Membrane-based recovery and dehydration of alcohols from fermentation broths – of materials and modules

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Motivation
Green Separations Research

• The sustainability of many commercial sectors is inexorably linked to the efficiency of separation technologies
  • Chemicals
  • Pharmaceuticals
  • Biofuels
  • Water/wastewater treatment
8 grand challenges identified:

#6 - Energy intensity of chemical processing

- energy- and cost-efficient separations alternatives are needed

Global energy use in 2003 = $380 \times 10^{15}$ BTU (380 Q/yr)

Separations = \(~15\%\) of total (~57 Q/yr)

6-Fold growth in global commodity production by 2040

“Business as usual” separations in 2040 = 340 Q/yr

Thermally driven separations must be avoided & phased out wherever possible
Membrane-Based Separation Processes

• **Filtration** – separation based on size
  - Particle-
  - Micro-
  - Ultra-
  - Nano-

• **Solution-Diffusion** – permeability-based separation
  - Pervaporation
  - Vapor Permeation
  - Osmosis (Forward and Reverse)
  - Dialysis (including electrodialysis)
Pervaporation = Permeation + Evaporation

Feed Liquid

Permeate Vapor

Non-Porous or Molecularly Porous Membrane (selective for Species 1)

Species 1
Species 2
Vapor Permeation – Pervaporation’s Sister

In Vapor Perm, the feed is a vapor instead of a liquid.

Non-Porous or Molecularly Porous Membrane
(selective for Species 1)

Feed Vapor

Permeate Vapor

Species 1

Species 2
Generic Pervaporation Process

- Feed Liquid
- Heater
- Pervaporation Module
- Retentate Liquid
- Discharge
- Permeate Vapor
- Condenser
- Condensed Permeate
- Vacuum Pump
- Vent

**Diagram Description:**
- Feed Liquid is pumped to the heater.
- The heated liquid passes through the pervaporation module.
- Part of the permeate vapor is vented, while another part is condensed in the condenser.
- The condensed permeate is collected.
- The retentate liquid is discharged.
Membrane Assisted Vapor Stripping (MAVS) – Recovers Latent & Sensible Heat from Vapor Permeation Streams

- Feed Liquid
- Vapor Stripping Column
- Make-up steam
- Effluent
- Condensed Ethanol Product
- Water Permeable Membrane
- Water-rich Permeate Vapor
- Ethanol-rich Retentate Vapor

Vapor Compressor ~ 5:1 ratio
Pervap & Vapor Perm Applications

- Dehydration of Organic Solvents
- Removal of VOCs from Wastewater
- Fermentation Product Recovery
  - biofuels (ethanol, acetone-butanol-ethanol)
  - flavor/aroma compounds
- Organic/Organic Separations
  - reducing sulfur in gasoline
PV/VP membranes can be of any type

- Polymeric
  - Rubbery or glassy polymers
- Inorganic
  - Ceramic, Zeolitic, Metallic, Glass/Silica
- Coating Process
  - Plasma-, Dip-, Cast-, Gel-, Seeded/Grown, Sprayed
- Composite
  - Multi-layer
  - Mixed Matrix
- Supported Liquid
- Charged or Uncharged
**PV/VP modules can be of any type**

- Plate & Frame
- Spiral wound
- Hollow fiber
- Tubular
What Materials/Manufacturing Problems Do They Have In Common?

• Seals and bonding of dissimilar materials
  ▪ Thermal, mechanical, & chemical stresses
    • Vacuum tight
    • Resistant to hot solvent & steam
    • Temperatures up to 130 °C

• Deposition of Defect-Free Thin Films
  ▪ Multi-layer fab

• Long-life selective layers

• Open feed and permeate flow paths

• High packing density
  ▪ Membrane area per unit of module volume
Fouling

• Internal
  ▪ Ex. Sorption in zeolite channels

• External
  ▪ Ex. Cake formation
Pervaporation Modules Are Available in Standard Membrane Formats:

Hollow Fiber, Spiral Wound, …
...Tubular, Monolithic,
…vibrating plate & frame system
Membranes

Typical composite membrane structure

Mixed Matrix Membranes: Zeolite dispersed in Silicone Polymer

50 wt% zeolite selective layer

Ultrafiltration Support
Zeolite in EPA Experimental MMM

- Zeolyst Int. CBV 28014
  - High-silica ZSM-5 (Si/Al = 137)
  - Porous, crystalline SiO₂ (MFI)
  - ~ 0.56 nm pores
  - 2.3 µm particles
PFP membranes are stable at high temperatures and high water contents.

After exposure to hot ethanol/water mixture at 130°C for 30 days.

Vapor Permeation

 kommerical hydrophilic

Permeate water concentration (wt%)

Feed water concentration (wt%)

Perfluoro membrane

Conventional hydrophilic membrane

Spiral-wound membrane module

Challenges:

- Stability of module components in hot ethanol/water mixtures
- Module performance

Low-cost Module Skids

Multiple module housings inside a single pressure vessel reduce cost
Secondary Components May Affect Membranes & Modules

“Simple” fermentation broth
Main Issues

- Stability of seals, adhesives, and membrane materials
- Formation of ultrathin selective layers
- High efficiency and low cost modules