Chemical Process Intensification.
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Model 5: Stochastic Optimisation for Process Intensification.
Lecture 5.3: Application of Optimisation Algorithms.

Welcome to massive open online course on Chemical Process Intensification. So, we are discussing the topics on module 5 as optimisation for process intensification. And in this lecture under this module 5 we will discuss something about applications of optimisation algorithms. We have already discussed some techniques methodology of that algorithms and also what are the different types of algorithms are actually present for analysis of chemical process based on this intensification of this process. And in this case we will then discuss about how that optimisation algorithms can be applied.

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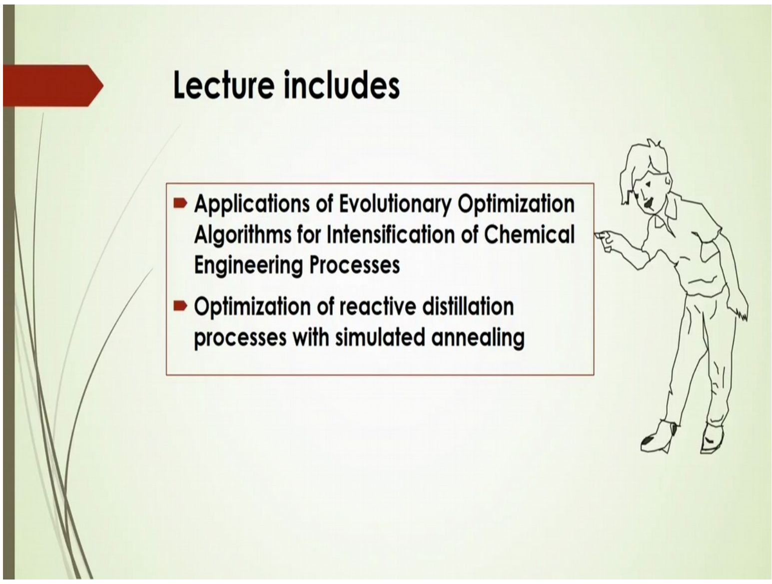

Lecture includes

- Applications of Evolutionary Optimization Algorithms for Intensification of Chemical Engineering Processes
- Optimization of reactive distillation processes with simulated annealing

So, we will discuss two portions of this lecture, here application of evolutionary optimisation algorithm, that is applied for chemical engineering processes. And also one example like that optimisation of reactive distillation process with certain specified optimisation algorithm like it is called simulated annealing.

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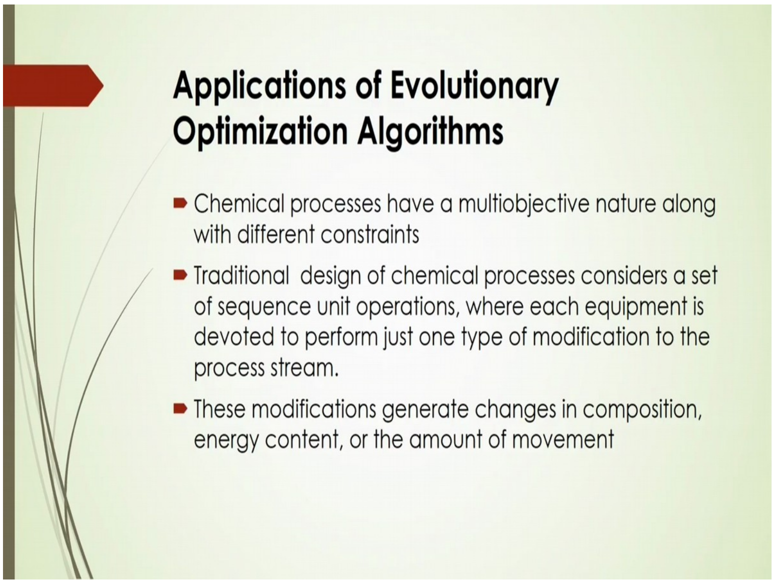

Applications of Evolutionary Optimization Algorithms

- Chemical processes have a multiobjective nature along with different constraints
- Traditional design of chemical processes considers a set of sequence unit operations, where each equipment is devoted to perform just one type of modification to the process stream.
- These modifications generate changes in composition, energy content, or the amount of movement

So, let us go back some extent of that optimisation algorithms where we have discussed the different types of algorithms for optimisation of single or multi-objective nature of that chemical engineering process. So, in that case evolutionary optimisation algorithm is one of the important algorithm by which you can apply or you can analyse that multi-objective nature chemical processes with different constraints.

And in this case the traditional design of the chemical process that we will consider is a set of sequences unit operations where each equipment is generally developed to perform just one type of modification to the process stream. And that modification actually generates changes in composition, energy content or that amount of you can say the movement of the phases there. And so that is why you can say that that chemical processes which will have multi-objective nature along with different constraints can be evaluated by the evolutionary optimisation algorithms.

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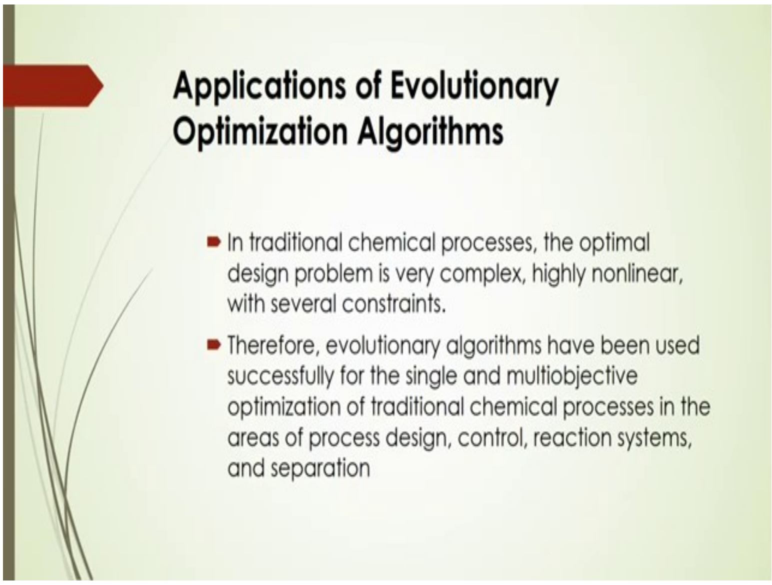

Applications of Evolutionary Optimization Algorithms

- In traditional chemical processes, the optimal design problem is very complex, highly nonlinear, with several constraints.
- Therefore, evolutionary algorithms have been used successfully for the single and multiobjective optimization of traditional chemical processes in the areas of process design, control, reaction systems, and separation

And this evolutionary optimisation algorithm in traditional chemical engineering processes. You will see the optimal design problems is very complex, highly nonlinear with several constraints. So, that is why evolutionary algorithms are generally successfully used for the single and multi-objective optimisation of those traditional chemical processes in the area as of process design, process control and also reaction systems parallelly separation also you can say there.

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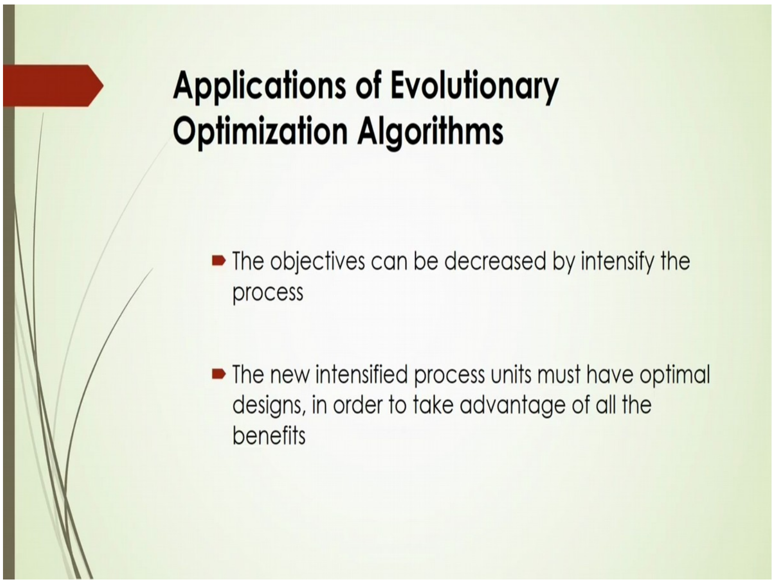

Applications of Evolutionary Optimization Algorithms

- The objectives can be decreased by intensify the process
- The new intensified process units must have optimal designs, in order to take advantage of all the benefits

So, that is why we are just going to discuss something about that application of that evolutionary optimisation algorithm. And in this case the objective can be decreased by intensify the process and the new intensified process units, it should be considered in such a way that it must have optimal design in order to take advantages of all benefits of the process.

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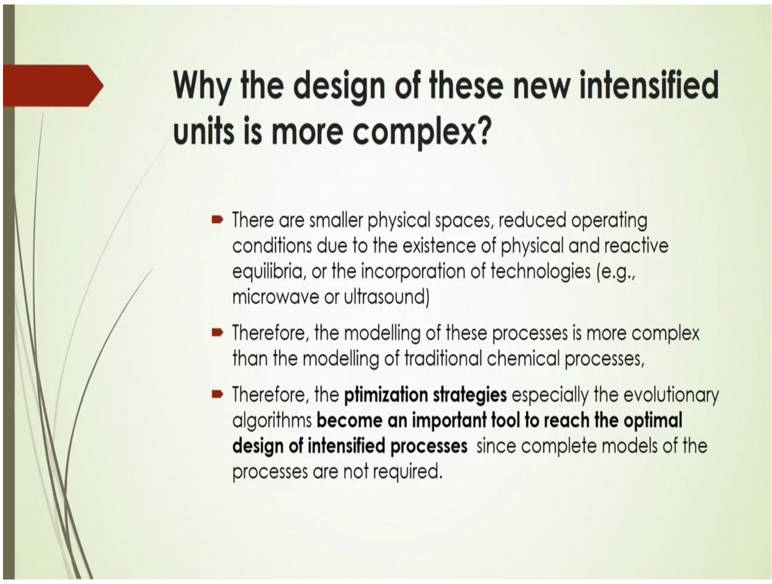

Why the design of these new intensified units is more complex?

- There are smaller physical spaces, reduced operating conditions due to the existence of physical and reactive equilibria, or the incorporation of technologies (e.g., microwave or ultrasound)
- Therefore, the modelling of these processes is more complex than the modelling of traditional chemical processes,
- Therefore, the **ptimization strategies** especially the evolutionary algorithms **become an important tool to reach the optimal design of intensified processes** since complete models of the processes are not required.

Now, why the design of this new intensified units is more complex whenever we are talking about that chemical engineering process intensification, of course, any process intensification we are talking that maybe that unit operations to be designed in such a way that will be more complex in some extent. So, why the design of those new intensified units should be more complex? In that case there are smaller physical spaces sometimes required in your process intensification.

In that case sometimes operating conditions to be reduced due to the existence of physical and reactive equilibrium or the incorporation of the technologies which are going to adapt for this process intensification like microwave techniques, ultrasound techniques to analyse or to design all those special technologies for the chemical process, it is very difficult to analyse based on the particular optimisation techniques. So, because there are various operating conditions to be considered for that tend to be very complex.

Therefore, the modelling of those process is more complex than the modelling of traditional chemical processes. For those cases you will see the optimisation strategies, especially the evolutionary algorithms become an important tool to reach the optimal design of intensified process, since the complete models of the process are not required in this case of evolutionary optimisation algorithm. So, this, the optimisation strategies is specially the evolutionary algorithm, that is why are very important to apply for such complex systems to get the optimal design of intensified processes.

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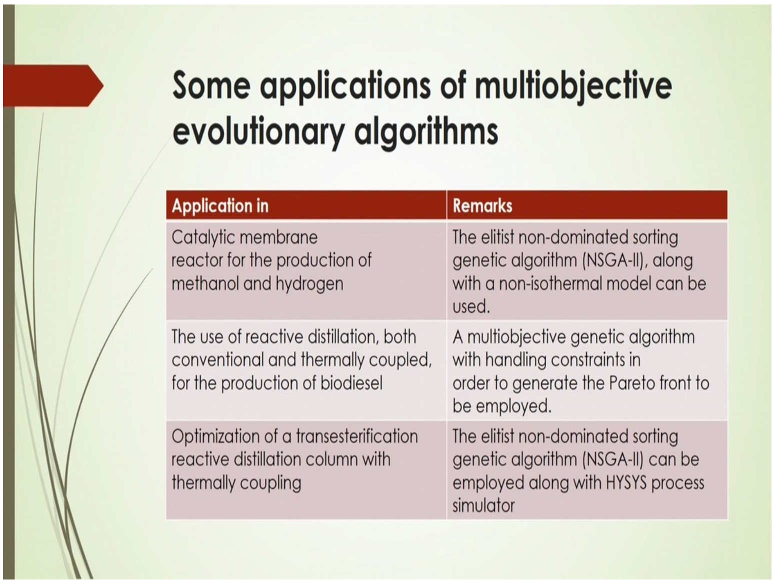

Some applications of multiobjective evolutionary algorithms

Application in	Remarks
Catalytic membrane reactor for the production of methanol and hydrogen	The elitist non-dominated sorting genetic algorithm (NSGA-II), along with a non-isothermal model can be used.
The use of reactive distillation, both conventional and thermally coupled, for the production of biodiesel	A multiobjective genetic algorithm with handling constraints in order to generate the Pareto front to be employed.
Optimization of a transesterification reactive distillation column with thermally coupling	The elitist non-dominated sorting genetic algorithm (NSGA-II) can be employed along with HYSYS process simulator

Some applications of multi-objective evolutionary algorithms are given here. You will see of course any process identified phenomena has different objectives whenever it will be executed any particular process synthesis there. So, in that case you have to solve those multi-objective operating conditions by those evolutionary algorithm. So, what are those special applications where you can apply the evolutionary algorithms based on that multi-objective function?

Now applications like catalytic membrane reactor for the production of methanol and hydrogen. In this case the elitist, non-dominated sorting genetic algorithm along with non-isothermal model can be actually considered to analyse the optimal solution of this particular process. So, we have already discussed the different types of genetic algorithms and what are the different steps and also sub algorithms of all those sets, already we have discussed in our previous lecture.

So, in that case this genetic algorithm that is non-dominated sorting genetic algorithm, it is called NSGA can be applied for such application of catalytic membrane reactor for the production of methanol and hydrogen. Another application like the use of reactive distillation where both conventional and thermally coupled systems are being used for the production of biodiesel. In that case again that multi-objective genetic algorithm with handling constraints in order to generate the Pareto front, that is set of optimal solutions that can be applied for the analysis of this reactive distillation.

Another important application there is called transesterification reaction there in reactive distillation column. In that case optimisation of that transesterification reaction in distillation, reactive distillation column with thermally coupling system to be done and for that optimisation the elitist non-dominated sorting again genetic algorithm can be used along with 5sys process simulator software there.

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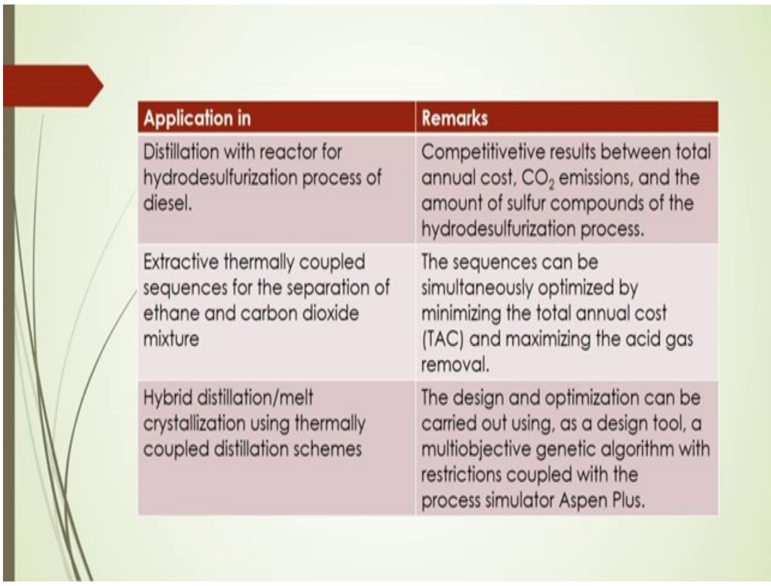

Application in	Remarks
Distillation with reactor for hydrodesulfurization process of diesel.	Competitivetive results between total annual cost, CO_2 emissions, and the amount of sulfur compounds of the hydrodesulfurization process.
Extractive thermally coupled sequences for the separation of ethane and carbon dioxide mixture	The sequences can be simultaneously optimized by minimizing the total annual cost (TAC) and maximizing the acid gas removal.
Hybrid distillation/melt crystallization using thermally coupled distillation schemes	The design and optimization can be carried out using, as a design tool, a multiobjective genetic algorithm with restrictions coupled with the process simulator Aspen Plus.

And also in the case of distillation with reactor for hydro desulphurisation process of diesel, there you can use some competitive results between total, annual cost, carbon dioxide emission and amount of sulphur compounds of the hydro desulphurisation process to be considered for the analysis of optimal solution, the distillation process with reactor for this beneficiation of the diesel by hydro desulphurisation. Another important application is called extractive thermally coupled, the sequences for the separation of ethane and carbon dioxide.

In this case you see that the sequences can be simultaneously optimised by minimising the total annual cost and maximising the acid gas removal there. So, in this case, it is very important that what are the sequences that you are going to consider there, in that particular extractive thermally coupled sequences for the separation of methane and carbon dioxide mixture? That should be optimised by the minimising the total annual cost and maximising the acid gas which is to be removed.

Hybrid distillation or melt crystallisation, that using thermally coupled distillation schemes can also be analysed for the optimisation process, where the design and optimisation can be carried out using as a design tool multi-objective genetic algorithm with restrictions that will be coupled with process simulator like Aspen plus.

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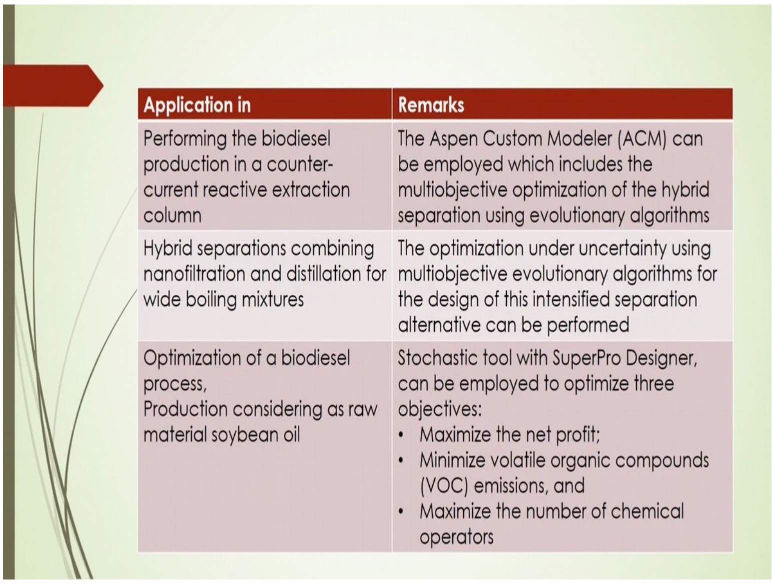

Application in	Remarks
Performing the biodiesel production in a counter-current reactive extraction column	The Aspen Custom Modeler (ACM) can be employed which includes the multiobjective optimization of the hybrid separation using evolutionary algorithms
Hybrid separations combining nanofiltration and distillation for wide boiling mixtures	The optimization under uncertainty using multiobjective evolutionary algorithms for the design of this intensified separation alternative can be performed
Optimization of a biodiesel process, Production considering as raw material soybean oil	Stochastic tool with SuperPro Designer, can be employed to optimize three objectives: • Maximize the net profit; • Minimize volatile organic compounds (VOC) emissions, and • Maximize the number of chemical operators

So, these are the applications. Another application like performing the biodiesel production in a counter current reactive extraction column. In that case you can use the Aspen custom modeler, which will actually include the multi-objective optimisation of the hybrid separation using evolutionary algorithms. And for the case of hybrid separations combining nano filtration and distillation for the wide boiling mixtures, the optimisation can be analysed under uncertainty using multi-objective evolutionary algorithms for the design of this intensified separation that alternative can be performed there.

And also optimisation of the biodiesel process like production of considering, in that case production that considers the raw material as a soya bean oil, in that case you can do that optimisation by stochastic tool with super pro designer tool and that is useful to optimise three objectives of this type of problem like maximise the net profit, maximise the number of chemical operators and also minimise the volatile, organic compounds that emitted during that production process.

So, you can optimise that biodiesel process based on the raw materials of the soya bean oil by this stochastic tool of super pro designer based on the objectives like maximisation of the net profit, minimisation of the volatile organic compounds, emission and also maximisation of the number of the number of chemical operators.

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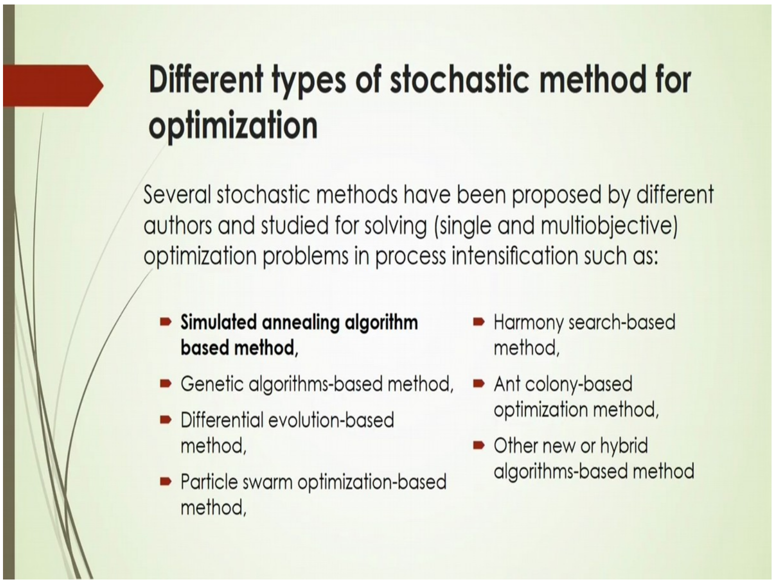

Different types of stochastic method for optimization

Several stochastic methods have been proposed by different authors and studied for solving (single and multiobjective) optimization problems in process intensification such as:

- **Simulated annealing algorithm based method,**
- Genetic algorithms-based method,
- Differential evolution-based method,
- Particle swarm optimization-based method,
- Harmony search-based method,
- Ant colony-based optimization method,
- Other new or hybrid algorithms-based method

Now what are the different types of the stochastic methods for optimisation are generally being used, that already we have discussed in our earlier lecture, the different types of optimisation algorithm, optimisation methods are available to analyse or to solve the single and multi-objective optimisation problems in process intensification.

So, here again we can have a list here like simulated annealing algorithm-based method, genetic algorithms based method, differential evolution-based method, particle swarm optimisation based method, harmony search-based method, Ant colony based optimisation method and other different types of methods which are being suggested by different investigators nowadays. Even refinement of those algorithms, new algorithms are nowadays coming, that is revealed by different investigators after their research.

So, these are a few stochastic methods which are already being discussed in the earlier lecture in details, what are the different advantage, disadvantage, pros and cons and even you know that how to apply those things already we have in our previous lecture. So, here we will actually concentrate on one optimisation method is called simulated annealing algorithm based method.

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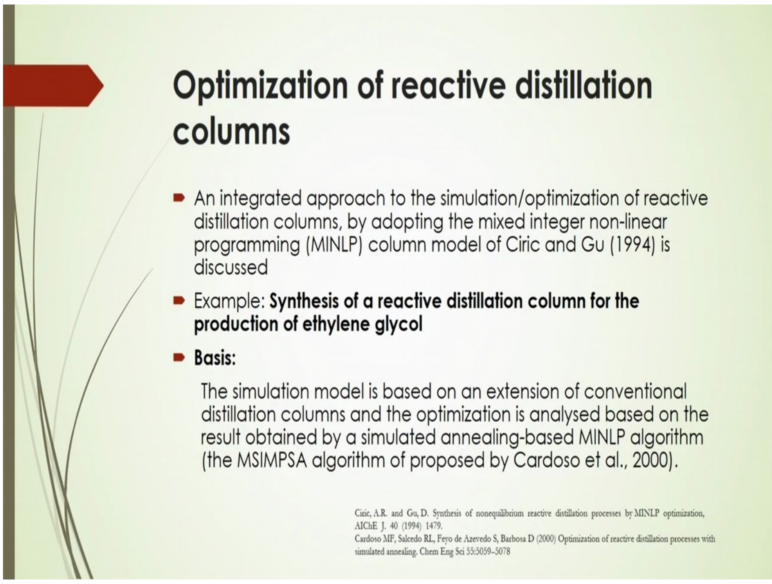

Optimization of reactive distillation columns

- An integrated approach to the simulation/optimization of reactive distillation columns, by adopting the mixed integer non-linear programming (MINLP) column model of Ciric and Gu (1994) is discussed
- Example: **Synthesis of a reactive distillation column for the production of ethylene glycol**
- **Basis:**

  The simulation model is based on an extension of conventional distillation columns and the optimization is analysed based on the result obtained by a simulated annealing-based MINLP algorithm (the MSIMPSA algorithm of proposed by Cardoso et al., 2000).

Ciric, A.R. and Gu, D. Synthesis of nonequilibrium reactive distillation processes by MINLP optimization, AIChE J. 40 (1994) 1479.
Cardoso MF, Salcedo RL, Feyo de Azevedo S, Barbosa D (2000) Optimization of reactive distillation processes with simulated annealing. Chem Eng Sci 55:5059–5078

Like if we consider the optimisation of reactive distillation column, in that case if we take that integration approach to the simulation or optimisation of the reactive distillation column, by adapting the mixer or also mixed integer nonlinear programming column model that is suggested by Ciric and Gu in 1994. So, this model actually it is called MINLP, that is called mixed integer nonlinear programming column model. And these models will be discussed here for this optimisation of reactive distillation column. In this case they have actually considered this synthesis of a reactive distillation column for the production of ethylene glycol.

So they have taken some basis for this simulation and the simulation model is based on an extension of conventional distillation columns and the optimisation is analysed based on that result obtained by simulated annealing based MINLP algorithm. And this is also called as MSIMPSA algorithm proposed by Cardoso et. al. in 2000 there. So, here we can say that if the simulated annealing based algorithm, it is called MSIMPSA, that is called that MINLP and which will be based on that simulated annealing. So, this algorithm, it is named as MSIMPSA algorithm, that is proposed by Cardoso et al.

And based on this SIMPSA algorithm, we can say that this similar trade annealing is a well established technique for the optimisation of combinatorial problems and also this can be done for the large scale functions that may assume several distinct discrete configurations, which are suggested in 1953.

And this simulated annealing based algorithm is suitable for the optimisation of mixed integer nonlinear programming problems, like you know that if you are considering that synthesis of non-equilibrium reactive distillation column, that you can apply this simulated annealing based algorithm.

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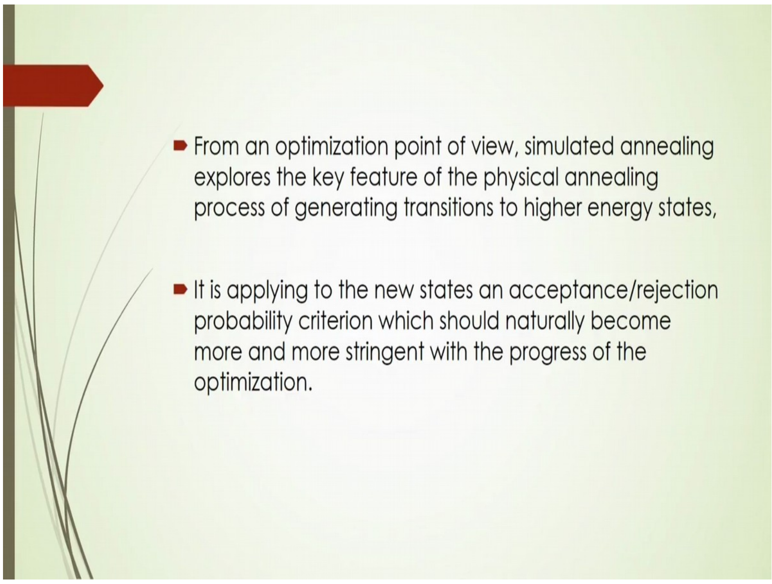

- From an optimization point of view, simulated annealing explores the key feature of the physical annealing process of generating transitions to higher energy states,
- It is applying to the new states an acceptance/rejection probability criterion which should naturally become more and more stringent with the progress of the optimization.

And from an optimisation point of view, this similar kit annealing explodes the key feature of the physical annealing process of generating transitions to higher energy states. And also it can be applied to the new states on whether it will be accepted or rejected, probability criterion on that particular acceptance and rejections, which should necessarily become more and more stringent with the progress of the optimisation.

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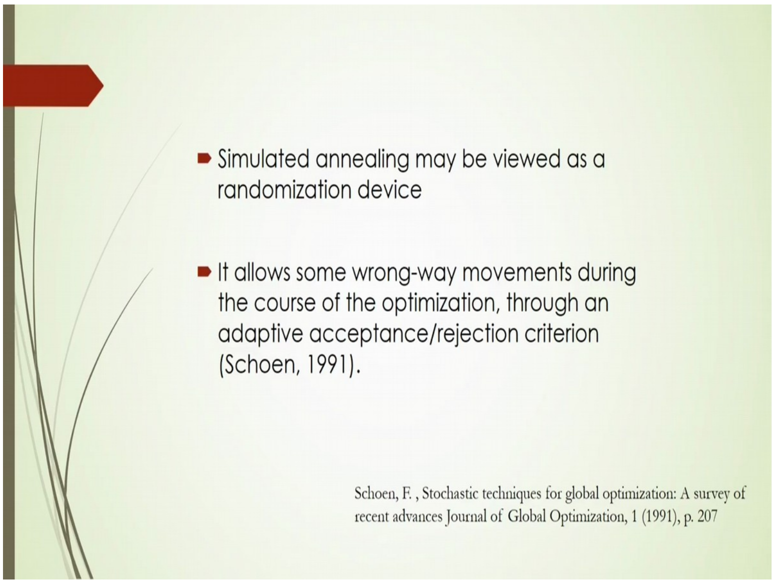

- Simulated annealing may be viewed as a randomization device
- It allows some wrong-way movements during the course of the optimization, through an adaptive acceptance/rejection criterion (Schoen, 1991).

Schoen, F. , Stochastic techniques for global optimization: A survey of recent advances Journal of Global Optimization, 1 (1991), p. 207

Now, these algorithms may be viewed as a randomisation device and it allows some wrong way movements during the course of optimisation. In that case you have to look at the picture where this wrong way movements during the course of the optimisation, whether it goes through an adaptive acceptance of or rejection criteria or not. So, that is actually observed by Schoen in 1991, this type of phenomena.

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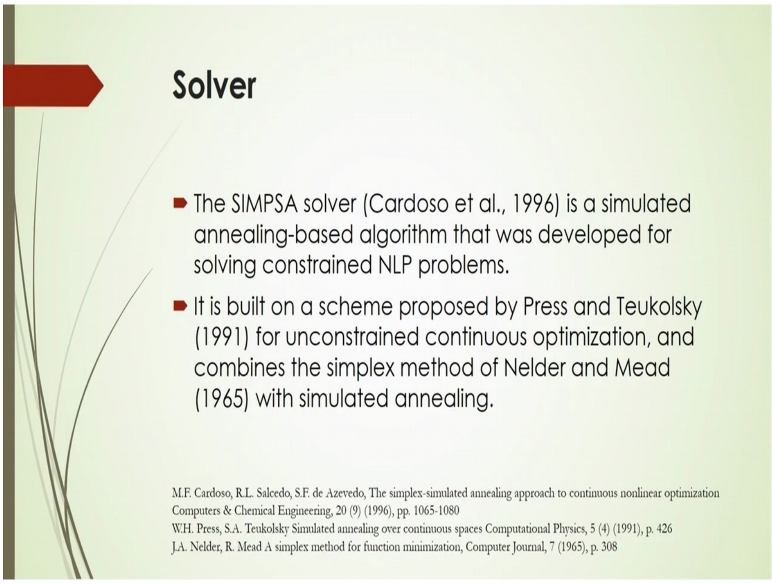

Solver

- The SIMPSA solver (Cardoso et al., 1996) is a simulated annealing-based algorithm that was developed for solving constrained NLP problems.
- It is built on a scheme proposed by Press and Teukolsky (1991) for unconstrained continuous optimization, and combines the simplex method of Nelder and Mead (1965) with simulated annealing.

M.F. Cardoso, R.L. Salcedo, S.F. de Azevedo, The simplex-simulated annealing approach to continuous nonlinear optimization Computers & Chemical Engineering, 20 (9) (1996), pp. 1065-1080
W.H. Press, S.A. Teukolsky Simulated annealing over continuous spaces Computational Physics, 5 (4) (1991), p. 426
J.A. Nelder, R. Mead A simplex method for function minimization, Computer Journal, 7 (1965), p. 308

What are the solver that you can use that for the optimisation of that particular problem of this reactive distillation column? In this case this SIMPSA solver, that suggested by Cardoso et al in 1996 can be used and it is a solver simulated annealing based algorithm that was developed for the solving constraints for the nonlinear programming problems. And it is generally built on a scheme that is proposed by Press and Teukolsky in 1991 for the unconstrained continuous optimisation and it combines the simplex method of, suggested by Nelder and Mead in 1965 with simulated annealing.

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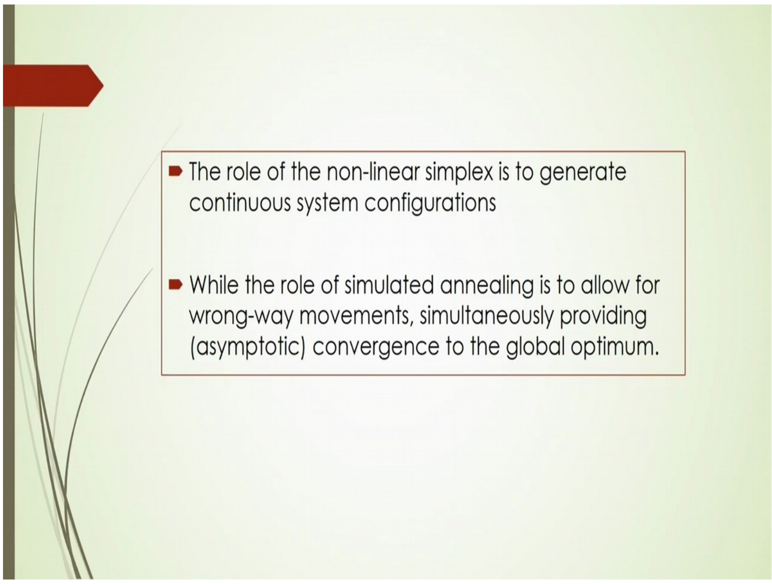

- The role of the non-linear simplex is to generate continuous system configurations
- While the role of simulated annealing is to allow for wrong-way movements, simultaneously providing (asymptotic) convergence to the global optimum.

And in this case the role of that nonlinear simplex will be to generate the continuous system configurations. Also while the role of similar tat annealing is to be there to allow for wrong way movements simultaneously providing convergence to the global optimum solution.

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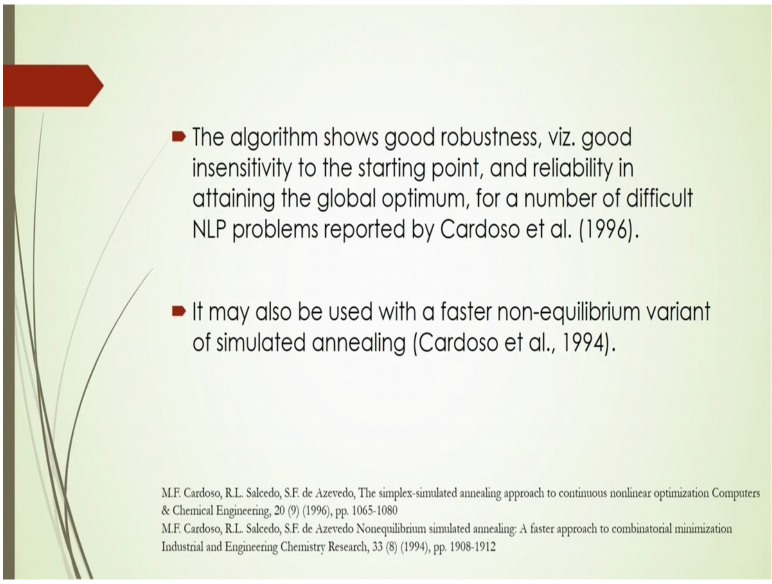

- The algorithm shows good robustness, viz. good insensitivity to the starting point, and reliability in attaining the global optimum, for a number of difficult NLP problems reported by Cardoso et al. (1996).
- It may also be used with a faster non-equilibrium variant of simulated annealing (Cardoso et al., 1994).

M.F. Cardoso, R.L. Salcedo, S.F. de Azevedo, The simplex-simulated annealing approach to continuous nonlinear optimization Computers & Chemical Engineering, 20 (9) (1996), pp. 1065-1080
M.F. Cardoso, R.L. Salcedo, S.F. de Azevedo Nonequilibrium simulated annealing: A faster approach to combinatorial minimization Industrial and Engineering Chemistry Research, 33 (8) (1994), pp. 1908-1912

And then this algorithm shows good robustness, like you no good insensitivity to the starting point and reliability and also you can say that how you can rely on this particular system that can attain the global optimum for a number of difficult NLP problems that is reported by Cardoso et al in 1996. It may also be used with a faster non-equilibrium variant of simulated annealing program like this that which has good insensitivity to the starting point and also has a reliability in attaining the global optimum solution.

Now MSIMPSA algorithm was developed by that Cardoso et al in 1997, it is coming actually based on that extension of the SIMPSA solver to deal with that mixed integer nonlinear programming problems. And in that case the continuous nonlinear solver is to be used to update the continuous parameters while the metropolis algorithm is used in an outer loop to update the complete set of decision variables.

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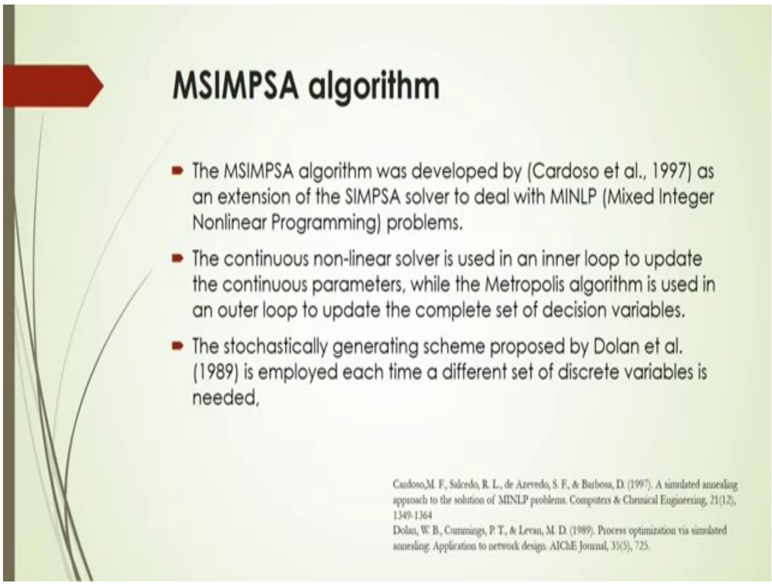

MSIMPSA algorithm

- The MSIMPSA algorithm was developed by (Cardoso et al., 1997) as an extension of the SIMPSA solver to deal with MINLP (Mixed Integer Nonlinear Programming) problems.
- The continuous non-linear solver is used in an inner loop to update the continuous parameters, while the Metropolis algorithm is used in an outer loop to update the complete set of decision variables.
- The stochastically generating scheme proposed by Dolan et al. (1989) is employed each time a different set of discrete variables is needed.

Cardoso,M. F., Salcedo, R. L., de Azevedo, S. F., & Barbosa, D. (1997). A simulated annealing approach to the solution of MINLP problems. Computers & Chemical Engineering, 21(12), 1349-1364

Dolan, W. B., Cummings, P. T., & Levan, M. D. (1989). Process optimization via simulated annealing: Application to network design. AIChE Journal, 35(5), 725.

So, the stochastically generating scheme proposed by Dolan et al can be employed each time a different set of discrete variables which will be required for this algorithm to analyse.

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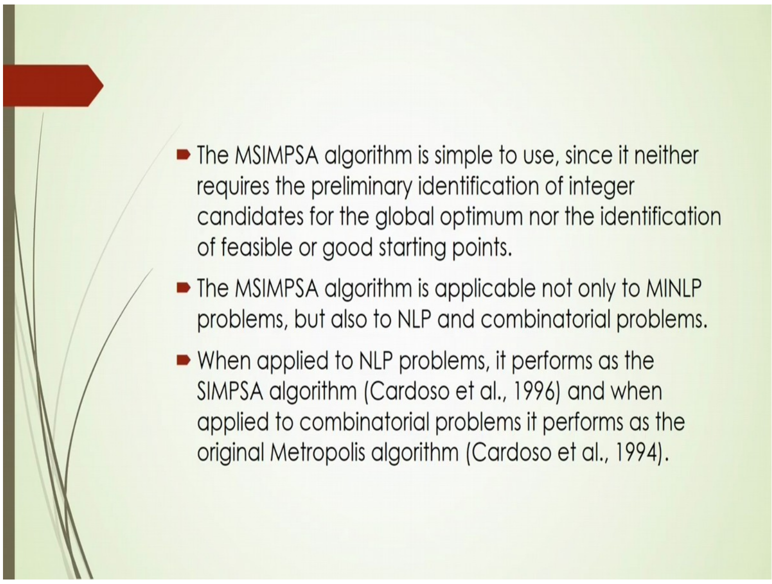

- The MSIMPSA algorithm is simple to use, since it neither requires the preliminary identification of integer candidates for the global optimum nor the identification of feasible or good starting points.
- The MSIMPSA algorithm is applicable not only to MINLP problems, but also to NLP and combinatorial problems.
- When applied to NLP problems, it performs as the SIMPSA algorithm (Cardoso et al., 1996) and when applied to combinatorial problems it performs as the original Metropolis algorithm (Cardoso et al., 1994).

And now this MSIMS algorithm is simple to use, since it neither requires the preliminary identification of integer candidates for the global optimum, nor the identification of feasible or good starting points there. So, in that case this M SIMS algorithm is applicable not only to that mixed integer nonlinear programming problems but also to the nonlinear programming and combinatorial problems also.

When if you are applying to this NLP problems, that is nonlinear programming problems, it may perform such the SIMS algorithm, that is suggested by Cardoso et al in 1996 and when applied to the combinatorial problems, it performs the original metropolis algorithm there. That is also given by Cardoso et al in 1994.

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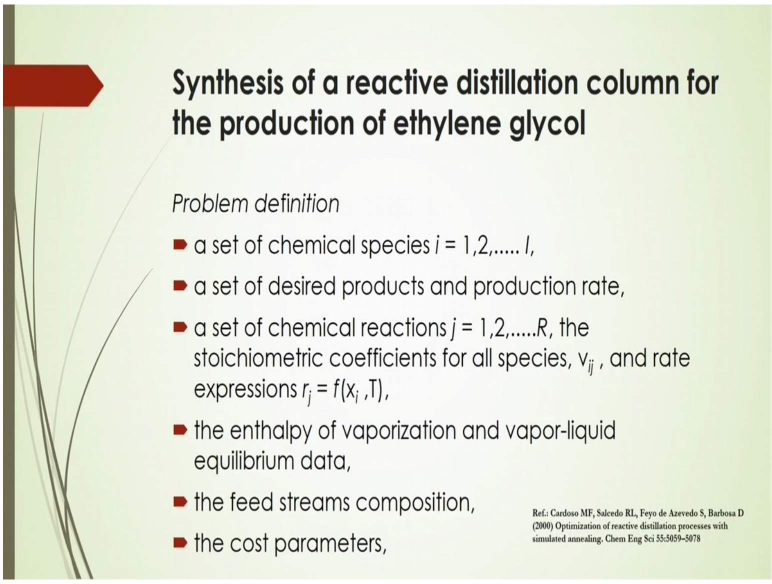

Synthesis of a reactive distillation column for the production of ethylene glycol

Problem definition

- a set of chemical species $i = 1,2,\ldots.. I$,
- a set of desired products and production rate,
- a set of chemical reactions $j = 1,2,\ldots..R$, the stoichiometric coefficients for all species, v_{ij}, and rate expressions $r_j = f(x_i, T)$,
- the enthalpy of vaporization and vapor-liquid equilibrium data,
- the feed streams composition,
- the cost parameters,

Ref.: Cardoso MF, Salcedo RL, Feyo de Azevedo S, Barbosa D (2000) Optimization of reactive distillation processes with simulated annealing. Chem Eng Sci 55:5059–5078

Now, let us have this synthesis of a reactive distillation column for the production of ethylene glycol that is described by Cardoso et al in 2000s, the paper published in chemical engineering science volume 55. So, they have given this problem definition like a set of chemical species, if you are representing by i, that will be equal to 1, 2, like this I. And also a set of desired products and production rate also.

And a set of chemical reactions denoted by *j*, like 1, 2,… R. The stoichiometric sufficient for all species is denoted by v_{ij}. And rate expressions are given as $r_j = f(x_i ,T)$, that will be a function of component fractions, you can say the compositions and also temperature. And the enthalpy of vaporisation and vapour liquid equilibrium data, the feed stream composition, the cost parameters. So, these are the problem definitions which are actually summarised like this.

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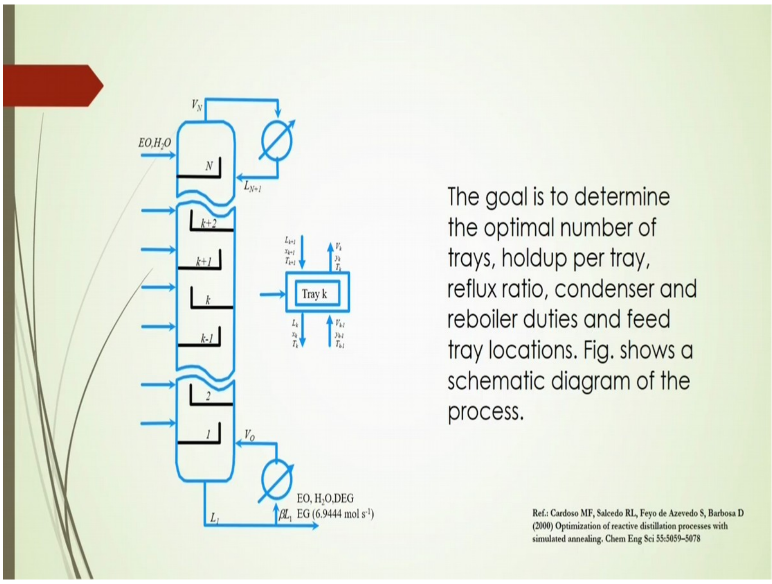

The goal is to determine the optimal number of trays, holdup per tray, reflux ratio, condenser and reboiler duties and feed tray locations. Fig. shows a schematic diagram of the process.

Ref.: Cardoso MF, Salcedo RL, Feyo de Azevedo S, Barbosa D (2000) Optimization of reactive distillation processes with simulated annealing. Chem Eng Sci 55:5059–5078

And they have considered this multi-trays distillation column there. And their goal was to determine the optimal number of trays here, hold up tray, hold up means what will be the volume fraction of that particular phases, the tray reflux ratio, condenser and reboiler duties and also what should be the feed tray locations that are to be optimised, that was their goal. So, it is shown in figure like this that process ethanol water mixture there and it will be supplied at different tray and what should be the optimal location of that feed tray and what should be the optimal reflux ratio condenser and reboiler duties.

So, I am not actually expressing how these operations, everybody knows that how distillation column is being operated, from the top that what is the vapour is coming up to distillation, some reflux, will be same and what will be going down, what will be an from the bottom also the heavy products to be boiled and then it will be supplied to that from the bottom. Like this the distillation, the conventional distillation column operation there. Now, in this case the main goal is to actually determine that optimum value of number of trays, hold-up per tray, reflux ratio, condenser and reboiler duties and also what should be the feed tray locations like these.

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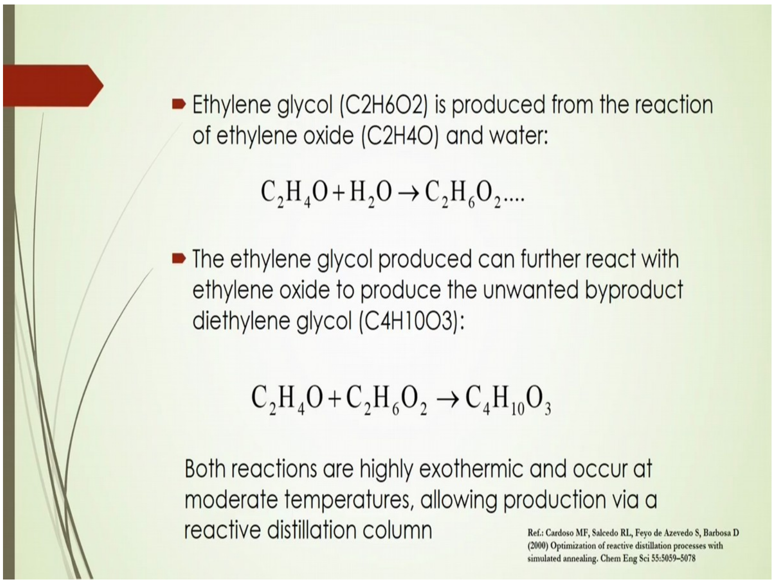

- Ethylene glycol (C2H6O2) is produced from the reaction of ethylene oxide (C2H4O) and water:

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2....$$

- The ethylene glycol produced can further react with ethylene oxide to produce the unwanted byproduct diethylene glycol (C4H10O3):

$$C_2H_4O + C_2H_6O_2 \rightarrow C_4H_{10}O_3$$

Both reactions are highly exothermic and occur at moderate temperatures, allowing production via a reactive distillation column

Ref.: Cardoso MF, Salcedo RL, Feyo de Azevedo S, Barbosa D (2000) Optimization of reactive distillation processes with simulated annealing. Chem Eng Sci 55:5059–5078

Now, what are the reactions actually being taken place here, in this particular reactive distillation column. So, in this case ethylene glycol is produced from the reaction of ethylene oxide and water there. So,

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2....$$

$$C_2H_4O + C_2H_6O_2 \rightarrow C_4H_{10}O_3$$

And the ethylene glycol produced can further react with ethylene oxide to produce the unwanted by-product that is diethylene glycol. And in this case both directions are you no highly exothermic and occur at moderate temperatures that will allow that production via reactive distillation column.

So, here in the slides, reactions are given, how the ethylene glycol is produced from the reaction of ethylene oxide and water and also ethylene glycol produced can further react with that ethylene oxide, that will give you that unwanted by-product is called diethylene glycol. Now, these both reactions of course will be exothermic and it will of course be carried out at a moderate temperature and in that case it will allow you the production via reactive distillation column.

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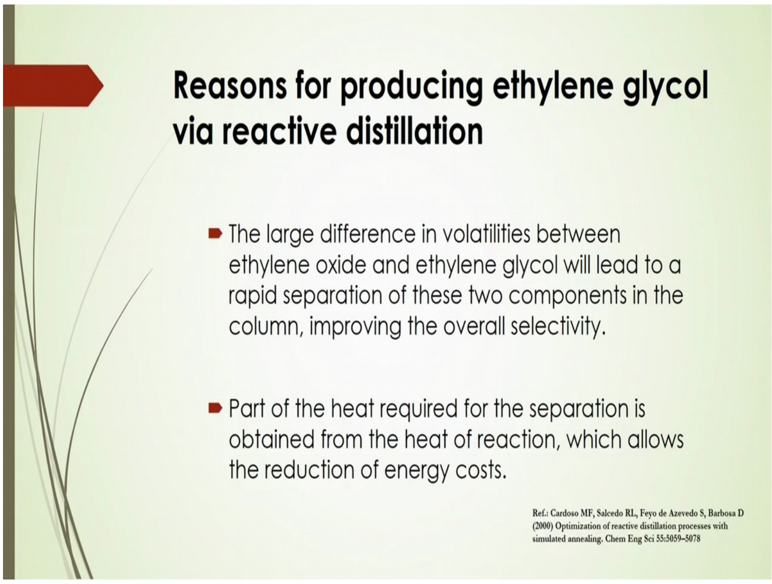

Reasons for producing ethylene glycol via reactive distillation

- The large difference in volatilities between ethylene oxide and ethylene glycol will lead to a rapid separation of these two components in the column, improving the overall selectivity.
- Part of the heat required for the separation is obtained from the heat of reaction, which allows the reduction of energy costs.

Ref.: Cardoso MF, Salcedo RL, Feyo de Azevedo S, Barbosa D (2000) Optimization of reactive distillation processes with simulated annealing. Chem Eng Sci 55:5059–5078

Now, why actually this production of ethylene glycol via reactive distillation. In this case the large difference in volatiles between ethylene oxide and ethylene glycol, that may lead to a rapid separation of these 2 components in the column that may improve the overall selectivity there. And part of the heat required for the separation that can be obtained from the heat of reaction, since it is exothermic reaction, which allows the reaction and also it may reduce the energy cost there. So, that is why reactive distillation is being actually chosen for the production of ethylene glycol via reactive distillation.

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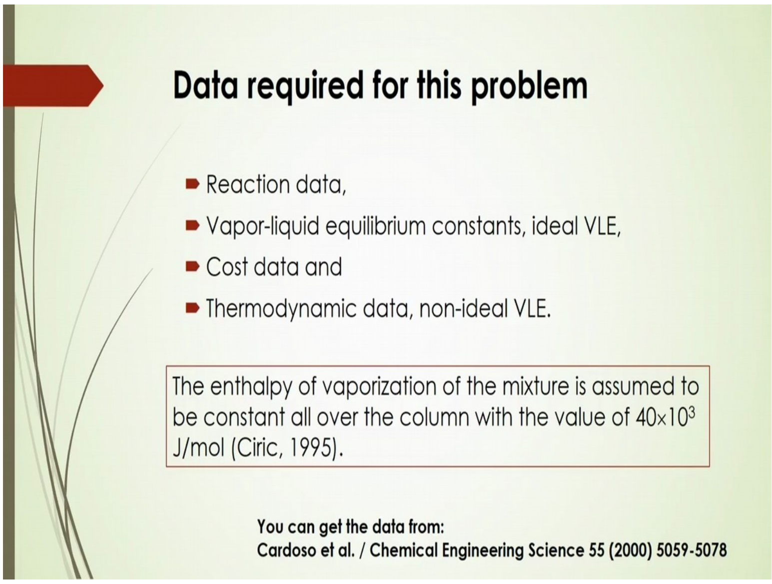

Data required for this problem

- Reaction data,
- Vapor-liquid equilibrium constants, ideal VLE,
- Cost data and
- Thermodynamic data, non-ideal VLE.

The enthalpy of vaporization of the mixture is assumed to be constant all over the column with the value of 40×10^3 J/mol (Ciric, 1995).

You can get the data from:
Cardoso et al. / Chemical Engineering Science 55 (2000) 5059-5078

And what are the data required for the problem here to optimise this process? In this case reaction data is required, vapour liquid equilibrium constants, ideal vapour liquid equilibrium data is required, what is the cost data and also what are the different thermodynamic data non-ideal vapour liquid equilibrium data, those are actually required for analysing this problem.

And this also very important to know that here the enthalpy of vaporisation of Mixture is assumed to be constant all over the column with the value of 40 into 10 to the power 3 joules per mole as per Ciric that is given in 1995. So, you make at these all data from this paper that is published by Cardoso et al in 2000s in chemical engineering science journal. So, you can take those data for further analysis there.

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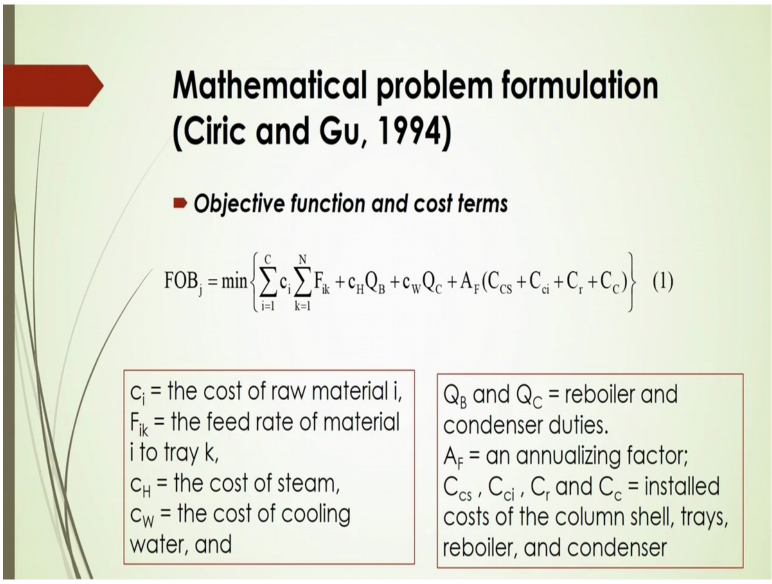

Mathematical problem formulation (Ciric and Gu, 1994)

- *Objective function and cost terms*

$$FOB_j = \min\left\{\sum_{i=1}^{C} c_i \sum_{k=1}^{N} F_{ik} + c_H Q_B + c_W Q_C + A_F (C_{CS} + C_{ci} + C_r + C_C)\right\} \quad (1)$$

c_i = the cost of raw material i,
F_{ik} = the feed rate of material i to tray k,
c_H = the cost of steam,
c_W = the cost of cooling water, and

Q_B and Q_C = reboiler and condenser duties.
A_F = an annualizing factor;
C_{CS} , C_{ci} , C_r and C_C = installed costs of the column shell, trays, reboiler, and condenser

Now, how to actually formulate that mathematical problem for those objective functions also cost terms there. So, as per Ciric and Gu, 1994, that objective function and the cost terms can be defined like this here.

$$FOB_j = \min\left\{\sum_{i=1}^{C} c_i \sum_{k=1}^{N} F_{ik} + c_H Q_B + c_W Q_C + A_F (C_{CS} + C_{ci} + C_r + C_C)\right\} \quad (1)$$

Where some rotations are given here as per equation 1, that ci will be equal to the cost of raw material i, F_{ik}, this is defined for the feed rate of material for i to tray k and CS referes the cost of the stream and CW is the cost of cooling water which is required for that distillation. And also you know that QB and QC, that will be reboiler and condenser duties which are very useful for that distillation operation. AF is actually referred to analysing factor and also

C_{CS}, C_{Ci}, C_R and C_C, all those terms are referred for the installed cost of the shell trays, reboiler and condenser respectively.

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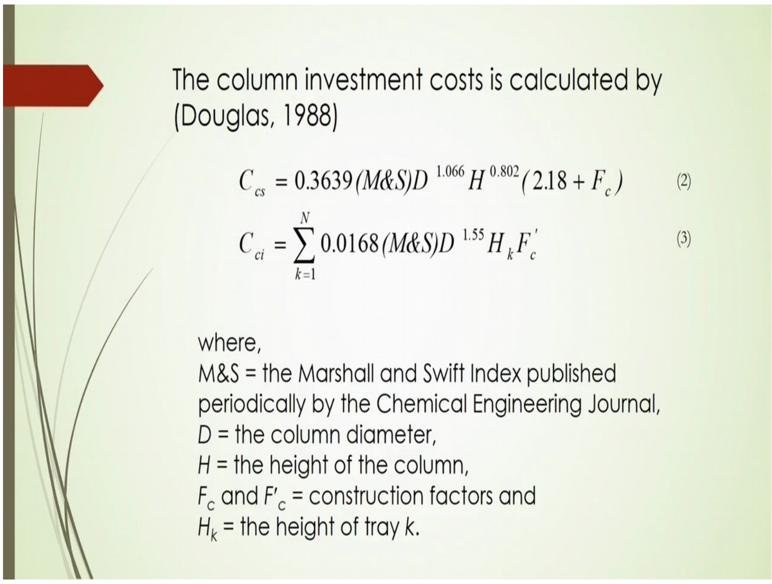

The column investment costs is calculated by (Douglas, 1988)

$$C_{cs} = 0.3639(M\&S)D^{1.066}H^{0.802}(2.18 + F_c) \qquad (2)$$

$$C_{ci} = \sum_{k=1}^{N} 0.0168(M\&S)D^{1.55}H_k F_c' \qquad (3)$$

where,
M&S = the Marshall and Swift Index published periodically by the Chemical Engineering Journal,
D = the column diameter,
H = the height of the column,
F_c and F'_c = construction factors and
H_k = the height of tray k.

So, here in this slide, those terms are given here.

And then how to calculate the call investment cost, that can be obtained from this equation numbers 2 and 3 are given in the slide here. It is given by Douglas in 1988 and this C_{CS} can be calculated from this equation number 2 and C_{Ci} can be calculated from this equation number 3, where the terms are defined here.

$$C_{cs} = 0.3639(M\&S)D^{1.066}H^{0.802}(2.18 + F_c)$$
$$C_{ci} = \sum_{k=1}^{N} 0.0168(M\&S)D^{1.55}H_k F_c'$$

M and S are actually represented here for the Marshall and Swift index that is published periodically by the chemical engineering journal. And D is a column diameter, H is the height of the column and F_C and F_c' dash are constructed factors. H_K is referred to as the height of the tray K. So, from these two equations you can calculate the investment and cost as per these equations.

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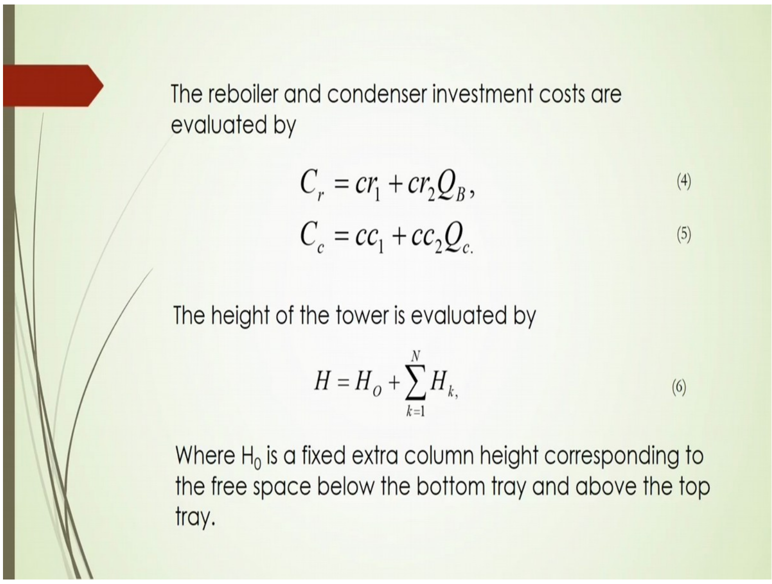

The reboiler and condenser investment costs are evaluated by

$$C_r = cr_1 + cr_2 Q_B, \quad (4)$$

$$C_c = cc_1 + cc_2 Q_{c.} \quad (5)$$

The height of the tower is evaluated by

$$H = H_O + \sum_{k=1}^{N} H_{k,} \quad (6)$$

Where H_0 is a fixed extra column height corresponding to the free space below the bottom tray and above the top tray.

And then how to calculate the reboiler and condenser investment costs, that can be actually calculated by these two equations of 4 and 5,

that is C_R, that is cost of reboiler, that will be equal to

$$C_r = cr_1 + cr_2 Q_B,$$
$$C_c = cc_1 + cc_2 Q_{c.}$$

And here the height of the tower is evaluated by H that will be equal to

$$H = H_O + \sum_{k=1}^{N} H_{k,}$$

if there is N number of trays, then you have to calculate that height respectively. Where, here H_0 is a fixed extra column height to be considered which will correspond to the free space below the bottom tray and above the top tray there.

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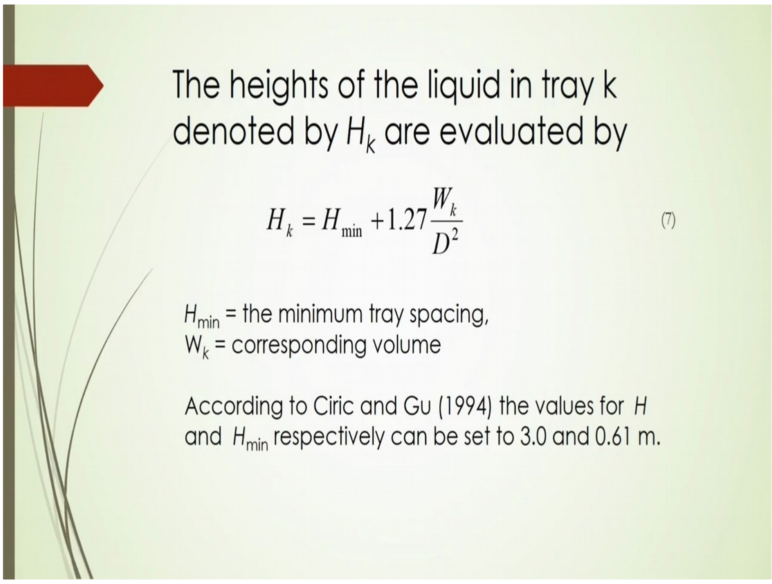

The heights of the liquid in tray k denoted by H_k are evaluated by

$$H_k = H_{\min} + 1.27\frac{W_k}{D^2} \quad (7)$$

H_{min} = the minimum tray spacing,
W_k = corresponding volume

According to Ciric and Gu (1994) the values for H and H_{min} respectively can be set to 3.0 and 0.61 m.

And here the heights of the liquid entry K, that will be denoted by H_K, that are calculated by

$$H_k = H_{\min} + 1.27\frac{W_k}{D^2}$$

And in this case, in the slide this HK, to be calculated based on that minimum tray-spacing and also what should be the corresponding volume to be considered here for the calculation of height of the liquid entry K.

So, this height of the liquid entry K actually as a function of that minimum tray spacing and corresponding volume of the liquid and also diameter of the column. According to this Ciric and Gu, the values for H and H min respectively can be set to 3.0 and 0.61 metres. So, as per this equation number 7, after substitution of this H min and also H, then what should be the W_K that also you can calculate.

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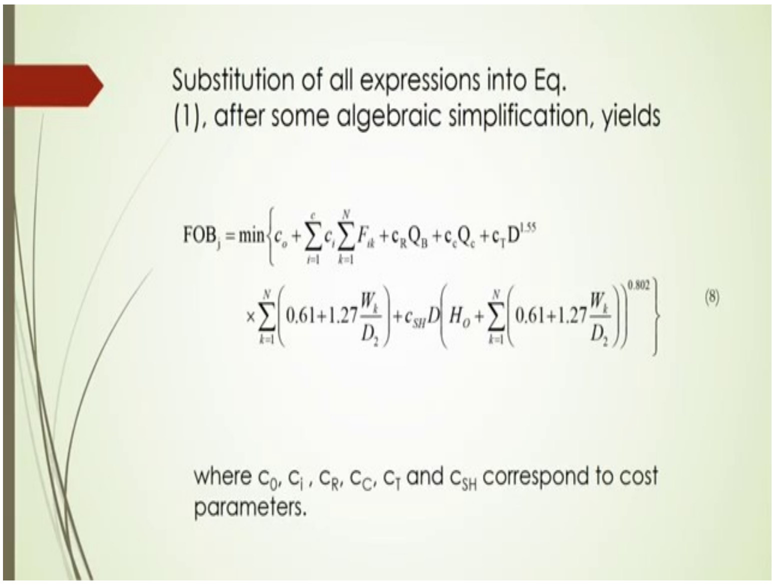

Substitution of all expressions into Eq. (1), after some algebraic simplification, yields

$$\mathrm{FOB_j} = \min\left\{ c_o + \sum_{i=1}^{c} c_i \sum_{k=1}^{N} F_{ik} + \mathrm{c_R Q_B} + \mathrm{c_c Q_c} + \mathrm{c_T D}^{1.55} \times \sum_{k=1}^{N}\left(0.61 + 1.27\frac{W_k}{D_2}\right) + c_{SH} D\left(H_O + \sum_{k=1}^{N}\left(0.61 + 1.27\frac{W_k}{D_2}\right)\right)^{0.802} \right\} \quad (8)$$

where c_0, c_i , c_R, c_C, c_T and c_{SH} correspond to cost parameters.

Now, substitution of all expressions into equation number 1, that is objective function after some algebraic simplifications, that will give you this equation number 8

$$\mathrm{FOB_j} = \min\left\{ c_o + \sum_{i=1}^{c} c_i \sum_{k=1}^{N} F_{ik} + \mathrm{c_R Q_B} + \mathrm{c_c Q_c} + \mathrm{c_T D}^{1.55} \times \sum_{k=1}^{N}\left(0.61 + 1.27\frac{W_k}{D_2}\right) + c_{SH} D\left(H_O + \sum_{k=1}^{N}\left(0.61 + 1.27\frac{W_k}{D_2}\right)\right)^{0.802} \right\}$$

and this equation will give you then the total objective function based on that different cost function and also cost parameters you can say.

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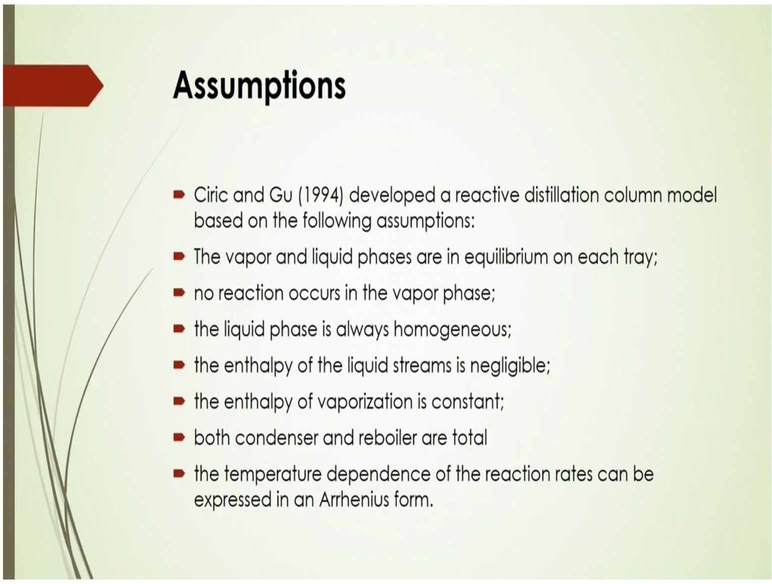

Assumptions

- Ciric and Gu (1994) developed a reactive distillation column model based on the following assumptions:
- The vapor and liquid phases are in equilibrium on each tray;
- no reaction occurs in the vapor phase;
- the liquid phase is always homogeneous;
- the enthalpy of the liquid streams is negligible;
- the enthalpy of vaporization is constant;
- both condenser and reboiler are total
- the temperature dependence of the reaction rates can be expressed in an Arrhenius form.

And after that you have to solve this problem optimisation problems by algorithm. So, for that you have to assume some constraints there. In this case as per Ciric and Gu in 1994, for this reactive distillation column and they have developed the reactive distillation column model based on the following assumptions like the vapour and liquid phases are to be in equilibrium on each tray that you have to consider. No reaction occurs in the vapour phase that also to be considered, the liquid phase is always has to be homogeneous, that is well mixed and the enthalpy of the liquid streams is to be neglected.

Also the enthalpy of the vaporisation should be considered as constant, both condenser and reboiler should be total and also the temperature dependence of the reaction rates can be expressed in an Arrhenius form. So, Arrhenius equation is to be used for that reaction to calculate the reaction rate and it should be temperature dependent.

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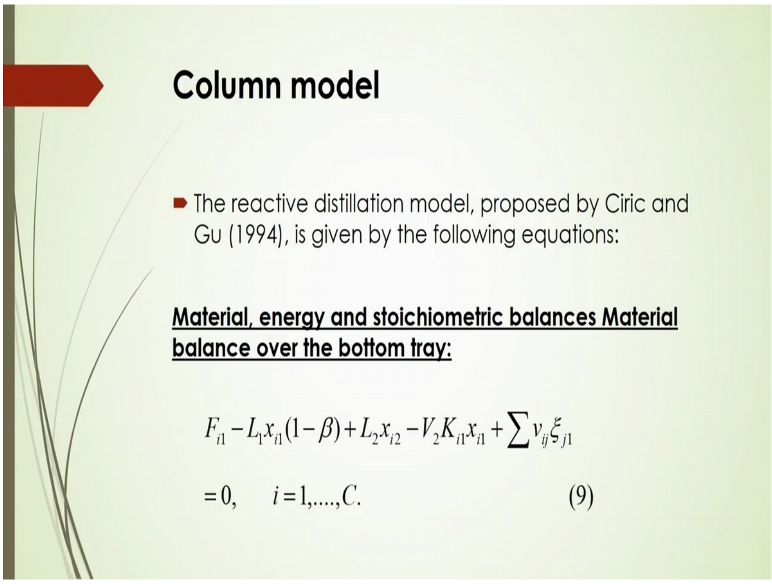

Column model

- The reactive distillation model, proposed by Ciric and Gu (1994), is given by the following equations:

Material, energy and stoichiometric balances Material balance over the bottom tray:

$$F_{i1} - L_1 x_{i1}(1-\beta) + L_2 x_{i2} - V_2 K_{i1} x_{i1} + \sum v_{ij}\xi_{j1}$$

$$= 0, \quad i = 1,....,C. \qquad (9)$$

And column model, how actually that column model is developed as per that Ciric and Gu. They have given the following equations from the material, energy and stoichiometric balances, that the material balance over the bottom tray, they have given this

$$F_{i1} - L_1 x_{i1}(1-\beta) + L_2 x_{i2} - V_2 K_{i1} x_{i1} + \sum v_{ij}\xi_{j1} = 0, \qquad i = 1,....,C.$$

where i equal to 1 to c. This is as per equation number 9, so you have to consider this equation number 9 for your calculations. So, as per this material balance over the bottom tray, that you can consider this equation number 9.

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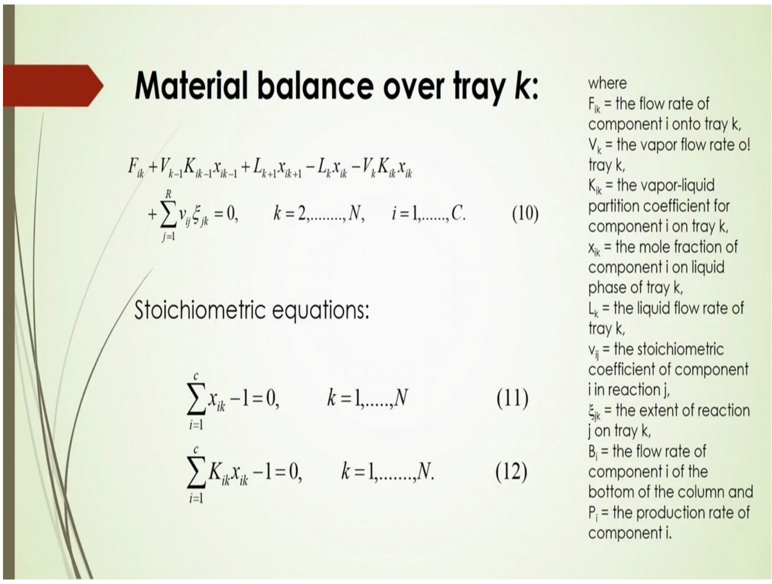

Material balance over tray k:

$$F_{ik}+V_{k-1}K_{ik-1}x_{ik-1}+L_{k+1}x_{ik+1}-L_kx_{ik}-V_kK_{ik}x_{ik}$$
$$+\sum_{j=1}^{R}v_{ij}\xi_{jk}=0, \qquad k=2,\dots\dots,N, \qquad i=1,\dots\dots,C. \qquad (10)$$

Stoichiometric equations:

$$\sum_{i=1}^{c}x_{ik}-1=0, \qquad k=1,\dots\dots,N \qquad (11)$$

$$\sum_{i=1}^{c}K_{ik}x_{ik}-1=0, \qquad k=1,\dots\dots,N. \qquad (12)$$

where
F_{ik} = the flow rate of component i onto tray k,
V_k = the vapor flow rate of tray k,
K_{ik} = the vapor-liquid partition coefficient for component i on tray k,
x_{ik} = the mole fraction of component i on liquid phase of tray k,
L_k = the liquid flow rate of tray k,
v_{ij} = the stoichiometric coefficient of component i in reaction j,
ξ_{jk} = the extent of reaction j on tray k,
B_i = the flow rate of component i of the bottom of the column and
P_i = the production rate of component i.

After that we have to do the material balance over the tray K,

$$F_{ik}+V_{k-1}K_{ik-1}x_{ik-1}+L_{k+1}x_{ik+1}-L_kx_{ik}-V_kK_{ik}x_{ik}$$
$$+\sum_{j=1}^{R}v_{ij}\xi_{jk}=0, \qquad k=2,\dots\dots,N, \qquad i=1,\dots\dots,C. \qquad (10)$$

this equation number 10 is giving the material balance over the tray K and what are the stoichiometric equations that can be actually obtained from this equation number 11 and 12 is given in the slide as

$$\sum_{i=1}^{c}x_{ik}-1=0, \qquad k=1,\dots\dots,N \qquad (11)$$
$$\sum_{i=1}^{c}K_{ik}x_{ik}-1=0, \qquad k=1,\dots\dots,N. \qquad (12)$$

So, summation of x_{ik}, that should be equal to 1 and summation of K_{ik} into x_{ik} should be equal to 1.

So, from this 11 and 12 equation number, you can calculate what should be the stoichiometric coefficients there. And in this case some notations are also given as per equation 10, 11, 12, so those notations to be actually considered for this particular equations for easy understanding of the different stream functions and other whatever parameters have to be there.

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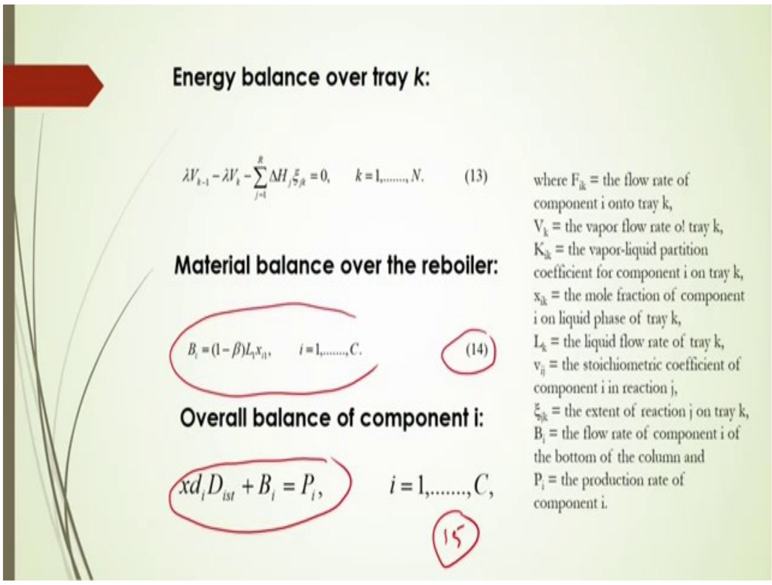

Energy balance over tray *k*:

$$\lambda V_{k-1} - \lambda V_k - \sum_{j=1}^{R} \Delta H_j \xi_{jk} = 0, \qquad k = 1,\ldots\ldots,N. \qquad (13)$$

Material balance over the reboiler:

$$B_i = (1-\beta)L_1 x_{i1}, \qquad i = 1,\ldots\ldots,C. \qquad (14)$$

Overall balance of component i:

$$xd_i D_{ist} + B_i = P_i, \qquad i = 1,\ldots\ldots,C,$$

15

where F_{ik} = the flow rate of component i onto tray k,
V_k = the vapor flow rate o! tray k,
K_{ik} = the vapor-liquid partition coefficient for component i on tray k,
x_{ik} = the mole fraction of component i on liquid phase of tray k,
L_k = the liquid flow rate of tray k,
v_{ij} = the stoichiometric coefficient of component i in reaction j,
ξ_{jk} = the extent of reaction j on tray k,
B_i = the flow rate of component i of the bottom of the column and
P_i = the production rate of component i.

And then you have to do the energy balance over the tray K, that equation 13 is giving its energy balance equation and material balance over the reboiler,

$$\lambda V_{k-1} - \lambda V_k - \sum_{j=1}^{R} \Delta H_j \xi_{jk} = 0, \qquad k = 1,\ldots\ldots,N. \qquad (13)$$

what would be that equation 14 is the material balance over the reboiler.

$$B_i = (1-\beta)L_1 x_{i1}, \qquad i = 1,\ldots\ldots,C. \qquad (14)$$

Whereas this overall balance of the component I can be expressed by this equation number, here if we consider it as equation number 15 as.

$$xd_i D_{ist} + B_i = P_i, \qquad i = 1,\ldots\ldots,C, \qquad (15)$$

So, this equation number 15 will give you the overall balance of component I. So, we are getting that material balance over tray K, energy balance over tray K, material balance over the reboiler, what should be the overall balance of component i.

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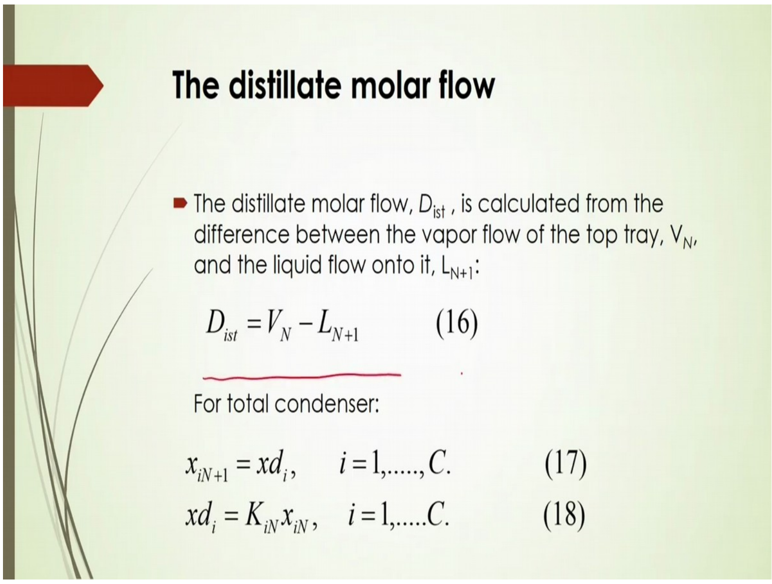

The distillate molar flow

- The distillate molar flow, D_{ist} , is calculated from the difference between the vapor flow of the top tray, V_N, and the liquid flow onto it, L_{N+1}:

$$D_{ist} = V_N - L_{N+1} \qquad (16)$$

For total condenser:

$$x_{iN+1} = xd_i, \quad i = 1,.....,C. \qquad (17)$$
$$xd_i = K_{iN}x_{iN}, \quad i = 1,.....C. \qquad (18)$$

And then you have to consider that distillate molar flow, so in that case this distillate molar flow D_{ist},

$$D_{ist} = V_N - L_{N+1} \qquad (16)$$

it will be denoted by that, so is calculated from the difference between the vapour flow of the top tray, that is V_N and the liquid flow onto it, that is denoted by L_{N+1}, that is as per equation number 16, then you can calculate the distillate molar flow that will be equal to V_N, that is vapour flow and also minus L_{N+1}, that is liquid flow.

So, for total condenser, you can consider that

$$x_{iN+1} = xd_i, \quad i = 1,.....,C. \qquad (17)$$
$$xd_i = K_{iN}x_{iN}, \quad i = 1,.....C. \qquad (18)$$ ’

that should be equal to xd_i and also xd_i should be is equal to $K_{iN}x_{iN}$. So, according to these equation numbers of 17 and 18, you can calculate what should be the mole fractions in tray N+1 and also N.

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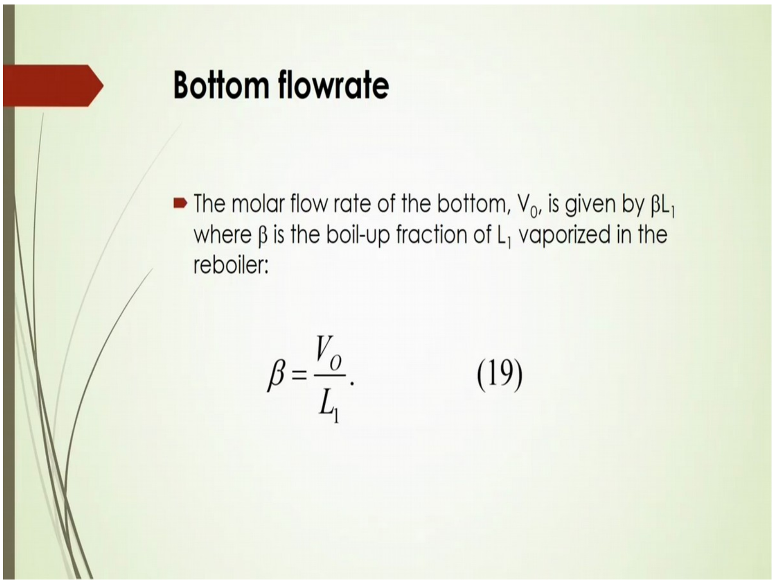

Bottom flowrate

- The molar flow rate of the bottom, V_0, is given by βL_1 where β is the boil-up fraction of L_1 vaporized in the reboiler:

$$\beta = \frac{V_O}{L_1}. \qquad (19)$$

And if you are considering the bottom flow rate, the molar flow rate of the bottom denoted by V_0 can be calculated by this beta into L, where beta is called boiler fraction of liquid stream L_1, that is vaporised in the reboiler, so beta should be equal to

$$\beta = \frac{V_O}{L_1}. \qquad (19)$$

that is given in the equation number 19 in the slide.

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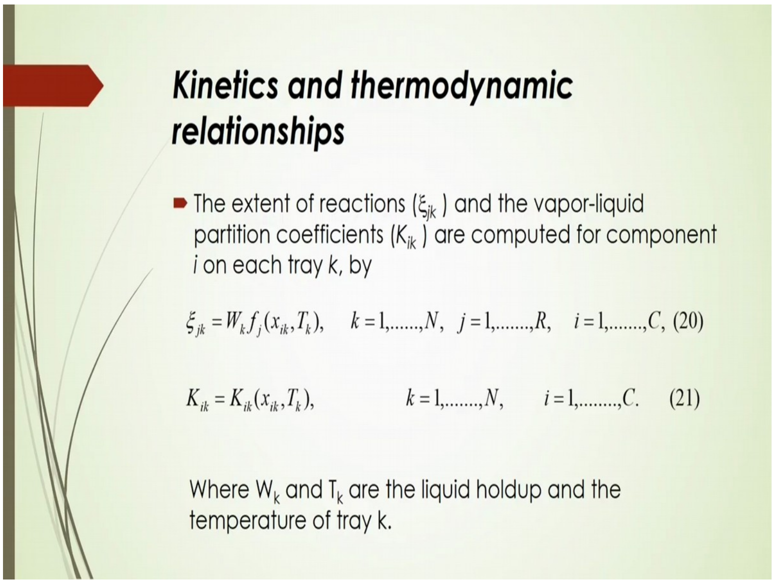

Kinetics and thermodynamic relationships

- The extent of reactions (ξ_{jk}) and the vapor-liquid partition coefficients (K_{ik}) are computed for component *i* on each tray k, by

$$\xi_{jk} = W_k f_j(x_{ik}, T_k), \quad k = 1, \ldots\ldots, N, \quad j = 1, \ldots\ldots, R, \quad i = 1, \ldots\ldots, C, \quad (20)$$

$$K_{ik} = K_{ik}(x_{ik}, T_k), \qquad k = 1, \ldots\ldots, N, \qquad i = 1, \ldots\ldots, C. \quad (21)$$

Where W_k and T_k are the liquid holdup and the temperature of tray k.

Now, after that you have to consider the kinetic and thermodynamic relationships. The extent of reactions ξ_{jk} and the vapour liquid partition coefficients or that is K_{ik} should be considered and those can be computed for component i on each tray by this equation 20 and also equation 21,

$$\xi_{jk} = W_k f_j(x_{ik}, T_k), \quad k = 1,......,N, \quad j = 1,.......,R, \quad i = 1,.......,C, \quad (20)$$

$$K_{ik} = K_{ik}(x_{ik}, T_k), \qquad k = 1,.......,N, \qquad i = 1,........,C. \qquad (21)$$

where this here W_K this and T_K are the liquid holdup and the temperature of the tray at K.

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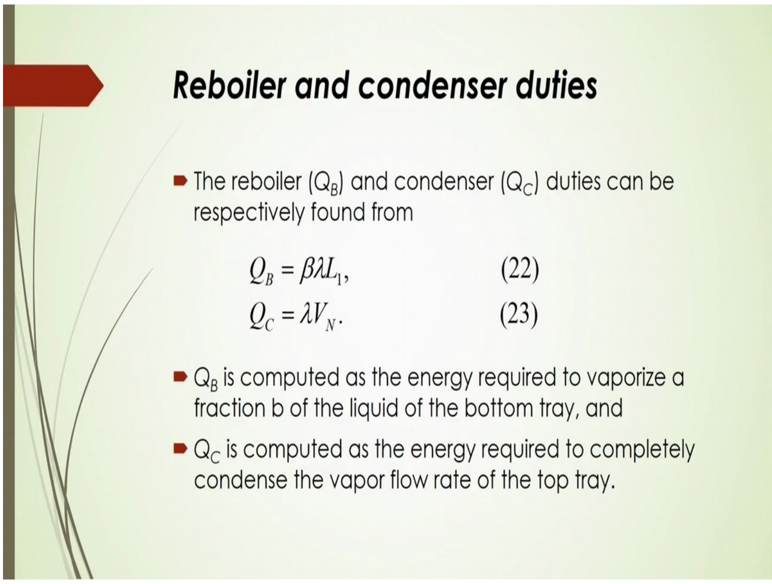

Reboiler and condenser duties

- The reboiler (Q_B) and condenser (Q_C) duties can be respectively found from

$$Q_B = \beta\lambda L_1, \qquad (22)$$
$$Q_C = \lambda V_N. \qquad (23)$$

- Q_B is computed as the energy required to vaporize a fraction b of the liquid of the bottom tray, and
- Q_C is computed as the energy required to completely condense the vapor flow rate of the top tray.

And this reboiler and condenser duties, how to calculate that, it can be calculated from this equation number 22 and 23.

$$Q_B = \beta\lambda L_1, \qquad (22)$$
$$Q_C = \lambda V_N. \qquad (23)$$

That is Q_B is equal to $\beta\lambda L_1$ and Q_C is equal to λV_N. And then Q_B is computed as the energy required to vaporise a fraction of B of the liquid of the bottom tray and Q_C is computed as the energy that is required to completely condensate the vapour flow rate of the top tray.

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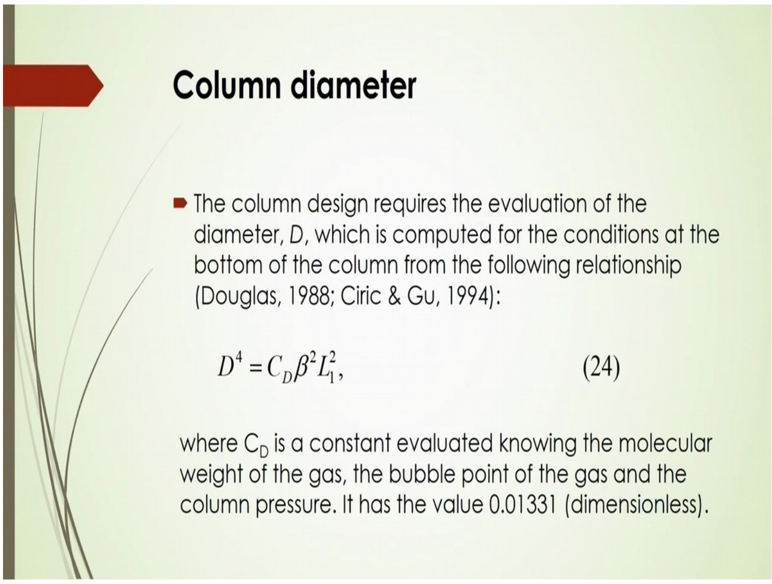

Column diameter

- The column design requires the evaluation of the diameter, D, which is computed for the conditions at the bottom of the column from the following relationship (Douglas, 1988; Ciric & Gu, 1994):

$$D^4 = C_D \beta^2 L_1^2, \qquad (24)$$

where C_D is a constant evaluated knowing the molecular weight of the gas, the bubble point of the gas and the column pressure. It has the value 0.01331 (dimensionless).

And then how to calculate that column diameter? The column design that will be required for the evaluation of the diameter D, which is computed or calculated for the conditions at the bottom of the column from the following equation, denoted by equation number 24,

$$D^4 = C_D \beta^2 L_1^2, \qquad (24)$$

that is given by Douglas in 1988 or you can follow that Ciric and Gu, 1994 paper. So, where in this case the C_D is a constant which is actually evaluated by knowing the molecular weight of the gas and the bubble point of the gas and the column pressure. So, it has a value of 0.01331 as a dimensionless as per you know that Ciric and Gu, that is given in 1994.

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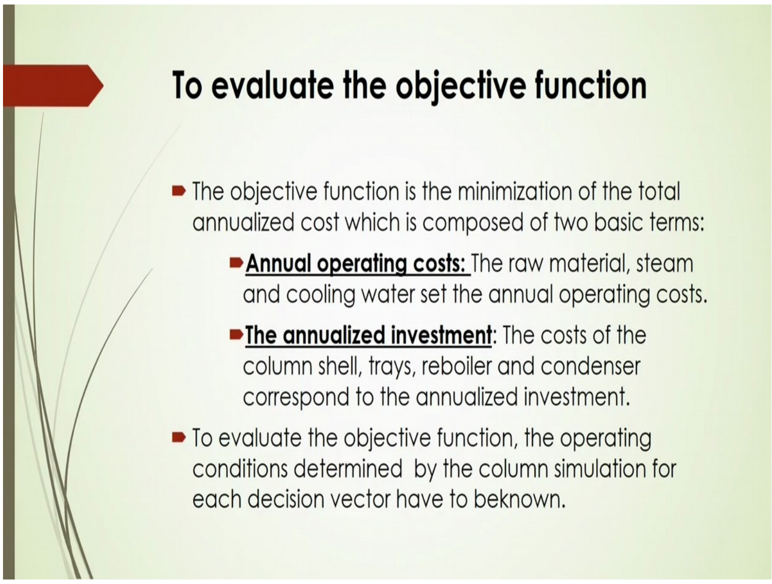

To evaluate the objective function

- The objective function is the minimization of the total annualized cost which is composed of two basic terms:
    - **Annual operating costs:** The raw material, steam and cooling water set the annual operating costs.
    - **The annualized investment**: The costs of the column shell, trays, reboiler and condenser correspond to the annualized investment.
- To evaluate the objective function, the operating conditions determined by the column simulation for each decision vector have to beknown.

Now, after that you have to evaluate the objective function. Now the objective function, that is actually minimisation of the total annualised cost, which is composed of two basic terms, to scold annual operating cost and the annualised investment. The annual operating cost actually it will come based on the raw materials, steam and cooling water, that aside for the operation annually and it will be considered that annual operating costs.

And then annualised investment should be the cost of the column shell trays, reboiler is, condenser, that will correspond to the annualised investment. And to evaluate this objective function, the operating conditions that will be determined by the column simulation for each decision vector that have to be known for that evaluation.

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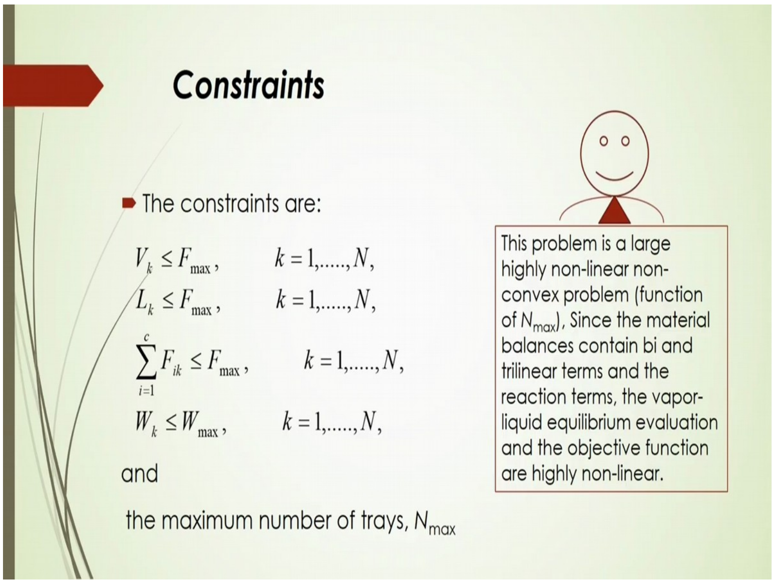

Constraints

- The constraints are:

$$
\begin{aligned}
&V_k \le F_{\max}, && k = 1,.....,N,\\
&L_k \le F_{\max}, && k = 1,.....,N,\\
&\sum_{i=1}^{c} F_{ik} \le F_{\max}, && k = 1,.....,N,\\
&W_k \le W_{\max}, && k = 1,.....,N,
\end{aligned}
$$

and

the maximum number of trays, N_{max}

This problem is a large highly non-linear non-convex problem (function of N_{max}). Since the material balances contain bi and trilinear terms and the reaction terms, the vapor-liquid equilibrium evaluation and the objective function are highly non-linear.

Now, in this case what are the constraints? The constraints are

$$
\begin{aligned}
&V_k \le F_{\max}, && k = 1,.....,N,\\
&L_k \le F_{\max}, && k = 1,.....,N,\\
&\sum_{i=1}^{c} F_{ik} \le F_{\max}, && k = 1,.....,N,\\
&W_k \le W_{\max}, && k = 1,.....,N,
\end{aligned}
$$

that V_k less than equal to F_{max}, here in the slides, all those constants are given, L_K should be less than equal to F_{max} and summation of F_{ik} should be less than equal to F max and W_K should be less than or equal to W_{max}.

And the maximum number of trays should be N_{max}. So, in this case you have to remember that this problem is a large highly nonlinear nonconvex problems function of N_{max}. Since the material balances contain you know that bi and tri linear terms and the reaction terms, in this case the vapour-liquid equilibrium evaluates and also the objective functions, all those are highly nonlinear. So, it will be very complex and to get that conversion or you can say it will be very highly nonconvex problem for you.

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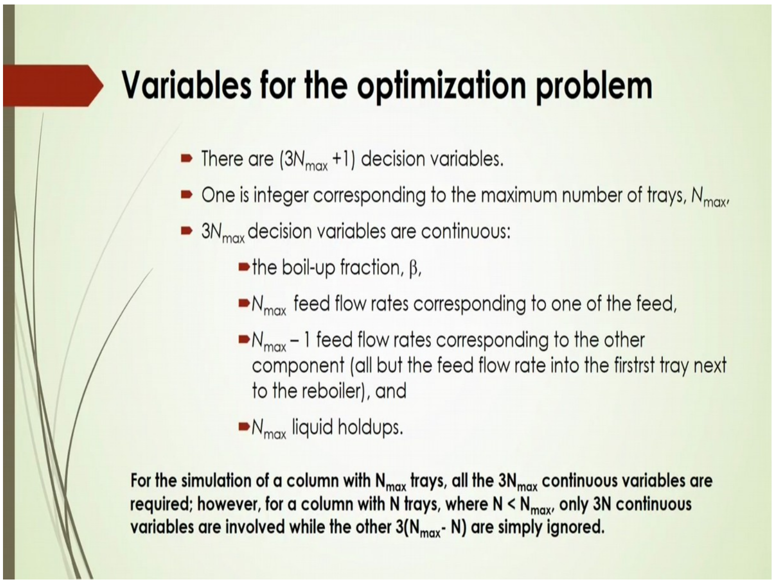

Variables for the optimization problem

- There are ($3N_{max}$ +1) decision variables.
- One is integer corresponding to the maximum number of trays, N_{max},
- $3N_{max}$ decision variables are continuous:
  - the boil-up fraction, β,
  - N_{max} feed flow rates corresponding to one of the feed,
  - N_{max} – 1 feed flow rates corresponding to the other component (all but the feed flow rate into the firstrst tray next to the reboiler), and
  - N_{max} liquid holdups.

For the simulation of a column with N_{max} trays, all the $3N_{max}$ continuous variables are required; however, for a column with N trays, where $N < N_{max}$, only 3N continuous variables are involved while the other $3(N_{max} - N)$ are simply ignored.

And in this case what are the variables for the optimisation problem to be considered? Indices there are $3N_{Max} + 1$ decision variable, one is integer corresponding to the maximum number of trace N_{max}. And you know 3 times of maximum number of trays should be decision variables that will also be continuous like the boiler fraction beta, the N max speed flow rates that will correspond to one of the feed and N_{max} -1 feed flow rates corresponds to the other component.

And in this case the feed flow rate into the 1st next to the reboiler to be considered here. And also N max liquid hold-ups to be considered there. So, for the simulation of the column with N_{max} trace, all the 3 times, that is $3N_{max}$ continuous variables are required. However in this case for a column with N trays, where N is less than N_{max}, only 3N continuous variables are involved, while the other 3 N_{max} minus N are simply ignored in this case.

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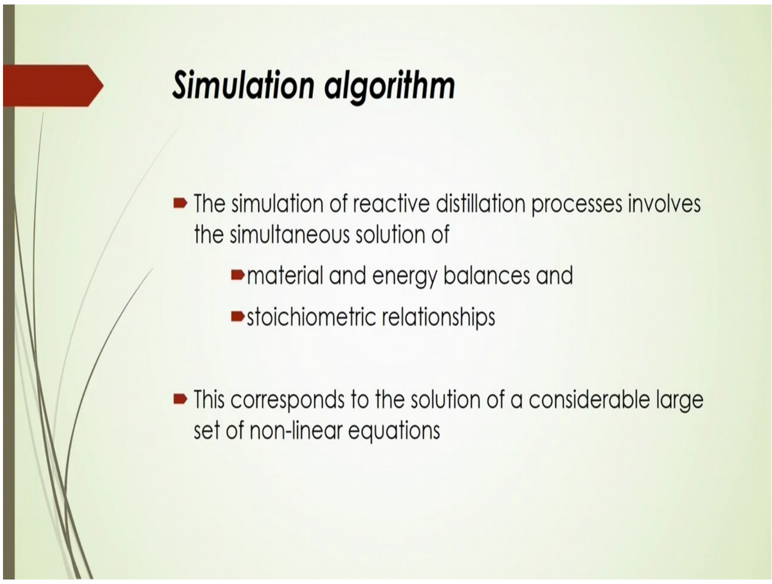
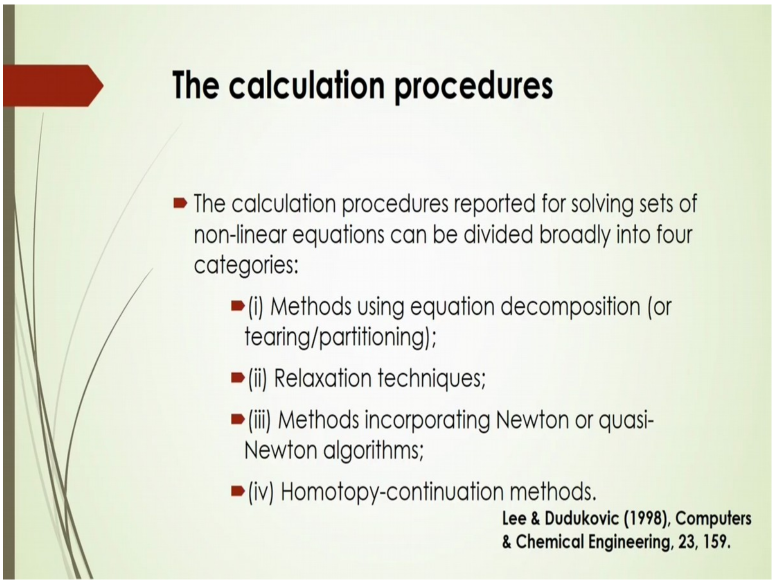


Simulation algorithm

- The simulation of reactive distillation processes involves the simultaneous solution of
    - material and energy balances and
    - stoichiometric relationships
- This corresponds to the solution of a considerable large set of non-linear equations



The calculation procedures

- The calculation procedures reported for solving sets of non-linear equations can be divided broadly into four categories:
    - (i) Methods using equation decomposition (or tearing/partitioning);
    - (ii) Relaxation techniques;
    - (iii) Methods incorporating Newton or quasi-Newton algorithms;
    - (iv) Homotopy-continuation methods.

Lee & Dudukovic (1998), Computers & Chemical Engineering, 23, 159.

And in this case for simulation purpose you have to use that simulation of reactive distillation process which will involve simultaneous solution of material and energy balances and stoichiometric relationships. This corresponds to the solution of a considerable large set of nonlinear equations.

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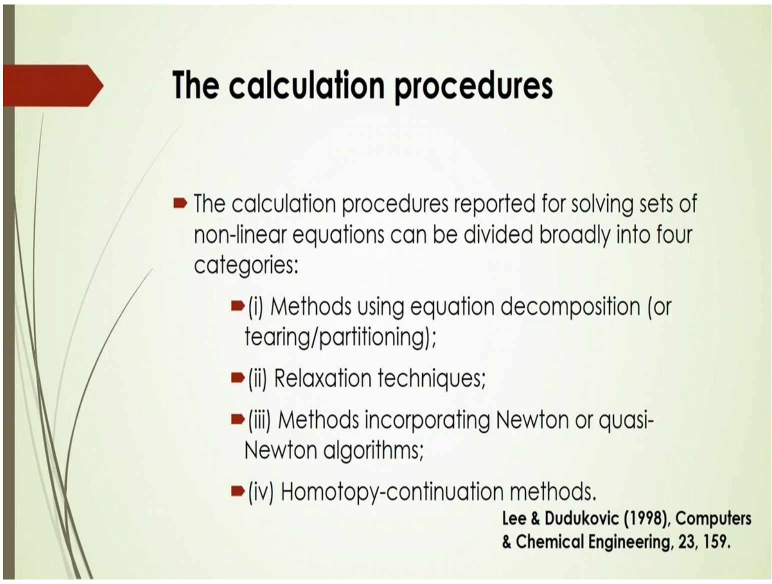

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  - (ii) Relaxation techniques;
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Lee & Dudukovic (1998), Computers & Chemical Engineering, 23, 159.

And for the calculation procedure that you have to know that consider this category is given in the slides like methods using equation for decomposition or tearing or partitioning relaxation techniques, methods in calculating Newton or quasi Newton algorithm homo-tropic continuation methods like this.

So, you can follow this Lee and DuduKovic that is published in computers and chemical engineering volume 3. And you can have the idea how to calculate that, the calculation procedure is there and detail is given there.

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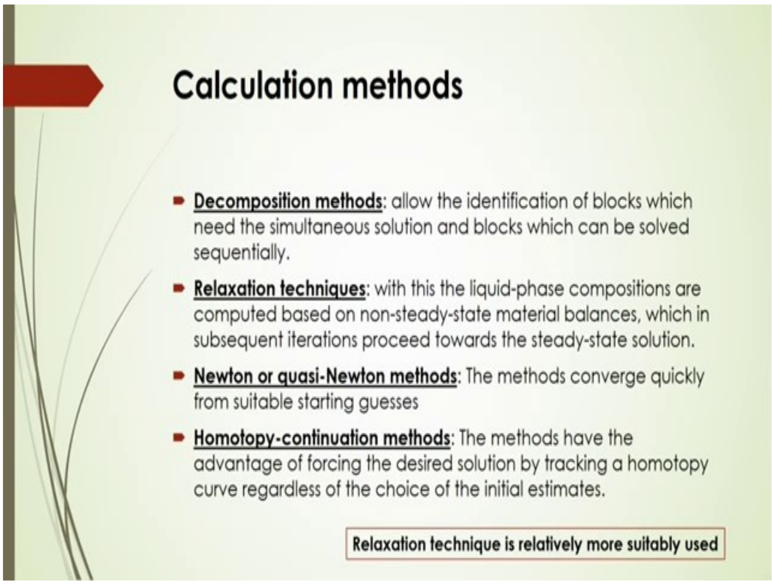

Calculation methods

- **Decomposition methods**: allow the identification of blocks which need the simultaneous solution and blocks which can be solved sequentially.
- **Relaxation techniques**: with this the liquid-phase compositions are computed based on non-steady-state material balances, which in subsequent iterations proceed towards the steady-state solution.
- **Newton or quasi-Newton methods**: The methods converge quickly from suitable starting guesses
- **Homotopy-continuation methods**: The methods have the advantage of forcing the desired solution by tracking a homotopy curve regardless of the choice of the initial estimates.

Relaxation technique is relatively more suitably used

Now, there are several methods, actually decomposition methods, relaxation techniques, Newton or quasi Newton methods, homo-tropic continuation methods there. Now, decomposition methods actually it will allow the identification of blocks which need the simultaneous solution and blocks which can be solved sequentially. Relaxation techniques, in this case liquid phase compositions are to be computed based on non-steady-state material balances and which in subsequent iterations proceed towards the steady-state solution there.

Newton or Quasi Newton methods in this case converge quickly for suitable starting guesses. And in case of homotopy continuation methods, the methods have the advantage of forcing the desired solution by tracking a homotopy curve regardless of the choice of the initial estimates. So among these various methods, relaxation technique is relatively more suitable to use for the calculations.

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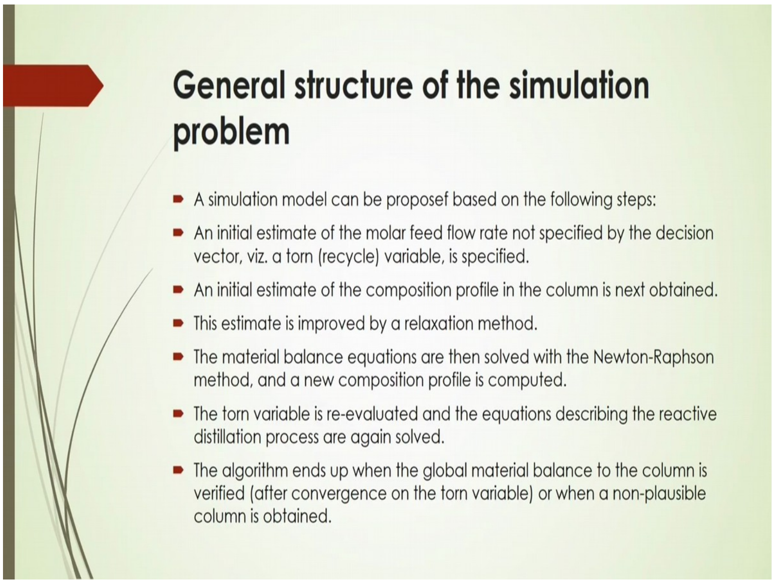

General structure of the simulation problem

- A simulation model can be proposef based on the following steps:
- An initial estimate of the molar feed flow rate not specified by the decision vector, viz. a torn (recycle) variable, is specified.
- An initial estimate of the composition profile in the column is next obtained.
- This estimate is improved by a relaxation method.
- The material balance equations are then solved with the Newton-Raphson method, and a new composition profile is computed.
- The torn variable is re-evaluated and the equations describing the reactive distillation process are again solved.
- The algorithm ends up when the global material balance to the column is verified (after convergence on the torn variable) or when a non-plausible column is obtained.

Now, general structure of the simulation problem, a simulation model can be proposed based on the following steps. Like this that an initial estimate of the molar feed flow rate, not specified by the decision vector, like a torn recycle or variable specified there. An initial estimate of the composition profile in the column to be next to be obtained and then this estimate can be improved by a relaxation method.

The material balance equations then to be solved within Newton Raphson method and a new composition profile is to be calculated. And the torn variable is to be re-evaluate it and the equations describing the reactive distillation process are again to be solved there. And the algorithms which should be ends up when the global material balance to the column is to be verified after convergence of the torn variable, also when a non-plausible column is obtained there.

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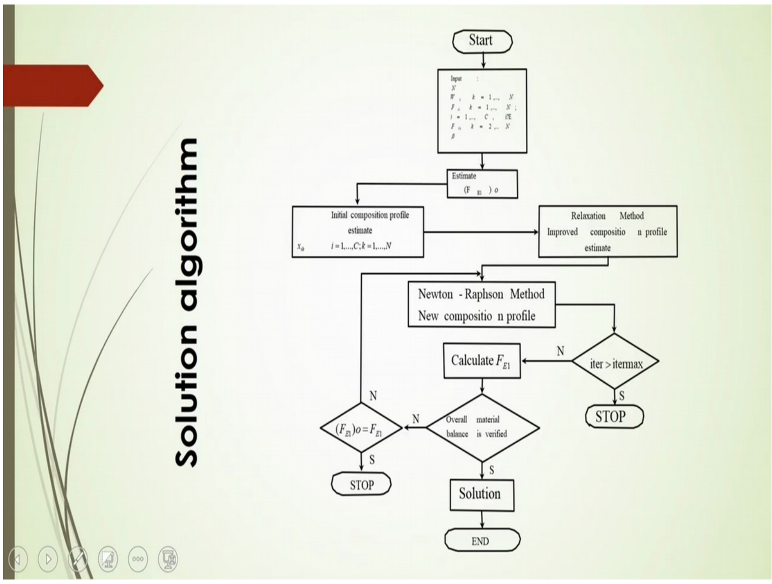

Solution algorithm

So, these are the solution algorithms are given in the slides, which goes through this slide one by one. You know that solution algorithm is given there. You can follow the solution method, how to actually in a systematic way that problem can be solved.

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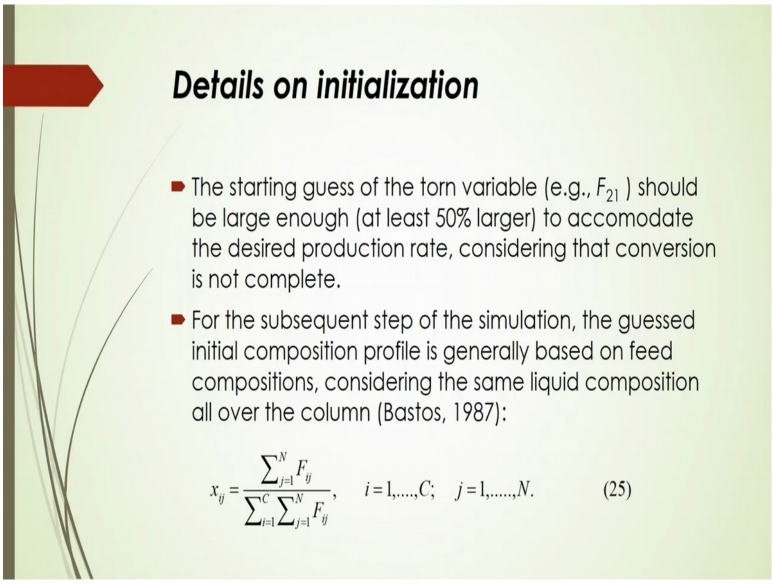

Details on initialization

- The starting guess of the torn variable (e.g., F_{21}) should be large enough (at least 50% larger) to accomodate the desired production rate, considering that conversion is not complete.
- For the subsequent step of the simulation, the guessed initial composition profile is generally based on feed compositions, considering the same liquid composition all over the column (Bastos, 1987):

$$x_{ij} = \frac{\sum_{j=1}^{N} F_{ij}}{\sum_{i=1}^{C}\sum_{j=1}^{N} F_{ij}}, \quad i = 1,....,C; \quad j = 1,.....,N. \qquad (25)$$

And in this case initiation is a very important one, that how to initiate that case of the torn, in that case it cannot be large enough but at least 50 percent larger to accommodate the desired production rate that will consider that conversion which is not complete there. For the subsequent steps of the simulation, you can guess the initial composition profile is generally based on the feed composition, considering the same liquid composition all over the column there. Like as per Bastos in 1987, you can use this equation number 25

$$x_{ij} = \frac{\sum_{j=1}^{N} F_{ij}}{\sum_{i=1}^{C} \sum_{j=1}^{N} F_{ij}}, \qquad i = 1,....,C; \quad j = 1,.....,N. \qquad (25)$$

for this initial composition guess.

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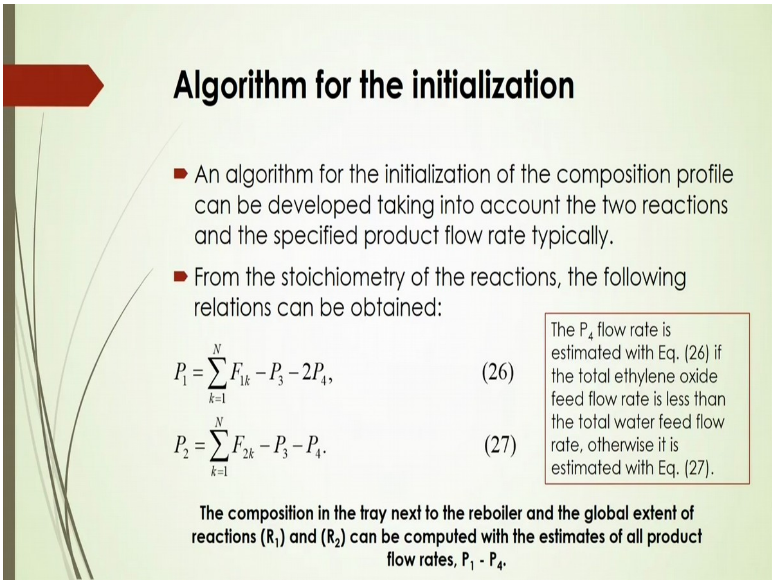

Algorithm for the initialization

- An algorithm for the initialization of the composition profile can be developed taking into account the two reactions and the specified product flow rate typically.
- From the stoichiometry of the reactions, the following relations can be obtained:

$$P_1 = \sum_{k=1}^{N} F_{1k} - P_3 - 2P_4, \qquad (26)$$

$$P_2 = \sum_{k=1}^{N} F_{2k} - P_3 - P_4. \qquad (27)$$

The P_4 flow rate is estimated with Eq. (26) if the total ethylene oxide feed flow rate is less than the total water feed flow rate, otherwise it is estimated with Eq. (27).

The composition in the tray next to the reboiler and the global extent of reactions (R_1) and (R_2) can be computed with the estimates of all product flow rates, P_1 - P_4.

Now, algorithm for the initialisation, in that case the algorithm for the initialisation of the composition profile can be developed taking into account the two reactions and the specified product flow rates typically from the stoichiometry of the reactions, the following reactions can be obtained, that is in equation number 26 and 27.

$$P_1 = \sum_{k=1}^{N} F_{1k} - P_3 - 2P_4, \qquad (26)$$

$$P_2 = \sum_{k=1}^{N} F_{2k} - P_3 - P_4. \qquad (27)$$

In the composition in the training through the reboiler and the global asset of the reactions can be computed with the estimates of the product flow rates like P_1-P_4, like this here.

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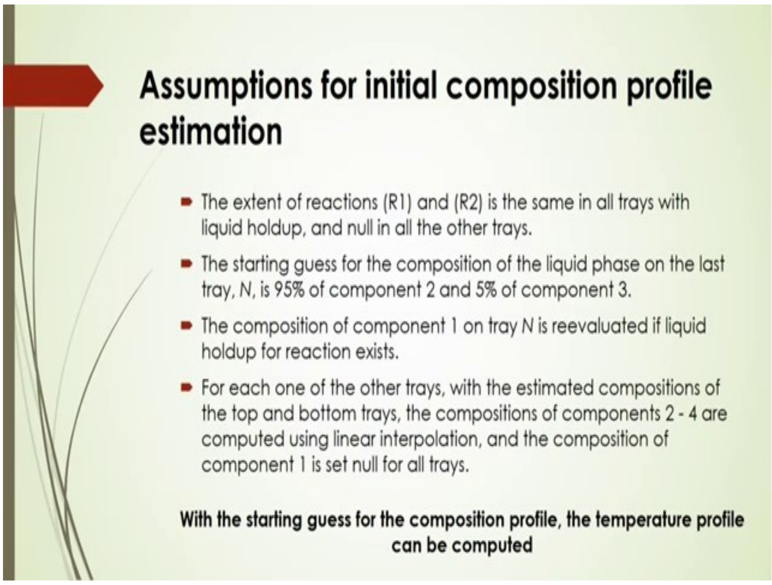

Assumptions for initial composition profile estimation

- The extent of reactions (R1) and (R2) is the same in all trays with liquid holdup, and null in all the other trays.
- The starting guess for the composition of the liquid phase on the last tray, *N*, is 95% of component 2 and 5% of component 3.
- The composition of component 1 on tray *N* is reevaluated if liquid holdup for reaction exists.
- For each one of the other trays, with the estimated compositions of the top and bottom trays, the compositions of components 2 - 4 are computed using linear interpolation, and the composition of component 1 is set null for all trays.

With the starting guess for the composition profile, the temperature profile can be computed

And assumptions for initial composition of profile estimation here in this case the extent of reactions that is R1 and R2 that has been given in earlier slides, that is should be is the same in all trays with liquid hold-up and null in all the other trays in that case. And the starting guess for the composition of the liquid phase on the last tray end is to be 95 percent of the component 2 and 5 percent of the component 3.

And the composition of that component 1 on the tray end is re-evaluated in the liquid holder for the reaction adjust. And for each one of the other trays with estimated composition of the top and bottom trays, composition of the component 2 to 4 are computed using the linear interpolation and the composition of the component 1 which is set null for all trays there. So, with the starting guess for the composition profile, the temperature profile can be computed there.

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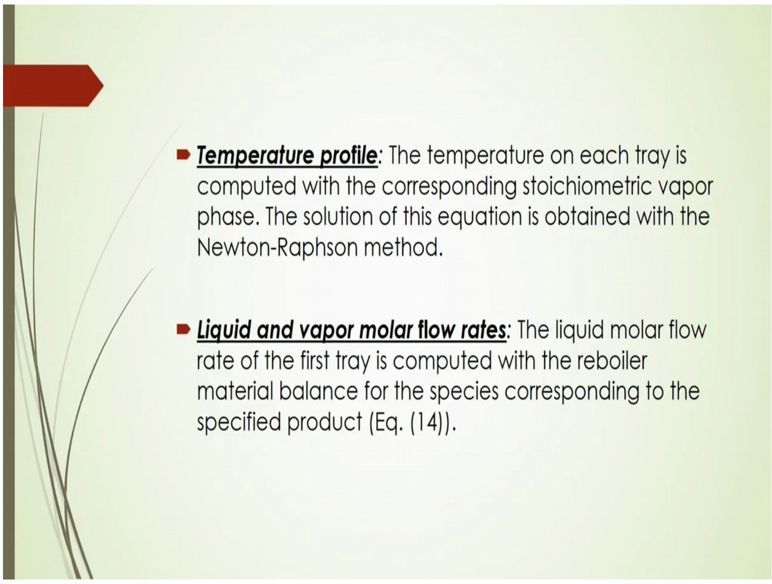

- **Temperature profile**: The temperature on each tray is computed with the corresponding stoichiometric vapor phase. The solution of this equation is obtained with the Newton-Raphson method.
- **Liquid and vapor molar flow rates**: The liquid molar flow rate of the first tray is computed with the reboiler material balance for the species corresponding to the specified product (Eq. (14)).

And the temperature on each tray can be computed with the corresponding stock metric vapour phase. The solution of this equation can be obtained with the Newton Raphson method. And also liquid and vapour molar flow rates also of the tray can be calculated with the reboiler material balance for the species that will correspond to the specified product.

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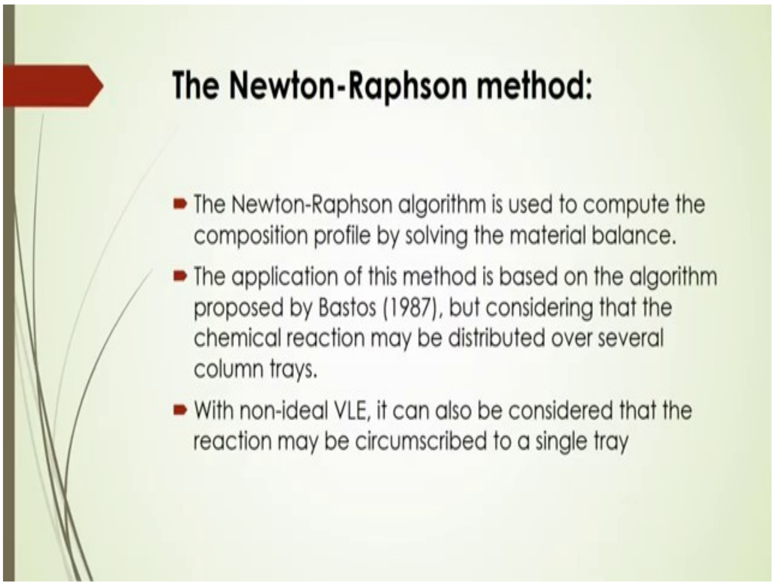

The Newton-Raphson method:

- The Newton-Raphson algorithm is used to compute the composition profile by solving the material balance.
- The application of this method is based on the algorithm proposed by Bastos (1987), but considering that the chemical reaction may be distributed over several column trays.
- With non-ideal VLE, it can also be considered that the reaction may be circumscribed to a single tray

Now, so what is this actually Newton Raphson method? The Newton Raphson method is used to compute that composition profile by solving the material balance. The application of this method is based on the algorithm proposed by Bastos in 1987 but considering that the chemical reaction may be distributed over the several column trays. And with non-ideal vapour liquid equilibrium, it can also be considered that the reaction may be circumscribed to a single tray.

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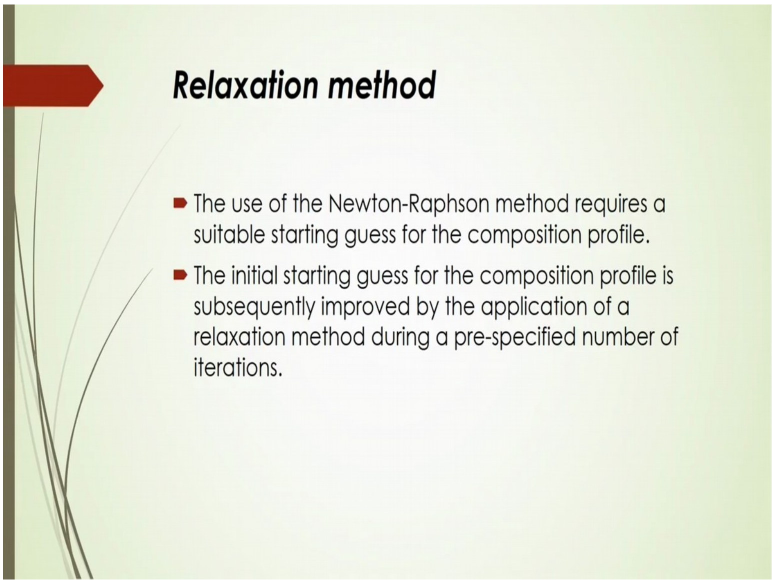

Relaxation method

- The use of the Newton-Raphson method requires a suitable starting guess for the composition profile.
- The initial starting guess for the composition profile is subsequently improved by the application of a relaxation method during a pre-specified number of iterations.

Whereas in the relaxation method, it can be used for the requirements where suitable starting guess for the composition profile is required. And also the initial starting guess for the composition profile is also subsequently to be improved by the application of a relaxation method during a pre-specified number of iterations.

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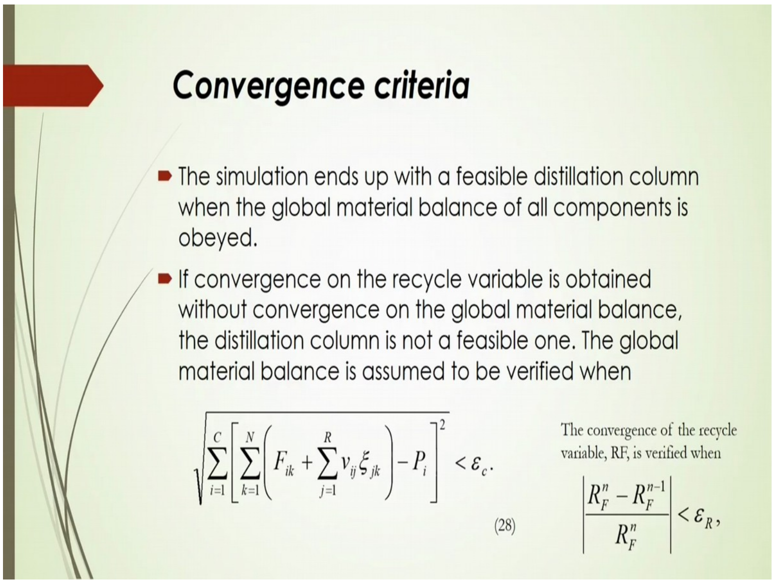

Convergence criteria

- The simulation ends up with a feasible distillation column when the global material balance of all components is obeyed.
- If convergence on the recycle variable is obtained without convergence on the global material balance, the distillation column is not a feasible one. The global material balance is assumed to be verified when

$$\sqrt{\sum_{i=1}^{C}\left[\sum_{k=1}^{N}\left(F_{ik}+\sum_{j=1}^{R}v_{ij}\xi_{jk}\right)-P_i\right]^2}<\varepsilon_c. \qquad (28)$$

The convergence of the recycle variable, RF, is verified when

$$\left|\frac{R_F^n-R_F^{n-1}}{R_F^n}\right|<\varepsilon_R,$$

Now, the convergence criteria also to be considered there, that during the simulation, with a feasible distillation column when the global material balance of all components should be obeyed, that simulation ends up. And if convergence on the recycle variable generally obtained without convergence on the global material balance.

In that case what you have to do is the distillation column is not a feasible one and in that case the global material balance is assumed to be verified when this equation

$$\sqrt{\sum_{i=1}^{C}\left[\sum_{k=1}^{N}\left(F_{ik}+\sum_{j=1}^{R}v_{ij}\xi_{jk}\right)-P_i\right]^2} < \varepsilon_c. \qquad (28)$$

Where

$$\left|\frac{R_F^n - R_F^{n-1}}{R_F^n}\right| < \varepsilon_R,$$

to be satisfied. The convergence of the recycle variable f is verified when this, here it is given in the slide, this one. So, this equation number 28 to be verified for the global material balance for the convergence criteria.

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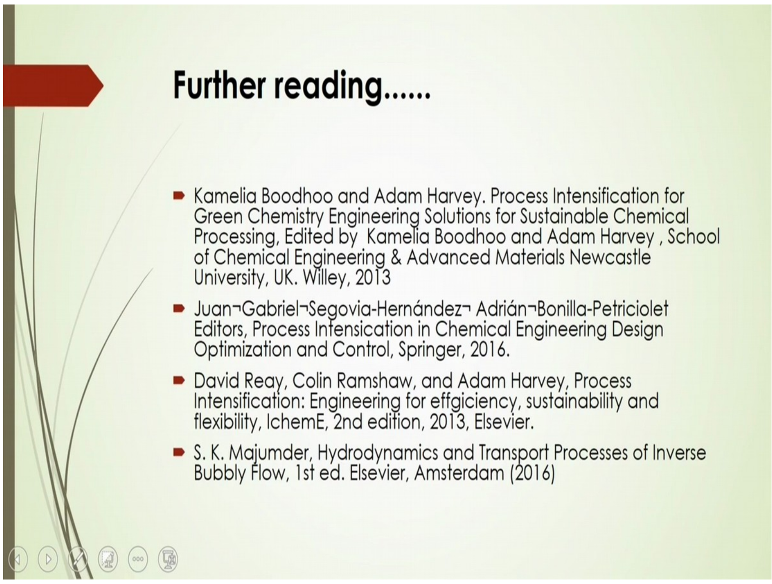

Further reading......

- 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. Willey, 2013
- Juan¬Gabriel¬Segovia-Hernández¬ Adrián¬Bonilla-Petriciolet Editors, Process Infensication in Chemical Engineering Design Optimization and Control, Springer, 2016.
- David Reay, Colin Ramshaw, and Adam Harvey, Process Intensification: Engineering for effgiciency, sustainability and flexibility, IchemE, 2nd edition, 2013, Elsevier.
- S. K. Majumder, Hydrodynamics and Transport Processes of Inverse Bubbly Flow, 1st ed. Elsevier, Amsterdam (2016)

So, I think I should stop here because there are several also materials also for the consideration of this optimal solution. So, I have given that basics of that optimisation techniques by the simulated annealing for this reactive distillation system, what are the different criteria, what are the different objective functions, what are the assumptions to be considered there.

So, I think you have some idea which may be helpful for further understanding of the optimisation problem for this chemical engineering process intensification. I would suggest you to go further with these textbooks, when some other you know that research papers that I have cited here in the slides also for your further understanding. Thank you.