# Multicomponent Distillation

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## Introduction

Distillation is the oldest separation process and the most widely used unit operation in industry. It involves the separation of a mixture based on the difference in the boiling point (or volatility) of its components. The reason for the wide acceptance of distillation is that, from both kinetic and thermodynamic points of view, distillation offers advantages over other existing processes for the separation of fluid mixtures:

1. Distillation has the potential for high mass transfer rates because, in general, in distillation there are no inert materials or solids present.
2. The thermodynamic efficiency for distillation is higher than the efficiency of most other available processes in the chemical industry.

Designing a distillation column involves: (1) selecting the type of column, mostly based on heuristics; (2) obtaining the vapour–liquid equilibrium data using thermodynamics; and (3) finding the design variables such as number of equilibrium stages and operating conditions required to obtain the desired separation based on mass and energy balances.

When the mixture to be separated contains two components, the design of a column can be accomplished by using *graphical methods*. However, for multicomponent systems the design methods are more difficult and are the focus of this article.

## Fundamentals

### Simple Distillation

Distillation began as a simple still. In such an operation, a liquid mixture is heated (see **Figure 1**). As a result, a vapour stream richer in the more volatile components comes off, while the liquid, richer in the less volatile components, remains in the still. The vapour stream is condensed and collected in the condenser.

The analysis of simple distillation for a binary mixture presented in 1902 by Lord Rayleigh marks the earliest theoretical work on distillation. Consider **Figure 1**. Let $F$ (moles) be the initial feed to the still and $x_F$ (mole fraction) be the composition of component $A$ of the mixture. Let $B$ be the number of moles of material remaining in the still, $x_B$ the mole fraction of component $A$ in the still, $x_D$ the mole fraction of component $A$ in the vapour d$B$ produced during an infinitesimal time interval d$t$. The differential material balance for component $A$ can be written as:

$$\ln\left(\frac{B}{F}\right) = \int_{x_F}^{x_B} \frac{\mathrm{d}x_B}{x_D - x_B} \qquad [1]$$

Complex mass and heat transfer processes occur in distillation processes and it is generally assumed that the vapour formed is in thermodynamic equilibrium with the liquid. Hence, the vapour composition ($x_D$) is related to the liquid composition ($x_B$) by an equilibrium relation of the functional form $x_D = f(x_B)$. Note that, because of the unsteady nature of simple distillation, the equilibrium relationship between $x_D$ and $x_B$ holds only for each infinitesimal time interval d$t$.

The exact equilibrium relationship for a particular mixture may be obtained from a thermodynamic analysis and is also dependent upon temperature and pressure.

### Thermodynamics and Equilibrium Data

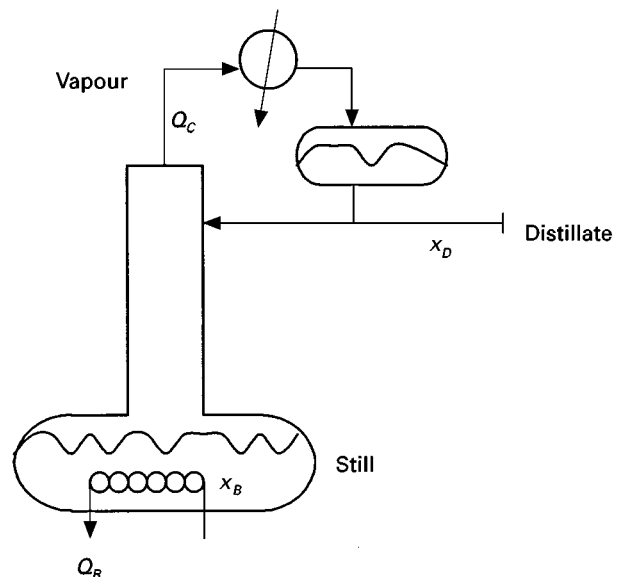Accurate and reliable thermodynamic data for vapour–liquid equilibrium is essential to distillation



**Figure 1** Simple distillation – a still.

design. For binary mixtures, these data are generally presented in the form of tables containing the liquid and vapour equilibrium compositions over a range of temperatures for a fixed pressure. The same information can also be plotted in what is called an $x$–$y$ diagram. For multicomponent mixtures, however, vapour liquid equilibrium data are difficult to represent in graphical or tabular form. In such case, $K$ values are used instead.

**$K$ value and relative volatility**   The $K$ value of a component $i$ is a measure of the tendency of such component to vaporize. A $K$ value is defined by:

$$K_i = \frac{y_i}{x_i} \qquad [2]$$

where $y_i$ is the equilibrium composition of the vapour phase for a composition $x_i$ of the liquid phase. $K$ values are a function of temperature, pressure and composition, and they are widely reported for binary and multicomponent mixtures. An associated concept is the relative volatility, $\alpha_{i,j}$, which is a measure of the ease of separation of components $i$ and $j$ by distillation:

$$\alpha_{i,j} = \frac{K_i}{K_j} \qquad [3]$$

**Ideal and nonideal systems**   An ideal system is one in which the liquid phase obeys Raoult's Law and the vapour phase obeys the ideal gas law. For such systems, the $K$ value is given by:

$$K_i = \frac{y_i}{x_i} = \frac{p_i^0}{P} \qquad [4]$$

where $p_i^0$ is the vapour pressure of pure component $i$ and $P$ is the pressure of the system. Note that $p_i^0$ is a function of temperature.

For a nonideal system, the $K$ values can also depend upon the composition of the mixture and are expressed in terms of fugacity coefficients, where $\phi_i^V$ is the vapour phase fugacity coefficient and $\gamma_i^L$ is the liquid phase activity coefficient, as given below:

$$K_i = \frac{\gamma_i^L}{\phi_i^V} \cdot \frac{p_i^0}{P} \qquad [5]$$

Azeotropic systems represent examples of nonideal mixtures for which eqn [5] has to be used.

### Classification of Distillation Processes

There are many criteria under which one can classify distillation: type of accessories, operating mode, design calculation assumptions, etc. Distillation can either be binary or multicomponent. According to the type of accessories used to increase the mass transfer in the separation process, a distillation column can be packed (use of packing) or staged (use of plates). It can be batch or continuous. Also, according to the assumptions made and accuracy expected in a distillation design calculation, a calculation technique can either be a shortcut method or a rigorous method.

**Packed columns and staged columns**   Although simple distillation in a still historically represents the start of the distillation process, a complete separation of the components of the mixture using this process is not possible. Therefore, the application of these stills is restricted to laboratory-scale distillation, where high purities are not required or when the mixture is easily separable.

One can look at simple distillation as consisting of one equilibrium stage where a liquid and a vapour are in contact with one another and mass and heat transfers take place between the two phases. If $N$ such stages are stacked one above the other, and are allowed to have successive vaporization and condensation, that results in a substantially richer vapour and weaker liquid (in terms of the more volatile component) in the condenser and the reboiler, respectively. This multistage arrangement is representative of a distillation column, where the vapour from the reboiler rises to the top and the liquid from the condenser is refluxed downwards (see **Figure 2**). The contact between the liquid and the vapour phase is established through accessories such as packing or plates. When the accessory is a stack of plates, then the result is a column of trays. Similarly, if the accessory is packing, the result is a packed column.

**Continuous distillation and batch distillation**   The basic difference between a batch column and a continuous column is that in continuous distillation the feed is continuously entering the column, while in batch distillation the reboiler is normally fed at the beginning of the operation. Also, while the top products are removed continuously in both batch and continuous operations, there is no bottom product in a conventional batch distillation. Since in a continuous operation the total product flow equals that of incoming feed or feeds, the process reaches a steady state. In batch distillation, on the other hand, the reboiler becomes depleted over time, so the process is unsteady. Such differences are illustrated in **Figure 3**.

Batch distillation is a direct extension of the simple distillation still, where the Rayleigh equation
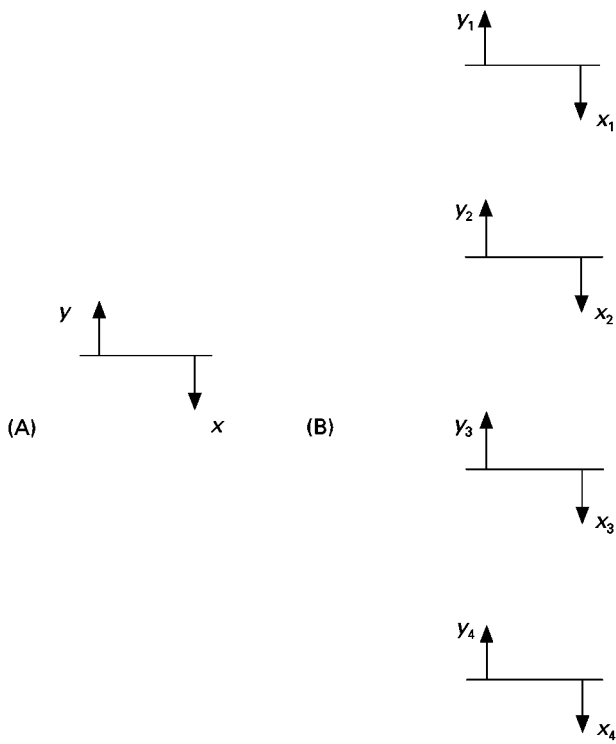
**Figure 2** Equilibrium processes. (A) Single stage; (B) multistage.

(eqn [1]) is applicable. However, in both batch and continuous distillation, multistage mass transfer and thermodynamic equilibrium stage calculations are used for obtaining the steady-state relationship be-

tween the product composition (instantaneous in case of batch) and feed composition.

## Multicomponent Multistage Equilibrium Calculations

This section is divided in two parts. In the first we discuss approximate methods (or shortcut methods); the second part corresponds to rigorous methods. The approaches are different depending upon the operation mode of the column, that is, a continuous operation or a batch operation.

In this section, our attention is focused on the approaches to the design of continuous columns. The reader can refer to the book by Diwekar (1995) for batch distillation calculations.

### Shortcut Methods

Approximate methods constitute a useful for the synthesis, analysis and design of distillation separations. The main advantage of shortcut methods is that they can provide the feasible region of operation. They also provide large saving in computer time, and sometimes, they are sufficiently accurate that more expensive rigorous methods are not justified.

**Concept of $N_{min}$ and $R_{min}$**   Minimum number of plates, $N_{min}$, and minimum reflux, $R_{min}$, are very important concepts in the design of distillation processes, as they are considered to be the limiting conditions in the operation of a distillation column.
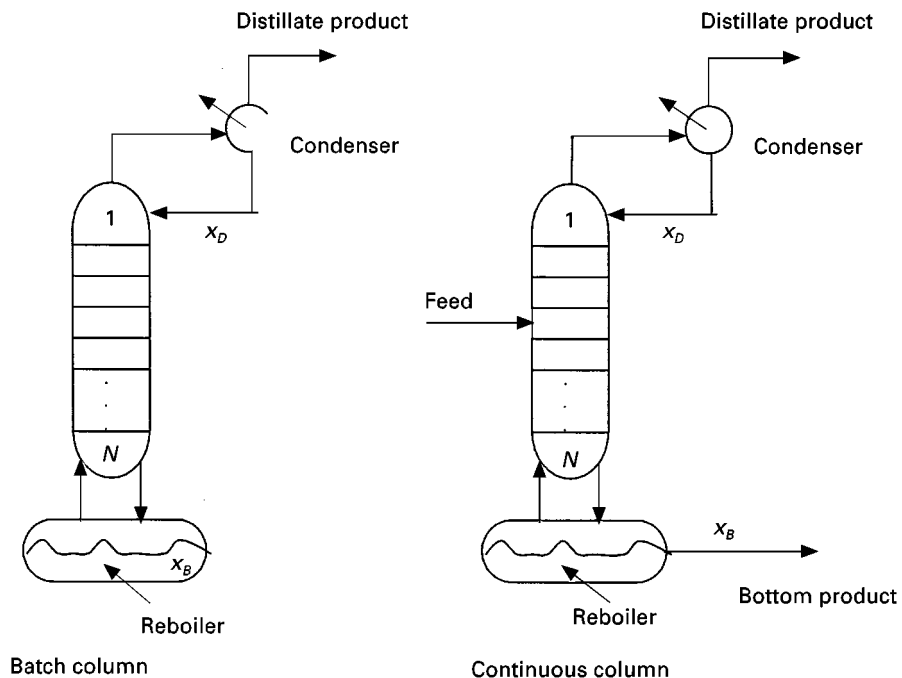


**Figure 3** Batch distillation versus continuous distillation.

$N_{\min}$ corresponds to the number of trays required for separation in a situation in which the external reflux ratio $R$ (ratio of the liquid refluxed to the distillate rate) of the column is infinite. This corresponds to total reflux operation.

$R_{\min}$ corresponds to the minimum value of the external reflux ratio required to achieve the specified separation in a situation in which the number of trays of the column is infinite.

**Fenske–Underwood–Gilliland method** The most popular of these shortcut methods is the Fenske-Underwood-Gilliland method (FUG). The basic assumptions of such a method are:

1. The system is ideal.
2. Constant molar overflow (as in the McCabe Thiele method for binary mixtures).
3. The separation is essentially taking place between the light key component and the heavy key component. The light key (lk) is the lightest component appearing in the bottom and the heavy key (hk) is the heaviest component appearing in the top.

In the FUG method:

1. Fenske's equation is used to calculate the minimum number of trays, $N_{\min}$.
2. Underwood's equation is used to estimate the minimum reflux, $R_{\min}$.
3. Gilliland's correlation is used to calculate the actual number of trays, $N$ (for any $R$ given), or the reflux ratio, $R$, (for any $N$ given) in terms of previous limiting values $N_{\min}$ and $R_{\min}$.

The Fenske equation is:

$$N_{\min} = \frac{\log\left[\left(\dfrac{x_{D_{lk}}}{x_{B_{lk}}}\right) \cdot \left(\dfrac{x_{B_{hk}}}{x_{D_{hk}}}\right)\right]}{\log(\alpha_{lk,hk})} \qquad [6]$$

where $\alpha_{lk,hk}$ is the relative volatility between the light key component and the heavy key component. Since it can be expected that the value of $\alpha$ changes for each tray of the column, the geometric average of this value is generally used:

$$\alpha^N = \alpha^N \cdot \alpha_{N-1} \dots \alpha_1 \qquad [7]$$

The Underwood equation can be written as:

$$\sum_i \frac{\alpha_i \cdot x_{i,D}}{\alpha_i - \theta} = R_{\min} + 1 \qquad [8]$$

where $\theta$ is a root of the equation:

$$\sum_i \frac{\alpha_i \cdot x_{i,F}}{\alpha_i - \theta} = 1 - q \qquad [9]$$

such that $\alpha_{hk} \leq \theta \leq \alpha_{lk}$. $\alpha_{hk}$ and $\alpha_{lk}$ are the relative volatilities of the key components (light and heavy) in the calculation. As stated earlier, such components are the ones that the designer uses as the basis for the separation.

Finally, the Gilliland correlation is given by:

$$\frac{N - N_{\min}}{N + 1} = 1 - \exp\left[\left(\frac{1 + 54.4G}{11 + 117.2G}\right) \cdot \left(\frac{G - 1}{G^{0.5}}\right)\right] \qquad [10]$$

where

$$G = \frac{R - R_{\min}}{R + 1} \qquad [11]$$

The main assumptions of the Underwood equation are the assumption of constant molar flow rates and an ideal system. Such assumptions constitute the main limitation of the algorithm.

## Rigorous Methods

Recent developments in computer hardware and software have made it possible to use rigorous methods for the design of distillation processes. In these methods, the assumption of constant molar flow rates is no longer considered. The implication of removing such an assumption is that rigorous methods not only consider mass balances, but also enthalpy balances for each of the trays of the column. Thus, rigorous methods require simultaneous convergence of mass and energy equations. Depending on the calculation sequence, there are several rigorous methods reported in the literature. The most important of these methods are: (1) Thiele–Geddes; (2) tridiagonal methods; (3) Naphtali–Sandholm; (4) inside-out algorithms; (5) $\Theta$ convergence methods; and (6) 2$N$ Newton methods. The method of Naphtali–Sandholm and the inside-out algorithm, which are commonly used nowadays, are discussed in this work to give an idea of the scope and applications of rigorous methods.

**MESH equations** Most rigorous methods involve the solution of the so-called MESH equations. For each stage $n$ in a distillation column (and for each component $i$ in a mixture of $C$ components), the equations representing mass balance (M), equilibrium relationships (E), summation of compositions (S) and energy balance (H), constitute the MESH equations. In addition, both $K$ values and enthalpies

are generally given as functions of temperatures, pressures and compositions. The generalized form of the MESH equations for the equilibrium stage shown in **Figure 4** and the expressions for $K$ values and enthalpies are present in **Table 1**.

**Naphtali–Sandholm method** In the Naphtali–Sandholm method, the number of variables of the MESH equations is reduced by the introduction of component flow rates and side streams. Furthermore, the summation of compositions are eliminated. Those modifications result in the equations presented in **Table 2**.

To solve the system of MESH equations given in Table 2, the vectors of variables and equations are ordered as follows. Variables:

$$\bar{X} = [\bar{X}_1, \bar{X}_2, \ldots, \bar{X}_n, \ldots, \bar{X}_N] \qquad [12]$$

where $N$ is the number of stages and

$$\bar{X}_n = [v_{n,1}, v_{n,2}, \ldots, v_{n,C}, T_n, l_{n,1}, l_{n,2}, \ldots, l_{n,C}]^{\mathrm{T}} \quad [13]$$

Equations:

$$\bar{F} = [\bar{F}_1, \bar{F}_2, \ldots, \bar{F}_n, \ldots, \bar{F}_N] \qquad [14]$$

where

$$\bar{F}_n = [\hat{H}_n, M_{n,1}, M_{n,2}, \ldots, M_{n,C}, E_{n,1}, E_{n,2}, \ldots, E_{n,C}]^{\mathrm{T}}$$
$$[15]$$

The solution process is iterative, using one of the several variations of the Newton method. Thus, corrections at each iteration $k$ are obtained from
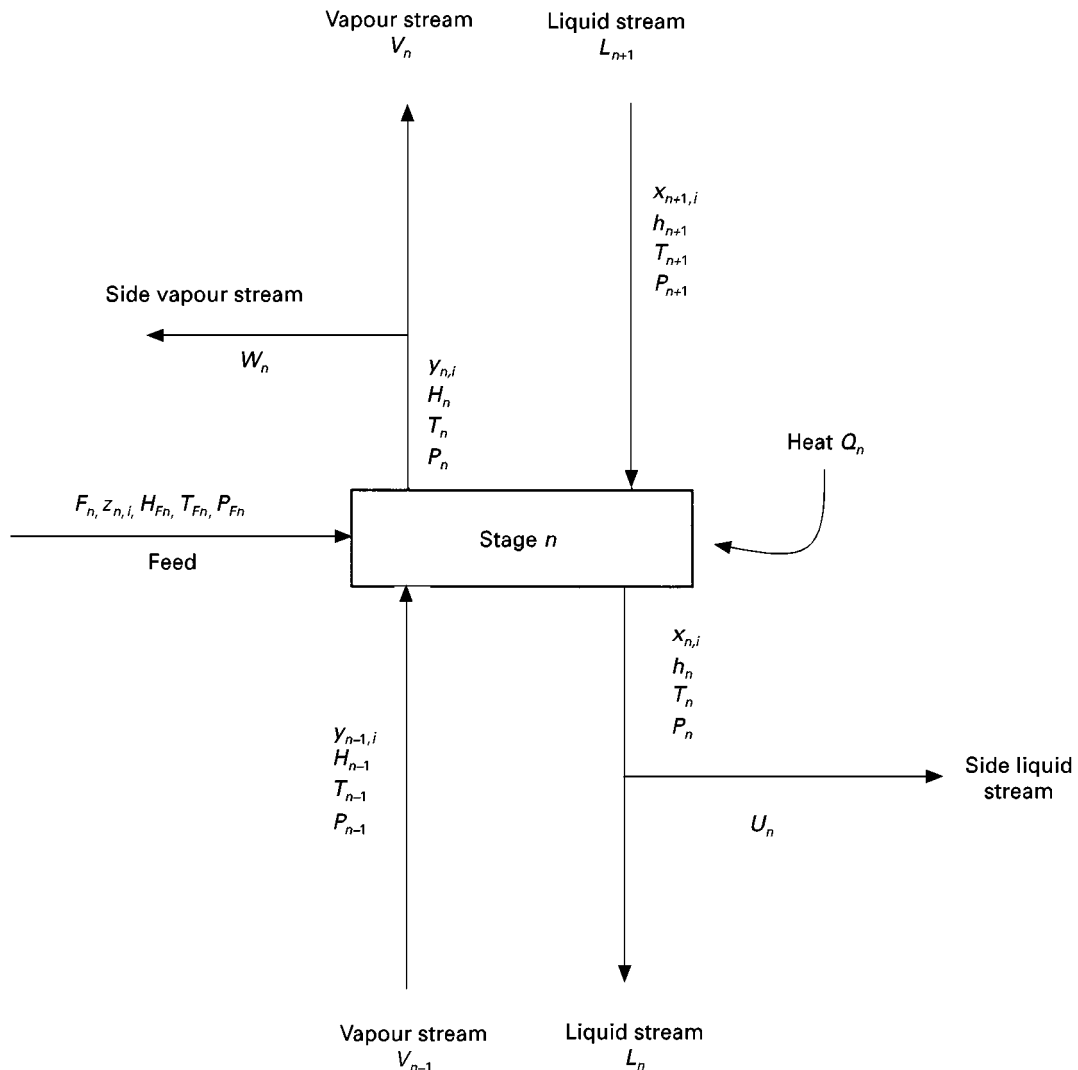


**Figure 4**  Equilibrium stage. Derivation of MESH equations.

**Table 1** MESH equations

| Relationship | Equation |
|---|---|
| **M**ass balance | $L_{n+1} \cdot x_{n+1,i} + V_{n-1} \cdot y_{n-1,i} + F_n \cdot z_{n,i} - (L_n + U_n) \cdot x_{n,i} - (V_n + W_n) \cdot y_{n,i} = 0$ |
| **E**quilibrium | $y_{n,i} = K_{n,i} \cdot x_{n,i}$ |
| **S**ummation of compositions | $\sum_i y_{n,i} - 1 = 0$ |
| **H** energy balance | $L_{n+1} \cdot h_{n+1} + V_{n-1} \cdot H_{n-1} + F_n \cdot H_{F_n} - (L_n + U_n) \cdot h_n - (V_n + W_n) \cdot H_n - Q_n = 0$ |
| **K** values and enthalpies | $K_{n,i} = K_{n,i}(T_n, P_n, x_n y_n)$ |
| | $H_{n,i} = H_{n,i}(T_n, P_n, y_n)$ |
| | $h_{n,i} = h_{n,i}(T_n, P_n, x_n)$ |

(classical Newton–Raphson equations):

$$\Delta \bar{F}^{(k)} = -\left[ \left( \frac{\partial \bar{F}}{\partial \bar{X}} \right)^{-1} \right]^{(k)} \cdot \bar{F}^{(k)} \qquad [16]$$

$$\bar{X}^{(k+1)} = \bar{X}^{(k)} + t \cdot \Delta \bar{X}^{(k)} \qquad [17]$$

where $t$ is such that $0 \leq t \leq 1$. $t$ is the factor that ensures progress toward the solution of the system at equations of each iteration.

**Inside-out algorithm** In the Naphtali–Sandholm method, the temperatures and component flowrates are the primary solution variables (see eqn [13]) and

**Table 2** MEH equations for method of Naphtali and Sandholm

| Relationship | Equation |
|---|---|
| Component flow rates and side streams | $v_{n,i} = y_{n,i} \cdot V_n$ |
| | $l_{n,i} = x_{n,i} \cdot L_n$ |
| | $f_{n,i} = z_{n,i} \cdot F_n$ |
| | $s_n = U_n / L_n$ |
| | $S_n = W_n / V_n$ |
| **M** | $M_{n,i} = l_{n,i} \cdot (1 + s_n) + v_{n,i} \cdot (1 + S_n)$ |
| | $\qquad - l_{n+1,i} - v_{n-1,i} - f_{n,i}$ |
| **E** | $E_{n,i} = K_{n,i} \cdot l_{n,i} \cdot \left( \sum_k v_{n,k} / \sum_k l_{n,k} \right) - v_{n,i} = 0$ |
| **H** | $\hat{H}_n = h_n \cdot (1 + s_j) \cdot \sum_i l_{n,i}$ |
| | $\qquad + H_n \cdot (1 + S_n) \cdot \sum_i v_{n,i}$ |
| | $\qquad - h_{n+1} \cdot \sum_i l_{n+1,i} - H_{n-1} \cdot \sum_i v_{n-1,i}$ |
| | $\qquad - H_{F_n} \cdot \sum_i f_{n,i} - Q_n = 0$ |

are used to generate the K values and enthalpies from complex correlations. Hence, such a method updates the primary variables in an outer loop, with the K values and enthalpies updated in an inner loop whenever the primary variables change.

In inside-out algorithms, the previous situation is reversed. These methods use complex K values and enthalpy correlations to generate parameters for simple K values and enthalpy models. Hence, these parameters become the variables for the outside loop. The inside loop then consists of the MESH equations. In every step through the outside loop, the simple K values and enthalpy models are updated by using the MESH variables from the inside loop. This sets up the next pass through the inside loop. The book by Kister (1992) provides detailed guidelines for the use of the various inside-out methods.

## Special Separations

When the components of a mixture have low relative volatilities, or when the mixture contains a large number of components, separation by distillation becomes difficult and expensive because a large number of trays or a large number of columns are required for the separation. Furthermore, some systems may show nonideal behaviour such as the formation of azeotropes or a reversal of the relative volatility with the change in pressure from top to bottom in a column. Complex systems which have these characteristics are common in the pharmaceutical and synthetic chemical industry.

This section presents a brief review of separations in which the traditional distillation process is altered, but the general principles of multicomponent distillation still apply. Three broad categories of such special separations exist: azeotropic distillation, extractive distillation and reactive distillation. Petroleum distillation will also be discussed since it represents a case

in which the complexity of the mixture (petroleum) requires special considerations for the separation.

## Azeotropic Distillation

Highly nonideal systems, with components having close boiling points among them, often produce azeotropes. Azeotropes can be identified by using an $x$–$y$ diagram. When an azeotrope is present, the equilibrium curve crosses the line $x = y$ (45° line), as shown in **Figure 5**.

Azeotropes limit the separation that can be achieved by conventional distillation. Sometimes it is possible to shift the equilibrium by changing the pressure of the system sufficiently to move the azeotrope away from the region where the separation must be made. Other cases, however, require the addition of a new material in order to achieve separation.

In azeotropic distillation, the equilibrium behaviour of the mixture is modified by adding a new material (called the solvent or entrainer). The added entrainer forms a minimum boiling point azeotrope with one or more components and distils overhead. The distillate is generally heterogeneous, that is, it is composed of two immiscible liquids when condensed. Such a heterogeneous nature facilitates the separation of the product from the entrainer.

## Extractive Distillation

Extractive distillation also involves the addition of the third component to the mixture (solvent or entrainer). However, in the case of extractive distillation, the solvent is a relatively high boiling point material, which is present at high concentration on each stage and exits at the bottom. To improve the efficiency of the process, the entrainer has to be added



**Figure 5** Azeotropic behaviour.

at the top of the column, so that its concentration on each stage will be enough to produce the desired effect in the equilibrium of the original mixture. Finally, the entrainer is separated from the bottoms product in another distillation column.

## Reactive Distillation

The idea of combining reaction and separation in a single apparatus has been extensively investigated. Doherty and Buzad (1992) present a survey of the available design techniques for reactive distillation. Reactive distillation is particularly attractive whenever a chemical reaction provides the favourable effect of reacting away azeotropic mixtures so that the behaviour of the liquid phase is simplified. In addition, it has been shown that reactive distillation has the potential of eliminating recycle costs when a liquid reaction involves a large excess of one reactant.

In general, the current trend in reactive distillation design is using experimental results from bench-scale problems in the initial stages of the design, and then using computer-aided simulation tools for scale-up and operability issues.

Possible profitable applications of reactive distillation processes are numerous. However, an incomplete understanding of the interactions of the many nonlinear phenomena such as chemical reaction, phase equilibrium, mass transfer and countercurrent flow has prevented the widespread use of such processes. Considerable research effort in the area is currently being conducted.

## Petroleum Distillation

Petroleum distillation is particularly difficult because of the large number of components of the mixture and large scale of the processes. This type of distillation involves products that are not easily identifiable components. Instead, separation is achieved in terms of pseudo-components, which are generally characterized in terms of their true boiling point ranges (TBP), an average relative molecular mass and an API gravity. TBP data are widely available and are generally presented in form of curves.

There are two main approaches to the design of petroleum distillation columns. The first consists of the solution of mass and energy balances based on empirical correlations, and is basically a calculation by hand. This approach was developed by Packie.

In the second approach, each pseudo-component is characterized for properties (such as vapour pressure and enthalpy) by using homologous-series approaches. Thus, rigorous mass and energy balances can then be applied to determine the separation in
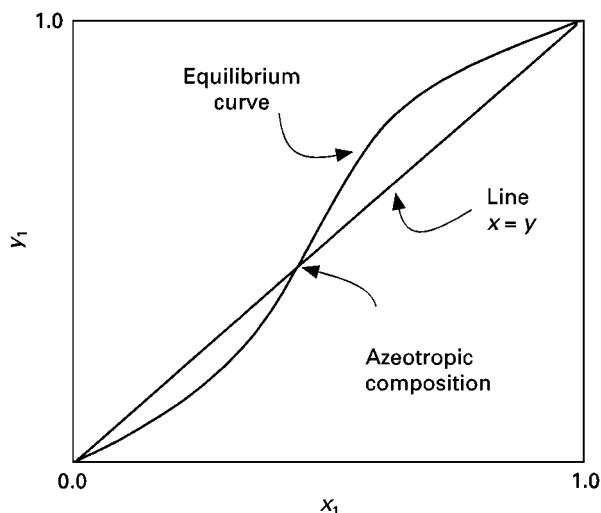
terms of the reflux ratio. Several efficient computer programs following this approach have been developed.

## Packed Columns

Several approaches exist for the design of packed columns. These are based on the concepts of number of transfer units (NTU), height of transfer units (HTU) and height equivalent to a theoretical plate (HETP). The last of these concepts is the most widely used.

Since methods for the design of staged distillation columns are well developed, a common approach is to calculate the number of trays $N$ using such approaches and then to find the height of the packed column, $h$, by the relation:

$$h = N \cdot \text{HETP} \qquad [18]$$

There exist various correlations for predicting the value of the HETP. One of most commonly used is the Sherwood correlation. It can be expected that HETP will change with respect to the operating conditions, physical properties of the liquid, etc., so, it is calculated in terms of correlations containing many factors.

## Nonequilibrium Distillation

All the mathematical methods (binary, rigorous, shortcut) presented earlier assume that each stage in the column is an equilibrium stage. In reality, however, this assumption is rarely satisfied.

### Stage Efficiency

An approach to nonequilibrium calculations is the use of the concept of stage efficiency. The most common approach is to modify the rigorous methods with the introduction of the so-called Murphree efficiency in the calculations. The Murphree efficiency in a stage calculation can be defined as:

$$E_{M_i}^L = \frac{x_{out,i} - x_{in,i}}{x_i' - x_{in,i}} \qquad [19]$$

for the liquid and

$$E_{M_i}^V = \frac{y_{out,i} - x_{in,i}}{y_i' - y_{in,i}} \qquad [20]$$

for the vapour. $x_i'$ are the compositions of the liquid that would be in equilibrium with the outlet composition of the vapour. $y_i'$ are the compositions of the liquid that would be in equilibrium with the outlet composition of the liquid.

### Mass Transfer Rates

It has been shown that stage efficiency prediction and scale-up are difficult and unreliable. For highly nonideal, polar and reactive systems, a transport phenomena approach for predicting mass transfer rates is preferred. Such mass transfer rates are calculated continuously along the column similarly to the HETP calculation for packed columns.

Nonequilibrium models for the calculation of mass transfer rates assume that, while the bulk vapour and liquid phase are not in equilibrium with each other, there is an equilibrium at the interface. Hence, the net loss or gain for a component at the interface is expressed in a rate form. For instance, the net gain by the vapour because of the transfer at the interface is:

$$N_{ij}^{v^o} = N_{ij}^v \cdot \mathrm{d}a_j \qquad [21]$$

where $N_{ij}^V$ is the vapour flux of the component at some point through the interface and $\mathrm{d}a_j$ is the interface area through which the flux passes. The mass transfer rates for liquid and vapour, $N_{ij}^V$ and $N_{ij}^L$, are dependent on the mass transfer coefficients for each phase. There exist several correlations for the heat and mass transfer coefficients and these are dependent on the compositions in the bulk phase, the temperatures in the bulk phase and interface, and on the packing or tray geometries.

## Industrial Applications

Distillation is by far the most widely used separation technique in the petroleum, natural gas and chemical industries so, applications of multicomponent distillation are numerous. A couple of industrial applications are described in this section.

### Primary Distillation of Crude Oil

A typical configuration for the distillation of a crude oil unit includes two main columns, an atmospheric tower and a vacuum tower (see **Figure 6**). In the atmospheric tower, crude oil is rectified (at a pressure no greater than 275.8 kPa (40 psi); to yield a distillate product containing light hydrocarbon gas, light and heavy naphtha, kerosene, diesel oil, and a bottom product of heavier components (TBP greater than 420°C). Each of the side streams of the atmospheric tower are sent to side strippers that have a partial reboiler or steam stripper. The side stream strippers serve to remove the light components. Stripping by
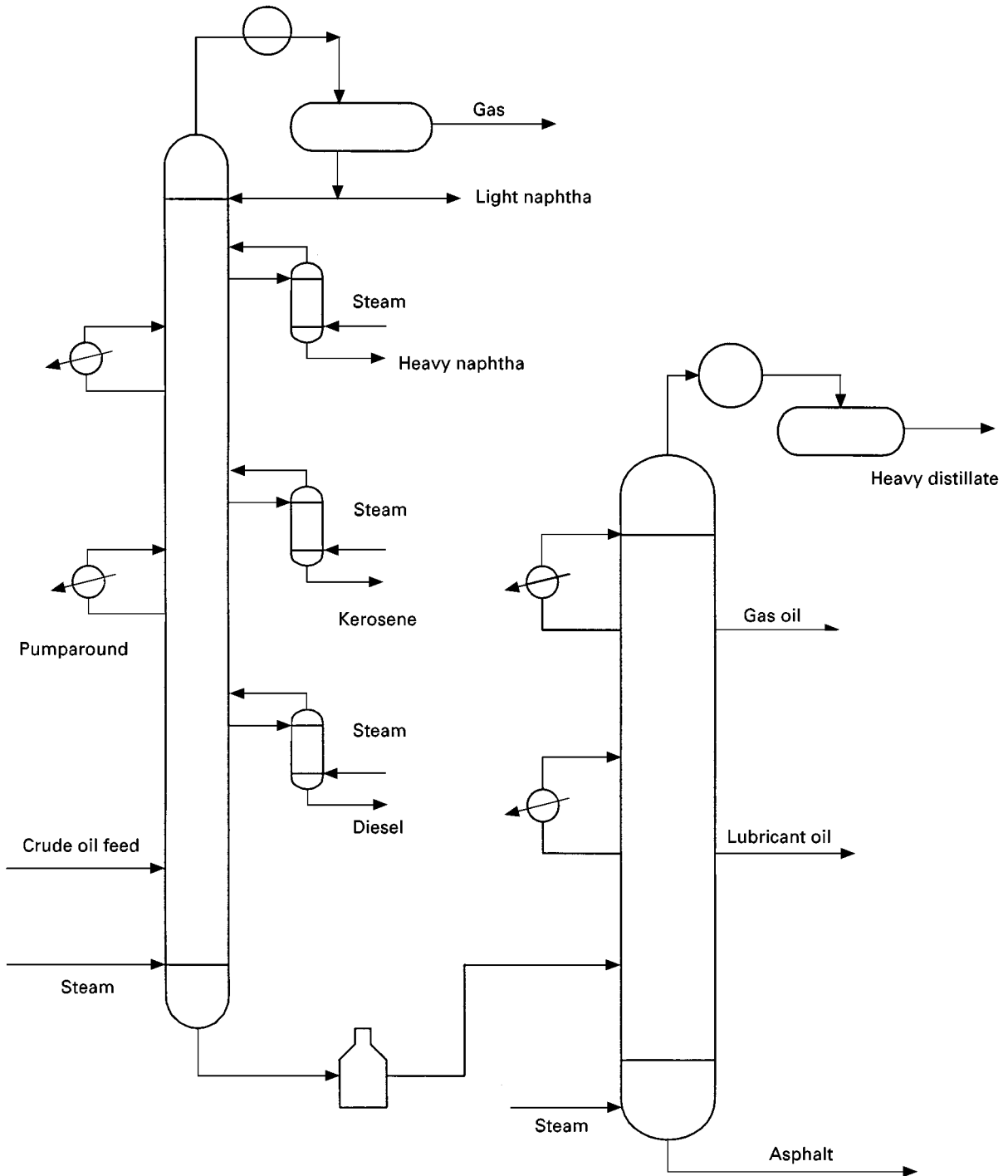
**Figure 6**  Crude oil distillation unit.

steam is also frequently used in the bottom of the tower.

The bottom product of the atmospheric tower is further separated by rectification in the vacuum tower. The feed-tray pressure of a vacuum tower is usually 6 kPa (45 Torr). Vacuum towers are mainly designed to obtain heavy distillates such as gas oil, lubricating oils and bunker fuels with asphalt as the bottom product.

The pump-around systems shown in both of the towers serve to make much larger liquid flows on the intermediate stages and produce a net increase in liquid flow. This serves as a point of control to keep the plates from running dry.

Highly developed procedures for the preliminary design of fractionators that process petroleum are commercially available through computer programs. The program 'REFINE' of the ChemShare Corporation and the 'PROCESS' (now PRO-II) program of Simulation Sciences Inc. are two examples.

### Ethylene and Propylene Production

The manufacture of ethylene and propylene is one of the most important operations of the petrochemical industry. In that process, ethylene and propylene are formed from the thermal cracking of other hydrocarbons, such as ethane, propane and naphtha. The mixture resulting from the thermal cracking is very complex. Hence, the mixture has to be separated into relatively pure ethylene and propylene, ethane and propane to be used as a recycle, methane and hydrogen to be used as fuel, and heavier products to be used for gasoline. A typical refinery gas feed to the separation system of this process contains hydrogen, ethylene, methane, ethane, propane, propylene and lower compositions of other heavy hydrocarbons. The distillation sequence most commonly used for the separation of the mixture is shown in **Figure 7**.

In a high pressure plant (no refrigeration is needed for condensation of products), the distillation sequence consists of five distillation columns:

1. Demethanizer
2. Deethanizer
3. Ethylene/ethane separator
4. Depropanizer
5. Propylene/propane separator.

Both the propylene/propane and the ethylene/ethane separator require high towers with large diameters because such mixtures contain components with very close relative volatilities. A plant that uses the configuration described here was built by Pullman Kellogg Inc., Houston, Texas.

In the case of a lower pressure plant, the deethanizer precedes the demethanizer because refrigeration is required for the feed of the demethanizer. So, by placing the deethanizer first, important utility savings are obtained.

## Future Work

Enormous progress has been made on the application and design of distillation technology. However, challenges still exist in some areas, which lead to the following ongoing research:

1. Improvement of mass transfer coefficients in packed distillation columns. Great effort is being made on the design of efficient packings and accurate correlation of their performance.
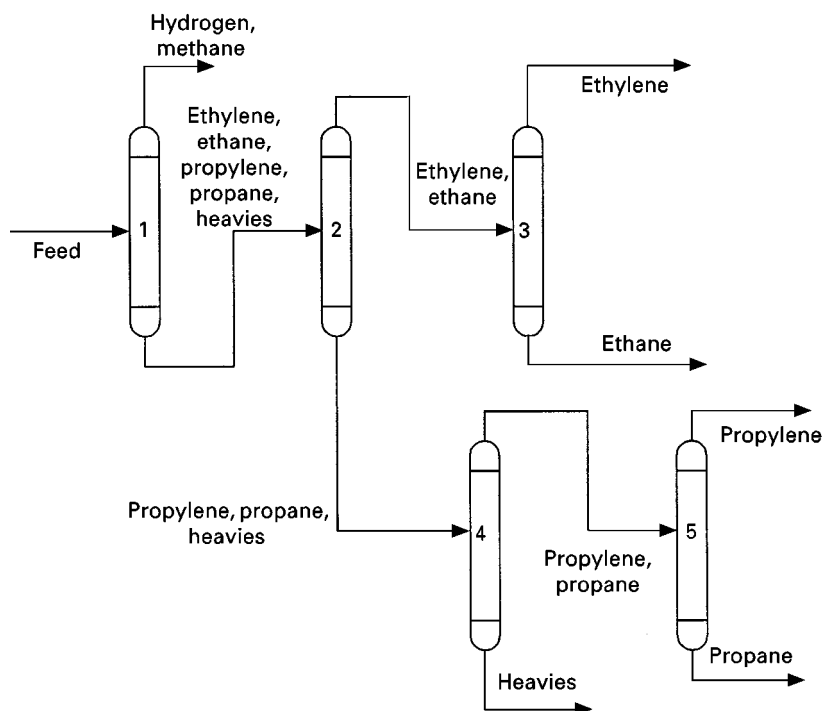


**Figure 7** Separation of products of the manufacture of ethylene and propylene.

2. The simulation, synthesis and design of reactive and azeotropic distillation. Such topics still constitute a gap in the knowledge of distillation technology.
3. Investigation of complex configurations for batch distillation processes.
4. Use of optimization methods for obtaining optimal configuration and design of batch and continuous distillation processes.
5. Online optimization and control of columns.

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

## Further Reading

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# Packed Columns: Design and Performance

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## Use of Packing in Distillation

Use of packing in mass transfer has its origins in the early 1800s for simple applications such as alcohol distillation, and in sulfuric acid plant absorbers. Glass balls, coke or even stones were used as packing materials. Nevertheless packings for distillation were not established until the 1930s with the use of regular shape materials such as ceramic Raschig rings and Berl saddles, as well as the availability of distillation calculations such as the McCabe–Thiele and Ponchon–Savarit methods. Early in the second half of the century, the use of packing for distillation went through a transformation, producing the second-generation packings (see **Table 1**). Regular and improved shape of packings, such as pall rings, became available with larger open areas that permitted a substantial increase both in capacity and column efficiency. In the 1960s Sulzer introduced the wire-mesh packings with very high efficiency (low height equivalent to a theoretical plate, HETP), resulting in a new transformation in the use of packings. In the 1970s

and 1980s all major mass-transfer equipment manufacturers developed structured packings. Compared to the traditional tray columns spectacular improvements in plant capacity were achieved, but also some projects were pitfalls, when the expected benefits did not materialize. Manufacturers started realizing that liquid distributors had to be improved, but there was no coherent understanding, nor correlations, that could lead to a safe distributor-column system design. Many manufacturers returned to trays, producing new improved designs, using the area under the downcomer for vapour flow: these trays are offered with new names that indicate their increased vapour flow capacity (Maxyflow, Superfrack, etc.). The need for good distribution and its effect on the column efficiency are now well understood, allowing safe design and efficient applications for random and structured packings in large industrial columns.

## General Concepts

Distillation separation is based in relative volatility that makes it possible to concentrate the more volatile components in the vapour phase while the less volatile ones remain in the liquid phase. Distillation columns are countercurrent vapour–liquid mass-transfer devices, where the required separation and purification of components is achieved.