Lecture 16.
Enhanced Distillation and Supercritical Extraction (2)
[Ch. 11]

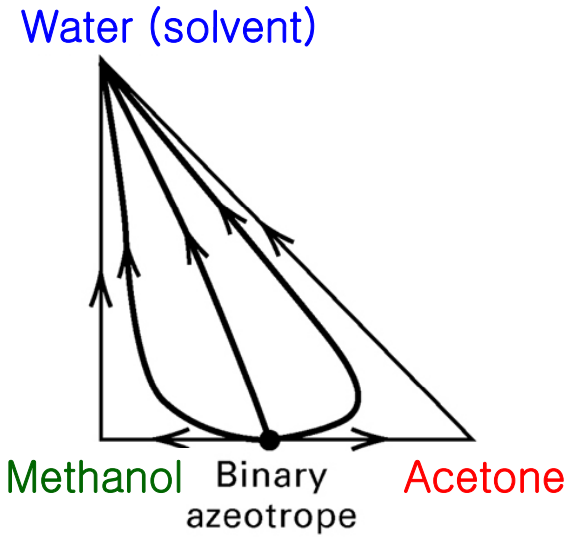
- Extractive Distillation
- Salt Distillation
- Pressure-Swing Distillation
- Supercritical-Fluid Extraction

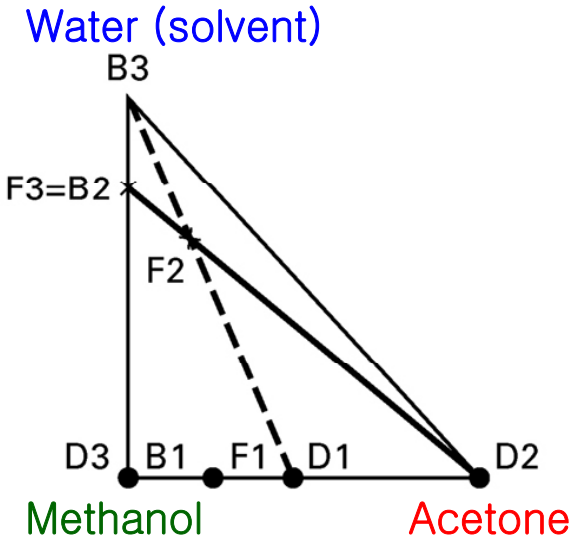
Extractive Distillation

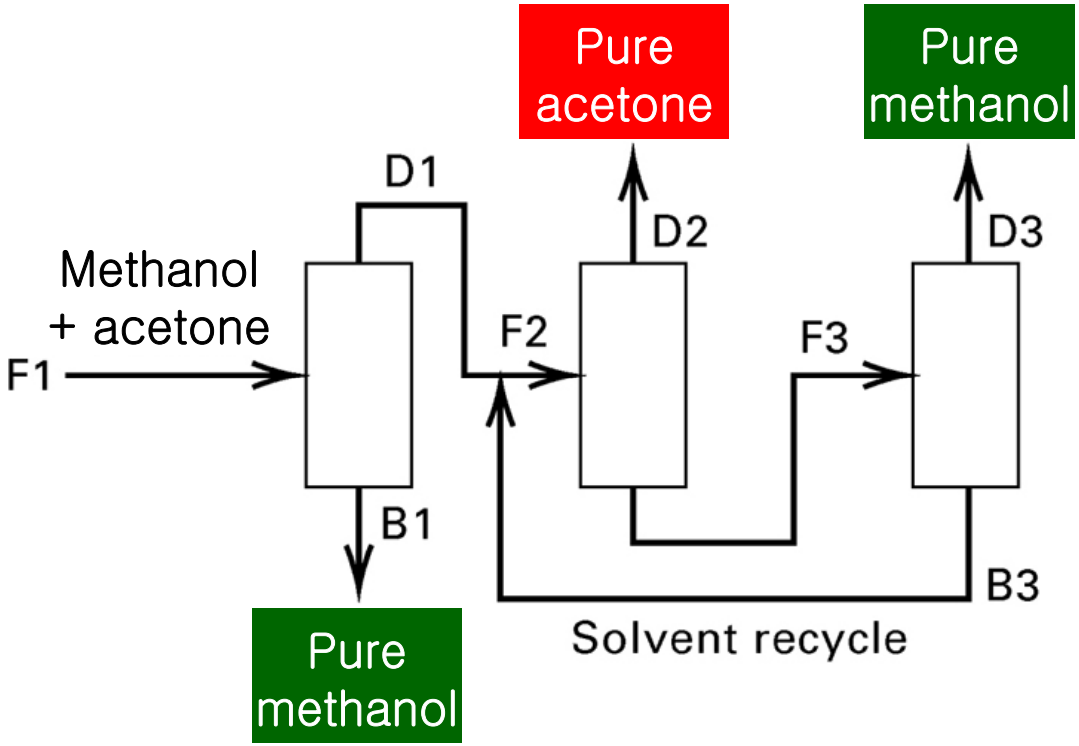
- Use
  - Mixture with azeotrope
  - Relative volatility of key components is below 1.1
- Minimum-boiling azeotrope feed
  : solvent with lower volatility than the key components → added to a tray above the feed stage and below the top
- Maximum-boiling azeotrope feed
  : solvent with different affinities for feed components → added with feed
- Requirement for solvent
  - Should not form an azeotrope with any component in the feed
  - General solvent-to-feed molar ratio is on the order of 1
  - Solvent is recovered from the bottoms for recycle

Distillation Sequence for Extractive Distillation

- Mixture of methanol and acetone (minimum-boiling azeotrope)





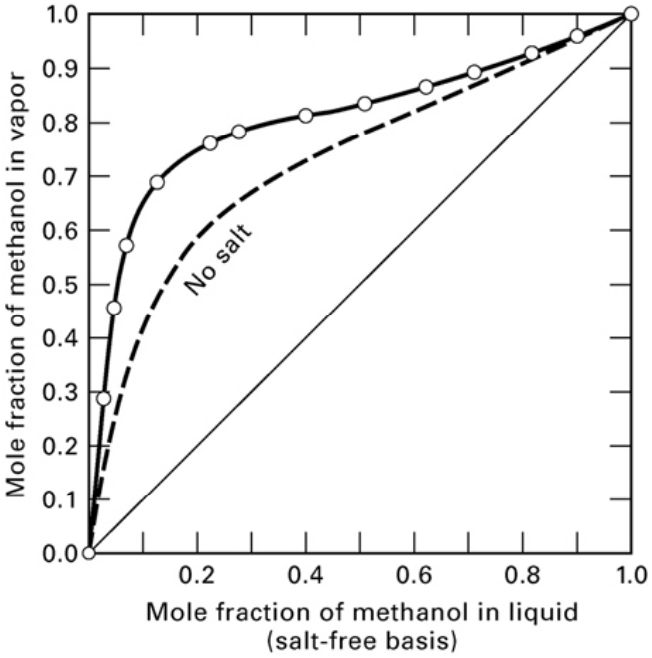


Salt Distillation (1)

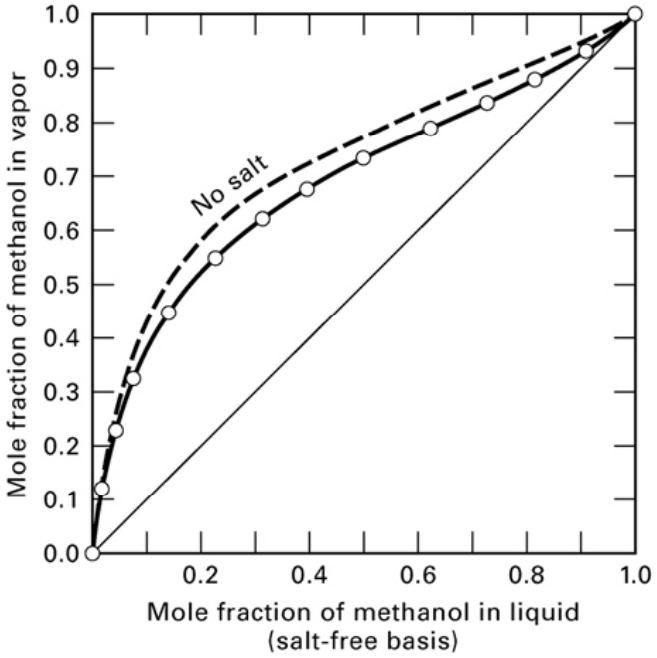
- Disadvantages of using water as solvent
  - Large amount of water is required
  - Water is stripped in acetone product

    ⇒ Water vapor pressure can be lowered using an aqueous inorganic salt solution (e.g. CaCl brine)

Salting-out of methanol by aqueous sodium nitrate



Salting-in of methanol by aqueous mercuric chloride



Salt Distillation (2)

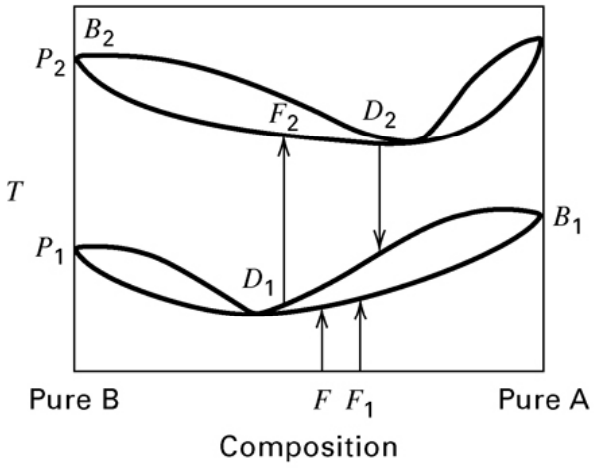
- Rather than using a solvent that contains a dissolved salt, the salt can be added as a solid or melt directly into the column by dissolving it in the liquid reflux

  → The salt is recovered from the aqueous bottoms by evaporation and crystallization

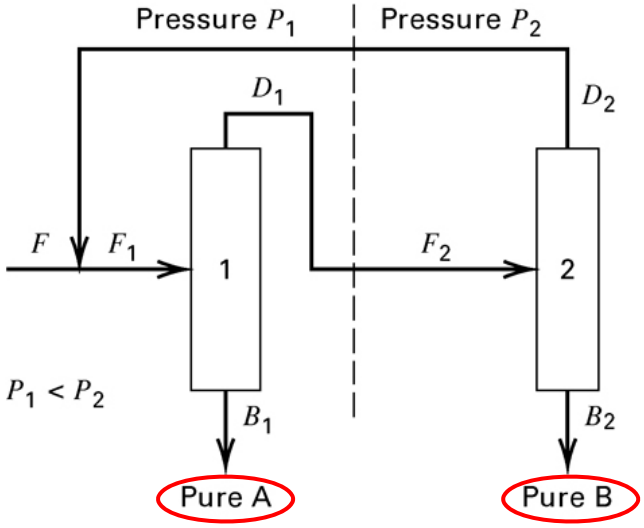
- Potential problems of salt distillation
  - Corrosion
  - The solubility of salt will be low in the reflux (rich in the more volatile component)
  - Bridging in the salt-feeding line
  - The reflux must be maintained near the boiling point to avoid precipitation of already dissolved salt

Pressure–Swing Distillation

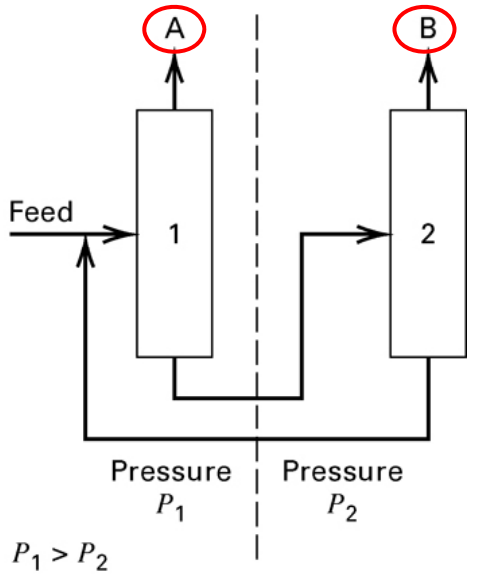
- Pressure-swing distillation (two-column distillation)
  - When a binary azeotrope disappears at some pressure or changes composition by 5 mol% or more
  - The recycle ratio is important in the design and depends on the difference in azeotropic composition for column pressures



Minimum-boiling azeotrope

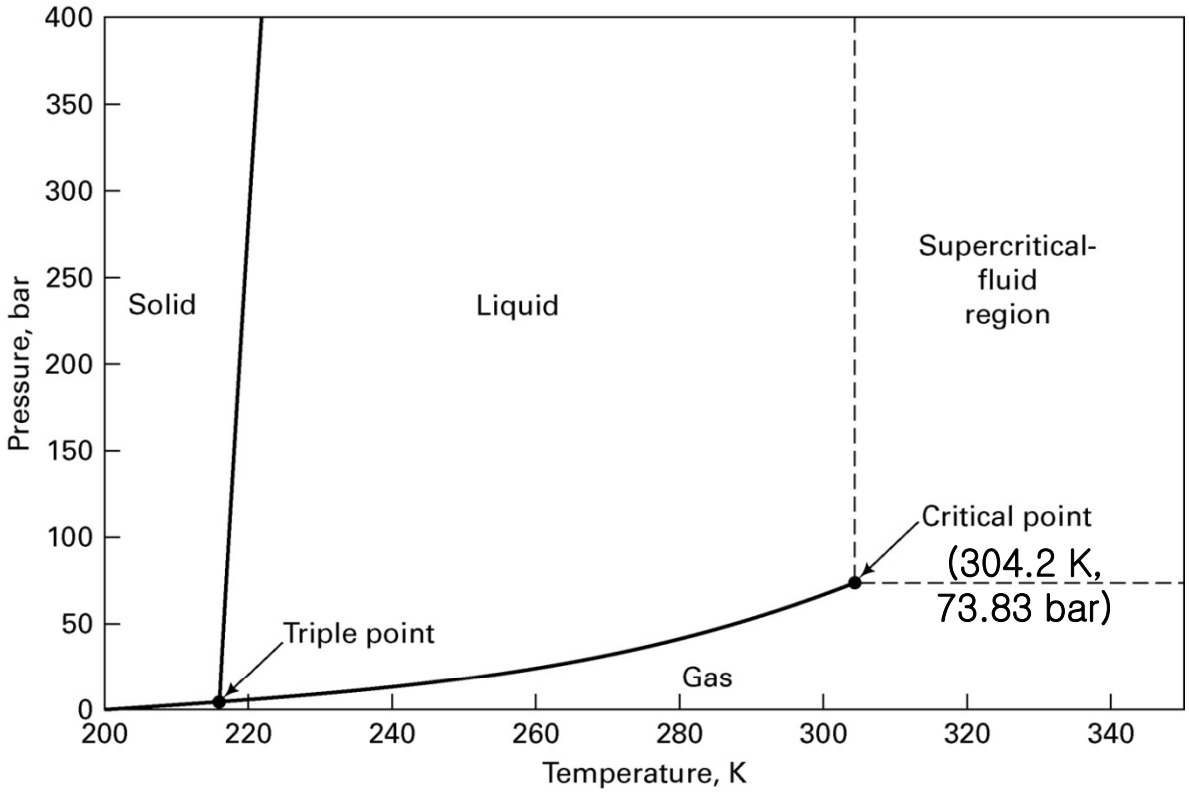


Maximum-boiling azeotrope

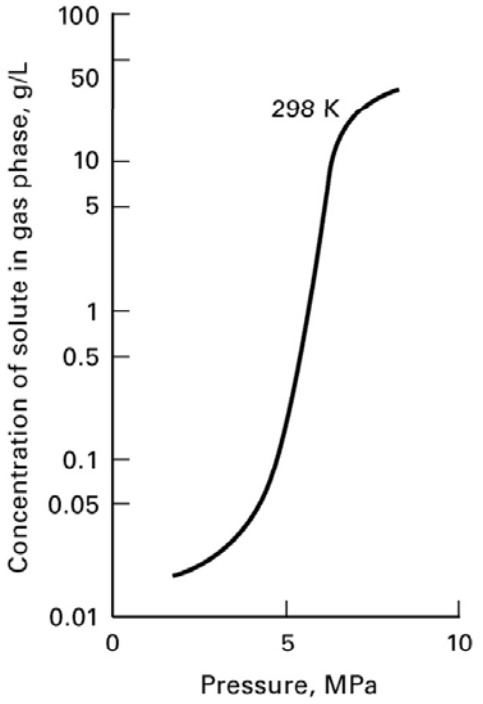


Supercritical-Fluid Extraction (1)

- Supercritical-fluid extraction (SFE), supercritical-gas extraction, supercritical extraction
  : solvent power of a compressed gas can undergo an enormous change in the vicinity of critical point



Supercritical -fluid region for CO_2



Solubility of pICB in supercritical ethylene

Supercritical-Fluid Extraction (2)

- Properties of supercritical fluid
  - Solvent density ↑ while the solubility of the solute ↑
  - As P ↑, closer packing of the solvent molecules allows them to surround and trap solute molecules
  - The diffusivity of solute is one to two orders of magnitude higher than in a normal liquid solvent
    → lower mass-transfer resistance in the solvent phase
  - Viscosity is an order of magnitude less than that of a normal liquid solvent
- SFE is most favorable for the extraction of small amounts of large, relatively nonvolatile solutes in solid or liquid
- Drawback: high solvent-compression costs
- Use: extraction of caffeine from coffee, hops oil from beer, and nicotine from tobacco

Supercritical-Fluid Extraction (3)

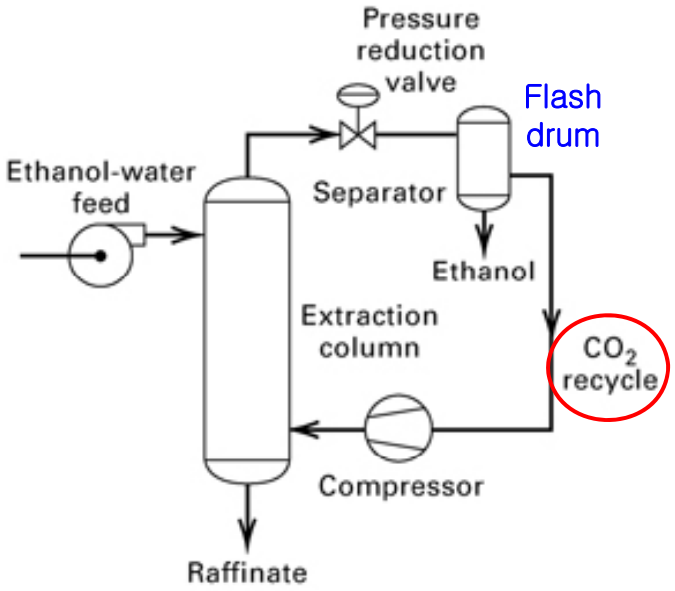
- Solvents for SFE

Solvent	Critical temperature, K	Critical pressure, MPa	Critical density, kg/m^3
Methane	192	4.60	162
Ethylene	283	5.03	218
Carbon dioxide	304	7.38	468
Ethane	305	4.88	203
Propylene	365	4.62	233
Propane	370	4.24	217
Ammonia	406	11.3	235
Water	647	22.0	322

- Carbon dioxide solvent
  - Desirable for undesirable, valuable, or heat-sensitive chemicals
  - Nonflammable, noncorrosive, nontoxic in low concentrations
  - Readily available, inexpensive, and safe
  - Relatively low viscosity and high diffusivity at supercritical condition

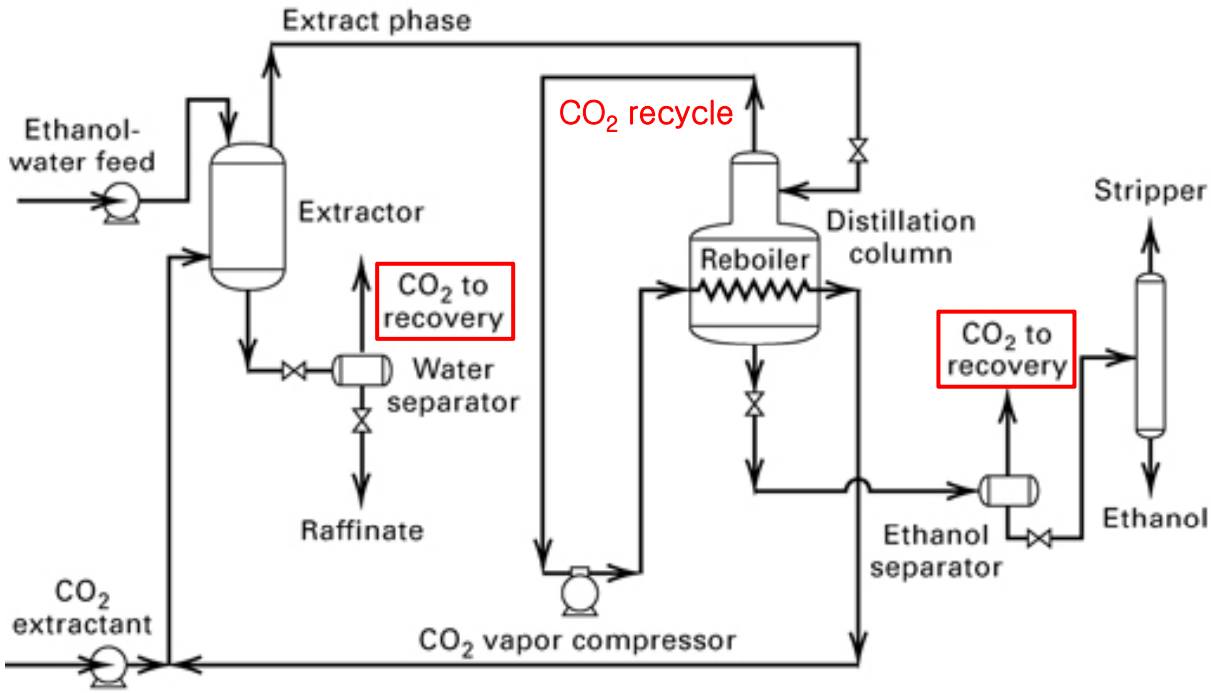
Supercritical-Fluid Extraction (4)

- Recovery of CO_2 in supercritical extraction processes (separation of ethanol and water)



Pressure reduction

High-pressure distillation



Supercritical–Fluid Extraction (5)

- Recovery of CO_2 in supercritical extraction processes (decaffeination of coffee)