

# Distillation

- Distillation is a method of separating mixtures based on differences in their volatilities in a boiling liquid mixture.
- Distillation is a unit operation, or a physical separation process, and not a chemical reaction.
- Commercially, distillation is used to separate crude oil into more fractions for specific uses such as transport, power generation and heating.
- Water is distilled to remove impurities, such as salt from seawater.
- Air is distilled to separate its components— oxygen, nitrogen, and argon—for industrial use.
- Distillation of fermented solutions has been used since ancient times to produce distilled beverages with a higher alcohol content.

# History

- The first clear evidence of distillation comes from Greek [alchemists](#) working in [Alexandria](#) in the first century AD. [Distilled water](#) has been known since at least ca. 200 AD. Arabs learned the process from the Egyptians and used it extensively in their [alchemical experiments](#).
- The first clear evidence from the distillation of alcohol comes from the [School of Salerno](#) in the 12th century. [Fractional distillation](#) was developed by Tadeo Alderotti in the 13th century.
- In 1500, [German](#) alchemist Hieronymus Braunschweig published the Book of the Art of Distillation, the first book solely dedicated to the subject of distillation. In 1651, [John French](#) published [The Art of Distillation](#) the first major English compendium of practice. This includes diagrams with people in them showing the industrial rather than bench scale of the operation.

- Early forms of distillation were batch processes using one vaporization and one condensation. Purity was improved by further distillation of the condensate. Greater volumes were processed by simply repeating the distillation.
- In the early 19th century the basics of modern techniques including pre-heating and reflux were developed, particularly by the French, then in 1830 a British [Patent](#) was issued for a whiskey distillation column, which worked continuously and may be regarded as the [archetype](#) of modern petrochemical units.
- In 1877, [Ernest Solvay](#) was granted a U.S. Patent for a tray column for [ammonia](#) distillation and the same and subsequent years saw developments of this theme for oil and spirits.

# Chemical Engineering Distillation

- With the emergence of [chemical engineering](#) as a discipline at the end of the 19th century, scientific rather than empirical methods could be applied.
- The developing [petroleum](#) industry in the early 20th century provided the impetus for the development of accurate design methods such as the [McCabe–Thiele method](#) and the [Fenske equation](#).
- The availability of powerful computers has also allowed direct [computer simulation](#) of distillation columns

# Equilibrium

- Idealized models of distillation are essentially governed by [Raoult's law](#) and [Dalton's law](#), and assume that [vapor-liquid equilibria](#) are attained.
- Raoult's law assumes that a component contributes to the total [vapor pressure](#) of the mixture in proportion to its percentage of the mixture and its vapor pressure when pure: partial pressure equals mole fraction multiplied by vapor pressure when pure.
- Dalton's law states that the total vapor pressure is the sum of the vapor pressures of each individual component in the mixture. When a multi-component liquid is heated, the vapor pressure of each component will rise, thus causing the total vapor pressure to rise. When the total vapor pressure reaches the pressure surrounding the liquid, [boiling](#) occurs and liquid turns to gas throughout the bulk of the liquid..

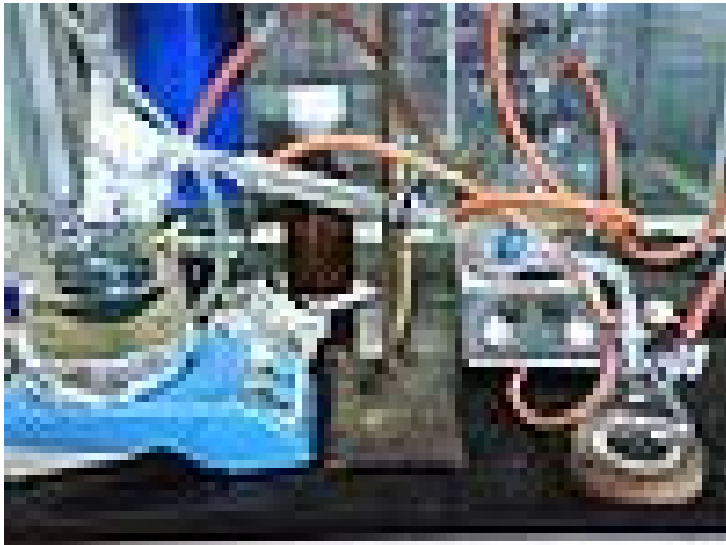
- The idealized model is accurate in the case of chemically similar liquids, such as [benzene](#) and [toluene](#).
- In other cases, severe deviations from Raoult's law and Dalton's law are observed, most famously in the mixture of ethanol and water. These compounds, when heated together, form an [azeotrope](#), which is a composition with a boiling point higher or lower than the boiling point of each separate liquid.
- Virtually all liquids, when mixed and heated, will display azeotropic behaviour. Although there are [computational methods](#) that can be used to estimate the behavior of a mixture of arbitrary components, the only way to obtain accurate [vapor-liquid equilibrium](#) data is by measurement.

# Batch still showing the separation of A and B.

- Heating an ideal mixture of two volatile substances A and B (with A having the higher volatility, or lower boiling point) in a batch distillation setup (such as in an apparatus depicted) until the mixture is boiling results in a vapor above the liquid which contains a mixture of A and B.
- The ratio between A and B in the vapor will be different from the ratio in the liquid: the ratio in the liquid will be determined by how the original mixture was prepared, while the ratio in the vapor will be enriched in the more volatile compound, A (due to Raoult's Law). The vapor goes through the condenser and is removed from the system.



# Lab batch distiller



- The result is that the ratio in the liquid mixture is changing, becoming richer in component B.
- This causes the boiling point of the mixture to rise, which in turn results in a rise in the temperature in the vapor, which results in a changing ratio of A : B in the gas phase.
- As distillation continues, there is an increasing proportion of B in the gas phase. This results in a slowly changing ratio A : B in the distillate.

# Continuous distillation

- Continuous distillation is an ongoing distillation in which a liquid mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams as time passes during the operation.
- Continuous distillation produces at least two output fractions, including at least one volatile distillate fraction, which has boiled and been separately captured as a vapor condensed to a liquid. There is always a bottoms (or residue) fraction, which is the least volatile residue that has not been separately captured as a condensed vapor.

- Continuous distillation differs from batch distillation in the respect that concentrations should not change over time. Continuous distillation can be run at a steady state for an arbitrary amount of time.
- For any source material of specific composition, the main variables that affect the purity of products in continuous distillation are the reflux ratio and the number of theoretical equilibrium stages (practically, the number of trays or the height of packing).
- Reflux is a flow from the condenser back to the column, which generates a recycle that allows a better separation with a given number of trays..

- Equilibrium stages are ideal steps where compositions achieve vapor–liquid equilibrium, repeating the separation process and allowing better separation given a reflux ratio.
- A column with a high reflux ratio may have fewer stages, but it refluxes a large amount of liquid, giving a wide column with a large holdup. Conversely, a column with a low reflux ratio must have a large number of stages, thus requiring a taller column

# Laboratory scale distillation

- Laboratory scale distillations are almost exclusively run as batch distillations.
- The device used in distillation, sometimes referred to as a still, consists at a minimum of a **reboiler** or *pot* in which the source material is heated, a **condenser** in which the heated vapour is cooled back to the liquid state, and a **receiver** in which the concentrated or purified liquid, called the **distillate**, is collected.
- Several laboratory scale techniques for distillation exist

# Several laboratory scale techniques

- **Simple distillation** : all the hot vapors produced are immediately channeled into a condenser that cools and condenses the vapors.
- **Fractional distillation** : be used in order to separate the components well by repeated vaporization–condensation cycles within a packed fractionating column.
- **Steam distillation** : a method for distilling compounds which are heat–sensitive
- **Vacuum distillation** : To boil very high boiling points compounds, it is often better to lower the pressure at which such compounds are boiled instead of increasing the temperature.
- **Molecular distillation** : vacuum distillation below the pressure of 0.01 torr

# Other types

- The process of [reactive distillation](#) involves using the reaction vessel as the still. In this process, the product is usually significantly lower-boiling than its reactants. As the product is formed from the reactants, it is vaporized and removed from the reaction mixture. This technique is an example of a continuous vs. a batch process; advantages include less downtime to charge the reaction vessel with starting material, and less workup.
- [Pervaporation](#) is a method for the separation of mixtures of liquids by partial vaporization through a non-porous [membrane](#).
- [Extractive distillation](#) is defined as distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent, that forms no azeotrope with the other components in the mixture.



# Industrial distillation

- Large scale industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation. The most widely used industrial applications of continuous, steady-state fractional distillation are in [petroleum refineries](#) [chemical plants](#).
- Industrial distillation is typically performed in large, vertical cylindrical columns known as **distillation towers** with diameters ranging from about 65 centimeters to 16 meters and heights ranging from 6 – 90 meters or more.
- When the feed has a diverse composition, liquid outlets at intervals up the column allow for the withdrawal of different products having different [boiling points](#).
- The "lightest" products (those with the lowest boiling point) exit from the top of the columns and the "heaviest" products (the highest boiling point) exit from the bottom and are often called the **bottoms**.

# Industrial distillation tower



- Design and operation of a distillation tower depends on the feed and desired products. Given a simple, binary component feed, analytical methods such as the [McCabe–Thiele method](#) or the [Fenske equation](#) can be used.
- For a multi–component feed, [simulation](#) models are used both for design and operation. Moreover, the efficiencies of the vapor–liquid contact devices (referred to as "plates" or "trays") used in distillation towers are typically lower than that of a theoretical 100% efficient [equilibrium stage](#).
- Hence, a distillation tower needs more trays than the number of theoretical vapor–liquid equilibrium stages.

# azeotropic distillation

- Interactions between the components of the solution create properties unique to the solution, as most processes entail nonideal mixtures, where [Raoult's law](#) does not hold.
- Such interactions can result in a constant-boiling [azeotrope](#) which behaves as if it were a pure compound (i.e., boils at a single temperature instead of a range). At an azeotrope, the solution contains the given component in the same proportion as the vapor, so that evaporation does not change the purity, and distillation does not effect separation.
- For example, [ethyl alcohol](#) and [water](#) form an azeotrope of 95.6% at 78.1 °C.

- If the azeotrope is not considered sufficiently pure for use, there exist some techniques to break the azeotrope to give a pure distillate.
- This set of techniques are known as **azeotropic distillation**. Some techniques achieve this by "jumping" over the azeotropic composition (by adding an additional component to create a new azeotrope, or by varying the pressure).
- Others work by chemically or physically removing or sequestering the impurity.
- For example, to purify ethanol beyond 95%, a drying agent or a (desiccant such as potassium carbonate) can be added to convert the soluble water into insoluble water of crystallization

- Immiscible liquids, such as water and toluene, easily form azeotropes.
- Commonly, these azeotropes are referred to as a low boiling azeotrope because the boiling point of the azeotrope is lower than the boiling point of either pure component.
- The temperature and composition of the azeotrope is easily predicted from the vapor pressure of the pure components, without use of Raoult's law.
- The azeotrope is easily broken in a distillation set-up by using a liquid-liquid separator (a decanter) to separate the two liquid layers that are condensed overhead. Only one of the two liquid layers is refluxed to the distillation set-up