H indicates the feasible product composition.

So the shaded region that you have obtained with help of the residue curve map that passing passes through point F as well as the lines F the line B F D as well as E F H gives us the feasible product composition. If you have F on the other side you will obtain pure ethylbenzene and the similar product composition region can also be obtained by drawing the appropriate material balance line.

So you should first establish the regions of feasible product compositions if we do that we will not be wasting much time and efforts in trying to converge distillation calculations when certain specified product compositions are not possible to obtain. So residue curve map or and the product composite feasible product compositions will tell us what compositions are possible to obtain and what compositions are not possible to be achieved so it will save our time and effort during distillation calculations.

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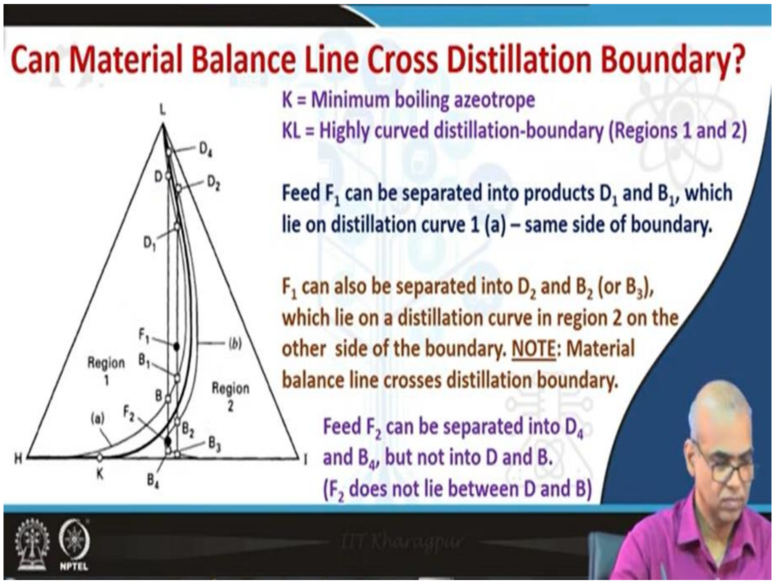

Can Material Balance Line Cross Distillation Boundary?

K = Minimum boiling azeotrope

KL = Highly curved distillation-boundary (Regions 1 and 2)

Feed F_1 can be separated into products D_1 and B_1, which lie on distillation curve 1 (a) – same side of boundary.

F_1 can also be separated into D_2 and B_2 (or B_3), which lie on a distillation curve in region 2 on the other side of the boundary. NOTE: Material balance line crosses distillation boundary.

Feed F_2 can be separated into D_4 and B_4, but not into D and B. (F_2 does not lie between D and B)

Now let us consider the cross distillation boundary. Can material balance line cross a distillation boundary it can do only when the distillation boundary is highly curved. So consider this residue curve map K represents a minimum boiling azeotrope and the K L represents a highly curved distillation boundary. So the region 1 and region 2 has been obtained by this distillation boundary.

If you consider the feed F 1; this can clearly be separated into D 1 and. B 1. Note that both are lying on the same residue curve indicated by A and they are on the same side of the of these particular residue curve the distillation boundary, both are in the region one. This is the valid feasible split or separation. F1 can also be separated by separated into D 2 and B 2. Now note that D 2 and B 2 lie on the other side of the distillation boundary, they are lying on the region 2.

So we have been able to cross the discussion boundary. This was possible because of the highly curved nature of the distillation boundary. So the feed F 1, which is lying on the on region 1 can be splitted into D 2 and B 2 which are lying on the region 2. Note that feed F 2 which is this point lying on the region 2 can be splitted into D 4 and B 4. So F 2 D 4 B 4 all are lying on region 2. This is a valid split. But can F 2 be split it into D and B which are lying on region 1? No, because F 2 does not lie between D and B.

So a feed mixture lying in region 1 can give compositions lying in region 2, it can cross the material balance line, it can cross the distillation boundary but we see that feed lying in the region 2 is unable to cross the distillation boundary. So feed which is lying in the region 2 cannot be splitted into 2 compositions lying in region 1. So this is because of the nature of the curvature. So with this we stop our discussion on residue curve map here.