

# Advanced Engineering Separations

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UG Notes



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# Nomenclature

## Roman

$B$	Bottom product flow	$\text{mol s}^{-1}$
$D$	Distillate flow	$\text{mol s}^{-1}$
$E$	Extract	$\text{kg s}^{-1}$
$E_A$	Extraction factor	—
$F$	Mass flow rate	$\text{kg s}^{-1}$
$f$	Fugacity	Pa
$K_D$	Partition coefficient	—
$L$	Liquid flow	$\text{mol s}^{-1}$
$N$	Number of stages	—
$n$	Molar flow rate	$\text{mol s}^{-1}$
$n$	Stage number	—
$R$	Raffinate	$\text{kg s}^{-1}$
$R$	Reflux ratio	—
$SF$	Split fraction	—
$SP$	Separation factor	—
$SR$	Split ratio	—
$V$	Vapour flow	$\text{mol s}^{-1}$
$x$	Mole fraction	—

## Greek

$\alpha$	Relative volatility	—
$\gamma$	Activity coefficient	—
$\mu$	Chemical potential	$\text{J mol}^{-1}$
$\phi$	Fugacity coefficient	—



## Course Information

Separations have been a key step in processing for thousands of years. Separations are crucial in chemical engineering; a typical chemical plant is a chemical reactor surrounded by separators. Raw materials are pre-purified in separation devices and fed to the chemical reactor; unreacted feed is separated from the reaction products and recycled back to the reactor. Products must be further separated and purified before they can be sold. Chemical plants commonly have from 40% to 70% of both capital and operating costs in separations.

This course has been developed to cover some of the widely used separation methods in industries and link fundamental theory to design. The course ILOs are:

- ILO 1.** Classify separation processes by type and select suitable separations for mixtures based on the properties of the components.
- ILO 2.** Design liquid-liquid extraction columns for ternary systems using the Hunter-Nash method.
- ILO 3.** Calculate the approximate design of multi-component distillation columns using short-cut models.
- ILO 4.** Assess simple and complex distillation column sequences using heuristic rules to find the optimal options.
- ILO 5.** Construct azeotropic distillation sequences using residue curve for ternary systems.

The course is built around this handbook, and the content within is supported by the lectures, tutorial questions, past exam papers, key concept videos, and a selection of online formative questions. Key videos can be accessed by scanning the QR codes found in these notes, or following the weblinks on blackboard. For a complete set of all the videos follow the [AdvancedEngineeringSeparations](#) channel on YouTube.

The tutorial questions are listed in 3 classifications,

**R** for revision questions. These refer to topics from previous courses, but will help your understanding of this course.

**E** for exam style questions. These are questions in the style which may appear in the exam.

**D** for design style questions. These are questions that may require you to look up more information, use a computer, or go beyond the core course.

For discussion of specific topics regarding this course with your fellow students or to communicate with the module leader, please use the Discussion Board and post your threads. The module leader will look on the board regularly and answer those uncleared questions, or come to the drop in session.





Chapter **1**

# Industrial Separations

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## 1.1 Chapter 1 ILOs

**ILO 1.1.** Classify separation processes by general separation method.

**ILO 1.2.** Select suitable separations for mixtures based on the properties of the components.

**ILO 1.3.** Define the quality of a separation process using key separation metrics.



Chapter Video

## 1.2 Introduction

Separations have been a key step in processes for thousands of years, those developed by early civilisations include extraction of metals from ores[5], evaporation of sea water to obtain salt[1], and the distillation of alcohol[3, 8].

Separations are crucial in chemical engineering; a typical chemical plant is a chemical reactor surrounded by separators, as shown by the schematic flow sheet of Figure 1.1. Raw materials are pre-purified in separation devices and fed to the chemical reactor; unreacted feed is separated from the reaction products and recycled back to the reactor. Products must be further separated and purified before they can be sold. Chemical plants commonly have from 40% to 70% of both capital and operating costs in separations[4].

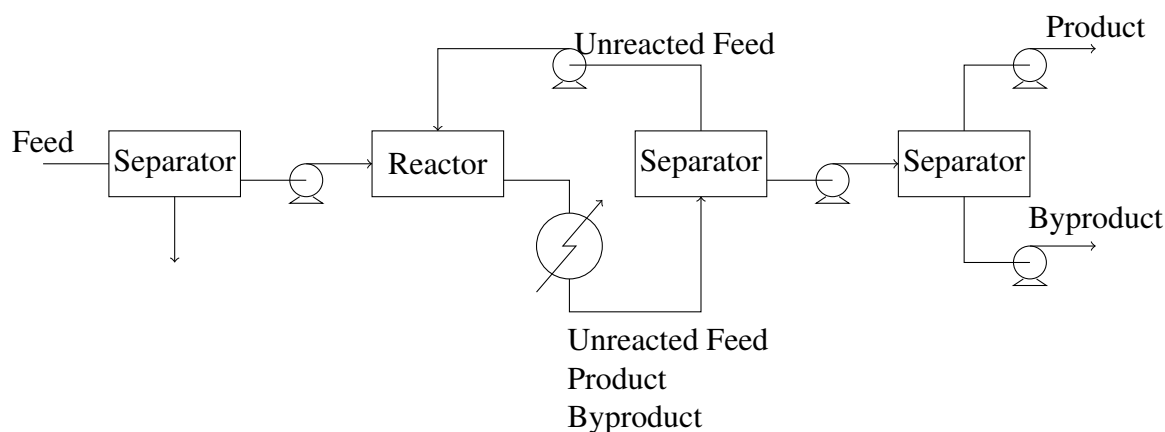


Figure 1.1: Example of a simple chemical process.

The exploitation and selection of the separation methods depends on the nature of the mixture but will be based on largely the so called phase separation. If the mixture is in a homogenous form, then another phase will have to be created, e.g. if the mixture is a vapour phase, then by a condenser a liquid phase can be created. However, if the mixture is in a heterogeneous form or the so called multiphase form, then the separation can be carried out relatively easily by exploiting the density difference between those multiple phases. It should be pointed out that any heterogeneous separation should be considered to be carried out first before any homogeneous separation, as the already existing advantages can be exploited.

## 1.3 Basic Separation Techniques

The creation of a mixture of chemical species from separate species is a spontaneous process that requires no energy input (though can take long amounts of time). The inverse process, separation of a chemical mixture into pure components, is not a spontaneous process and thus requires energy. A mixture to be separated may be single or multiphase. If it is multiphase, it is usually advantageous to first separate the phases.

In a general separation process both species and phase separation can occur; the feed and products may be vapour, liquid, or solid; one or more separation operations may be taking place; and the products differ in composition and may differ in phase. In each separation operation, the mixture components are induced to move into different, separable spatial

locations or phases by any one or more of the five basic separation methods shown in Figure 1.2. However, in most instances, the separation is not perfect, and if the feed contains more than two species, two or more separation operations may be required.

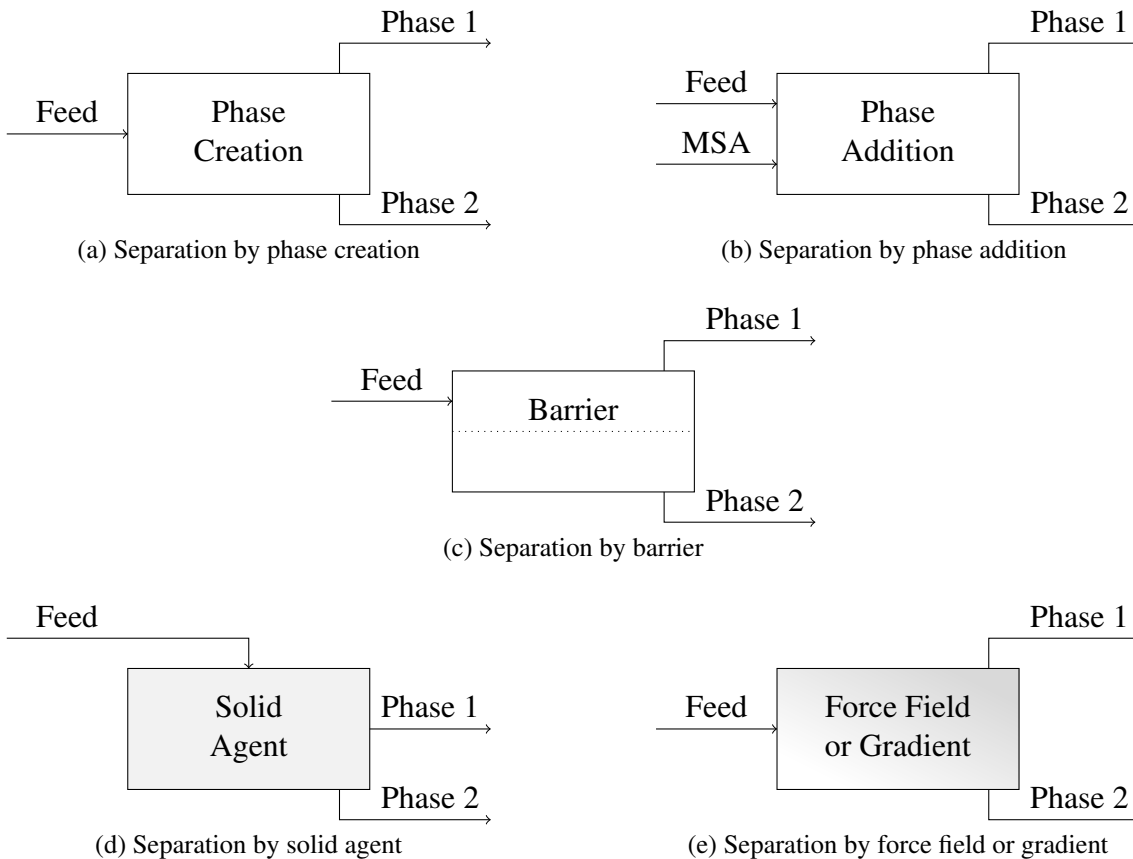


Figure 1.2: Basic separation techniques: (a) separation by phase creation; (b) separation by phase addition; (c) separation by barrier; (d) separation by solid agent; (e) separation by force field or gradient.

The most common separation technique, shown in Figure 1.2(a), creates a second phase, immiscible with the feed phase, by energy (heat and/or shaft-work) transfer or by pressure reduction. Common operations of this type are distillation, which involves the transfer of species between vapour and liquid phases, exploiting differences in volatility (e.g. vapour pressure or boiling point) among the species; and crystallisation, which exploits differences in melting point. A second technique, shown in Figure 1.2(b), adds another fluid phase, which selectively absorbs, extracts, or strips certain species from the feed. The most common operations of this type are liquid-liquid extraction, where the feed is liquid and a second, immiscible liquid phase is added; and absorption, where the feed is vapour, and a liquid of low volatility is added.

In both cases, species solubilities are significantly different in the added phase. Less common, but of growing importance, is the use of a barrier (shown in Figure 1.2(c)), usually a polymer membrane, which involves a gas or liquid feed and exploits differences in species permeabilities through the barrier. Also of growing importance are techniques that involve contacting a vapour or liquid feed with a solid agent, as shown in Figure 1.2(d). Most commonly, the agent consists of particles that are porous to achieve a high surface area, and differences in species adsorbability are exploited. Finally, external fields (centrifugal, thermal, electrical, flow, etc.), shown in Figure 1.2(e), are applied in specialised

cases to liquid or gas feeds, with electrophoresis being especially useful for separating proteins by exploiting differences in electric charge and diffusivity.

For the techniques of Figure 1.2, the size of the equipment is determined by rates of mass transfer of each species from one phase or location to another, relative to mass transfer of all species. The driving force and direction of mass transfer is governed by the departure from thermodynamic equilibrium, which involves volatilities, solubilities, etc. Fluid mechanics and heat transfer play important roles in separation operations. The extent of separation possible depends on the exploitation of differences in molecular, thermodynamic, and transport properties of the species. Properties of importance are:

#### 1. Molecular properties

Molecular weight	Polarizability
van der Waals volume	Dielectric constant
van der Waals area	Electric charge
Molecular shape (acentric factor)	Radius of gyration
Dipole moment	

#### 2. Thermodynamic and transport properties

Vapour pressure	Adsorptivity
Solubility	Diffusivity

Values of these properties appear in handbooks, reference books, and journals. Many can be estimated using process simulation programs. When property values are not available, they must be estimated or determined experimentally if a successful application of the separation operation is to be achieved.

## 1.4 Separations by Phase Addition or Creation

If the feed is a single-phase solution, a second separable phase must be developed before separation of the species can be achieved. The second phase is created by an energy-separating agent (ESA) and/or added as a mass-separating agent (MSA). An ESA involves heat transfer or transfer of work to or from the mixture. An example of work is the creation of vapour from a liquid phase by reducing the pressure. An MSA may be partially immiscible with one or more mixture components and frequently is the constituent of highest concentration in the added phase. Alternatively, the MSA may be miscible with a liquid feed mixture, but may selectively alter partitioning of species between liquid and vapour phases.

When immiscible fluid phases are contacted, intimate mixing is used to enhance mass-transfer rates so that the maximum degree-of-partitioning of species can be approached rapidly. After phase contact, the phases are separated by employing gravity and/or an enhanced technique such as centrifugal force. Table 1.1 includes the most common separation operations based on interphase mass transfer between two phases, one of which is created by an ESA or added as an MSA.

The equipment symbols shown in Table 1.1 correspond to the simplest configuration for each operation. More complex versions are frequently desirable. For example, a more complex version of the absorber could have a reboiler and several feeds. Design procedures must handle such complex equipment. Also, it is possible to conduct chemical reactions within separation equipment, e.g. reactive distillation[9].

When the feed mixture includes species that have widely different vapour pressures (boiling points) then partial condensation or partial vapourisation could be adequate to achieve the desired separation. The second phase is created when a vapour feed is partially condensed by removing heat or a liquid feed is partially vapourised by adding heat. Alternatively, partial vapourisation can be initiated by reducing the feed pressure with a valve or turbine (flash vapourisation). In both operations, the resulting vapour phase is enriched with the more easily vapourised species, while the liquid phase is enriched with respect to the less-volatile species. The two phases are then separated by gravity.

Often, the separation achieved by a single stage process is inadequate because the volatility differences among the species are not sufficiently large. In that case, multiple partial condensation and vapourisation stages can be used, distillation. Distillation is the most commonly used industrial separation process and involves multiple contacts between counter-currently flowing liquid and vapour phases.

When the volatility difference between species is so small as to necessitate more than about 100 trays extractive distillation can be considered. Here, a miscible MSA, acting as a solvent, increases the volatility difference among species in the feed, thereby reducing the number of trays. This MSA can also increase relative volatilities of species enough to break azeotropes.

If it is difficult to condense the vapour leaving the top of a distillation column, a liquid MSA, called an absorbent, can be fed to the top tray in place of reflux. If the feed is a vapour then the stripping section of the column is not needed, and the operation is referred to as absorption. Absorbers generally do not require an ESA and are frequently conducted at ambient temperature and elevated pressure. Species in the feed vapour dissolve in the absorbent depending on their solubility.

The inverse of absorption is stripping, where a liquid mixture is separated, often at elevated temperature and ambient pressure, by contacting the feed with a vapour stripping agent. If trays are needed above the feed tray to achieve the separation, a condenser with reflux can be used at the top of the column to produce a refluxed stripper, often called steam distillation if the MSA used is steam. Additional separation operations may be required to recover MSAs for recycling.

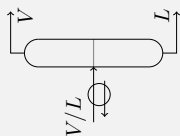
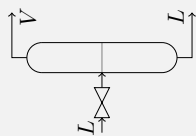
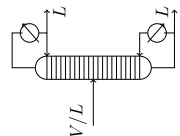
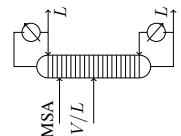
Liquid-liquid extraction is typically used when distillation is impractical, especially when the mixture is temperature sensitive. One or two solvents are added (potentially at different locations) which selectively dissolve only one or a fraction of the components in the feed. Several counter-currently arranged stages may be necessary. As with extractive distillation, additional operations are required to recover solvent from the streams leaving the extraction operation.

Since many chemicals are processed wet but sold as dry solids, a common manufacturing step is drying. Although the only requirement is that the vapour pressure of the liquid to be evaporated from the solid be higher than its partial pressure in the gas stream, dryer design and operation represents a complex problem. In addition to the effects of such external conditions as temperature, humidity, air flow, and degree of solid subdivision on drying rate, the effects of internal diffusion conditions, capillary flow, equilibrium moisture content, and heat sensitivity must be considered.

Evaporation is defined as the transfer of volatile components of a liquid into a gas by heat transfer. Applications include humidification, air conditioning, and concentration of aqueous solutions.

Crystallisation is carried out in some organic, and in almost all inorganic, chemical plants where the desired product is a finely divided solid. Crystallisation is a purification step, so the conditions must be such that impurities do not precipitate with the product. In solution crystallisation, the mixture, which includes a solvent, is cooled and/or the solvent is evaporated. In melt crystallisation, two or more soluble species are separated by partial freezing.

Table 1.1: Separation Operations Based on Phase Creation or Addition. Greyed rows are not covered by this course.

Separation Operation	Symbol	Feed Phase	Created or Added Phase	Separating Agent / Property	Industrial Example	Course
Partial condensation or vaporisation		Vapour and/or liquid	Liquid or vapour	Heat transfer (ESA) Vapour pressure (Relative volatility)	Recovery of H <sub>2</sub> and N <sub>2</sub> from ammonia by partial condensation and high-pressure phase separation	CHEN10082 Engineering Thermodynamics
Flash vaporisation		Liquid	Vapour	Pressure reduction Vapour pressure (Relative volatility)	Recovery of water from sea water	CHEN10082 Engineering Thermodynamics
Distillation		Liquid and/or Vapour	Vapour and liquid	Heat transfer (ESA) and sometimes work Relative volatility	Purification of styrene	CHEN20072 Distillation and Absorption This course will cover multicomponent and distillation sequencing
Extractive distillation		Liquid and/or Vapour	Vapour and liquid	Liquid solvent (MSA) and heat transfer (ESA) Modified relative volatility / Solubility	Separation of ethanol from water[7]	This course

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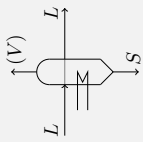
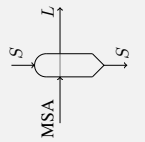
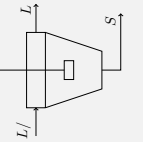


Table 1.1 – Continued from previous page

Separation Operation	Symbol	Feed Phase	Created or Added Phase	Separating Agent / Property	Industrial Example	Course
Absorption		Vapour	Liquid	Liquid (MSA) Solubility	Separation of carbon dioxide from combustion products by absorption with aqueous solutions of an ethanolamine	CHEN20072 Distillation and Absorption
Stripping		Liquid	Vapour	Stripping (MSA) Solubility	Stream stripping of naphtha, kerosene, and gas oil side cuts from crude distillation unit to remove light ends	CHEN20072 Distillation and Absorption
Liquid-liquid extraction		Liquid	Liquid	Liquid (MSA) Solubility	Recovery of penicillin from aqueous fermentation medium by methyl isobutyl ketone. Recovery of aromatics	This course
Drying		Liquid and often solid	Vapour	Gas (MSA) and/or heat transfer (ESA) Vapour pressure	Removal of water from polyvinylchloride with hot air in a fluid-bed dryer	CHEN10082 Engineering Thermodynamics
Evaporation		Liquid	Vapour	Heat transfer (ESA) Vapour pressure	Evaporation of water from a solution of urea and water	CHEN10082 Engineering Thermodynamics

Continued on next page

Table 1.1 – Continued from previous page

Separation Operation	Symbol	Feed Phase	Created or Added Phase	Separating Agent / Property	Industrial Example	Course
Crystallisation		Liquid	Solid (and vapour)	Heat transfer (ESA) Solubility	Recovery of a pro-tease inhibitor from an organic solvent. Crystallisation of <i>p</i> -xylene from a mixture with <i>m</i> -xylene	CHEN40052 Interface and Colloid Science
Leaching		Solid	Liquid	Liquid solvent (MSA) Solubility of solid components	Removal of caffeine from coffee beans with methylene chloride	
Coagulation Flocculation		Liquid/solid	Polymers and salts	(MSA) van der Waals force	Removal of small particulates from sewage in waste water treatment	

## 1.5 Separations by Barriers

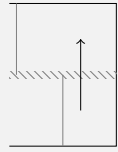
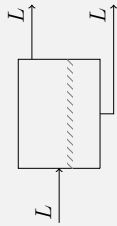
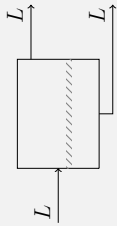
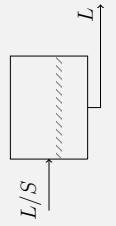
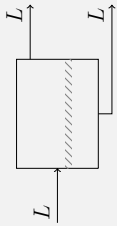
Use of microporous and nonporous membranes as semipermeable barriers for selective separations is gaining adherents. Membranes are fabricated mainly from natural fibers and synthetic polymers, but also from ceramics and metals. Membranes are fabricated into flat sheets, tubes, hollow fibers, or spiral-wound sheets, and incorporated into commercial modules or cartridges. For microporous membranes, separation is effected by rate of species diffusion through the pores; for nonporous membranes, separation is controlled by differences in solubility in the membrane and rate of species diffusion. The most complex and selective membranes are found in the trillions of cells in the human body.

Table 1.2 lists the main membrane-separation operations. Osmosis involves transfer, by a concentration gradient, of a solvent through a membrane into a mixture of solute and solvent. This membrane is almost impermeable to the solute. In reverse osmosis the transport of solvent is forced in the opposite direction by imposing a pressure, higher than the osmotic pressure, on the feed side.

Dialysis is the transport by a concentration gradient of small solute molecules through a porous membrane. The molecules unable to pass through the membrane are small, insoluble, non-diffusible particles. Microporous membranes selectively allow small solute molecules and/or solvents to pass through the membrane, while preventing large dissolved molecules and suspended solids from passing through, these filtration separations are generally classified by the size of the particles. Microfiltration refers to the retention of molecules from 0.02 to 10  $\mu\text{m}$ . Ultrafiltration, refers to the retention of molecules that range from 1 to 20  $\mu\text{m}$ . To retain molecules down to 0.1  $\mu\text{m}$ , nonporous membranes can be used in hyperfiltration. Gases can be separated in a similar manor by selective gas permeation.

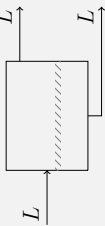
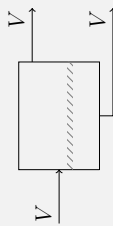
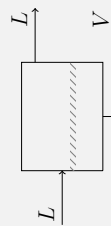
Pervaporation involves the transport of evaporated material through a nonporous membrane. This method, which can be used to separate azeotropic mixtures, uses much lower pressures than reverse osmosis and filtration, but the heat of vaporization must be supplied.

Table 1.2: Separation Operations Based on a Barrier. Greyed rows are not covered by this course.

Separation Operation	Symbol	Feed Phase	Separating Agent	Industrial Example	Course
Osmosis		Liquid	Nonporous membrane		
Reverse osmosis		Liquid	Nonporous membrane with pressure gradient	Desalination of sea water	
Dialysis		Liquid	Porous membrane with pressure gradient	Recovery of caustic from hemicellulose	
Filtration		Liquid and Solid	Porous film or bead of granular material	Removal of crystals from feed stock liquid	CHEN20061 Solid Fluid Systems
Microfiltration		Liquid	Microporous membrane with pressure gradient	Removal of bacteria from drinking water	

*Continued on next page*

Table 1.2 – Continued from previous page

Separation Operation	Symbol	Feed Phase	Separating Agent	Industrial Example	Course
Ultrafiltration		Liquid	Microporous membrane with pressure gradient	Separation of whey from cheese	
Gas permeation		Vapour	Nonporous membrane with pressure gradient	Hydrogen enrichment	
Pervaporation		Liquid	Nonporous membrane with pressure gradient	Separation of azeotropic mixtures	

## 1.6 Separations by Solid Agents

Separations that use solid agents are listed in Table 1.3. The solid, in the form of a granular material or packing, is the adsorbent itself, or it acts as an inert support for a thin layer of adsorbent. The separation is achieved by selective adsorption or chemical reaction with species in the feed. Adsorption is confined to the surface of the solid adsorbent, unlike absorption, which occurs throughout the absorbent. The active separating agent eventually becomes saturated with solute and must be regenerated or replaced. Such separations are often conducted batchwise or semicontinuously; however, equipment is available to simulate continuous operation.

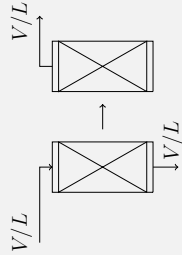
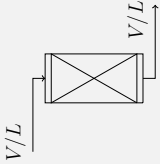
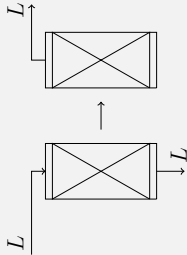
Adsorption is generally used to remove species in low concentrations and is followed by desorption to regenerate the adsorbents, which include activated carbon, aluminum oxide, silica gel, and synthetic sodium or calcium aluminosilicate zeolites (molecular sieves). The sieves are crystalline and have pore openings of fixed dimensions, making them very selective. Equipment consists of a cylindrical vessel packed with a bed of solid adsorbent particles through which the gas or liquid flows. Because regeneration is conducted periodically, two or more vessels are used, one desorbing while the other(s) adsorb(s). If the vessel is vertical, gas flow is best employed downward. With upward flow, movement can cause particle attrition, pressure-drop increase, and loss of material. However, for liquid mixtures, upward flow achieves better flow distribution. Regeneration occurs by one of four methods:

1. vapourisation of the adsorbate with a hot purge gas (thermal-swing adsorption),
2. reduction of pressure to vapourise the adsorbate (pressure-swing adsorption),
3. inert purge stripping without change in temperature or pressure, and
4. displacement desorption by a fluid containing a more strongly adsorbed species.

Chromatography separates gas or liquid mixtures by passing them through a packed bed. The bed may be solid particles (gas-solid chromatography or a solid-inert support coated with a viscous liquid (gas-liquid chromatography)). Because of selective adsorption on the solid surface, or absorption into liquid absorbents followed by desorption, components move through the bed at different rates, thus effecting the separation.

Ion exchange resembles adsorption in that solid particles are used and regenerated. However, a chemical reaction is involved.

Table 1.3: Separation operations based on solid agents. Greyed rows are not covered by this course.

Separation Operation	Symbol	Feed Phase	Separating Agent / Property	Industrial Example	Course
Adsorption		Vapour or liquid	Solid adsorbent Adsorbance	Purification of <i>p</i> -xylene	CHEN40061 Adsorption & Ion Exchange
Chromatography		Vapour or liquid	Solid adsorbent or liquid adsorbent on a solid support Adsorbance	Separation and pu- rification of proteins from complex mix- tures. Separation of xylene isomers and ethylbenzene	CHEN40061 Adsorption & Ion Exchange
Ion exchange		Liquid	Resin with ion- active sites Adsorbance	Demineralization of water	CHEN40061 Adsorption & Ion Exchange

## 1.7 Separations by External Field or Gradient

External fields can take advantage of differing degrees of response of molecules and ions to force fields. Table 1.4 lists common techniques and combinations.

When feed mixtures have different densities then gravity settling could be adequate to achieve the desired separation. The more dense material settles to the bottom of the settler and the less dense material rises to the top. This allows dense material to be taken from the bottom and the light material from the top. This separation can be used to separate gas-liquid, gas-solid, liquid-liquid, and liquid-solid systems.

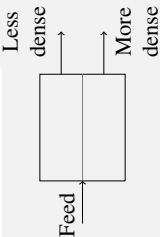
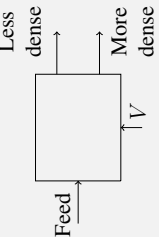
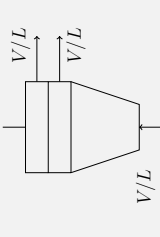
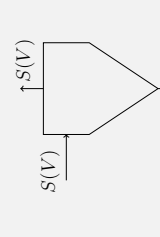
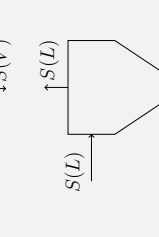
If the difference in densities is only small this separation can take a long time. Therefore, the separation force can be increased by exchanging gravity for rotational inertia. The two main options for this are centrifugation and cyclones. In centrifugation the contents are rotated at high speed in a rotating container, where as in cyclones the material is rotated due to its own inertia.

Electrolysis is the passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials. Electrolysis requires an electrolyte, substance containing free ions which are the carriers of electric current in the electrolyte; a direct current (DC) supply, provides the energy necessary to create or discharge the ions in the electrolyte; and two electrodes, an electrical conductor which provides the physical interface between the electrical circuit providing the energy and the electrolyte. A permeable membrane can be added to the system preventing migration of species of like charge, this is called electrodialysis.

In field-flow fractionation an electrical or magnetic field or thermal gradient is established perpendicular to a laminar-flow field. Components of the mixture travel in the flow direction at different velocities, so a separation is achieved. A related device is a small-particle collector where the particles are charged and then collected on oppositely charged metal plates.



Table 1.4: Separation operations by external field or gradient. Greyed rows are not covered by this course.

Separation Operation	Symbol	Feed Phase	Force Field or Gradient	Industrial Example	Course
Gravity Settling		Vapour or liquid or solid	Gravity		CHEN20061 Solid Fluid systems
Flotation		Solid in Liquid	Gravity Reduction in density from gas bubbles		Removal of precious metals from waste ores in mining
Centrifugation		Vapour or liquid	Centrifugal field	Separation of uranium isotopes	CHEN20061 Solid Fluid Systems
Cyclone		Solid (and vapour)	Centrifugal field	Remove sawdust from air at Saw mills	CHEN20061 Solid Fluid Systems
Hydrocyclone		Solid (and Liquid)	Centrifugal field	Remove sand, staples, and plastics from paper pulp	

*Continued on next page*

Table 1.4 – Continued from previous page

Separation Operation	Symbol	Feed Phase	Force Field or Gradient	Industrial Example	Course
Electrolysis		Liquid	Electrical force field	Concentration of heavy water	
Electrodialysis		Liquid	Electrical force field and membrane	Desalination of sea water [6]	
Field-flow fractionation		Liquid	Laminar flow in force field [2]	Separation of cells and platelets from blood	
Magnetic Separation		Solids in solids or liquid	Magnetic force	Ferrous scrap are to be separated from other waste from recycling	

## 1.8 Component Recoveries

If no chemical reaction occurs and the process operates in a continuous, steady-state fashion, then for each component  $i$ , in a mixture of  $C$  components, the molar (or mass) flow rate in the feed,  $n_i^{(F)}$ , equals the sum of the product molar (or mass) flow rates,  $n_i^{(p)}$ , for that component in the  $N$  product phases,  $p$ ,

$$n_i^{(F)} = \sum_{p=1}^N n_i^{(p)} \quad (1.8.1)$$



Summary Video

To solve equation 1.8.1 for values of  $n_i^{(p)}$  from specified values of  $n_i^{(F)}$  an additional  $N - 1$  independent expressions involving  $n_i^{(p)}$  are required. This gives a total of  $NC$  equations in  $NC$  unknowns. If a single-phase feed containing  $C$  components is separated into  $N$  products,  $C(N - 1)$  additional expressions are needed. If more than one stream is fed to the separation process,  $n_i^{(F)}$  is the summation for all feeds.

### 1.8.1 Split Fractions and Split Ratios

Chemical plants are designed and operated to meet specifications given as component recoveries and product purities. For each separation process, feed components are partitioned between the outlets (often 2) according to a split fraction or split ratio that depends on the properties of the components and the separator. The split fraction,  $SF$ , for component  $i$  in separator  $k$  is the fraction found in the product,  $p$ ,

$$SF_{i,k} = \frac{n_{i,k}^{(p)}}{n_{i,k}^{(F)}} \quad (1.8.2)$$

Alternatively, a split ratio,  $SR$ , between two products,  $p_1$  and  $p_2$ , is,

$$SR_{i,k} = \frac{n_{i,k}^{(p_1)}}{n_{i,k}^{(p_2)}} = \frac{SF_{i,k}}{(1 - SF_{i,k})} \quad (1.8.3)$$

$SF$  may be a better degree-of-separation indicator than  $SR$  because  $SF$  is bounded between 0 and 1, while  $SR$  can range from 0 to a large value. Two other measures of success can be applied to each separation or to an entire process. One is the percent recovery of a designated product. The other is product purity.

### 1.8.2 Separation Factor

Some separation operations are incapable of making a sharp split between key components and can effect the desired recovery of only a single component. For these, either a single separation stage is utilised, or the feed enters at one end (not near the middle) of a multistage separator. The split ratio ( $SR$ ), split fraction ( $SF$ ), recovery, or purity that can be achieved for the single key component depends on a number of factors. For these, a

measure of the relative degree of separation between two key components,  $i$  and  $j$ , is the separation factor or power,  $SP$ , defined in terms of the component splits as measured by the compositions of the two products, (1) and (2),

$$SP_{i,j} = \frac{\frac{C_i^{(1)}}{C_i^{(2)}}}{\frac{C_j^{(1)}}{C_j^{(2)}}} \quad (1.8.4)$$

where  $C$  is some measure of composition.  $SP$  is readily converted to the following forms in terms of split fractions or split ratios,

$$SP_{i,j} = \frac{SR_i}{SR_j} \quad (1.8.5)$$

$$SP_{i,j} = \frac{\frac{SF_i}{1 - SF_i}}{\frac{SF_j}{1 - SF_j}} \quad (1.8.6)$$

## 1.9 References

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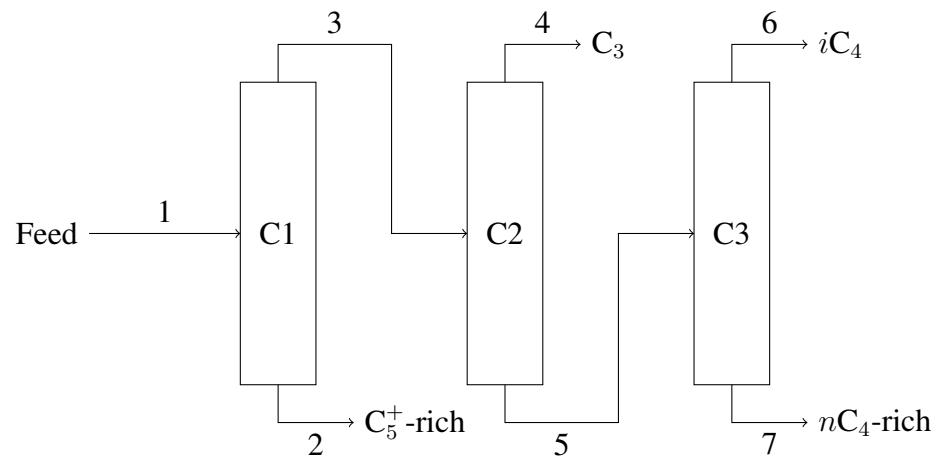
## 1.10 Problems

E1 How can we separate a mixture of 10 vol% ethanol in water to produce

- (a) 50 vol% ethanol in water?
- (b) 99 vol% ethanol in water?

- E2 For each of the following binary mixtures, a separation operation is suggested. Explain why the operation will or will not be successful.
- (a) Separation of air into oxygen-rich and nitrogen-rich products by distillation.
  - (b) Separation of *m*-xylene from *p*-xylene by distillation.
  - (c) Separation of benzene and cyclohexane by distillation.
  - (d) Separation of isopropyl alcohol and water by distillation.
  - (e) Separation of penicillin from water in a fermentation broth by evaporation of the water.

E3 The system of 3 distillation columns below are used to separate a mixture of hydrocarbons with stream compositions given in the table. Calculate the split fraction,  $SF$ , split ratio,  $SR$ , and the recovery of  $C_3H_8$ .



Component	lbmol h <sup>-1</sup> in Stream						
	1 Feed to C1	2 C <sub>5</sub> <sup>+</sup>	3 Feed to C2	4 C <sub>3</sub>	5 Feed to C3	6 iC <sub>4</sub>	7 nC <sub>4</sub> -rich
C <sub>2</sub> H <sub>6</sub>	0.60	0.00	0.60	0.60	0.00	0.00	0.00
C <sub>3</sub> H <sub>8</sub>	57.00	0.00	57.00	54.80	2.20	2.20	0.00
iC <sub>4</sub> H <sub>10</sub>	171.80	0.10	171.70	0.60	171.10	162.50	8.60
nC <sub>4</sub> H <sub>10</sub>	227.30	0.70	226.60	0.00	226.60	10.80	215.80
iC <sub>5</sub> H <sub>12</sub>	40.00	11.90	28.10	0.00	28.10	0.00	28.10
nC <sub>5</sub> H <sub>10</sub>	33.60	16.10	17.50	0.00	17.50	0.00	17.50
C <sub>6</sub> <sup>+</sup>	205.30	205.30	0.00	0.00	0.00	0.00	0.00
<b>Total</b>	<b>735.60</b>	<b>234.10</b>	<b>501.50</b>	<b>56.00</b>	<b>445.50</b>	<b>175.50</b>	<b>270.00</b>

E4 For the system shown in E3 also calculate the

- (a) recovery of  $iC_4H_{10}$ .
- (b) split fraction of  $C_3H_8$  in column 1.
- (c) purity of the  $C_3H_8$  product.
- (d) split ratio of  $iC_4H_{10}$  in column 3.
- (e) separation factor between  $C_3H_8$  and  $iC_4H_{10}$  in column 2.



- E5 A feed,  $F$ , of  $100 \text{ kmol h}^{-1}$  of air containing 21 mol%  $\text{O}_2$  and 79 mol%  $\text{N}_2$  is to be partially separated by a membrane unit according to each of four sets of specifications. Compute the amounts, in  $\text{kmol h}^{-1}$ , and compositions, in mol%, of the two products (retentate,  $R$ , and permeate,  $P$ ). The membrane is more permeable to  $\text{O}_2$ .
- (a) 50% recovery of  $\text{O}_2$  to the permeate and 87.5% recovery of  $\text{N}_2$  to the retentate.
  - (b) 50% recovery of  $\text{O}_2$  to the permeate and 50 mol% purity of  $\text{O}_2$  in the permeate.
  - (c) 85 mol% purity of  $\text{N}_2$  in the retentate and 50 mol% purity of  $\text{O}_2$  in the permeate.
  - (d) 85 mol% purity of  $\text{N}_2$  in the retentate and a split ratio of  $\text{O}_2$  in the permeate to the retentate equal to 1.1.



# Liquid-Liquid Extraction

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## 2.1 Chapter 2 ILOs

- ILO 2.1.** Choose suitable solvents and explain why they are suitable for the separation.
- ILO 2.2.** Use the lever-arm rule to calculate flow rates on ternary diagrams.
- ILO 2.3.** Demonstrate knowledge of general design considerations for liquid-liquid extraction.
- ILO 2.4.** Calculate single stage liquid-liquid equilibrium using ternary diagrams
- ILO 2.5.** Apply the Hunter-Nash method to allow calculation of the number of equilibrium stages needed for a single section liquid-liquid extraction system.
- ILO 2.6.** Recall the types of equipment used for liquid-liquid extraction.



Chapter Video 1



Chapter Video 2

## 2.2 Introduction

In liquid-liquid extraction (also called solvent extraction or extraction), a liquid feed of two or more components is contacted with a second liquid phase, called the solvent, which is immiscible or only partly miscible with one or more feed components and completely or partially miscible with one or more of the other feed components. Thus, the solvent partially dissolves certain species of the liquid feed, effecting at least a partial separation of the feed components.

The solvent may be a pure compound or a mixture. If the feed is an aqueous solution, an organic solvent is used; if the feed is organic, the solvent is often water. Important exceptions occur in metallurgy for the separation of metals and in bioseparations for the extraction from aqueous solutions of proteins that are denatured or degraded by organic solvents.

Extraction has been practiced since the time of the Romans, who used molten lead to separate gold and silver from molten copper by extraction[3]. However, it was not until the early 1930s that Lazăr Edeleanu invented the first large-scale extraction process. The Edeleanu process[1] is used in the petroleum refining industry, whereby liquid sulphur dioxide is used to extract aromatics from liquid kerosene at around  $-20^{\circ}\text{C}$ . Liquid  $\text{SO}_2$  selectively dissolves the aromatics leaving behind the low aromatic content kerosene as the finished product, resulting in cleaner-burning kerosene. Liquid-liquid extraction has grown in importance since then because of the demand for temperature-sensitive products, higher-purity requirements, better equipment, and availability of solvents with higher selectivity, and is an important method in bioseparations.

This chapter covers the simplest liquid-liquid extraction, which involves only a ternary system consisting of two miscible feed components — the carrier,  $C$ , and the solute,  $A$  — plus solvent,  $S$ , a pure compound. Components  $C$  and  $S$  are at most only partially soluble, but solute  $A$  is completely or partially soluble in  $S$ . During extraction, mass transfer of  $A$  from the feed to the solvent occurs, with less transfer of  $C$  to the solvent, or  $S$  to the feed. Nearly complete transfer of  $A$  to the solvent is seldom achieved in just one stage. Therefore, in practice, a number of stages are used.

In general, extraction is preferred over distillation for:

1. Dissolved or complexed inorganic substances in organic or aqueous solutions
2. Removal of a contaminant present in small concentrations
3. A high-boiling component present in relatively small quantities in an aqueous waste stream
4. Recovery of heat-sensitive materials, where extraction may be less expensive than vacuum distillation
5. Separation of mixtures according to chemical type rather than relative volatility
6. Separation of close-melting or close-boiling liquids, where solubility differences can be exploited.
7. Separation of mixtures that form azeotropes.

### 2.2.1 Partition coefficient

The solute in the mixture is separated by its different solubility in the 2 immiscible solvents. This difference in solubility can be represented by the distribution (partition) coefficient,

$$K_{DA} = \frac{x_A^{(S)}}{x_A^{(C)}} \quad (2.2.1)$$

This value should be greater than one, or a large a solvent-to-feed ratio will be required. The partition coefficient is an equilibrium constant, and this equilibrium is based on the chemical potential,  $\mu$ , of the solute being equal in each phase,

$$\begin{aligned} \mu_A^{(S)} &= \mu_A^{(C)} \\ \mu_A^{0,(S)} + RT \ln x_A^{(S)} &= \mu_A^{0,(C)} + RT \ln x_A^{(C)} \\ \frac{x_A^{(S)}}{x_A^{(C)}} &= \exp\left(\frac{\mu_A^{0,(C)} - \mu_A^{0,(S)}}{RT}\right) = K_{DA} \end{aligned} \quad (2.2.2)$$

The standard chemical potential can be represented in terms of the molar volumes as the solubility parameter, so that,[2]

$$K_{DA} = \exp\left(\frac{v_A(\delta_A - \delta_C)^2 - v_A(\delta_A - \delta_S)^2}{RT}\right) \quad (2.2.3)$$

An example of some solubility parameters of commonly used liquid-liquid extraction materials are given in Table 2.1.

The separation can also be represented by the extraction factor, which takes into account the flow rates of the solvent and carrier,<sup>1</sup>

$$E_A = \frac{K'_{DA} F_S}{F_C} \quad (2.2.4)$$

When the degree of solute extraction is not particularly high and/or when a large extraction factor can be achieved, an extractor will not require many stages. This is fortunate because mass-transfer resistance in liquid-liquid systems is high and stage efficiency is low in contacting devices, even if mechanical agitation is provided.

### 2.2.2 Solvent Selection

The key to an effective extraction process is a suitable solvent. The ideal solvent should have,

1. High selectivity for the solute relative to the carrier to minimize the need to recover carrier from the solvent
2. High capacity for dissolving the solute to minimize solvent-to-feed ratio

<sup>1</sup> $K'_{DA}$  is the distribution or partition coefficient in terms of mass or mole ratios (instead of mass or mole fractions).  $F_S$  and  $F_C$  are the flow rate of the solvent and carrier respectively.

Table 2.1: Some example solubility parameters of common liquid-liquid extraction materials[4].

Solvent	$\delta / \text{cal}^{1/2} \text{cm}^{-3/2}$
Amyl acetate	8.32
Benzene	9.15
Butanol	11.30
Butyl acetate	8.46
Carbon disulphide	9.97
Carbon tetrachloride	8.65
Chloroform	9.21
Cyclohexane	8.18
Ethanol	12.92
Hexane	7.24
Hexanol	10.7
Acetone	9.77
Perfluorohexane	5.9
Toluene	8.91
Water	23.5

3. Minimal solubility in the carrier
4. A volatility sufficiently different from the solute that recovery of the solvent can be achieved by distillation, but not so high that a high extractor pressure is needed, or so low that a high temperature is needed if the solvent is recovered by distillation
5. Stability to maximise the solvent life and minimise the solvent makeup requirement
6. Inertness to permit use of common materials of construction
7. Low viscosity to promote phase separation, minimise pressure drop, and provide a high-solute mass-transfer rate
8. Nontoxic and nonflammable characteristics to facilitate its safe use
9. Availability at a relatively low cost
10. Moderate interfacial tension to balance the ease of dispersion and the promotion of phase separation
11. Large difference in density relative to the carrier to achieve a high capacity in the extractor
12. Compatibility with the solute and carrier to avoid contamination
13. Lack of tendency to form a stable scum layer at the phase interface
14. Desirable wetting characteristics with respect to extractor internals

Solvent selection is a compromise among all the properties listed above. However, initial consideration is usually given to selectivity and environmental concerns, and second to capacity and cost.

## 2.3 General Design Considerations

Liquid-liquid extractors involve more variables than vapour-liquid operations because liquids have more complex structures than gases. To determine stages, one of the three cascade arrangements in Figure 2.1, or an even more complex arrangement, must be selected.

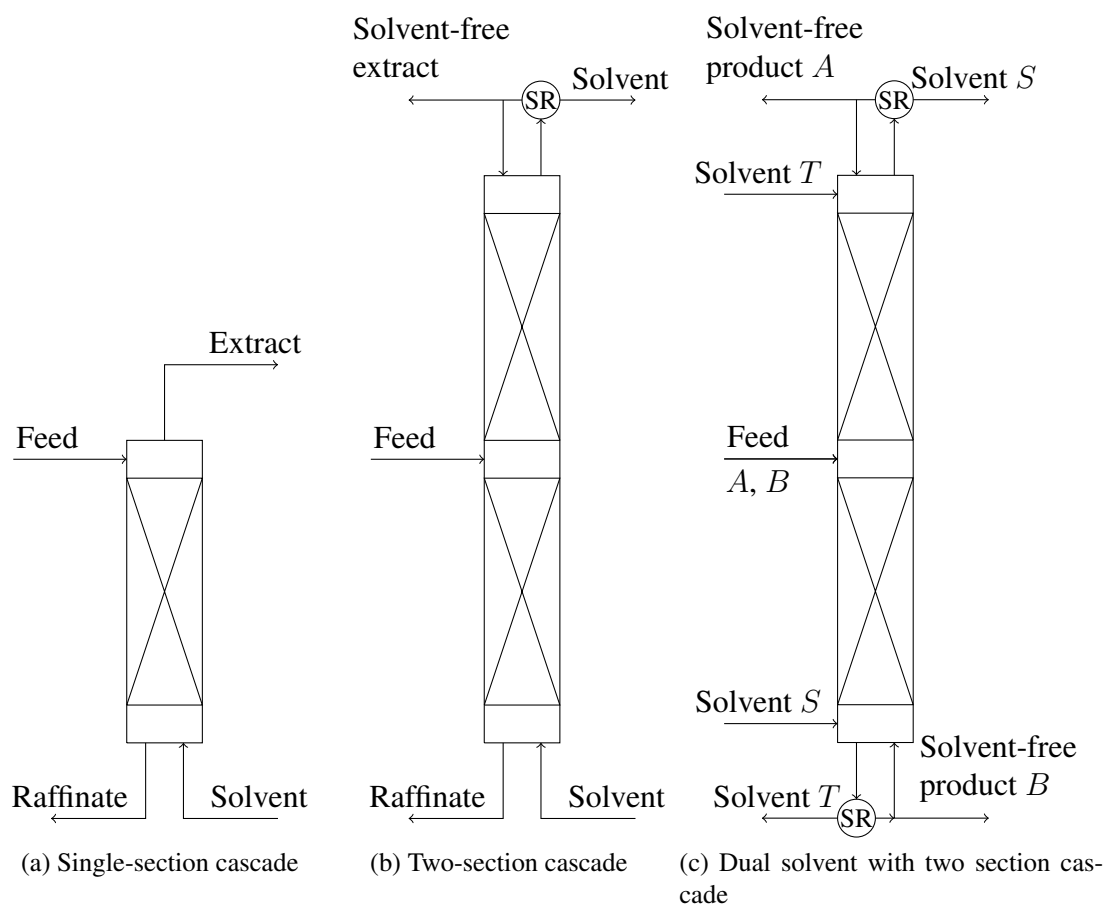


Figure 2.1: Common liquid-liquid extraction cascade configurations: (a) single-section cascade; (b) two-section cascade; (c) dual solvent with two section cascade.

The single-section cascade of Figure 2.1(a), which is similar to that used for absorption and stripping, will transfer solute in the feed to the solvent. The two-section cascade of Figure 2.1(b) is similar to that used for distillation. Solvent enters at one end and reflux, derived from the extract, enters at the other end. The feed enters in between. With two sections, depending on solubilities, it is sometimes possible to achieve a separation between feed components; if not, a dual-solvent arrangement with two sections, as in Figure 2.1(c), with or without reflux at the ends, may be advantageous. The configurations in Figure 2.1 are shown with packed sections, but any extraction equipment may be chosen. Operative factors are:

1. Entering feed flow rate, composition, temperature, and pressure
2. Type of stage configuration (one- or two-section)
3. Desired degree of recovery of one or more solutes for one-section cascades
4. Degree of feed separation for two-section cascades



5. Choice of solvent(s)
6. Operating temperature
7. Operating pressure (greater than the bubble point)
8. Minimum-solvent flow rate and actual-solvent flow rate as a multiple of the minimum rate for one-section cascades or reflux rate and minimum reflux ratio for two-section cascades
9. Number of equilibrium stages
10. Emulsification and scum-formation tendency
11. Interfacial tension
12. Phase-density difference
13. Maximum residence time to avoid degradation
14. Type of extractor
15. Extractor cost and power requirement

## 2.4 Representation of Multi-phase Liquid-Liquid Systems

Extraction calculations of liquid systems are most conveniently carried out with ternary equilibrium diagrams; this is due to the fact that 3 liquids are generally in equilibrium with each other.

In Figure 2.2, for a general system, the bold line is the equilibrium curve, also called the binodal curve because the plait point separates the curve into an extract to the left and a raffinate to the right. Mixtures of the 3 liquid system inside the equilibrium curve are not stable and separate into two immiscible phases. The red lines are tie-lines connecting compositions of these equilibrium phases.

Figure 2.3 shows some of the key different types of multi-phase systems found for 3 liquid systems. Type 1 has one pair of partially immiscible liquids with both of these miscible in the third liquid, e.g. Figure 2.3(a) where liquids A and B are immiscible in each other but both are miscible in liquid C. Type 2 has two pairs of partially immiscible liquids with two of the liquids being miscible, e.g. Figure 2.3(b) where liquids A and B are immiscible in each other and liquids B and C are also immiscible in each other but A and C are miscible.

If the two 2 phase boundaries are large enough then they can meet creating a large 2 phase region, e.g. Figure 2.3(c). The two 2 phase boundaries can also join and form a 3 phase region, e.g. Figure 2.3(d) where any total composition falling inside the middle triangle separates into 3 liquid phases with the compositions of a, b, and c.

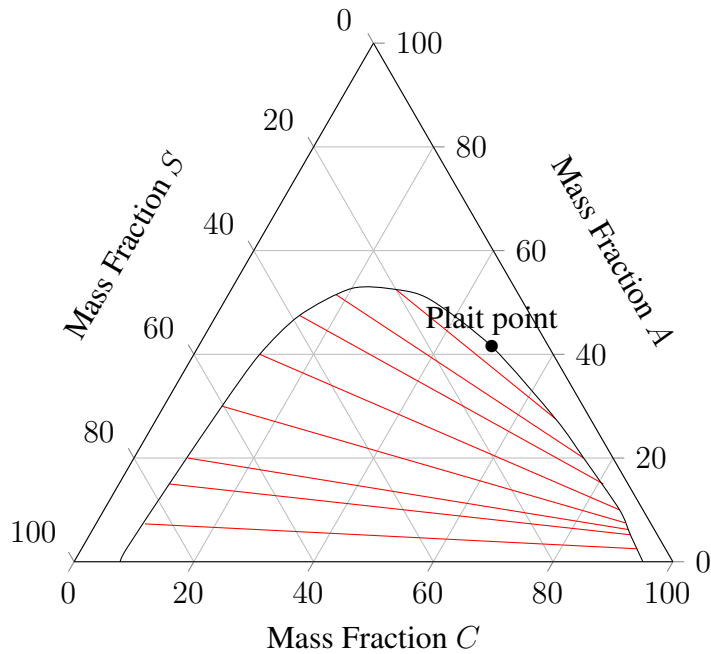


Figure 2.2: Example ternary phase diagram for a 2 phase liquid-liquid system.

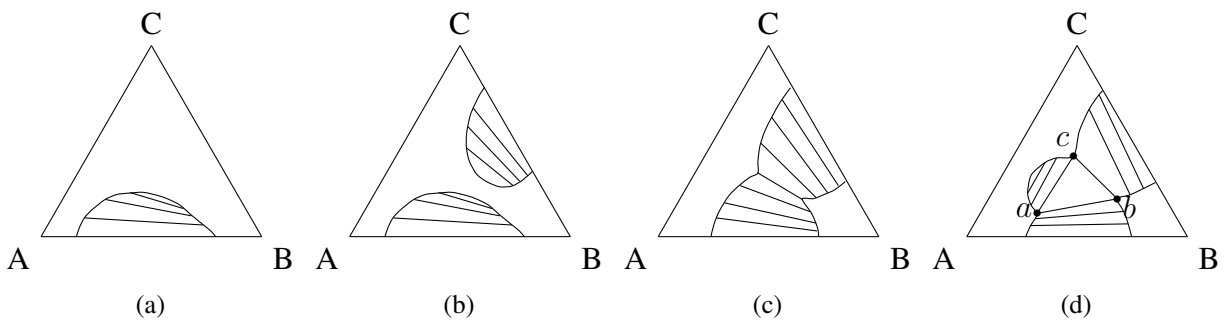


Figure 2.3: Some examples of liquid-liquid system, (a) Type 1, (b) Type 2 non-meeting, (c) Type 2 meeting, and (d) 3 liquid phases.

## 2.5 Single Stage Liquid-Liquid Extraction

Adding a solvent,  $S$  to a mixture of a solute,  $A$ , and a carrier,  $C$ , allows the solute to dissolve into the solvent, producing two output streams; the extract,  $E$ , and the raffinate,  $R$ ; Figure 2.4.

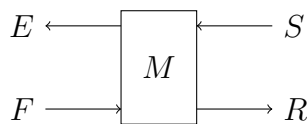


Figure 2.4: Single equilibrium stage liquid-liquid extraction.

An overall total mass balance can be generated for the system, as we know that the total amount of material entering the system must equal that exiting the system. We can also refer to the total amount in the system as  $M$ , i.e. the total mixture,

$$F + S = M = E + R \quad (2.5.1)$$

As well as an overall total mass balance we can also produce an overall mass balance for each component in the mixture,

$$\begin{aligned}
 (x_A)_F F + (x_A)_S S &= (x_A)_M M = (x_A)_E E + (x_A)_R R \\
 (x_C)_F F + (x_C)_S S &= (x_C)_M M = (x_C)_E E + (x_C)_R R \\
 (x_S)_F F + (x_S)_S S &= (x_S)_M M = (x_S)_E E + (x_S)_R R
 \end{aligned}
 \tag{2.5.2}$$

This process can be represented on a ternary diagram. For example, the following feed and solvent specifications,

Feed (F)	Solvent (S)
$F = 400 \text{ kg}$	$S = 100 \text{ kg}$
$(x_A)_F = 0.25$	$(x_A)_S = 0.00$
$(x_C)_F = 0.75$	$(x_C)_S = 0.00$
$(x_S)_F = 0.00$	$(x_S)_S = 1.00$

can be taken and plotted in Figure 2.5.

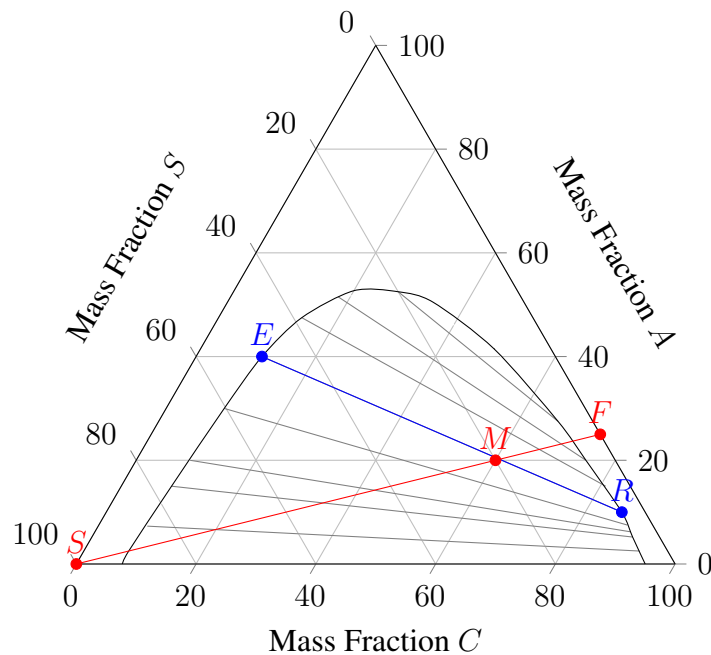


Figure 2.5: Ternary phase diagram for a general solute-carrier-solvent system.

By material balances (equations 2.5.1 and 2.5.2), the composition of  $M$  is,

$$\begin{aligned}
 M &= F + S = 400 + 100 = 500 \text{ kg} \\
 (x_A)_M M &= 0.25 \cdot 400 + 0 \cdot 100 = 100 \text{ kg} \\
 (x_A)_M &= 100/500 = 0.20 = 20.0 \% \\
 (x_C)_M M &= 0.75 \cdot 400 + 0 \cdot 100 = 300 \text{ kg} \\
 (x_C)_M &= 300/500 = 0.60 = 60.0 \% \\
 (x_S)_M M &= 0 \cdot 400 + 1 \cdot 100 = 100 \text{ kg} \\
 (x_S)_M &= 100/500 = 0.20 = 20.0 \%
 \end{aligned}$$

This mixing point,  $M$ , can be located on Figure 2.5. It can be seen that is point,  $M$ , is located on the straight line connecting  $F$  and  $S$  (red line). Therefore,  $M$  could be located knowing just one value of  $(x_i)_M$ , say,  $(x_S)_M$ .

With point  $M$  located, the composition of exiting extract,  $E$ , and raffinate,  $R$ , is determined from the equilibrium tie line that the mixing point lies on (blue line),

Raffinate Product	Extract Product
$(x_A)_R = 0.100$	$(x_A)_E = 0.400$
$(x_C)_R = 0.861$	$(x_C)_E = 0.110$
$(x_S)_R = 0.039$	$(x_S)_E = 0.490$

From the material balances (equations 2.5.1 and 2.5.2) the flow rates of the extract and raffinate can then be calculated. With  $M = 500$  kg this means that the mass of the extract and raffinate are,  $R = 322$  kg and  $E = 178$  kg.

## 2.6 Lever-Arm Rule

As noted when the feed, solvent, and mixing point were plotted on Figure 2.5; they all lie on a straight line. Taking the material balances for two of the components (equation 2.5.2),

$$\begin{aligned}(x_A)_F F + (x_A)_S S &= (x_A)_M M \\ (x_C)_F F + (x_C)_S S &= (x_C)_M M\end{aligned}$$

these can be combined with the overall total mass balance,  $F + S = M$ , to give,

$$\frac{F}{S} = \frac{(x_A)_S - (x_A)_M}{(x_A)_M - (x_A)_F} = \frac{(x_C)_S - (x_C)_M}{(x_C)_M - (x_C)_F} \quad (2.6.1)$$

The points must therefore lie on a straight line with the mixing position set by the amounts of the solvent and the feed<sup>1</sup>, as the differences can be thought of as vector line lengths,

$$\frac{F}{S} = \frac{\overline{SM}}{\overline{FM}} \quad (2.6.2)$$

So in our previous example we could have found the position of  $M$  by taking,

$$\begin{aligned}\frac{400 \text{ kg}}{100 \text{ kg}} &= \frac{\overline{SM}}{\overline{FM}} \\ \overline{SM} &= 4\overline{FM}\end{aligned}$$

and measuring the line lengths.

<sup>1</sup>As proof equation 2.6.1 can then be rearranged into the form of an equation for a straight line,

$$(x_C)_M = \frac{(x_C)_S - (x_C)_F}{(x_A)_S - (x_A)_F} (x_A)_M + \frac{(x_C)_F (x_A)_S - (x_C)_S (x_A)_F}{(x_A)_S - (x_A)_F}$$



Summary Video

## 2.7 Hunter-Nash Graphical Equilibrium-Stage Method

For a single stage system the extract and raffinate compositions are limited by the liquid-liquid equilibrium tie lines. Often these compositions are not suitable for the separation that is needed. To improve the separation a multi-stage method can be used.

Stagewise extraction calculations for Type I and Type II systems are most conveniently carried out with ternary equilibrium diagrams. Consider a counter-current flow,  $N$ -equilibrium-stage extractor operating isothermally in steady-state, continuous flow, as in Figure 2.6.

Stages are numbered from the feed end. Thus, the final extract is  $E_1$  and the final raffinate is  $R_N$ . Equilibrium is assumed at each stage, so for any stage  $n$ , the components in extract  $E_n$  and raffinate  $R_n$  are in equilibrium.



Summary Video

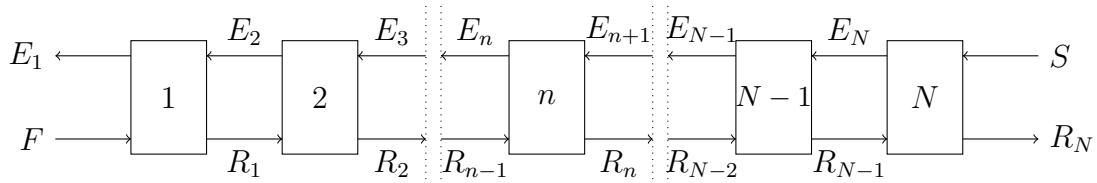


Figure 2.6: Counter-current flow,  $N$ -equilibrium-stage liquid-liquid extraction cascade.

Mass transfer of all species occurs at each stage. The feed,  $F$ , contains the carrier,  $C$ , the solute,  $A$ , and potentially the solvent,  $S$ , up to the solubility limit. Entering solvent,  $S$ , can contain  $C$  and  $A$ , but preferably contains little of either. Most liquid-liquid equilibrium data are listed and plotted in mass rather than mole concentrations, therefore we can say that  $F$  is the mass flow rate of feed to the cascade,  $S$  is the mass flow rate of solvent to the cascade,  $E_n$  is the mass flow rate of extract leaving stage  $n$ ,  $R_n$  is the mass flow rate of raffinate leaving stage  $n$ ,  $(y_i)_n$  is the mass fraction of species  $i$  in extract leaving stage  $n$ , and  $(x_i)_n$  is the mass fraction of species  $i$  in raffinate leaving stage  $n$ .

Although Figure 2.6 implies that the extract is the light phase, either phase can be the light phase. Phase equilibrium is represented on an equilateral-triangle diagram, e.g. Figure 2.5. In this case the ternary system is  $A$  (solute),  $C$  (carrier), and  $S$  (solvent) at a temperature,  $T$ . The tie lines slope upward from the  $C$  side toward the  $S$  side, at equilibrium,  $A$  has a concentration higher in  $S$  than in  $C$ . Thus, in this example,  $S$  is an effective solvent for extracting  $A$  from  $C$ .

In general when designing liquid-liquid extraction equipment to determine the number of stages several specifications are made; typically these are  $F$ ,  $(x_i)_F$ ,  $(y_i)_S$ ,  $T$ ,  $S$ , and  $(x_i)_{R_N}$ . Although other options can be used e.g.  $F$ ,  $(x_i)_F$ ,  $(y_i)_S$ ,  $T$ ,  $(x_i)_{R_N}$ , and  $(y_i)_{E_1}$  if the exit compositions are important, or  $F$ ,  $(x_i)_F$ ,  $(y_i)_S$ ,  $T$ ,  $(x_i)_{R_N}$ , and  $N$  if the design is for a retrofit of existing equipment. All the exiting phases,  $(x_i)_{R_N}$ , and  $(y_i)_{E_1}$ , lie on the equilibrium curve.

For example we will consider the typical set of specifications, with the procedures for the other sets being minor modifications, e.g. calculation of  $S$  from a suitable mixing point, and an iterative procedure with a given  $N$ . The technique, sometimes called the Hunter-Nash method[5], involves three kinds of constructions on the triangular diagram,

and is more difficult than the McCabe-Thiele staircase method for distillation. Although the procedure below is illustrated here only for a Type I system, parallel principles apply to a Type II system. The construction steps are shown as follows.

### 2.7.1 Step 1 - Calculation of the Mixing Point

As in the single stage separation an overall total mass balance can be written for the whole system,

$$F + S = R_N + E_1 = M \quad (2.7.1)$$

and for the an overall component mass balance can be written too,

$$F(x_i)_F + S(x_i)_S = R_N(x_i)_{R_N} + E_1(x_i)_{E_1} = M(x_i)_M \quad (2.7.2)$$

The first step is the same a in the single stage extraction, which is to calculate the mixing point,  $M$ , which can be calculated from equations 2.7.1 and 2.7.2 or using the lever-arm rule.

Assuming the same feed and solvent specifications as in section 2.5,

Feed	Solvent
$F = 400 \text{ kg}$	$S = 100 \text{ kg}$
$(x_A)_F = 0.25$	$(x_A)_S = 0.00$
$(x_C)_F = 0.75$	$(x_C)_S = 0.00$
$(x_S)_F = 0.00$	$(x_S)_S = 1.00$

we can plot the feed,  $F$ , solvent,  $S$ , and mixing point,  $M$ , on Figure 2.7.

### 2.7.2 Step 2 - Product Mass Balance

The difference from the single stage extraction is that the final extract,  $E_1$ , and the final raffinate,  $R_N$ , now do not need to be based on the equilibrium tie line (as we will have multiple equilibrium stages). The position of either product is specified and then the other calculated by a mass balance (equations 2.7.1 and 2.7.2), i.e. a straight line which passes between  $E_1$ ,  $M$ , and  $R_N$ .

In this example, we will specify  $(x_A)_{R_N} = 0.025 = 2.5\%$ , i.e. the desired exit concentration. As this point lies on the equilibrium curve,  $R_N$  can be located and the values of  $(x_C)_{R_N} = 92.8\%$  and  $(x_S)_{R_N} = 4.7\%$  can be read from Figure 2.7. A straight line drawn from  $R_N$  through  $M$  locates  $E_1$  at the equilibrium-curve intersection, from which the composition of  $E_1$  can be read. Values of the flow rates  $R_N$  and  $E_1$  can then be determined from the overall material balance equations, or from Figure 2.7 by the lever-arm rule.

With  $M = 500 \text{ kg}$ ; by either method the results are,

Raffinate Product	Extract Product
$R_N = 295.5 \text{ kg}$	$E_1 = 204.5 \text{ kg}$
$(x_A)_R = 0.025$	$(x_A)_E = 0.457$
$(x_C)_R = 0.928$	$(x_C)_E = 0.126$
$(x_S)_R = 0.047$	$(x_S)_E = 0.417$

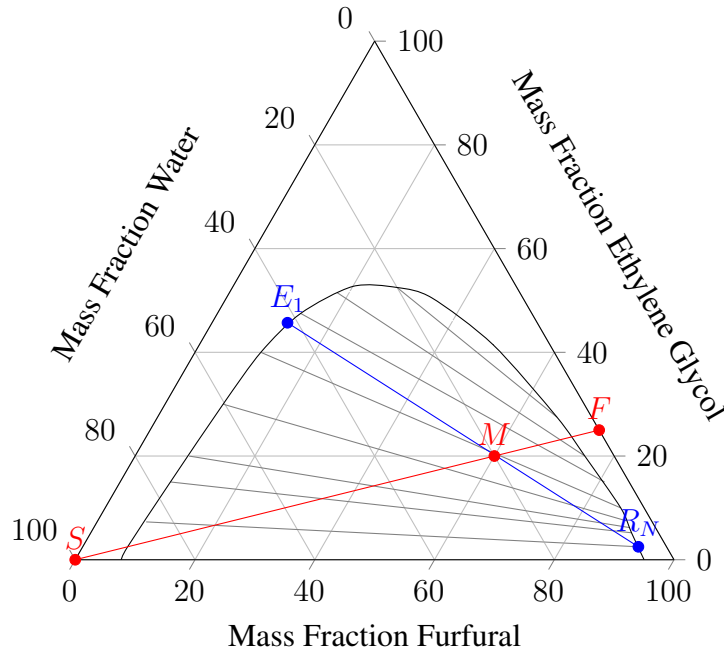


Figure 2.7: Construction 1: Location of product points.

### 2.7.3 Step 3 - Calculation of the Operating Lines

For vapour-liquid cascades, e.g. distillation and absorption, an operating line can be determined that is the locus of passing streams in a the cascade. Referring to Figure 2.6, a material balance can be generated around stage  $n$ ,

$$R_{n-1} + E_{n+1} = R_n + E_n = M \quad (2.7.3)$$

This can be rearranged to give the difference in flows,  $\Delta$ , at both sides of the stage,

$$R_{n-1} - E_n = R_n - E_{n+1} = \Delta \quad (2.7.4)$$

This value of  $\Delta$  must be the same for every stage including the first the last stage such that,

$$F - E_1 = R_N - S = \Delta \quad (2.7.5)$$

This process can be repeated for each component around stage  $n$ ,

$$R_{n-1}(x_i)_{R_{n-1}} + E_{n+1}(x_i)_{E_{n+1}} = R_n(x_i)_{R_n} + E_n(x_i)_{E_n} = M(x_i)_M \quad (2.7.6)$$

which means that the difference in component flows is,

$$R_{n-1}(x_i)_{R_{n-1}} - E_n(x_i)_{E_n} = R_n(x_i)_{R_n} - E_{n+1}(x_i)_{E_{n+1}} = \Delta(x_i)_\Delta \quad (2.7.7)$$

Because the passing streams are differenced,  $\Delta$  defines a difference point, not a mixing point,  $M$ . From the same geometric considerations that apply to a mixing point, a difference point also lies on a line through the points involved<sup>1</sup>. However, whereas  $M$  lies

<sup>1</sup>The component balance equation can be rearranged for that of a straight line,

$$(x_i)_\Delta = \frac{R_{n-1}(x_i)_{R_{n-1}} - E_n(x_i)_{E_n}}{R_{n-1} - E_n} = \frac{R_n(x_i)_{R_n} - E_{n+1}(x_i)_{E_{n+1}}}{R_n - E_{n+1}}.$$

inside the diagram and between the two end points,  $\Delta$  usually lies outside the triangular diagram along an extrapolation of the line through two points such as  $\overline{FE_1}$ ,  $\overline{SR_N}$ .

To locate this difference point, two straight lines are drawn through the passing-stream point pairs  $(E_1, F)$  and  $(S, R_N)$  (equation 2.7.5) established from Figure 2.7 and shown in Figure 2.8. These lines are extrapolated until they intersect at the difference point  $\Delta$ . These lines and point  $\Delta$  are shown in Figure 2.8.

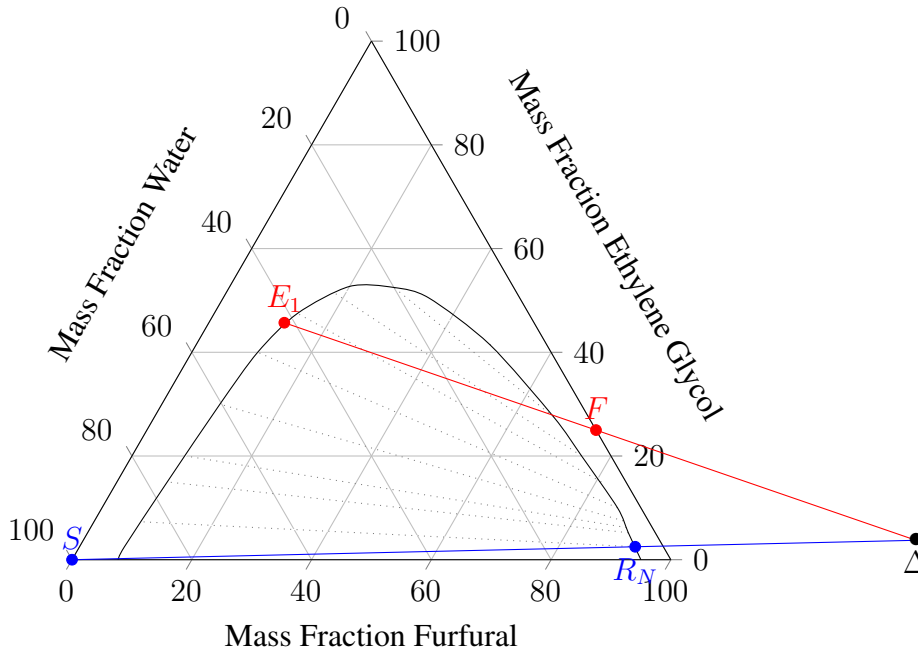


Figure 2.8: Construction 2: Location of operating points. Red line is the  $F - E_1$  operating line and the blue line is the  $R_N - S$  operating line.

Straight lines drawn through points for any other pair of passing streams, such as  $(E_n, R_{n-1})$ , must also pass through point  $\Delta$ . Thus, the difference point becomes an operating point for the extraction, and lines drawn through pairs of points for passing streams and extrapolated to point  $\Delta$  are operating lines.

The operating point,  $\Delta$ , lies on the feed or raffinate side of the diagram in Figure 2.8. Depending on the relative amounts of feed and solvent and the slope of the tie lines, point  $\Delta$  may lie on the solvent or feed side of the diagram, and inside or outside of the diagram.

### 2.7.4 Step 4 - Tie Lines and Equilibrium Lines

The next part of the construction involves the tie lines that define the equilibrium curve, which is divided into the two sides (raffinate and extract) by the plait point. A material balance around stage  $n$  for any of the three components is,

$$(x_i)_{n-1} R_{n-1} + (y_i)_{n+1} E_{n+1} = (x_i)_n R_n + (y_i)_n E_n \quad (2.7.8)$$

Because  $R_n$  and  $E_n$  are in equilibrium, their composition points are at the two ends of a tie line. Typically, a diagram will not contain all tie lines needed; they may be added by centering them between existing tie lines.



Equilibrium stages are stepped off by alternate use of tie lines and operating lines, as shown in Figure 2.9, where constructions have been employed to locate the stages points. Starting at the feed end from point  $E_1$  and referring to Figure 2.9, it is seen that  $R_1$  is in equilibrium with  $E_1$ .  $R_1$  passes  $E_2$ . Therefore,  $E_2$  lies at the intersection of the straight operating line drawn through points  $R_1$  and  $\Delta$ , and back to the extract side of the equilibrium curve. From  $E_2$ ,  $R_2$  is located with a tie line (equilibrium).

Continuing in this fashion by alternating between equilibrium tie lines and operating lines, the specified point  $R_N$  is reached or passed. In Figure 2.9, 4 equilibrium stages are required, where equilibrium stages are counted by the number of equilibrium tie lines used.

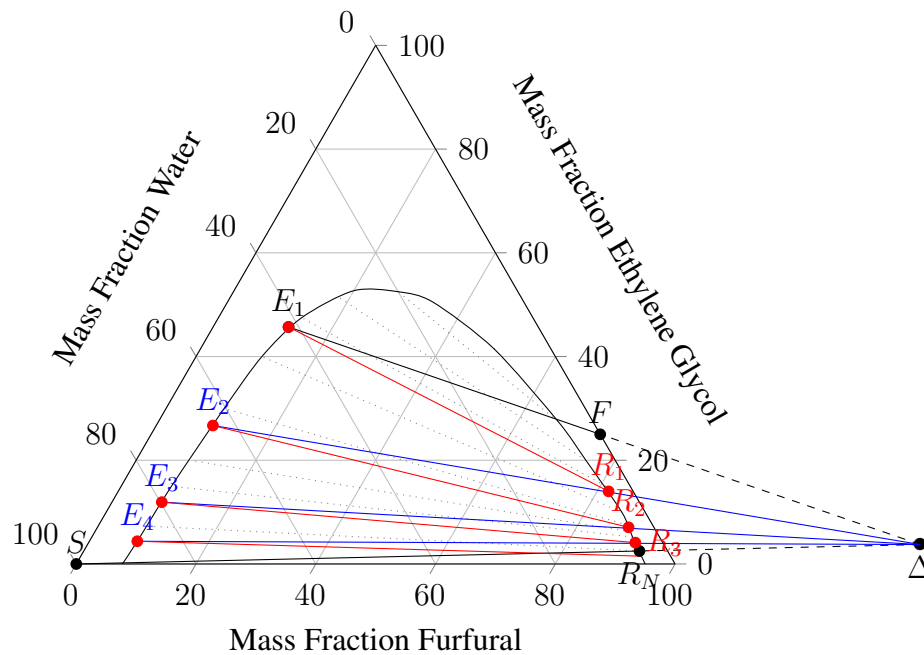


Figure 2.9: Construction 3: Determination of the extraction stages. Red lines are the equilibrium tie lines, blue lines are the operating difference lines between equilibrium stages.

## 2.8 Minimum and Maximum Solvent-to-Feed Flow-Rate Ratios

The procedure above for determining the number of equilibrium stages needed to achieve a desired solute extraction for a given solvent-to-feed ratio presupposes that this ratio is,

- greater than the minimum ratio, which corresponds to an infinite number of stages, and
- less than the maximum ratio that would prevent the formation of the required second liquid phase.

### 2.8.1 Minimum Ratio

In practice, one usually determines the minimum ratio first. This is done by solving with  $N = \infty$ , where, as in distillation, absorption, and stripping, the infinity of stages occurs at an equilibrium-curve and operating-line pinch point. In ternary systems, the pinch point occurs when a tie line coincides with an operating line. The calculation is involved because the pinch point is not always at the feed end of the cascade.

Each tie line is assumed to be a pinch point by extending each tie line until it intersects the line  $\overline{SR}$ . In this manner, a sequence of intersections  $\Delta_1, \Delta_2$ , etc., is found. If these points lie on the raffinate side of the diagram, the pinch point corresponds to the point  $\Delta_{min}$  located at the greatest distance from  $R_N$ , Figure 2.10.

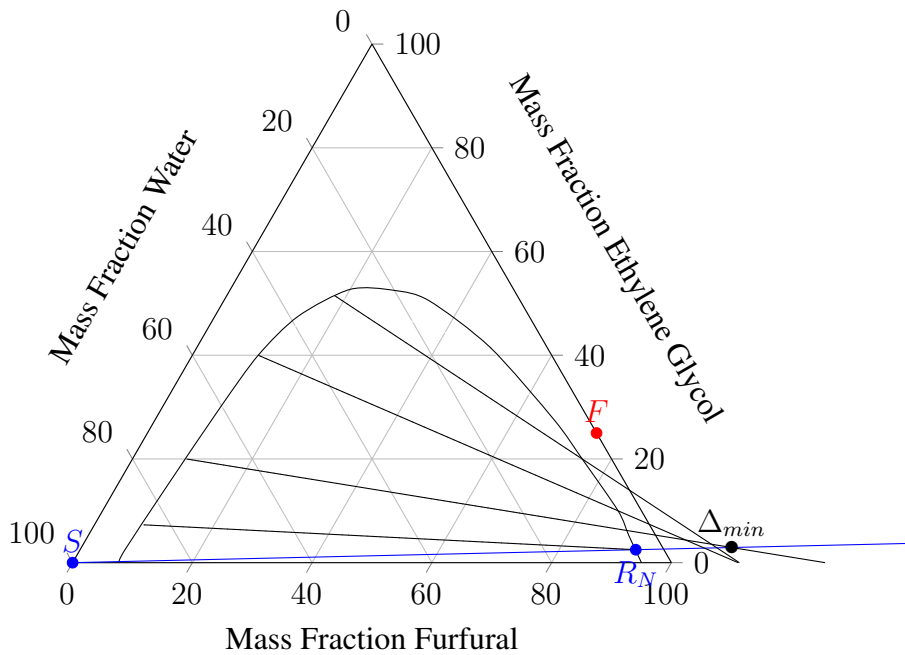


Figure 2.10: Construction to find the minimum solvent to feed ratio for equilibrium lines slopping towards the raffinate side.

If the intersection points lie on the extract side of the diagram, the pinch point corresponds to the point  $\Delta_{min}$  located at the closest distance to  $S$ , Figure 2.11.

Joining the  $\Delta_{min}$  to the feed point,  $F$ , we can get the  $E_{min}$  value. Joining the  $E_{min}$  to  $R$  gives the mixing point,  $M_{min}$ . The  $(S/F)_{min}$  value can be calculated by the lever-arm rule, Figure 2.12.

### 2.8.2 Maximum Ratio

If  $M$  in Figure 2.12 is moved along the  $\overline{FS}$  line towards  $S$ , the intersection for  $(S/F)_{max}$  occurs at the point shown on the extract side of the binodal curve, Figure 2.13. This is the maximum amount of solvent that can be added with the mixture composition within the 2 phase region. If the mixture falls outside the 2 phase region there is only one phase, so there can't be any extraction.

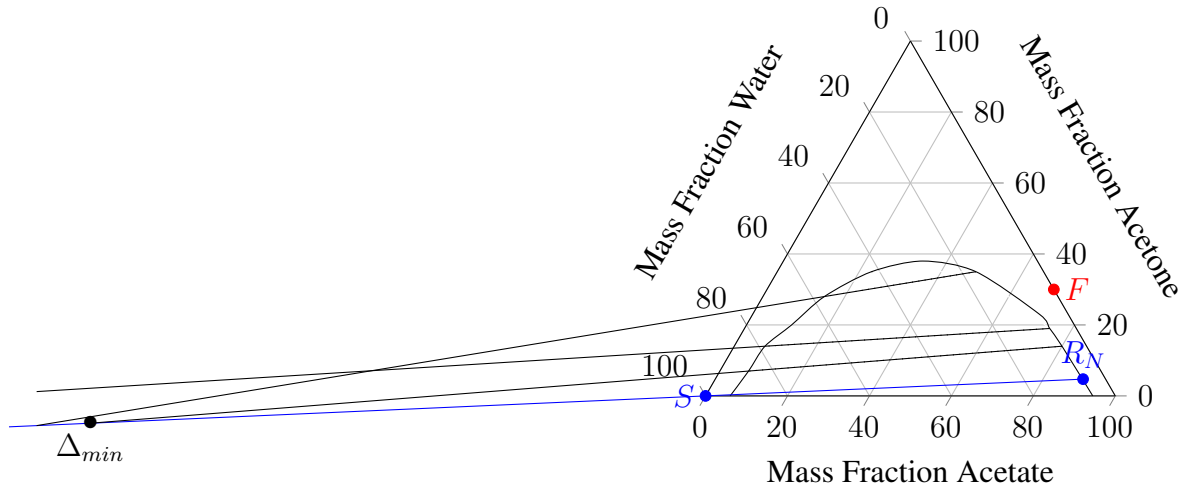


Figure 2.11: Construction to find the minimum solvent to feed ratio for equilibrium lines sloping towards the extract side.

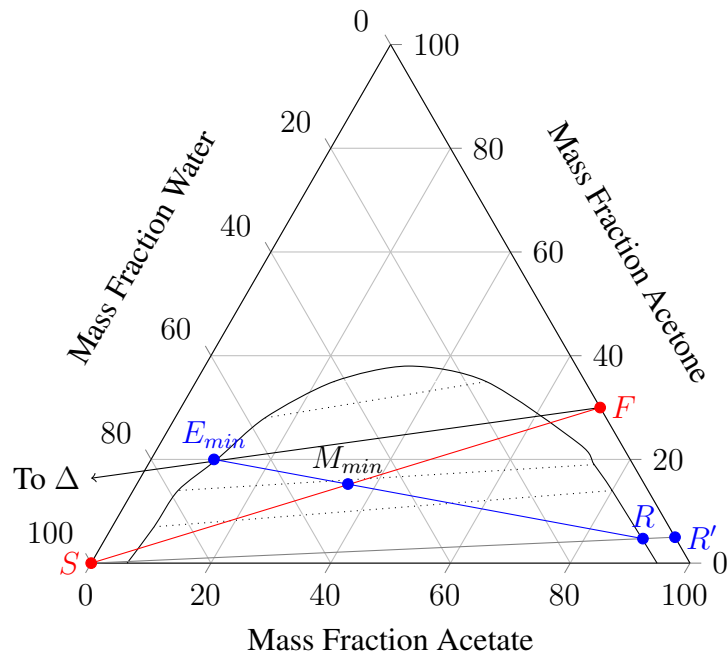


Figure 2.12: Determination of  $M_{min}$ .

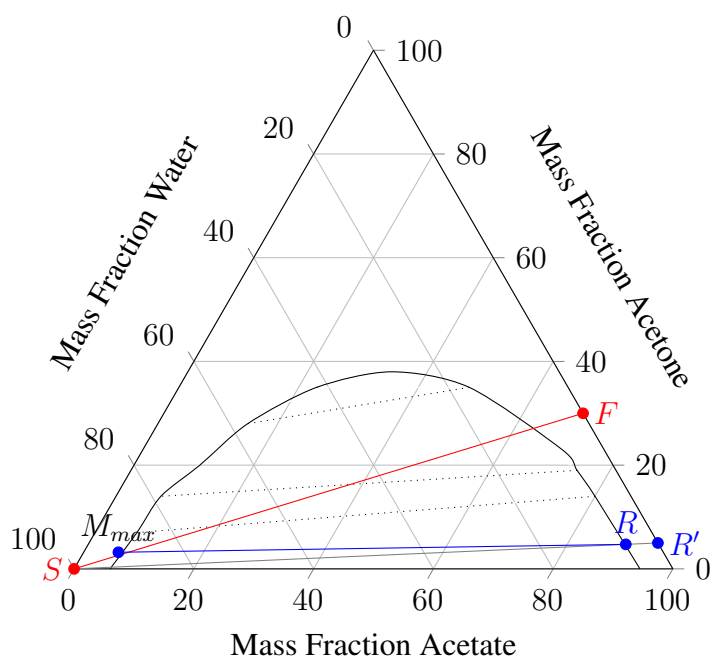


Figure 2.13: Determination of  $M_{max}$ .

## 2.9 Equipment for Solvent Extraction

Equipment similar to that used for absorption, stripping, and distillation is sometimes used for extraction, but such devices are inefficient unless liquid viscosities are low and differences in phase density are high. Generally, centrifugal and mechanically agitated devices are preferred. Regardless of the type of equipment, the number of equilibrium stages required is computed first. Then the size of the device is obtained from experimental HETP or mass-transfer-performance-data characteristic of that device. In extraction, some authors use the acronym HETS, height equivalent to a theoretical stage, rather than HETP. Also, the dispersed phase, in the form of droplets, is referred to as the discontinuous phase, the other phase being the continuous phase.

### 2.9.1 Mixer-Settlers

In mixer-settlers, the two liquid phases are first mixed in a vessel (Figure 2.14(a)) by one of several types of impellers, and then separated by gravity-induced settling (Figure 2.14(b)). Any number of mixer-settler units may be connected together to form a multistage, countercurrent cascade.

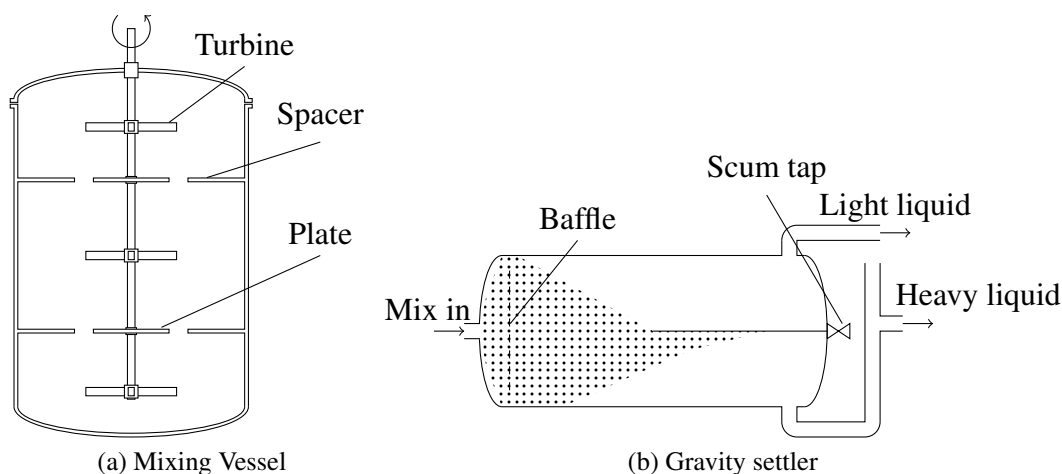


Figure 2.14: Mixer-Settler equipment (a) Compartmented mixing vessel with turbine agitators, (b) Horizontal gravity-settling vessel.

During mixing, one of the liquids is dispersed in the form of small droplets into the other liquid. The dispersed phase may be either the heavier or the lighter phase. The mixing is commonly conducted in an agitated vessel with sufficient residence time so that a reasonable approach to equilibrium (e.g. 80% to 90%) is achieved. The vessel may be compartmented as in Figure 2.14(a). If dispersion is easily achieved and equilibrium rapidly approached, as with liquids of low interfacial tension and viscosity, the mixing step can be achieved by alternative, more energy efficient means, e.g. impingement in a jet mixer, by turbulence in a nozzle mixer, orifice mixer, or other in-line mixing device.

The settling step is by gravity in a settler (decanter). In Figure 2.14(b) a horizontal vessel, with an impingement baffle to prevent the jet of the entering two-phase dispersion (emulsion) from disturbing the gravity-settling process, is used. Vertical and inclined vessels are also common. A major problem in settlers is emulsification in the mixing vessel, which may occur if the agitation is so intense that the dispersed droplet size falls below 1

to  $1.5\ \mu\text{m}$  (micrometers). When this happens, coalescers, separator membranes, meshes, electrostatic forces, ultrasound, or chemical treatment are required to speed settling. If the phase-density difference is small, the rate of settling can be increased by substituting centrifugal for gravitational force.

Each mixer-settler can be thought of as one theoretical stage.

## 2.9.2 Spray Columns

The simplest and one of the oldest extraction devices is the spray column. Either the heavy phase or the light phase can be dispersed, as seen in Figure 2.15. The droplets of the dispersed phase are generated at the inlet, usually by spray nozzles.

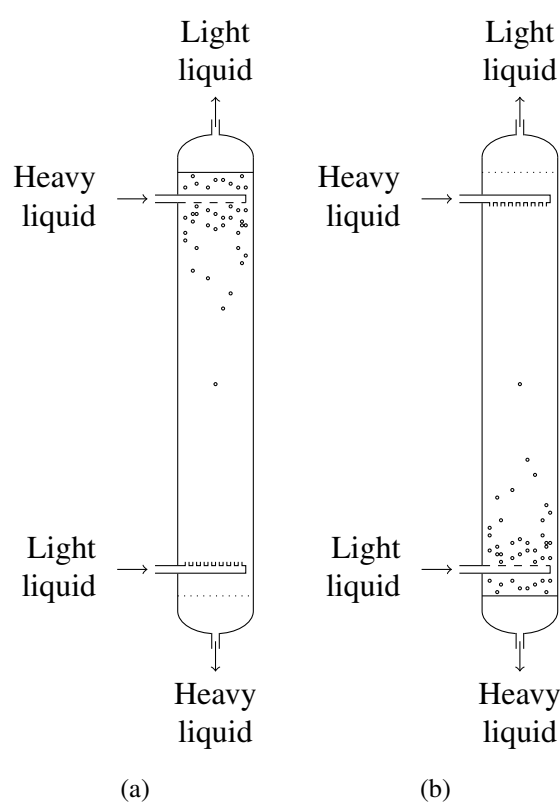


Figure 2.15: Spray columns: (a) light liquid dispersed, heavy liquid continuous; (b) heavy liquid dispersed, light liquid continuous.

Because of lack of column internals, throughputs are large, depending upon phase-density difference and phase viscosities. As in gas absorption, axial dispersion (backmixing) in the continuous phase limits these devices to applications where only one or two stages are required. Axial dispersion is so serious for columns with a large diameter-to-length ratio that the continuous phase is completely mixed, and spray columns are thus rarely used, despite their low cost. The HETP for spray towers depends on the properties of the liquids and the dimensions of the column[6–9].

Spray towers can be used e.g. when there is an irreversible reaction occurring in one of the phases. Spray towers are thus used in waste acid neutralisation. In these cases the column volume may be set by the reaction rate, not the mass transfer, and the height is not designed only based on HETP.

### 2.9.3 Packed Columns

Axial dispersion in a spray column can be reduced, but not eliminated, by packing the column. This also improves mass transfer by breaking up large drops to increase interfacial area, and promoting mixing in drops by distorting droplet shape. With the exception of Raschig rings, the packings used in distillation and absorption are suitable for liquid-liquid extraction, but choice of packing material is more critical.

A material preferentially wetted by the continuous phase is preferred. Figure 2.16 shows performance data, in terms of HTU, for Intalox saddles in an extraction service as a function of continuous,  $U_C$ , and discontinuous,  $U_D$ , phase superficial velocities. Because of backmixing, the HETP is generally larger than for staged devices; hence packed columns are suitable only when few stages are needed.

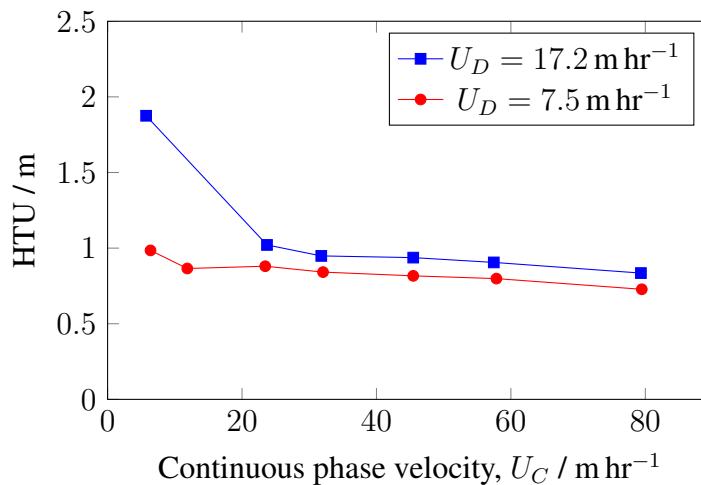


Figure 2.16: Efficiency of 1-inch Intalox saddles in a column 60 inches high with MEK–water–kerosene [10].  $U_D$  is the dispersed phase velocity.

### 2.9.4 Plate Columns

Sieve plates reduce axial mixing and promote a stagewise type of contact. The dispersed phase may be the light or the heavy phase. For the former, the dispersed phase, analogous to vapour bubbles in distillation, flows up the column, with redispersion at each tray. The heavy phase is continuous, flowing at each stage through a downcomer, and then across the tray like a liquid in a distillation tower. If the heavy phase is dispersed, upcomers are used for the light phase. Columns have been built with diameters larger than 4.5 m. Holes from 0.64 to 0.32 cm in diameter and 1.25 to 1.91 cm apart are used, and tray spacings are closer than in distillation - 10 to 15 cm for low-interfacial-tension liquids. Plates are usually built without outlet weirs on the downspouts.

If operated properly, extraction rates in sieve-plate columns are high because the dispersed-phase droplets coalesce and re-form on each sieve tray. This destroys concentration gradients, which develop if a droplet passes through the entire column undisturbed. Sieve-plate extractors are subject to the same limitations as distillation columns: flooding, entrainment, and, to a lesser extent, weeping. An additional problem is scum formation at phase interfaces due to small amounts of impurities.

## 2.9.5 Columns with Mechanically Assisted Agitation

If interfacial tension is high, the density difference between liquid phases is low, and/or liquid viscosities are high, gravitational forces are inadequate for proper phase dispersal and turbulence creation. In that case, mechanical agitation is necessary to increase interfacial area per unit volume, thus decreasing mass-transfer resistance. For packed and plate columns, agitation is provided by an oscillating pulse to the liquid, either by mechanical or pneumatic means.

The most prevalent agitated columns are those that employ rotating agitators, such as those in Figure 2.17, driven by a shaft extending axially through the column. The agitators create shear mixing zones, which alternate with settling zones.

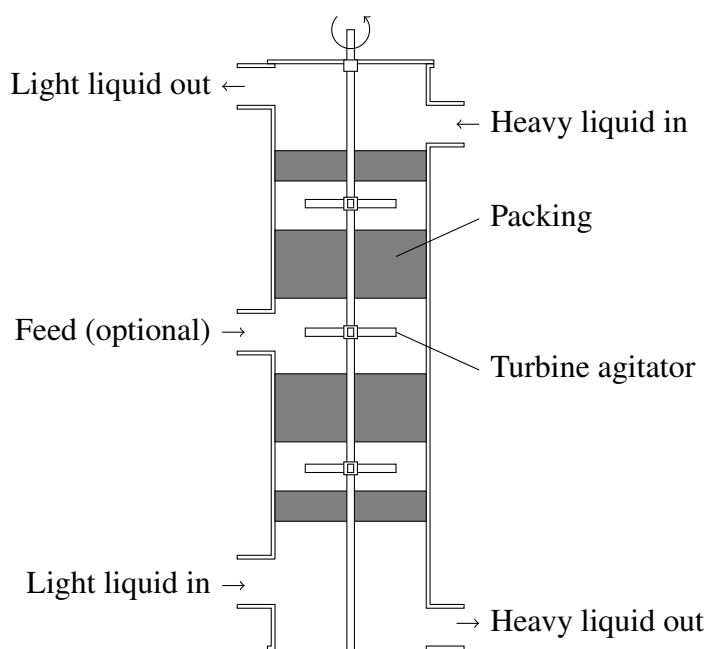


Figure 2.17: Commercial extractor with mechanically assisted agitation.

## 2.10 References

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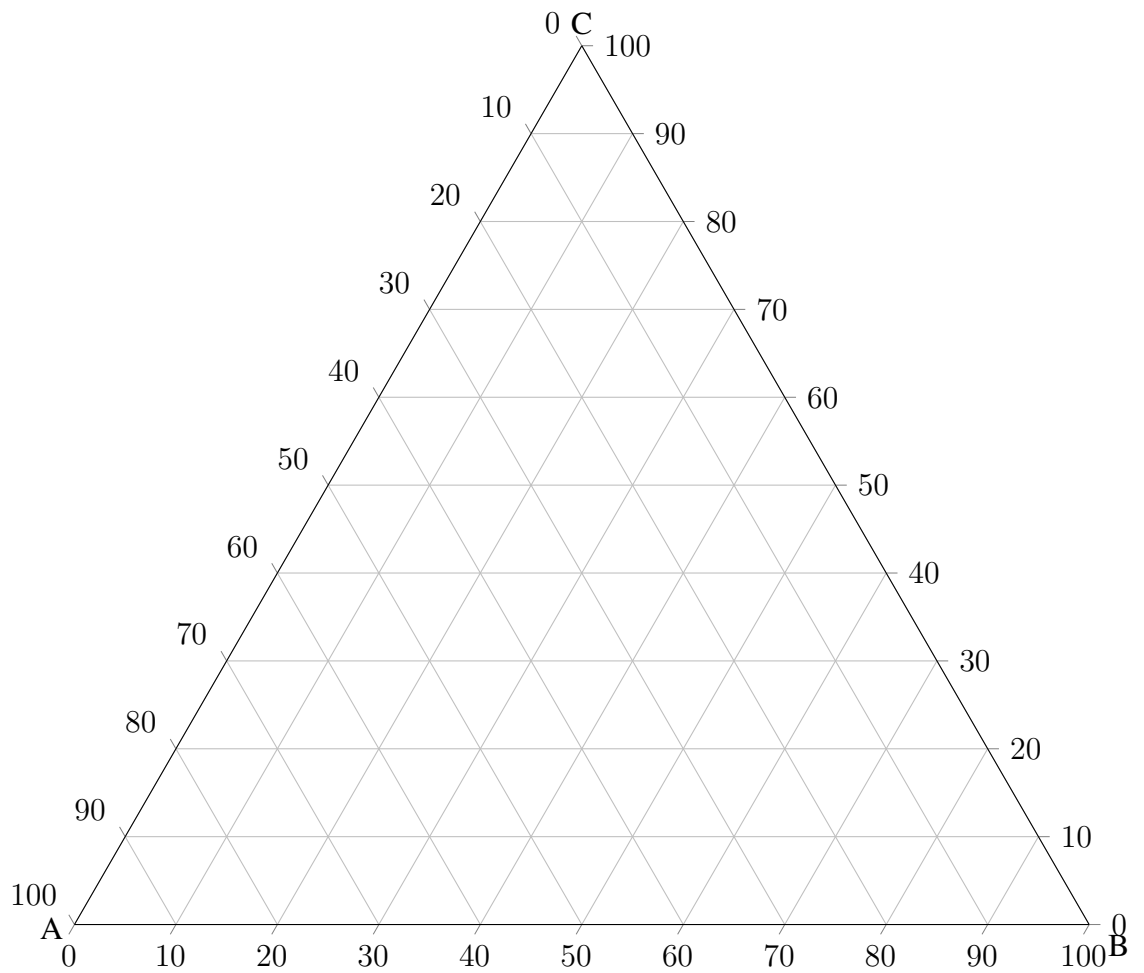
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## 2.11 Problems

R1 Plot the points that refer to

- (a) Pure B
- (b) 70% B and 20% A
- (c) A composition of 0.1 A, 0.5 B, 0.4 C



E1 Determine the composition of the equilibrium phases produced when a 45 % w/w ethylene glycol and 55 % water solution is contacted with twice its weight of pure furfural solvent at 25 °C and 101 kPa. [Phase 1 - 32.0 wt% Ethylene Glycol, Phase 2 - 8.5 wt% Ethylene Glycol].

Furfural (w/w %)	Ethylene Glycol (w/w %)	Water (w/w %)
95.0	0.0	5.0
90.3	5.2	4.5
86.1	10.0	3.9
75.1	20.0	4.9
66.7	27.5	5.8
49.0	41.5	9.5
34.3	50.5	15.2
27.5	52.5	20.0
13.9	47.5	38.6
11.0	40.0	49.0
9.7	30.0	60.3
8.4	15.0	76.6
7.7	0.0	92.3

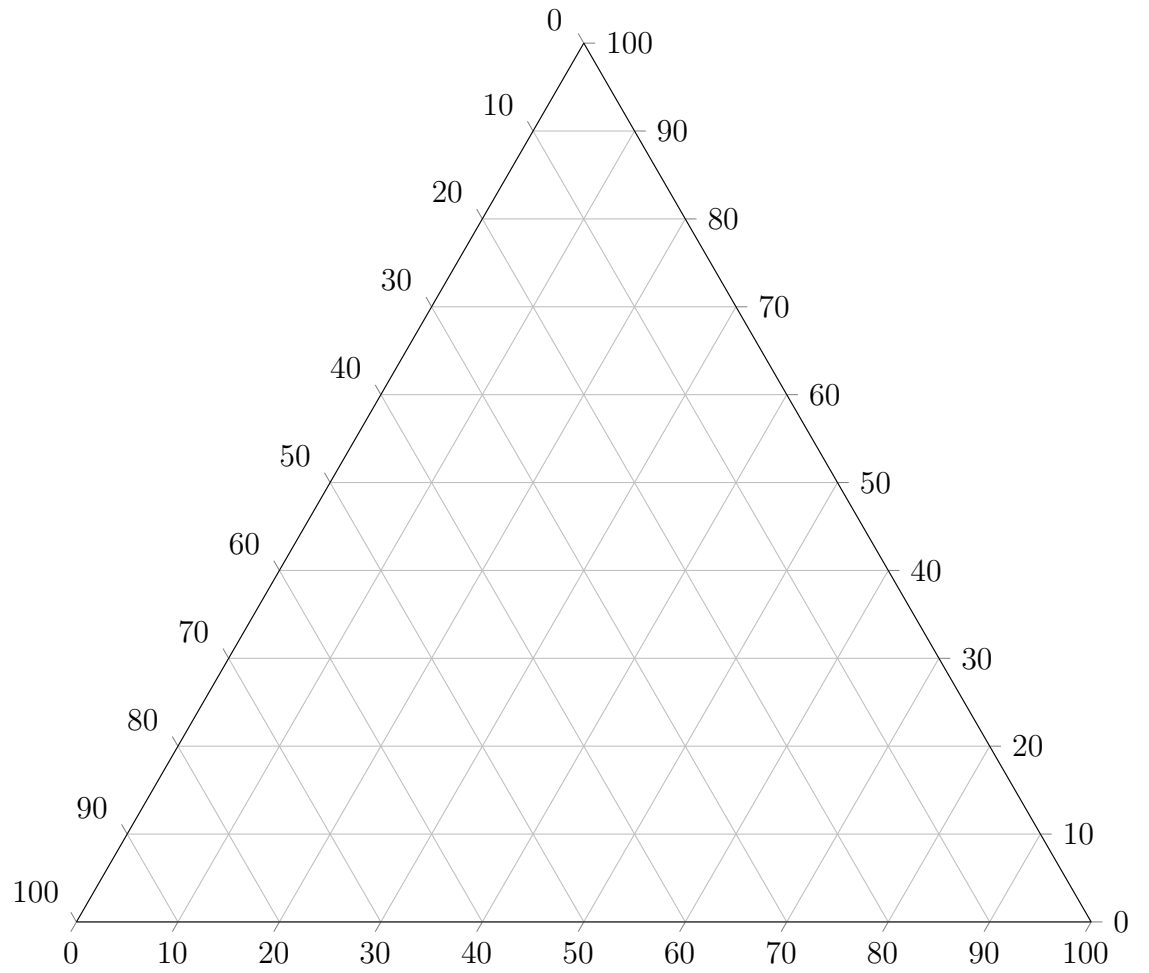
Equilibrium miscibility data

EG in Water (w/w %)	EG in Furfural (w/w %)
41.5	41.5
52.5	27.5
51.5	20.0
47.5	15.0
40.0	10.0
30.0	7.5
20.0	6.2
15.0	5.2
7.3	2.5

Mutual Equilibrium (Tie Line) data.



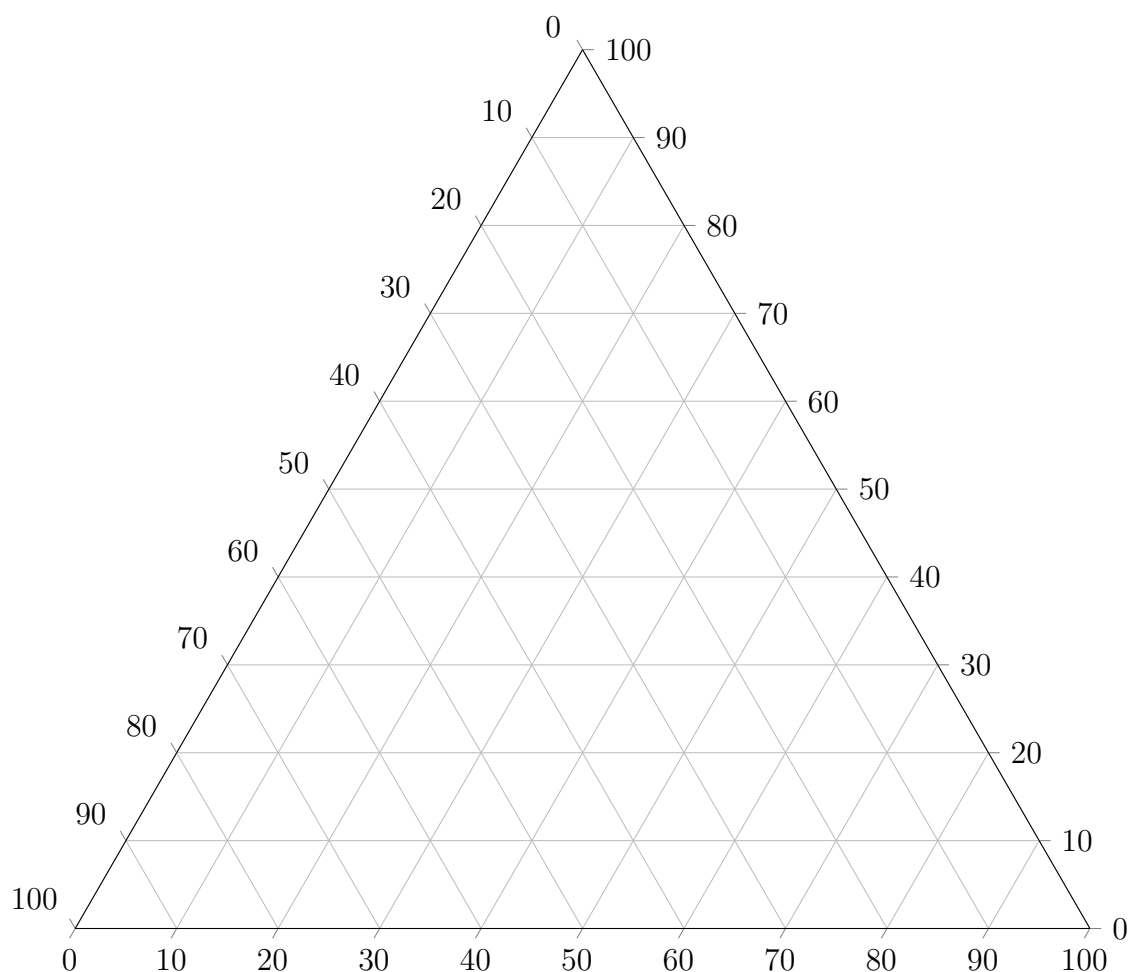
Solution Video



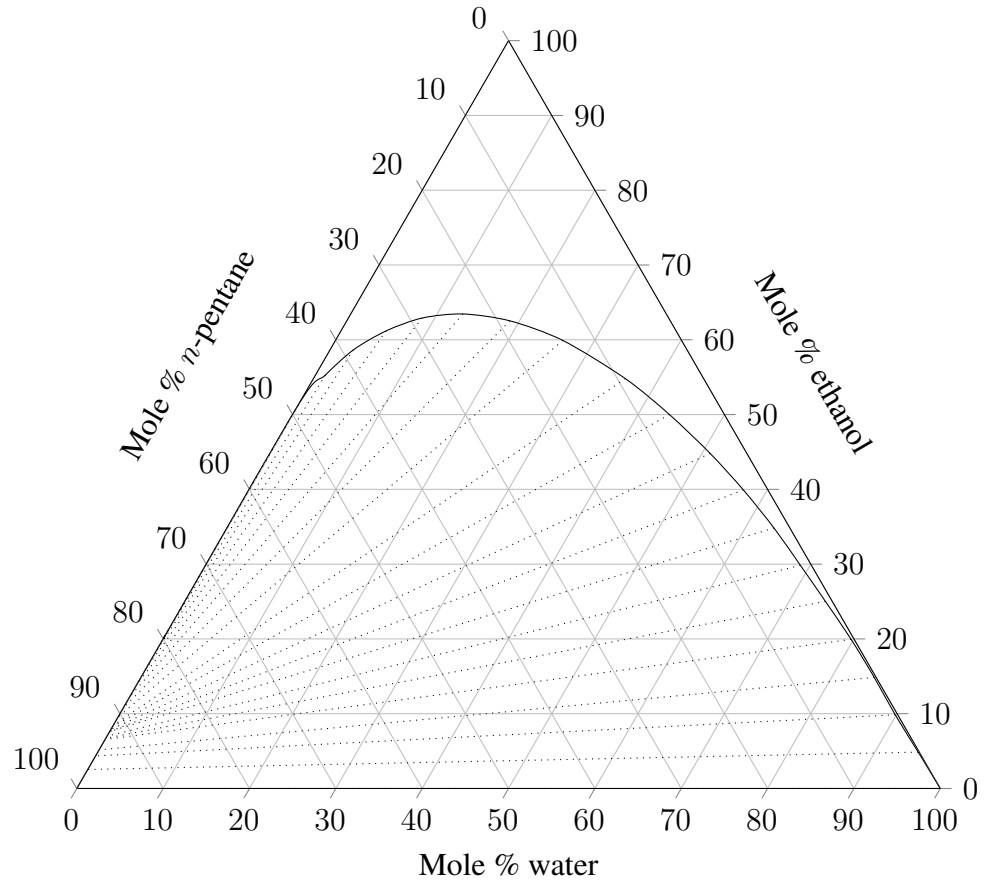
E2 A feed with a flow rate of  $1000 \text{ kg h}^{-1}$  contains 30 %wt acetic acid in isopropyl ether. The acetic acid is to be extracted with water. Equilibrium data are given in the table, in which it can be seen that water and ether have significant mutual solubility.

Mass fraction in water phase			Mass fraction in ether phase		
Acetic acid	water	Isopropyl ether	Acetic acid	water	Isopropyl ether
0.0069	0.981	0.012	0.0018	0.005	0.993
0.0141	0.971	0.015	0.0037	0.007	0.989
0.0289	0.955	0.016	0.0079	0.008	0.984
0.0642	0.917	0.019	0.0193	0.010	0.971
0.1330	0.844	0.023	0.0482	0.019	0.933
0.2550	0.711	0.034	0.1140	0.039	0.847
0.3670	0.589	0.044	0.2160	0.069	0.715

- (a) Represent the equilibrium data in the table in composition space (e.g. mass fraction acetic acid vs mass fraction water).
- (b) Estimate the flow rate and composition of the two liquid phases obtained if  $2500 \text{ kg h}^{-1}$  water is mixed with the feed. Represent the single-stage phase separation in the composition space diagram. [Phase 1 - 9.86 wt% Acetic acid, Phase 2 - 3.35 wt% Acetic acid]

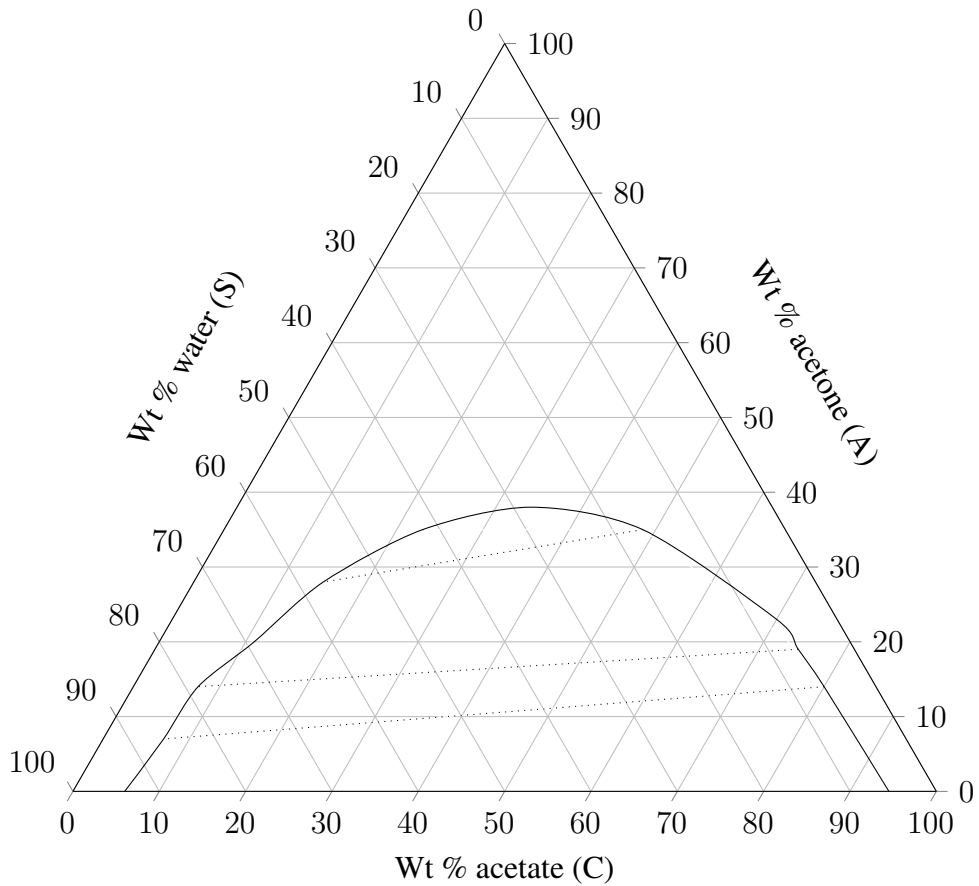


- E3 A process produces a stream consisting of 20 mol% ethanol and 80 mol% *n*-pentane. This is to be separated into a product of *n*-pentane with only 5 mol% ethanol present using a solvent of water. If the flow rate of the feed is  $720 \text{ kmol hr}^{-1}$  and the flow rate of the solvent is  $100 \text{ kmol hr}^{-1}$  how many stages are needed for the separation? [3 stages]



E4 Acetone is to be extracted from a 30 wt% acetone (A) and 70 wt% ethyl acetate (C) feed at 30 °C, using pure water (S) as the solvent. The final raffinate is to contain 5 wt% acetone on a water-free basis.

- Find the actual raffinate composition. [4.725 wt% acetone, 5.5 wt% water]
- Determine the minimum and maximum solvent-to-feed ratios (NB. you might need to use some extra paper to draw the lines). [min = 1, max = 10]
- Find the number of equilibrium stages required if  $S/F = 3$ . [3 stages]



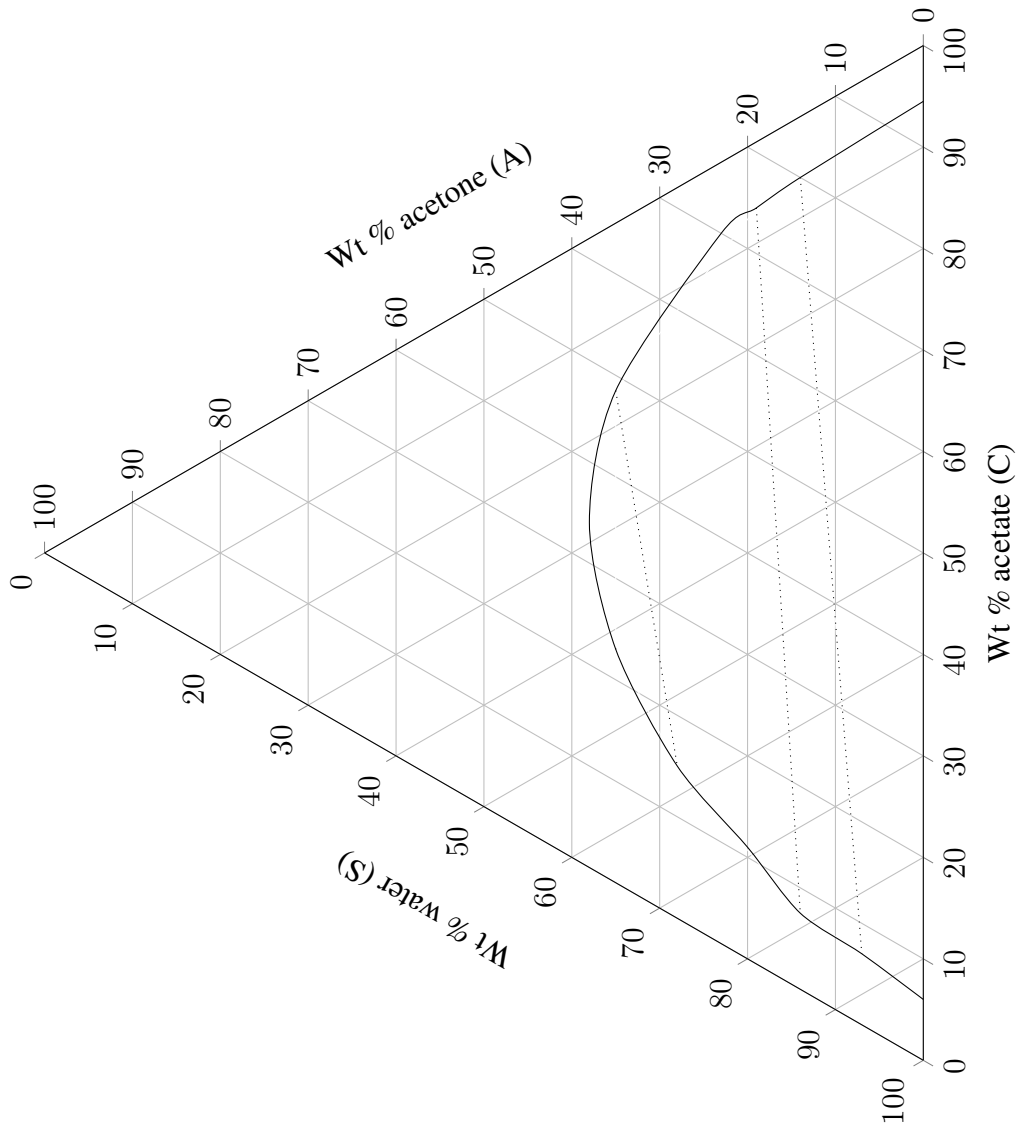


- D1 In question E4 above, a feed of 30 wt% acetone and 70 wt% ethyl acetate was extracted with pure water in a single-section, counter-current cascade to obtain a raffinate of 5 wt% acetone on a water (solvent-free basis).

An enrichment section can be added to the system to allow less water content in the extract. Use the equilibrium diagram over the page to calculate the number of stages to produce an extract of only 50 wt% water with a  $S/F$  ratio of 1.43.



Method Video



# Multi-Component Distillation

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## 3.1 Chapter 3 ILOs

**ILO 3.1.** Define the average relative volatility for components in a multi-component mixture.

**ILO 3.2.** Explain the key assumptions used in the short-cut design equations.

**ILO 3.3.** Use the short-cut design equations to approximately design multi-component distillation columns.

**ILO 3.4.** Assess considerations for multi-component distillation design.



Chapter Video

## 3.2 Introduction

In a brief statement, distillation is a method of separating homogeneous mixtures based on the difference in volatilities of the components in the mixtures. Distillation is a unit operation, or a physical separation process, and not a chemical reaction. Distillation often produces an overhead distillate (can be either vapour or liquid) and a bottom product (almost always liquid), whose compositions differ from that of the feed.

Unlike absorption and stripping, the second phase created in distillation is normally by thermal vaporisation or condensation rather than by introducing a second phase that may contain an additional component or components not present in the feed mixture.

Distillation normally requires repeated vaporisation and condensation and is the most common method for the separation of fluid mixtures with fluid products. The driving force for such a separation is the difference between the compositions of the vapour and liquid phases at equilibrium. Distillation is suitable for a wide range of throughputs and feed concentration and can produce high product purity, e.g. in the industry of recovering and purifying small biomolecules such as ethanol, acetone, and *n*-butanol, and solvent (e.g. organic alcohols, acids, and ketones) in biochemical industry. However, in bioseparation of large biological metabolites, polymers or the products that are thermolabile, distillation is not often seen.

Multistage distillation is the most widely used industrial method for separating chemical mixtures. However, it is a very energy-intensive technique, especially when the relative volatility of the key components being separated is low ( $< 1.5$ ). About two-thirds of the distillation energy was consumed by petroleum refineries, where distillation is used to separate crude oil into petroleum chemicals.

Even distillation is widely used in the chemical industry, but it may not be suitable for:

- Low molecular weight materials.
- High molecular weight heat-sensitive materials.
- Components with a low concentration.
- Classes of components.
- Mixtures with low relative volatility or which exhibit azeotropic behaviour.
- Mixtures of condensable and non-condensable components.

As for binary mixtures, vapour-liquid equilibrium is governed by equation 3.3.2, when there are more than two components in the mixture as in Figure 3.1, the calculations become more complicated. In principle, the design equations for binary distillation still apply but  $N - 1$  balance equations in an  $N$  component mixture make solutions harder to obtain. It is also worth noting that short-cut distillation models are useful for initialising more rigorous models and design methods.

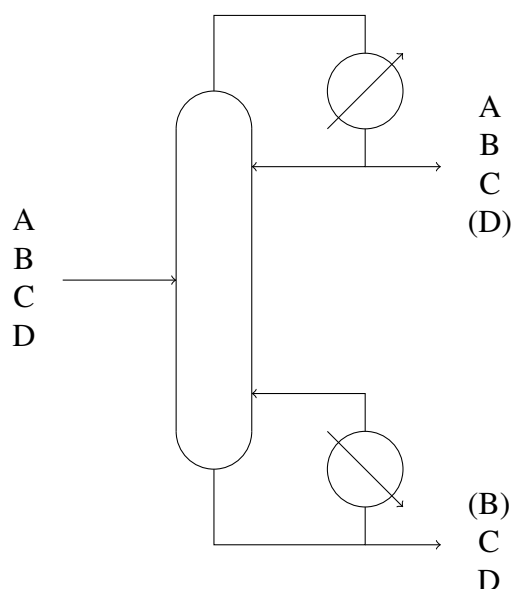


Figure 3.1: Multi-component distillation, where B and D are light and heavy key components and C is the intermediate boiling component.

### 3.3 Vapour-Liquid Equilibrium

The status of a matter existing in our physical world is determined by pressure and temperature. At the right temperature and pressure, a matter can be solid, liquid or vapour. In thermodynamics, the three phases can coexist - interpreted as phase equilibrium at a particular point of temperature and pressure. In distillation, we are normally concerned with the vapour-liquid equilibrium in multi-component mixtures.

We first introduce a concept - fugacity. In a pure liquid, the vapour generated by its escaping molecules necessarily has the same composition as that of the liquid. However, in a mixture, the composition of the vapour is not the same as that of the liquid, the vapour is richer in that component whose molecules have greater tendency to escape from the liquid phase. This tendency is measured by fugacity. Therefore, fugacity is a measure of the tendency of a component of a liquid mixture to escape, or vaporize, from the mixture. The fugacity of a component in a mixture is essentially the pressure that it exerts in the vapour phase when in equilibrium with the liquid mixture. It is the effective pressure of a real gas that differs from the behaviour of an ideal gas.

Thus, for each component in the mixture, when the vapour and liquid are in thermodynamic equilibrium, we have:

$$f_i^V = f_i^L \quad (3.3.1)$$

where  $f_i^V$  is the fugacity of component  $i$  in the vapour phase and  $f_i^L$  is the fugacity of the component  $i$  in the liquid phase.

Defining the vapour phase fugacity coefficient  $\phi_i^V$  and the liquid phase fugacity coefficient

$\phi_i^L$  and activity coefficient  $\gamma_i$ , when the system pressure is  $P$ , we have:

$$\begin{aligned} f_i^V &= \phi_i^V y_i P \\ f_i^L &= \phi_i^L x_i P \end{aligned}$$

or

$$f_i^L = \gamma_i x_i f_0 \quad (3.3.2)$$

where  $f_0$  is the standard state fugacity of component  $i$  at the temperature of the system,  $x_i$  and  $y_i$  are the molar fractions of component  $i$  in liquid and vapour phases, respectively.

For moderate pressures  $f_0$  is usually taken to be the saturated vapour pressure  $p_i^0$

$$f_i^L = \gamma_i x_i P_i^0 \quad (3.3.3)$$

The above equations can be combined (using equation 3.3.1) to give an expression for the equilibrium 'constant' or  $K$ -value,  $K_i$ ,

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} = \frac{\gamma_i P_i^0}{\phi_i^V P} \quad (3.3.4)$$

At moderate pressure,  $\phi_i^V \rightarrow 1$

$$K_i = \frac{\gamma_i P_i^0}{P} \quad (3.3.5)$$

When the liquid phase behaves as an ideal solution ( $\gamma_i \rightarrow 1$ ), this expression simplifies to

$$K_i = \frac{P_i^0}{P} \quad (3.3.6)$$

which is the so called Raoult's Law.

Figure 3.2 shows an example of the vapour-liquid equilibrium in an ideal binary mixture: Benzene-Toluene mixture at 1 atm.

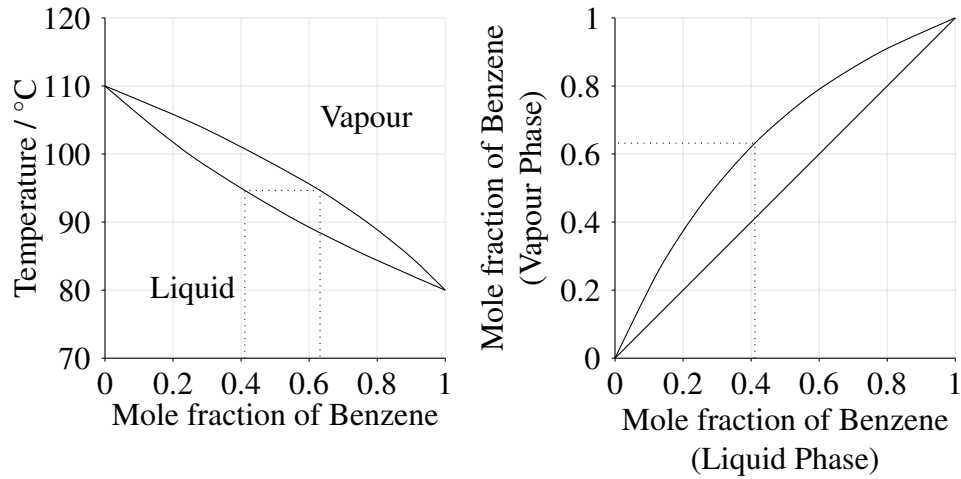


Figure 3.2: Vapour-liquid equilibrium of Benzene-Toluene mixture at 1 atm. The same equilibrium pair is shown in both styles of plot.

### 3.4 Short-cut methods for multi-component distillation

In short-cut design for multi-component distillation, the basic assumptions include,

1. constant relative volatility, which is the most important assumption for most problems although not often a good assumption for mixtures with non-ideal behaviour, and
2. constant molar overflow i.e. constant molar vapour and liquid flowrates.

There are a number of short-cut methods for simple columns including,

- Fenske equation: Minimum number of stages,  $N_{min}$ .
- Hengstebeck-Geddes method: Distribution of non-key components.
- Underwood equations: Minimum reflux ratio,  $R_{min}$ .
- Gilliland correlation: Actual number of stages, given the actual reflux ratio,  $R_{min}$  and  $N_{min}$ .

It should be pointed out that all these methods have approximations that the designer must understand. Otherwise, incorrect preliminary decisions on the choice of separator and operating conditions might be made.

#### 3.4.1 Relative volatility

We first introduce relative volatility - a ratio of the  $K$ -values of two components:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} \quad (3.4.1)$$



The geometric mean of the top and bottom product  $\alpha$  values is most commonly used in the short-cut calculations,

$$(\alpha_{ij})_{mean} = \sqrt{(\alpha_{ij})_{top} (\alpha_{ij})_{bottom}} \quad (3.4.2)$$

From equation 3.4.1, it is clear that the relative volatilities of distillate and bottom product depend on product compositions, but normally product compositions are not known and an iterative procedure may be required to estimate them using short-cut models.

### 3.4.2 The Fenske equation

The Fenske equation[5] is used to estimate the minimum number of the theoretical stages,

Assumptions:

- Total Reflux

Figure 3.3 shows two stages in a simple distillation column, where  $y_L$  and  $y_H$  refer to the compositions of light and heavy components in the vapour and  $x_L$  and  $x_H$  refer to the compositions of light and heavy components in the liquid.

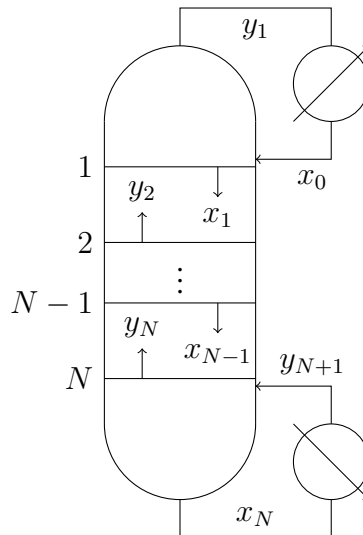


Figure 3.3: Simple distillation column for deriving the Fenske equation.

According to the definition of the relative volatility, equation 3.4.1, on each stage,

$$\alpha_{LH,n} = \frac{\left(\frac{y_{L,n}}{x_{L,n}}\right)}{\left(\frac{y_{H,n}}{x_{H,n}}\right)} \quad (3.4.3)$$

$$\alpha_{LH,n} = \frac{y_{L,n}x_{H,n}}{y_{H,n}x_{L,n}}$$

which can be transformed into:

$$\left(\frac{y_L}{y_H}\right)_n = \alpha_{LH,n} \left(\frac{x_L}{x_H}\right)_n \quad (3.4.4)$$

At the bottom of the column the mass balance is given by the stripping section operating line (remembering the assumption of constant  $L/V$ ),

$$y_{n+1} = \frac{L}{V}x_n - \frac{B}{V}x_D \quad (3.4.5)$$

As the column is run under total reflux there is no bottom product, i.e.  $B = 0$ , therefore,

$$y_{n+1} = \frac{L}{V}x_n \quad (3.4.6)$$

This is true for all components in the system, which means that,

$$\begin{aligned} \frac{y_{L,n+1}}{y_{H,n+1}} &= \frac{\left(\frac{L}{V}\right) x_{L,n}}{\left(\frac{L}{V}\right) x_{H,n}} \\ \left(\frac{y_L}{y_H}\right)_{n+1} &= \left(\frac{x_L}{x_H}\right)_n \end{aligned} \quad (3.4.7)$$

Combining equation 3.4.7 with 3.4.4 (taken for  $n + 1$ ) gives,

$$\alpha_{LH,n+1} \left(\frac{x_L}{x_H}\right)_{n+1} = \left(\frac{y_L}{y_H}\right)_{n+1} = \left(\frac{x_L}{x_H}\right)_n \quad (3.4.8)$$

For the each stage in the column we therefore have,

$$\begin{aligned} \left(\frac{x_L}{x_H}\right)_{N-1} &= \alpha_{LH,N} \left(\frac{x_L}{x_H}\right)_N \\ &\vdots \\ \left(\frac{x_L}{x_H}\right)_1 &= \alpha_{LH,2} \left(\frac{x_L}{x_H}\right)_2 \\ \left(\frac{x_L}{x_H}\right)_0 &= \alpha_{LH,1} \left(\frac{x_L}{x_H}\right)_1 \end{aligned} \quad (3.4.9)$$

Combining equation 3.4.9 produces,

$$\left(\frac{x_L}{x_H}\right)_0 = \prod_{n=1}^N \alpha_{LH,n} \left(\frac{x_L}{x_H}\right)_N \quad (3.4.10)$$

As the composition of the liquid entering the column at the top is equal to the distillate composition, and that leaving the column at the bottom is equal to the bottoms composition, then,

$$\left(\frac{x_L}{x_H}\right)_D = \prod_{n=1}^N \alpha_{LH,n} \left(\frac{x_L}{x_H}\right)_B \quad (3.4.11)$$

If we then define,

$$\bar{\alpha}_{LH} = \left(\prod_{n=1}^N \alpha_{LH,n}\right)^{1/N} \quad (3.4.12)$$

Which can be approximated by equation 3.4.2. Therefore,

$$\begin{aligned} \left(\frac{x_L}{x_H}\right)_D &= \prod_{n=1}^N \alpha_{LH,n} \left(\frac{x_L}{x_H}\right)_B \\ \left(\frac{x_L}{x_H}\right)_D &= \bar{\alpha}_{LH}^N \left(\frac{x_L}{x_H}\right)_B \\ \bar{\alpha}_{LH}^N &= \left(\frac{x_L}{x_H}\right)_D \left(\frac{x_H}{x_L}\right)_B \end{aligned} \quad (3.4.13)$$

As this analysis is for total reflux this means that the number of stages is the minimum number,  $N_{min}$ ,

$$N_{min} = \frac{\log \left[ \left(\frac{x_L}{x_H}\right)_D \left(\frac{x_H}{x_L}\right)_B \right]}{\log \bar{\alpha}_{LH}} \quad (3.4.14)$$

or equivalently,

$$N_{min} = \frac{\log \left[ \frac{D_L B_H}{D_H B_L} \right]}{\log \bar{\alpha}_{LH}} \quad (3.4.15)$$

If can also be expressed in terms of the recovery of the key components,  $r$ ,

$$N_{min} = \frac{\log \left[ \frac{r_{D,L} r_{B,H}}{1 - r_{D,L} 1 - r_{B,H}} \right]}{\log \bar{\alpha}_{LH}} \quad (3.4.16)$$

Equation 3.4.14 is the original form of the Fenske equation for calculating the minimum number of theoretical stages. When  $\bar{\alpha}$  is extended to be the geometric mean of the relative volatilities of the light and heavy key components in a multiple component system. Equation 3.4.14 are still approximately valid and largely useful for estimating the minimum number of the theoretical stages.

### 3.4.3 The Hengstebeck-Geddes Method

All components distribute between distillate and bottoms at total reflux; while at minimum reflux conditions, none or only a few of the nonkey components distribute. Distribution ratios for these two limiting conditions are given in Figure 3.4 [11].

For total reflux, the Fenske equation results in a plot as a straight line on log-log coordinates. Such that taking equation 3.4.15 for to general components,  $i$  and  $j$ ,

$$\begin{aligned} N_{min} &= \frac{\log \left[ \frac{D_i B_i}{D_j B_j} \right]}{\log \alpha_{i,j}} \\ N_{min} \log \alpha_{i,j} &= \log \left( \frac{D_i}{B_i} \right) - \log \left( \frac{D_j}{B_j} \right) \\ \log \left( \frac{D_i}{B_i} \right) &= \log \left( \frac{D_j}{B_j} \right) + N_{min} \log \alpha_{i,j} \end{aligned} \quad (3.4.17)$$

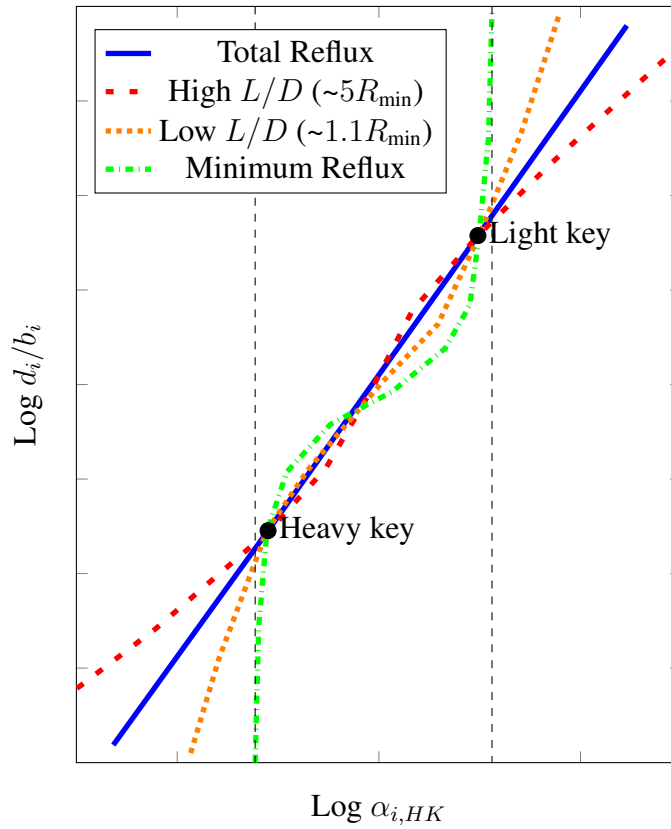


Figure 3.4: The Hengstebeck-Geddes relation (adapted from [11]).

As it can be said that  $\alpha_{i,j} = \alpha_{i,r}\alpha_{r,j}$ , where  $r$  refers to a reference component, equation 3.4.17 can be rearranged to be,

$$\begin{aligned} \log\left(\frac{D_i}{B_i}\right) &= \log\left(\frac{D_j}{B_j}\right) + N_{min} \log \alpha_{i,r} + N_{min} \log \alpha_{r,j} \\ \log\left(\frac{D_i}{B_i}\right) &= \log\left(\frac{D_j}{B_j}\right) + N_{min} \log \alpha_{i,r} - N_{min} \log \alpha_{j,r} \\ \log\left(\frac{D_i}{B_i}\right) &= \log\left(\frac{D_j}{B_j} \alpha_{j,r}^{-N_{min}}\right) + N_{min} \log \alpha_{i,r} \end{aligned} \quad (3.4.18)$$

which is known as the Hengstebeck-Geddes method [6]. If we take the heavy key,  $H$ , as the reference component, then the straightline equation can be written for each component,  $i$ , in the system as,

$$\log \frac{D_i}{B_i} = A + C \log \alpha_{i,H} \quad (3.4.19)$$

where  $C$  is equal to  $N_{min}$  and  $A$  can be conveniently obtained from the heavy key component as,

$$A = \log\left(\frac{D_H}{B_H}\right) \quad (3.4.20)$$

For minimum reflux, the Underwood equations (below) can be used to estimate the component distributions. Product-distribution curves for a given reflux might be expected to lie between the lines for total and minimum reflux. However, this is not the case, and product distributions are complex. Near  $R_{min}$ , product distribution (curve 3) lies between

the two limits (curves 1 and 4). However, for a high reflux ratio, non-key distributions (curve 2) may lie outside the limits, thus causing inferior separations.

As the reflux ratio is decreased from total reflux while maintaining the key-component splits, stage requirements increase slowly at first, but then rapidly as minimum reflux is approached. Initially, large decreases in reflux cannot be compensated for by increasing stages. This causes inferior nonkey distributions. As  $R_{min}$  is approached, small decreases in reflux are compensated for by large increases in stages; and the separation of non-key components becomes superior to that at total reflux.

It appears reasonable to assume that, at a near-optimal reflux ratio of 1.3, nonkey-component distribution is close to that estimated by the Fenske equation for total-reflux conditions.

### 3.4.4 The Underwood Equation

The Underwood equation[12, 13] is widely used in estimating the minimum reflux ratio for multiple component systems even though it usually underestimates the minimum reflux ratio.

At the point of the minimum reflux ratio, there is a pinch point in the system, Figure 3.5

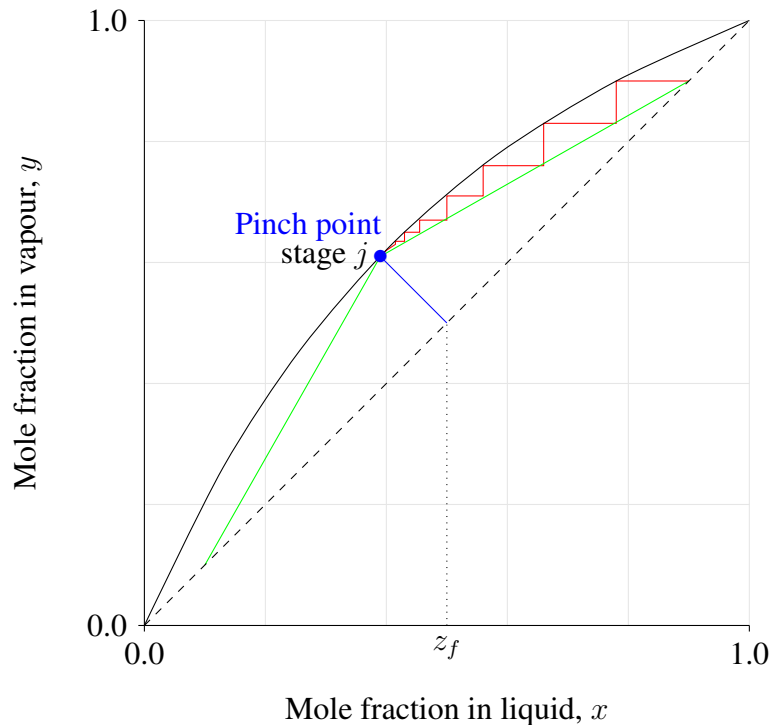


Figure 3.5: Pinch point condition for a binary system.

At this pinch point the concentration at stage  $j$  stays the same on the plates above and below,

$$\begin{aligned} x_{j-1} &= x_j = x_{j+1} \\ y_{j-1} &= y_j = y_{j+1} \end{aligned} \quad (3.4.21)$$

The pinch point is also on the equilibrium curve such that,

$$y_{j,i} = K_i x_{j,i} \quad (3.4.22)$$

Taking a mass balance over the rectifying section (i.e. pinch point up to the distillate) gives,

$$V_{min} y_{j+1,i} = L_{min} x_{j,i} + D x_{D,i} \quad (3.4.23)$$

Substituting equation 3.4.22 into equation 3.4.23 gives,

$$V_{min} y_{j+1,i} = L_{min} \frac{y_{j,i}}{K_i} + D x_{D,i} \quad (3.4.24)$$

and from equation 3.4.21,

$$V_{min} y_{j,i} = L_{min} \frac{y_{j,i}}{K_i} + D x_{D,i} \quad (3.4.25)$$

This can be rearranged for  $y_{j,i}$  as,

$$\begin{aligned} V_{min} y_{j,i} - L_{min} \frac{y_{j,i}}{K_i} &= D x_{D,i} \\ y_{j,i} \left( V_{min} - \frac{L_{min}}{K_i} \right) &= D x_{D,i} \\ y_{j,i} &= \frac{D x_{D,i}}{\left( V_{min} - \frac{L_{min}}{K_i} \right)} \end{aligned} \quad (3.4.26)$$

As we don't know the position of the pinch point, we don't know the individual compositions of  $y_{j,i}$ , however we do know that the sum of the vapour fractions of all the components is equal to one, so that,

$$1 = \sum \frac{D x_{D,i}}{\left( V_{min} - \frac{L_{min}}{K_i} \right)} \quad (3.4.27)$$

The equilibrium constant for any component can be given by the relative volatility and the equilibrium constant of the reference component  $K_i = \alpha_{i,r} K_r$ , so that,

$$1 = \sum \frac{D x_{D,i}}{\left( V_{min} - \frac{L_{min}}{\alpha_{i,r} K_r} \right)} \quad (3.4.28)$$

This can now be rewritten as in a simplified form as an expression for  $V_{min}$ ,

$$\begin{aligned} 1 &= D \sum \frac{x_{D,i}}{\frac{V_{min}}{\alpha_{i,r}} \left( \alpha_{i,r} - \frac{L_{min}}{V_{min} K_r} \right)} \\ V_{min} &= D \sum \frac{\alpha_{i,r} x_{D,i}}{\left( \alpha_{i,r} - \frac{L_{min}}{V_{min} K_r} \right)} \end{aligned} \quad (3.4.29)$$

This same method analysis can also be performed on the stripping section of the column to produce,

$$-V'_{min} = B \sum \frac{\alpha_{i,r} x_{B,i}}{\left(\alpha_{i,r} - \frac{L'_{min}}{V'_{min} K'_r}\right)} \quad (3.4.30)$$

Under the assumptions of constant molar overflow and constant relative volatility it can be proved that,

$$\frac{L_{min}}{V_{min} K_r} = \frac{L'_{min}}{V'_{min} K'_r} = \phi \quad (3.4.31)$$

Substituting equation 3.4.31 into equations 3.4.29 and 3.4.30 produces to key linked equations for the minimum vapour flows,

$$V_{min} = D \sum \frac{\alpha_{i,r} x_{D,i}}{(\alpha_{i,r} - \phi)} \quad (3.4.32)$$

$$V'_{min} = -B \sum \frac{\alpha_{i,r} x_{B,i}}{(\alpha_{i,r} - \phi)} \quad (3.4.33)$$

$$(3.4.34)$$

These key equations allow us to generate the two Underwood equations. For the first equation, a mass balance around the feed stage gives,

$$V_{min} - V'_{min} = F(1 - q) \quad (3.4.35)$$

Substituting equations 3.4.32 and 3.4.33 in this gives,

$$\begin{aligned} \sum \frac{\alpha_{i,r} D x_{D,i}}{(\alpha_{i,r} - \phi)} + \sum \frac{\alpha_{i,r} B x_{B,i}}{(\alpha_{i,r} - \phi)} &= F(1 - q) \\ \sum \frac{\alpha_{i,r} (D x_{D,i} + B x_{B,i})}{(\alpha_{i,r} - \phi)} &= F(1 - q) \end{aligned} \quad (3.4.36)$$

From an overall column mass balance,

$$D x_{D,i} + B x_{B,i} = F z_{F,i} \quad (3.4.37)$$

Substituting this into equation 3.4.36 gives, the first Underwood equation,

$$1 - q = \sum \frac{\alpha_{i,r} z_{F,i}}{(\alpha_{i,r} - \phi)} \quad (3.4.38)$$

As this only contains information about the feed it allows us to calculate  $\phi$ . Note, there are multiple roots to this equation, Figure 3.6; each root of  $\phi$  lies between an adjacent pair of relative volatilities of distributing species. Generally the root we are looking for is  $\alpha_{HK} < \phi < \alpha_{LK}$  if the heavy key is the reference for the volatility.

The value of  $\phi$  can then be used to find the minimum reflux ratio,  $R_{min}$  from,

$$R_{min} = \frac{V_{min}}{D} - 1 \quad (3.4.39)$$

Substituting  $V_{min}$  from equation 3.4.32 gives the second Underwood equation,

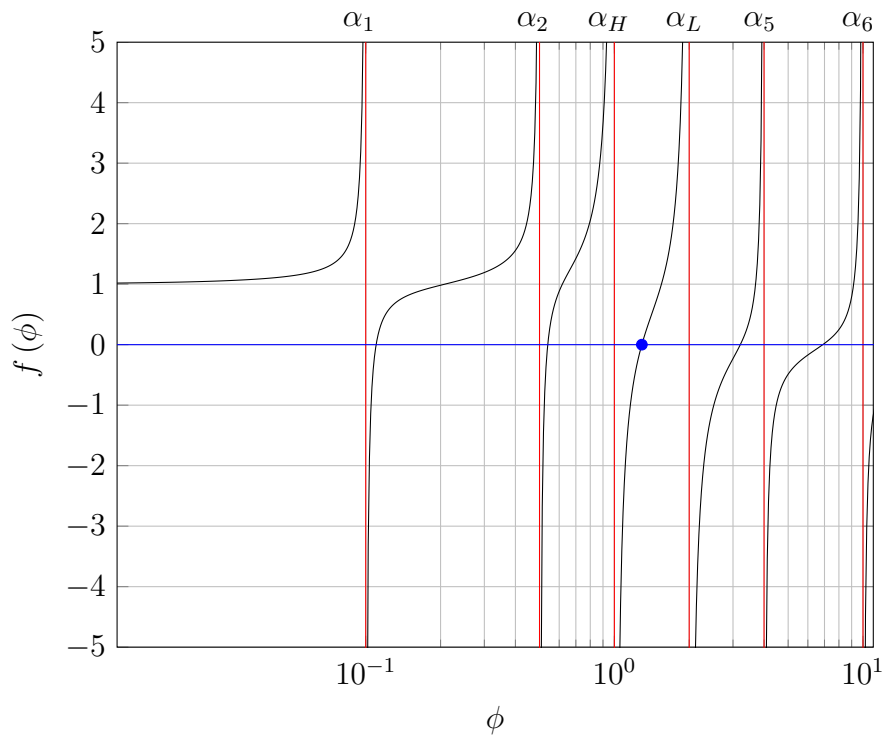


Figure 3.6: Graphical solution to the first Underwood equation for an example of 6 components.

$$R_{min} + 1 = \sum \frac{\alpha_{i,r} x_{D,i}}{(\alpha_{i,r} - \phi)} \quad (3.4.40)$$

The Underwood minimum reflux equations are widely used, but often without examining the possibility of non-key distributions. In addition, the assumption is frequently made that  $R_{min}$  equals the reflux ratio without pinch points of the non-key components.

When the Underwood assumptions appear valid and a negative minimum reflux ratio is computed, a rectifying section may not be needed for the separation. The Underwood equations show that the minimum reflux depends mainly on feed condition and  $\alpha$  and, to a lesser extent, on degree of separation, as is the case with binary distillation. As with binary distillation, a minimum reflux ratio exists in a multi-component system for a perfect separation between the LK and HK. The Underwood method can also be extended for use with multiple feeds [2].

For calculations at actual reflux conditions with a process simulator by the computer programs knowledge of  $R_{min}$  is not essential, but  $N_{min}$  must be known if the split between two components is to be specified.

### 3.4.5 The Gilliland correlation

The Gilliland correlation[7] is probably the most widely used empirical relation in practical distillation design for the calculation of the number of the theoretical stages under a given reflux ratio.

As shown in Figure 3.7, the correlation was established between  $Y = (N - N_{min}) / (N + 1)$  and  $X = (R - R_{min}) / (R + 1)$ . As the minimum number of theoretical stages,  $N_{min}$  and



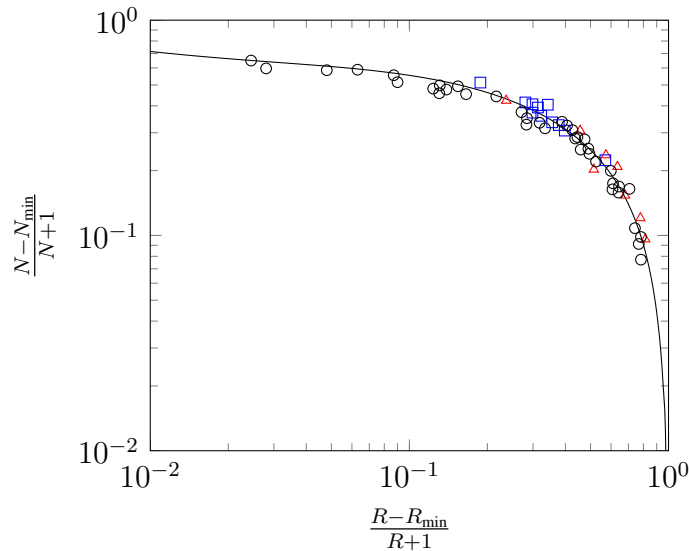


Figure 3.7: The Gilliland correlation. Data plotted:  $\circ$  from Gilliland [7, 10],  $\square$  from van Winkle and Todd [14], and  $\triangle$  from Brown-Martin [3]. Line plotted from equation 3.4.41 by Molokanov [9].

minimum reflux ratio,  $R_{min}$  can be obtained from Fenske equation and the Underwood equation, respectively, as long as the actual reflux ratio,  $R$ , is given, then the actual number of the theoretical stages,  $N$ , can be calculated according to the values given in the correlation. The data used covers the range of parameters,

- Number of components: 2 to 11
- $\alpha$ : 1.11 to 4.05
- $q$ : 0.28 to 1.42
- $R_{min}$ : 0.53 to 9.09
- Pressure: vacuum to 600 psig
- $N_{min}$ : 3.4 to 60.3

It is worth noting that the Gilliland correlation presents a graphical correlation, using the design data. This correlation is effectively accurate for  $X < 0.17$ . This graphical correlation has been fitted to an equation [9],

$$\frac{N - N_m}{N + 1} = 1 - \exp \left[ \left( \frac{1 + 54.5\Psi}{11 + 117.2\Psi} \right) \left( \frac{\Psi - 1}{\Psi^{0.5}} \right) \right] \quad \text{where} \quad \Psi = \frac{R - R_m}{R + 1} \quad (3.4.41)$$

A more accurate correlation should utilize a parameter involving the feed condition,  $q$ . As feed conditions range from subcooled liquid to superheated vapour the number of stages required for the separation decreases. However, this effect is small unless  $\alpha_{LK,HK}$  is high.

### 3.4.6 The Erbar-Maddox correlation

Similar to the Gilliland correlation, the Erbar-Maddox correlation [4] also relates the actual number of theoretical stages to the actual reflux ratio, the minimum reflux ratio and

the minimum number of theoretical stages.

This is also an empirical correlation, it is sometimes considered more reliable than the Gilliland correlation, but its use is not as widespread as the latter, Figure 3.8.

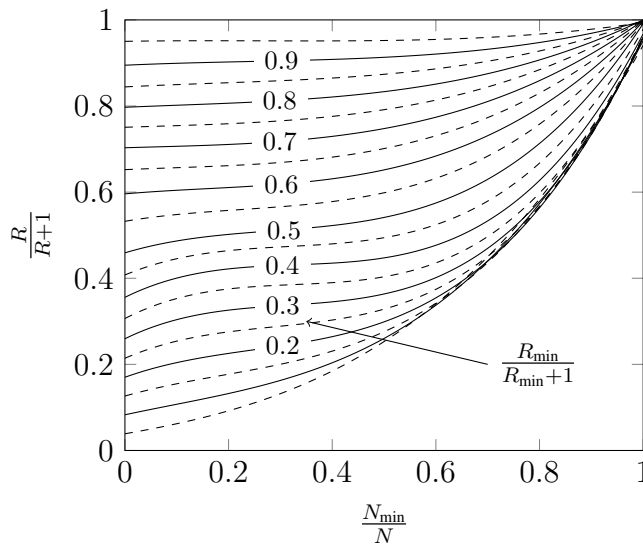


Figure 3.8: The Erbar-Maddox correlation [4] using prediction equations from [1].

### 3.4.7 The Kirkbride Correlation

Implicit in the application of the Gilliland correlation is the specification that stages be distributed optimally between the rectifying and stripping sections. The optimal feed stage can be located by assuming that the ratio of stages above the feed to stages below is the same as the ratio determined by applying the Fenske equation to the separate sections at total reflux conditions.

Unfortunately, this is not reliable except for fairly symmetrical feeds and separations.

A better approximation of the optimal feed-stage location can be made with the Kirkbride empirical equation [8],

$$\log \left( \frac{N_r}{N_s} \right) = 0.206 \log \left[ \left( \frac{B}{D} \right) \left( \frac{x_{HK,f}}{x_{LK,f}} \right) \left( \frac{x_{LK,b}}{x_{HK,d}} \right)^2 \right] \quad (3.4.42)$$

where  $N_r$  is the number of stages in the rectifying section (above feed stage),  $N_s$  is the number of stages in the stripping section (below feed stage),  $x_{HK,f}$  is the mole fraction of heavy key component in feed,  $x_{LK,f}$  is the mole fraction of light key component in feed,  $B$  and  $D$  are the distillate and bottoms flow rates respectively,  $x_{LK,b}$  is the mole fraction of light key component in bottom product, and  $x_{HK,d}$  is the mole fraction of heavy key component in distillate.

### 3.4.8 Procedures of the short-cut design

For shortcut distillation design, several commercial software packages are available for simulations, optimizations, and optimal controls. Most of these packages are usually limited to conventional systems as they were developed in early or late 1980s.

Normally, in the use of the shortcut design, the following steps are required, for a feed of known composition, flow rate, thermal condition and pressure,

1. Specify top product phase, i.e. total or partial condenser.
2. Select light and heavy key components.
3. Specify mole fraction of light key in the bottoms and heavy key in the distillate.
4. Specify pressure of condenser and reboiler.
5. Estimate the relative volatilities for the top, bottom and feed point of the column.
6. Use the Fenske equation to calculate  $N_{min}$ .
7. Use the Hengstebeck-Geddes method to estimate the split of the non-key components.
8. Repeat steps 5 to 7 until  $N_{min}$  doesn't change.
9. Use the Underwood equations to calculate  $R_{min}$ .
10. Pick a  $R/R_{min}$  value.
11. Use the Gilliland correlation to calculate the actual number of stages,  $N$ .
12. Use the Kirkbride correlation to calculate the ratio of the rectifying to stripping number of stages.

### 3.5 Rigorous Model for Multi-component Distillation

A common design for distillation columns is that the condenser at the top of the column is assumed to be a complete condenser (i.e. all the vapour that enters the condenser leaves as a liquid at the same temperature with no-sub-cooling). This means that this does not represent an equilibrium stage. The first plate below the condenser is where the final stage of the enrichment occurs.

#### Calculation of Plate Vapour-Liquid Equilibrium

The composition of the vapour on the plate,  $y_j$ , is known from calculation of the previous plate<sup>1</sup>. Therefore it is possible to calculate the composition of the liquid on the same tray,  $x_j$ , as it is in equilibrium.

The temperature of the plate is calculated using a mole weighted vapour pressure<sup>2</sup>,

$$\sum \frac{y_i}{K_i} = 1 \quad (3.5.1)$$

The values of  $y_i/K_i$  produced are then the values of  $x_i$  for that plate, the  $x_j$ s.

<sup>1</sup>In the case of the first plate the composition of  $y_1$  is of course equal to that of the distillate,  $x_d$ , which is also equal to  $x_0$

<sup>2</sup>The pressure at this point can be considered constant throughout the column and equal to that of the feed

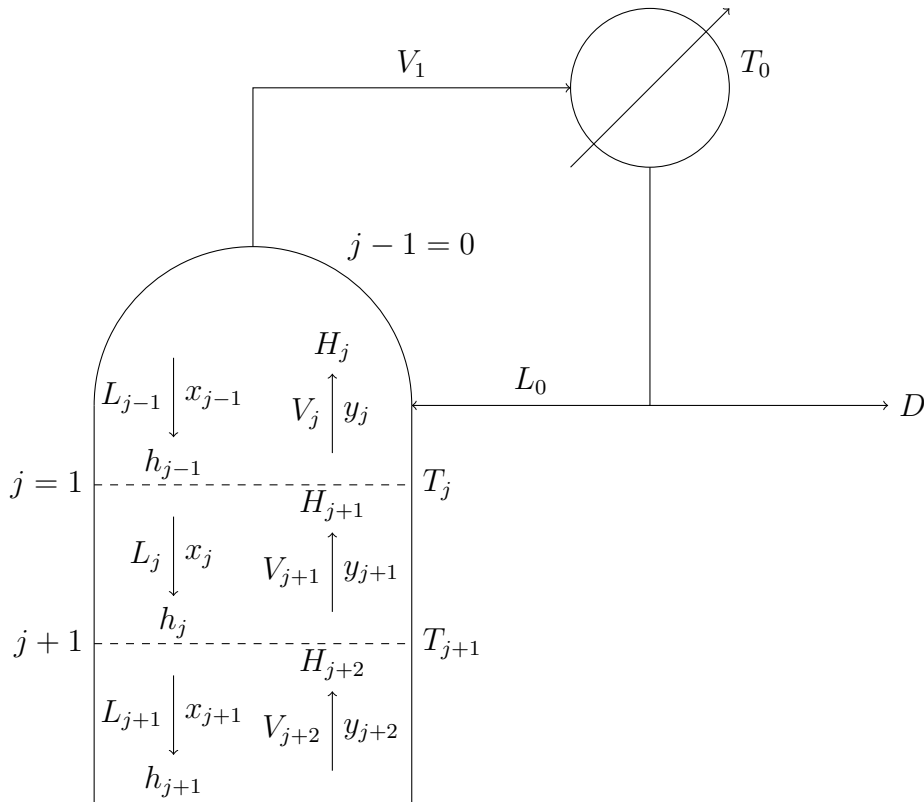


Figure 3.9: Mass and energy flow in the top of a distillation column.

### Plate Mass and Energy Balance

The second step for calculating the plate is to make an estimate for the composition of the vapour arriving from the next plate,  $y_{j+1}$ . Assuming that there is no chemical reaction then the molar flow from each plate should equal that to each plate,

$$L_j + V_j = L_{j-1} + V_{j+1} \quad (3.5.2)$$

and the flow of each component should also be constant,

$$x_j L_j + y_j V_j = x_{j-1} L_{j-1} + y_{j+1} V_{j+1} \quad (3.5.3)$$

Combining these two equation gives  $y_{j+1}$ ,

$$y_{j+1} = \frac{(L_{j-1} + V_{j+1} - V_j) x_j + y_j V_j - x_{j-1} L_{j-1}}{V_{j+1}} \quad (3.5.4)$$

At this point however the value of  $V_{j+1}$  is unknown, but as an initial guess assumed to be equal to  $V_j$ . The values of  $L_{j-1}$  and  $V_j$  are known from the previous plate balance<sup>1</sup>.

<sup>1</sup>The value of  $V_1$  and  $L_0$  can be calculated from the distillate flow rate,  $D$ , and the reflux ratio,  $R$ , calculated from the short cut calculation,

$$\begin{aligned} V_1 &= (R + 1) D \\ L_0 &= R D \end{aligned}$$

The liquid flow down from the plate,  $L_j$ , and the vapour flow rate up from the next plate,  $V_{j+1}$  can also be calculated using a heat balance,

$$h_j L_j + H_j V_j = h_{j-1} L_{j-1} + H_{j+1} V_{j+1} \quad (3.5.5)$$

where  $H$  is the vapour enthalpy and  $h$  is the liquid enthalpy calculated from the calculated plate temperature and the estimate of  $y_{j+1}$ .

Rearranging this equation in terms of  $L_j$  and combining with the molar flow balance (equation 3.5.2) gives,

$$L_j = \frac{H_j V_j - h_{j-1} L_{j-1} + H_{j+1} (L_{j-1} - V_j)}{H_{j+1} - h_j} \quad (3.5.6)$$

Also from the molar flow balance (equation 3.5.2),

$$L_j = L_{j-1} + V_{j+1} - V_j \quad (3.5.7)$$

therefore iterating the value of  $V_{j+1}$  until the values of  $L_j$  calculated by the last two equations are equal solves the plate.

## 3.6 Considerations in Multi-component Distillation

There are some general considerations in designing a multi-component distillation. As many components are present in the feed, fixing the recovery or mole fraction of a single component does not specify the product composition or temperature; also, the selection of the key components is a process engineering decision, usually based on the objectives of the separation. Mass and energy balances are solved iteratively. It is useful to use commercial process simulation software to carry out the calculations. The short-cut design equations allow initial estimates of design variables and column performance to be obtained prior to rigorous simulation. Practical experience shows that convergence of rigorous simulation can be facilitated by good initial estimates.

### 3.6.1 Choice of distillation operating parameters

In determining the distillation operating parameters, usually the feed composition and flow rate are considered fixed. The product specifications are usually given in the design problem statement and may be expressed in terms of recovery of certain components, product purities or specific compositions.

The operating parameters to be selected by the design engineer would normally include,

- Operating pressure.
- Reflux ratio.
- Feed condition.
- Feed stage location.
- Type of condenser.

In the preliminary distillation design, it is necessary for the design to be on the basis of the whole system rather than a specific part as distillation columns are energy-intensive any heat integration of distillation columns can significantly reduce the energy costs.

The heat integration opportunities for heat recovery in distillation columns can be created and the operating pressure, reflux ratio and feed condition can have effects on those opportunities thus their selection should be carefully considered.

### Operating pressure

It is clear that the condenser temperature sets the distillation operating pressure as the vapour comes out of the top of the column. There are two types of condensers: total and partial condensers, Figure 3.10.

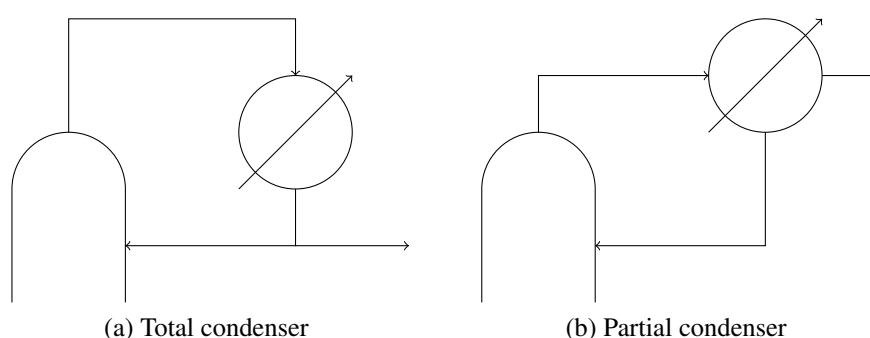


Figure 3.10: Condenser options.

A total condenser means all the vapour is to be condensed leaving only liquid as the top product, in such cases, pressure should be fixed. Additionally, if cooling water is to be used as the heat transfer agent, the bubble point of the overhead product should be typically  $10^{\circ}\text{C}$  above the summer cooling water temperature. If air cooling is to be used, the bubble point of the overhead product should be typically  $20^{\circ}\text{C}$  above the summer air temperature.

For a partial condenser: vapour is taken as the top product. The above criteria for the total condenser are applied to the dew point of the vapour top product.

There are exceptions for determining operating pressure in a distillation column, e.g.

- In the separation of gases and light hydrocarbons, a very high operating pressure may be required as a result of trying to operate the condenser against cooling water or air cooling, therefore, a combination of high operating pressure and low temperature condensation using refrigeration may be needed.
- For distilling high molecular weight materials, process constraints may restrict the maximum temperature of the distillation to avoid product decomposition, a vacuum operation must be used to reduce the boiling temperature.
- In a sequence of columns, the condenser of one operating at a high pressure may provide heat to the reboiler of another operating at a lower pressure thus heat recovery opportunities can be created.

The effect of pressure on distillation is shown in Figure 3.11 in an example of separating a benzene-toluene-ethylbenzene-styrene mixture.

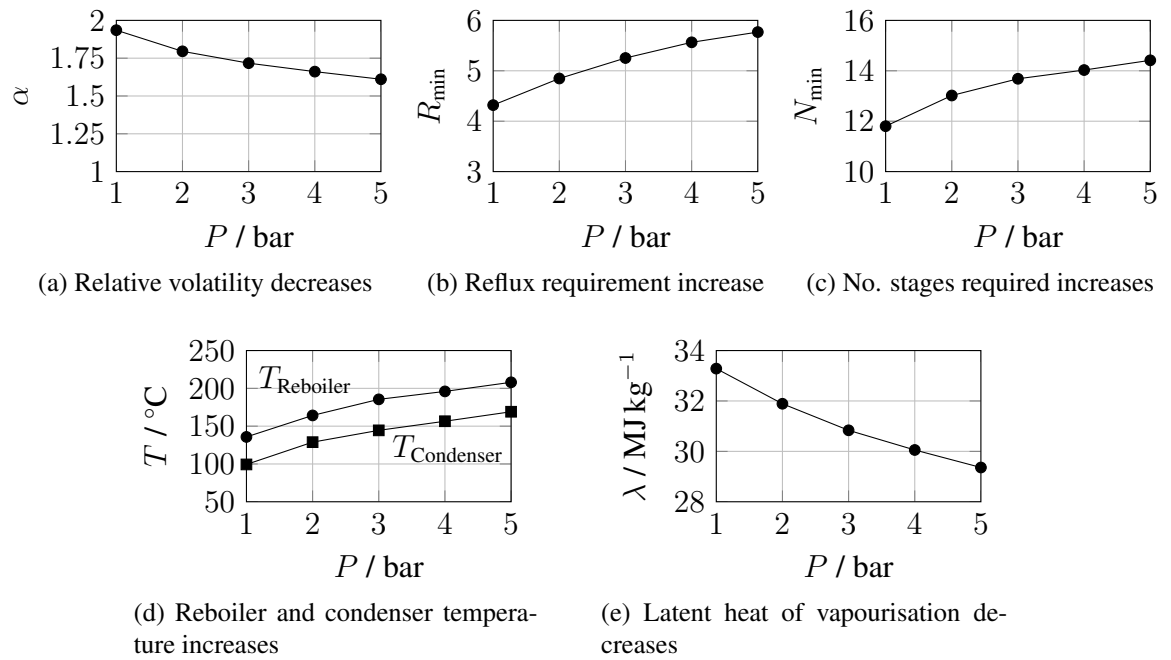


Figure 3.11: The effects of pressure on (a) relative volatility of components, (b) reflux, (c) number of theoretical stages, (d) reboiler and condenser temperatures, and (e) the latent heat of the vaporisation.

### Effect of temperature on utility costs

The temperature of a distillation column has significant effects on utility costs as the typical utility costs depend on the temperature and source of heating or cooling. Figure 3.12 shows such effects.

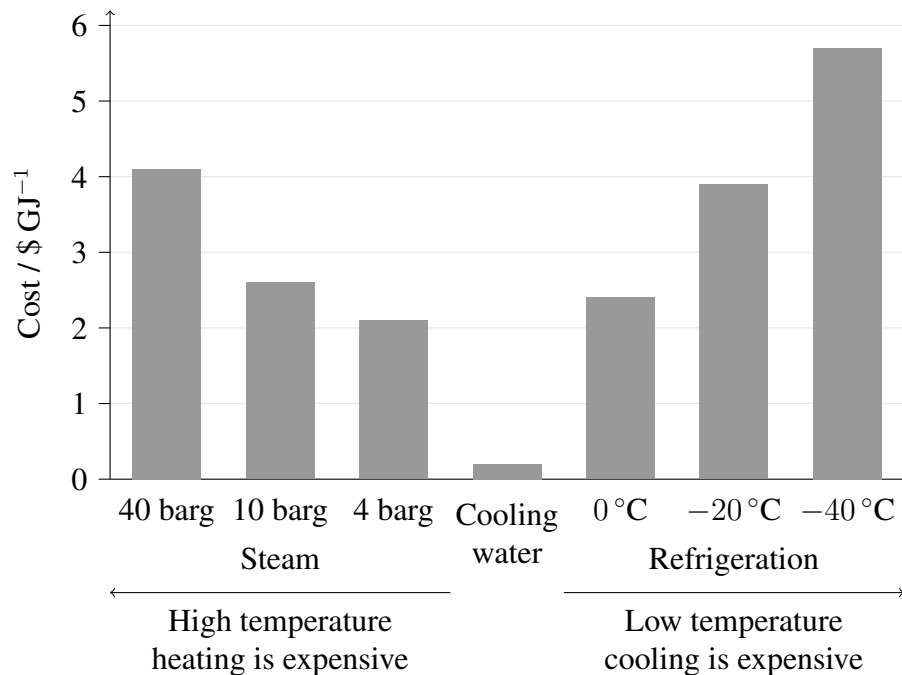


Figure 3.12: The effect of temperature on utility costs.

As seen from Figure 3.12, water used as the cooling agent would lower the costs signifi-

cantly thus is the most economic source of creating condensation. This result is also based on a simulation of separating a benzene-toluene-ethylbenzene-styrene mixture.

### 3.6.2 Choice of reflux ratio

The reflux ratio has a direct effect on the number of theoretical stages. There are two extreme situations: minimum and total reflux ratio.

In the case of the minimum reflux ratio, an infinite number of stages would be required which would incur a very high capital cost but minimise the energy requirements thus the operating cost is low. However, in case of total reflux ratio, a minimum number of stages is required, which means low capital cost but needs to maintain high energy supply resulting in high operating costs. Figure 3.13 shows the variation of the number of stages with the reflux ratio for the same benzene-toluene-ethylbenzene-styrene mixture.

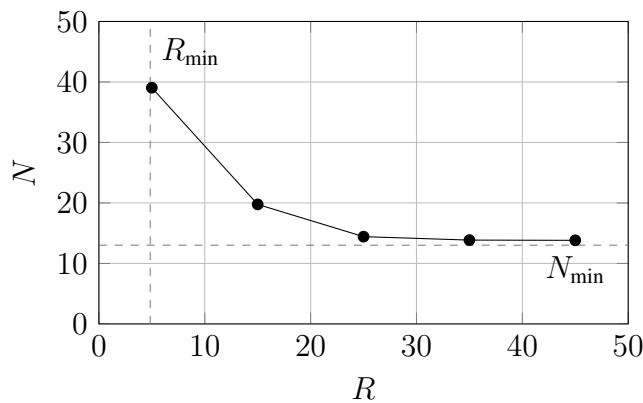


Figure 3.13: Effect of reflux ratio on the number of theoretical stages.

To avoid the two extremes, the actual reflux will lie between the minimum and the total ratio. Figure 3.14 illustrates that there are capital-energy trade-offs, to lower the total cost, and that there is often an optimum reflux ratio.

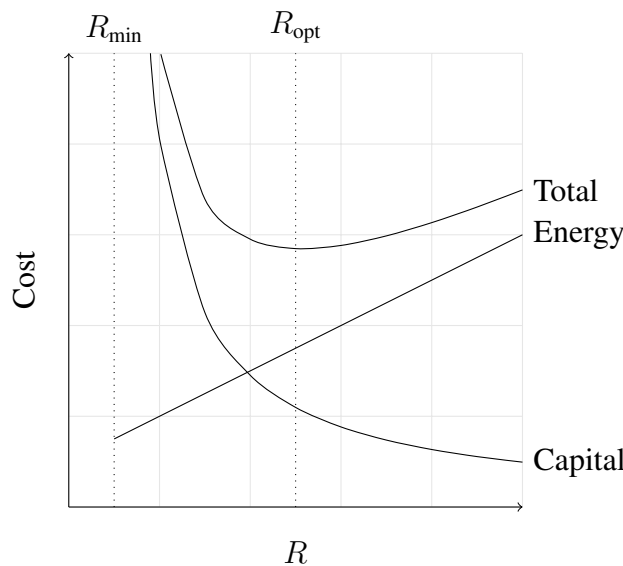


Figure 3.14: Trade-offs between the capital and energy costs.



The Rule of thumb for the choice of the optimum reflux ratio can be expressed as within the range of 1.1 to 1.3 times of the minimum reflux ratio. This rule of thumb assumes that heating and cooling duties will be provided by the utility system. Also, the reflux ratio should only be optimised in the context of the overall process heating and cooling requirements. Table 3.1 shows some industrial examples and the conditions used; this shows that the guide reflux ratio is not always the optimum for a variety of reasons.

Table 3.1: Representative commercial distillation operations.

Binary Mixture	Average Relative Volatility	Number of Pressure / psia	Typical Operating Reflux Ratio	Reflux to Minimum
1,3-Butadiene/vinyl acetylene	1.16	130	75	1.70
Vinyl acetate/ethyl acetate	1.16	90	15	1.15
<i>o</i> -Xylene/ <i>m</i> -xylene	1.17	130	15	1.12
Isopentane/ <i>n</i> -pentane	1.30	120	30	1.20
Isobutane/ <i>n</i> -butane	1.35	100	100	1.15
Ethylbenzene/styrene	1.38	34	1	1.71
Propylene/propane	1.40	138	280	1.06
Methanol/ethanol	1.44	75	15	1.20
Water/acetic acid	1.83	40	15	1.35
Ethylene/ethane	1.87	73	230	1.07
Acetic acid/acetic anhydride	2.02	50	15	1.13
Toluene/ethylbenzene	2.15	28	15	1.20
Propane/1,3-butadiene	2.18	40	120	1.13
Ethanol azeotrope/water	2.21	60	15	1.35
Isopropanol/water	2.23	12	15	1.28
Benzene/toluene	3.09	34	15	1.15
Methanol/water	3.27	60	45	1.31
Cumene/phenol	3.76	38	1	1.21
Benzene/ethylbenzene	6.79	20	15	1.14
HCN/water	11.20	15	50	1.36
Ethylene oxide/water	12.68	50	50	1.19
Formaldehyde/methanol	16.70	23	50	1.17
Water/ethylene glycol	81.20	16	4	1.20

### Choice of feed condition and feed stage location

The feed condition and feed stage location are two other important factors that would affect the heating duty energy cost significantly.

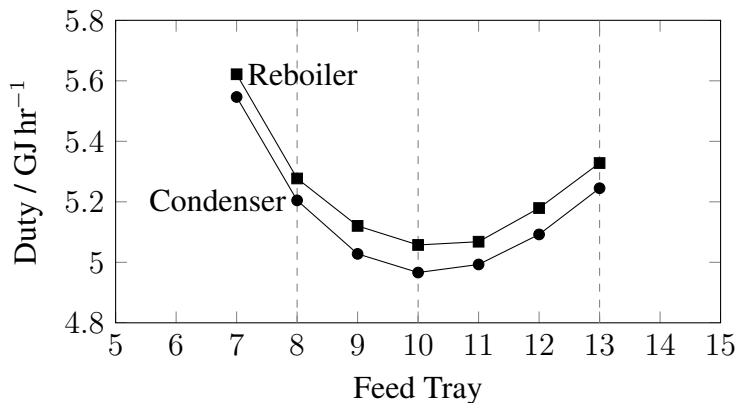
The feed condition,  $q$ , value affects the vapour and liquid flow rates in the column. A simple rule is that the feed temperature usually lies between the extreme temperatures of the column (condenser and reboiler temperatures).

- $q = 1$ , (saturated liquid feed) is preferred. This makes the column pressure easy to control by pumping the liquid to the correct pressure.
- If  $q = 0$  (saturated vapour feed), a compressor, rather than a pump, is needed, as it is harder to adjust the pressure of a vapour feed than a liquid feed.
- Superheated or subcooled feeds cannot participate in the separation process until thermal equilibrium is achieved
- In columns with multiple feeds, it is not unusual to use feeds with  $q < 0$  or  $q > 1$ , which would be determined by the practical needs.

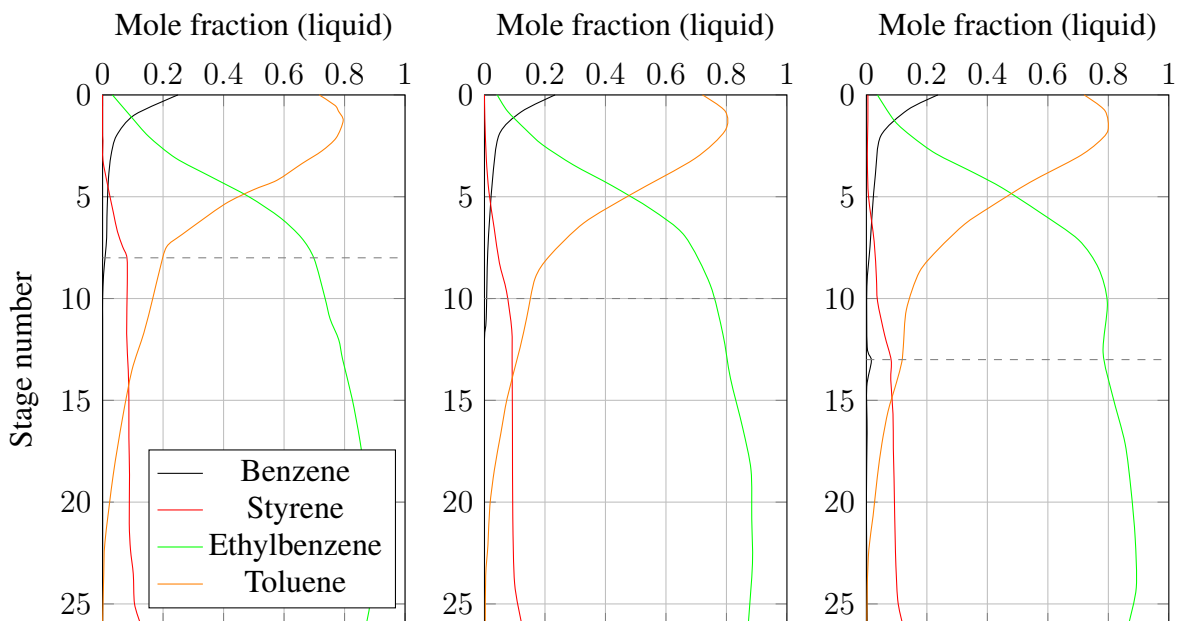
Therefore, heating or cooling the feed can reduce overall energy costs. Preheating the feed typically decreases the reboiler duty and may increase the condenser duty. Cooling the feed, conversely, tends to decrease the condenser duty and may increase the reboiler duty. The best feed condition can only be determined by considering heat recovery opportunities with the overall process.

The choice of feed stage location should follow the best match with the feed stage in terms of composition and temperature or using the Kirkbride equation to provide an initial estimate. It should be noted that poor matches are thermodynamically unfavourable, leading to higher energy requirements. In multi-component distillation, it is highly unlikely that the composition of all components can be matched.

Again, in the simulation of separating a Benzene-toluene-ethylbenzene-styrene mixture, a comparison shown in Figure 3.15 between different feeding stages is made to highlight the fact that heating duty depends on the match between the feed compositions and that of the components on a particular stage.



(a) Change in duty of the condenser and reboiler with feed stage



(b) Composition with feed at stage 8

(c) Composition with feed at stage 10

(d) Composition with feed at stage 13

Figure 3.15: Heating duty depending on the match between the feed condition and the composition of the component on the stage. (a) Variation in heat duty, (b)-(d) composition of components on the stages with different feed stage positions.

Note in Figure 3.15, when the feed composition and feed stage composition are not well matched, significant disruptions to the composition profiles have been observed.

### Type of condenser

As shown in Figure 3.10, there are two types of condensers: total and partial condensers. The total condenser produces liquid product for intermediate or final product storage or the top product is to be fed to another distillation at a higher pressure. The partial condenser reduces the condenser duty and avoid expensive refrigeration as not all vapour is condensed.

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### 3.8 Problems

- R1 A mixture of 44 mol% Benzene and 56 mol% Toluene needs to be separated into a product of at least 98 mol% Benzene and one of at least 98 mol% Toluene. It has been suggested by the plant engineer that this could be achieved using a distillation column at 1 atm with a Reflux ratio twice the minimum reflux ratio and a saturated liquid feed. How many stages are needed for this distillation column? [13 trays plus partial reboiler]

$x$	$y$
0.0	0.00
0.1	0.21
0.2	0.38
0.3	0.51
0.4	0.62
0.5	0.71
0.6	0.78
0.7	0.85
0.8	0.91
0.9	0.96
1.0	1.00

VLE Data for benzene with toluene at 1 atm.



Solution Video

E1 A de-ethaniser is to be designed for the separation summarised in the table below. Estimate the minimum number of stages required for the separation. [12 stages]

Component	Feed flow rate (kmol h <sup>-1</sup> )	Specified recovery to distillate (kmol h <sup>-1</sup> )	Average volatility
methane	160		8.22
ethane	370	368	2.42
propane	240	2	1.00
<i>n</i> -butane	25		0.378
<i>n</i> -pentane	5		0.150

Feed temperature (°C) 32

E2 A distillation column is used to separate a mixture of 30% mol propane in propylene to obtain 99% mol propylene and 98% mol propane.

- (a) Calculate the column pressure if the reboiler temperature is 370 K and the condenser temperature is 317 K. [18 bar]
- (b) Calculate  $R_{min}$  if the feed condition at a column operating pressure is
- saturated liquid, [ $\phi = 1.25, R_{min} = 0.65$ ]
  - saturated vapour, [ $\phi = 1.61, R_{min} = 1.09$ ]
  - 50% mol vapour. [ $\phi = 1.38, R_{min} = 0.79$ ]
- (c) Calculate the reboiler duty for the case that the feed flow rate is  $500 \text{ kmol h}^{-1}$  and the reflux ratio is 1.1 times  $R_{min}$ . Take the heat of vapourisation of the bottom product to be  $11330 \text{ kJ kmol}^{-1}$ . [ $3053.6 \text{ MJ h}^{-1}$ ,  $6768.9 \text{ MJ h}^{-1}$ ,  $4573.5 \text{ MJ h}^{-1}$ ]

Use the Antoine equation to estimate relative volatilities,

$$p_i^0 = \exp \left[ A_i - \frac{B_i}{T + C_i} \right]$$

where:  $p_i^0$  is the saturated vapour pressure in bar and  $T$  is the temperature in K.

Component	$A_i$	$B_i$	$C_i$
Propane	9.1058	2154.9	-25.16
Propylene	9.5749	1999.1	-17.61

E3 A distillation column is to be designed to separate Hexane from Cyclohexane. The feed consisting of 50 mol% Hexane enters the column as a saturated liquid at 346.77 K. The distillate consisting of 95 mol% Hexane exits the column at 342.38 K and the bottom product consisting of 5 mol% Hexane exits the column at 352.97 K. What is the minimum number of stages and the minimum reflux ratio needed for the separation.

The saturated vapour pressure of the components can be given by:

$$p_i^0 = 10 \left( A_i - \frac{B_i}{C_i + T} \right)$$

with parameters of:

Component	$A$	$B$	$C$	$T_{\min}$	$T_{\max}$
Hexane (H)	4.1297	1246.33	-40.162	178	508
Cyclohexane (C)	3.9706	1206.47	-50.014	280	354

The activity coefficient for each component can be given by:

$$\ln \gamma_i = -\ln [x_i + \Lambda_{ij}(1 - x_i)] + (1 - x_i) \left( \frac{\Lambda_{ij}}{x_i + \Lambda_{ij}(1 - x_i)} - \frac{\Lambda_{ji}}{(1 - x_i) + \Lambda_{ji}x_i} \right)$$

with parameters of:

$$\Lambda_{\text{HC}} = 0.8276$$

$$\Lambda_{\text{CH}} = 1.1103$$



- D1 Use the short-cut method to design a distillation column to separate the mixture in the table below, with a recovery of 95% of C5 to the distillate and 97% of C6 to the bottom product. Use a saturated liquid feed at 298 K with a column pressure equal to the feed pressure.

Alkane	mol fraction
C3	0.05
C4	0.10
C5	0.40
C6	0.35
C7	0.10

The saturation pressure in kPa for any straight chained hydrocarbon length  $n$  can be approximated to<sup>a</sup>,

$$P_i^0 = 1.78382 \times 10^4 \phi^n$$

$$\phi = \exp \left[ -427.248 \left( \frac{1}{T} - 1.029807 \times 10^{-3} \right) \right]$$

<sup>a</sup>L. Caldwell and D.S. van Vuuren, (1986), On the formation and composition of the liquid phase in Fischer-Tropsch reactors, *Chemical Engineering Science*, **41**:89-96



Solution Video



# Distillation Sequencing

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## 4.1 Chapter 4 ILOs

**ILO 4.1.** Appraise simple distillation sequences using heuristic rules to find optimal sequences.

**ILO 4.2.** Compare distillation sequences with the calculation of key performance indicators.

**ILO 4.3.** Develop distillation sequences using complex distillation columns.

**ILO 4.4.** Analyse the reasons for the advantages of complex distillation columns.



Chapter Video

## 4.2 Introduction

In almost any chemical industry, the mixtures intended to be separated are not simple binary mixtures, they normally contain more than two components. If the mixture is homogeneous as discussed in the previous chapters, distillation would be the most commonly used method for separating those multiple components. However, if the products required are not only two but more than that, then generally a separation sequence is needed to make the separation of the components in a viable and economic way. This is called distillation sequencing; the separations carried out based on distillation does not have only one sequence but other alternatives. The problem then becomes how to sieve those sequences and choose the best option.

## 4.3 Sequencing Simple Distillation Columns

A simple distillation column means that a single feed, two products, the key components are adjacent in volatility and the column has a reboiler and a condenser as shown in Figure 4.1.

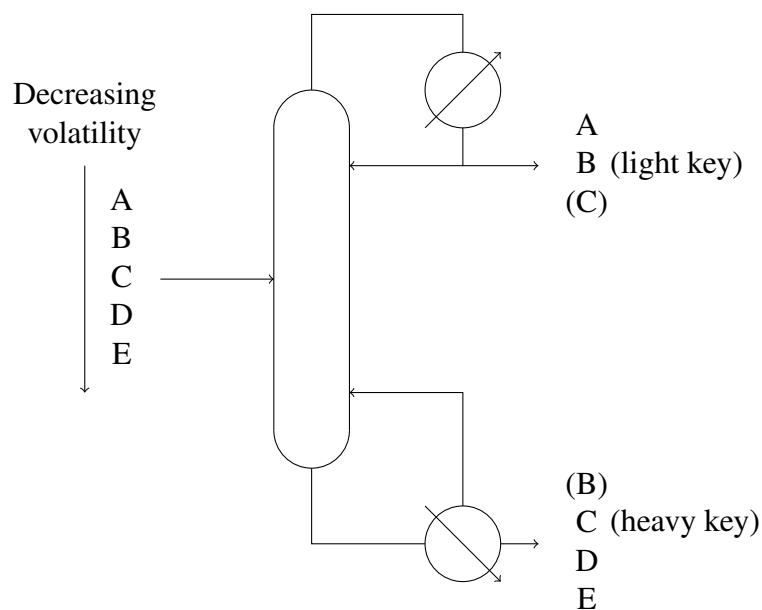


Figure 4.1: A simple column.

Suppose there is a homogeneous mixture with three components, A, B and C in which A is the lightest component and C is the heaviest component, to be separated, we can show there are in fact two alternative sequences - a direct sequence and an indirect sequence.

**A direct sequence** means in each column, the lightest component is taken as the overhead product.

**An indirect sequence** means the heaviest component is taken as the bottom product in each column.

The two sequences are illustrated in Figure 4.2.

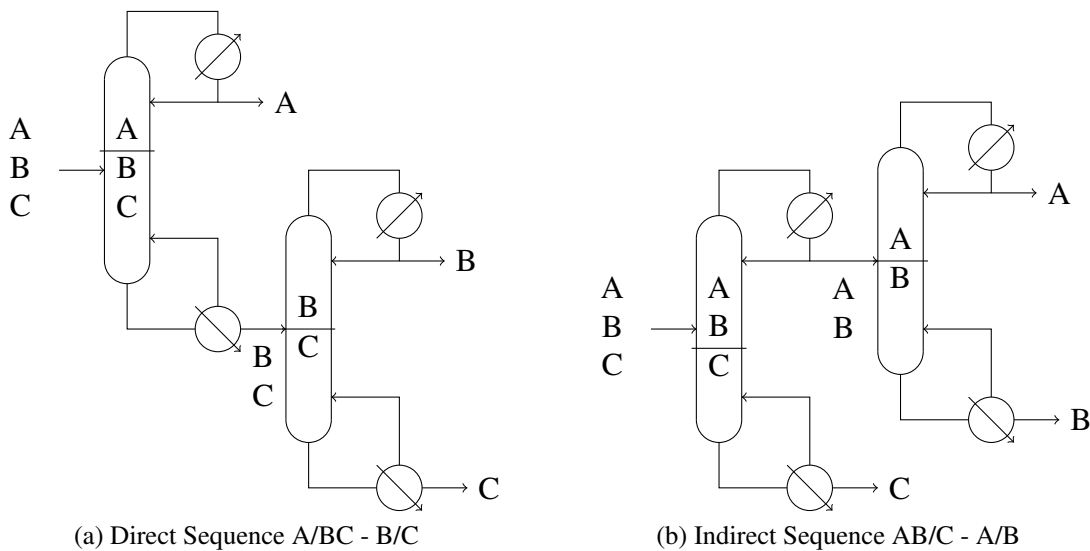


Figure 4.2: The direct and indirect sequences.

As seen in Figure 4.2, in the two sequences, each column has a reboiler and a condenser. It is worth noting that the direct sequence often requires less energy than the indirect one; this is because the light component is only vaporised once. However, the indirect sequence can be quite energy efficient compared to the direct one if the light component in the feed has a low flowrate but the heavy component has a high flowrate. This is because feeding a high flowrate of heavy component to both of the columns in the direct sequence is more important than vaporising the light component twice in the indirect sequence.

In a three component mixture, there are only two sequences. When the number of components in a mixture increases, the number of sequences increases dramatically. Figure 4.3 shows the alternative sequences for the separation of a five-component mixture.

Table 4.1 shows how dramatic the number of sequences changes with the increase of the number of the components in the mixture.

Table 4.1: Number of sequences changes with the number of components.

Number of components	Number of possible sequences
2	1
3	2
4	5
5	14
⋮	⋮
10	4862

As seen from Table 4.1, as the number of components increases to 10, the number of sequences increases to 4862. It is almost impossible to try so many sequences. Therefore, the problem becomes: how do we screen for the best few sequences and what criteria should we use to choose between alternative sequences? The way forward is to use simplified methods to identify several promising sequences and then evaluate these options further through rigorous simulations.

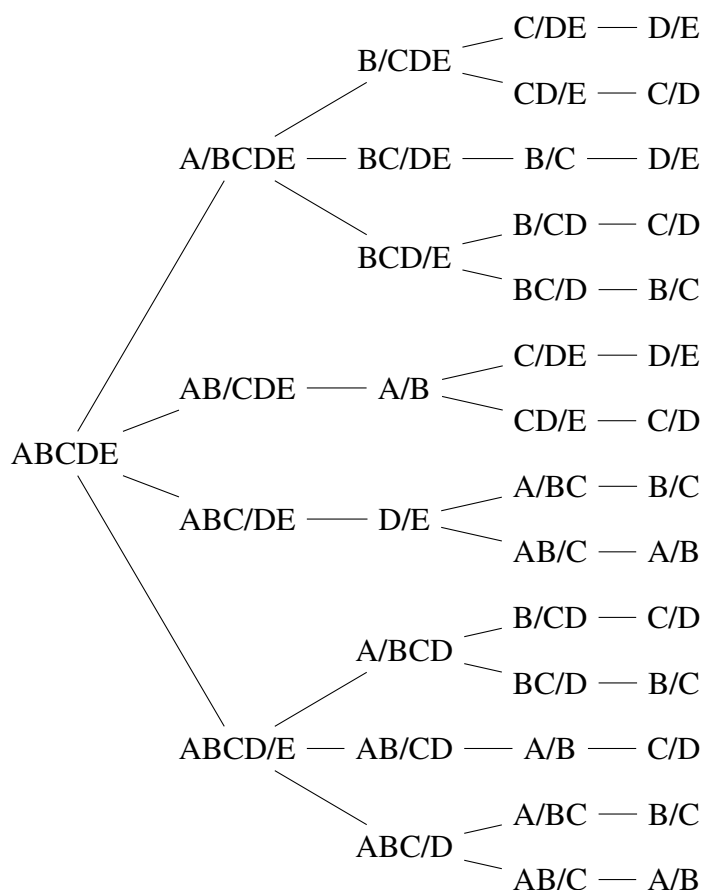


Figure 4.3: Alternative sequences for separating a five component mixture.

## 4.4 Distillation Columns Sequencing Heuristics

Certainly, not every sequence is to be feasible, there are practical constraints to sequencing columns including,

- Remove early: hazardous component, reactive and heat-sensitive components and corrosive components.
- Decomposition in the reboilers would contaminate products, which means no finished products should be taken from bottoms of columns.
- For those compounds which polymerise when distilled would require chemicals added to inhibit polymerisation but they tend to be involatile and end up in the column bottoms, so it would be necessary to take finished products overhead.
- For those components that are difficult to condense, a total condensation would normally be required under low-temperature refrigeration and/or very high operating pressures. The light components are normally removed from the top of the first column to minimise use of refrigeration and high pressures.

However, there are some heuristics developed for sequencing columns, they are useful as a guide line.

**Heuristic 1** Separations where the relative volatility of the key components is close to unity or which exhibit azeotropic behaviour should be performed in the absence of non-key components (Difficult separations typically require large reflux ratios - by

removing extraneous components, the internal flows in the column are reduced.) - Do the most difficult separation last.

**Heuristic 2** Sequences which remove the lightest components alone by one in column overheads should be favoured. In other words, favour the direct sequence (Less material is vaporised if only the lightest component is removed overhead, as in Figure 4.9(a).)

**Heuristic 3** A component comprising a large fraction of the feed should be removed first (The inventory in subsequent columns is kept to a minimum.)

**Heuristic 4** Favour near equimolar splits between top and bottom products in individual columns (The mass load in subsequent columns will be more evenly distributed in the sequence.)

However, difficulties can arise when those heuristics are in conflict with each other. Heuristics can be contradictory to each other but they do have advantages such as they incorporate engineering experience and insights and the designer stays in control (compared to automated screening techniques). However, they are still qualitative guidance, it is thus necessary to have some quantitative measures to classify the relative performance of the sequences.

## 4.5 Performance Indicators

Some quantitative performance indicators are proposed for screening distillation sequences. These are,

- Total vapour load.
- Total energy demand.
- Operating cost.
- Capital cost.
- Total annualised cost including capital, energy trade-offs, and the consideration of heat integration.

### 4.5.1 Vapour load

Vapour load of a column is a meaningful performance indicator, as it relates to heat duties in the reboiler and condenser (operating costs tend to dominate overall costs), size of reboiler and condenser also the column diameter.

Vapour load can be calculated using short-cut methods (e.g. Underwood Equation). The sum of the vapour loads for the sequence would provide a quantitative indicator of the performance of the sequence. However, it has limitations such as it is not directly related to energy demand or operating costs and the capital costs are only partially accounted for. The calculation of vapour load can be made using the reflux ratio as shown in Figure 4.4.



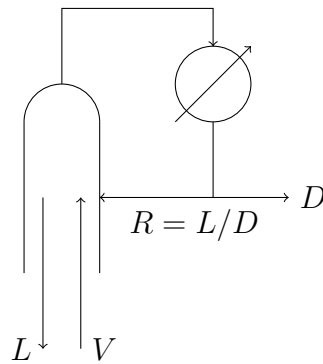


Figure 4.4: Schematic representation of the vapour load.

As the minimum reflux ratio  $R_{min}$  can be calculated from the Underwood equation and the minimum vapour load  $V_{min}$  based on  $R_{min}$  is,

$$V_{min} = (R_{min} + 1) D \quad (4.5.1)$$

The typical values of  $R$  (1.1 - 1.3 times of  $R_{min}$ ) have implicitly accounted for a capital-energy trade-offs.

The total vapour load in a distillation sequence is thus the addition of the vapour load for each column.

### 4.5.2 Energy demand

Energy demand is another useful indicator and allows total energy cost to be estimated. The energy demand can be calculated from the energy balances effectively from the vapour load. It should be pointed out that the heat of vaporisation depends on composition and temperature of stream (use product composition).

For a total condenser shown in Figure 4.5(a), the vapour to be condensed is  $V$ , thus the energy needed for the condensation is,

$$Q_{condenser} = V \cdot \Delta H^{vap} \quad (4.5.2)$$

where  $\Delta H^{vap}$  is the enthalpy of vaporisation.

Similarly, for a partial condenser, Figure 4.5(b),

$$Q_{condenser} = L \cdot \Delta H^{vap} \quad (4.5.3)$$

where  $L = RD$ .

### 4.5.3 Costs

- Operating costs. This can be determined by knowing the reboiler, condenser and preheat duties, and given costs of utilities (e.g. steam, cooling water, refrigeration power). It should be noted that costs of utilities are highly site-specific and vary significantly from time to time.

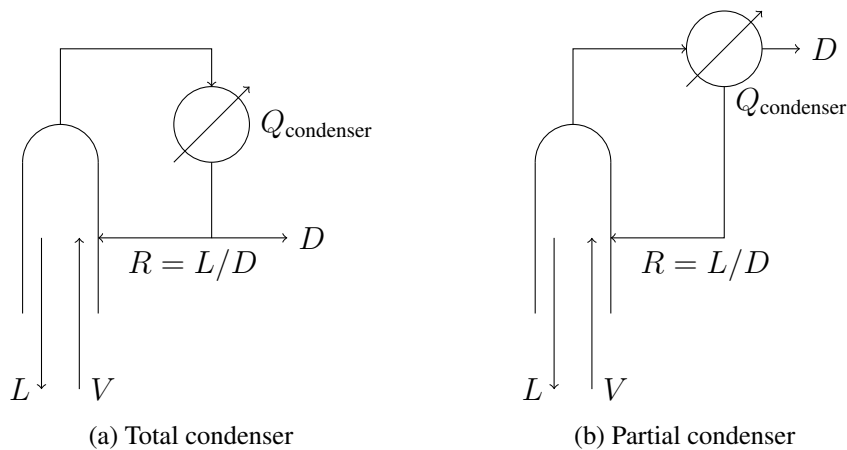


Figure 4.5: Energy demand for condensers.

- Capital costs. This can also be estimated, based on short-cut design results, e.g. using the Fenske equation to calculate the minimum number of theoretical stages ( $N_{min}$ ) then using the Gilliland correlation to relate reflux ratio and number of stages to  $R_{min}$  and  $N_{min}$ . However, the capital cost models are typically highly inaccurate ( $\pm 30\text{-}50\%$ ) and the actual cost of a installed equipment is typically 4 times purchase cost of the equipment.
- Total annualised costs account for both operating and capital costs.

## 4.6 Distillation Sequencing with Complex Columns

In addition to simple distillation columns, complex distillation columns can be considered. These can have more than 2 product streams, or have linking between columns by two-directional flows with one column having no condenser, or no reboiler - often referred to as thermally coupled distillation columns.

In sequencing distillation with complex columns, heuristics for simple columns are still available and useful as they provide qualitative guidance with insights; however, extra heuristics for the complex columns are also available.



Summary Video

### 4.6.1 Side-Stream Columns

A side-stream distillation column may replace two simple columns for some applications, sometimes at considerable savings in energy and investment. Intuitively, the side stream should contain primarily middle boiling components from a multicomponent mixture. Side streams may be useful when the middle boilers are the main product, as in a pasteurization column where the lighter trace components leave overhead.

Based on experience of using these column types, and simulations of ideal systems [2] heuristics have been suggested for when these columns provide a potential economic advantage.

**Heuristic 1** For a pure sidestream product, for a three component mixture, A-B-C, if the feed has  $B > 50\%$  and  $C < 5\%$ , use a vapour sidestream, as B is more volatile than the other dominant component, C, at the draw stage. As shown in Figure 4.6(a).

**Heuristic 2** For a pure sidestream product, for a three component mixture, A-B-C, if the feed has  $B > 50\%$  and  $A < 5\%$ , use a liquid sidestream, as B is less volatile than the other dominant component, A, at the draw stage. As shown in Figure 4.6(b).

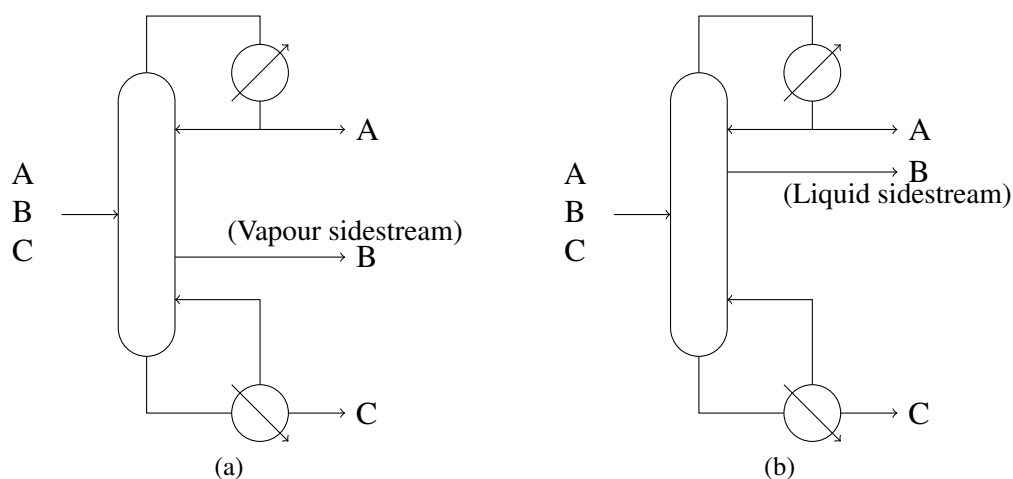


Figure 4.6: (a) Vapour side-stream for separating middle and heavy components, (b) Liquid side-stream for separating middle and light components.

## 4.6.2 Side-stripper arrangement

The use of complex nonstandard distillation columns can sometimes lead to substantial savings in capital costs as well as in energy consumption in comparison with conventional one-feed two-product distillation columns. Complex columns are also suitable for retrofit design, since they can often be implemented with only small modifications to existing columns.

As can be seen from Figure 4.7(a), for the side-stripper arrangement, the column on the right hand side effectively takes liquid from and feeds vapour to the left column. For the right column a condenser is saved.

The side-stripper sequence is a reconfiguration for the indirect sequence, Figure 4.2(b). As in the indirect sequences Figure 4.8(a), the left hand column produces only the bottom product and has part of the condensed liquid being fed into the right column and part of the liquid being refluxed. The idea was to remove the total condenser from the left column and to connect two streams to the right column, therefore to take liquid from the right column but feed vapour to it as needed (Figure 4.8(b)), which was then rearranged to become Figure 4.8(c).

Based on experience of using side-strippers, and calculations on energy use [1] heuristics have been suggested for when these columns provide a potential economic advantage. Figure 4.9(b) shows the percent savings when using a side stripper over the equivalent two simple column system.

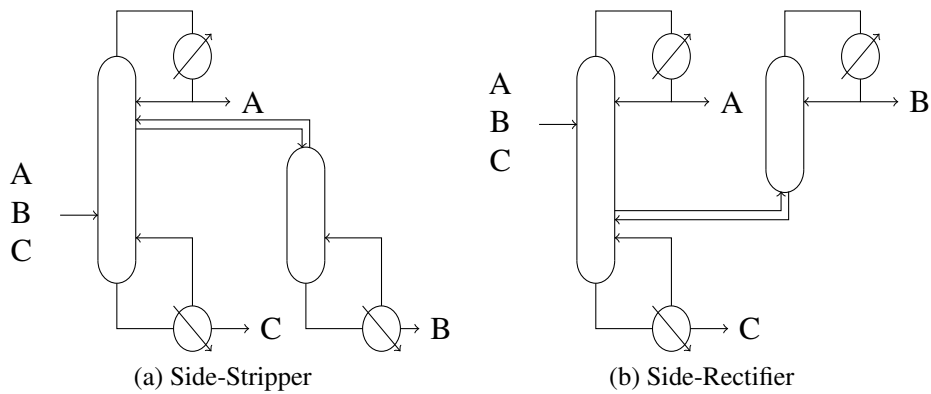


Figure 4.7: Thermally coupled distillation configurations, (a) side-stripper and (b) side-rectifier.

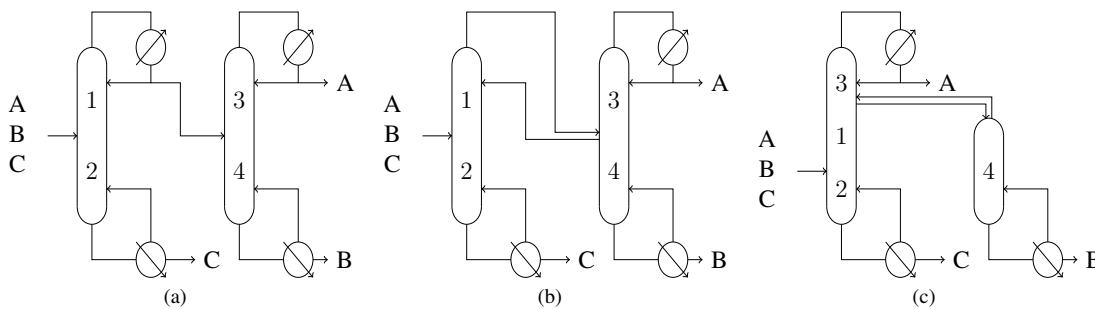


Figure 4.8: Thermal coupling for indirect sequences, (a) the indirect sequence, (b) the thermally-coupled indirect sequence, and (c) side-stripper arrangement.

**Heuristic** For a three component mixture, A-B-C, if the feed has  $B < 30\%$  and there is more C than A, use a side-stripper. As shown in Figure 4.8.

### 4.6.3 Side-rectifier arrangement

As can be seen from Figure 4.7(b), for the side-rectifier arrangement, the column on the right hand side effectively takes vapour from and feeds liquid to the left column. For the right column a reboiler is saved.

The side-rectifier sequence is a reconfiguration for the direct sequence, Figure 4.2(a). As in the direct sequences Figure 4.10(a), the left hand column produces only the top product and has part of the bottom liquid being fed into the right column and part of the liquid reboiled into the column. The idea was to remove the reboiler from the left column and to connect two streams to the right column, therefore to take vapour from the right column but feed liquid to it as needed (Figure 4.10(b)), which was then rearranged to become Figure 4.10(c).

Based on experience of using side-rectifiers, and calculations on energy use [1] heuristics have been suggested for when these columns provide a potential economic advantage, this is essentially the inverse of Figure 4.9(b).

**Heuristic** For a three component mixture, A-B-C, if the feed has  $B < 30\%$  and there is more A than C, use a side-rectifier. As shown in Figure 4.10.

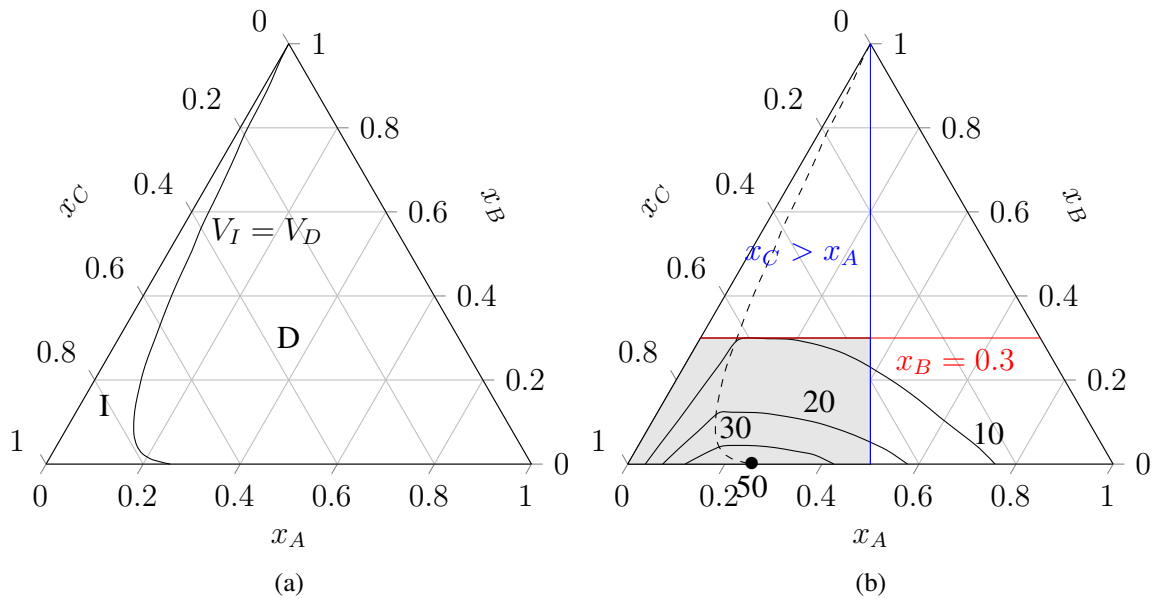


Figure 4.9: Energy savings for using a side-stripper system based on the assumption of ideal separation following the calculations of [1]. (a) Comparison of energy use for the direct vs indirect sequence, section marked D is where the energy use of the direct sequence is less, and section marked I is where the energy use of the indirect sequence is less. (b) Comparison of the energy use in a side stripper arrangement versus the lowest energy two column system, the contour lines are percent energy saving and the grey shaded is the best region for the use a side-stripper.

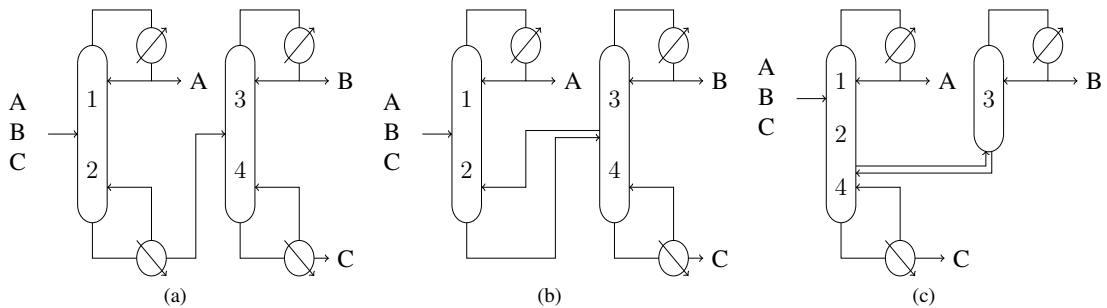


Figure 4.10: Thermal coupling for direct sequences, (a) the direct sequence, (b) the thermally-coupled direct sequence, and (c) the side-rectifier arrangement.

### 4.6.4 Pre-fractionation arrangements

The pre-fractionation arrangement is also a type of thermal coupling for distillation sequences. In such cases, the products are taken from the column on the right (Figure 4.11(a)), the left column has non-adjacent key components separated and fitted with a partial condenser and a partial reboiler, in such a connection, the column on the right has two feeds and three products. Similar considerations as to the side-stripper and side-rectifier arrangements can be made for rearranging such a connection to remove the condenser and the reboiler from the left column but to connect two streams on both top and bottom of it to the right column. This has been shown in Figure 4.11(b) also called the Petlyuk arrangement.

Figure 4.11(c) further simplifies the connection in Figure 4.11(b) by combining the two

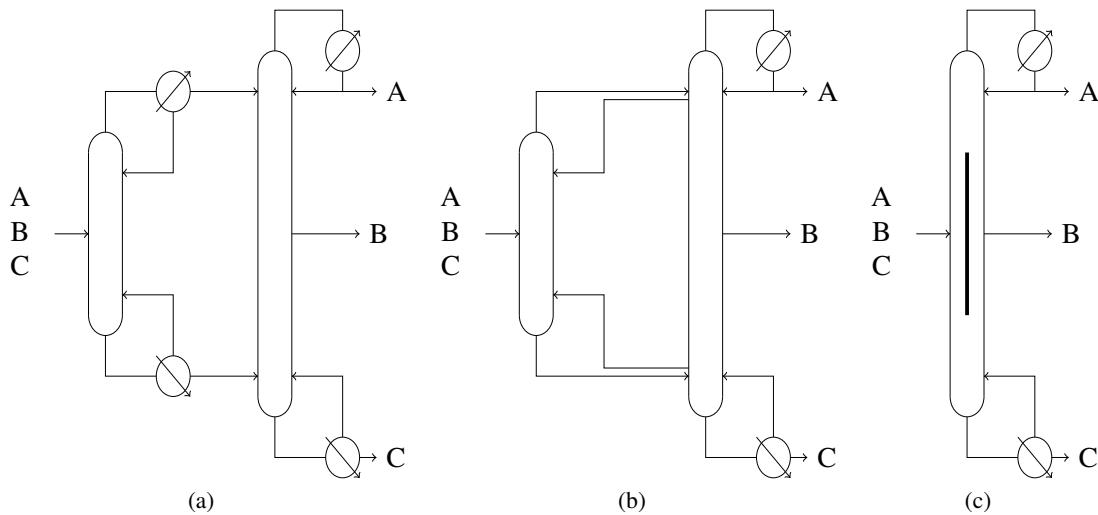


Figure 4.11: Thermal coupling for pre-fractionation sequences, (a) two columns with partial condenser on first column, (b) thermally-coupled pre-fractionator (Petlyuk column), and (c) dividing wall column.

columns into one so-called dividing wall column. The three arrangements have equal mass balances for all components but in the dividing column, the capital cost may be reduced significantly as not only does it remove the condenser and the reboiler but it is in a combined single shell structure. The disadvantages in such dividing wall columns are it may be sometimes difficult to cope with the differences in temperature and pressure operated in the combined two columns.

**Heuristic** For a three component mixture, A-B-C, when the middle-boiling component comprises a large fraction of the feed and  $\alpha_{AB}$  is similar to  $\alpha_{BC}$ , it is then useful to consider a pre-fractionator arrangement. As shown in Figure 4.11.

The condition  $\alpha_{AB}$  is similar to  $\alpha_{BC}$  is important as B is then more uniformly distributed in the A and C streams fed into the right column. The pre-fractionator arrangement typically requires 30% less energy than conventional column arrangements, due to the composition profile.

Figure 4.12(a) is the conventional direct sequence arrangement for separating a three component mixture. The composition profile for the middle boiling product B is shown in Figure 4.12(b). As seen from Figure 4.12(b), the top product in Column 1 is only A and the bottom stream has a high concentration of B, when this stream is fed into Column 2, as B is the product in the top of the column so B will experience a process called remixing to reach the top of Column 2 as the product being taken out from this column. This means that it is highly possible that the composition of the bottom stream from Column 1 as the feed into Column 2 is not matching the composition of the stage at the feeding location. A mismatching between the feed composition and that of the feeding stage will require more energy consumption for the fact of remixing - concentration redistribution.

However, in the pre-fractionation arrangement, the energy loss for remixing can be significantly reduced, this is due to a uniform distribution of the middle boiling component in the top and bottom streams of the left column as feeds to the right column. This is illustrated in Figure 4.13.

As no product has been taken from the left column, component B would be uniformly distributed in the top and bottom streams into the right column, thus there is no redistribution

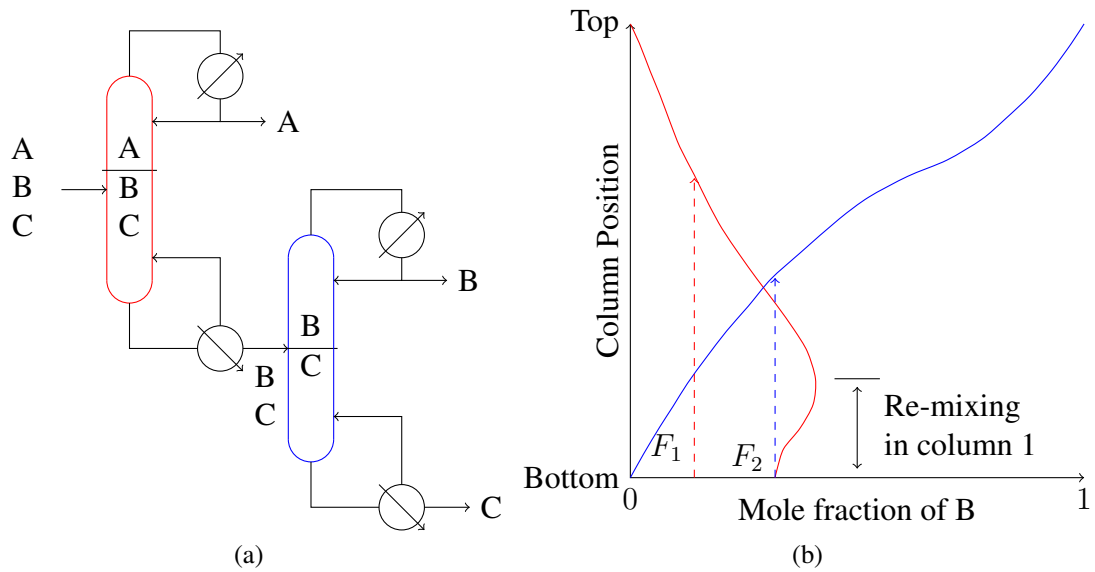


Figure 4.12: Separating a three component mixture with the (a) conventional direct sequence and (b) the composition profile of component B.

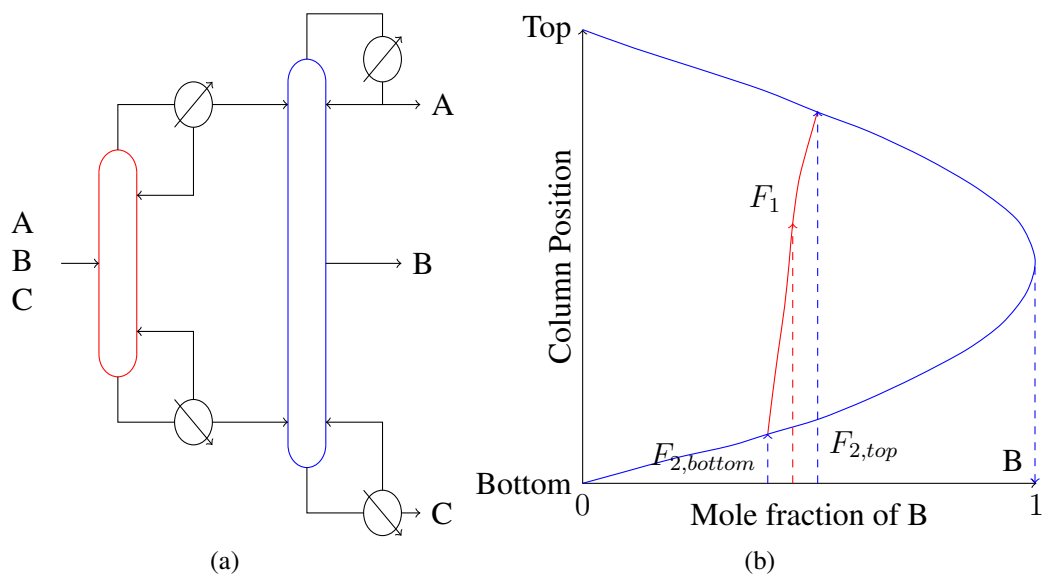


Figure 4.13: Composition profile of component B in the pre-fractionation arrangement.

of B taking place in the right column. This then gives a considerably greater freedom to match the composition of the feed streams from the left column with that of the feeding stages in the right column thus reduces energy consumption in remixing. In fact, the improved thermodynamic efficiency (heat duties reduced) in pre-fractionation arrangements is essentially due to reduced vapour load.

## 4.7 Utility Considerations with Thermally Coupled Columns

As been discussed in the last section, thermal coupling arrangements have great capabilities to reduce energy consumption compared to that from the conventional arrangements. Thus, it is necessary in the design distillation sequences, to take this into account. Such

thermal coupling would result in the side-stripper, side-rectifier and Petlyuk configurations and the pre-fractionation arrangement.

In thermally coupled arrangements, heating and/or cooling is provided to an upstream column directly by a process stream from the downstream column, rather than indirectly through a heat exchanger. Therefore, thermal coupling leads to energy savings as remixing is reduced such as in the pre-fractionator arrangement compared to conventional column arrangements, a reduction in total vapour flow is expected.

However, those thermally coupled arrangement have larger temperature ranges than simple column sequences as shown in Figure 4.14.

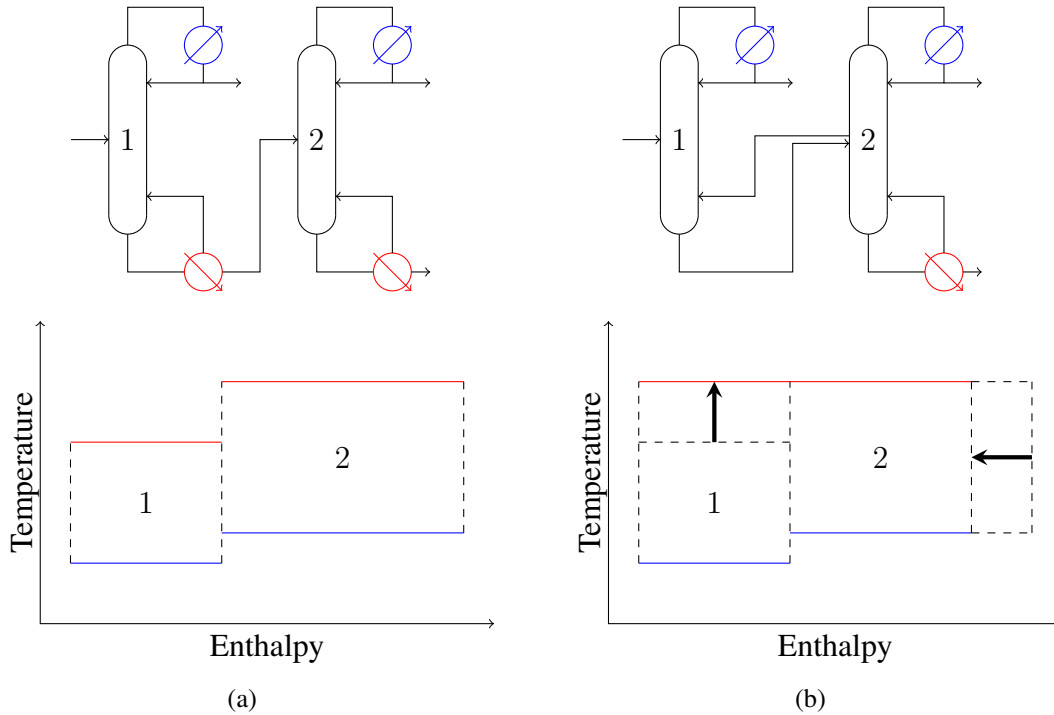


Figure 4.14: Comparison of temperature range between (a) the direct sequence and (b) the side rectifier arrangement.

It should be noted in the thermally coupled arrangement, although less energy is required in a single reboiler, all it is running at higher temperatures. Whether operating costs are reduced depends on which utilities are required, and on their relative costs, thus the heat integration opportunities created may be compromised.



## 4.8 Decomposition of Complex Columns for Design

When it comes to mass and energy balance analysis, it is practically useful to decompose complex columns into multiple columns so that short-cut calculations can be carried out relatively easily. Thermally coupled columns can be decomposed into a combination of side stream columns and simple columns. The mass and energy balances are equivalent for the complex column configurations and the decomposed multi-column sequence. However, the capital costs would then depend on the actual configurations used. Generally speaking, the cost of complex column configuration is less than that of the equivalent sequence of columns.



Summary Video

There are mainly two steps used for the modelling. First, design the upstream column using a hypothetical reboiler or condenser to obtain approximate flow rates and compositions of the linking streams. Second, model the downstream column(s) as a side-stream column using the extended Underwood equation for a side-stream columns.

### 4.8.1 Side-stripper decomposition

It is always the case that a side-stripper arrangement is for an indirect sequence. Thus, the decomposition of a side-stripper would follow that two condensers are needed for the top of the two columns, and, the right column takes vapour from the left column and feeds liquid into it. Such decomposition is shown in Figure 4.15.

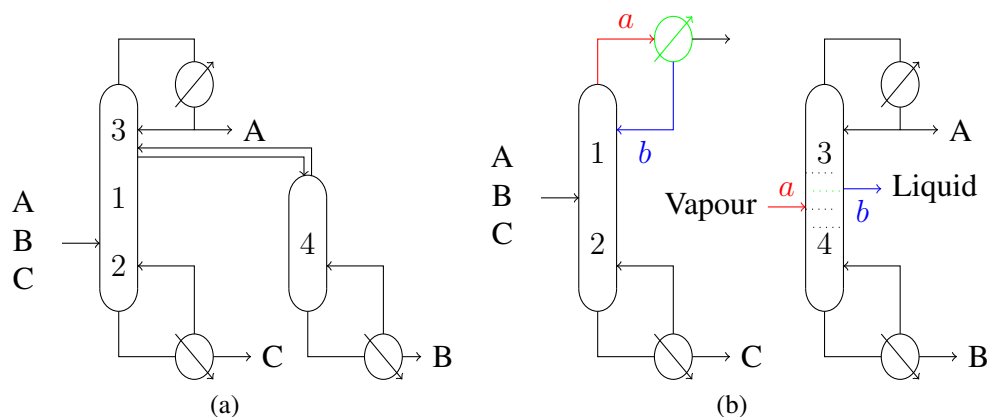


Figure 4.15: The decomposition of a side-stripper; (a) original side-stripper and (b) the decomposed sequence of a simple column with theoretical condenser and liquid side-stream column.

The right column in Figure 4.15 indicates that the side stream column is a liquid and the side stream should be one plate above feed plate. This is because this is the equivalent of one stage of equilibrium. The added partial condenser on the left column is equivalent to this one stage in the right column.

### 4.8.2 Side-rectifier decomposition

The side-rectifier decomposition is similar to that of the side-stripper decomposition. The difference is that a side-rectifier arrangement is for a direct sequence thus two reboilers are needed for the bottom of the two columns, and, the right column takes liquid from the left one and feeds vapour into it. This is shown in Figure 4.16.

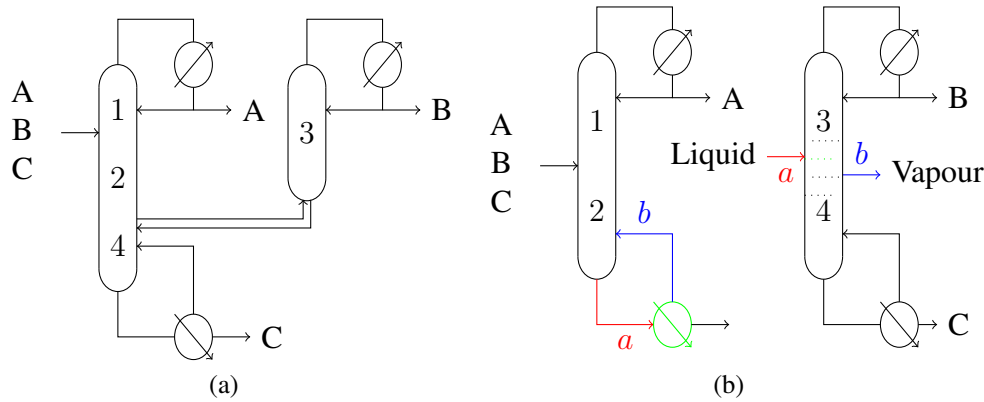


Figure 4.16: The decomposition of a side-rectifier; (a) original side-rectifier and (b) the decomposed sequence of a simple column with theoretical reboiler and vapour side-stream column.

If in the decomposition, a vapour side stream is needed from the right column, the side stream should be taken from a plate below the feed plate. This is because this is the equivalent of one stage of equilibrium. The added partial reboiler on the left column is equivalent to this one stage in the right column.

### 4.8.3 Pre-fractionator decomposition

In the decomposition for a pre-fractionation arrangement, as no product would be taken from the left column, it is relatively simpler. It can be made by adding a partial condenser and a partial reboiler to the left column and feeding the top and bottom streams into the right column. If there are also side streams being drawn from the right column, based on the phase status, the drawing stage should also follow that explained for the side-stripper and side-rectifier decompositions, Figure 4.17.

### 4.8.4 Extension to Underwood Equations for Side Stream Columns

As the Underwood equation is used to calculate the minimum reflux ratio under the conditions of given the feed composition, feed condition and relative volatilities of the components, the vapour flow in the column at minimum reflux,  $V_{min}$ , can also be determined [3],

$$V_{min} = M \sum_{i=1}^n \frac{\alpha_{i,R} x_{i,M}}{\alpha_{i,R} - \theta} \quad (4.8.1)$$

where  $M$  is the flow of net overhead product as shown in Figure 4.18(a) and  $\theta$  is calculated according to equation 3.4.38 with  $\alpha_{A,R} > \theta > \alpha_{B,R}$ .

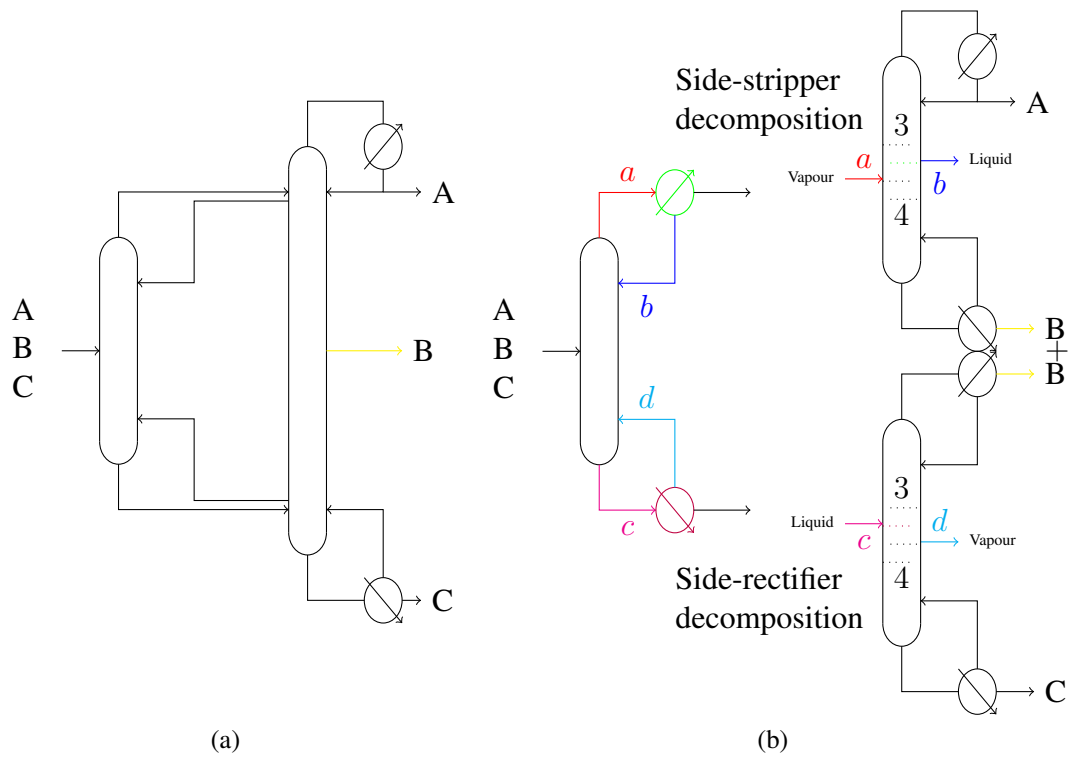


Figure 4.17: The decomposition of a pre-fractionator; (a) original pre-fractionator and (b) the decomposed sequence of a simple column with theoretical condenser and reboiler, and vapour side-stream and liquid side-stream columns.

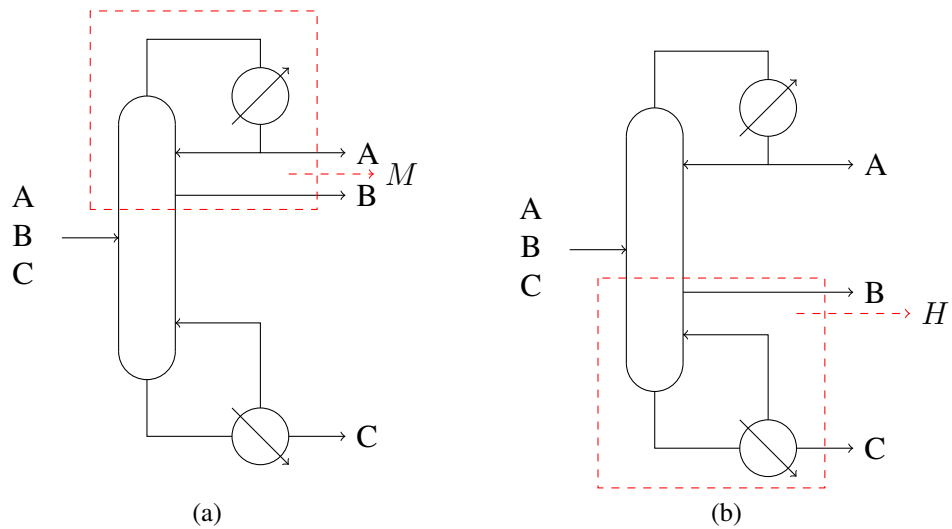


Figure 4.18: A side stream column (a) with the net overhead product and (b) with the net bottom product.

Similarly, for a side-stream below the feed as shown in Figure 4.18(b), the minimum vapour flow can also be calculated as,

$$-V_{min} = H \sum_{i=1}^n \frac{\alpha_{i,R} x_{i,H}}{\alpha_{i,R} - \theta} \quad (4.8.2)$$

where  $H$  is the flow of the net bottom product and  $\alpha_{B,R} > \theta > \alpha_{C,R}$ .

## 4.9 References

- [1] Glinos, K. and Malone, M. F. [1988], ‘Optimality regions for complex column alternatives in distillation systems’, *Chemical Engineering Research and Design* **66**, 229–240.
- [2] Rooks, R. E., Malone, M. F. and Doherty, M. F. [1996], ‘A geometric design method for side-stream distillation columns’, *Industrial & Engineering Chemistry Research* **35**, 3653–3664.
- [3] Triantafyllou and Smith [1992], *Chemical Engineering Research and Design* **70**, 118–132.

## 4.10 Problems

E1 The mixture of A, B, C and D shown in the table below is to be separated into pure component products using a sequence of distillation columns.

Apply heuristics to identify one or two promising sequences of simple distillation columns, as well as one or two sequences including complex distillation configurations, to carry out the desired separation. Assume that the relative volatilities are constant.



Solution Video

Component	Molar composition	Relative volatility between adjacent components
A	0.20	2.33
B	0.50	2.33
C	0.25	1.148
D	0.05	—

E2 The mixture of benzene, toluene and xylene isomers shown in the table below is to be separated into pure component products using a sequence of distillation columns. Three sequences are proposed,

- Sequence 1: B / T *pX* *oX* – T / *pX* *oX* – *pX* / *oX* (direct sequence)
- Sequence 2: B T / *pX* *oX* – B / T – *pX* / *oX*
- Sequence 3: B T *pX* / *oX* – B T / *pX* – B / T (indirect sequence)

Component	Molar composition	Relative volatility at 1 atm
Benzene	0.40	6.215
Toluene	0.35	2.673
<i>p</i> -Xylene	0.20	1.148
<i>o</i> -Xylene	0.05	1

Total flow rate 180 kmol h<sup>-1</sup>

Temperature 99.2 °C (saturated liquid)

Pressure 1 atm

Use the total vapour load and reboiler duty to compare the proposed sequences. Identify the most promising sequence. The reflux ratio is assumed to be 1.1 times of the  $R_{min}$  for each column. Short-cut distillation models are used to simulate the individual simple distillation columns that are used in the distillation sequences proposed. The table below presents the results of these simulations, where complete separation of the key components is assumed in each column. The feeds to all columns are saturated liquids; all columns are assumed to operate at a constant pressure of 1 atm.

Separation	$R_{min}$	$N_{min}$	$\Delta H_{feed}^{vap}$ (kJ kmol <sup>-1</sup> )	$T_{condenser}$ (°C)	$T_{reboiler}$ (°C)
B / T <i>pX</i> <i>oX</i>	1.49	19.7	35170	80.2	120.1
B T / <i>pX</i> <i>oX</i>	0.63	19.6	35170	91.2	139.8
B T <i>pX</i> / <i>oX</i>	1.96	111.3	35170	97.4	143.6
B / T <i>pX</i>	1.50	19.8	34764	80.2	118.6
B T / <i>pX</i>	0.61	19.5	34764	91.2	139.0
T / <i>pX</i> <i>oX</i>	1.43	22.1	35476	110.3	139.8
T <i>pX</i> / <i>oX</i>	3.74	129.3	35476	118.6	143.6
B / T	1.36	20.0	32599	80.2	110.3
T / <i>pX</i>	1.34	22.8	35182	110.3	139.0
<i>pX</i> / <i>oX</i>	10.31	151.2	36349	138.9	143.6

B: Benzene; T: Toluene; *pX*: *p*-Xylene; *oX*: *o*-Xylene

E3 Discuss the difference between simple distillation sequencing and thermally coupled sequencing in the aspects,

- (a) Operating lines
- (b) Middle boiling component distribution
- (c) Configuration
- (d) Total vapour load
- (e) Energy consumption and capital cost
- (f) Feed composition requirement

E4 Discuss any restrictions for dividing wall columns.



D1 For the options you have identified in question E1 design the best distillation sequence using the short-cut design rules if the total feed is  $300 \text{ kmol h}^{-1}$ . Some useful information,

Component	Boiling point / °C	Liquid density / $\text{kg m}^{-3}$	Molecular weight / Da
A	36	0.5	72
B	68	0.6	86
C	98	0.7	100
D	151	0.8	128



# Azeotropic Distillation

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## 5.1 Chapter 5 ILOs

**ILO 5.1.** Explain the presence of different azeotrope types using the modified Raoult's law.

**ILO 5.2.** Demonstrate the use of ternary diagrams to represent distillation columns.

**ILO 5.3.** Analyse residue curve maps to find feasible distillation column separations.

**ILO 5.4.** Construct approximate residue curve maps on ternary diagrams.

**ILO 5.5.** Design azeotropic distillation sequences using ternary diagrams.



Chapter Video 1



Chapter Video 2



Chapter Video 3

## 5.2 Azeotropic mixtures

Departures from Raoult's law commonly manifest themselves in the formation of azeotropes. Many close boiling, non-ideal mixtures form azeotropes, particularly those of different chemical types. Azeotropic-forming mixtures exhibit either maximum- or minimum-boiling points at some composition, corresponding, respectively, to negative and positive deviations from Raoult's law. Vapour and liquid compositions are identical for an azeotrope; thus, all  $K$  values are 1,  $\alpha_{AB} = 1$ , and no separation can take place,

$$y_i P = x_i \gamma_i P^0 \quad (5.2.1)$$

with  $x_i = y_i$  at the non-trivial solutions of 0 and 1.

If only one liquid phase exists, it is a homogeneous azeotrope; if more than one liquid phase is present, the azeotrope is heterogeneous. By the Gibbs phase rule, at constant pressure in a two-component system, the vapour can coexist with no more than two liquid phases; in a ternary mixture, up to three liquid phases can coexist with the vapour, and so on.

Figures 5.1, 5.2, and 5.3 show three types of azeotropes. The most common by far is the **minimum-boiling homogeneous azeotrope**, e.g. isopropyl ether-isopropyl alcohol, shown in Figure 5.1. At a temperature of 70°C, the maximum total pressure is greater than the vapour pressure of either component, as shown in Figure 5.1(a), because activity coefficients are greater than 1. The  $y$ - $x$  diagram in Figure 5.1(b) shows that for a pressure of 1 atm, the azeotropic mixture is at 78 mol% ether. Figure 5.1(c) is a  $T$ - $x$  diagram at 1 atm, where the azeotrope is seen to boil at 66°C. In Figure 5.1(a), for 70°C, the azeotrope occurs at 123 kPa, for 72 mol% ether. Thus, the azeotropic composition and temperature shift with pressure. In distillation, minimum-boiling azeotropic mixtures are approached in the overhead product.

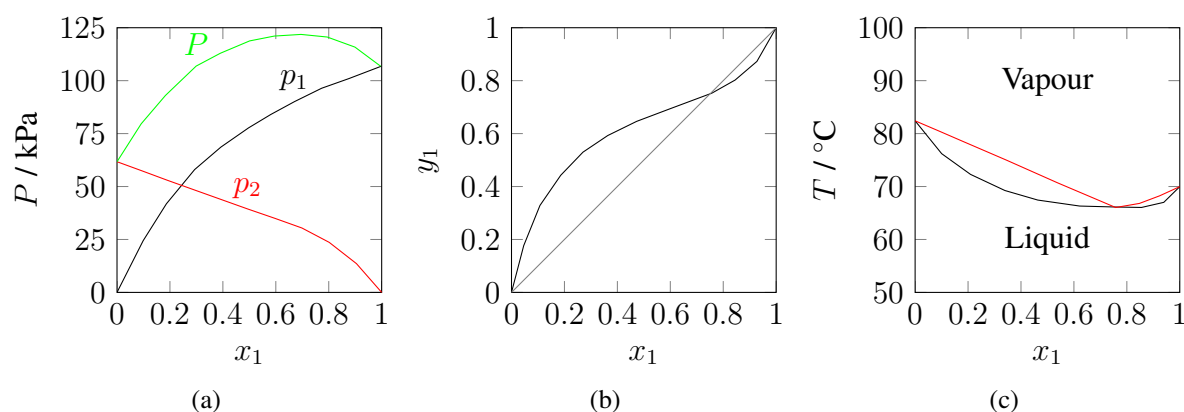


Figure 5.1: Minimum-boiling-point azeotrope, isopropyl ether (1) - isopropyl alcohol (2) system: (a) partial and total pressures at 70°C; (b) vapour-liquid equilibria at 101 kPa; (c) phase diagram at 101 kPa.

For the **maximum-boiling homogeneous azeotropic** acetone-chloroform system in Figure 5.2(a), the minimum total pressure at 60°C is below the vapour pressures of the pure components because activity coefficients are less than 1. The azeotrope is approached in the bottoms product in a distillation operation. Phase compositions at 1 atm are shown in Figures 5.2(b) and (c).

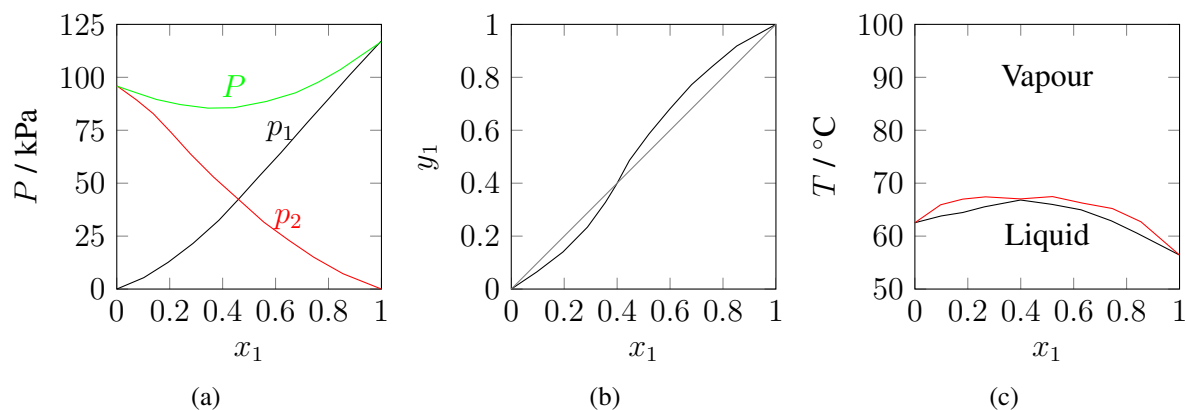


Figure 5.2: Maximum-boiling-point azeotrope, acetone (1) - chloroform (2) system: (a) partial and total pressures at 60°C; (b) vapour–liquid equilibria at 101 kPa; (c) phase diagram at 101 kPa pressure.

**Heterogeneous azeotropes** are minimum-boiling because activity coefficients must be significantly greater than 1 to form two liquid phases. The grey region in Figure 5.2(a) for the water-*n*-butanol system is a two-phase region, where total and partial pressures remain constant as the amounts of the phases change, but phase compositions do not. The  $y$ - $x$  diagram in Figure 5.2(b) shows a horizontal line over the immiscible region, and the phase diagram of Figure 5.2(c) shows a minimum constant temperature.

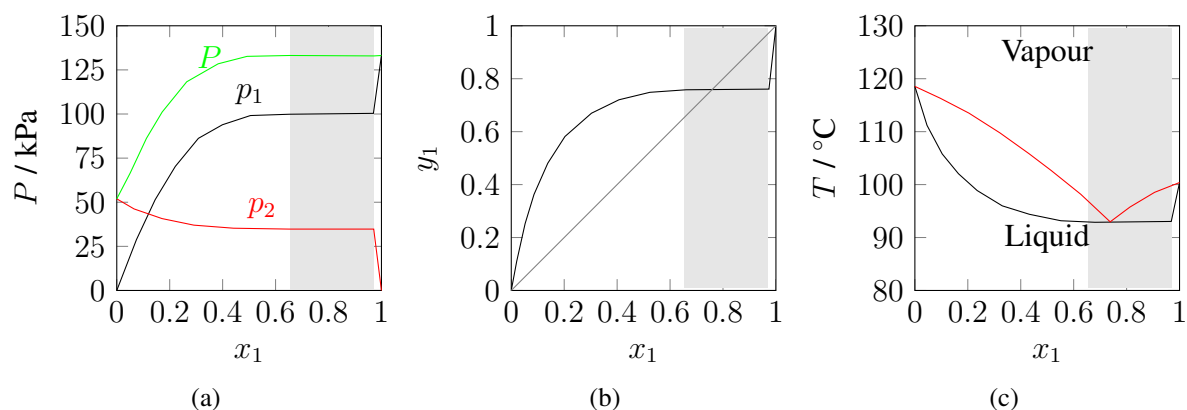


Figure 5.3: Minimum-boiling-point (two liquid phases) water (1) - *n*-butanol(2) system: (a) partial and total pressures at 100°C; (b) vapour-liquid equilibria at 101 kPa; (c) phase diagram at 101 kPa pressure. Grey zone is the liquid 2-phase region.

To avoid azeotrope limitations, it is sometimes possible to shift the equilibrium by changing the pressure sufficiently to “break” the azeotrope, or move it away from the region where the required separation is to be made. For example, ethyl alcohol and water form a homogeneous minimum-boiling azeotrope of 95.6 wt% alcohol at 78.15°C and 101.3 kPa. However, at vacuums of less than 9.3 kPa, no azeotrope is formed.

## 5.3 Triangular Graphs

In the distillation of a ternary mixture, possible equilibrium compositions do not lie uniquely on a single, isobaric equilibrium curve because the Gibbs phase rule gives an additional degree of freedom. The other compositions are determined only if the temperature, pressure, and composition of one component in one phase are fixed.

The composition of a ternary mixture can be represented on a triangular diagram (like in Chapter 2, either equilateral or right, where the three apexes represent pure components). Although Stichlmair [4] shows that vapour-liquid phase equilibria at a fixed pressure can be plotted by letting the triangular grid represent the liquid phase, with superimposing lines of constant equilibrium-vapour composition for two of the three components, Figure 5.4, this representation is seldom used. It is more useful, when developing a feasible-separation process for a ternary mixture, to plot only equilibrium-liquid-phase compositions on the triangular diagram.

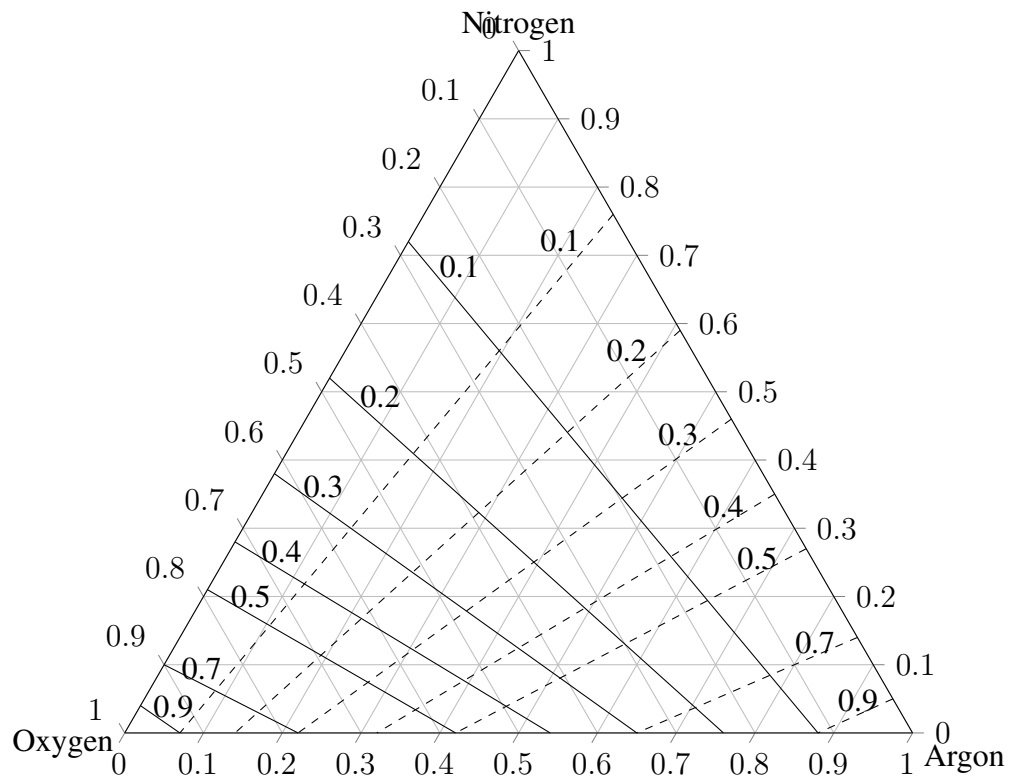


Figure 5.4: Example Stichlmair ternary diagram for a mixture of nitrogen, oxygen, and argon [4], axis are  $x_{O_2}$ ,  $x_{N_2}$ , and  $x_{Ar}$  while solid lines are  $y_{O_2}$  and dashed lines are  $y_{Ar}$ .

Figure 5.5, where compositions are in mole fractions, shows plots of this type for three different ternary systems. Each curve is the locus of possible equilibrium-liquid-phase compositions during distillation of a mixture, starting from any point on the curve. The boiling points of the three components and their binary and/or ternary azeotropes are included on the diagrams.

The zeotropic system of Figure 5.5(a) does not form any azeotropes. If the mixture of these three components is distilled, there is only one distillation region. Accordingly, the distillate can be nearly pure A, or the bottoms can be nearly C. However, nearly pure B, the intermediate-boiling component, cannot be produced as a distillate or bottoms. To separate this ternary mixture into the three components, a sequence of two columns is

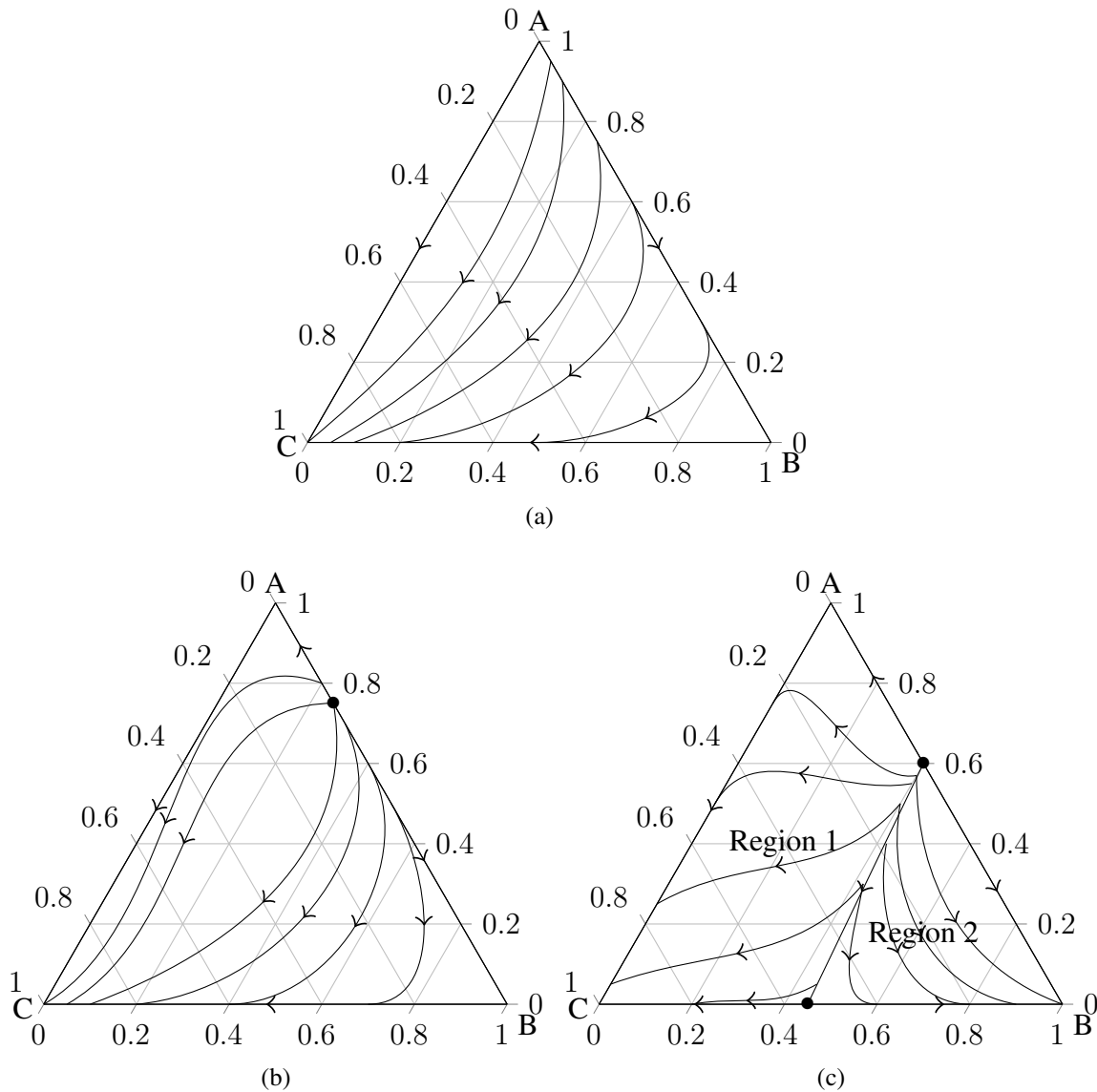


Figure 5.5: Residue curves for liquid-phase compositions of ternary systems. Lowest-boiling component is A, the intermediate-boiling component is B, and the highest-boiling component is C. (a) Mixture not forming an azeotrope, (b) Mixture forming one minimum-boiling azeotrope, and (c) Mixture forming two minimum-boiling azeotropes.

used, as shown in Figure 5.6, where the feed, distillate, and bottoms product compositions must lie on a straight, total-material balance line within the triangular diagram. In the direct sequence of Figure 5.6(a), the feed,  $F$ , is first separated into distillate A and a bottoms of B and C; then B is separated from C in the second column. In the indirect sequence of Figure 5.6(b), a distillate of A and B and a bottoms of C are produced in the first column, followed by the separation of A from B in the second column. When a ternary mixture forms an azeotrope, the products from a single distillation column depend on the feed composition, as for a binary mixture. However, unlike the case of the binary mixture, where two distillation regions, are well defined, the determination of distillation regions for azeotrope-forming ternary mixtures is complex. Consider the example of Figure 5.5(b), for a mixture of A, B, and C, which are in the order of increasing boiling point. The only azeotrope formed is a minimum-boiling binary azeotrope between A and B.

For this type of system, no distillation boundaries for the ternary mixture exist, even



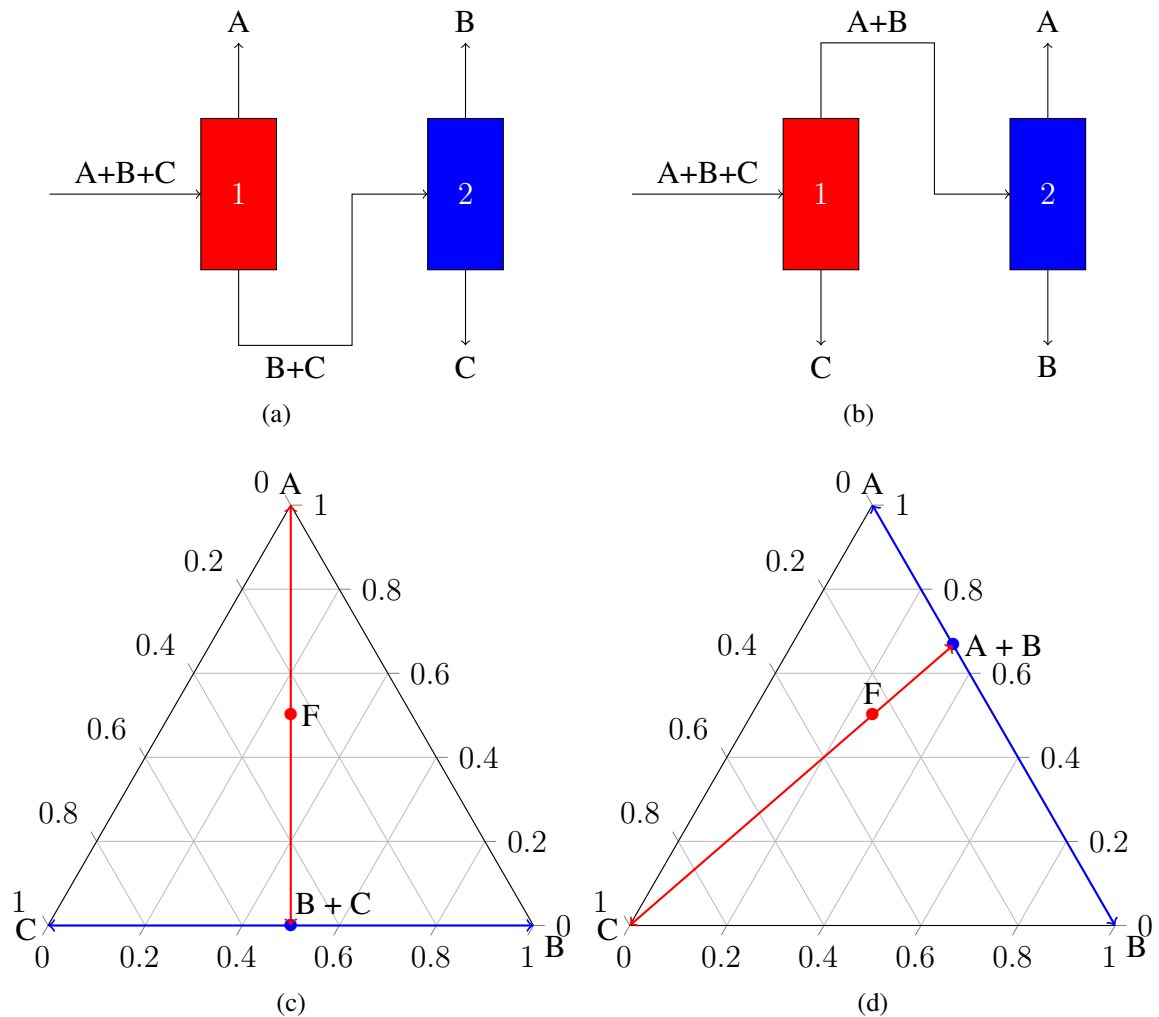


Figure 5.6: Distillation sequences for ternary zeotropic mixtures, (a) and (c) Direct sequence, (b) and (d) Indirect sequence. Red is the first column material balance, blue is the second column balance.

though an azeotrope is present. A feed composition located within the triangular diagram can be separated into two binary products, consistent with the total-material-balance line. Ternary distillate or bottoms products can be avoided if the column split is properly selected, e.g. like the system in Figure 5.7(a).

The more complex case of the ternary mixture with 2 azeotropes is presented in Figure 5.5(c); A and B form a minimum-boiling binary azeotrope, and B and C do the same. A triangular diagram for this system is separated by a distillation boundary into Regions 1 and 2. A column material-balance line connecting the feed to the distillate and bottoms cannot cross this distillation boundary, thus restricting the possible distillation products. For example, a mixture with a feed composition inside Region 2 cannot produce a bottoms of C, the highest-boiling component in the mixture. It can be distilled to produce a distillate of the A-B azeotrope and a bottoms of a mixture of B and C, or a bottoms of B and a distillate of all three components. If the feed lies in Region 1 of Figure 5.5(c), it is possible to produce the A-B azeotrope and a bottoms of a mixture of A and C, or a bottoms of C and a distillate of an A and B mixture, e.g. Figure 5.7(b). Thus, each region produces unique products<sup>1</sup>.

<sup>1</sup>It should be noted that if the distillation boundary is very curved it is in fact possible to cross for

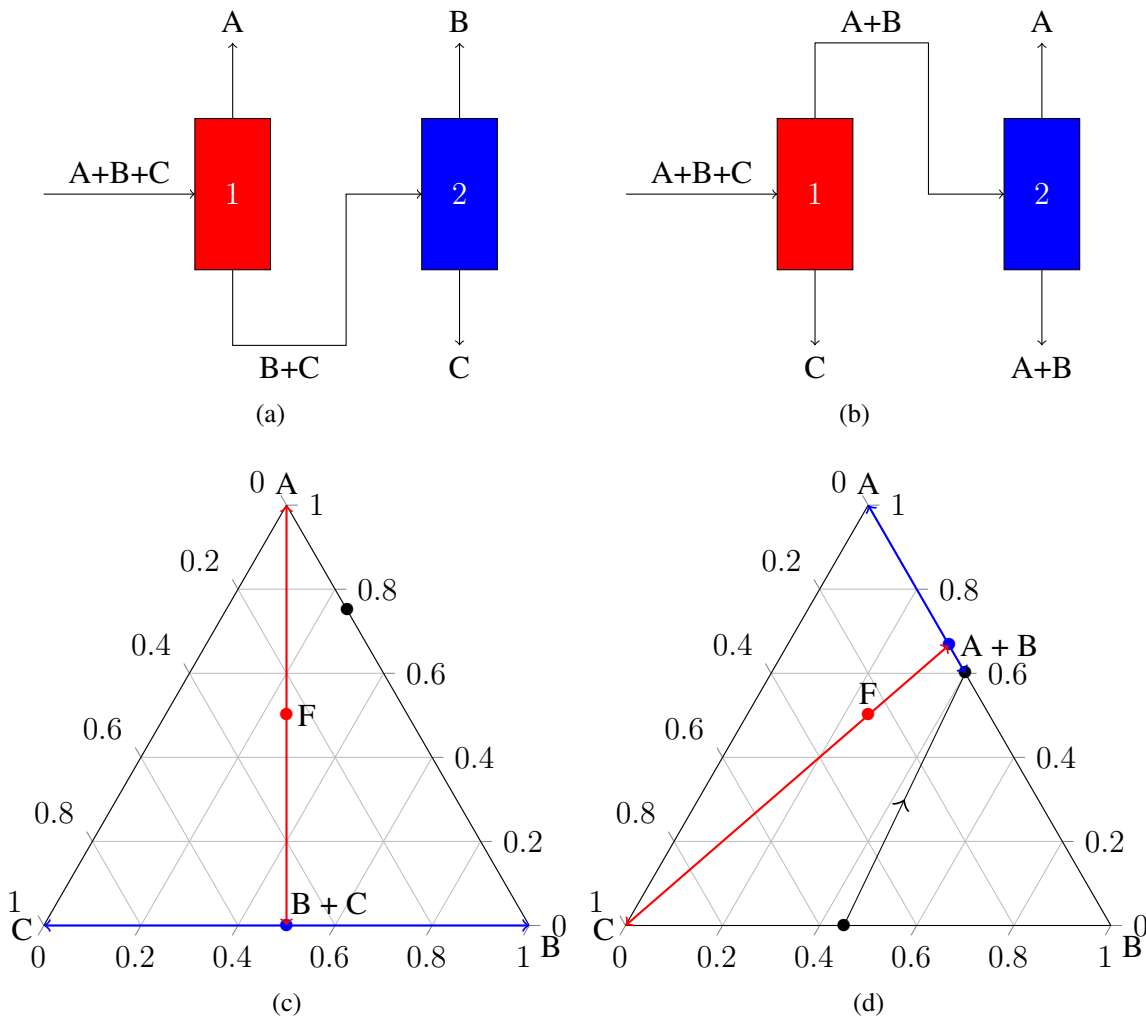


Figure 5.7: Distillation sequences for ternary azeotropic mixtures, (a) Direct sequence for a single azeotrope system, (b) Indirect sequence for a two azeotrope system. Red is the first column material balance, blue is the second column balance.

### 5.3.1 Residue-Curve Maps

Consider the simple batch distillation (no trays, packing, or reflux). For any ternary mixture component, a material balance for its vapourisation from the still, assuming that the liquid is perfectly mixed and at its bubble point, can be written as,

$$\frac{dx_i}{dt} = (y_i - x_i) \frac{1}{W} \frac{dW}{dt} \tag{5.3.1}$$

where  $x_i$  is the mole fraction of component  $i$  in  $W$  moles of a perfectly mixed liquid residue in the still, and  $y_i$  is the mole fraction of component  $i$  in the vapour leaving the still (instantaneous distillate) in equilibrium with  $x_i$ . As  $W$  decreases with time,  $t$ , it is possible to combine  $W$  and  $t$  into a single variable,  $\xi^1$ . As  $W(t)$  decreases monotonically

<sup>1</sup>certain situations.

$$\frac{d\xi}{dt} = -\frac{1}{W} \frac{dW}{dt} \tag{5.3.2}$$

Let the initial condition be  $\xi = 0$  and  $W = W_0$  at  $t = 0$ . Then the solution to equation 5.3.2 for  $\xi$  at time

with time,  $\xi(t)$  must increase monotonically with time and is considered a dimensionless time. Thus, for the ternary mixture, the distillation process can be modelled by,

$$\frac{dx_i}{d\xi} = (x_i - y_i), \quad i = 1, 2 \quad (5.3.4)$$

If equation 5.3.4 is written in a forward-finite-difference form, the following set of differential-algebraic equations can be used to solve the residue curves, assuming that a second liquid phase does not form,

$$\frac{x_{i,\xi+\Delta\xi} - x_{i,\xi}}{\Delta\xi} = x_{i,\xi} - y_{i,\xi}, \quad i = 1, 2 \quad (5.3.5)$$

$$\sum_{i=1}^3 x_i = 1 \quad (5.3.6)$$

$$y_i = K_i x_i, \quad i = 1, 2, 3 \quad (5.3.7)$$

and the bubble-point-temperature equation,

$$\sum_{i=1}^3 K_i x_i = 1 \quad (5.3.8)$$

where, in the general case,  $K_i = K_i(T, P, x, y)$ .

Thus, the system consists of seven equations in nine variables,  $P$ ,  $T$ ,  $x_1$ ,  $x_2$ ,  $x_3$ ,  $y_1$ ,  $y_2$ ,  $y_3$ , and  $\xi$ . With the pressure fixed, the next seven variables can be computed from equations 5.3.5 to 5.3.8 as a function of the ninth variable,  $\xi$ , from a specified initial condition. The calculations can proceed in the forward or backward direction of  $\xi$ . The results, when plotted on a triangular graph, are residue curves because the plot follows, with time, the liquid-residue composition in the still. A collection of residue curves, at a fixed pressure, is a residue curve map.

On a triangular diagram, all pure-component vertices and azeotropic points - whether binary azeotropes on the borders of the triangle or a ternary azeotrope within the triangle - are singular or fixed points of the residue curves because at these points,  $dx = d\xi = 0$ .

In the vicinity of these points, the behaviour of a residue curve depends on the two eigenvalues of equation 5.3.4. At each pure-component vertex, the two eigenvalues are identical. At each azeotropic point, the two eigenvalues are different. Three cases, illustrated by each of three pattern groups in Figure 5.8, are possible,

**Case 1**, both eigenvalues are negative. This is the point reached as  $\xi$  tends to  $\infty$ , and is where all residue curves in a given region terminate. Thus, it is the component or azeotrope with the highest boiling point in the region. This point is a stable node.

**Case 2**, both eigenvalues are positive. This is the point where all residue curves in a region originate, and is the component or azeotrope with the lowest boiling point in the region. This point is an unstable node.

$t$  is,

$$\xi(t) = \ln \left( \frac{w_0}{W(t)} \right) \quad (5.3.3)$$

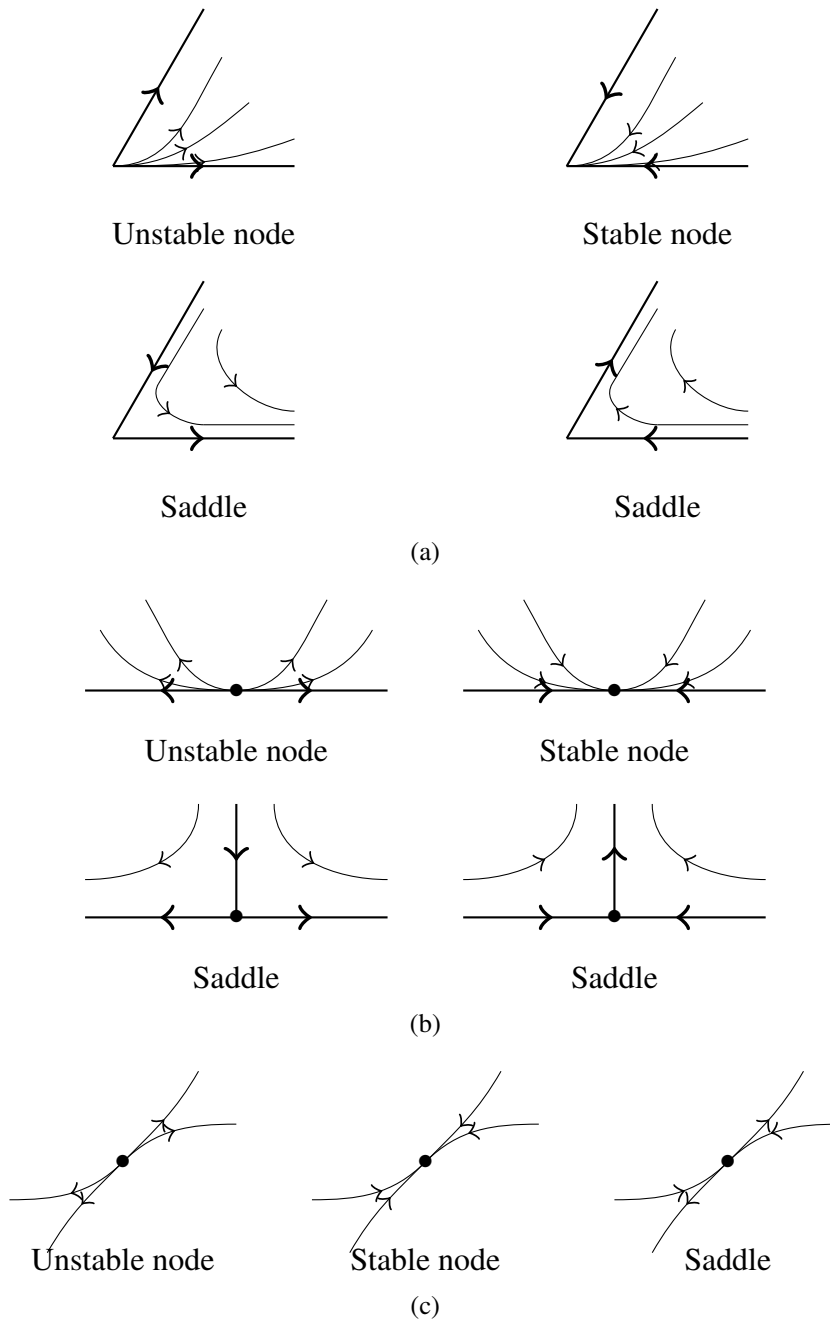


Figure 5.8: Residue-curve patterns, (a) near pure-component vertices, (b) near binary azeotropes, and (c) near ternary azeotropes.

**Case 3**, one eigenvalue is positive and one is negative. Residue curves within the triangle move toward and then away from such saddle points. For a given region, all pure components and azeotropes intermediate in boiling point between the stable node and the unstable node are saddles.

### 5.3.2 Distillation-Curve Maps

A residue curve represents the changes in residue composition with time as the result of a simple, one-stage batch distillation. The curve points in the direction of increasing time, from a lower-boiling state to a higher-boiling state. An alternative representation for distillation on a ternary diagram is a distillation curve for continuous, rather than batch,

distillation. The curve is most readily obtained for total reflux at a constant pressure (like for the derivation of the Fenske equation, section 3.4.2). The calculations are made down or up the column, starting from any composition. Consider making the calculations by moving up the column, starting from a stage designated as Stage 1. Between equilibrium stages  $j$  and  $j + 1$ , at total reflux, passing vapour and liquid streams have the same composition. Thus,

$$x_{i,j+1} = y_{i,j} \quad (5.3.9)$$

Also, liquid and vapour streams leaving the same stage are in equilibrium,

$$y_{i,j} = K_{i,j}x_{i,j} \quad (5.3.10)$$

To calculate a distillation curve, an initial liquid-phase composition,  $x_{i,1}$ , is assumed. This liquid is at its bubble-point temperature, which is determined from equation 5.3.8, which also gives the equilibrium-vapour composition,  $y_{i,1}$  in agreement with equation 5.3.10. The composition,  $x_{i,2}$ , of the passing liquid stream is equal to  $y_{i,1}$  by equation 5.3.9. The process is then repeated to obtain  $x_{i,3}$ , then  $x_{i,4}$ , and so forth. The sequence of liquid-phase compositions, which corresponds to the operating line for the total-reflux condition, is plotted on the triangular diagram. The distillation curve is analogous to the 45° line on a McCabe–Thiele diagram.

Distillation curves can be computed more rapidly than residue curves, and closely approximate them. A collection of distillation curves, including lines for distillation boundaries, is a distillation-curve map, an example of which is given in Figure 5.9. The dashed lines are the distillation curves, which approximate the solid-line residue curves. This system has two minimum-boiling binary azeotropes, one maximum-boiling binary azeotrope, and a ternary saddle azeotrope. The map shows four distillation boundaries, designated by A, B, C, and D. These computed boundaries, which define four distillation regions (1 to 4), are all curved lines rather than the approximately straight lines.

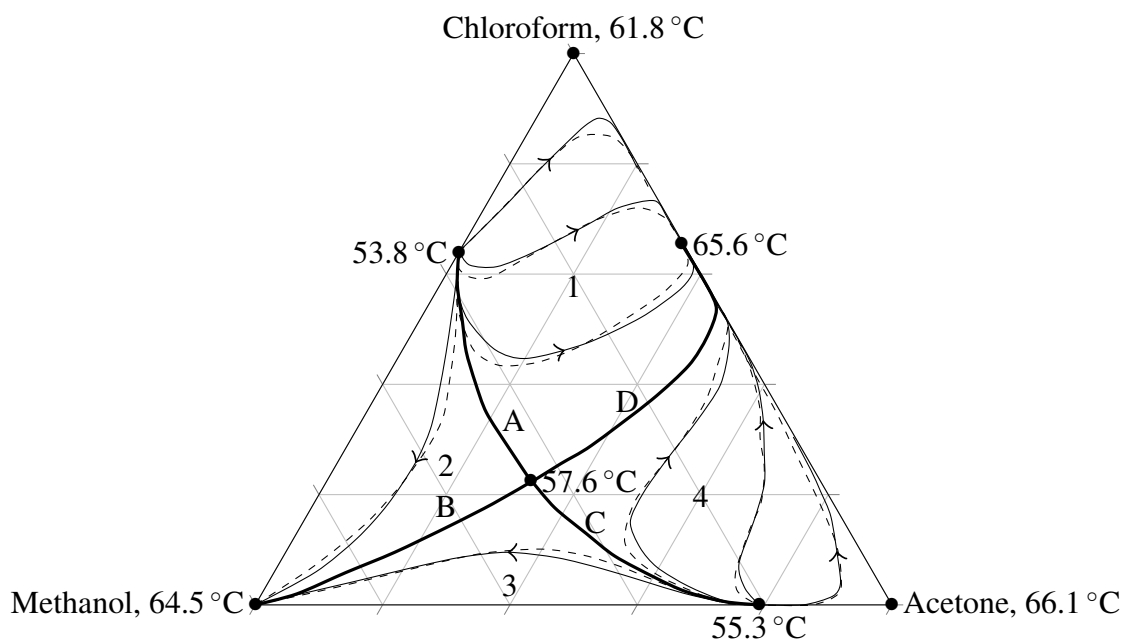


Figure 5.9: Comparison of residue curves (solid lines) to distillation curves (dashed lines).

Figure 5.10 shows an example of an actual distillation column with a finite reflux ratio ( $R = 1$ ) plotted on a residue curve plot for Hexane, Octane, and Decane. The rectifying

section (red dots) approximately follows the residue curve that  $D$  is on. The stripping section (blue dots) also follows the same residue curve from the other direction, starting at  $B$ . There is some deviation around the feed point (stage 11), due to the fact that the feed addition affects the equilibrium in column. The green line is the approx mass balance between the feed (green dot), and the trays in the rectifying and stripping sections.

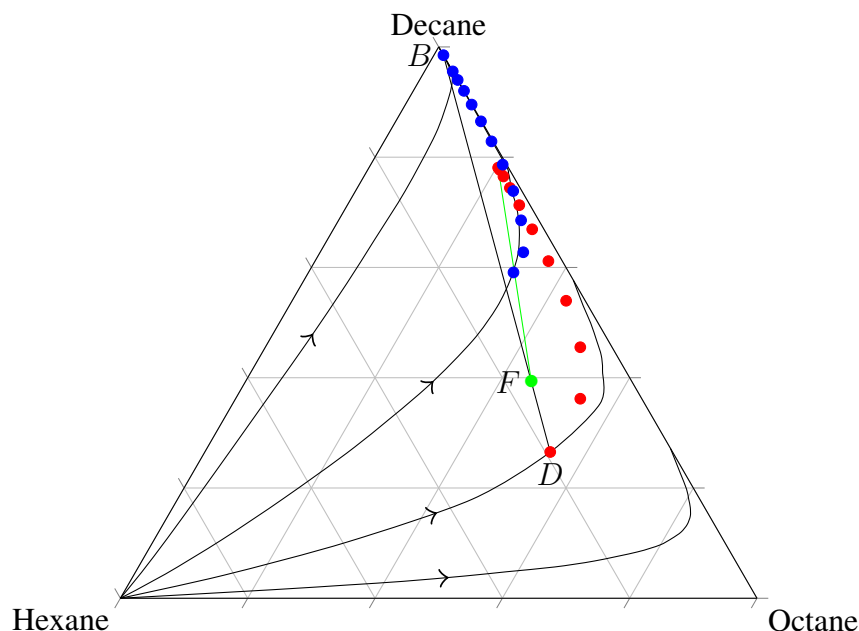


Figure 5.10: Actual distillation column plotted on a residue curve plot for Hexane, Octane, and Decane. Column has 20 stages, a reflux ratio of 1, and feed stage 11. Green line is the balance on the feed stage with the rectifying section (red dots), the stripping section (blue dots), and the feed (green dot).

### 5.3.3 Approximate Residue-Curve Maps

Calculation of a residue-curve map requires a considerable effort. However, process simulators such as ASPEN PLUS can compute residue maps. Alternatively, the classification of singular points as stable nodes, unstable nodes, and saddles provides a rapid method for approximating a residue-curve map, including approximate distillation boundaries, from just the pure component boiling points and azeotrope boiling points and compositions. Boiling points of pure substances are available in handbooks and databases, and extensive listings of binary azeotropes are found in many sources.

Based on experimental evidence for ternary mixtures, with very few exceptions there are at most three binary azeotropes and one ternary azeotrope. Accordingly, the following set of restrictions applies to a ternary system,

$$N_1 + S_1 = 3 \quad (5.3.11)$$

$$N_2 + S_2 = B \leq 3 \quad (5.3.12)$$

$$N_3 + S_3 = 1 \text{ or } 0 \quad (5.3.13)$$

where  $N$  is the number of stable and unstable nodes,  $S$  is the number of saddles,  $B$  is the number of binary azeotropes, and the subscript is the number of components at the

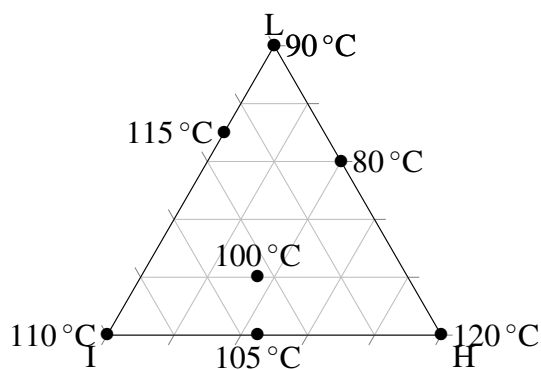
node (stable or unstable) or saddle. Thus,  $S_2$  is the number of binary azeotrope saddles. A topological relationship among  $N$  and  $S$  is,

$$2N_3 - 2S_3 + 2N_2 - B + N_1 = 2 \quad (5.3.14)$$

The topological relationships are useful for rapidly sketching, on a ternary diagram, an approximate residue-curve map, including distillation boundaries. The procedure involves the following nine steps,

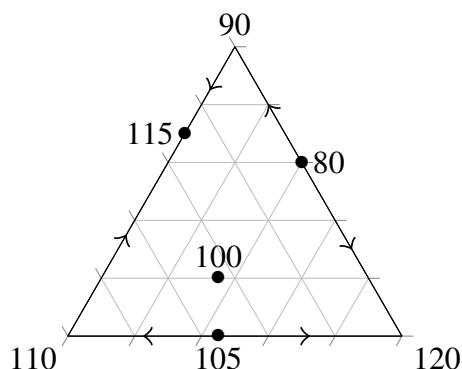
### Step 1

Label the ternary diagram with the pure-component, normal-boiling-point temperatures. It is preferable to designate the top vertex of the triangle as the low boiler (L), the bottom-right vertex as the high boiler (H), and the bottom-left vertex as the intermediate boiler (I). Plot the composition points for the binary and ternary azeotropes and add labels for their normal boiling points. This determines the value of  $B$ . In this example, two minimum-boiling and one maximum-boiling binary azeotropes and one ternary azeotrope. Thus,  $B = 3$ .



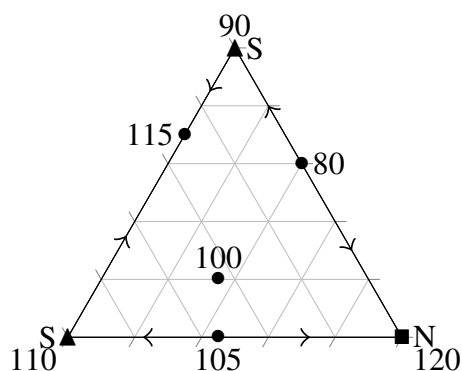
### Step 2

Draw arrows on the edges of the triangle, in the direction of increasing temperature, for each pair of adjacent species.



### Step 3

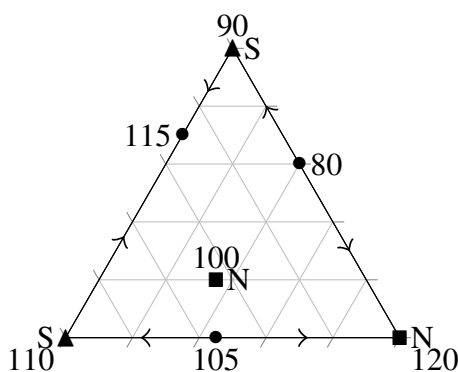
Determine the type of singular point for each pure component vertex by using Figure 5.8 with the arrows drawn in Step 2. This determines the values for  $N_1$  and  $S_1$ . In this example L is a saddle because one arrow points toward L and one points away from L; H is a stable node because both arrows point toward H, and I is a saddle. Therefore,  $N_1 = 1$  and  $S_1 = 2$ .



**Step 4** (for a ternary azeotrope only)

Determine the type of singular point for the ternary azeotrope, if one exists. The point is a node if (a)  $N_1 + B < 4$ , and/or (b) excluding the pure-component saddles, the ternary azeotrope has the highest, second-highest, lowest, or second-lowest boiling point of all species. Otherwise, the point is a saddle. This determines the values for  $N_3$  and  $S_3$ .

In this example,  $N_1 + B = 1 + 3 = 4$ . However, excluding L and I because they are saddles, the ternary azeotrope has the second lowest boiling point. Therefore, the point is a node, and  $N_3 = 1$  and  $S_3 = 0$ . The type of node, stable or unstable, is still to be determined.

**Step 5** (for a ternary saddle only)

Connect the ternary saddle, by straight lines, to all binary azeotropes and to all pure-component nodes (but not to pure-component saddles), and draw arrows on the lines to indicate the direction of increasing temperature. Determine the type of singular point for each binary azeotrope, by using Figure 5.8 with the arrows drawn in this step. This determines the values for  $N_2$  and  $S_2$ . These values should be consistent with equations 5.3.12 and 5.3.13. If  $N_1 + B = 6$ , then special checks must be made [1, 2], or the residue-curve-map structure should be computed by equations 5.3.4 to 5.3.8.

This completes the development of the approximate residue-curve map, with no further steps needed. This step does not apply to the example, because the ternary azeotrope is not a saddle.

**Step 6**

Determine the number of binary nodes,  $N_2$ , and binary saddles,  $S_2$ , from equations 5.3.12 and 5.3.14, where equation 5.3.14 can be solved for  $N_2$  to give

$$N_2 = \frac{2 - 2N_3 + 2S_3 + B - N_1}{2} \quad (5.3.15)$$

For this example,  $N_2 = (2 - 2 + 0 + 3 - 1) / 2 = 1$ . From equation 5.3.12,  $S_2 = 3 - 1 = 2$ .

**Step 7**

Count the binary azeotropes that are intermediate boilers (i.e., that are not the highest- or the lowest-boiling species), and call that number  $B_{ib}$ . Make the following two data-consistency checks: (a) The number of binary azeotropes,  $B$ , less  $B_{ib}$ , must equal  $N_2$ , and (b)  $S_2$  must be  $\leq B_{ib}$ . For the example system, these are the L-I and I-H azeotropes so  $B_{ib} = 2$ ,  $B - B_{ib} = 1$ ,  $N_2 = 1$ , and  $S_2 = 2$ . If these two consistency checks are not satisfied, one or more of the boiling points may be in error.

**Step 8**

If  $S_2 \neq B_{ib}$ , this procedure cannot determine a unique residue-curve-map structure, which therefore must be computed from equations 5.3.4 to 5.3.8. If  $S_2 = B_{ib}$ , there is a unique structure, which is completed in Step 9. For this example,  $S_2 = B_{ib} = 2$ ; therefore, there is a unique map.



**Step 9**

In this final step, the distillation boundaries (connections), if any, are determined and entered on the triangular diagram as straight lines, and, if desired, one or more representative residue curves are sketched as curved lines within each distillation region. This step applies to cases of  $S_3 = 0$ ,  $N_3 = 0$  or 1, and  $S_2 = B_{ib}$ . In all cases, the number of distillation boundaries equals the number of binary saddles,  $S_2$ .

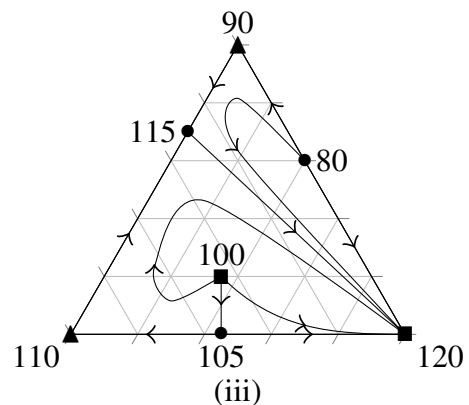
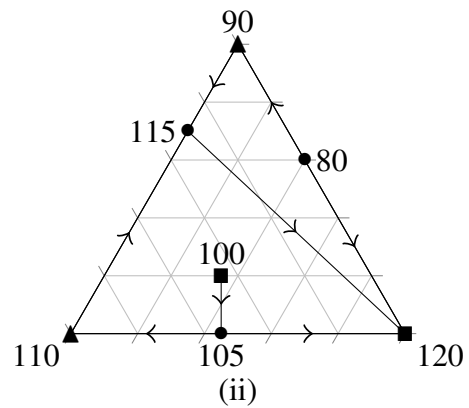
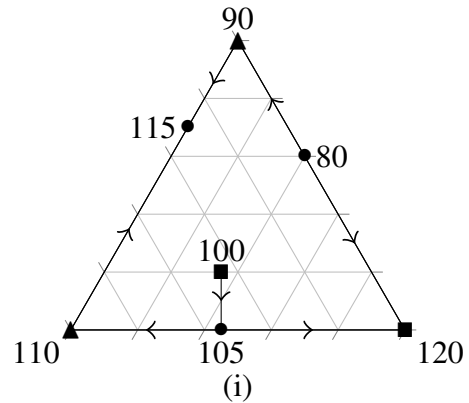
- Each binary saddle must be connected to a node (pure component, binary, or ternary).
- A ternary node must be connected to at least one binary saddle.
- Thus, a pure-component node cannot be connected to a ternary node,
- and an unstable node cannot be connected to a stable node.

The connections are made by determining a connection for each binary saddle such that (a) a minimum-boiling binary saddle connects to an unstable node that boils at a lower temperature and (b) a maximum-boiling binary saddle connects to a stable node that boils at a higher temperature.

It is best to first consider connections with the ternary node and then examine possible connections for the remaining binary saddles. In this example,  $S_2 = 2$ , with these saddles denoted as L-I, a maximum-boiling azeotrope at 115 °C, and as I-H, a minimum-boiling azeotrope at 105 °C. Therefore, two connections are made to establish two distillation boundaries. The ternary node at 100 °C cannot connect to L-I because 100 °C is not greater than 115 °C. The ternary node can, however, connect, as shown in (i), to I-H because 100 °C is lower than 105 °C. This marks the ternary node as unstable.

The connection for L-I can only be to H, as shown in (ii), because it is a node (stable), and 120 °C is greater than 115 °C. This completes the connections.

Finally, as shown in (iii), three typical, but approximate, residue curves are added to the diagram. These curves originate from unstable nodes and terminate at stable nodes.



### 5.3.4 Feasible Product-Composition Regions at Total Reflux

The feasible-distillation regions for azeotrope-forming ternary mixtures are not obvious. Fortunately, residue-curve maps can be used to make preliminary estimates of regions of feasible-product compositions for non-ideal ternary systems. These regions are determined by superimposing a column material-balance line on either type of curve-map diagram. Consider first the simpler zeotropic ternary system in Figure 5.11(a), which shows an isobaric residue-curve map with three residue curves. Suppose a ternary feed  $F$  in Figure 5.11(a) is continuously distilled isobarically to produce distillate  $D$  and bottoms  $B$ . A straight line that connects the distillate and bottoms compositions must pass through the feed composition at some intermediate point to satisfy the material-balance equations. Three random material-balance lines are included in the figure. For a given line,  $D$  and  $B$  composition points, designated by coloured squares, must lie on the same residue curve. This causes the material-balance line to intersect the residue curve at these two points and be a chord to the residue curve.

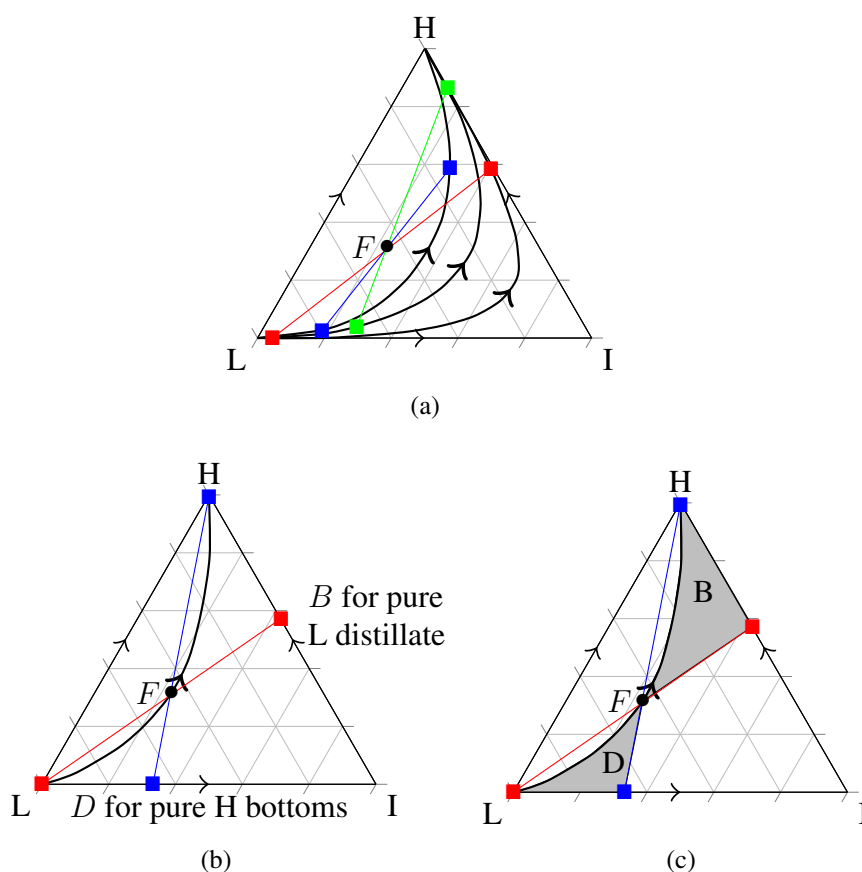


Figure 5.11: Product-composition regions for a zeotropic system. (a) Material-balance lines and residue curves, (b) Residue curve through the feed point with the extrem product lines, and (c) Product-composition regions shown shaded.

The limiting distillate-composition point for this zeotropic system is pure low-boiling component, L. From the material-balance line passing through  $F$ , shown as the red line in Figure 5.11(b), the corresponding bottoms composition with the least amount of component L is point  $B$ . At the other extreme, the limiting bottoms-composition point is high-boiling component H. A material-balance line from this point, through feed point  $F$ , ends at  $D$ , shown as the blue line in Figure 5.11(b).

These two lines and the residue curve define the feasible product-composition regions, shown as the shaded regions in Figure 5.11(c). Note that, because for a given feed both the distillate and bottoms compositions must lie on the same residue curve, the shaded feasible regions lie between the feed residue curve and the side of the material balance line opposite the extreme end of the residue curve, i.e. the bottom product side is bounded by the material balance line from the extreme distillate product, the red line. Because of its appearance, the feasible-product-composition region is called a bow-tie region.

For azeotropes, where distillation boundaries are present, a feasible-product-composition region exists for each distillation region. Two examples are shown in Figure 5.12. Figure 5.12 has two distillation regions caused by two minimum-boiling binary azeotropes. A curved distillation boundary connects the minimum-boiling azeotropes. In the lower, right-hand distillation region (1), the lowest-boiling species is the *n*-octane-2-ethoxyethanol minimum-boiling azeotrope, while the highest-boiling species is 2-ethoxyethanol. Accordingly, for feed  $F_1$ , straight lines are drawn from the points for each of these two species, through the point  $F_1$ , and to a boundary (either a distillation boundary or a side of the triangle). Shaded, feasible-product-composition regions are then drawn on the outer side of the residue curve that passes through the feed point. The result is that distillate compositions are confined to shaded region  $D_1$  and bottoms compositions are confined to shaded region  $B_1$ . For a given  $D_1$ ,  $B_1$  must lie on a straight line that passes through  $D_1$  and  $F_1$ .  $D_1$  and  $B_1$  must also lie on the same residue curve.

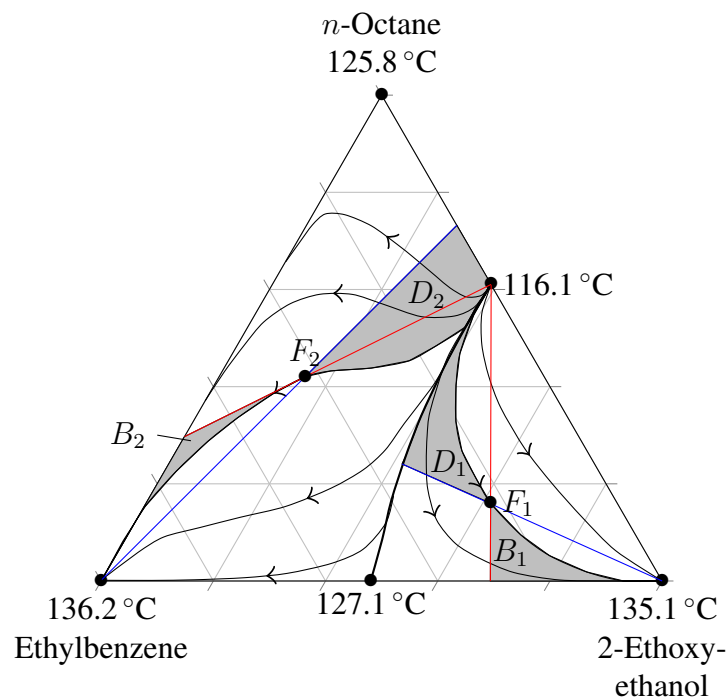


Figure 5.12: Product-composition regions for given feed compositions. Ternary mixture with two minimum-boiling binary azeotropes at 1 atm.

A complicated situation is observed in distillation Region 2 on the left side of Figure 5.12, where the lowest-boiling species is the binary azeotrope of octane and 2-ethoxyethanol, while the highest-boiling species is ethylbenzene. The complicating factor in Region 2 is that feed  $F_2$  lies on or close to an inflection point of an S-shaped distillation curve. In this case feasible-product-composition regions may lie on either side of the residue curve passing through the feed point; however, following the same rule of the region being

between the residue curve and the material balance line with the extreme other product, then the region is placed correctly.

In Figures 5.11 and 5.12 each bow-tie region is confined to its distillation region, defined by the distillation boundaries. In all cases, the feed, distillate, and bottoms points on the material-balance line lie within a distillation region, with the feed point between the distillate and bottoms points. The material-balance lines do not cross the distillation-boundary lines.

### 5.3.5 Extension to Short-cut Equations for Azeotropic Systems

In Section 3.4 the short-cut method was discussed for multi-component distillation. One of the key assumptions for this method is a constant relative volatility (or approximately constant). When a system has an azeotrope it is clear that the relative volatility is not constant. Take Figure 5.13(a) as an example system, at  $x_1 = 0.05$   $\alpha = 2.55$  while at  $x_1 = 0.95$   $\alpha = 0.47$ , this means that it is not possible to use the short-cut method. Taking an average relative volatility from the feed, distillate, and bottom product composition gives a value of  $\alpha = 1.82$ , which would be represented by the red line, which is not similar to the actual VLE.

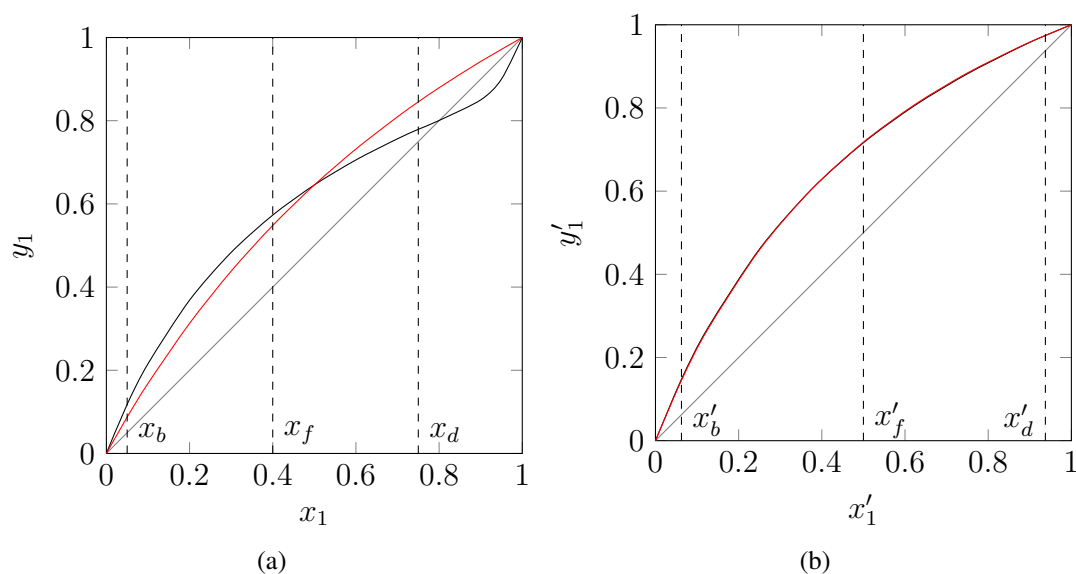


Figure 5.13: Example azeotropic system transformation using equation 5.3.16[5, 6]. (a) The original azeotropic VLE in black, and a constant relative volatility system with the same average as the large region in the original system in red. (b) The transformed system for the large region VLE in black, and a constant relative volatility system with the same average as the transformed region in red.

The short-cut method can still be used for systems of this type by transforming the region of interest using the method of Vogelpohl[5, 6]. It should be noted that this method will give results that are even more approximate than for zeotropic systems, but the key is the consistency of the relative volatility.

This method transforms the co-ordinate system using:

$$x'_i = \frac{x_i}{a}, \quad y'_i = \frac{y_i}{a} \quad (5.3.16)$$

where  $a$  is the composition of the azeotrope. The new value of the relative volatility for each pair of  $x'_i$  and  $y'_i$  can be given by,

$$\alpha' = \frac{y'_i(1-x'_i)}{x'_i(1-y'_i)} \quad (5.3.17)$$

For example taking the large region in Figure 5.13(a), using equation 5.3.16 with the azeotrope composition,  $a = 0.8$ , produces Figure 5.13(b). The average relative volatility of the transformed system is then  $\alpha' = 2.54$ , which when plotted is very similar to the transformed VLE.

This method has been extended to more components, by using a matrix transformation[3]. Take Figure 5.14(a) as an example system, the relative volatility for the feed (F), bottom product (B), and distillate (D) are given by Table 5.1. However, the relative volatility of the azeotrope is unknown and the distillation boundary makes the methyl acetate pure component inaccessible from the region of the separation.

Table 5.1: Example ternary azeotropic system for methanol(M), ethanol (E), and methyl acetate (MA)

Component	B	F	D
MA	5.49	4.44	3.02
M	1.77	1.97	2.91
E	1.00	1.00	1.00

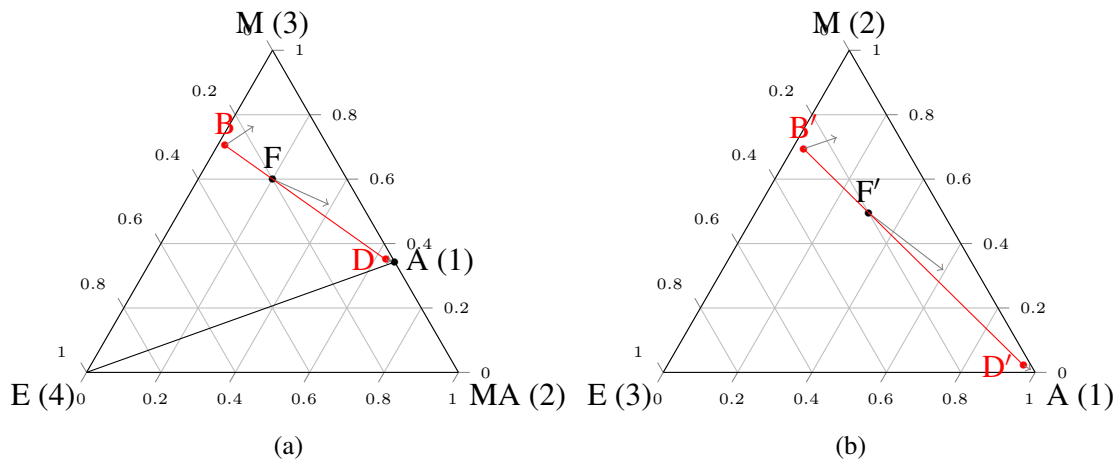


Figure 5.14: Example ternary azeotropic system for methanol(M), ethanol (E), and methyl acetate (MA); this system has one azeotrope (A). The numbers represent the order of the boiling points. (a) The original ternary azeotropic system with an example separation shown in red, the grey arrows show the vapour phase composition in equilibrium with the liquid phase composition of the points. (b) The transformed system using equation 5.3.18[3] with the same separation shown in red, the grey arrows show the vapour phase composition in equilibrium with the liquid phase composition of the points in the transformed co-ordinate system.

This method transforms the co-ordinate system using:

$$\mathbf{X} = \mathbf{M}\mathbf{X}' \quad (5.3.18)$$

where  $\mathbf{X}$  is the original liquid composition, in boiling point order,  $\mathbf{M}$  is the singular point matrix of the 3 corners of the region  $\mathbf{X}$  is in, in boiling point order, and  $\mathbf{X}'$  is the translated liquid composition. This can also be carried out for the vapour compositions.

The new value of the relative volatility for each pair of  $x'_i$  and  $y'_i$  can be given by,

$$\alpha' = \frac{y'_i x'_H}{y'_H x'_i} \quad (5.3.19)$$

For example taking the separation in the large region in Figure 5.14(a), using equation 5.3.18 with the azeotrope composition produces Figure 5.14(b) as,

$$\begin{bmatrix} x'_A \\ x'_M \\ x'_E \end{bmatrix} = \begin{bmatrix} 0.6574 & 0 & 0 \\ 0.3426 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} \begin{bmatrix} x_{MA} \\ x_M \\ x_E \end{bmatrix}$$

Where the  $\mathbf{M}$  matrix is the three singular points of the separation region in boiling point order (A, M, E) horizontally where the co-ordinates are in terms of the pure components in boiling point order (MA, M, E) vertically. The transposed relative volatility for the feed ( $F'$ ), bottom product ( $B'$ ), and distillate ( $D'$ ) are given by Table 5.2. The short-cut method can then be used with these new  $x'$  values and the average relative volatilities.

Table 5.2: Example relative volatilities for the transposed ternary azeotropic system for methanol(M), ethanol (E), and azeotrope (A) system

Component	B'	F'	D'
A	5.49	4.44	3.02
M	1.72	1.46	1.10
E	1.00	1.00	1.00

Although this method provides an approximate design and will work with any number of components, there are limitations. The first is if there are more singular points in a region than original components the matrix  $\mathbf{M}$  has no inverse. The second is that distillation boundaries are approximated to be straight lines, if the boundaries are not straight lines then the resulting approximation will be poor, and the order of the component relative volatilities can change. Finally the more non-ideal the components the more inaccurate the method will become as the relative volatilities will vary across the column.

## 5.4 Separations for Azeotropes

When  $\alpha < 1.10$ , separation by ordinary distillation may be uneconomical, and even impossible if an azeotrope forms. In that event, the following techniques referred to as enhanced distillation, should be explored,

**Pressure-Swing Distillation (changing  $P$ )**, Separates a mixture that forms a pressure-sensitive azeotrope by utilizing two columns in sequence at different pressures.

**Extractive Distillation (changing  $\alpha$ )**, Uses large amounts of a relatively high-boiling solvent to alter the liquid-phase activity coefficients so that the  $\alpha$  of key components becomes more favourable. Solvent enters the column a few trays below the

top, and exits from the bottom without forming any azeotropes. If the column feed is an azeotrope, the solvent breaks it. It may also reverse key-component volatilities. A variant of this is salt distillation where a nonvolatile ionic salt, which stays in the liquid phase as it passes down the column, is used to modify the  $\alpha$ .

**Homogeneous Azeotropic Distillation (changing  $\alpha$ ),** A method of separating a mixture by adding an entrainer that forms a homogeneous minimum- or maximum-boiling azeotrope with feed component(s). Where the entrainer is added depends on whether the azeotrope is removed from the top or the bottom of the column.

**Heterogeneous Azeotropic Distillation (add secondary separation mechanism),** A minimum boiling heterogeneous azeotrope is formed by the entrainer. The azeotrope splits into two liquid phases in the overhead condenser. One liquid phase is sent back as reflux; the other is sent to another separation step or is a product.

**Reactive Distillation (changing species),** A chemical that reacts selectively and reversibly with one or more feed constituents is added, and the reaction product is then distilled from the non-reacting components. The reaction is later reversed to recover the separating agent and reacting component. This operation, referred to as catalytic distillation if a catalyst is used, is suited to reactions limited by equilibrium constraints, since the product is continuously separated. Reactive distillation also refers to chemical reaction and distillation conducted simultaneously in the same apparatus.

If an azeotrope is formed in a process of separating a multiple component mixture, normally the azeotrope is isolated as a whole then separated separately. This way is treating the azeotrope as a single component from other components. Normally, an azeotrope is formed between two components - binary azeotrope, however, it is possible that an azeotrope may contain multiple components.

### 5.4.1 Pressure Swing Distillation

If a binary azeotrope disappears at some pressure, or changes composition by 5 mol% or more over a moderate range of pressure, consideration should be given to using two ordinary distillation columns operating in series at different pressures. This process is referred to as pressure-swing distillation.

Figure 5.15 illustrated this method for a minimum boiling binary azeotrope.

As seen from the right hand of Figure 5.15, the left column is operated at a lower pressure  $P_1$ , as the boiling temperature of the azeotrope is lower than both A and B components, so the bottom product would only be B but the top product is the azeotrope. This more volatile azeotrope is then fed into the right column operating at a higher pressure, as seen from the left graph of this figure, as the composition of A in the azeotrope at the higher pressure is lower than that in higher pressure, when the azeotrope is fed into a column operating at a higher pressure, part of A in the azeotrope from higher pressure would be released, thus the bottom product from the right column would just be pure A.

Pressure swing distillation is a simple and effective way of overcoming the boundary presented by a binary azeotrope, it requires two columns; a pump would need to be used to elevate pressure and no additional material (i.e. entrainer or solvent) needed. However, azeotropes are often insensitive to changes in pressure. Also, when the difference in azeotrope compositions is small, large recycle flows are needed, which makes pressure

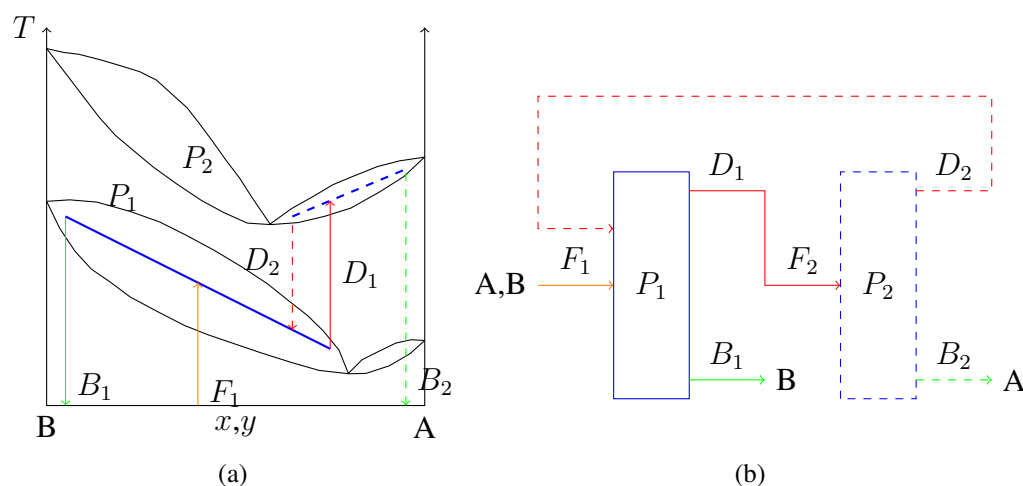


Figure 5.15: Pressure swing to break a minimum boiling binary azeotrope, (a) the VLE data and (b) the distillation sequence.

swing method ineffective with some negative impact on capital and operating costs of process, due to the high cost of gas compression.

## 5.4.2 Extractive Distillation

Extractive distillation is used to separate azeotropes and close-boiling mixtures. If the feed is a minimum-boiling azeotrope, a solvent (the entrainer), with a lower volatility than the key components of the feed mixture, is added to a tray just a few trays below the top of the column so that,

- the solvent is present in the down-flowing liquid, and
- little solvent is stripped and lost to the overhead vapour.

If the feed is a maximum boiling azeotrope, the solvent enters the column with the feed.

The components in the feed must have different solvent affinities so that the solvent causes an increase in  $\alpha$  of the key components, to the extent that separation becomes feasible and economical. The solvent should not form an azeotrope with any components in the feed. Usually, a molar ratio of solvent to feed on the order of 1 is required. The bottoms are processed to recover the solvent for recycle and complete the feed separation.

In selecting a solvent for extractive distillation, a number of factors are considered, including availability, cost, corrosivity, vapour pressure, thermal stability, heat of vapourisation, reactivity, toxicity, infinite-dilution activity coefficients in the solvent of the components to be separated, and ease of solvent recovery for recycle.

Initial screening is based on the measurement or prediction of infinite-dilution activity coefficients. Generally successful solvents for extractive distillation are highly hydrogen-bonded liquids such as water, amino-alcohols, amides, and phenols that form three-dimensional networks of strong hydrogen bonds; and alcohols, acids, phenols, and amines that are composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine).

Figure 5.16 shows the typical three column extractive distillation sequence, consisting of



ordinary distillation concentrating the feed to the azeotrope composition, followed by the extractive distillation with the added solvent, and then ordinary distillation to recover the solvent. Often a pre-concentration distillation column is used as this reduces the amount of material passing through the two distillation columns with the solvent. This reduced the size of these columns and the amount of solvent needed, thus the cost of the system is reduced. If the feed composition is similar to the azeotrope the it may not be necessary to have the pre-concentration distillation column - this is an economic balance.

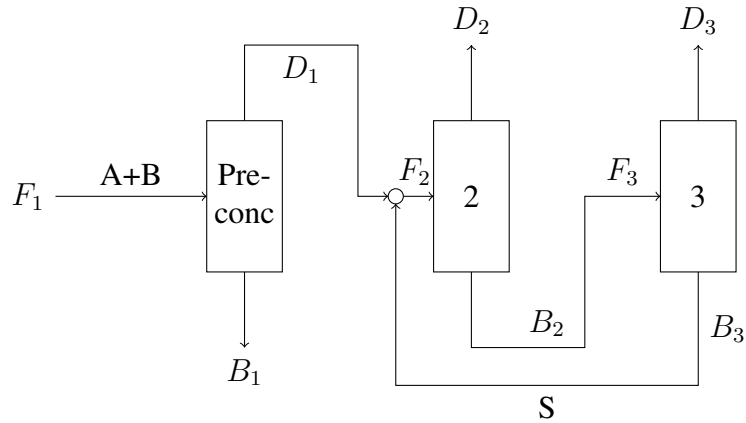


Figure 5.16: Typical 3 column extractive distillation sequence.

For the sequence shown in Figure 5.16 the columns can be represented on a ternary diagram, Figure 5.17. This allows the compositions in the columns to be approximated and used in short-cut calculations.

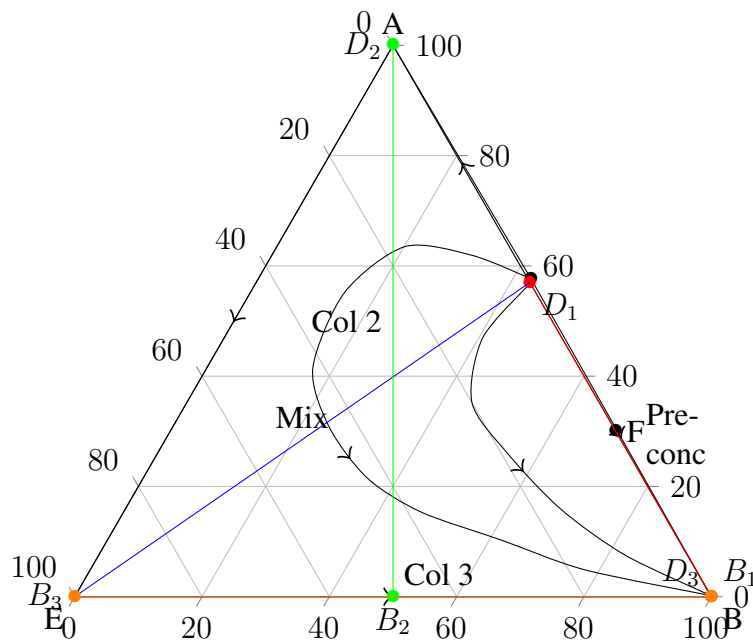


Figure 5.17: Typical 3 column extractive distillation sequence, Figure 5.16, shown on an example ternary diagram with residue curves.

If the boiling point of the solvent is much higher than the boiling points of the components in the feed, then a good approximation is that the solvent never vapourises, thus the system can be thought of as a binary system, but with a modified activity coefficient between the feed components. An example of this can be seen for the Butadiene and Butane

system in Figure 5.18. At 1 atm there is an azeotrope between Butadiene (B.P.  $-4.4^{\circ}\text{C}$ ) and Butane (B.P.  $-0.2^{\circ}\text{C}$ ) preventing separation via simple distillation, Figure 5.18(a). Adding N-Methyl-2-pyrrolidone (NMP) (B.P.  $202.0^{\circ}\text{C}$ ) to the mixture effects the activity coefficient between Butadiene and Butane and removes the azeotrope producing the equilibrium given by Figure 5.18(b). In fact, the activity coefficient is effected so much that Butadiene becomes the least volatile component rather than the most volatile component. As the boiling point of NMP is so much higher than that of the other two components, it does not really vapourise in the distillation column and just passes down the column as a liquid.

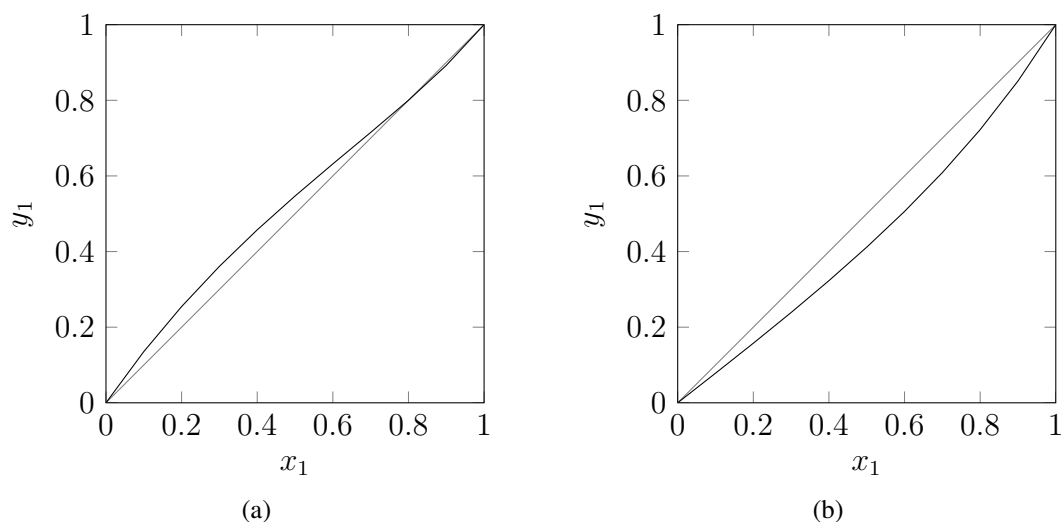


Figure 5.18: Vapour-Liquid equilibrium at 1 atm for (a) Butadiene(1) and Butane(2) and (b) Butadiene(1) and Butane(2) in the presence of N-Methyl-2-pyrrolidone (NMP), 2 parts NMP to 1 part Butadiene/Butane.

An alternative to adding a pure solvent is to add a salt solution or salt melt to the azeotropic mixture (often called salt distillation). This allows a extra modification to the  $\alpha$ . The vapour pressure of the dissolved salt is so small that it never enters the vapour, provided entrainment is avoided.

Salt distillation is accompanied by several problems. First and foremost is corrosion, particularly with aqueous chloride-salt solutions, which may require stainless steel or a more expensive corrosion-resistant material. Feeding and dissolving a salt into the reflux poses problems as the solubility of salt will be low in the reflux because it is rich in the more-volatile component, the salt being most soluble in the less-volatile component. Salt must be metered at a constant rate and the salt-feeding mechanism must avoid bridging and prevent the entry of vapour, which could cause clogging when condensed. The salt must be rapidly dissolved, and the reflux must be maintained near the boiling point to avoid precipitation of already-dissolved salt. In the column, presence of dissolved salt may increase foaming, requiring addition of antifoaming agents and/or column-diameter increase. There is also potential that the salt may crystallise within the column. However, the concentration of the less-volatile component (e.g., water) increases down the column, so the solubility of salt increases down the column while its concentration remains relatively constant. Thus, the possibility of clogging and plugging due to solids formation is unlikely.

### 5.4.3 Homogeneous Azeotropic Distillation

As seen in the previous section, an azeotrope can be separated by extractive distillation, using a solvent that has a higher boiling than the feed components and does not form any azeotropes with either component. However, this restricts the number of solvents that can be used.

Alternatively, the separation can be made by homogeneous azeotropic distillation, using an entrainer not subject to such restrictions. Like extractive distillation, a sequence of two or three columns can be used. For a suitable entrainer, E, the two components, A and B, to be separated, or any product azeotrope, must lie in the same distillation region of the residue-curve map. Thus, a distillation boundary cannot be connected to the A-B azeotrope. Furthermore, A or B, but not both, must be a saddle.

Figure 5.19 shows a typical two column homogeneous azeotrope distillation sequence, consisting of a distillation column with the added solvent, and then an ordinary distillation to recover the solvent as an azeotrope.

### 5.4.4 Heterogeneous Azeotropic Distillation

For homogeneous azeotropic distillation it is required that A and B lie in the same distillation region of the residue-curve map as the residue forms an azeotrope with one of them. To allow this to occur, one of the azeotropes formed needs to be a maximum-boiling azeotrope, which are much rarer than minimum-boiling azeotropes. These constraints are often so restrictive that it is often difficult to find a feasible entrainer.



Summary Video

A better, alternative technique that finds wide use is heterogeneous azeotropic distillation to separate close-boiling binaries and minimum-boiling binary azeotropes by employing an entrainer that forms a binary and/or ternary heterogeneous (two-phase) azeotrope. A heterogeneous azeotrope has two or more liquid phases. If it has two, the overall, two-liquid-phase composition is equal to that of the vapour phase. Thus, all three phases have different compositions. If the overhead vapour from the azeotropic column is close to the composition of the heterogeneous azeotrope when condensed, two liquid phases form in a decanter (a strenuous attempt is made to restrict the formation of two liquid phases to the decanter because when two liquid phases form on a tray, the tray efficiency decreases).

After separation, most or all of the entrainer-rich liquid phase is returned to the column as reflux, while most or all of the other liquid phase is sent to the next column for further processing, Figure 5.20(a). The distillation sequence can also include a separate preconcentrator, Figure 5.20(b).

As the two liquid phases from the azeotropic column top product usually lie in different distillation regions of the residue-curve map, the restriction that dooms homogeneous azeotropic distillation is overcome. Thus, in heterogeneous azeotropic distillation, the components to be separated need not lie in the same distillation region.

Figure 5.21 shows a typical two column heterogeneous azeotrope distillation sequence plotted on a ternary diagram, consisting of an azeotropic distillation column with the heterogeneous azeotrope being condensed and separated settled into two liquid phases,  $L_1$

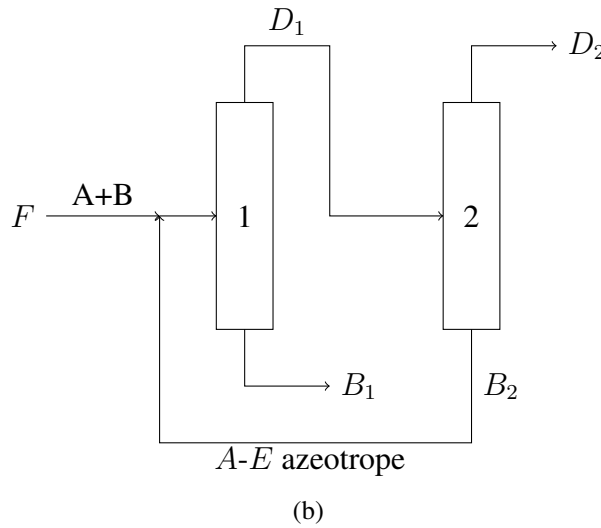
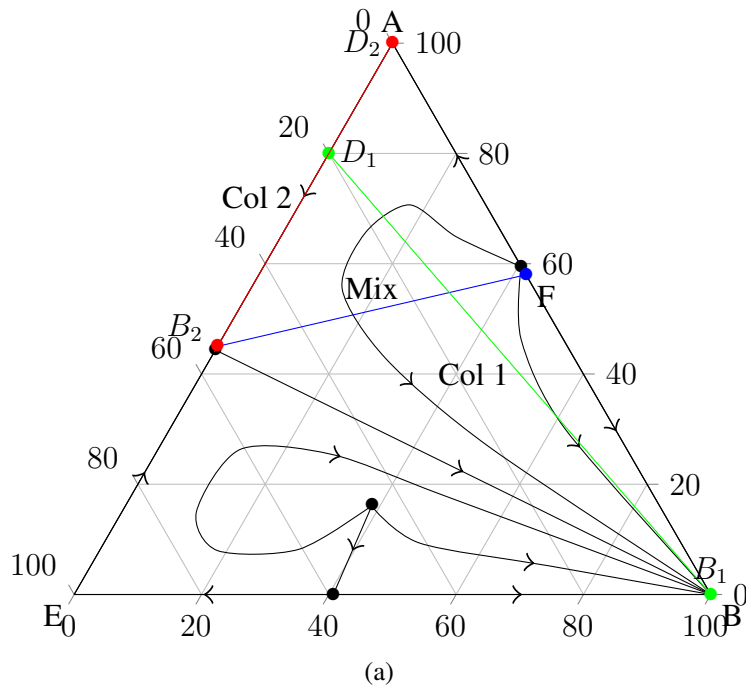


Figure 5.19: Typical 2 column homogeneous azeotropic distillation sequence, shown on an example ternary diagram with residue curves.

and  $L_2$ . The liquid phase with the most solvent tends to be fed back into the azeotropic column. The other liquid phase is fed into a simple distillation column where the remaining solvent is separated.

### 5.4.5 Reactive Distillation

Reactive distillation denotes simultaneous chemical reaction and distillation. The reaction usually takes place in the liquid phase or at the surface of a solid catalyst in contact with the liquid. The separation of a close-boiling or azeotropic mixture of components A and B can be enhanced if a chemically reacting entrainer E is introduced into the column. If A is the lower-boiling component, it is preferable that E be higher boiling than B and that it react selectively and reversibly with B to produce reaction product C, which also has a higher boiling point than component A and does not form an azeotrope with A, B, or E.

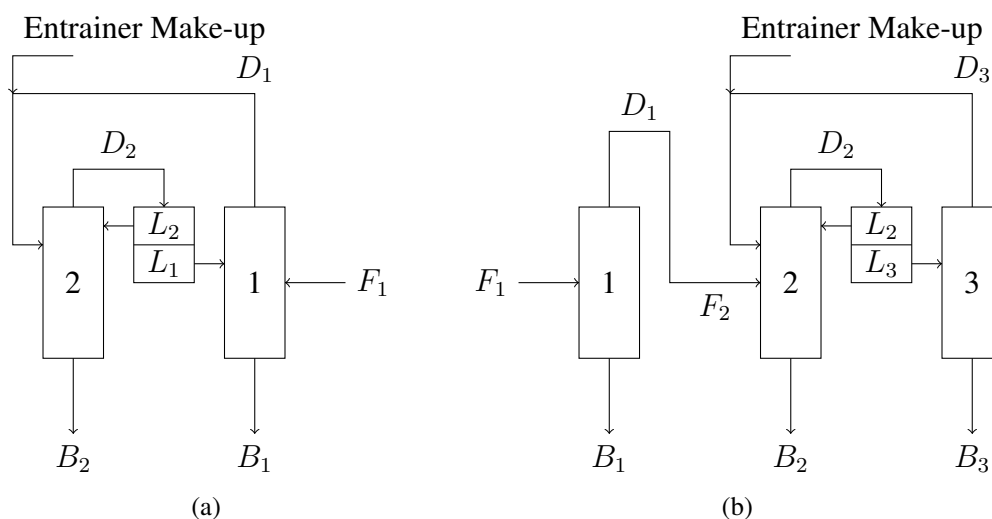


Figure 5.20: Distillation sequence for heterogeneous azeotropic distillation; (a) two column design, column 1 is the combined pre-concentrator/entrainer recovery column and column 2 is the Azeotropic column; and (b) three column design, column 1 is the pre-concentrator column, column 2 is the Azeotropic column, and column 3 is the entrainer recovery column.

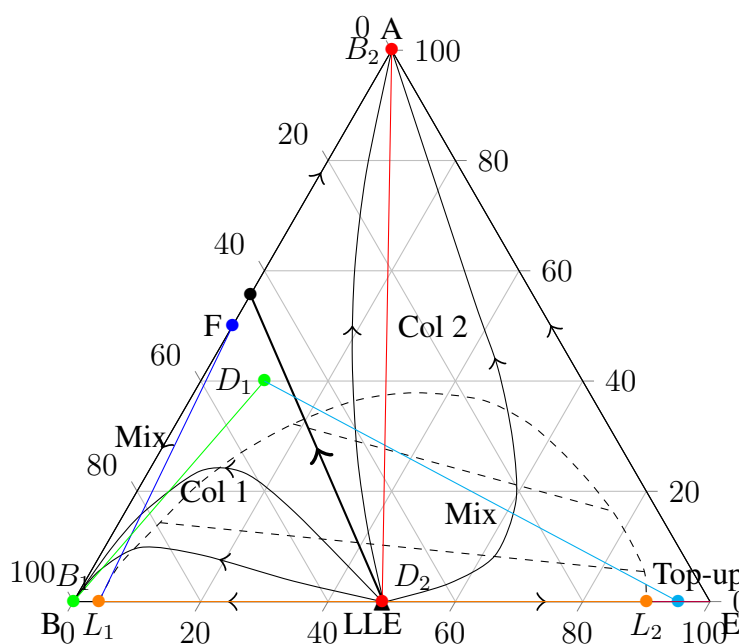


Figure 5.21: Typical 2 column heterogeneous azeotropic distillation sequence, Figure 5.20(a), shown on an example ternary diagram with residue curves and liquid-liquid equilibrium.

Component A is removed as distillate, and components B and C, together with any excess E, are removed as bottoms. Components B and E are recovered from C in a separate distillation, where the reaction is reversed ( $C \rightarrow B + E$ ); B is taken off as distillate, and E is taken off as bottoms and recycled to the first column.

Reactive distillation should be considered whenever the following hold,

1. The chemical reaction occurs in the liquid phase, in the presence or absence of a homogeneous catalyst, or at the interface of a liquid and a solid catalyst.

2. Feasible temperature and pressure for the reaction and distillation are the same. That is, reaction rates and distillation rates are of the same order of magnitude.
3. The reaction is equilibrium-limited so that if one or more of the products can be removed by distillation, the reaction can be driven to completion; thus, a large reactant excess is not necessary for a high conversion. This is particularly advantageous when excess reagent recovery is difficult because of azeotrope formation. For reactions that are irreversible, it is more economical to take the reactions to completion in a reactor and then separate the products in a distillation column. In general, reactive distillation is not attractive for supercritical conditions, for gas-phase reactions, and for reactions at high temperatures and pressures and/or that involve solids.

Careful consideration must be given to the configuration of reactive distillation columns. Important factors are feed entry and product-removal stages, the possible need for intercoolers and interheaters when the heat of reaction is appreciable, and obtaining required residence time for the liquid phase.

## 5.5 References

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- [6] Vogelpohl, A. [2002], ‘On the relation between ideal and real mixtures in multicomponent distillation’, *Chemical Engineering & Technology* **25**(9), 869–872.

## 5.6 Problems

- E1 Plot a portion of a residue curve for *n*-propanol (1), isopropanol (2), and benzene (3) at 1 atm starting from a bubble-point liquid with 20 mol% each of 1 and 2, and 60 mol% of component 3 (78.67 °C).

Use Raoult's law with regular-solution theory for estimating the liquid-phase activity coefficients.

The normal boiling points of the three components in °C are 97.3, 82.3, and 80.1, respectively.

Minimum-boiling azeotropes are formed at 77.1 °C for components 1, 3 and at 71.7 °C for 2, 3.



Solution Video

Useful information:

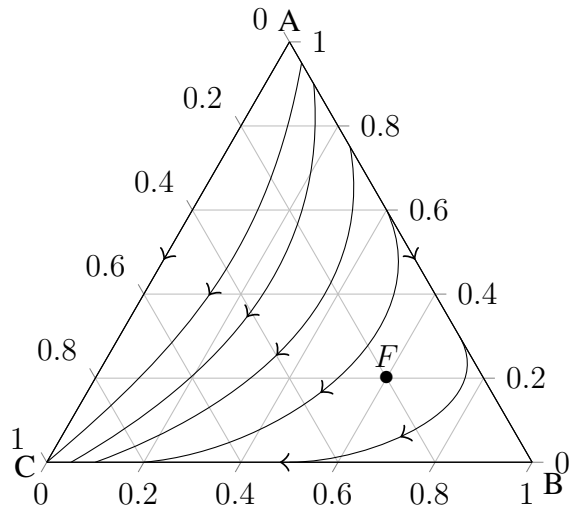
$$R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}.$$

$$K_i = \frac{\gamma_{iL} P_i^\circ}{P} \quad \ln(p^\circ [\text{kPa}]) = A - \frac{B}{T [^\circ\text{C}] + C}$$

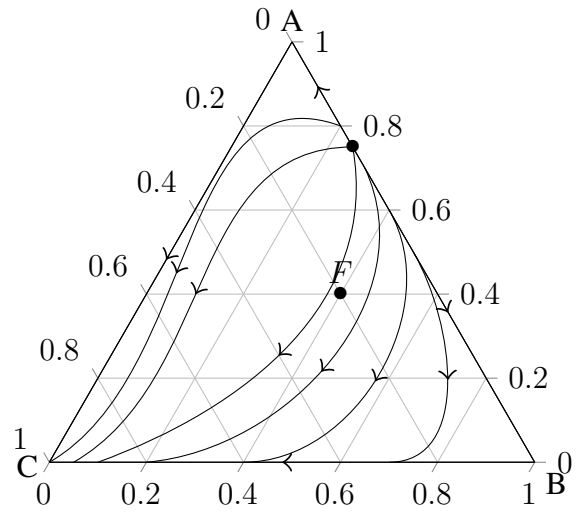
$$\ln \gamma_{iL} = \frac{v_{iL} \left( \delta_i - \sum_{j=1}^n \Phi_j \delta_j \right)^2}{RT} \quad \Phi_j = \frac{x_j v_{jL}}{\sum_{k=1}^n x_k v_{kL}}$$

Component	$\delta / \text{cal}^{1/2} \text{ cm}^{-3/2}$	$v / \text{cm}^3 \text{ mol}^{-1}$	$A$	$B$	$C$
<i>n</i> -propanol	12.0	74.72	16.1154	3483.67	205.807
isopropanol	11.6	76.4	16.6796	3640.2	219.61
Benzene	9.2	89.04	13.7819	2726.81	217.572

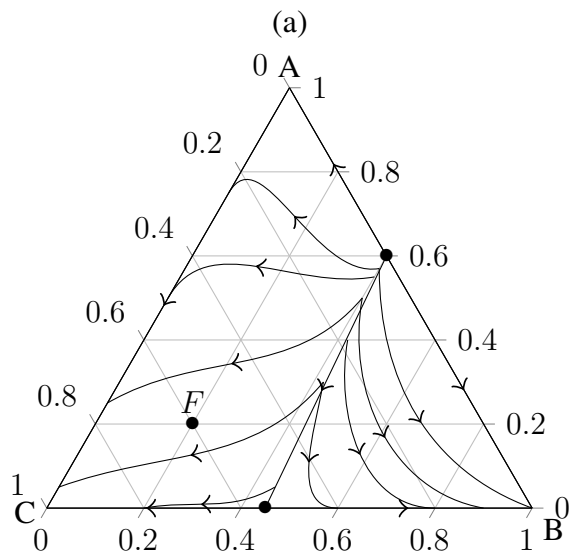
E2 For the feed positions below, find the feasible product regions.



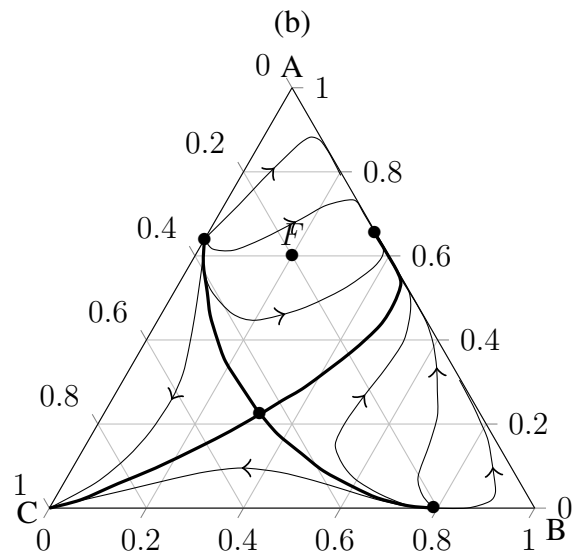
(a)



(b)



(c)



(d)



E3 For the normal hexane-methanol-methyl acetate system at 1 atm, sketch a residue-curve map on a right-triangular diagram, and indicate the distillation boundaries. Determine for each azeotrope and pure component whether it is a stable node, an unstable node, or saddle.

Methanol - b.p. = 64.65 °C

Methyl acetate - b.p. = 57.1 °C

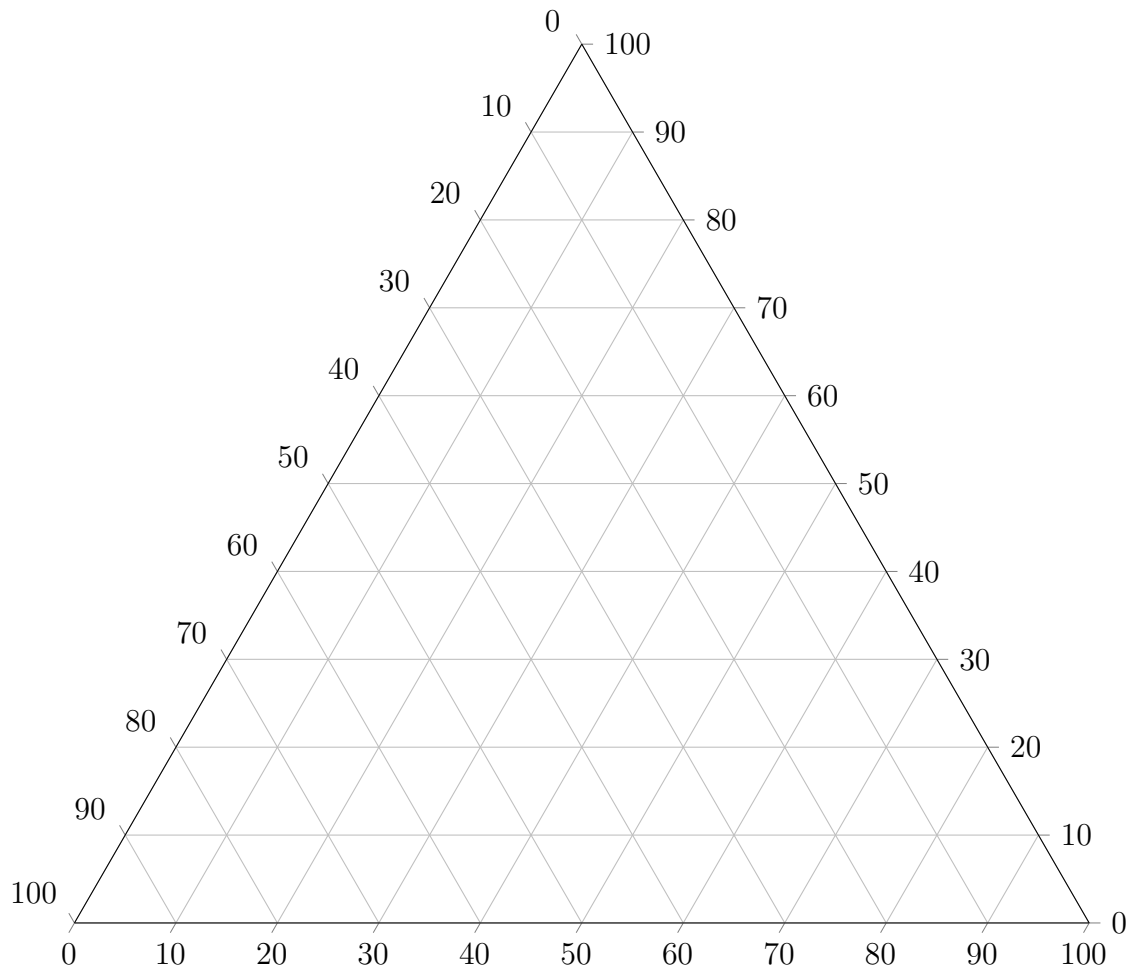
*n*-hexane - b.p. = 69.0 °C

Methanol 18.7 wt%, Methyl acetate 81.3 wt% - b.p. = 53.8 °C

Methanol 28.0 wt%, *n*-hexane 72.0 wt% - b.p. = 50.6 °C

Methyl acetate 60.7 wt%, *n*-hexane 39.3 wt% - b.p. = 51.8 °C

Methanol 14.0 wt%, Methyl acetate 27.0 wt%, *n*-hexane 59.0 wt% - b.p. = 45.0 °C



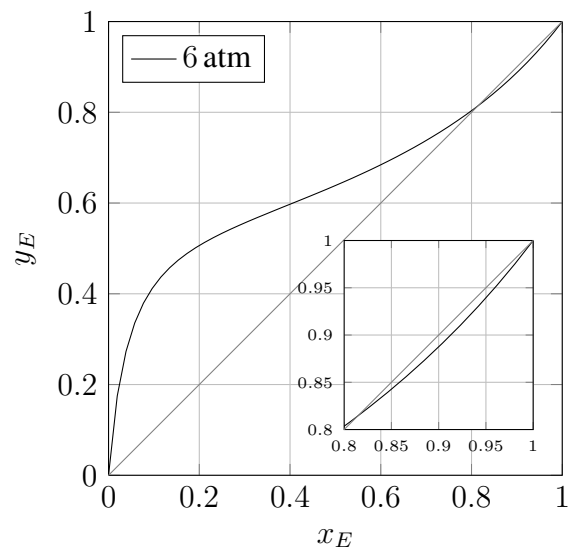
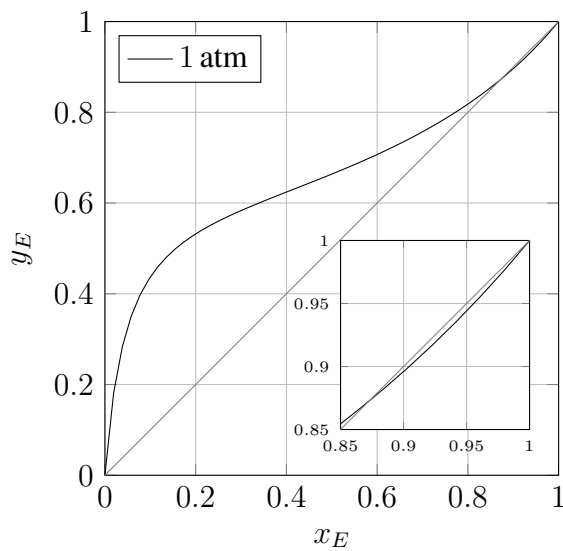
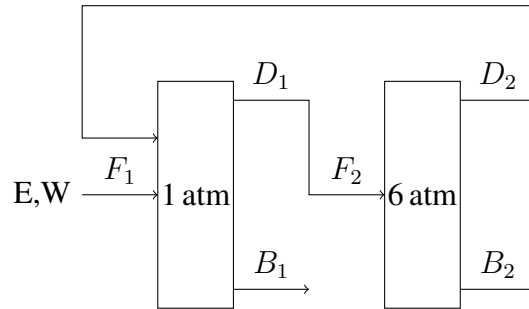
E4 A distillation column is to be designed to separate two components. The feed consisting of 40 mol% component 1 enters the column as a saturated liquid. A distillate consisting of 75 mol% component 1 and a bottom product consisting of 5 mol% component 1 are produced. What is the minimum number of stages and the minimum reflux ratio needed for the separation. The VLE for the system is:

$x_1$	$y_1$
0.000	0.000
0.050	0.118
0.100	0.215
0.200	0.368
0.300	0.483
0.400	0.573
0.500	0.646
0.600	0.706
0.700	0.757
0.750	0.779
0.800	0.800
0.900	0.850
0.950	0.900
1.000	1.000

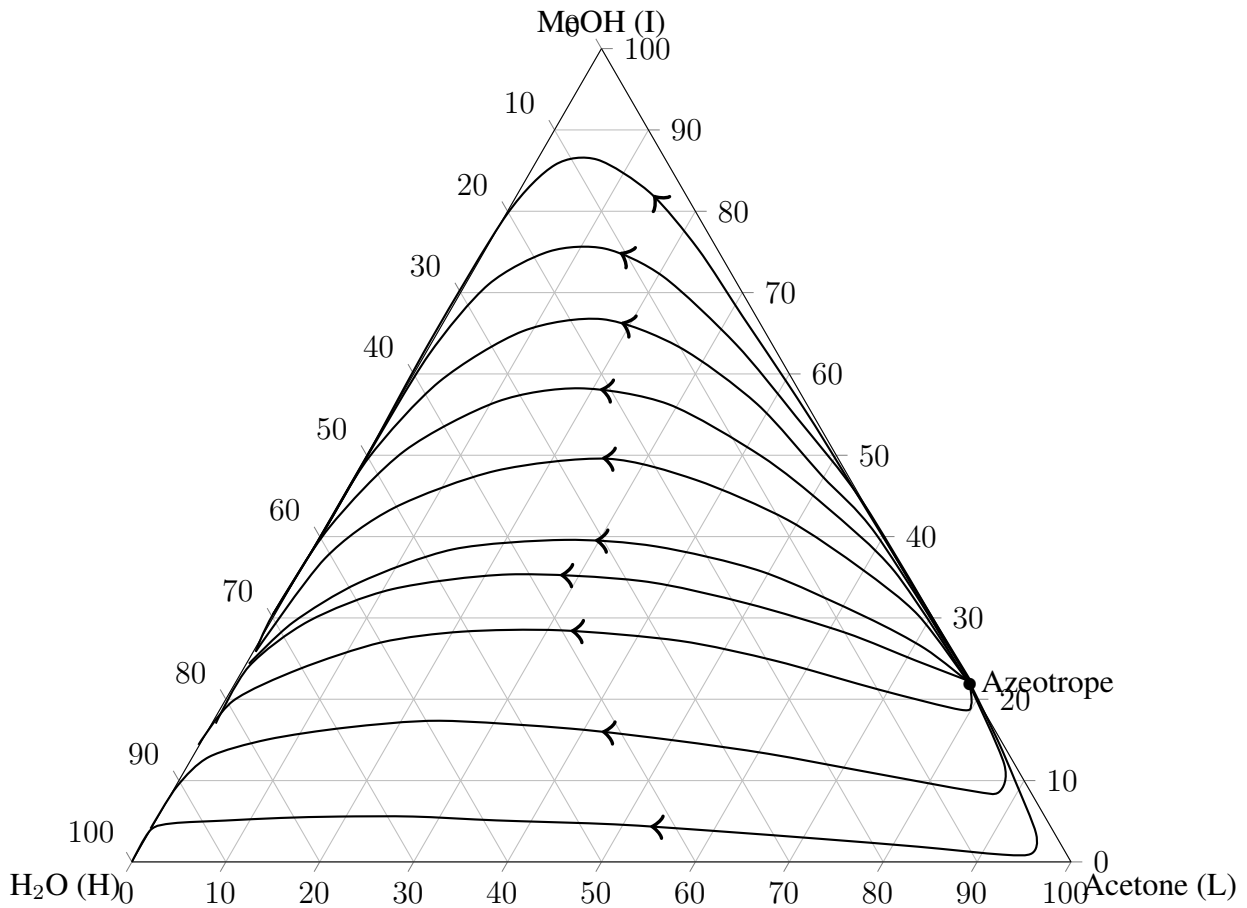
E5 Pressure swing distillation is used to separate  $100 \text{ kmol hr}^{-1}$  of a mixture of 40 mol% ethanol with water into products with 99 mol% purity.

Based on the sequence and the VLE below,

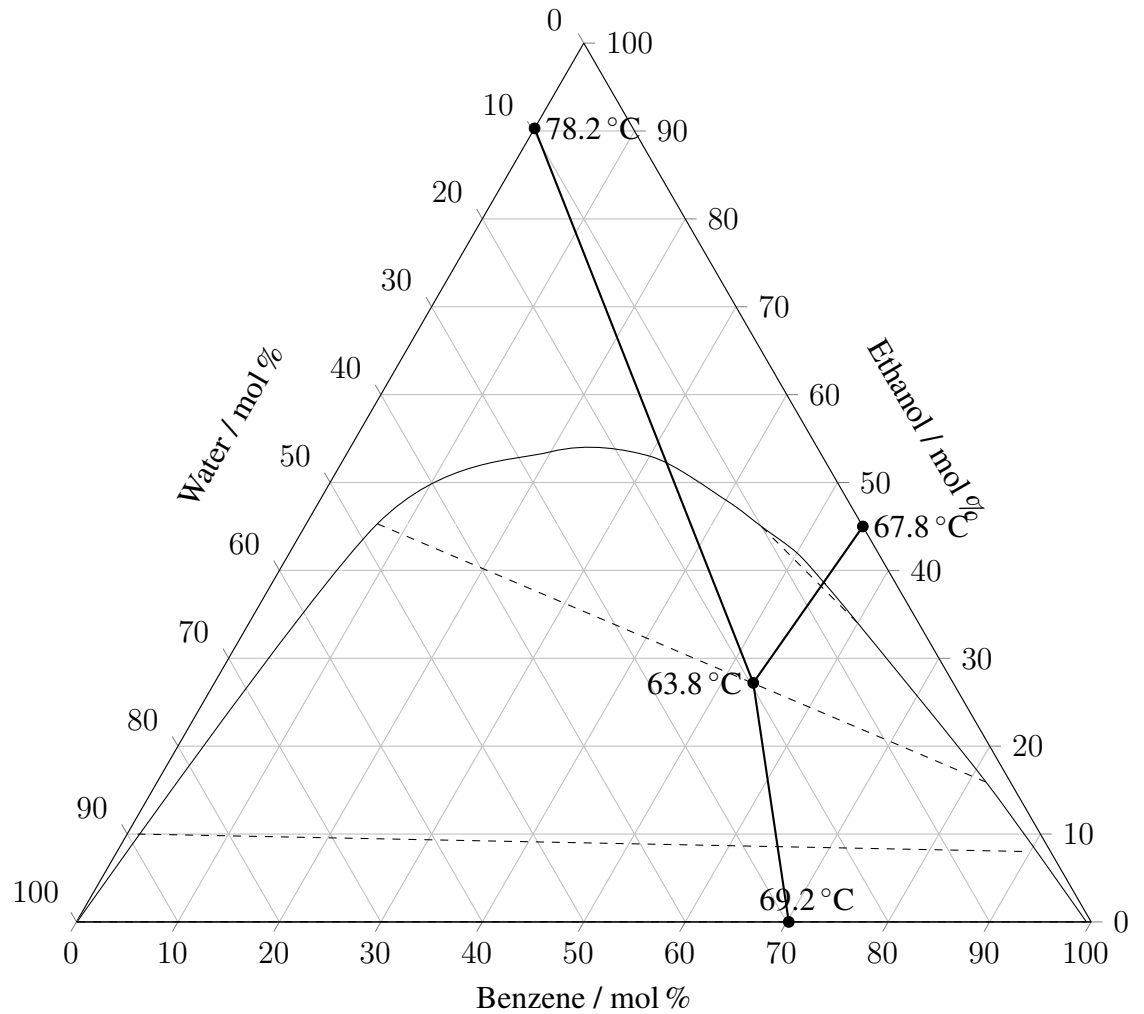
- Identify the compositions of  $B_1$ ,  $D_1$ ,  $B_2$  and  $D_2$
- Determine the flowrates of  $B_1$  and  $B_2$
- Determine the flowrates of  $D_1$  and  $D_2$



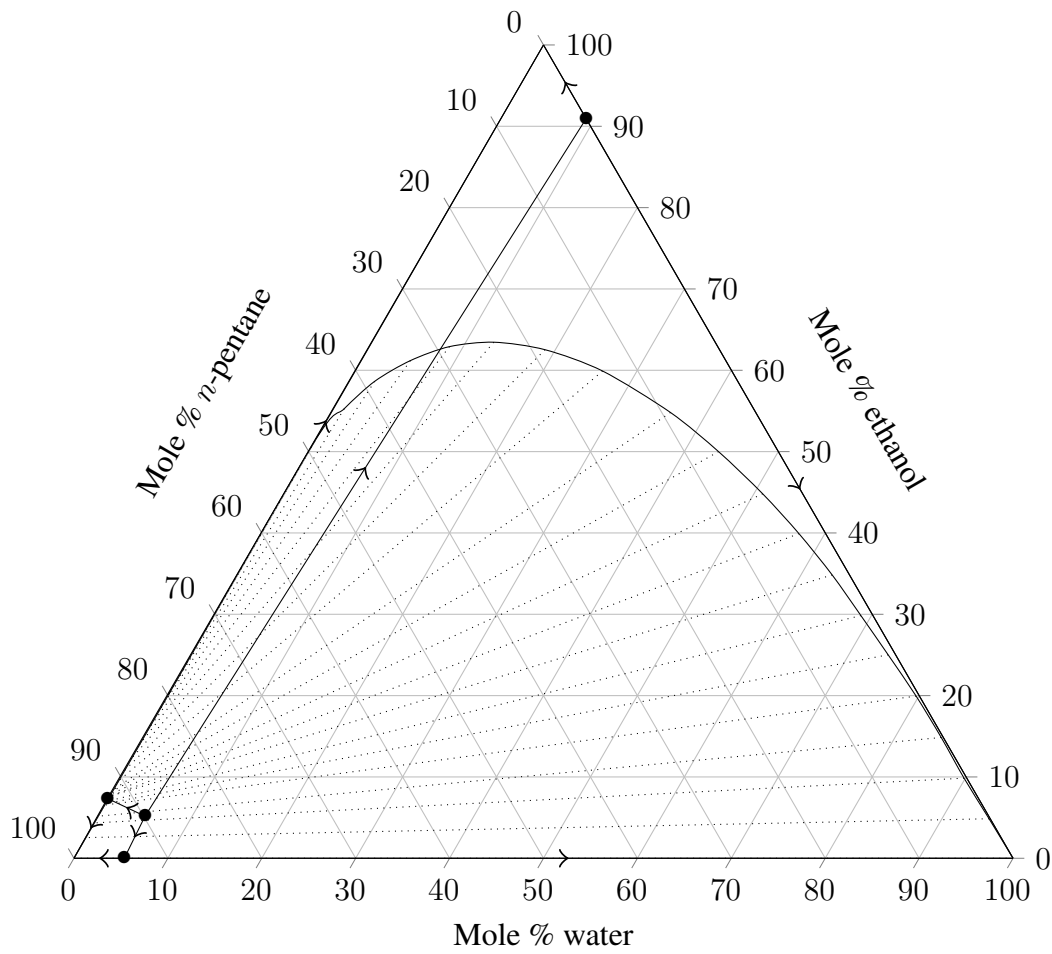
E6 Forty mol s<sup>-1</sup> of a bubble-point mixture of 75 mol% acetone and 25 mol% methanol at 1 atm is separated by extractive distillation, using water as the solvent, to produce an acetone product of not less than 95 mol% acetone, a methanol product of not less than 98 mol% methanol, and a water stream for recycle of at least 99.9 mol% purity. Prepare a preliminary process design using the traditional three-column sequence consisting of ordinary distillation followed by extractive distillation, and then ordinary distillation to recover the solvent, Figure 5.16.



- E7 Design a two-column distillation sequence (Figure 5.20(a)) to separate 150 mol/s of an azeotropic mixture of ethanol and water at 1 atm into nearly pure ethanol and nearly pure water using heterogeneous azeotropic distillation with benzene as the entrainer.



E8 Design a three-column distillation (Figure 5.20(b)) sequence to separate a feed of 20% ethanol in water into products of at least 99% purity using heterogeneous azeotropic distillation with a pentane entrainer.



Chapter **6**

# Revision

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## 6.1 Introduction

This section does not aim to provide the full information and detail for the separations listed, it is simply there as revision of topics covered in previous courses, which could be useful during this course.

## 6.2 Flash Equilibrium

For a vapour in equilibrium with a liquid the mole fraction in the vapour,  $y_i$ , and liquid,  $x_i$ , phases are linked by,

$$\begin{aligned} P y_i &= x_i \gamma_i P_i^o \\ y_i &= \frac{\gamma_i P_i^o}{P} x_i = K_i x_i \end{aligned} \quad (6.2.1)$$



Summary Video

For a non-condensable gas, i.e. a temperature far above the boiling point, this expression doesn't work and the solubility must be taken into account, e.g. oxygen dissolved in water, with an expression like Henry's Law,

$$\begin{aligned} P y_i &= H_i x_i \\ y_i &= \frac{H_i}{P} x_i = K_i x_i \end{aligned} \quad (6.2.2)$$

A simple flash system can be represented by Figure 6.1.

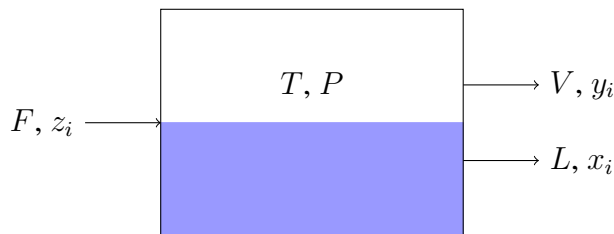


Figure 6.1: Representation of a flash vessel separation.

A mass balance for a component  $i$  in this system can be given by,

$$F z_i = L x_i + V y_i \quad (6.2.3)$$

Substituting  $y_i$  from equation 6.2.1,

$$\begin{aligned} F z_i &= L x_i + V K_i y_i \\ &= (F - V) x_i + V K_i x_i \\ &= F x_i + V x_i (K_i - 1) \\ x_i &= \frac{F z_i}{F + V (K_i - 1)} \\ &= \frac{z_i}{1 + \frac{V}{F} (K_i - 1)} \end{aligned} \quad (6.2.4)$$

The sum of the mole fractions of each component must add to 1 such that,  $\sum x_i = 1$  and  $\sum y_i = 1$ , therefore:

$$\begin{aligned} 0 &= \sum_i y_i - \sum_i x_i \\ &= \sum_i (K_i x_i - x_i) \\ &= x_i (K_i - 1) \end{aligned} \tag{6.2.5}$$

Substituting  $x_i$  from equation 6.2.4 produces the Rachford-Rice Flash equation,

$$\sum_i \frac{z_i (K_i - 1)}{1 + \frac{V}{F} (K_i - 1)} = 0 \tag{6.2.6}$$

This equation can be solved iteratively to calculate the vapourised fraction,  $V/F$ , for the given temperature and pressure of the system.

### 6.3 McCabe-Thiele Method

The main assumptions of the McCabe-Thiele method are:

- Constant Molar Overflow (CMO) - The flow rate of the vapour and the liquid in the column sections are constant and do not change from tray to tray.
- Adiabatic and Isobaric - There are no heat losses within the system and the pressure doesn't change in the column.
- Parallel Enthalpy Lines (PEL) - The saturated liquid and saturated vapour (molar) enthalpy curves,  $h_L(x)$  and  $h_V(y)$  respectively, are parallel lines, i.e. the molar enthalpy of vaporisation,  $\lambda_M$ , of the mixture is constant and independent of composition.



Summary Video

Taking a mass balance on the top of the distillation column, Figure 6.2.

$$\begin{aligned} V y_n &= L x_{n+1} + D x_d \\ y_n &= \frac{L}{V} x_{n+1} + \frac{D}{V} x_d \\ Y_n - \frac{L}{V} x_{n+1} &= \frac{D}{V} x_d \end{aligned} \tag{6.3.1}$$

Taking a mass balance on the enrichment section, Figure 6.3.

$$\begin{aligned} V y_{n-1} + L x_{n+1} &= V y_n + L x_n \\ y_{n-1} &= \frac{L}{V} x_n + y_n - \frac{L}{V} x_{n+1} \end{aligned} \tag{6.3.2}$$

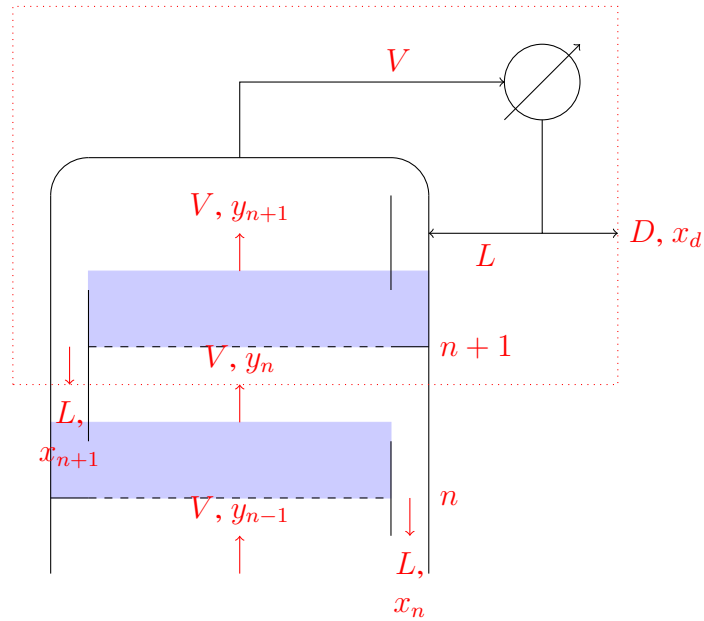


Figure 6.2: Mass balance around the top of distillation column.

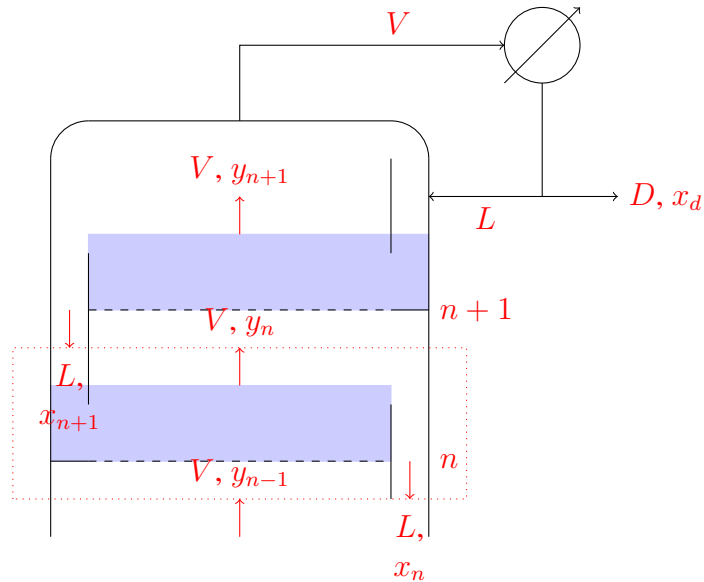


Figure 6.3: Mass balance on the enrichment section of a distillation column.

Substituting equation 6.3.1 into this equation gives,

$$\begin{aligned} y_{n-1} &= \frac{L}{V}x_n + \frac{D}{V}x_d \\ y_n &= \frac{L}{V}x_{n+1} + \frac{D}{V}x_d \end{aligned} \quad (6.3.3)$$

This is the enrichment section operating line (ESOL). Equation 6.3.3 can also be written

in terms of the reflux ratio,  $R = L/D$  as,

$$\frac{L}{V} = \frac{L}{L+D} = \frac{\frac{L}{D}}{\frac{L}{D}+1} = \frac{R}{R+1} \quad (6.3.4)$$

$$\frac{D}{V} = \frac{D}{L+D} = \frac{1}{\frac{L}{D}+1} = \frac{1}{R+1} \quad (6.3.5)$$

Therefore,

$$y_n = \frac{R}{R+1}x_{n+1} + \frac{1}{R+1}x_d \quad (6.3.6)$$

At the top of the column  $y_{n+1} = x_{n+1} = x_d$  as the condenser is a complete condenser, this means that,

$$\begin{aligned} y_n &= \frac{R}{R+1}x_d + \frac{1}{R+1}x_d \\ &= \frac{R+1}{R+1}x_d = \frac{R+1}{R+1}x_d \\ &= x_d \end{aligned} \quad (6.3.7)$$

This process can also be repeated for the stripping section of the column which gives the stripping section operating line (SSOL),

$$y_m = \frac{L_m}{V_m}x_{m+1} - \frac{B}{V_m}x_b \quad (6.3.8)$$

At the bottom of the column  $x_{m+1} = x_b$ , thus from equation 6.3.8  $y_m = x_b$ .

A mass balance on the feed is shown in Figure 6.4.

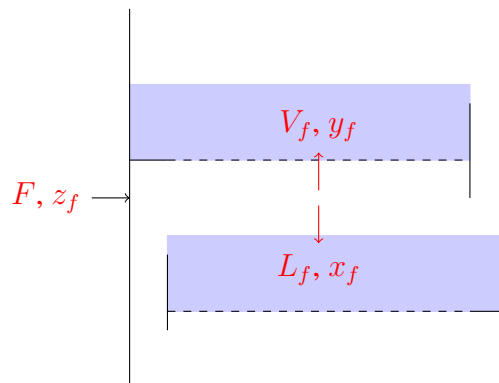


Figure 6.4: Mass balance on the feed section of a distillation column.

$$\begin{aligned} Fz_f &= V_f y_f + L_f x_f \\ V_f y_f &= Fz_f - L_f x_f \\ y_f &= -\frac{L_f}{V_f}x_f + \frac{F}{V_f}z_f \end{aligned} \quad (6.3.9)$$

This is the feed operating line (FOL). Equation 6.3.9 can also be written in terms of the feed quality,  $q = L_f/L$  as,

$$-\frac{L_f}{V_f} = -\frac{L_f}{F - L_f} = \frac{\frac{L_f}{F}}{\frac{L_f}{F} - 1} = \frac{q}{q - 1} \quad (6.3.10)$$

$$\frac{F}{V_f} = \frac{F}{F - L_f} = \frac{1}{1 - \frac{L_f}{F}} = \frac{1}{1 - q} \quad (6.3.11)$$

Therefore,

$$y_f = \frac{q}{q - 1}x_f + \frac{1}{1 - q}z_f \quad (6.3.12)$$

Knowledge of VLE data along with equations 6.3.12 and 6.3.6 allows a graphical calculation of the number of stages needed for the separation. To do this the equality line is plotted,  $y = x$  followed by the position of the top product,  $(x_d, x_d)$ ; feed,  $(z_f, z_f)$ ; and the bottom product,  $(x_b, x_b)$  shown as the red points in Figure 6.5.

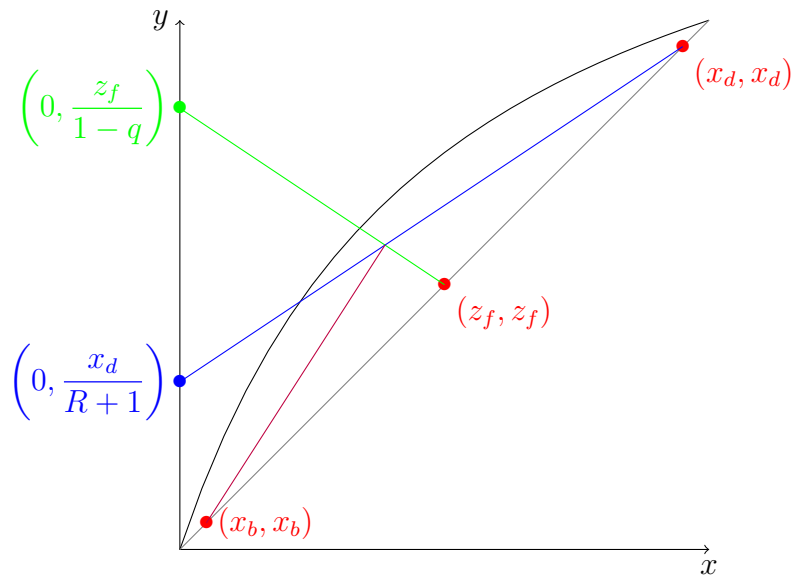


Figure 6.5: Graphical McCabe-Thiele operating lines. Feed line in green, enrichment section operating line in blue, and stripping section operating line in purple.

The feed operating line, equation 6.3.12, can be plotted on the graph as it is known it starts at the feed point,  $(z_f, z_f)$ , and at the y-axis (i.e.  $x = 0$ ) the y coordinate is  $z_f/(1 - q)$ . This is shown as the green line in Figure 6.5.

After the feed line, the enrichment section operating line, equation 6.3.6, can be plotted on the graph as it is known it starts at the distillate product point,  $(x_d, x_d)$ , and at the y-axis (i.e.  $x = 0$ ) the y coordinate is  $x_d/(R + 1)$ . This is shown as the blue line in Figure 6.5.

The stripping section operating line can then be drawn by joining the the bottom product point,  $(x_b, x_b)$ , with the point where the feed operating line and the enrichment section operating line meet. This is shown as the purple line in Figure 6.5.

Now that the operating lines are drawn, the stages can be calculated by drawing between the operating lines and the equilibrium line as shown by the red lines in Figure 6.6. This process is continued until the last red line is below the bottom product position.

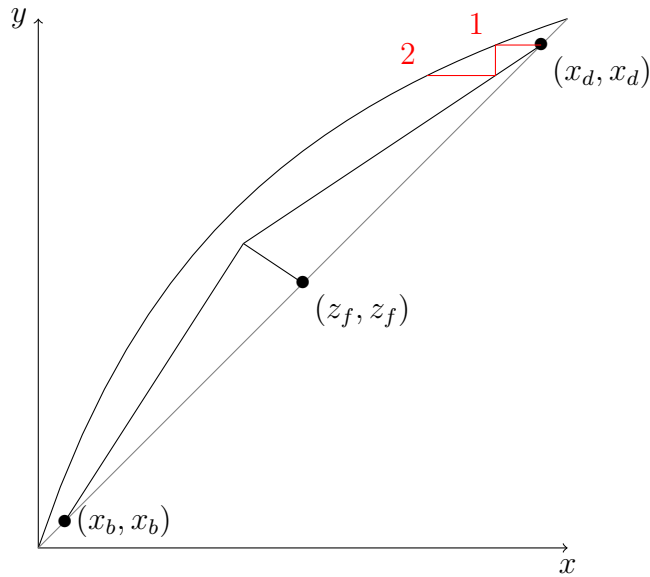


Figure 6.6: Graphical McCabe-Thiele equilibrium stages drawn on the operating lines.

## 6.4 Ponchon-Savarit Method

The Ponchon-Savarit method has advantages over the McCabe-Thiele method as it doesn't require the PEL or CMO assumptions.

Taking a mass and energy balance on the top of the distillation column, Figure 6.7.



Summary Video

An energy balance around the top of the column is,

$$V_n h_{V,n} = L_{n+1} h_{L,n+1} + D h_{L,d} + \dot{Q}_C \quad (6.4.1)$$

Defining  $h'_d = h_{L,d} + \dot{Q}_C/D$  means that,

$$V_n h_{V,n} = L_{n+1} h_{L,n+1} + D h'_d \quad (6.4.2)$$

From a total mass balance  $L_{n+1} + D = V_n$ , therefore,

$$\begin{aligned} (L_{n+1} + D) h_{V,n} &= L_{n+1} h_{L,n+1} + D h'_d \\ L_{n+1} (h_{V,n} - h_{L,n+1}) &= D (h'_d - h_{V,n}) \\ \frac{L_{n+1}}{D} &= \frac{h'_d - h_{V,n}}{h_{V,n} - h_{L,n+1}} \end{aligned} \quad (6.4.3)$$

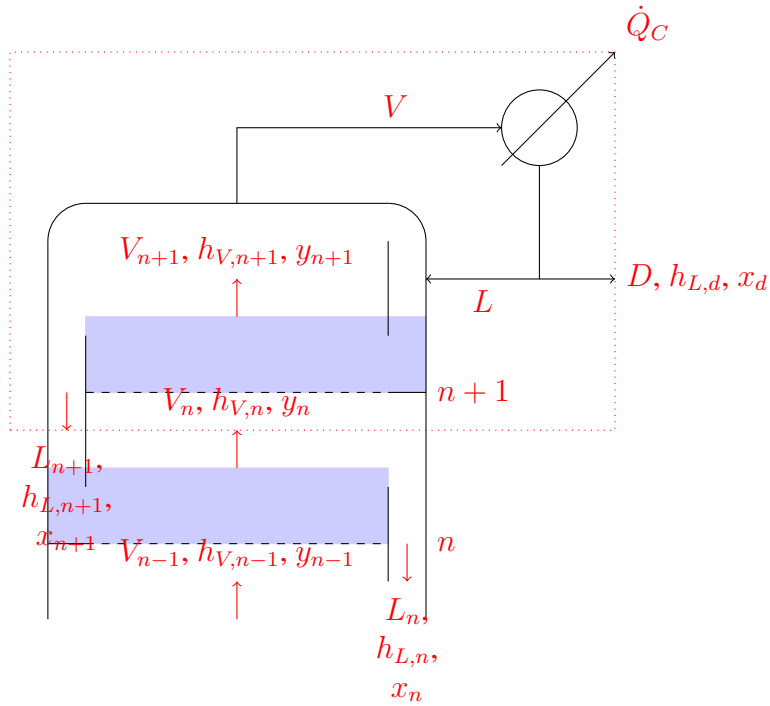


Figure 6.7: Mass and energy balance around the top of distillation column.

A mass balance for the top of the column is,

$$\begin{aligned}
 V_n y_n &= L_{n+1} x_{n+1} + D x_d \\
 (L_{n+1} + D) y_n &= L_{n+1} x_{n+1} + D x_d \\
 L_{n+1} (y_n - x_{n+1}) &= D (x_d - y_n) \\
 \frac{L_{n+1}}{D} &= \frac{x_d - y_n}{y_n - x_{n+1}}
 \end{aligned} \tag{6.4.4}$$

Comparing equations 6.4.3 and 6.4.4 produces,

$$\begin{aligned}
 \frac{h'_d - h_{V,n}}{h_{V,n} - h_{L,n+1}} &= \frac{x_d - y_n}{y_n - x_{n+1}} \\
 \frac{h'_d - h_{V,n}}{x_d - y_n} &= \frac{h_{V,n} - h_{L,n+1}}{y_n - x_{n+1}}
 \end{aligned} \tag{6.4.5}$$

This form of equation means that key pairs line on the same straight line, these are:  $(y_n, h_{V,n})$ ,  $(x_{n+1}, h_{L,n+1})$ , and  $(x_d, h'_d) = P_C$ .

The same approach can also be carried out around the bottom of the column to give,

$$\frac{h_{V,m} - h'_b}{y_m - x_b} = \frac{h_{V,m} - h_{L,m+1}}{y_m - x_{m+1}} \tag{6.4.6}$$

where  $h'_b = h_{L,b} - \dot{Q}_R/B$ .

This form of equation means that key pairs line on the same straight line, these are:  $(y_m, h_{V,m})$ ,  $(x_{m+1}, h_{L,m+1})$ , and  $(x_b, h'_b) = P_R$ .

A mass and energy balance can also be taken over the whole column. For the mass balance,

$$F z_f = B x_b + D x_d \tag{6.4.7}$$

As  $F = B + D$  then,

$$\begin{aligned}
 (B + D) z_f &= Bx_b + Dx_d \\
 B(z_f - x_b) &= D(x_d - z_f) \\
 \frac{B}{D} &= \frac{x_d - z_f}{z_f - x_b}
 \end{aligned} \tag{6.4.8}$$

For the energy balance,

$$\begin{aligned}
 Fh_f + \dot{Q}_R &= Dh_{L,d} + \dot{Q}_C + Bh_{L,b} \\
 Fh_f &= Dh_{L,d} + \dot{Q}_C + Bh_{L,b} - \dot{Q}_R \\
 Fh_f &= Dh'_d + Bh'_b \\
 (B + D)h_f &= Dh'_d + Bh'_b \\
 B(h_f - h'_b) &= D(h'_d - h_f) \\
 \frac{B}{D} &= \frac{h'_d - h_f}{h_f - h'_b}
 \end{aligned} \tag{6.4.9}$$

Combining equations 6.4.8 and 6.4.9 gives,

$$\begin{aligned}
 \frac{x_d - z_f}{z_f - x_b} &= \frac{h'_d - h_f}{h_f - h'_b} \\
 \frac{h_f - h'_b}{z_f - x_b} &= \frac{h'_d - h_f}{x_d - z_f}
 \end{aligned} \tag{6.4.10}$$

This form of equation means that key pairs line on the same straight line, these are:  $(x_d, h'_d) = P_C$ ,  $(x_b, h'_b) = P_R$ , and  $(z_f, h_f) = F$ .

This means that the operating points can be plotted on the enthalpy data graph for the system of interest on Figure 6.8. The condenser operating point,  $P_C$ , in red is above the  $h_V$  line by the amount  $\dot{Q}_C/D$ , this amount is related to the reflux ratio. For a total condenser,

$$\begin{aligned}
 V &= L + D \\
 &= RD + D = (R + 1)D \\
 \dot{Q}_C &= V(h_V - h_L) \\
 &= (R + 1)(h_V - h_L)D \\
 \frac{\dot{Q}_C}{D} &= (R + 1)(h_V - h_L)
 \end{aligned} \tag{6.4.11}$$

The feed point,  $F$ , in green is plotted as the point  $(z_f, h_f)$  and  $h_f$  is related to the feed quality as,

$$q = \frac{h_V - h_f}{h_V - h_L} \tag{6.4.12}$$

The reboiler operating point,  $P_R$ , in blue can then be plotted as it is on a straight line from  $P_C$  through  $F$  and at the x-coordinate of  $x_b$ , this position allows the calculation of the reboiler duty from  $h'_b$ .



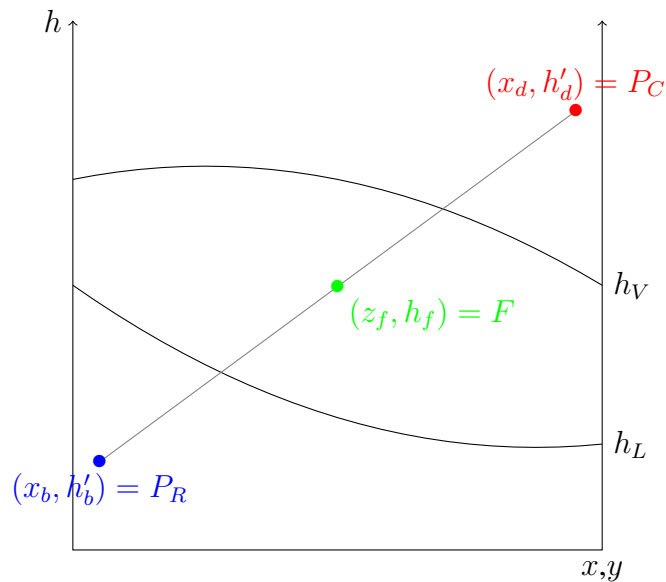


Figure 6.8: Graphical Ponchon-Savarit operating points. Feed point in green, condenser operating point in red, and reboiler operating point in blue.

Now that the operating points are plotted, the number of stages needed for the separation can be determined as in Figure 6.9. Starting at the top of the column,  $x_d$ , the liquid fraction can be determined from the VLE data and then the  $h_L$  value, red lines. The vapour composition of the stage below can then be calculated joining the liquid composition to the condenser operating point, green line. This is the equivalence of the operating line in the McCabe-Thiele method.

Now the liquid composition on the same stage can be determined from the VLE chart, blue, and then back to the condenser operating point, purple line. This process is repeated until the lines pass the line through the feed point, after this the reboiler operating point,  $P_R$  is used with the VLE data.

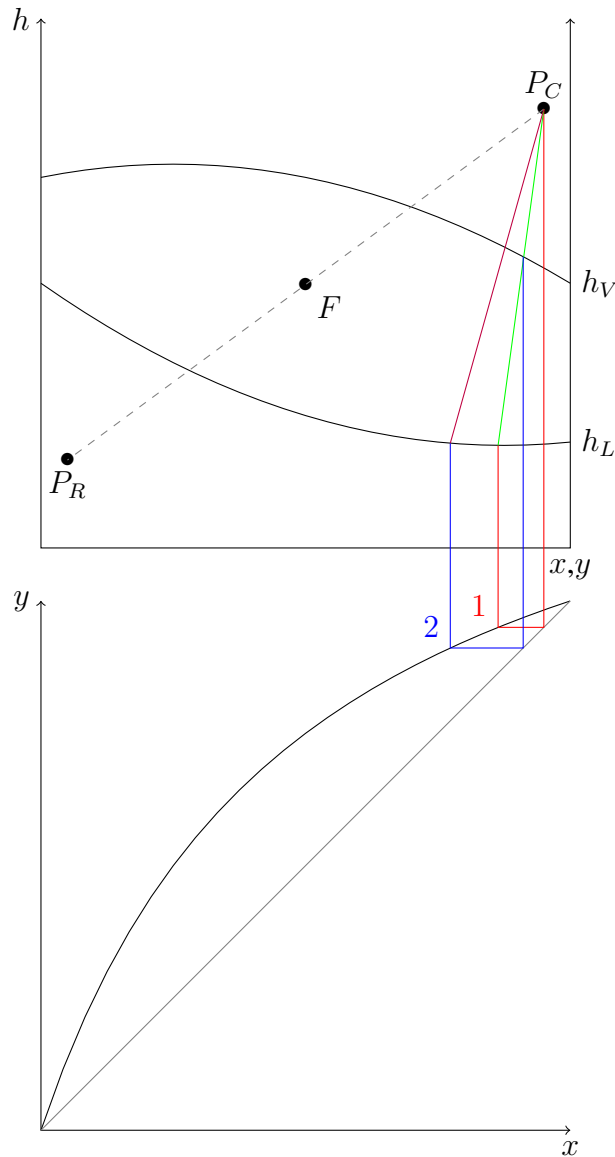


Figure 6.9: Graphical Ponchon-Savarit stages drawn from the operating points coupled with the VLE data.

## 6.5 Absorption/Desorption

In absorption/desorption there is a gas phase and a liquid phase and a solute which passes between the two phases. The gas and liquid phases are insoluble in each other.



Summary Video

For convenience key variables are used:

- $L'$  is the solute-free liquid flow rate
- $G'$  is the solute-free gas flow rate

- $X$  is the mole ratio of solute in the liquid to the solute-free liquid, i.e.

$$X_A = \frac{x_A}{1 - x_A} \quad (6.5.1)$$

- $Y$  is the mole ratio of solute in the gas to the solute-free gas, i.e.

$$Y_A = \frac{y_A}{1 - y_A} \quad (6.5.2)$$

The mass balance is shown in Figure 6.10 for the top of the column as the red border,

$$\begin{aligned} G'Y_n + L'X_{T+1} &= G'Y_T + L'X_{n+1} \\ Y_n &= \frac{L'}{G'}X_{n+1} + Y_T - \frac{L'}{G'}X_{T+1} \end{aligned} \quad (6.5.3)$$

For the bottom of the column as the green border,

$$\begin{aligned} G'Y_0 + L'X_{n+1} &= G'Y_n + L'X_1 \\ Y_n &= \frac{L'}{G'}X_{n+1} + Y_0 - \frac{L'}{G'}X_1 \end{aligned} \quad (6.5.4)$$

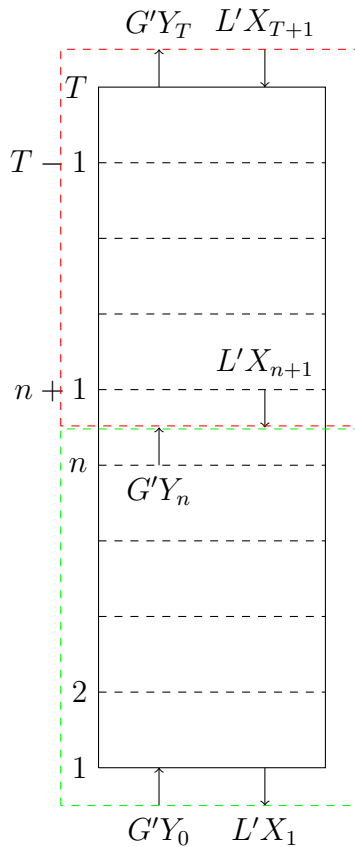


Figure 6.10: Absorption column mass balance.

Equations 6.5.3 and 6.5.4 are the same line with a gradient of  $L'/G'$  and pass through points  $(X_1, Y_0)$  and  $(X_{T+1}, Y_T)$ .

### 6.5.1 Scrubbing

For Absorption the liquid gets more concentrated as it goes down the column, i.e. the solute is absorbed from the gas phase carrier into the liquid solvent.

This means that the operating line, shown in red, is above the solubility line, Figure 6.11. As with the McCabe-Thiele method the stages, shown in blue, are determined by stepping between the equilibrium line and the operating line.

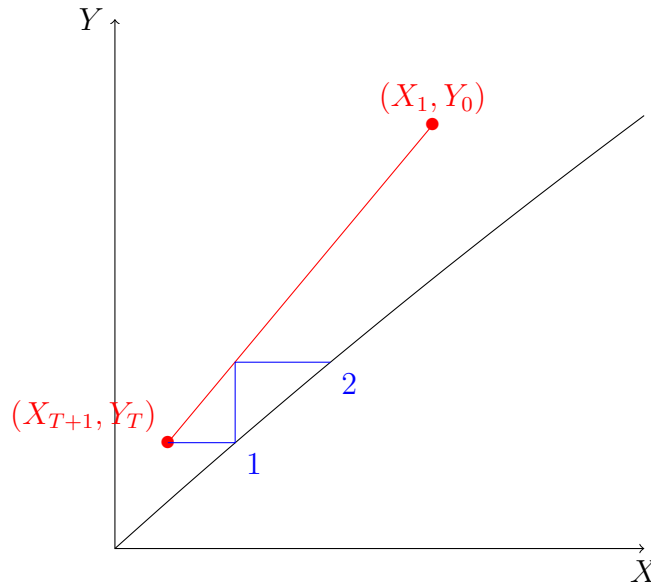


Figure 6.11: Graphical scrubbing operating lines. Operating line in red, stages in blue.

### 6.5.2 Stripping

For Desorption the liquid gets less concentrated as it goes down the column, i.e. the solute is desorbed from the liquid phase carrier into the gas solvent.

This means that the operating line, shown in red, is below the solubility line, Figure 6.12. As with the McCabe-Thiele method the stages, shown in blue, are determined by stepping between the equilibrium line and the operating line.

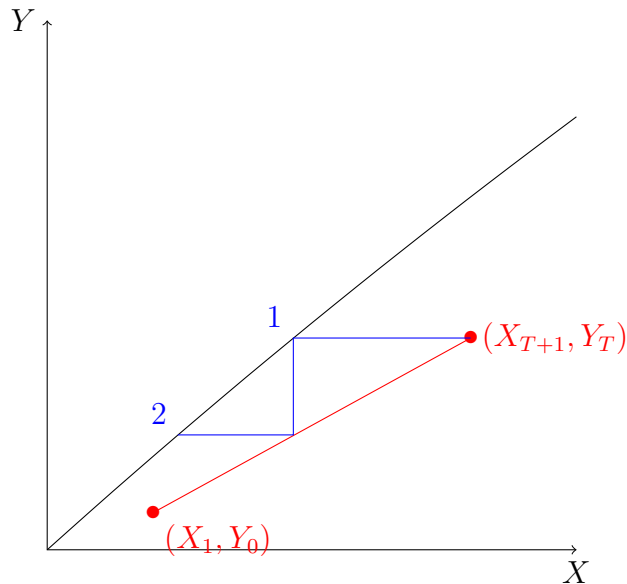


Figure 6.12: Graphical stripping operating lines. Operating line in red, and stages in blue.

## 6.6 Liquid-Liquid Extraction

Liquid-liquid extraction uses a solvent, S, to remove a solute, A, from an original carrier, C. If an assumption is made that the carrier and the solvent do not dissolve in each other (then their flow rate is constant through the column), and the fraction of the solute is relatively small then a method similar to absorption can be used to calculate the number of stages needed for the separation.

As with absorption key variables are used to make the equations easier to solve:

- $X$  is the mass ratio of solute, A, to the carrier, C, in the feed/raffinate phase i.e.

$$X_A = \frac{\text{mass of A}}{\text{mass of C}} \quad (6.6.1)$$

- $Y$  is the mass ratio of solute, A, to the solvent, S, in the solvent/extract phase i.e.

$$Y_A = \frac{\text{mass of A}}{\text{mass of S}} \quad (6.6.2)$$

The mass balance is shown in Figure 6.13 for the whole of the column as the red border, remembering that the carrier flow is  $C$  and the solvent flow is  $S$ , and don't change in the column,

$$\begin{aligned} CX_0 + SY_{T+1} &= CX_T + SY_1 \\ C(X_0 - X_T) &= S(Y_1 - Y_{T+1}) \\ \frac{C}{S} &= \frac{Y_1 - Y_{T+1}}{X_0 - X_T} \end{aligned} \quad (6.6.3)$$

As in absorption this defines a straight line with a gradient of  $C/S$  that passes through points  $(X_0, Y_1)$  and  $(X_T, Y_{T+1})$ .

The operating line, shown in red, is below the solubility line, Figure 6.14. As with the McCabe-Thiele method the stages, shown in blue, are determined by stepping between the equilibrium line and the operating line.

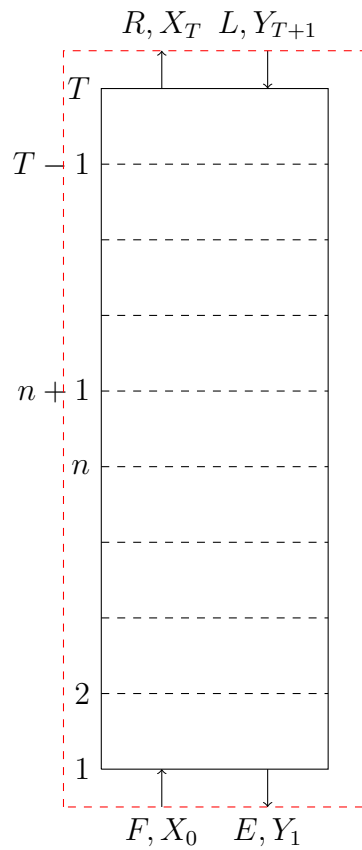


Figure 6.13: Liquid-liquid extraction column mass balance.

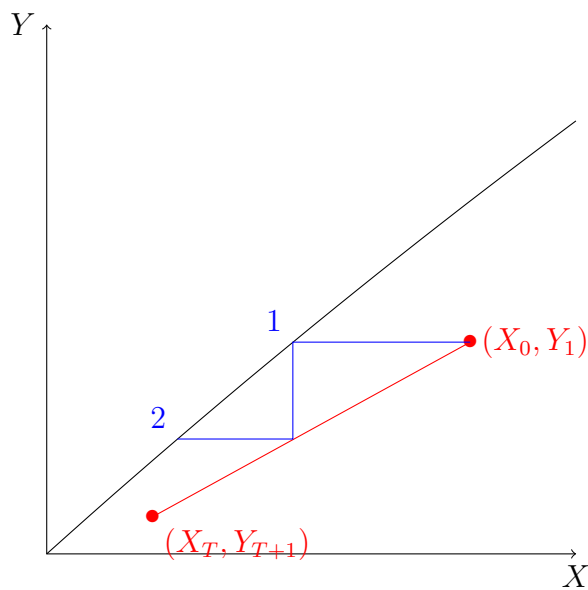


Figure 6.14: Graphical liquid-liquid extraction operating lines. Operating line in red, and stages in blue.