some organic chemicals. In fact, some thermal decompositions have been shown to be autocatalytic. It therefore may be well to consider flash distillation of the crude product prior to subjecting it to fractional distillation to remove trace non-volatiles and/or nonvolatiles which would accelerate decomposition or lead to excessively high pot temperatures. In some cases one might consider the addition of a stabilizing agent to the pot to retard decomposition.

Closing Remarks

With all of the above having been stated, fractional distillation, particularly at reduced pressure, can be viewed as an opportunity to see physical chemistry at work. When selecting a system one hopes will result in satisfactory partition of components it will be helpful to consider properties other than the boiling point. For example, if a mixture of intermolecularly bound substances is to be separated by distillation, their partition is likely to be more difficult than the differentials between their boiling points would indicate. On the other hand, a mixture of alkanes may well be more easily separable than comparison of their boiling points would otherwise indicate. In any case practice is necessary, both conducting distillations and selecting systems for distillation. Once experience has been gained it is satisfying to be able to rationalize the results of a fractionation in terms of physico-chemical principles. One positive note: since distillation does not result in loss of product, in the worst case one can recombine all the fractions and redistill using different conditions and, if necessary, a different system.

Modelling and Simulation

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Introduction

Rigorous computer modelling of all types of fractionation columns has become a necessary part of the development and design process. There are numerous software products available to do these calculations. An understanding of the basic mathematics used in these programmes is helpful to select, use and troubleshoot a column model. Explained here are the basic equations, numerical and solution methods commonly used.

Stage and Column Models

A rigorous method describes a column as a group of equations and is the mathematical engine to solve and satisfy these equations to calculate the operating conditions of the column.

Column design and performance calculations present the column at steady state, that is, what enters the column matches what leaves it (material and energy balances), i.e.:

$$\sum \text{(molar feed flow rates)} = \sum \text{(molar product flow rates)}$$

$$\sum \text{(mass feed flow rates)} = \sum \text{(mass product flow rates)}$$

$$\sum \text{(moles of any component in the feeds)} = \sum \text{(moles of the component in the products)}$$

$$\text{Feed enthalpy} + \text{Heat added} = \text{Product enthalpy} + \text{Heat removed}$$

Figure 1 shows a complex column with one feed and one side product. The top stage of the column is a partial condenser, with a vapour product, D, and a liquid product, d. The reflux is the liquid, L_0, and the reflux ratio is $L_0/(D + d)$. The bottoms product, B, leaves stage $\mathrm{N} + 1$, the reboiler. The stages are numbered from the top, with the condenser as stage 0, the top tray in the column, stage 1, the bottom tray, stage N, and the reboiler, as stage $\mathrm{N} + 1$.

An ideal or equilibrium stage is where vapour and liquid entering and leaving the stage are perfectly mixed and there are no inhibitions to material transfer between the phases. The material and energy flows in and out of a simple stage, with no feeds or side products, is stage j depicted in Figure 2, and i represents the component number. Components are numbered from 1 to the last, C.

The enthalpy terms, H_j and h_j, are molar enthalpies of the vapour and liquid leaving the stage, respectively. These molar enthalpies are multiplied by the total flow rates, V_j and L_j, leaving the stage to give the total energy leaving the stage in each phase.

The feed stage model (stage f in **Figure 2**) for an equilibrium stage assumes that the feed liquid mixes

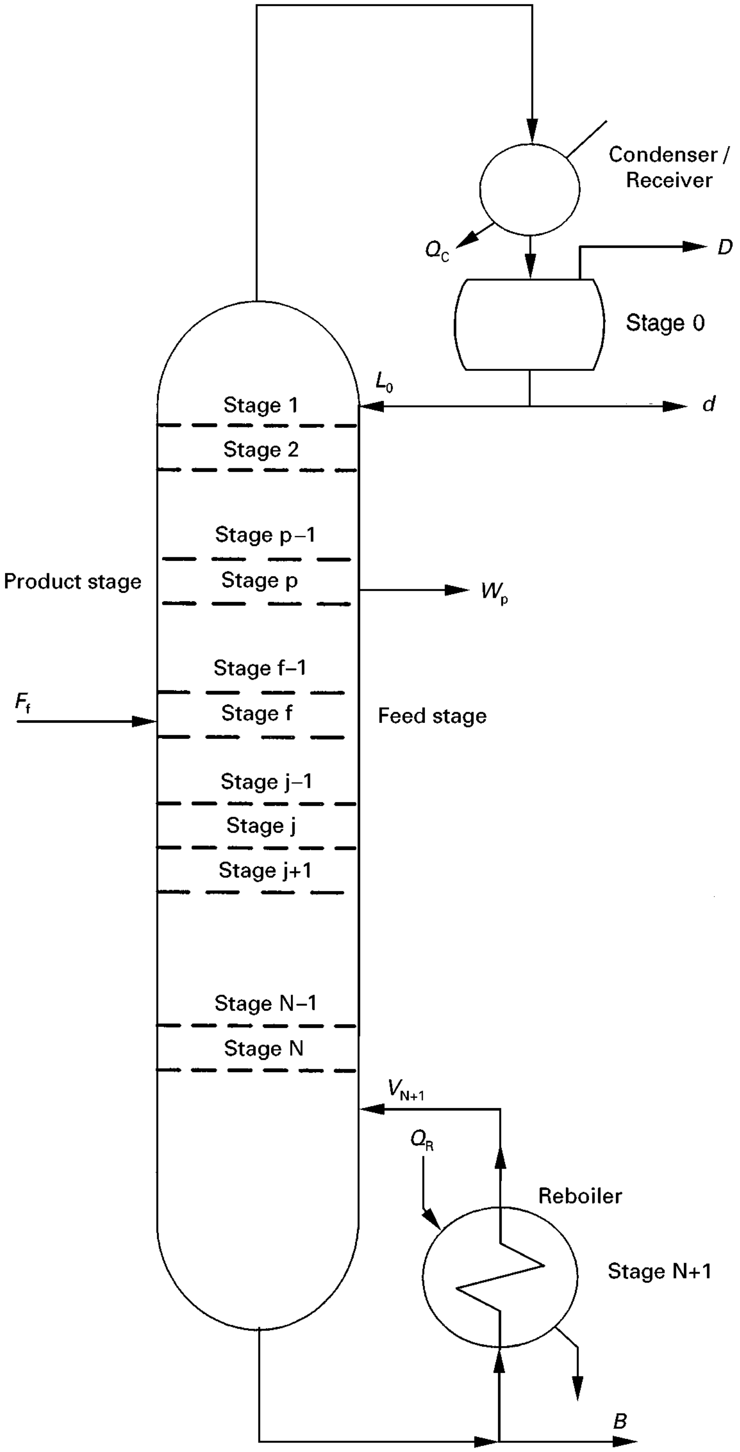

Figure 1 Overall column model with external variables.

with the liquid entering the feed stage while feed vapour mixes with vapour leaving the stage (though special consideration is made for the vapour feed at the bottom of absorber/stripper columns). The distribution is found by an adiabatic flash of the feed at the feed stage pressure before the feed enters the column. Regardless of whether the feed is subcooled liquid or superheated vapour, or if true mixing occurs, the assumption of an equilibrium stage is maintained in most rigorous methods.

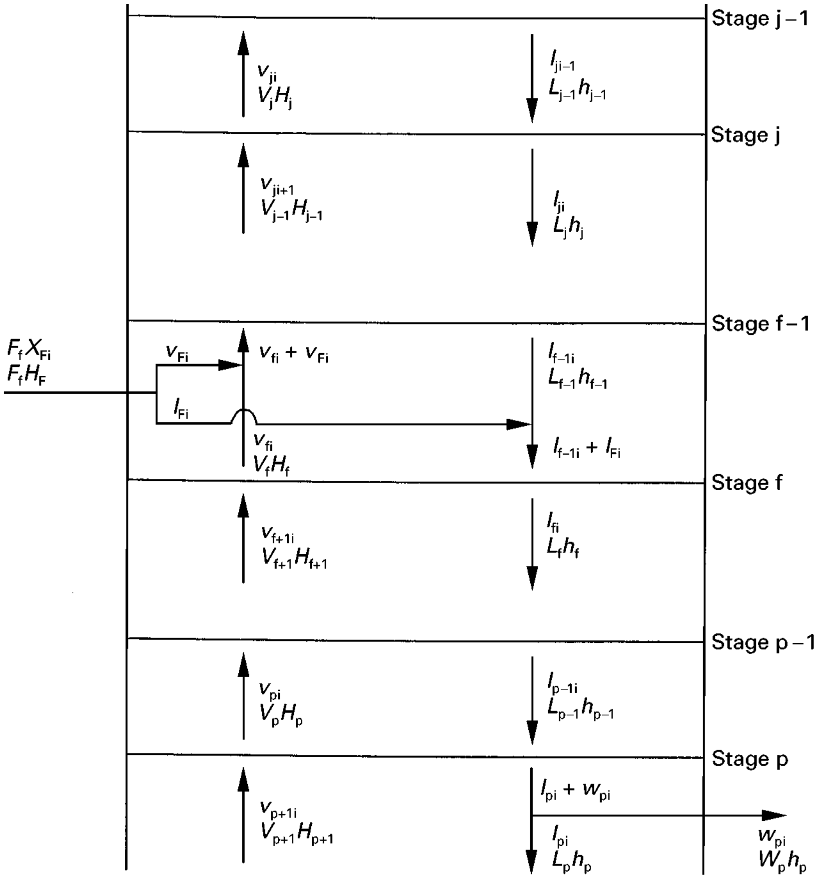

Figure 2 Model of stage variables.

Similar models are drawn for the bottom and top stages of any column, plus other equipment such as product withdrawal stages (stage p of Figure 2), pump-around returns and draws, and inter-reboilers and inter-condensers. Since a reflux, reboiler vapour, feeds, or returns are often subcooled, superheated, or very different in composition from the material on the stage, the assumption of an equilibrium stage rapidly becomes invalid.

Equations of Distillation Modelling

The basic equations below fully describe a distillation column. These equations define the overall column total material balances, energy balances, and product compositions. Internal to the column, they describe equilibrium conditions, internal (stage-to-stage) component and total material balances, and internal energy balances. The independent variables of a column are the product rates and compositions, internal vapour and liquid rates and compositions, and stage temperatures. Equilibrium constants, also called *K* values, and mixture enthalpies are dependent variables. Each stage is assumed to be at equilibrium (a theoretical stage), though an efficiency can be applied in the equations.

The equations were first referred to as the MESH equations by Wang and Henke (1966). The MESH acronym stands for:

Material or flow rate balance equations, both component and total.
Equilibrium equations including the bubble and dew point equations.
Summation or Stoichiometric equations or composition constraints.
Heat or enthalpy or energy balance equations.

The MESH variables are referred to as state variables. These are:

- Stage temperatures, T_j
- Internal total vapour and liquid rates, V_j and L_j
- Stage compositions, y_{ji} and x_{ji}, or instead, component vapour and liquid rates, v_{ji} and l_{ji}

The equilibrium equation is:

$$y_{ji} = K_{ji}x_{ji} \quad \text{or} \quad v_{ji}/V_j = K_{ji}l_{ji}/L_j$$

The equilibrium constant or K-value, K_{ji}, can be a complex function itself, dependent on the compositions, x_{ji} and y_{ji}

$$K_{ji} = K_{ji}(T_j, P_j, x_{ji}, y_{ji})$$

The dependence of K_{ji} on x_{ji} and y_{ji} often appears in the MESH equations. The component rates can also be expressed in the terms of each other, giving:

$$v_{ji} = l_{ji}(K_{ji}V_j/L_j) = l_{ji}S_{ji}$$

and

$$l_{ji} = v_{ji}(L_j/K_{ji}V_j) = v_{ji}A_{ji}$$

$K_{ji}V_j/L_j$ is termed the stripping factor, S_{ji}, while $L_j/K_{ji}V_j$ is termed the absorption factor, A_{ji}.

The summation equation or composition constraints simply states that the sum of the mole fractions on each stage is equal to unity. For the liquid phase:

$$\sum_{i=1}^{C} x_{ji} - 1 = 0 \quad \text{or} \quad \sum_{i=1}^{C} l_{ji}/L_j - 1 = 0 \quad \text{or}$$
$$\sum_{i=1}^{C} y_{ji}/K_{ji} - 1 = 0$$

and for the vapour phase:

$$\sum_{i=1}^{C} y_{ji} - 1 = 0 \quad \text{or} \quad \sum_{i=1}^{C} v_{ji}/V_j - 1 = 0 \quad \text{or}$$
$$\sum_{i=1}^{C} K_{ji}x_{ji} - 1 = 0$$

For a simple column (single feed, no side products), the overall component balance equation is:

$$f_i - d_i - b_i = 0$$

The component balance for the simple stage (no feed or side product), j, of Figure 2, is:

$$v_{ji+1} + l_{ji-1} - v_{ji} - l_{ji} = 0$$

The component balance for feed stage, f, of Figure 2 will add the liquid portion of the feed, l_{Fi}, while the vapour portion, v_{Fi}, is added to the component balance for stage f − 1. For the product stage, p, the material withdrawn, w_{pi}, is subtracted from the component material balance. By convention, material leaving a tray has a negative value and material entering a tray has a positive value.

The total material balances are organized in the same manner as the component balances. The total material balance for the simple stage of Figure 2 is:

$$V_{j+1} + L_{j-1} - V_j - L_j = 0$$

The same convention applies to feed and product trays where the total flow rate of a feed, F_f, is positive and the product, W_p, is negative.

The equilibrium equation and the composition constraint are combined to get the bubble point equation:

$$\frac{1}{\sum_{i=1}^{C} l_{ji}} * \sum_{i=1}^{C} K_{ji}l_{ji} - 1 = 0$$

and the dew point equation:

$$\frac{1}{\sum_{i=1}^{C} v_{ji}} * \sum_{i=1}^{C} \frac{v_{ji}}{K_{ji}} - 1 = 0$$

These, or some variation, are important in some methods to find the stage temperature, especially for more narrow boiling mixtures.

The energy balance equations are required in any rigorous method. In narrow-boiling mixtures, they influence the internal total flow rates. In wide-boiling mixtures and in columns where there are great heat effects (e.g. oil refinery fractionators) they also strongly influence stage temperatures. The overall energy balance for a column with one feed and side product is:

$$FH_F - DH_D - Bh_B - WH_W + Q_R - Q_C = 0$$

The enthalpy terms, H and h, are per mole of mixture. Note that the enthalpies of the top and side products are written so that a vapour or liquid enthalpy can be substituted, depending on the phase of the product. The energy balance for the simple stage, j, of Figure 2 is:

$$v_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j = 0$$

The enthalpies (energy per mole) for each phase are functions of temperature, pressure and composition:

$$H_j = H_j(T_j, P_j, y_{ji})$$

$$h_j = h_j(T_j, P_j, x_{ji})$$

For feed stages, side product stages, and stages with inter-condensers or inter-reboilers, additional terms are included in the energy balance equations. The energy balance for the reboiler is:

$$L_N h_N - V_{N+1} H_{N+1} - B h_{N+1} + Q_R = 0$$

and for a partial condenser with both vapour and liquid products:

$$V_1 H_1 - L_0 h_0 - d h_0 - D H_0 - Q_C = 0$$

Subcooling is accounted for in h_0 (the enthalpy of the reflux, L_0, and the liquid distillate, d).

Most computer simulations work with ideal stages but to characterize a stage for the deviation from ideality or equilibrium, stage efficiencies are often used in some software. Commonly, a Murphree vapour efficiency is used for each component, given as:

$$E_{\mathrm{MVji}} = \frac{y_{\mathrm{ji}} - y_{\mathrm{ji-1}}}{y^*_{\mathrm{ji}} - y_{\mathrm{ji-1}}}$$

where y^*_{ji} is what the vapour composition would be if the vapour were in equilibrium with the actual liquid on the stage and y_{ji} and $y_{\mathrm{ji-1}}$ are actual vapour compositions. If the absorption factor is used, the vapour efficiency can be expressed in terms of variables already presented:

$$E_{\mathrm{MVji}} = \frac{v_{\mathrm{ji}} - v_{\mathrm{ji+1}}(V_{\mathrm{j}}/V_{\mathrm{j+1}})}{(K_{\mathrm{ji}} V_{\mathrm{j}}/L_{\mathrm{j}}) l_{\mathrm{ji}} - v_{\mathrm{ji+1}}(V_{\mathrm{j}}/V_{\mathrm{j+1}})}$$

A vaporization efficiency, E_{ji}, based on the Murphree efficiency is defined as:

$$E_{\mathrm{ji}} = E_{\mathrm{MVji}} + (1 - E_{\mathrm{MVji}}) \frac{y_{\mathrm{ji+1}}}{K_{\mathrm{ji}} x_{\mathrm{ji}}}$$

This can be used in the MESH equations to account for stage nonideality. This vaporization efficiency is applied to the equilibrium constant, K_{ji}, and appears as the product $E_{\mathrm{ji}}K_{\mathrm{ji}}$. The vaporization efficiency does solve a computational problem in placing an efficiency in the MESH equations. A major disadvantage of the vaporization efficiency is that it does vary with composition. Near the top of a high purity column, as $y_{\mathrm{ji+1}}$ and x_{ji} approach unity, E_{ji} also approaches unity, and so a vaporization efficiency does not truly reflect stage nonidealities.

Another efficiency method is the bypass method where some of the vapour flow of a component entering the stage is sent to the next stage to account for its inefficiency in separation. The bypass method cannot be used on trays that have material leaving or entering from outside the column such as a feed tray, product draw tray, pump-around return or draw tray, or side-stripper return or draw tray. The bypass method will cause one of these trays to be out of mass balance. Some of the trays adjacent to these trays are also affected by these actions. In some columns, this eliminates a large number of trays and makes results difficult to apply.

Caution then should be used in any choice of efficiency. More often, it is usually best to perform the rigorous calculation using ideal stages and then apply an overall column efficiency based on sound engineering judgement and experience to account for stage nonideality, and calculate the number of actual trays or packing height.

Rigorous Computational Methods

Classification of the Methods

The rigorous methods can be divided into four basic classes. These are:

- The bubble point methods (BP)
- The sum-rates methods (SR)
- The 2*N* Newton methods
- The global Newton or simultaneous correction (SC) methods.

The BP methods get their name because the stage temperatures are found by directly solving the bubble point equation. The BP methods generally work best for narrow-boiling, ideal or nearly ideal systems; where composition has a greater effect on temperature than the latent heat of vaporization.

The sum-rates (SR) method is suitable for modelling absorbers and strippers with extremely wide-boiling systems, especially those with non-condensables. In these columns, temperatures are the dominant variables and are found by a solution of the stage energy balances. Compositions do not have as great an influence in calculating the temperatures as do heat effects or latent heats of vaporization.

The 2*N* Newton methods calculate temperatures and total flow rates together but compositions are still calculated in a separate, dependent step. The name 2*N* Newton means that there are two equations per stage for a total of $2 \times N$ functions and variables per column solved simultaneously by a Newton–Raphson method. The 2*N* Newton methods have been shown to work well for wide-boiling mixtures including refinery fractionators, absorber-stripper columns and reboiled absorbers.

The first three classes are referred to as equation tearing or decoupling methods because the MESH equations are divided and grouped or partitioned and paired with MESH variables to be solved in a series of steps. The SC methods attempt to solve all of the MESH equations and variables together. Additional classes are:

- Inside-out methods
- Relaxation methods
- Homotopy–continuation methods
- Nonequilibrium models.

The relaxation, inside-out and homotopy–continuation methods are extensions of whole or part of the first four methods in order to expand the range of columns, and to solve difficult systems or columns. The nonequilibrium models are rate-based or transport phenomena-based methods that do away altogether with the ideal stage concept and eliminate any use of efficiencies. They are best suited for columns where a theoretical stage is difficult to define and efficiencies are difficult to predict or apply by any means.

Numerical Methods – The Newton–Raphson Technique

The MESH equations form a large system of interrelated, nonlinear, algebraic equations. The mathematical method used to solve all or part of these equations as a group is the Newton–Raphson method. An understanding of the numerical method is needed to understand the performance of all column methods. Detailed discussion of the Newton–Raphson method and its variations can be found in Holland's (1981) text.

The Newton–Raphson is an approximation technique. It assumes in the derivatives that the MESH equations are linear over short distances and the slopes will point towards the answers. The MESH equations can be far from linear and the predictions can take the next trial well off the curves, and move away from the solution. In some rigorous methods based on Newton–Raphson, a poor set of starting values can cause the calculation never to approach a solution. Also, the calculation can oscillate, with values swinging to either side of the solution. The independent variables calculated in a trial need to move the column to a solution. The software should include means to prevent or detect these problems and improve stability, e.g. by damping or limiting the change to the next set of variables. A Newton–Raphson method will normally take even steps toward the solution.

Global Newton Methods

One group of methods that is very popular is the global Newton methods, also called the simultaneous correction (SC) methods. A common one is that of Naphtali and Sandholm (1971), but there are numerous applications in the literature and global Newton methods have been extended to include additional equations and variables for solving three-phase and reactive distillation columns.

In the global Newton methods, all of the equations are solved together in a Newton–Raphson technique. The methods vary in their choice of variables and MESH equations for the Newton–Raphson calculation but none of the MESH equations are solved in any separate step. In the BP, SR and $2N$ Newton methods, the component balances and compositions lag the other MESH calculations (since K values and enthalpies are generated using the compositions from the previous trial) and compositions of each component are calculated independently of the others MESH variables. These are major disadvantages with highly nonideal systems, where K values (especially activity coefficients γ_{ji}) and enthalpies are highly composition dependent and where the composition of one component cannot be readily decoupled from those of others. The global Newton method includes the component balances among the Newton–Raphson independent functions and compositions join other MESH variables as independent variables.

The global Newton methods are the most sensitive of the rigorous methods to the quality of the initial values and often require initial values near the answer. This, and applying the methods to a full range of column equipment and specifications, is their greatest problem. Variations on global Newton methods are used in the inside-out, relaxation, homotopy and nonequilibrium methods, where their power and reliability is extended.

Inside-out Methods

The inside-out algorithm has become one of the most popular methods because of its robustness and its ability to be applied to the solution of a wide variety of columns. The inside-out concept was developed by Boston (1980). Russell (1983) presented an inside-out method that works well for many refinery fractionators. The inside-out methods are now the methods of choice for mainstream column simulation and have displaced other methods.

In older methods, the MESH variables of temperatures, total flow rates and component flow rates are the primary solution variables and are used to generate the K values and enthalpies from complex correlations. These methods update the MESH variables in an outer loop with the K values and enthalpies updated whenever the MESH variables change. The inside-out concept reverses this by using the complex K value and enthalpy correlations to generate parameters for simple K value and enthalpy models. These parameters are unique for each stage and become the variables for the outside loop. The inside loop consists of the MESH equations and is a variation on other methods. In every step through the outside loop, the simple models are updated using MESH variables from the inside loop. This sets up the next pass through the inside loop. Since the K values and enthalpies are simple, the inside loop works well for a wide range of mixtures and is little affected by the nonideality of mixtures or the quality of the initial values.

The outer loop K value model is based on a simple composition-independent K method:

$$\ln K_{\mathrm{bj}} = A_{\mathrm{j}} + B_{\mathrm{j}}(1/T_{\mathrm{j}} - 1/T^*)$$

where T^* is a reference temperature for the K value correlation. Outer loop variables, A_{j} and B_{j}, are generated for each stage from a reference K_{bjRef} of a composite component:

$$\ln K_{\mathrm{bjRef}} = \sum_{i=1}^{C} w_{\mathrm{i}} \ln K_{\mathrm{ji(actual)}}$$

where the w_{i} are weight factors. The temperatures and compositions used to get the $K_{\mathrm{ji(actual)}}$ are the latest from the inside loop. Simple relative volatilities are among the outside loop variables, and are used in the K_{b} method to calculate the temperatures and whenever K values are needed in the inside loop:

$$\alpha_{\mathrm{ji}} = K_{\mathrm{ji(actual)}}/K_{\mathrm{bjRef}}$$

These simple relative volatilities change little over the range of temperatures that is seen on a given stage and greatly simplify temperature and composition calculations in the inside loop. For nonideal mixtures, an activity coefficient for each component accounts for composition effects in the inside loop. This activity coefficient has a simple model, similar to the K_{b} model:

$$\ln \gamma^*_{\mathrm{ji}} = a_{\mathrm{ji}} + b_{\mathrm{ji}} x_{\mathrm{ji}}$$

where the new outer loop variables, a_{ji} and b_{ji}, for each component are determined from the actual activity coefficient model at the current stage temperature and stage composition.

The simple K values used in the inside loop are easily determined from:

$$K_{\mathrm{ji(simple)}} = K_{\mathrm{bj}} \alpha_{\mathrm{ji}} \gamma^*_{\mathrm{ji}}$$

Simple models for the enthalpy of a phase are also used to reduce effects such as that caused by components moving past their critical conditions. Thus, the outside loop calculation consists of updating the terms of the simple K value, activity and enthalpy models which are updated after each inside loop solution using the latest temperatures and compositions from the inside loop.

The inside loop consists of the actual calculation of the MESH variables using the simple K value and enthalpy models. Boston initially used an inside loop solution method similar to a bubble point method and from that it may appear that the Boston method is most appropriate for narrow-boiling mixtures. However, the forcing style of the method also allows it to work well for wide-boiling mixtures. The Boston method works well for tall, high purity (superfractionator) type columns, but has been extended to absorbers, to three-phase distillation, and to reactive distillation by using other arrangements of the MESH equations.

The Boston method includes a middle loop to allow for column specifications and constraints. The arrangement of equations in the inner loop, where the solution of the MESH variables occur, may allow for only a few control or specified variables, such as fixed reflux ratio and product rates. The middle loop adjusts the control variables to meet the specifications. The middle loop can be built as an optimization method with process specification equations and economic objectives and constraints.

Russell's (1983) method differs from Boston's in the inside loop by a solution method of the MESH equations that includes specifications for product quality, stage temperatures, internal flow rates, etc., without the use of a middle loop to solve these. Here, for each heat exchanger in the column, plus each additional side product, an additional specification and operating variable is added to the problem. Russell's method has been found to work well for refinery fractionators with side strippers and other similar columns.

Relaxation Methods

A relaxation method finds a steady-state solution of a column as if it were an operating column changing with time. The column is initialized using some realistic condition and then makes steps to the steady-state conditions by successive approximations of the unsteady-state distillation equations. These unsteady-state equations are modifications to the MESH equations to include changes in the MESH variables with respect to time. This mimics the physical start-up of the column, but the objective is not to follow the dynamic operation but to seek the steady-state solution.

Homotopy–Continuation Methods

Homotopy or continuation methods are applied to difficult-to-solve columns, and are a simple means of forcing a solution. The MESH equations can be difficult to solve, due either to the nature of the column (many feeds or side products, side strippers, near minimum reflux, etc.) or to the nonidealities of the *K* values or enthalpies. For three-phase systems, azeotropic systems or systems of columns with two or more feed/recycle stream combinations, there may be more than one calculated solution. The method must be forced to reach the desired solution. Homotopy methods begin with a known solution of the column and from there follow a path to the desired solution. The known solution can be at different conditions or with much simpler *K* value and enthalpy methods and stepped changes are made from there, solving the column equations at each step, until the final solution is reached.

Nonequilibrium or Rate-based Methods

Stage efficiency prediction and scale-up from ideal or equilibrium stages to the actual design can be difficult and unreliable for many columns. For highly nonideal, polar and reactive systems, such as amine absorbers and strippers, prediction and use of efficiencies is particularly difficult. In such mixtures, mass transfer and not equilibrium often limits the separation.

Nonequilibrium methods attempt to get around the difficulty of predicting efficiencies by replacing the equilibrium stage concept. Instead, they apply a transport phenomena approach for predicting mass transfer rates. Here, the bulk vapour and liquid phases are not at equilibrium with each other, but there is equilibrium at the interface between phases with a movement from the bulk phase through the interface (**Figure 3**). The net loss or gain of material and energy at the interface is expressed as transfer rates. The mass and energy transfer rates are dependent on the mass and energy transfer coefficients for each phase which are in turn dependent on composition and conditions of each bulk phase and at the interface.

The correlations for the mass and heat transfer coefficients and interface also take into account packing or tray geometries for the actual column. The total mass and energy rates are calculated from integrating the mass and energy fluxes across the total interface surface.

Krishnamurthy and Taylor (1986) present and test a nonequilibrium model which includes rate equations among the traditional MESH equations. These include individual mass and energy balances in the vapour and the liquid and across the interface. An equilibrium equation exists for the interface only. The solution methods for these equations are the same as the global Newton methods.

The total mass transfer rates are added to an expanded set of the MESH equations called the MERQ equations. The new MERQ acronym stands for:

Material balances for each component – one for the bulk vapour, one for the bulk liquid and one across the interface.
Energy balance equations – one for the bulk vapour, one for the bulk liquid and one across the interface.
Rate equations for mass transfer for all but one component – one from the interface to the bulk vapour and one from the bulk liquid to the interface, plus one energy transfer rate equation from the liquid to the vapour.
eQuilibrium equation at the interface only.

Outlook

New rigorous methods for fractionation modelling may no longer be forthcoming and most enhancements will be driven by greater acceptance of nonequilibrium methods, and to other methods by their application to more complex fractionators and difficult systems of components. Teaching concepts of equations and solution may be limited to what is necessary to understand a programme's options, diagnostics and why a programme acts in a certain manner. There should be greater emphasis on knowledge of the physical reality of a column and where the actual process is sensitive, to help set up a problem. Software improvements are needed more in analysis and troubleshooting thought processes, tools and reports. Some of these tools may be a return to use of pre-computer tools such as *x-y*, McCabe–Thiele, and Hengstebeck diagrams and shortcut methods. While computers continue to become more common, faster and easier to use, they should never be a substitute for sound engineering experience and judgement.

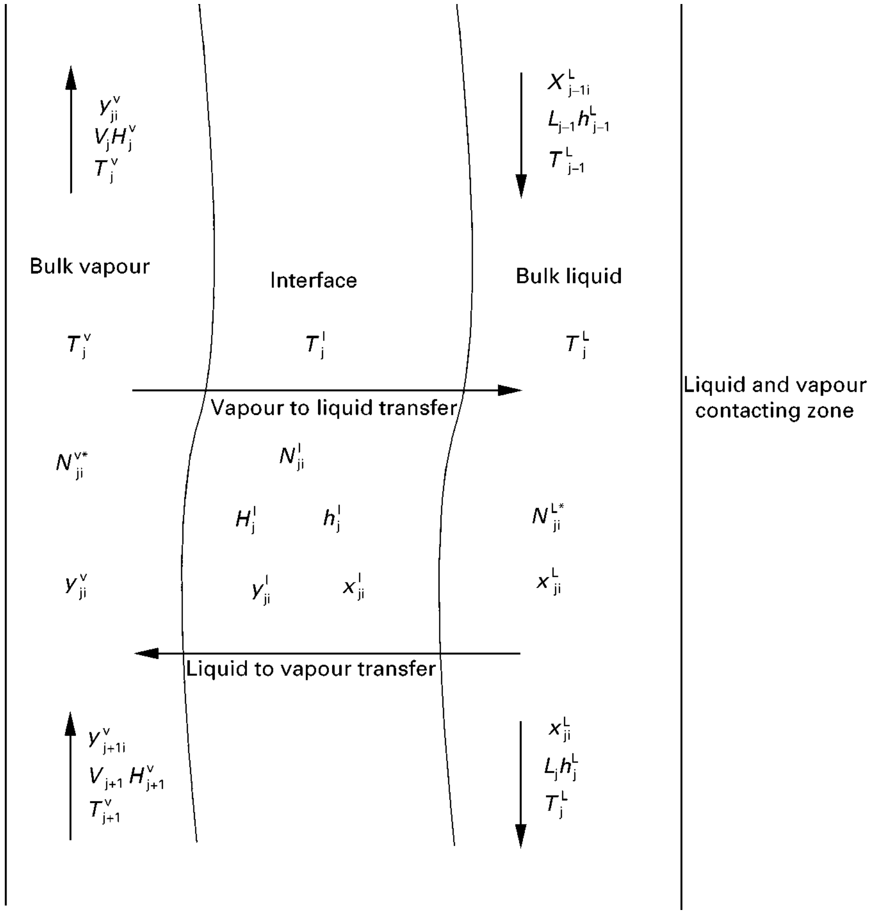

Figure 3 Model of a nonequilibrium separation and mass transfer.

See also: **II/Distillation:** Historical Development; Theory of Distillation; Vapour-Liquid Equilibrium: Correlation and Prediction; Vapour-Liquid Equilibrium: Theory.

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