

Lecture 10

Enhanced distillation and supercritical extraction

When two or more components differ in boiling point by less than approximately 50°C and form a nonideal-liquid solution, the relative volatility may be below 1.10. Then, separation by ordinary distillation may be uneconomical and if an azeotrope forms even impossible. In that event, the following separation techniques, referred to as enhanced distillation by Stichlmair, Fair, and Bravo, should be explored:

1. **Extractive Distillation:** A method that uses a large amount of a relatively high-boiling solvent to alter the liquid-phase activity coefficients of the mixture, so that the relative volatility of the key components becomes more favorable. The solvent enters the column above the feed entry and a few trays below the top, and exits from the bottom of the column without causing an azeotrope to be formed. If the feed to the column is an azeotrope, the solvent breaks it. Also, the solvent may reverse volatilities.

2. **Salt Distillation:** A variation of extractive distillation in which the relative volatility of the key components is altered by dissolving a soluble, ionic salt in the top reflux. Because the salt is nonvolatile, it stays in the liquid phase as it passes down the column.

3. **Pressure-Swing Distillation:** A method for separating a pressure-sensitive azeotrope that utilizes two columns operated in sequence at two different pressures.

4. **Homogeneous Azeotropic Distillation:** A method of separating a mixture by adding an entrainer that forms a homogeneous minimum- or maximum-boiling azeotrope with one or more feed components. The entrainer is added near the top of the column, to the feed, or near the bottom of the column, depending upon whether the azeotrope is removed from the top or bottom.

5. **Heterogeneous Azeotropic Distillation:** A more useful azeotropic-distillation method in which a minimum-boiling heterogeneous azeotrope is formed by the entrainer. The azeotrope splits into two liquid phases in the overhead condensing system. One liquid phase is sent back to the column as reflux, while the other liquid phase is sent to another separation step or is a product.

6. **Reactive Distillation:** A method that adds a separating agent to react selectively and reversibly with one or more of the constituents of the feed. The reaction product is subsequently distilled from the nonreacting components. The reaction is then reversed to recover the separating agent and the other reacting components. Reactive distillation also refers to the case where a chemical reaction and multistage distillation are conducted simultaneously in the same apparatus to produce other chemicals. This combined operation, sometimes referred to as catalytic distillation if a catalyst is used, is especially suited to chemical reactions limited by equilibrium constraints, since one (or more) of the products of the reaction is (are) continuously separated from the reactants.

For ordinary distillation of multicomponent mixtures, the determination of feasible distillation sequences, the design of the columns in the sequence by rigorous

methods, and the optimization of the column operating conditions are tedious, but are relatively straightforward. In contrast, determining and optimizing feasible, enhanced-distillation sequences is a considerably more difficult task. In particular, rigorous calculations of enhanced distillation frequently fail because of liquid-solution nonidealities and/or the difficulty of specifying feasible separations. To significantly reduce the chances of failure, especially for ternary systems, graphical techniques, described by Partin and developed largely by Doherty and co-workers, and by Stichlmair and co-workers, as referenced later, provide valuable guidance for the development of feasible, enhanced-distillation sequences prior to making rigorous calculations. This lecture presents an introduction to the principles of these graphical methods and applies them to enhanced distillation. Doherty and Malone, Stichlmair and Fair, and Siirola and Barnicki give more detailed treatments of enhanced distillation.

Also included is a discussion of supercritical extraction, which differs considerably from conventional liquid-liquid extraction because of strong nonideal effects, and also requires considerable care in the development of an optimal system. The principles and techniques in this chapter are largely restricted to ternary systems; enhanced distillation and supercritical extraction are most commonly applied to such systems because the expense of these operations often requires that a multicomponent mixture first be reduced, by distillation or other means, to a binary or ternary system.

Extractive distillation is used to separate azeotropes and other mixtures that have key components with a relative volatility below about 1.1 over an appreciable range of concentration. If the feed is a minimum-boiling azeotrope, a solvent, with a lower volatility than the key components of the feed mixture, is added to a tray above the feed stage and a few trays below the top of the column so that (1) the solvent is present in the downflowing liquid phase to the bottom of the column, and (2) little solvent is stripped and lost to the overhead vapor. If the feed is a maximum-boiling azeotrope, the solvent enters the column with the feed. The components in the feed must have different affinities for the solvent so that the solvent causes an increase in the relative volatility 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. Generally, a molar ratio of solvent-to-feed on the order of 1 is required to achieve this goal. The bottoms from the extractive distillation column is processed further to recover the solvent for recycle and complete the feed separation. The name, extractive distillation, was introduced by Dunn et al. in connection with the commercial separation of toluene from a paraffin-hydrocarbon mixture, using phenol as solvent.

The use of water as a solvent in the extractive distillation of acetone and methanol has the two disadvantages that a large amount of water is required to adequately alter the relative volatility and, even though the solvent is introduced into the column several trays below the top tray, enough water is stripped by vapor traffic into the distillate to reduce the acetone purity to 95.6 mol%. The water vapor pressure can be lowered, and thus the purity of acetone distillate increased, by use of an aqueous inorganic salt solution as the solvent. For example, a 1927 patent

application by Othmer describes the use of a concentrated, calcium-chloride brine. Not only does calcium chloride, which is highly soluble in water, reduce the volatility of water, but it also has a strong affinity for methanol. Thus, the relative volatility of acetone with respect to methanol is further enhanced. The separation of the brine solution from methanol is easily accommodated in the subsequent distillation step, with the brine solution recycled to the extractive distillation column. The vapor pressure of the dissolved salt is so small that it never enters the vapor phase, provided that entrainment is avoided. An even earlier patent by Van Raymbeke describes the extractive distillation of ethanol from water by using solutions of calcium chloride, zinc chloride, or potassium carbonate in glycerol.

Solute extraction from a liquid or solid mixture is usually accomplished with a liquid solvent at conditions of temperature and pressure that lie substantially below the critical temperature and pressure of the solvent. Following the extraction step, the solvent and dissolved solute are subjected to a subsequent separation step, such as distillation, to recover the solvent for recycle and purify the solute.

In 1879, Hannay and Hogarth reported that solid potassium iodide could be dissolved in ethanol, as a dense gas, at supercritical conditions of $T > T_c = 516\text{K}$ and $P > P_c = 65\text{ atm}$. The iodide could then be precipitated from the ethanol by reducing the pressure. This process was later referred to as supercritical-fluid extraction, supercritical-gas extraction, supercritical extraction (SCE), dense-gas extraction, or destruction (a combination of distillation and extraction). By the 1940s, as chronicled by Williams, proposed practical applications of SCE began to appear in the patent and technical literature. Figure 1 shows the supercritical fluid region for CO_2 , which has a critical point of 304.2 K and 73.83 bar.

The solvent power of a compressed gas can undergo an enormous change in the vicinity of its critical point. Consider, for example, the solubility of *p*-iodochlorobenzene (*p*ICB) in ethylene, as shown in Figure 2, at 298 K for pressures from 2 to 8 MPa. This temperature is 1.05 times the critical temperature of ethylene (283 K) and the pressure range straddles the critical pressure of ethylene (5.1 MPa). At 298 K, *p*ICB is a solid (melting point = 330 K) with a vapor pressure of the order of 0.1 ton; At 2 MPa, if *p*ICB formed an ideal-gas solution with ethylene, the mole fraction of *p*ICB in the gas in equilibrium with pure, solid *p*ICB would be extremely small at about 6.7×10^{-6} or a concentration of 0.00146 g/L. The experimental concentration from Figure 2 is 0.015 g/L, which is an order of magnitude higher because of nonideal-gas effects. If the pressure is increased from 2 MPa to almost the critical pressure at 5 MPa (an increase by a factor of 2.5), the equilibrium concentration of *p*ICB is increased about 10-fold to 0.15 g/L. At 8 MPa, the concentration begins to level out at 40 g/L, which is 2,700 times higher than predicted from the vapor pressure for an ideal-gas solution. It is this dramatic increase in solubility of a solute at near-critical conditions of a solvent that makes SCE of interest.

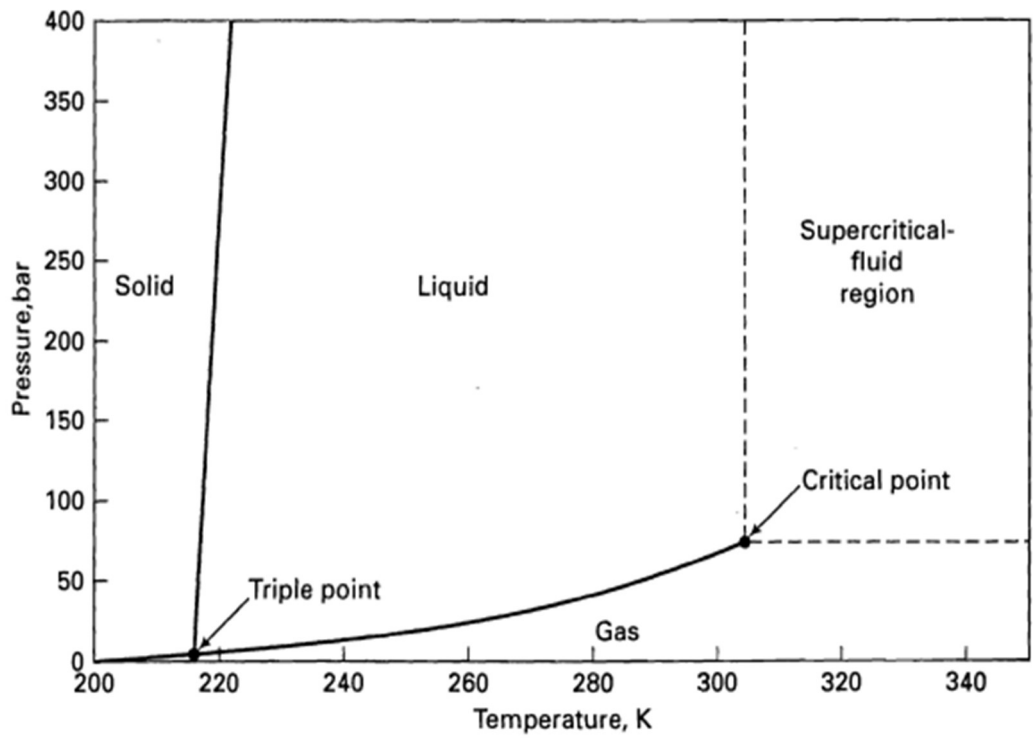


Figure 1 - Supercritical fluid region for CO₂

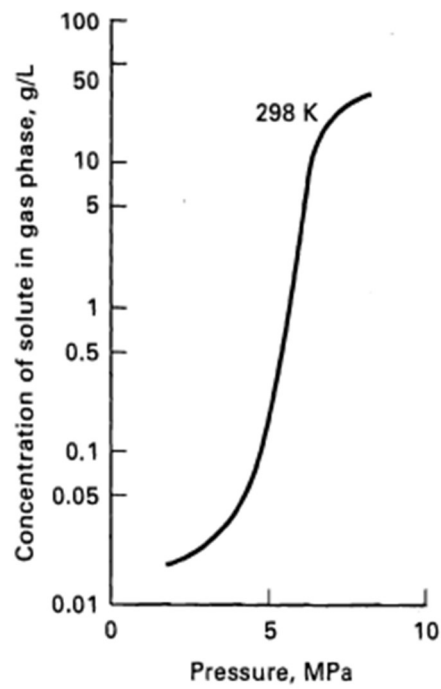


Figure 2 - Effect of pressure on solubility of pICB in supercritical ethylene