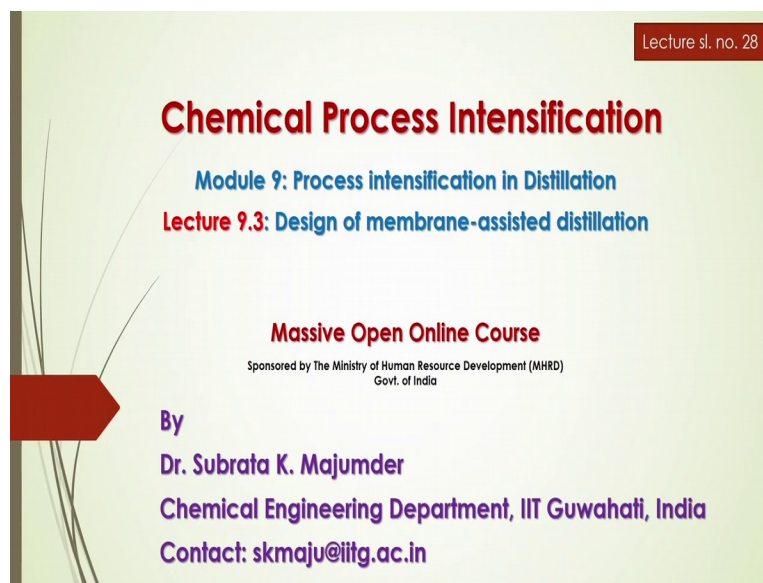


Chemical Process Intensification
Professor Subrata K. Majumder
Department of Chemical Engineering
Indian Institute of Technology Guwahati
Module 9
Lecture No 9.3
Design of Membrane-assisted Distillation

Welcome to massive open online course on chemical process intensification, so we are discussing something about the process intensification in distillation, so in this module we will discuss more about that process intensification in distillation.

(Refer Slide Time: 0:57)



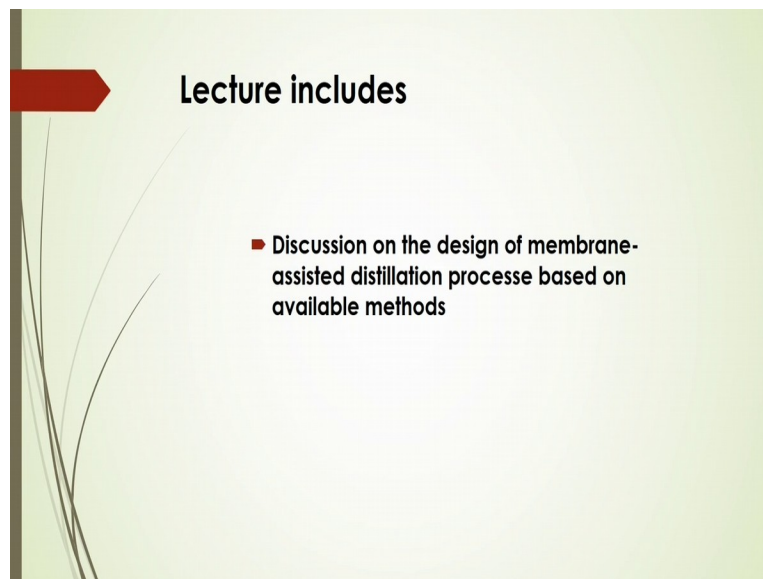
Lecture sl. no. 28

Chemical Process Intensification

Module 9: Process intensification in Distillation
Lecture 9.3: Design of membrane-assisted distillation

Massive Open Online Course
Sponsored by The Ministry of Human Resource Development (MHRD)
Govt. of India

By
Dr. Subrata K. Majumder
Chemical Engineering Department, IIT Guwahati, India
Contact: skmaju@iitg.ac.in



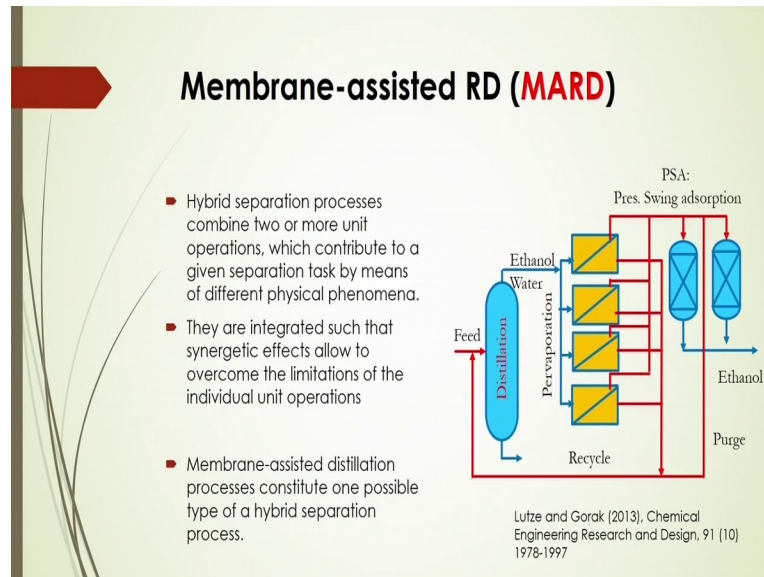
Lecture includes

- Discussion on the design of membrane-assisted distillation processes based on available methods

So in this lecture we will discuss design of membrane assisted distillation and we will discuss something design aspect of membrane assisted distillation process based on available

methods and how that design criteria is to be selected as well as what are the different actually methods of designing that will be discussed in this lecture.

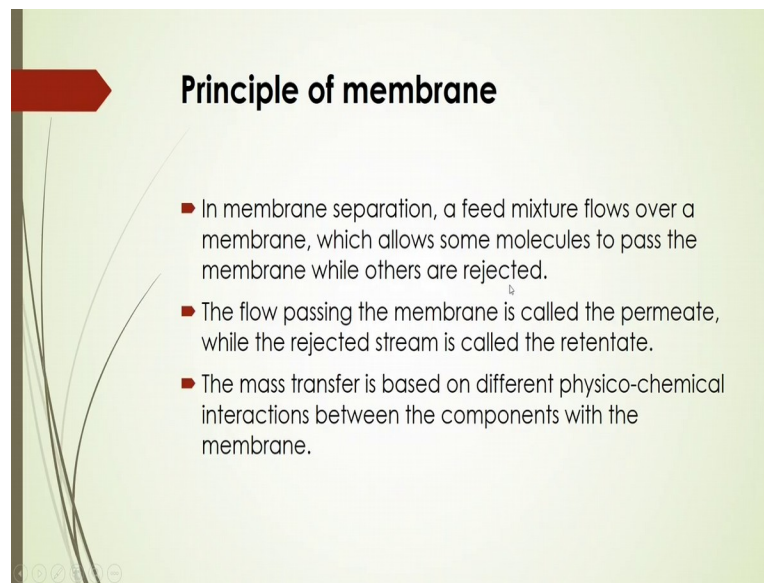
(Refer Slide Time: 1:26)



So we know that, hybrid process of you know reactive distillation process is one of the important aspects of process intensification and in that case the integration with this membrane is very important and then hybrid separation processes combines 2 or more unit operations which contributes to a given separation task by means of different, you know physical phenomena and based on that different physical phenomena and also some mechanism of different you know, aspects of you know, integration process.

So they are integrated such that synergetic effects allow to work on the limitations of the individual unit operations. In that case membrane assisted distillation process may contribute one of **the, you** know, important possible type of you know hybrid separation process. So in this figure it is shown that one example that is given by Lutze and Gorak in 2013, that they have actually described that you know, hybrid forces of distillation conjugated with the membrane system and if you are shown this how membranes are actually being utilised after getting separation by this distillation process and then from that overhead product, how that products will be separated by intensified way by this membrane process and then after that you know that, removing some unwanted you know by-products by this membrane that can be actually sent to that you know, from adsorption system. So this is one of important you know that hybrid separation process conjugating with membrane and adsorption process after, you know that, operation of distillation process.

(Refer Slide Time: 3:50)



Principle of membrane

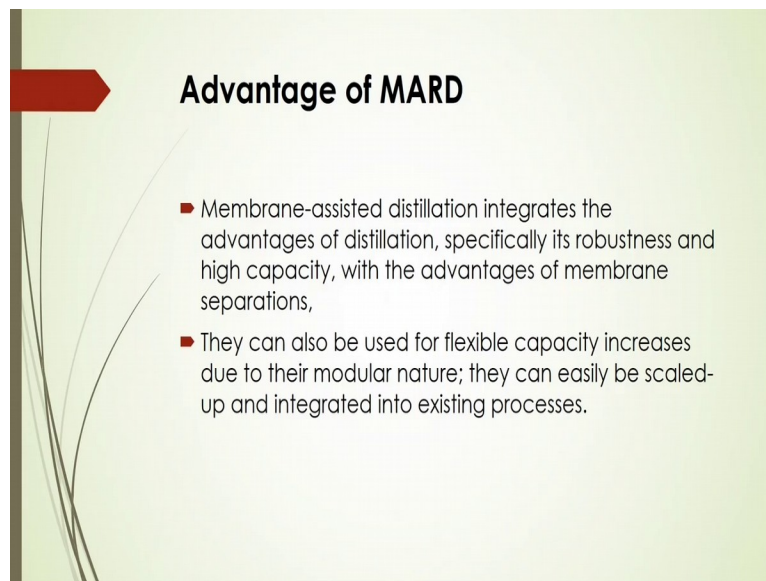
- In membrane separation, a feed mixture flows over a membrane, which allows some molecules to pass the membrane while others are rejected.
- The flow passing the membrane is called the permeate, while the rejected stream is called the retentate.
- The mass transfer is based on different physico-chemical interactions between the components with the membrane.

And you know that, whenever you are going to use this membrane process of course that, you have to know some principles of that membrane. So in membrane separation, a feed mixture flows over a membrane which actually allows some molecules to pass the membrane while others are rejected and then flow passing the membrane is called the permeate while the rejected stream is called the retentate.

The mass transfer is based on the different physico-chemical interaction between the components with the membrane, so we will discuss more about that membrane, different types of membranes, even how that membrane is being actually synthesised and also you know that how membrane are being you know that, procured and how that principle of this membrane will be working on different separation process will discuss in the you know, next modules.

So here just briefing that, that membranes will be acting as separator where, you know that through which some molecules will be passed where, some other molecules will be rejected whenever it will be passing through that membrane separator. It is basically a barrier whenever any mixture components will be passed through that barrier some components will be pass based on that pore size of that membrane barrier and also whenever flow will be passing the membrane, it will be called as permeate and whatever rejected stream will be you know, retained by that membrane it will be called retentate and by this case that there will be mass transfer that is one component will be passing through that membrane that mass transfer phenomena will be based on the different physic-chemical interactions between components with the membrane.

(Refer Slide Time: 5:58)

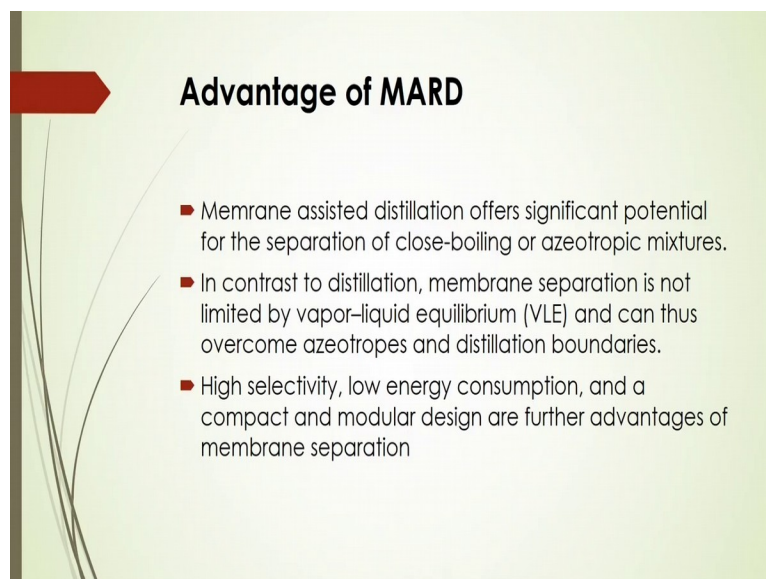


Advantage of MARD

- Membrane-assisted distillation integrates the advantages of distillation, specifically its robustness and high capacity, with the advantages of membrane separations,
- They can also be used for flexible capacity increases due to their modular nature; they can easily be scaled-up and integrated into existing processes.

Now if you are considering that you know, membrane assisted reactive distillation then what should be the advantage there, then only you can say that the process intensification will be there based on some advantages. Now membrane assisted distillation integrates the advantages of distillation, specially its robustness and high-capacity with the advantages of membrane separations. They can also be used for flexible capacity that increases due to their molecule phenomena and also modular based membrane procurement also gives some advantageous for the, you know that, increase of capacity of that membrane. They can easily be you know scaled up and integrated into existing processes, so that is why membrane assisted you know reactive distillation are important.

(Refer Slide Time: 7:07)

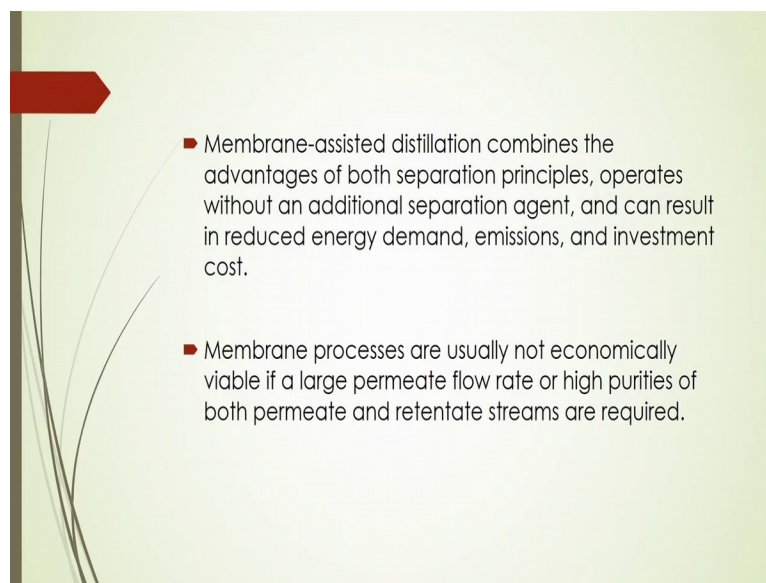


Advantage of MARD

- Membrane assisted distillation offers significant potential for the separation of close-boiling or azeotropic mixtures.
- In contrast to distillation, membrane separation is not limited by vapor-liquid equilibrium (VLE) and can thus overcome azeotropes and distillation boundaries.
- High selectivity, low energy consumption, and a compact and modular design are further advantages of membrane separation

Also you will see that it will offer some significant potential for the separation of close boiling or azeotropic mixtures. Sometimes it is very difficult to control the separation of azeotropic mixtures by the distillation and if you use that hybrid separation by this membrane system it will be sometimes easier to separate that close boiling mixture, which is called azeotropic mixture. And in contrast to distillation, membrane separation is not limited by you can say, vapour-liquid equilibrium and can thus overcome azeotropes and you know, distillation boundaries. High selectivity, low energy consumption and a compact and modular design are further you know, advantages of membrane separation.

(Refer Slide Time: 8:00)



You will see that this type of, you know hybrid separation process that is membrane assisted distillation processes it will actually combines the advantages of both separation principles, operates without an additional separation agent and also it can be used to reduce the energy demand, emissions and investment cost. Membrane processes are also used, you know sometimes, you know to get that high purity in the permeate and retentate but, there will be some limitations for that, since it is a small scale sometimes it is not viable for you know, that large scale processes and also, sometimes this membrane processes are not economically viable if a large permeate flow rate or high purity is of both permeate and retentate streams are required there.

(Refer Slide Time: 9:03)

Design Aspects

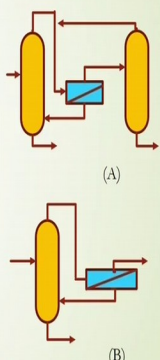
- A major obstacle for considering hybrid processes as design options in industrial practice is the **complexity of the design task**.
- Need for suitable design methods
- It starts with the identification of potential process variants and the selection of a suitable membrane.
- Computational tool can predict permeability and selectivity to support membrane selection
- Database information and expert knowledge is required to identify the suitable membrane

Now what are the different design aspects of this hybrid processes of membrane assisted, you know reactive distillation process. You will see that a major obstacle for considering hybrid processes as you know, design options in industrial practice which is mainly the complexity of the design task and for that it is required to need you know, for suitable design methods and that actually starts with the identification of potential process variants and selection of suitable membrane. Computational tool can predict permeability and selectivity to support that membrane selection. Database information and expert knowledge is also required to identify the suitable membrane by which you can have or designed that hybrid separation with distillation based on this membrane separation process.

(Refer Slide Time: 10:09)

Different configurations of (MARD)

- **Configuration A:** the feed mixture is separated until occurrence of a separation boundary, e.g., a low boiling azeotrope, which exits as a distillate.
- **Configuration B:** may consist of a membrane at the bottom if a homogenous catalyst containing some reactant needs to be recycled into a reactive distillation via a retentate recycle



You will see that there are different configuration of that membrane assisted reaction distillation systems like A, B, C, D here will show that in this slides can have these 2 configuration of A and B. You will see in the configuration A, the feed mixture is separated until occurrence of a separation boundary. Example it will allow a azeotrope boiling that is you know, a low boiling azeotrope which exists at a distillate and in the configuration B it may consist of a membrane at the bottom if homogeneous catalyst that contain some reactant that needs to be recycled into a you know, reactive distillation via the retentate recycle.

(Refer Slide Time: 11:04)

■ **Configuration C:** represents the high selectivity of the membrane used to pre-fractionate the mixture, which relieves the distillation column. This process may lead to smaller distillation columns and lower reflux ratios.

■ **Configuration D:** the membrane is used to separate a three-component mixture.

Each of these configurations offers multiple design degrees of freedom (DDoF).

As shown in figure here in the slides, the configuration C it represents the high selectivity of the membrane which is used to you know, pre-fractionate the mixture and also it relieves the distillation columns. This process may lead to smaller distillation columns and also, sometimes it will give the lower reflux ratio. In case of configuration D you will see that it may be used to separate a three-component mixture before you know, that entering to that distillation column that membrane will be used to separate some unwanted materials there and then three-component mixture to be you know, separate by this you know, hybrid separation process. Now you have to remember that whenever you are using these different types of configurations you have to consider some you know design degrees of freedom there, so of this configuration offers multiple design degrees of freedom.

(Refer Slide Time: 12:16)

■ For each distillation column the followings are need to be determined

- the number of equilibrium trays
- the location of feed and side streams and
- the energy duties

■ The membrane process can comprise of multiple stages, which have to be specified by

- membrane area
- feed pressure
- Temperature and
- permeate pressure

All DDoF should be optimized simultaneously in order to take full advantage of both separation principles

Now for each distillation column, the followings are also to be need to be determined like the number of equilibrium trays, the location of the feed and also side streams is there or not, the energy duties also. The membrane process can also comprise of multiple stages which have to be specified by membrane area, **feed pressure and temperature** and permeate pressure. Now all these degrees of freedom you know design degrees of freedom should be optimised simultaneously in order to take full advantage of both separation principles of membrane as well as you know, distillation.

(Refer Slide Time: 13:06)

Synthesis framework for design

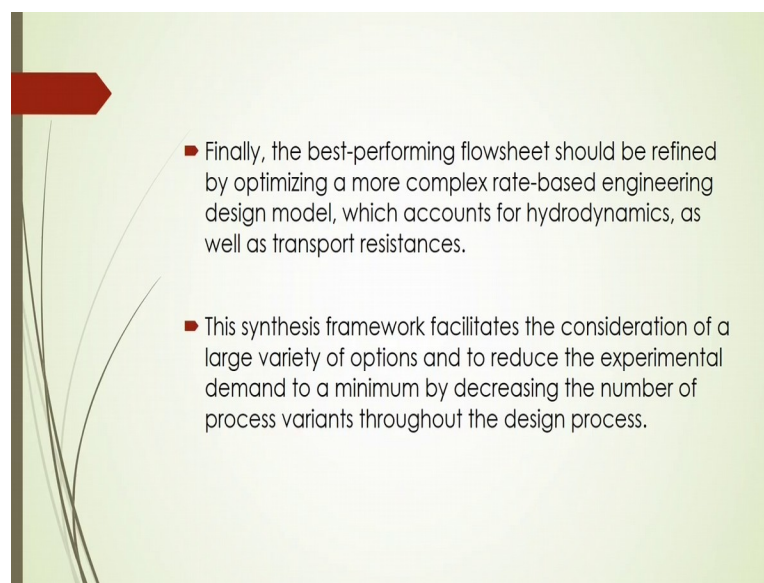
- For the design for complex hybrid processes, a synthesis framework can be used (Marquardt et al., 2008; Skiborowski et al., 2013)
- It is required to generate the process variants after first screening based on shortcut models in order to assess feasibility and effort of a separation.
- The most useful variants are subsequently optimized using more detailed models by means of mixed-integer nonlinear programming (MINLP).
- The model relies on mass and energy balances, rigorous physical property models, and either equilibrium-controlled or kinetically limited mass transfer models.

Marquardt, Wolfgang; Kossack, Sven; Kraemer, Korbinian, A framework for the systematic design of hybrid separation processes, Chinese Journal of Chemical Engineering (2008), 14 (3), 333-342
Skiborowski, Mirko; Harwardt, Andreas; Marquardt, Wolfgang, Conceptual design of distillation-based hybrid separation processes, Annual Review of Chemical and Biomolecular Engineering (2013), 4 (1), 45-68

Now, how to design for this generally some you know, framework should be used for design of this type of hybrid separation process for this membrane and distillation. In that case

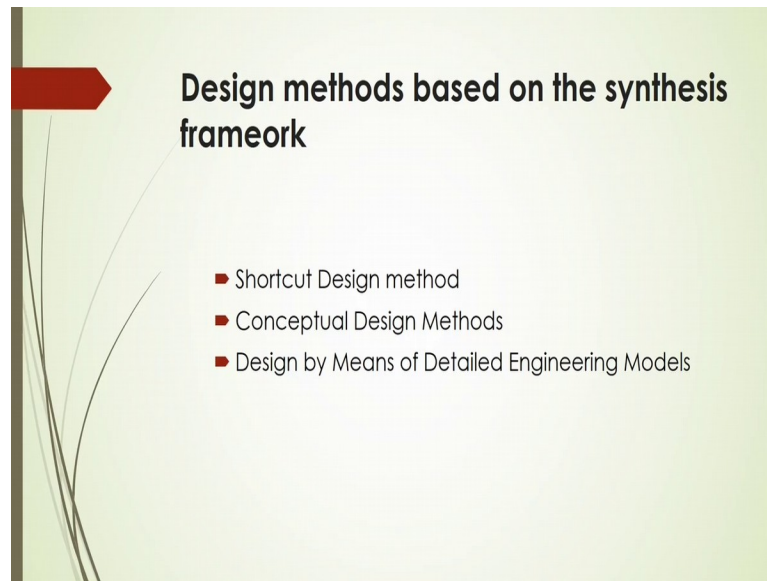
synthesis framework is very important for the design for this complex hybrid processes, synthesis framework can be used that is actually suggested by Marquardt et al. 2008 later on in 2013 Skiborowski they have extended you know, this synthesis framework model by Marquardt et al. 2008 and in that case it is required to generate the process variants after first screening based on shortcut models in order to assess feasibility and effort of a separation and the most useful you know, variants are subsequently optimised using you know, more detailed models by means of mixed integer non-linear programming there. Already we have discussed different aspects of optimisation of you know, non-linear programming system they are in the earlier you know, that modules that optimisation modules there and in that case this model relies on mass and energy balances, rigorous physical property models and either equilibrium controlled or kinetically limited mass transfer models. So this has to be you know that, remember that based on synthesis framework you can design this you know, this hybrid processes just by considering the optimization tool of you know, mixed integer nonlinear programming.

(Refer Slide Time: 15:06)



Finally the best performing flow sheet should be you know, refined by optimizing a more complex rate-based engineering design model, which accounts for hydrodynamics as well as transport resistances. This synthesis framework facilitates the consideration of a large variety of options and to reduce the experimental demand to a minimum by decreasing the number of you know, process variants throughout the design processes.

(Refer Slide Time: 15:44)

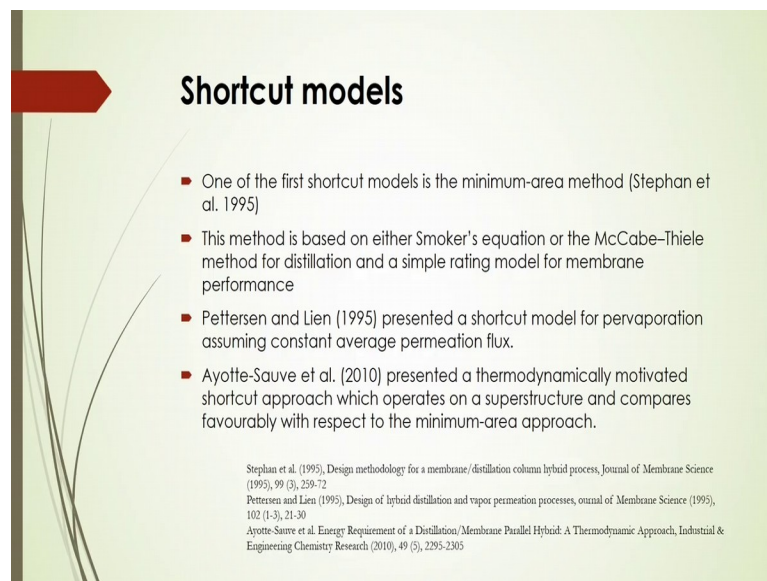


Design methods based on the synthesis framework

- Shortcut Design method
- Conceptual Design Methods
- Design by Means of Detailed Engineering Models

Now based on this synthesis framework what are the methods, generally 3 methods are available to design based on this synthesis framework. Those are shortcut design methods, conceptual design methods and final one is design by means of detailed engineering models.

(Refer Slide Time: 16:06)



Shortcut models

- One of the first shortcut models is the minimum-area method (Stephan et al. 1995)
- This method is based on either Smoker's equation or the McCabe-Thiele method for distillation and a simple rating model for membrane performance
- Pettersen and Lien (1995) presented a shortcut model for pervaporation assuming constant average permeation flux.
- Ayotte-Sauve et al. (2010) presented a thermodynamically motivated shortcut approach which operates on a superstructure and compares favourably with respect to the minimum-area approach.

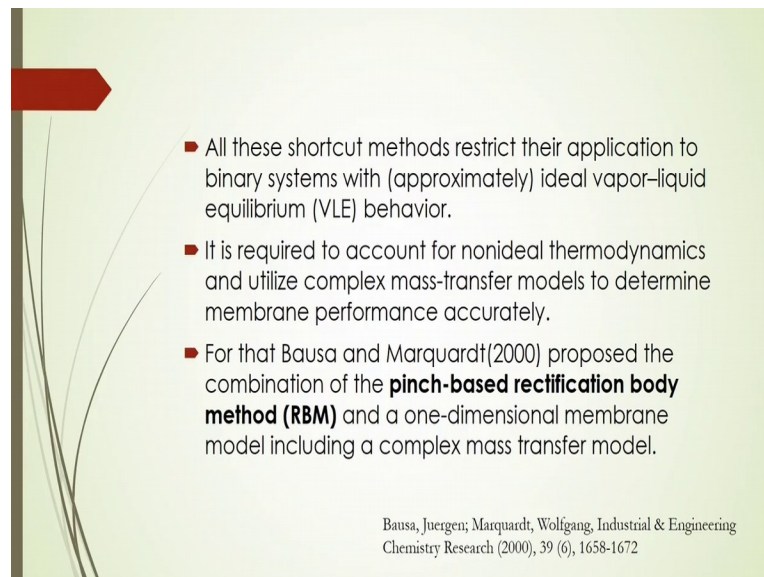
Stephan et al. (1995), Design methodology for a membrane/distillation column hybrid process, Journal of Membrane Science (1995), 99 (3), 259-72
Pettersen and Lien (1995), Design of hybrid distillation and vapor permeation processes, Journal of Membrane Science (1995), 102 (1-3), 21-30
Ayotte-Sauve et al. Energy Requirement of a Distillation/Membrane Parallel Hybrid: A Thermodynamic Approach, Industrial & Engineering Chemistry Research (2010), 49 (5), 2295-2305

What is that Shortcut models? One of the first shortcut models is the minimum area method it is actually developed by Stephan et al 1995 and this method is based on either Smoker's equation or the, you know McCabe-Thiele method for distillation. McCabe-Thiele method is very important for designing a distillation column that is basic you know understanding of that design of distillation column. I think those who have done the B. Tech program in Chemical engineering in the mass transfer operations and even in unit operations this you

know, distillation process are actually taught and they are this McCabe-Thiele methods are actually taught for you know, design of distillation column. So in that case this you know shortcut models that method is based on either this you know McCabe-Thiele method or Smoker's equation for the distillation and a simple rating models for membrane performance.

In 1995 Pettersen and Lien presented a shortcut model for pervaporation assuming constant average permeation flux for the membrane performance analysis. Also Ayotte-Sauve et al. in 2010 presented another important models which will be you know, based on thermodynamics phenomena, so they have presented the thermodynamically motivated shortcut approach which operates on a superstructure and compares favourably with respect to the minimum area approach.

(Refer Slide Time: 17:58)

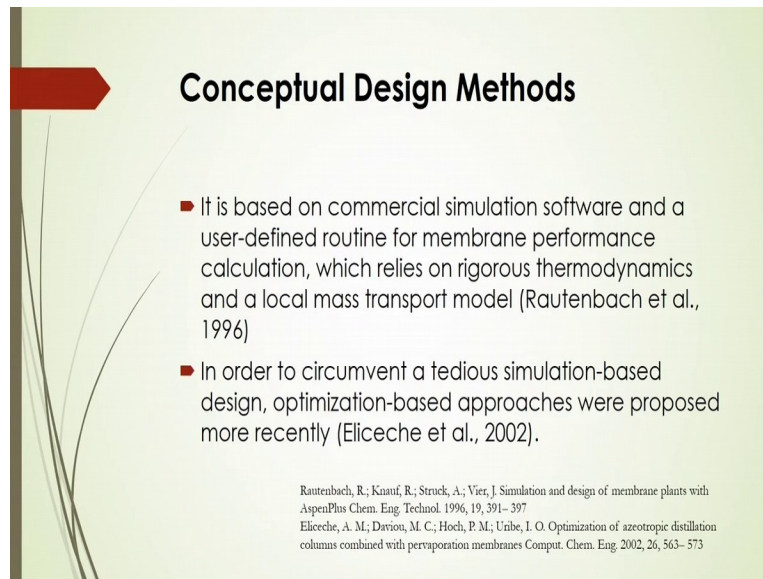


- All these shortcut methods restrict their application to binary systems with (approximately) ideal vapor-liquid equilibrium (VLE) behavior.
- It is required to account for nonideal thermodynamics and utilize complex mass-transfer models to determine membrane performance accurately.
- For that Bausa and Marquardt(2000) proposed the combination of the **pinch-based rectification body method (RBM)** and a one-dimensional membrane model including a complex mass transfer model.

Bausa, Juergen; Marquardt, Wolfgang, Industrial & Engineering Chemistry Research (2000), 39 (6), 1658-1672

All this shortcut methods of course, restrict their application to binary systems with ideal vapour-liquid equilibrium behaviour, in that case it is required to account for you know, non-ideal thermodynamics and utilise complex mass-transfer models to determine the membrane performance accurately and for that what you have to do, you have to follow some pinch based rectification body methods that is suggested by Bausa and Marquardt 2000 and also you can follow that one dimensional membrane model which may include a complex mass transfer model and then conceptual design methods are this method is based on commercial simulation software and a user defined routine for the membrane performance analysis which relies on rigorous thermodynamic and local mass transfer model and it is actually developed by Rautenbach et al 1996.

(Refer Slide Time: 19:11)



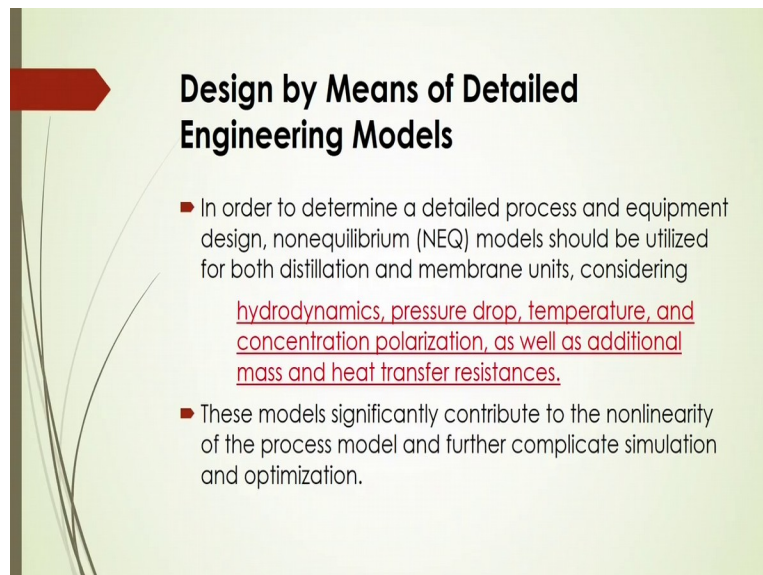
Conceptual Design Methods

- It is based on commercial simulation software and a user-defined routine for membrane performance calculation, which relies on rigorous thermodynamics and a local mass transport model (Rautenbach et al., 1996)
- In order to circumvent a tedious simulation-based design, optimization-based approaches were proposed more recently (Eliceche et al., 2002).

Rautenbach, R.; Knauf, R.; Struck, A.; Vier, J. Simulation and design of membrane plants with AspenPlus Chem. Eng. Technol. 1996, 19, 391–397
Eliceche, A. M.; Daviou, M. C.; Hoch, P. M.; Unbe, I. O. Optimization of azeotropic distillation columns combined with pervaporation membranes Comput. Chem. Eng. 2002, 26, 563–573

In order to circumvent a tedious simulation based design you can you know, follow the Eliceche et al. 2002 model which is given for the optimisation based models for analysis of this you know performance of the you know, that membrane processes. So these are the models that you can use or methods you can use for conceptual design.

(Refer Slide Time: 19:40)



Design by Means of Detailed Engineering Models

- In order to determine a detailed process and equipment design, nonequilibrium (NEQ) models should be utilized for both distillation and membrane units, considering hydrodynamics, pressure drop, temperature, and concentration polarization, as well as additional mass and heat transfer resistances.
- These models significantly contribute to the nonlinearity of the process model and further complicate simulation and optimization.

And also, you can use other models like the design by means of detailed engineering models and in that case to determine a detailed process and equipment design you have to follow non-equilibrium models for both distillation and membrane units and in that case you have to consider the hydrodynamics, pressure drop, temperature and concentration polarisation as well as additional mass and heat transfer resistances and these models significantly

contributes to the non-linearity of the process models and further complicates simulation and optimisation.

(Refer Slide Time: 20:26)



Optimization Model

- The Hybrid process optimization constitutes an aggregation of superstructure models for each subprocess.
- The superstructure model for the distillation columns is based on the MESH equations,
- The model of a membrane network comprises multiple membrane stages with interstage heating and possible interior recycles.
- Each stage of membrane is generally modeled by one-dimensional, differential mass and enthalpy balances, incorporating a detailed and experimentally validated local mass transfer model.
- All models rely on rigorous thermodynamics

Now what are those that optimisation model, in this case this hybrid process optimisation generally you know, build upon the basis of aggregation of superstructure models for each sub processes. The superstructure model for the distillation column is actually based on the MESH equation. The model of a membrane network comprises multiple membrane stages with **inter-stage** heating and also possible interior recycles. Now each stage of membrane is generally modelled by one-dimensional, differential mass and enthalpy balances that may incorporate a detailed and experimentally you know, validated local mass transfer model and all the models of course, will be rely on the rigorous thermodynamic analysis.

(Refer Slide Time: 21:31)

Distillation Column Model

- Viswanathan and Grossmann (1993) first introduce the optimization of a single distillation column by a superstructure model for homogeneous ideal systems.
- Bauer and Stichlmair (1995) extended this approach to nonideal and azeotropic mixtures.

Viswanathan, J.; Grossmann, I. E. An alternate MINLP model for finding the number of trays required for a specified separation objective *Comput. Chem. Eng.* 1993, 17, 949–955
 Bauer, M. H.; Stichlmair, J. Synthesis and optimization of distillation sequences for the separation of azeotropic mixtures *Comput. Chem. Eng.* 1995, 19, 15–20

And Viswanathan and you know, Grossmann 1993 first introduce the optimisation of a single distillation column by a superstructure model for homogeneous ideal systems and later on in 1995 Bauer and Stichlmair, 1995, extended this Viswanathan and Grossmann model to you know, non ideal and also azeotropic mixtures.

(Refer Slide Time: 22:07)

General superstructure for a distillation column

It is based on the concept of a variable reflux column. The variable locations of feed and side stream trays as well as reflux and boil-up trays facilitate the decision on the discrete design degrees of freedom (DDoF).

Column Tray (n)

The superstructure for a distillation column with one side and two feed streams.

And here in this slides says general superstructure for the distillation column is shown. You will see that this superstructure is basically based on the concept of a you know, variable reflux column, the variable locations of the feed and side stream trays as well as reflux and boil-up trays that facilitates the decision on the discrete design and also design degrees of freedom. You see in this figure here there are maybe several feed streams will be there and

also side streams will be there and then here are this boil up of course they are as reflux with reflux also to be considered here and then the superstructure for a distillation column with one-side and two feed streams are shown here in this slide.

(Refer Slide Time: 23:13)

Mass and enthalpy balance

- The mass and enthalpy balances for an arbitrary tray n are given by

$$L_n x_{n,i} + V_n y_{n,i} = L_{n-1} x_{n-1,i} + V_{n+1} y_{n+1,i} + F_1 z_{F_1,i} b_{F_1,n} + F_2 z_{F_2,i} b_{F_2,n} - S z_{S,i} b_{S,n} + R_D x_{R,i} b_{R,n} + R_B y_{B,i} b_{B,n}$$

$$i = 1, \dots, n_c \quad (1)$$

(L_n, x_n, h_n^L)
the flow rate, composition vector, and enthalpy for the liquid on tray n

(V_n, y_n, h_n^V)
the flow rate, composition vector, and enthalpy for the vapour on tray n

$$L_n h_n^L + V_n h_n^V = L_{n-1} h_{n-1}^L + V_{n+1} h_{n+1}^V + F_1 h_{F_1} b_{F_1,n} + F_2 h_{F_2} b_{F_2,n} - S h_S b_{S,n} + R_D h_R^L b_{R,n} + R_B h_B^V b_{B,n}$$

$$(F_1, z_{F_1}, h_{F_1}) \quad (F_2, z_{F_2}, h_{F_2}) \quad (S, z_S, h_S) \quad (R_D, x_R, h_R^L) \quad (R_B, y_B, h_B^V)$$

Flowrate, composition and enthalpy for feed streams, the side stream, the reflux, and the boil-up stream respectively. The binary variables $b_{F_1,n}$, $b_{F_2,n}$, $b_{S,n}$, $b_{R,n}$, and $b_{B,n}$ encode the decisions regarding feed, recycle, and side streams related to stage n .

And if you do the mass and enthalpy balance for this you know superstructure column then you will see that the mass and enthalpy balances for an arbitrary tray if you consider n that can be written and expressed by the equation number 1 and 2 here.

$$L_n x_{n,i} + V_n y_{n,i} = L_{n-1} x_{n-1,i} + V_{n+1} y_{n+1,i} + F_1 z_{F_1,i} b_{F_1,n} + F_2 z_{F_2,i} b_{F_2,n} - S z_{S,i} b_{S,n} + R_D x_{R,i} b_{R,n} + R_B y_{B,i} b_{B,n}$$

$$i = 1, \dots, n_c \quad (1)$$

$$L_n h_n^L + V_n h_n^V = L_{n-1} h_{n-1}^L + V_{n+1} h_{n+1}^V + F_1 h_{F_1} b_{F_1,n} + F_2 h_{F_2} b_{F_2,n} - S h_S b_{S,n} + R_D h_R^L b_{R,n} + R_B h_B^V b_{B,n}$$

$$(2)$$

In this case these are the equations are shown and in this case we will see L_n, X_n and h_n^L these are actually denoted for you know, the flow rate composition vector and enthalpy for the liquid on that tray n . Whereas V_n, Y_n and h_n^V it represents the flow rate, composition vector and enthalpy for the vapour on the tray n . Whereas this F_1, z_{F_1}, h_{F_1} here this $F_2, z_{F_2}, h_{F_2}, S, h_S,$

$R_D, x_R, h_R^L, R_B, y_B, h_B^V$ all are generally flow rate composition and enthalpy for feed streams, the side streams, the reflux and the boil up stream respectively. The binary variables here you will see b_{F1n} , b is for binary, b_{F2} , b_{Bn} , b_{Rn} and b_{Sn} that encode the decision regarding feed, recycle and side streams related to stage n .

(Refer Slide Time: 24:55)

■ Arbitrary composition $z_{s,j}$ and enthalpy h_s for the side stream allows:

- to withdraw either a liquid or a vapor stream from one tray, or
- to selectively remove a single component, which is of special importance for initialization

■ The mass and enthalpy balances are complemented by the summation constraints

$$\sum_{i=1}^{n_c} x_{n,i} = 1 \quad (3)$$

$$\sum_{i=1}^{n_c} y_{n,i} = 1 \quad (4)$$

and the equilibrium relations: $y_{n,i} = K_{n,i} x_{n,i}, \quad i = 1, \dots, n_c \quad (5)$

$K_{n,i}$ = the distribution coefficient, $x_{n,i}$ and $y_{n,i}$ = liquid and vapor phase composition at equilibrium temperature T_n and pressure p .

After that what you have to do that arbitrary composition Z_{S_i} and enthalpy h_s for the side stream to be considered which allow to you know that, withdraw either a liquid or a vapour stream from one tray or to selectively remove a single component which is of you know special importance for the initialization. The mass and enthalpy balances are complemented by the summation that will have some constraints and then summation constraints can be represented by this equation number 3 and 4

$$\sum_{i=1}^{n_c} x_{n,i} = 1 \quad (3)$$

$$\sum_{i=1}^{n_c} y_{n,i} = 1 \quad (4)$$

and the equilibrium relations of course will be considered for the you know, as a complementary equation there here $y_{n,i}$ that should be equal to $K_{n,i} x_{n,i}$ where i is equal to 1 to n_c , here $K_{n,i}$ represents the distribution coefficient $x_{n,i}$ and $y_{n,i}$ are liquid and vapour phase composition and of course, it will be at equilibrium temperature and pressure.

(Refer Slide Time: 26:18)

Distribution coefficient

- The distribution coefficient, can be derived from equal chemical potentials of the liquid and vapor phase, which can be expressed as

$$K_{n,i} = \frac{\gamma_i(x_{n,i}, T_n) \cdot F_{p,i}(T_n, p) \cdot \varphi_i^0(T_n) \cdot p_i^0(T_n)}{\varphi_i(T_n, p, y_{n,i}) \cdot p}, \quad i = 1, \dots, n_c \quad (6)$$

N.B.: The exact formulation depends on the thermodynamic models selected to predict the individual quantities.

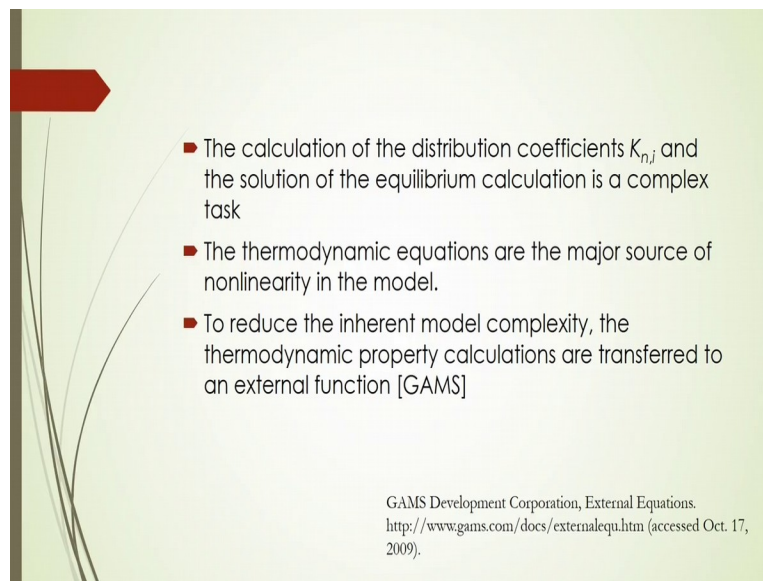
Where	$\gamma_i(x_{n,i}, T_n)$	= Activity coefficients,
	$F_{p,i}(T_n, p)$	= Poynting factors (Numerical factors name after John Henry Poynting, a Physicist, UK)
	$\varphi_i^0(T_n)$	= Pure component fugacity factors
	$p_i^0(T_n)$	= vapor pressures,
	$\varphi_i(T_n, p, y)$	= fugacity coefficients for the vapor mixture of component i .

What are those then distribution coefficient how it can be actually estimated? The distribution coefficient can be derived from equal chemical potentials of the liquid and vapour phase which can be expressed as given by this equation number 6 where $K_{n,i}$ is equal to this here.

$$K_{n,i} = \frac{\gamma_i(x_{n,i}, T_n) \cdot F_{p,i}(T_n, p) \cdot \varphi_i^0(T_n) \cdot p_i^0(T_n)}{\varphi_i(T_n, p, y_{n,i}) \cdot p}, \quad i = 1, \dots, n_c \quad (6)$$

So from this equation 6 you can calculate this distribution coefficient. In this case some parameters where it is denoted and it is given as a notation here $\gamma_i(x_{n,i}, T_n)$ is a function it will be activity coefficients, F_p is appointing factor that is numerical some factors name after John Henry Poynting, a Physicist that is United King based Physicist and here this φ_i^0 denotes the pure components fugacity factors and vapour pressures are denoted by you know p_i^0 whereas fugacity coefficients for the vapour mixture of competent i to be represented by this φ_i . So in this case you have to note down that the exact formulation that depends on thermodynamic models that is selected to predict the individual quantities.

(Refer Slide Time: 27:52)



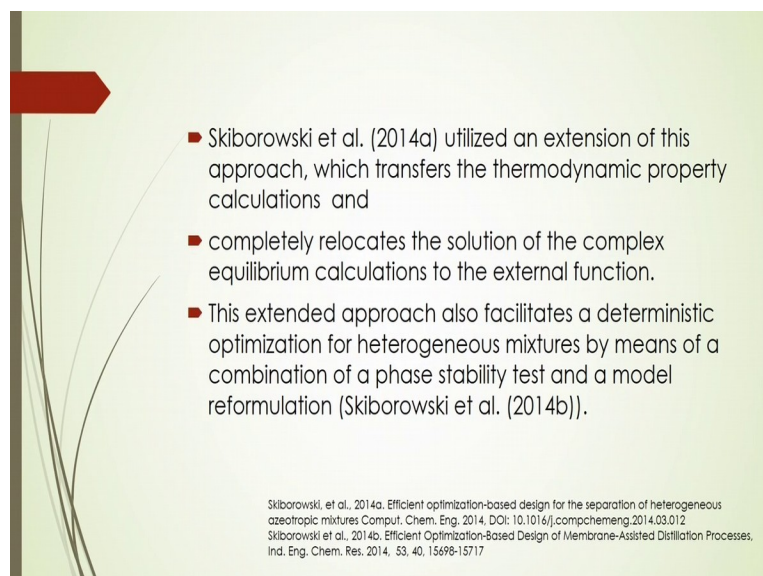
A slide with a light green background and a dark green vertical bar on the left. A red arrow points to the right. The slide contains three bullet points and a citation at the bottom right.

- The calculation of the distribution coefficients $K_{n,j}$ and the solution of the equilibrium calculation is a complex task
- The thermodynamic equations are the major source of nonlinearity in the model.
- To reduce the inherent model complexity, the thermodynamic property calculations are transferred to an external function [GAMS]

GAMS Development Corporation, External Equations.
<http://www.gams.com/docs/externalequ.htm> (accessed Oct. 17, 2009).

And the calculation of the distribution coefficient and the solution of the equilibrium calculation of course it is a tedious job and it is very complex method and the thermodynamic equations are the major source of non-linearity in the model and in this case to reduce the inherent model complexity, the thermodynamic property calculations of course to be transferred to an you know, external function that is called GAMS. You know that some tool that is developed by, you know GAMS Development Corporation and they have given some external equations based on which you can solve this problem and it is given, this website is given there so you can contact with **the Corporation** to you know, solve this problems based on their you know, external equations.

(Refer Slide Time: 28:52)



A slide with a light green background and a dark green vertical bar on the left. A red arrow points to the right. The slide contains three bullet points and a citation at the bottom right.

- Skiborowski et al. (2014a) utilized an extension of this approach, which transfers the thermodynamic property calculations and
- completely relocates the solution of the complex equilibrium calculations to the external function.
- This extended approach also facilitates a deterministic optimization for heterogeneous mixtures by means of a combination of a phase stability test and a model reformulation (Skiborowski et al. (2014b)).

Skiborowski, et al., 2014a. Efficient optimization-based design for the separation of heterogeneous azeotropic mixtures Comput. Chem. Eng. 2014. DOI: 10.1016/j.compchemeng.2014.03.012
Skiborowski et al., 2014b. Efficient Optimization-Based Design of Membrane-Assisted Distillation Processes, Ind. Eng. Chem. Res. 2014, 53, 40, 15698-15717

And also important to note that this extension of this approach of course to be considered which transfers the thermodynamic property calculations that is given by Skiborowski et al 2014 and as far they are actually approach it completely relocates the solution of the complex equilibrium calculations to the external function and this extended approach also facilitates a deterministic optimisation for you know, heterogeneous mixture by means of a combination of a phase stability tests and also model reformulation. This is also you know that, given by Skiborowski et al. 2014.

(Refer Slide Time: 29:51)

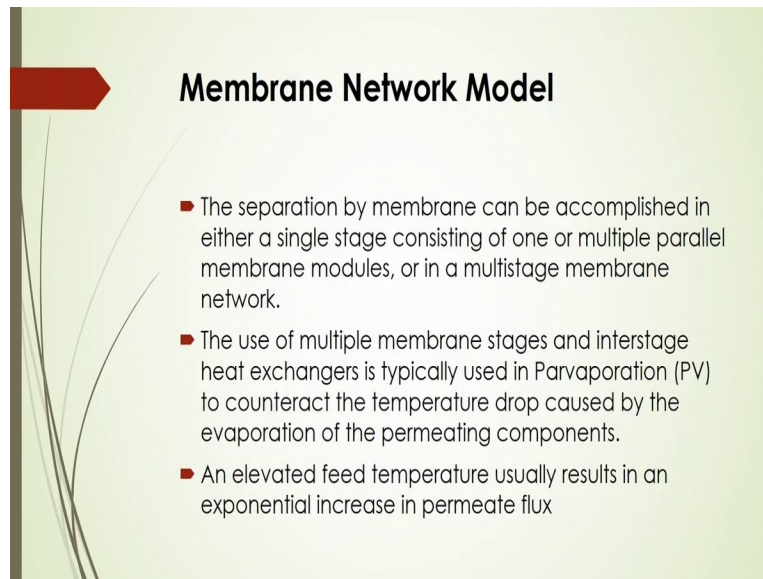
Design Degrees of Freedom of Distillation column

- The design degrees of freedom of a distillation column comprises:
 - the number of trays n_{trays} ,
 - the feed tray $n_{\text{feed, tray}}$ and side stream tray $n_{\text{side, tray}}$,
 - the operating pressure p ,
 - the reboiler and condenser heat duties Q_B and Q_C .

In order to optimize the number of trays, the feed and side stream locations, the binary decision variables ($b_{F,n}$, $b_{r,n}$, $b_{B,n}$, $b_{R,n}$, and $b_{S,n}$) need to be determined.

Now another one important aspect to actually consider for the design is called design degrees of freedom of distillation column, in this case the design degree of freedom of a distillation column that comprises the number of trays, the feed tray and the side stream tray, the operating pressure, the reboiler and condenser heat duties. In order to optimise the number of trays, the feed and side stream locations, the binary decision variables like $b_{F,n}$, $b_{r,n}$, $b_{B,n}$, $b_{R,n}$, and $b_{S,n}$ all those b need to be of course, determined.

(Refer Slide Time: 30:32)

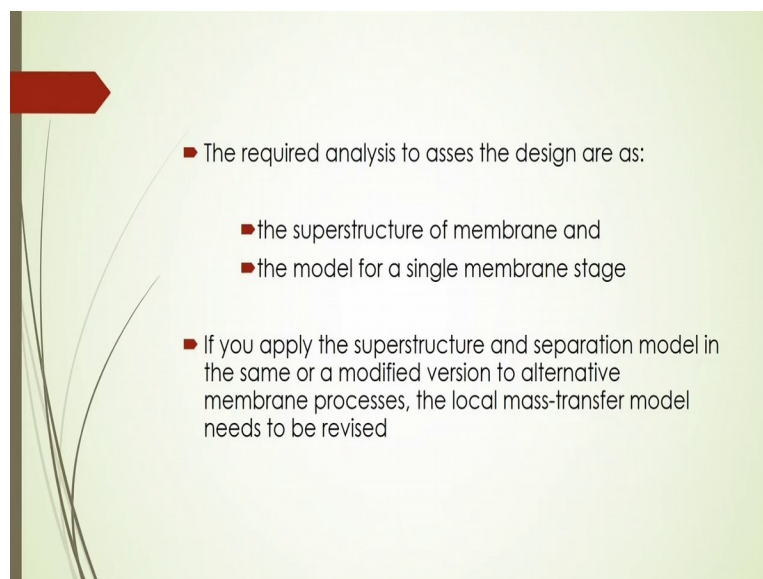


Membrane Network Model

- The separation by membrane can be accomplished in either a single stage consisting of one or multiple parallel membrane modules, or in a multistage membrane network.
- The use of multiple membrane stages and interstage heat exchangers is typically used in Parvaporation (PV) to counteract the temperature drop caused by the evaporation of the permeating components.
- An elevated feed temperature usually results in an exponential increase in permeate flux

And, then you have to consider that member network model to analyse that membrane, in that case the separation by membrane can be accomplished in either a single stage that may consist of one or multiple parallel membrane modules or in a multistage membrane network. The use of multiple membrane stages and interstage heat exchangers is typically used in Parvapouration to counteract the temperature drop that may caused by the evaporation of the you know, permeating components and elevated feed temperature also results in an exponential increase in permeate flux that you have to also consider wisely.

(Refer Slide Time: 31:27)

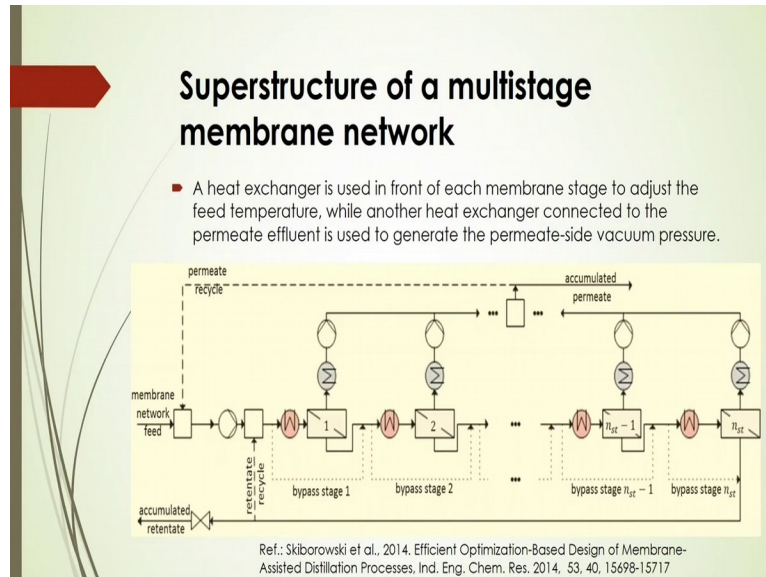


- The required analysis to asses the design are as:
 - the superstructure of membrane and
 - the model for a single membrane stage
- If you apply the superstructure and separation model in the same or a modified version to alternative membrane processes, the local mass-transfer model needs to be revised

And some you analysis of course to be required to assess that sign like the superstructure of the membrane how to actually procure and also the model for a single membrane stage and

also its selections. If you apply the superstructure and separation model in the same or modified version to you know, alternative membrane processors in that case the local mass transfer model you have to revise.

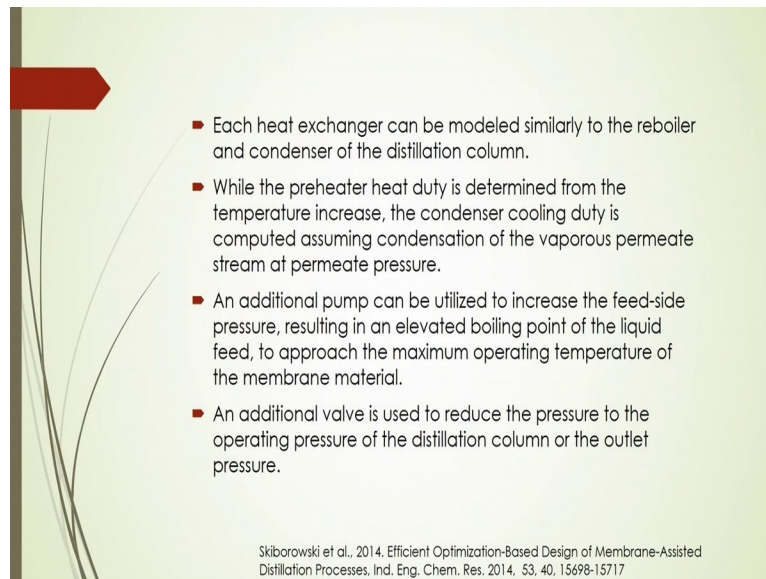
(Refer Slide Time: 32:00)



Superstructure of a multistage membrane network is shown here in a slide, in this case you will see that a heat exchanger is used in front of each membrane stage to adjust the feed temperature, while another heat exchanger connected to the membrane, the permeate side in that case it is used to generate the permit side vacuum pressure.

So these things to be considered whenever you are going to you know that, analyse based on the superstructure and separation model in the same or a modified version of alternative membrane processes for you know that or by, you know that...model, so these things to be considered.

(Refer Slide Time: 32:56)

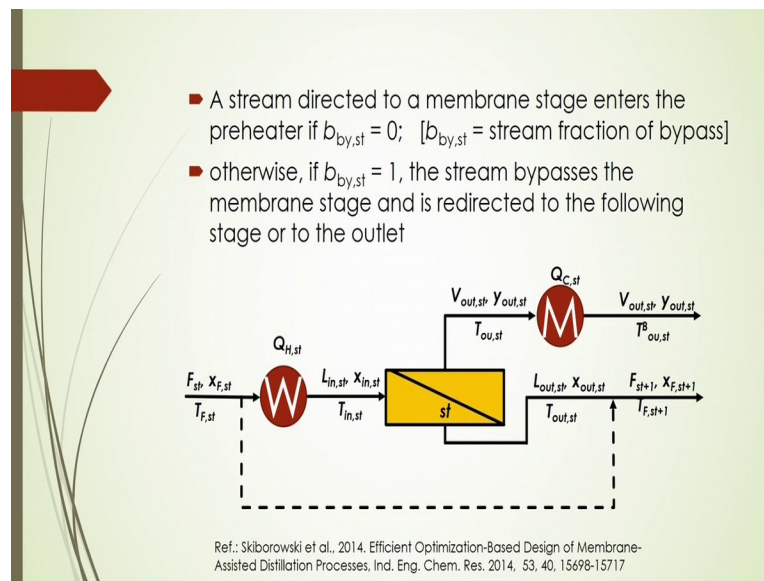


- Each heat exchanger can be modeled similarly to the reboiler and condenser of the distillation column.
- While the preheater heat duty is determined from the temperature increase, the condenser cooling duty is computed assuming condensation of the vaporous permeate stream at permeate pressure.
- An additional pump can be utilized to increase the feed-side pressure, resulting in an elevated boiling point of the liquid feed, to approach the maximum operating temperature of the membrane material.
- An additional valve is used to reduce the pressure to the operating pressure of the distillation column or the outlet pressure.

Skiborowski et al., 2014. Efficient Optimization-Based Design of Membrane-Assisted Distillation Processes. Ind. Eng. Chem. Res. 2014, 53, 40, 15698-15717

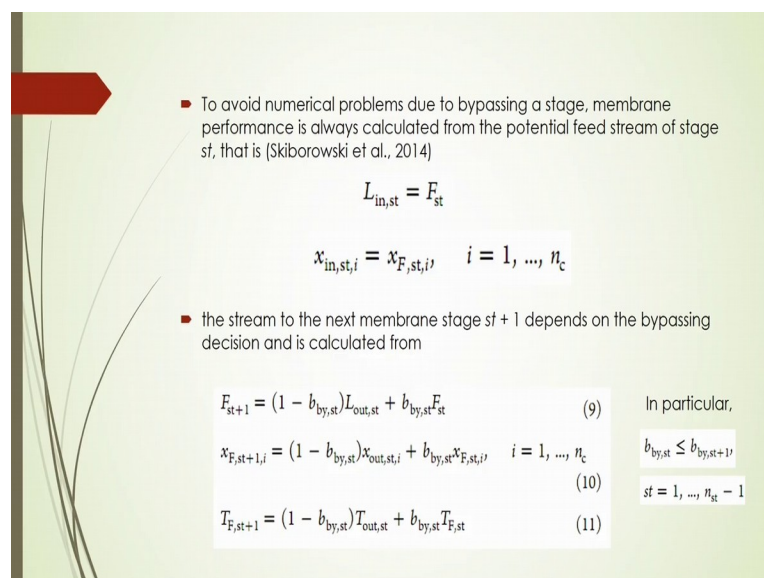
And each heat exchanger can be modelled similarly to the reboiler and condenser of the distillation column. While the preheater heat duty is determined from the temperature increase, the condenser cooling duty and those are to be computed assuming the condensation of the vaporous permeate stream at permeate pressure. In this case an additional pump are suggested to utilised to increase the feed stream pressure resulting in an elevated boiling point of the liquid feed, to approach the maximum operating temperature of the membrane material. Also you will see that additional valve is sometime used to reduce the pressure to the operating pressure of the distillation column or the outlet pressure and for this membrane network also internal recycles can significantly improve efficiency and also reduce the cost. By optimisation of the membrane area you can determine the number of membrane stages and also, if you want to facilitate the robust optimisation of the number of membrane stages of course you have to opt the bypass stream which is integrated into the superstructure for the each membrane stage. Of course it is suggested by this Skiborowski et al. in 2014.

(Refer Slide Time: 34:36)



And a stream that is directed to the membrane stage that is enters the preheater in this case, if this bypass you know that fraction, bypass stream fraction if it is 0 then the stream directed to the membrane stage that is enters to the preheater. If suppose bypass stream fraction is equal to 1, so in that case the stream bypass, the membrane stage is redirected the following stage or to the outlets\ here in this figure as shown in the slide.

(Refer Slide Time: 35:18)



And to avoid the numerical problems due to the bypassing stage in that case membrane performance which allows the calculation from the potential feed stream of stage that is here given by Skiborowski et al. 2014, as per their suggestion that should be in let flow rate of this liquid should be is equal to you know, F_{st} that is at the stage what is the feed

amount there. So x in stage i that will be x_F stage i where i is equal to 1 to n stage and in that case the stream to next membrane stage that is, stage plus 1 depends on the bypassing decision and that can be calculated from this equations here given in 9, 10 and 11.

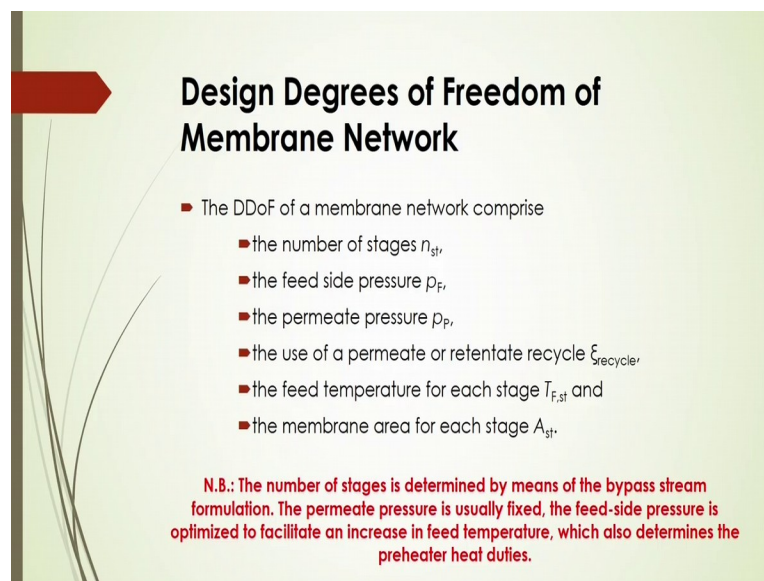
$$F_{st+1} = (1 - b_{by,st})L_{out,st} + b_{by,st}F_{st} \quad (9)$$

$$x_{F,st+1,i} = (1 - b_{by,st})x_{out,st,i} + b_{by,st}x_{F,st,i}, \quad i = 1, \dots, n_c \quad (10)$$

$$T_{F,st+1} = (1 - b_{by,st})T_{out,st} + b_{by,st}T_{F,st} \quad (11)$$

In this case you have to of course, note down the inequality for this you know that bypass fraction should be less than equals to that bypass fraction of stages of n plus 1.

(Refer Slide Time: 36:33)



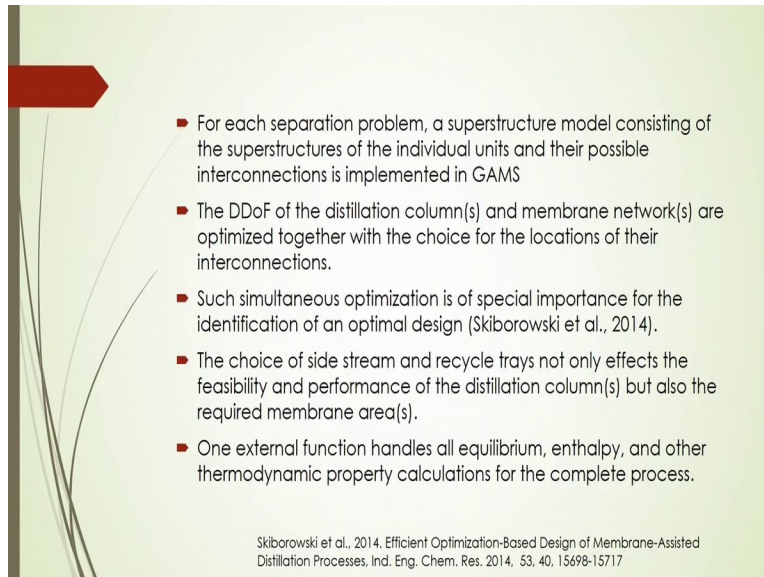
Design Degrees of Freedom of Membrane Network

- The DDoF of a membrane network comprise
 - the number of stages n_{st} ,
 - the feed side pressure p_F ,
 - the permeate pressure p_p ,
 - the use of a permeate or retentate recycle $\xi_{recycle}$,
 - the feed temperature for each stage $T_{F,st}$ and
 - the membrane area for each stage A_{st} .

N.B.: The number of stages is determined by means of the bypass stream formulation. The permeate pressure is usually fixed, the feed-side pressure is optimized to facilitate an increase in feed temperature, which also determines the preheater heat duties.

Now what will be the design degrees of freedom of membrane network, the design degrees of freedom of membrane network that of course, consists of a number of stages the feed side pressure, the permeate pressure, the use of a permeate or retentate recycle, the feed temperature for each stage and the membrane area for this stage. In this case you have to note down that the number of stage is determined by means of the bypass stream formulation and the permeate pressure is usually fixed and the feed side pressure is optimise to facilitate an increase in feed temperature which also determines the preheated heat duties.

(Refer Slide Time: 37:31)



- For each separation problem, a superstructure model consisting of the superstructures of the individual units and their possible interconnections is implemented in GAMS
- The DDoF of the distillation column(s) and membrane network(s) are optimized together with the choice for the locations of their interconnections.
- Such simultaneous optimization is of special importance for the identification of an optimal design (Skiborowski et al., 2014).
- The choice of side stream and recycle trays not only effects the feasibility and performance of the distillation column(s) but also the required membrane area(s).
- One external function handles all equilibrium, enthalpy, and other thermodynamic property calculations for the complete process.

Skiborowski et al., 2014. Efficient Optimization-Based Design of Membrane-Assisted Distillation Processes, Ind. Eng. Chem. Res. 2014, 53, 40, 15698-15717

For each separation problem, whenever you are considering the superstructure model that may consist of the superstructure of the individual units and their possible interconnections and of course in that case it is to be implemented in GAMS tools. The design degrees of freedom of the distillation column and the membrane networks are optimised together with that choice for the locations of their interactions such simultaneous optimisation is of special importance for the identification of an optimal design. That is actually given, there's a statement for this you know importance by Skiborowski et al. 2014 and you know that the choice of side stream and recycle trays not only affects that feasibility and performance of the distillation columns but also required that membrane areas as per conclusion of Skiborowski et al. 2014 and also, as according to their perception that one external function that may handles all equilibrium, enthalpy and other thermodynamic property calculations for the complete process.

(Refer Slide Time: 38:49)

Separation Model

- A membrane stage is usually comprised of multiple parallel membrane modules containing membrane sheets of fixed area
- A fixed length l_{st} and a variable width w_{st} are assumed in each membrane stage $st = 1, \dots, n_{st}$ to manipulate the total membrane area A_{st} .

Now for that if you are considering that membrane that will be used for separations after distillation, so what should be modelled to be used for that membrane **separation?** So a membrane stage which is usually comprised of multiple you know, parallel membranes modules that contains membrane sheets of fixed area, a fixed length l_{st} and a variable with w_{st} are shown figure in the slides are assumed in each membrane stages to you know, manipulate the total membrane area are that is denoted by A_{ST} .

(Refer Slide Time: 39:35)

- The membrane feed enters stage st with flow rate $L_{in, st}$, compositions $x_{in, st}$, and temperature $T_{in, st}$ on the retentate side, which operates at pressure $p_{p, st}$.
- Mass transfer through the membrane occurs along the flow direction z with permeation flux J and compositions m .
- The permeated stream evaporates on the permeate side due to the vacuum pressure $p_{p, st}$, which is sustained by condensation of the permeate stream with flow rate $V_{out, st}$ and compositions $Y_{out, st}$.
- The permeate pressure is limited by the condensation temperature $T_{out, st}^B$

And in this case the membrane feed enters a stage with flow rate compositions temperature on the retentate side which operates at pressure P . The mass transfer through the membrane that also to be considered that occurs along the flow direction z with permeation flux J and

compositions. The permeated stream evaporates on the permeate side due to the vacuum pressure which is sustained by condensation of the permeate stream with flow rate that is V out and the composition Y out that is in the outlet stream. The permeate pressure is limited by the condensation temperature there in the outlet streams.

(Refer Slide Time: 40:20)

- The change of the retentate and permeate stream along the membrane length z is described by means of the differential mass and enthalpy balances

$$\frac{dL_i}{dz} = -J_i \cdot w_{st}, \quad i, \dots, n_c \quad (12)$$

$$\frac{dV_i}{dz} = J_i \cdot w_{st}, \quad i, \dots, n_c \quad (13)$$

$$\frac{dh^L}{dz} = \frac{J}{L} w_{st} (h^L - h^V) \quad (14)$$

L_i and V_i = the local molar flow rates of component i on the retentate and permeate sides,

J_i = the local flux of component i from the retentate to the permeate side.

The molar enthalpy of the liquid retentate h^L and the vapor enthalpy of the permeate flux h^V are required in order to account for the temperature drop due to the evaporation of the permeate flux.

And in that case you have to you know, assist the change of retentate and permeate stream along the membrane lengths and that can be described by means of the differential mass and enthalpy balance here given, as in equation number 12, 13 and 14.

$$\frac{dL_i}{dz} = -J_i \cdot w_{st}, \quad i, \dots, n_c \quad (12)$$

$$\frac{dV_i}{dz} = J_i \cdot w_{st}, \quad i, \dots, n_c \quad (13)$$

$$\frac{dh^L}{dz} = \frac{J}{L} w_{st} (h^L - h^V) \quad (14)$$

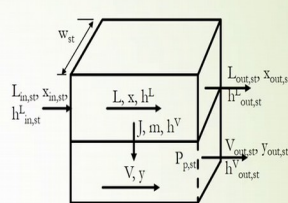
In this case you have to remember that molar enthalpy of the liquid retentate and the vapour enthalpy of the permeate flux which will be required in order to account for the temperature drop due to evaporation of the permit flux.

(Refer Slide Time: 40:54)

■ Additional algebraic equations are required to relate the component flow rates to the overall flow rates and compositions:

$$L = \sum_i^{n_c} L_i, L_i = x_i \cdot L, i, \dots, n_c \quad (15)$$

$$V = \sum_i^{n_c} V_i, V_i = y_i \cdot V, i, \dots, n_c \quad (16)$$

$$J = \sum_i^{n_c} J_i, J_i = m_i \cdot J, i, \dots, n_c \quad (17)$$


For the integration of the ordinary differential equations (ODEs) (eq 12–14) an efficient implicit Runge–Kutta method or other suitable method can be used.

Additional algebraic equation also to be required to you know, relate the component flow rates to the overall flow rates and compositions and equation number 15, 16 and 17

$$L = \sum_i^{n_c} L_i, L_i = x_i \cdot L, i, \dots, n_c \quad (15)$$

$$V = \sum_i^{n_c} V_i, V_i = y_i \cdot V, i, \dots, n_c \quad (16)$$

$$J = \sum_i^{n_c} J_i, J_i = m_i \cdot J, i, \dots, n_c \quad (17)$$

will represent those additional algebraic equations to relate that component flow with the overall flow rates and compositions. For the integration of the ordinary differential equations you can use you know, Runge-Kutta method or other suitable methods also you can use to solve these you know ordinary differential equations.

(Refer Slide Time: 41:37)

Local Mass-Transfer Model

- The transport of a component through the membrane can either be modeled by means of the solution-diffusion (SD) or pore-flow (PF) model.
- In most cases, mass transfer is described by means of a semiempirical model for the local flux

$$J_i = Q_i \cdot DF_i \quad i = 1, \dots, n_c$$

- This is based on experimentally validated permeances Q_i .
- The driving force DF_i is given by the difference in chemical potential,
- The driving force is often simplified to the difference in fugacities, activities, or partial pressures, depending on the type of membrane process.

And also for assessment of this membrane performance you have to you know that, consider that local mass transfer model in that case the transport of that component through the membrane can either be modelled by means of that solution diffusion or pore flow model. In most cases mass transfer is described by means of a semiempirical model for the local flux as shown in equation here in the slides

$$J_i = Q_i \cdot DF_i, \quad i = 1, \dots, n_c$$

and this is because of you know that there will be some driving force by difference in chemical potential and also this is based on the experimentally validated permeances that is Q and the driving force is often simplified to the difference in fugacities, activities or potential pressures that may depend on the type of, you know membrane process.

(Refer Slide Time: 42:36)



Solution Strategy

- The solver in GAMS Model can be used for decomposition and the relocation of the equilibrium calculations to the external function.
- A complex MINLP problem has to be solved, which requires careful initialization and a tailored solution strategy
- First determine a feasible solution utilizing the full process structure, that is, all column trays and membrane stages included in the superstructure.

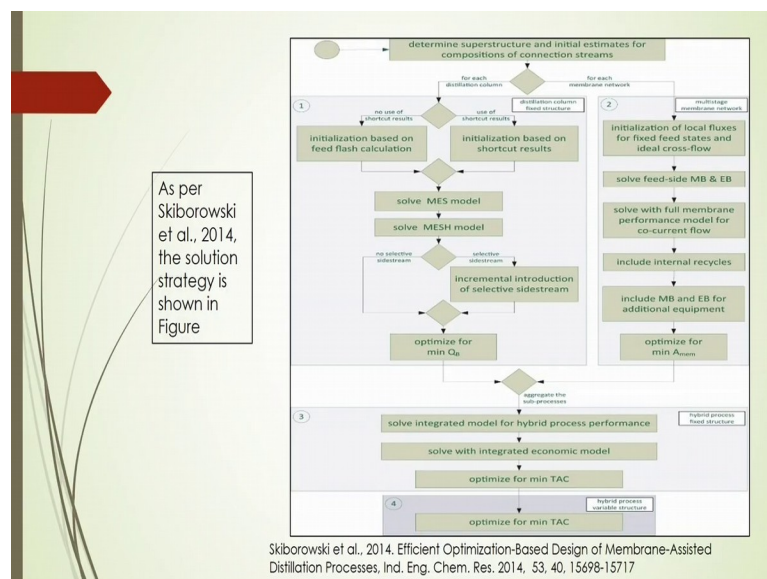
Now all those things that we have got different design equations for the distillation as well as membranes, now how to actually solve those design equations to get that you know optimum solution for that. In that case you can use solver in GAMS Model for decomposition and relocation of the equilibrium calculation to the external function and also a complex you know, non-linear program in problems has to be solved which requires careful initialisation and a tailored solution strategy and first determine a feasible solution that utilising the full process structure for the whole column and also all column trays and you know, membrane stages included in the superstructure.

(Refer Slide Time: 43:33)

- The optimal process is then determined by reducing the process structure and adjusting the operating conditions.
- For process optimization, an objective function needs to be defined, to reflect both operating and capital cost in form of total annualized cost (TAC).
- Operating cost mainly depend on heat exchanger duties and membrane replacement.
- Capital cost estimation for distillation columns is based on sizing equations
- The capital cost of the membrane process are simply related to the membrane area.

And also one of the important things that you have to consider for this optimum design in that case, you know that capital cost estimation for the distillation column is to be considered and that should be actually based on the sizing equation and those are related to the membrane area and also you know that, some cost function to be considered which is actually reflecting both operating and capital cost in form of total annualised cost and the optimal process is then determined by reducing the process structure and adjusting the operating conditions and optimal annual cost.

(Refer Slide Time: 44:22)



Now, as per Skiborowski et al. 2014 some solution strategy is shown in figure, here shown in slides their compact solution strategy is given in this slide. I suggest you to go through this

you know that figures to get that you know, compact idea of you know the solution strategy for the design solution of the hybrid process of membrane assisted distillation column.

(Refer Slide Time: 44:54)



Further reading.....

- David Reay, Colin Ramshaw, and Adam Harvey, Process Intensification: Engineering for efficiency, sustainability and flexibility, IChemE, 2nd edition, 2013, Elsevier.
- Kamelia Boodhoo and Adam Harvey. Process Intensification for Green Chemistry Engineering Solutions for Sustainable Chemical Processing, Edited by Kamelia Boodhoo and Adam Harvey, School of Chemical Engineering & Advanced Materials Newcastle University, UK. Wiley, 2013
- Juan Gabriel Segovia-Hernández, Adrián Bonilla-Petriciolet Editors, Process Intensification in Chemical Engineering Design Optimization and Control, Springer, 2016.
- Skiborowski et al., 2014. Efficient Optimization-Based Design of Membrane-Assisted Distillation Processes, Ind. Eng. Chem. Res. 2014, 53, 40, 15698-15717



Thank You

And also I would suggest to go for the reading, for better understanding of this you know membrane-based you know, distillation system, reactive distillation system and these are some reference that are included for your you know, better understanding of this membrane assisted reactive distillation process. So thank you for your attention for this lecture, next lecture we will discuss with some other module that is extraction module. So I would suggest you to follow those extraction models for the process intensification. Thank you.