

## DISTILLATION OR RECTIFICATION

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### Summary

Distillation (or rectification) is the most important technique for separating fluid mixtures into pure substances. Distillation is extensively used in chemical, petrochemical, pharmaceutical and food industries. This article presents a concise description of the state of the art and of novel developments. The first section deals with the basic principles of distillation processes, for instance, vapor liquid equilibrium and separation mechanisms in countercurrent columns. In the focus are binary as well as multicomponent systems. The second section deals with the equipment of industrial distillation. The design principles of tray columns and packed columns are explained, and typical operational data are given, for instance, capacity, pressure drop and separation efficiency. The last section deals with the conceptual design of complete

separation processes such as: batch distillation, reactive distillation, azeotropic distillation, and extractive distillation. Some examples of important industrial distillation processes are also presented, i.e. sea water desalination, air separation, crude oil refinery and production of absolute alcohol.

## 1. Introduction

Distillation, in Europe often called rectification, is by far the most important technique for separating fluid mixtures in the process industries, and consensus is that it will remain so for years to come. Approximately 95 % of all liquid separations are carried out by distillation processes. This exceptional role played by distillation is founded on the fact that distillation is the only separation technique that is capable to fractionate a fluid mixture into its pure constituents. The disadvantages of distillation are a risk of thermal degradation of the species and a high energy demand.

Distillation uses a very simple principle that consists of three steps. Firstly, generation of a two phase system, secondly, mass transfer across the interface and thirdly, separation of the two phases. This principle is very effective and, therefore, it is also applied to other separation processes. However, in most alternative separation processes, e.g. absorption, adsorption, and extraction, the two phase system is created by the addition of an external substance (entrainer or solvent) that has to be removed later on in an additional separation process. In distillation however, the two phase system (vapor-liquid) is generated by a supply of heat which can easily be removed later on.

Distillation (lat. *destillare* = dripping down) is a very old technique dating back to the first century A.D. Today, distillation is highly developed in all respects, i.e. fundamentals (thermodynamics, vapor liquid equilibrium), process design as well as equipment (packed columns, tray columns). Distillation columns up to 10 m in diameter and 100 m in height can be safely designed, constructed and operated. They dominate the image of many industrial sites, e.g. chemical plants or oil refineries, see Figure 1.



Figure 1: Chemical plant with distillation columns.

## 2. Fundamentals

The basic principle of distillation is to bring a liquid into intimate contact with a vapor so that mass transfer between the two coexistent phases takes place. The driving force for the interfacial mass transfer is the endeavor of each system to reach a state of equilibrium. Therefore, a good knowledge of vapor liquid equilibrium is of essential importance for the design of distillation processes. In distillation, the concentrations of the vapor ( $y$ ) and the liquid ( $x$ ) must be different.

In a distillation unit, the liquid is at the boiling point and the vapor at the dew point. A liquid mixture is at its boiling point if the sum of the partial pressures of all components is equal to the total pressure of the system. According to this condition, a liquid mixture approaches the boiling point either by rising the temperature or by decreasing the pressure. Analogously, a vapor mixture reaches the dew point either by decreasing the temperature or by increasing the pressure. The region between the boiling and the dew points is used in distillation processes.

### 2.1. Vapor Liquid Equilibrium

At equilibrium, the two coexistent phases have the same temperature  $T$ , the same total pressure  $p$ , and the same partial pressures  $p_i$  of all components  $i$ . The partial pressure in the vapor phase is determined by Dalton's law:

$$p_i = y_i \cdot p \quad (1)$$

The partial pressure in the liquid phase is described by Raoult's law, and under supercritical temperatures by Henry's law:

$$\text{Raoult } p_i = \gamma_i \cdot x_i \cdot p_i^0 \quad \text{or} \quad \text{Henry } p_i = \gamma_i \cdot x_i \cdot H_{i,j} \quad (2)$$

In these equations,  $\gamma_i$  denotes the activity coefficient of component  $i$ , which is unity for ideal mixtures. For non-ideal mixtures, it can be either larger or smaller than unity. The values of the activity coefficients depend on all components in the mixture at hand. According to the present state of the art, the values of the activity coefficients are calculated from the free excess enthalpy  $g^E$ . The free excess enthalpy is a thermodynamic quantity which describes the non-ideal behavior of a liquid mixture. There are several well known  $g^E$  functions e.g. van Laar, Margules, Wilson, NRTL, UNIQUAC etc. The parameters in these empirical equations are determined from experimental equilibrium data. Thus, the excess enthalpy only provides a thermodynamically consistent interpolation of the phase equilibrium. A more rigorous method is based on equations of state (e.g. Van-der-Waals, Soave-Redlich-Kwong, Peng-Robinson, Virial equation etc.). However, the use of these equations of state is presently restricted to special applications, for instance, to the processing of natural gas.

### 2.1.1. Binary Mixtures

The vapor liquid equilibrium of binary mixtures is shown in Figure 2 for the cases A: ideal mixtures, B: mixtures with total mixing gap in the liquid, and C: mixtures with an irreversible instantaneous reaction in the liquid.

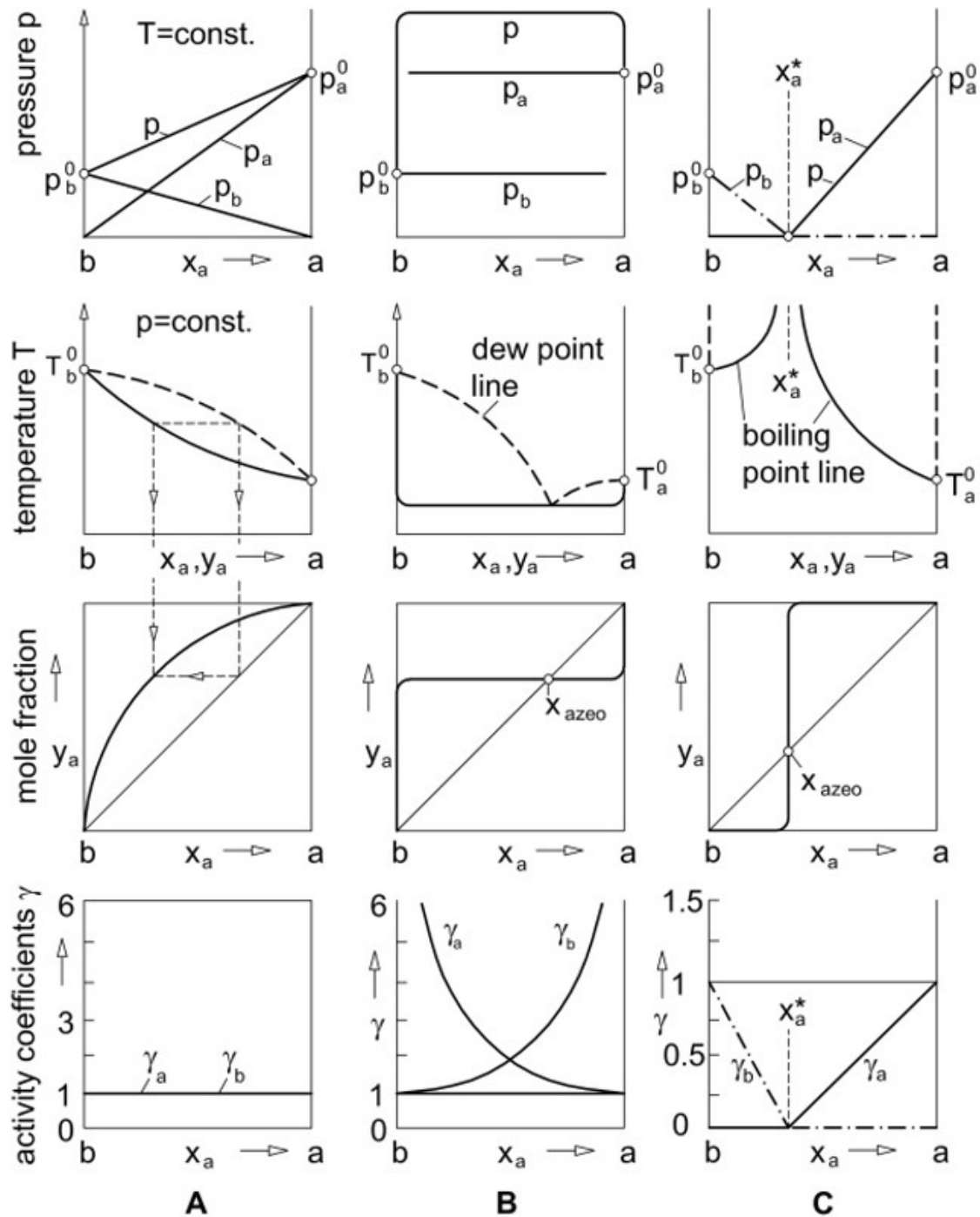


Figure 2: Vapor liquid equilibrium of three binary mixtures. A: ideal system, B: system with a mixing gap in the liquid phase, C: system with irreversible chemical reaction in the liquid phase.

The partial pressures  $p_i$  and the total pressure  $p$  versus the molar concentration  $x$  of the liquid phase at constant temperature are plotted in the upper row. Ideal mixtures show a linear dependence of the pressures on liquid concentration. System B, with a total mixing gap, exhibits an increase of total pressure  $p$ . System C, with chemical

reaction, is characterized by a decrease of the total pressure  $p$ .

The second row shows the boiling and dew point temperatures versus the concentration at constant pressure. In ideal systems, both temperatures monotonously decrease with rising concentrations  $x$  of the low boiler  $a$ . System B shows a boiling and a dew point minimum which is caused by the rise of the total pressure of the mixture. Analogously, system C shows a maximum of the boiling and dew point temperatures.

In the third row of Figure 2, the concentration  $y^*$  of the vapor is plotted versus the concentration  $x$  of the liquid at constant pressure. For ideal systems, the following equation holds:

$$y^* = \frac{\alpha \cdot x}{1 + (\alpha - 1) \cdot x} \quad (3)$$

Here,  $\alpha$  denotes the relative volatility, defined as:  $\alpha \equiv p_a^0 / p_b^0$ .

In the two non-ideal mixtures (systems B and C) the equilibrium curves intersect the diagonal of the diagram. At the point of intersection, vapor and liquid have the same concentration ( $y^* = x$ ). This point is of great importance for distillation. It is called azeotrope.

The fourth row of Figure 2 shows the dependence of the activity coefficients on the liquid concentration  $x$ . System B is characterized by strong intermolecular repulsion forces; hence both activity coefficients  $\gamma_a$  and  $\gamma_b$  are larger than unity. In system C with a chemical reaction (i.e. intermolecular attraction forces), both activity coefficients are smaller than unity. The smaller the concentration of a component  $i$ , the bigger (system B) or smaller (system C) is its activity coefficient  $\gamma_i$ .

Figure 2 shows the three extreme cases of vapor liquid equilibrium. The behavior of real systems, shown in Figure 3, lies in between. The system benzene/toluene is nearly ideal. Here, the intermolecular forces are the same for all molecules. In the systems at the left hand side of Figure 3, the intermolecular forces are increasingly repulsive. In those shown at the right hand side, the intermolecular forces are increasingly attractive.

### Azeotropes

The existence of azeotropes is of primary importance for distillation because at this point, the vapor and the liquid phases have the same concentration, i.e.  $y_i^* = x_i$ . A maximum azeotrope is characterized by a boiling point maximum, and a minimum azeotrope by a boiling point minimum. In multicomponent mixtures, saddle point azeotropes with an intermediate boiling point can exist. At the azeotrope, the mixture behaves like a pure substance. Azeotropes are a barrier to distillation; therefore, the knowledge of azeotropic concentrations is essential for the design of distillation processes. However, alternative separation processes, e.g. absorption, adsorption,

extraction etc., can overcome azeotropes.

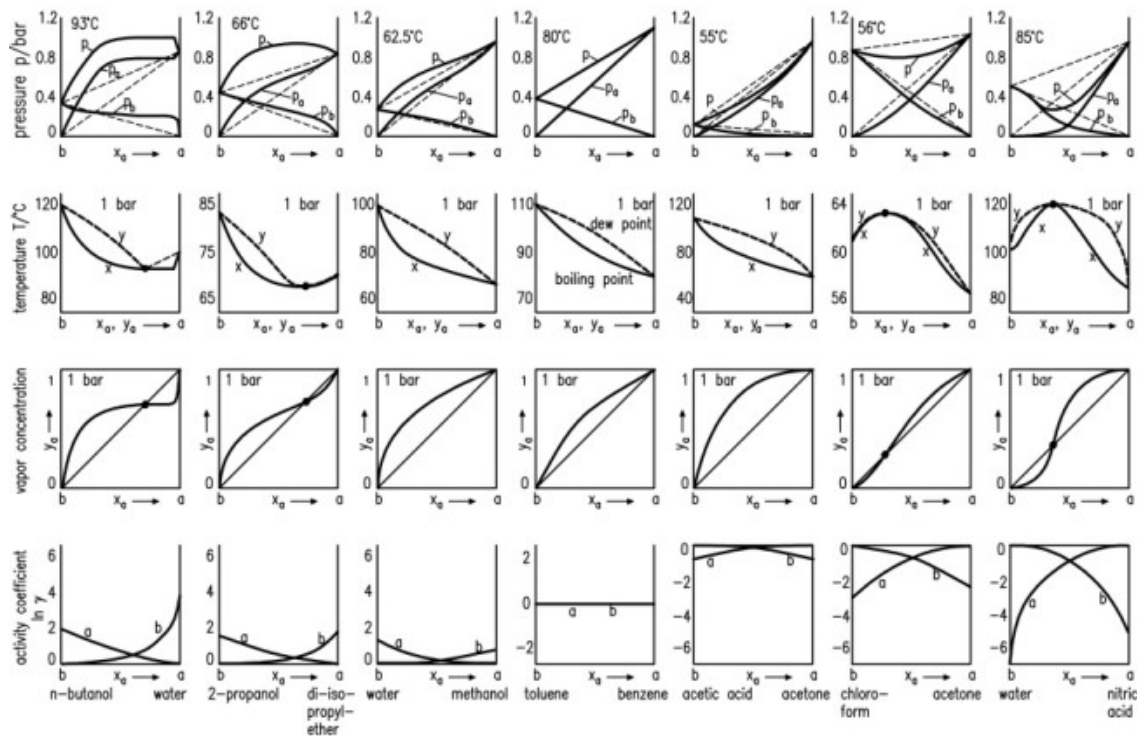


Figure 3: Vapor liquid equilibrium of some real mixtures.

### 2.1.2. Ternary Mixtures

In ternary systems, the vapor liquid equilibrium is also calculated from Dalton's and Raoult's laws. With the definitions  $\alpha_{ac} \equiv p_a^0 / p_c^0$  and  $\alpha_{bc} \equiv p_b^0 / p_c^0$ , equation (3) can be written for ideal systems:

$$y_a^* = \frac{\alpha_{ac} \cdot x_a}{1 + (\alpha_{ac} - 1) \cdot x_a + (\alpha_{bc} - 1) \cdot x_b} \quad \text{and} \quad y_b^* = \frac{\alpha_{bc} \cdot x_b}{1 + (\alpha_{ac} - 1) \cdot x_a + (\alpha_{bc} - 1) \cdot x_b} \quad (4)$$

For non-ideal systems, the values of the activity coefficients have to be calculated from  $g^E$  functions. The ternary coefficients can be determined from experimental data of all binary systems in the mixture.

In ternary mixtures, the vapor liquid equilibrium is graphically represented by distillation lines in a triangular diagram. Distillations lines are given by a sequence of equilibrium stages calculated via the following recursion formula:

$$x_0 \rightarrow y_0^* = x_1 \rightarrow y_1^* = x_2 \rightarrow y_2^* = x_3 \rightarrow y_3^* = \dots \quad (5)$$

Starting from a liquid concentration  $x_0$ , the equilibrium concentration  $y_0^*$  of the

coexistent vapor is determined. This vapor is totally condensed, resulting in a liquid with the same concentration,  $x_1 = y_0^*$ , etc. A sequence of such equilibrium stages constitutes a distillation line. Distillation lines follow the course of a ball rolling down the boiling point surface shown in Figure 4. Thus, distillation lines always start at a local temperature maximum and end at a local temperature minimum. In azeotropic mixtures, there may exist several start and end points of distillation lines. The regions with different start or end points are separated from each other by boundary distillation lines that always run between local temperature extremes of the same type (either maxima or minima). Boundary distillation lines are barriers to ternary distillation, similar to azeotropes in binary mixtures.

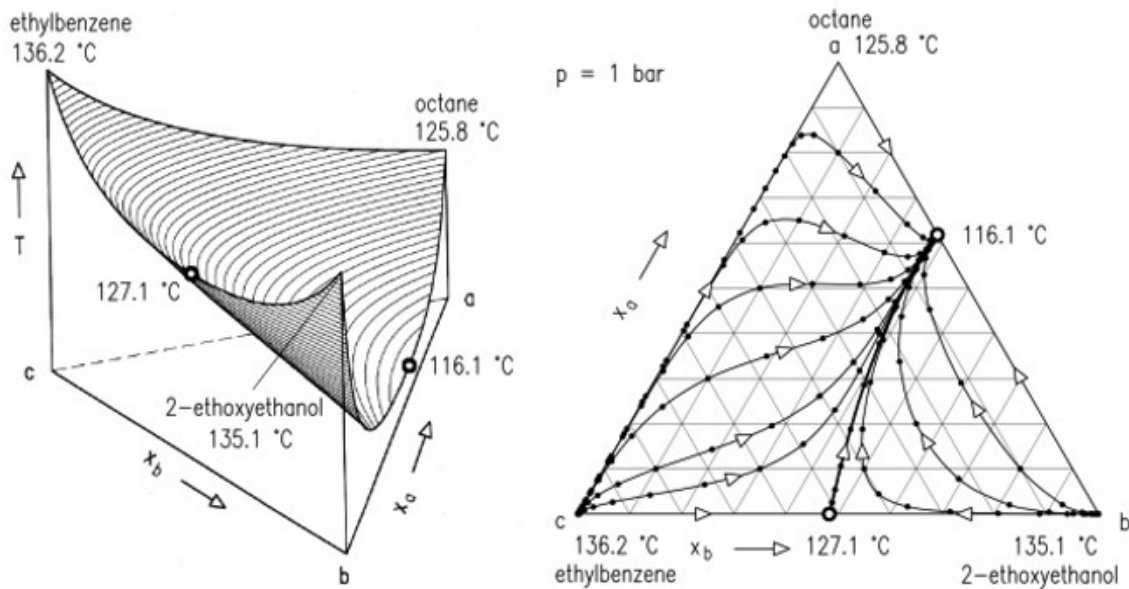


Figure 4: Boiling point surface and distillation lines of the system octane/2-ethoxyethanol/ethylbenzene. ● azeotropes.

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### **Biographical Sketch**

**Johann G. Stichlmair** is Professor of Chemical Engineering at the Technical University of Munich, Germany. A graduate of the Technical University of Munich, he holds a master's (Dipl.-Ing.) and a doctoral (Dr.-Ing.) degree of the same university. He worked several years in industry (Linde, QVF) before he became a full professor at the University of Essen (1980) and Munich (1993). Besides winning several professional awards (Arnold Eucken Award, Kirschbaum Medal), he served nine years as chairman of the German Working Party on Absorption, Distillation and Extraction. From 1995 to 1998 he was vice president of the German Society of Chemical Engineers. He is author of more than 130 papers in scientific journals and of four books.