

## Distillation

Distillation is a separation operation based on differences in volatility. If a mixture containing substances that differ in their volatility is brought to ebullition, the composition of the vapors released will be different from that of the boiling liquid. After condensation, the vapors constitute the ‘distillate’. The remaining liquid is called ‘residue’ or ‘bottoms’.

One of the oldest separation processes, distillation is of central importance in the chemical process industry. In the food sector, its main application is in the production of ethanol and alcoholic beverages from fermented liquids. Other food-related applications include the recovery, fractionation and concentration of volatile aromas as well as recovery of organic solvents (desolventation) in the production of edible oils by solvent extraction and removal of undesirable odorous substances (e.g. deodorization of cream). Distillation may be carried out as a batch or as a continuous process.

### Vapor–Liquid Equilibrium (VLE)

Consider a binary liquid solution consisting of substances A and B. If the mixture behaves as an ideal solution, the vapor pressure of substance A,  $p_A$ , is given by Raoult’s law (Francois-Marie Raoult, French chemist, 1830–1901), as formulated in Eq. (1):

$$p_A = x_a p_A^0 \quad \dots\dots \text{Eq. (1)}$$

where:

$x_a$  = concentration of A in the solution, in mol fraction

$p_A^0$  = vapor pressure of pure A, at the temperature of the solution.

If, furthermore, the vapor phase behaves as an ideal gas mixture, then Dalton’s law (John Dalton, English physicist and chemist, 1766–1844) applies. The partial pressure of A in the vapor is then:

$$\bar{p}_A = y_A P \quad \dots\dots \text{Eq. (2)}$$

where:

$y_A$  = concentration of A in the vapor phase, in mol fraction

$P$  = total pressure.

At equilibrium, the partial pressure of A in the gas must be equal to the vapor pressure of A over the solution. The equilibrium concentration of A in the vapor,  $y_A^*$  is then given by Eq. (3):

$$y_A^* = x_A \frac{p_A^0}{P} \quad \dots\dots \text{Eq. (3)}$$

Unless the total pressure is abnormally high, the assumption of ideal gas mixture for the gas phase is fairly safe. In contrast, few liquids of interest in food processing behave like ideal solutions. For example, the vapor pressure behavior of ethanol–water mixtures deviates considerably from Raoult’s law. The vapor pressure of component A over a non-ideal solution is given by Eq. (4):

$$p_A = \gamma_A x_A p_A^0 \quad \dots \text{Eq. (4)}$$

where:

$\gamma_A$  is the activity coefficient of A in the solution. The activity coefficient is not constant but varies with the temperature and the composition of the mixture. The equilibrium concentration of A in the vapor phase is then:

$$y_A^* = x_A \gamma_A \frac{p_A^0}{P} \quad \dots \text{Eq. (5)}$$

The use of Eq. (5) for the prediction of vapor–liquid equilibrium (VLE) data is problematic, mainly because of the difficulty to find activity coefficient values for mixtures, as a function of temperature and composition. Another expression used for the prediction of VLE data is the ‘relative volatility’ defined as follows:

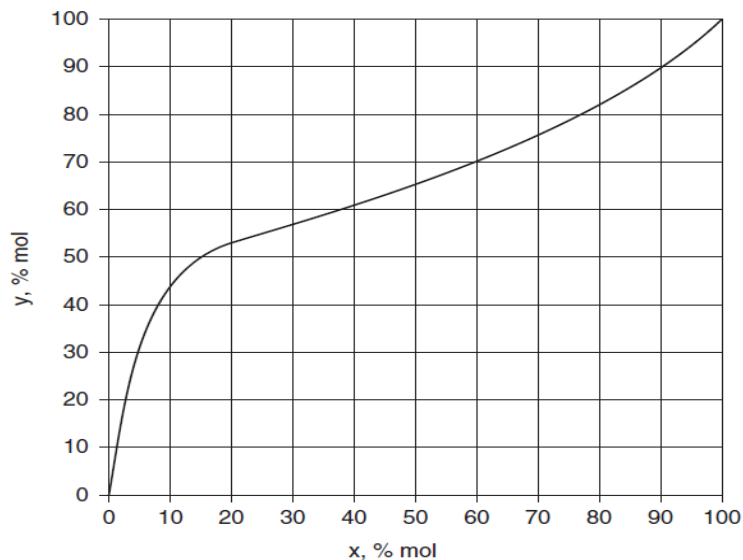
$$\alpha_{A \rightarrow B} = \frac{y_A^* (1 - x_A)}{x_A (1 - y_A^*)} \quad \dots \text{Eq. (6)}$$

where:  $\alpha_{A \rightarrow B}$  is the volatility of A relative to B.

In an ideal solution, the relative volatility is simply the ratio of the vapor pressures of the pure components A and B. Within a limited range of concentrations, the relative volatility may be assumed to be fairly constant.

Detailed experimental VLE data for many mixtures of industrial interest are available in the literature. Data for the ethanol–water system are given in Table 1 and as a graph in Figure 1.

One of the peculiarities of the ethanol–water solution is the formation of an azeotrope at the ethanol concentration of 0.894 (mol fraction). An azeotrope is a homogeneous mixture that has the same composition in the vapor phase as in the liquid phase at boiling point. Therefore, an azeotrope behaves in distillation as a pure substance and not as a mixture. It is therefore impossible to separate an azeotrope into its components by simple distillation. The ethanol–water azeotrope has a boiling point of 78.15 °C at atmospheric pressure, slightly lower than that of pure ethanol. Many mixtures of two or three substances are known to form azeotropes.



**Figure 1.** Ethanol–water vapor–liquid equilibrium curve, in mol%

**Table 1.** Vapor–liquid equilibrium data for ethanol–water mixtures at 1 atm

Ethanol in liquid % mol or % mass	Ethanol in vapor	
	% mol	% mass
0	0.0	0.0
1	6.5	10.0
3	20.5	24.8
5	32.2	38.0
10	43.7	52.0
15	50.1	59.5
20	53.2	64.8
25	55.4	68.6
30	57.5	71.4
35	59.4	73.3
40	61.4	74.7
45	63.2	75.9
50	62.2	77.1
55	67.6	78.2
60	70.3	79.4
65	72.6	80.7
70	75.4	82.2
75	78.6	83.9
80	82.1	85.9
85	85.8	88.3
90	89.8	91.3
95	94.7	95.0
97	96.8	96.9
99	98.95	98.9
100	100	100
Azeotrope mixture	89.40	95.57

## **Steam Distillation**

Steam distillation is one of the principal methods for the manufacture of essential oils and fragrances. Essential oils are mostly mixtures of terpenoid substances. They have relatively high boiling temperatures (frequently above 200°C). Their recovery by ordinary distillation at atmospheric pressure is impractical because they undergo thermal decomposition at such high temperatures. They can be recovered by vacuum distillation but a more economical approach is steam distillation.

Essential oils are practically insoluble in water. The total vapor pressure of a mixture of immiscible substances is equal to the sum of the vapor pressures of the pure components. Consequently, such a mixture will boil at a temperature lower than the boiling point of each of the components. A mixture of an essential oil and water will therefore boil at a temperature below 100°C at atmospheric pressure. This is the basic effect on which steam distillation is based. Saturated steam is bubbled through the material containing essential oils (juices, extracts, spices, herbs etc.). The essential oils are volatilized into the steam and entrained towards the condenser. When the vapors are condensed, a liquid consisting of two immiscible layers is obtained, from which the essential oil is separated by centrifugation or by decantation.

## **Vacuum Distillation**

Reduction of the total pressure in the distillation column provides another means of distilling at lower temperatures. When the vapour pressure of the volatile substance reaches the system pressure, distillation occurs. With modern efficient vacuum-producing equipment, vacuum distillation is tending to supplant steam distillation. In some instances, the two methods are combined in vacuum steam distillation.

## **Applications of distillation**

### ***a) Manufacture of Whisky***

Whisky is a spirit produced by the distillation of a mash of cereals, which may include barley, corn, rye and wheat, and is matured in wooden casks. There are three types of Scotch and Irish whisky: malt whisky produced from 100% malted (germinated) barley, grain whisky produced from unmalted cereal grains and blended whisky which contains 60– 70% grain whisky and 30–40% malt whisky.

### ***b) Manufacture of Neutral Spirit***

A multicolumn distillation plant is used for producing neutral spirits from fermented mash. A typical system would be comprised of five columns: a whisky-separating column, an aldehyde column, a product-concentrating column, an aldehyde-concentrating column and a fusel oils concentrating column. The whisky-separating column is fitted with sieve plates, with some bubble cap plates near the top of the column. The other four columns are fitted with bubble cap plates. The fermented mash containing 7% (v/v) of alcohol is fed to near the top of the whisky-separating column. The overhead distillate from this column is fed to the aldehyde

column. The bottom product from this column is pumped to the middle of the product concentrating column. The end product, neutral spirit, is withdrawn from near the top of this column.

***c) Recovery of solvents from oil after extraction***

Most of the solvent can be recovered by evaporation using a film evaporator. However, when the solution becomes very concentrated, its temperature rises and the oil may be heat-damaged. The last traces of solvent in the oil may be removed by steam distillation or stripping with nitrogen.

***d) Concentration of Aroma Compounds from Juices and Extracts***

By evaporating 10–30% of the juice in a vacuum evaporator, most of the volatile aroma compounds leave in the vapour. This vapour can be fed to a distillation column. The bottom product from the column is almost pure water and the aroma concentrate leaves from the top of the column. This is condensed and may be added back to the juice or extract prior to drying. Fruit juices and extract of coffee may be treated in this way.

***e) Extraction of Essential Oils from Leaves, Seeds, etc.***

This may be achieved by steam distillation. The material in a suitable state of subdivision is placed on a grid or perforated plate above heated water. In some cases the material is in direct contact with the water or superheated steam may be used. If the oil is very heat sensitive distillation may be carried out under vacuum.