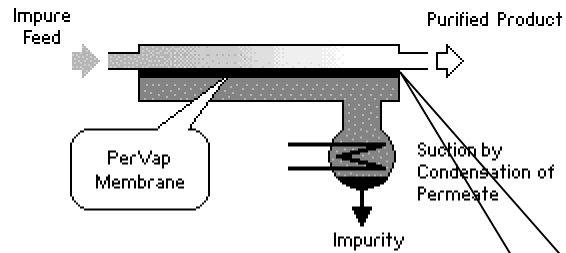
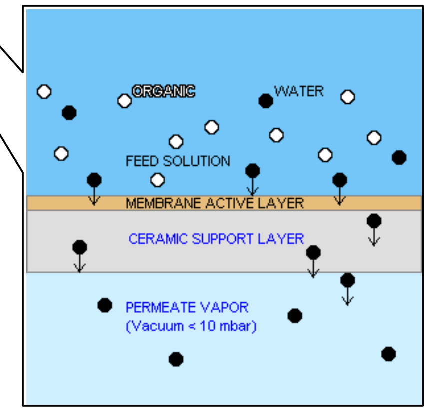
Membrane Technology

- Pervaporation



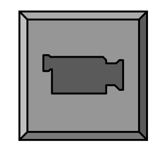


- Discovered 1917.

- Only operation with phase change.

- Non-Porous Membranes.

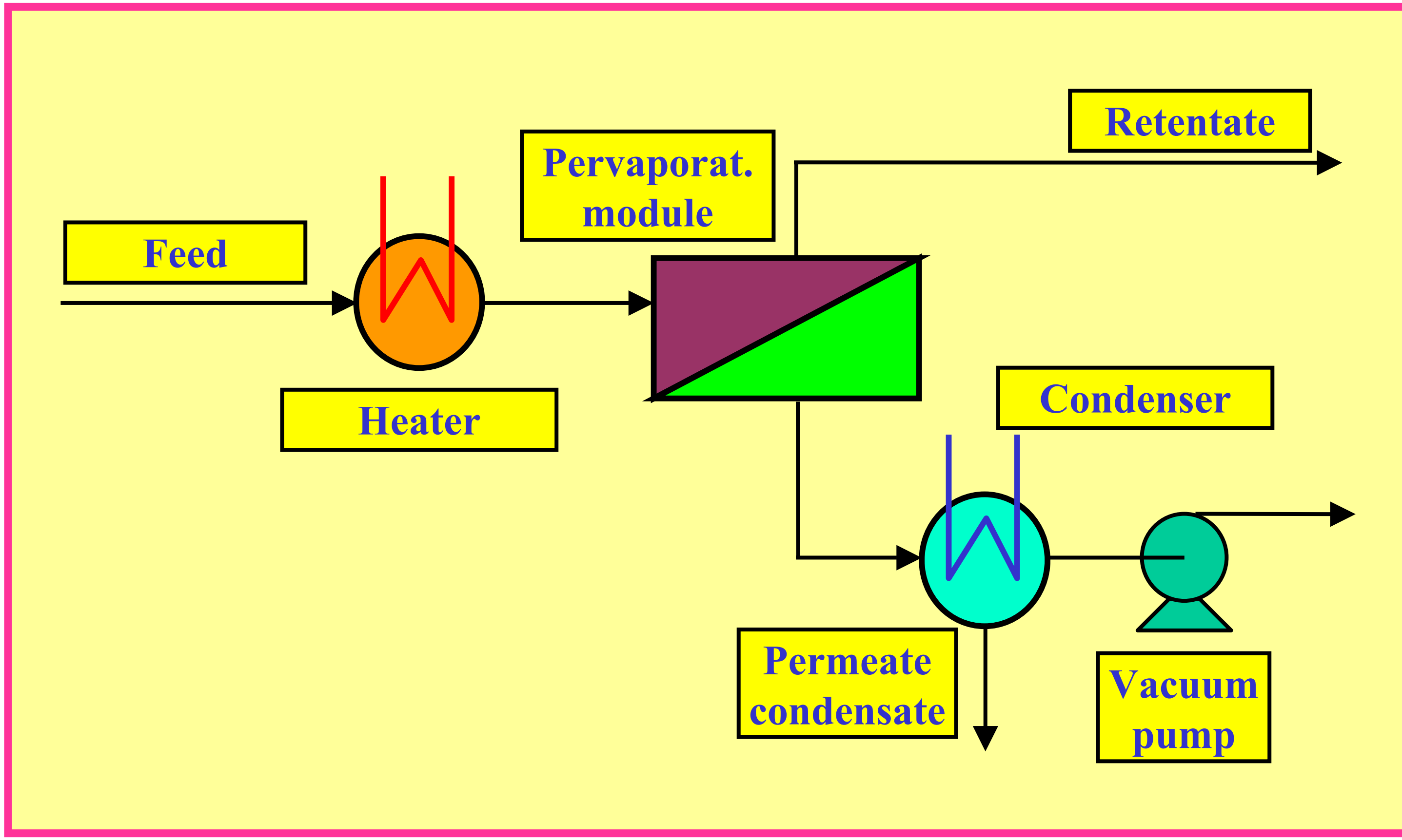
- Mechanism solution-diffusion.



- Driving force: difference in partial pressure.

-Vacuum (<40 mm Hg), dilution (inert gas, N_2) or temperature difference.

- Pervaporation



General Pervaporation system.

- Pervaporation

- Industrial applications.

- Alternative to distillation when thermodynamic limitations.

  - Low energy costs.
  - Low investment costs.
  - Better selectivity, without thermodynamic limitations.
  - Clean and closed operation.
  - No process wastes.
  - Compact and scalable units.

- Pervaporation

- Drawbacks:

  - Scarce Membrane market.
  - Low permeate flows.
  - Limited applications:

    - Organic substances dehydratation.

    - Recovery of volatile compounds at low concentrations.

    - Separation of azeotropic mixtures.

- Pervaporation.

- Do not mistake with a distillation where a membrane is just separating phases.

- Three steps mechanisms:

  - Selective absorption on the membrane.
  - Dissolution at the membrane.
  - Diffusion through the membrane.

- Pervaporation

- The membrane is active in this process.

- The permeability coefficient (P) of a compound depends on the solubility (S) and the diffusivity (D), in the polymeric phase, of the crossing compound

$$P_i = S_i\,(c_i, c_j)\cdot D_i\,(c_i, c_j)$$

- Simplificated transport equation:

$$J_i = \frac{P_i}{d}\cdot\left(x_i\cdot\gamma_i\cdot p_i^o - y_i\cdot p_p\right)$$

J_i: flux of component *i* d: membrane thickness x_i: molarfraction in liquid γ_i: activity coefficient
p_i^o: vapour pressure y_i: molar fraction at permeate p_p: pressure at permeate side

- Pervaporation

- Main membrane parameters:

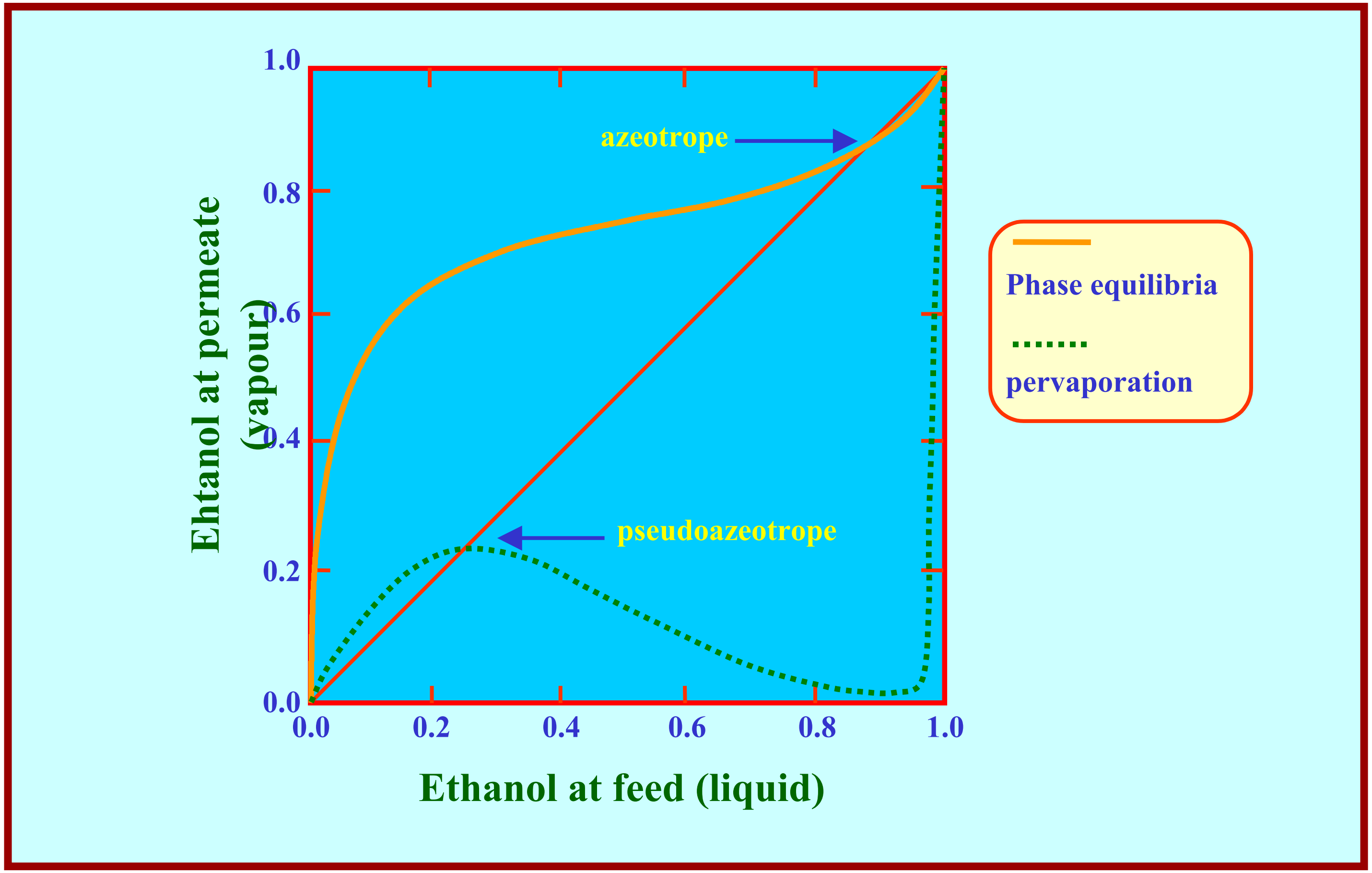
- Separation factors

$$\alpha_{A,B} = \frac{C_{A,p}/C_{B,p}}{C_{A,f}/C_{B,f}} = \frac{\beta_A}{\beta_B}$$

- Enrichment factors

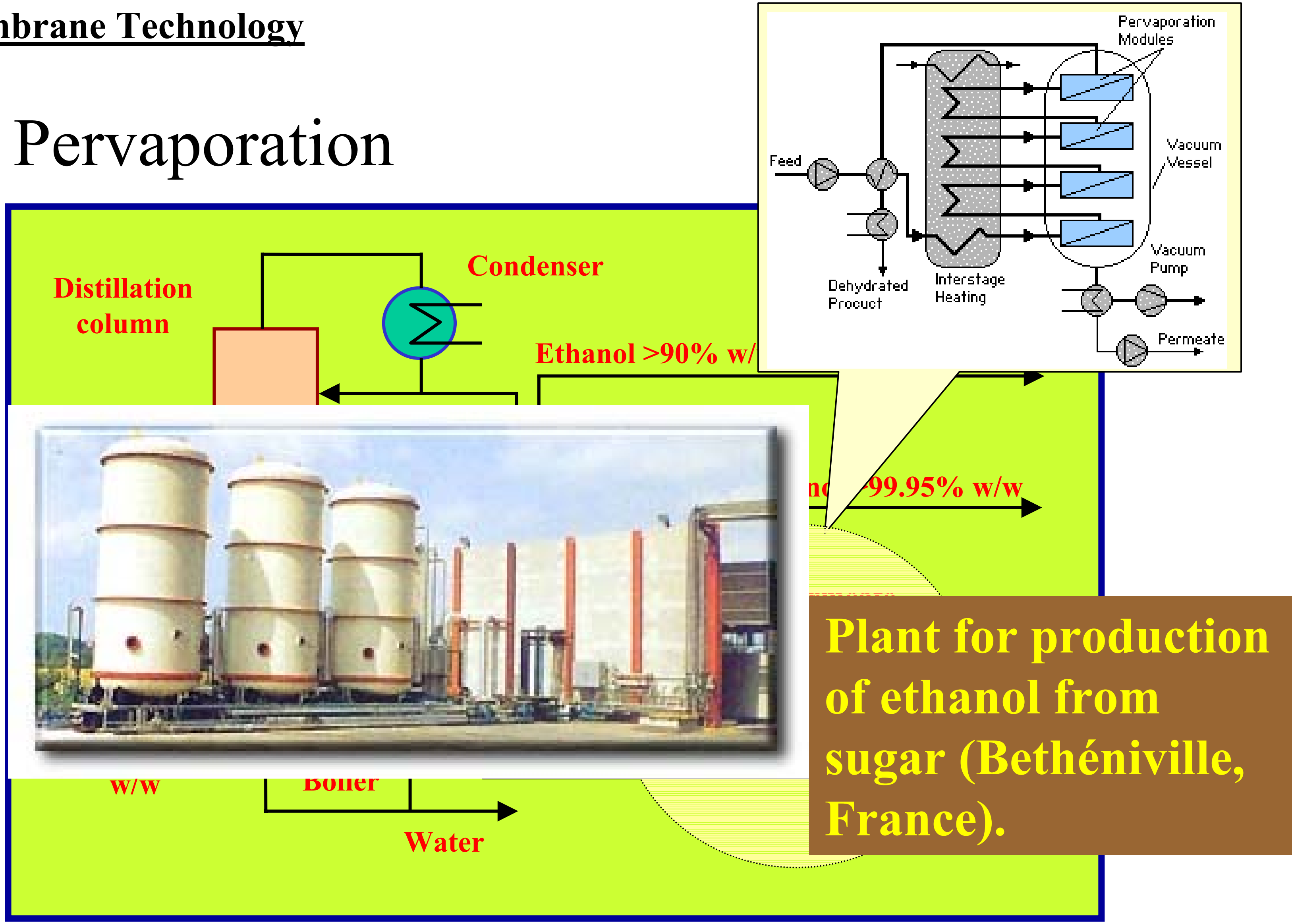
$$\beta_A = \frac{C_{A,p}}{C_{A,f}}$$

- Pervaporation



Pervaporation process of an ethanol/water mixture with a PVA membrane.

- Pervaporation



Combination of distillation and pervaporation for the production of pure ethanol.

- Pervaporation

Dehydration of organic solvents.

Organic solvents to apply pervaporation.

Methanol	Alil alcohol	Ethyl Acetate	Tricloretilene
Ethanol	Furfurol	Buthyl acetate	Tetrachloretane
n-Propanol	Methylfurfurol	Diethyl ether	Tretrahydrofurane
Isopropanol	Diethilenglicol	Diisopropyl ether	Aniline
n-Buthanol	Acetone	Dipropyl ether	Benzene
t-Buthanol	Buthanone	Ethyl propyl ether	Toluene
2-Penthanol	Cyclohexanone	Chloroform	Xylene
Hexanol	Methyl ethyl Ketone	Methyl Chloride	Ethylen diamine
Cyclohexanol	Metil isobuthyl Ketone	Chlorethylene	Ethanol amine
Isoamilic Alcohol	Caprolactame	Dichloro ethylene	Diethyl amine

- Hydrophilic membranes: PVA, PAN...

- Pervaporation

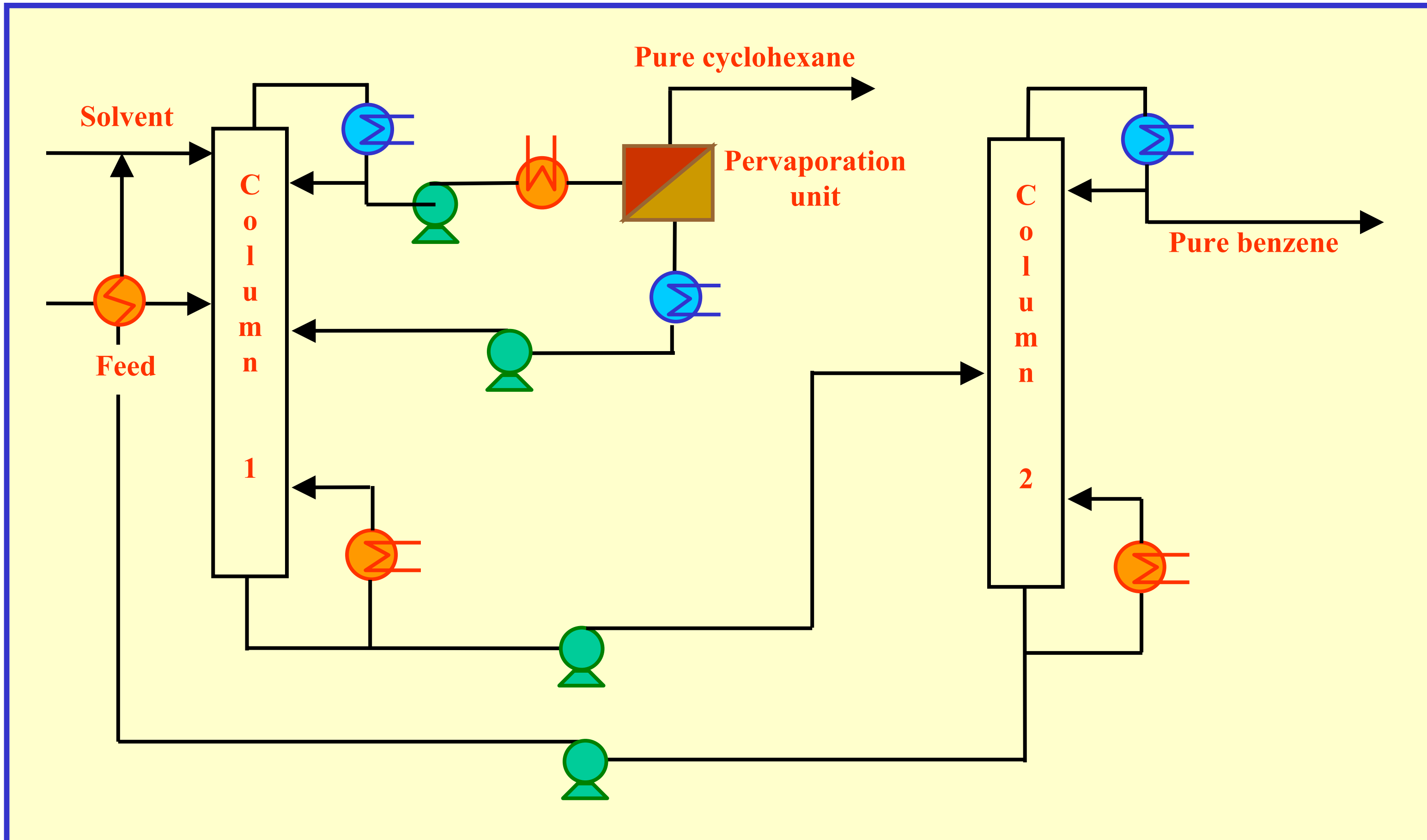
- Organic compounds recovery.
  - For volatile compounds.
  - Economically competitive.
  - Hydrophobic membranes: PDMS and derivatives.
- Azeotrope breaking of organic compounds.
  - Studied at lab scale.
  - Low selectivity.

- Pervaporation

Lab scale separations reported.

Mixture	Membrane	Selectivity
Ethylbenzene/xylene	Polyethylene	Not available
p-xilene/o-xilene	Polyethylene	Not available
m-xilene/p-xilene	Polypropilene	m-Xylene
Dichlor ethane/trichlor ethane	Poliamide/polyeth	Dichlorethane
Benzene/cyclohexane	Polyimide	Benzene
Acetone/cyclohexane	Polyimide	Acetone

- Pervaporation



Hybrid process: extractive distillation and pervaporation for the production of pure benzene and cyclohexane .

- Gas permeation

- Since 50's.

- Membranes: porous and no porous.

- Several possible mechanisms for gas transport:

  X Viscous Flow.

  √ Knudsen Flow.

  √ Solution-diffusion.

- The last two are selective.

- Gas Permeation

- Knudsen Flow (porous membranes). When the porous diameter is on the range of the average free space of the molecule (kinetic theory for gases).

$$J_i = \frac{\varepsilon}{d \cdot \tau} \cdot \frac{D_k}{R \cdot T} \cdot \Delta P_i$$

Transport equation

$$D_k = \frac{2}{3} \cdot r \cdot \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}}$$

Knudsen diffusivity

<u>Enrichment</u>

$$\frac{J_i}{J_j} = \sqrt{\frac{M_j}{M_i}}$$

ε: porosity
τ: tortuosity
T: temperature
r: porus radi
M: MW
d: membrane thickness
R: gas constant
ΔP: transmembrane P

- Gas permeation

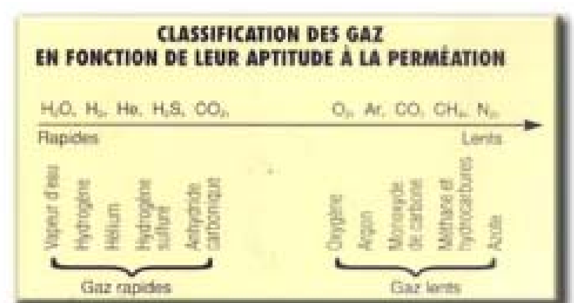
-Solution-diffusion (non-porous membranes).

$$P_i = S_i \cdot D_i$$

The selectivity is referred to the separation factors of the compounds to be separated

$$\alpha_{ij} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \cdot \left(\frac{S_i}{S_j}\right)$$

There are “slow” and “fast gases” for a determined membrane.



- Gas permeation

  - Driving force: partial pressure gradient.
  - Working pressure: up to 100 bar.
  - Non-porous polymeric membranes:

    PDMS, CA, PS, PES i PI

  - Ceramic Membranes (small pores for Knudsen).

  - Metallic membranes (Pd and Ag alloys).

- Gas permeation

- Asymmetric membranes.
- Thin polymer on a structural porous material.
- Preferred configuration Hollow Fiber or Spiral, others like flat or tubular also possible.

- Applied in petrochemistry.

- Purification of H_2, CO_2, CH_4 and gaseous hydrocarbons of difficult distillation.

- Nitrogen purification.

- Gas permeation

- Some examples:

- Enrichment, recovery and dehydration of N_2.

- H_2 recovery in residual flows of proceses, purge o natural gas.

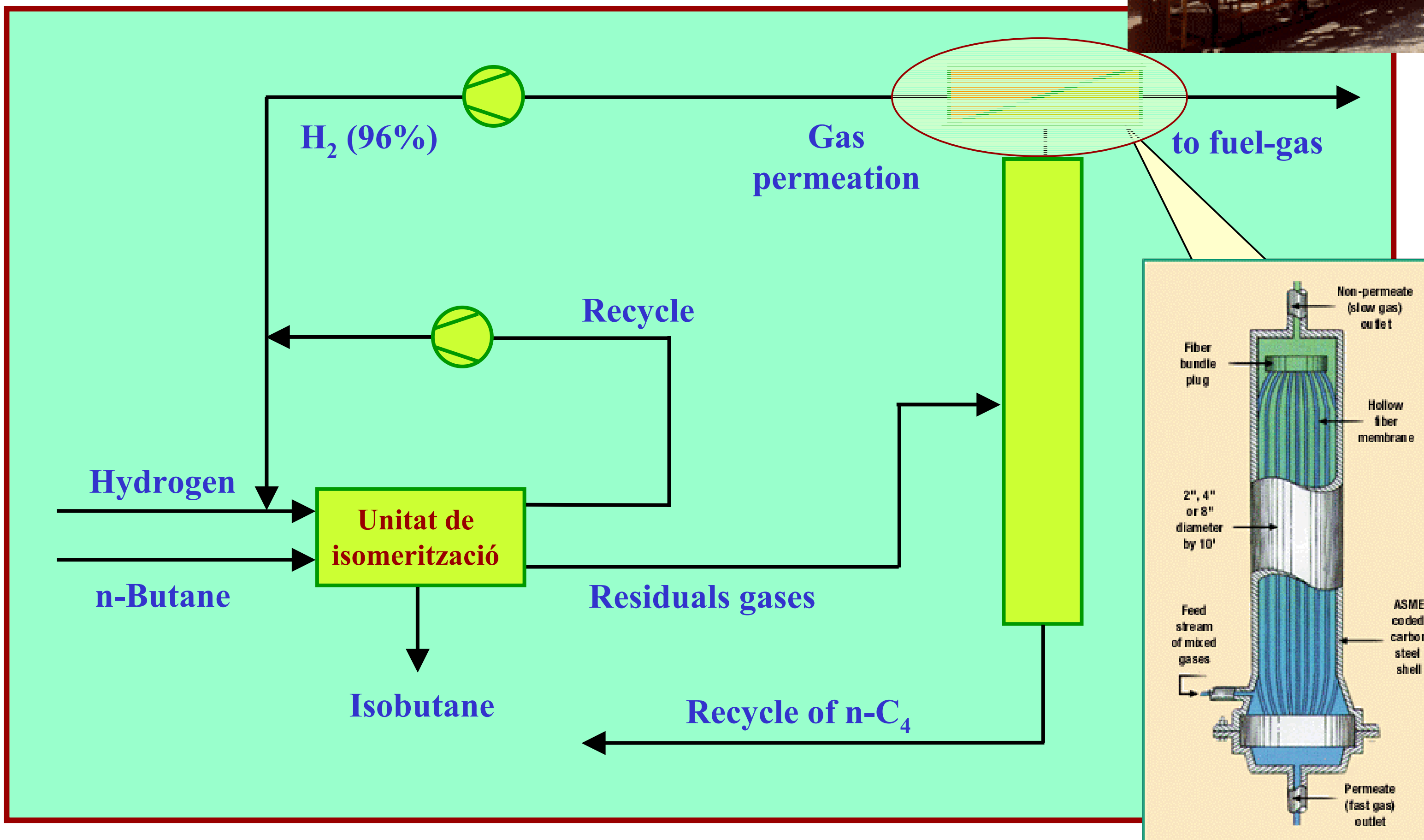
- Adjust of the ratio H_2/CO synthesis gas.

- Acid gas removal (CO_2, H_2S) from natural gas.

- Helium recovery from natural gas and other sources.

- VOC removal from process flow.

- Gas permeation



Hydrogen recovery in a butane isomeration plant.

A typical PRISM® Separator (Airproducts)

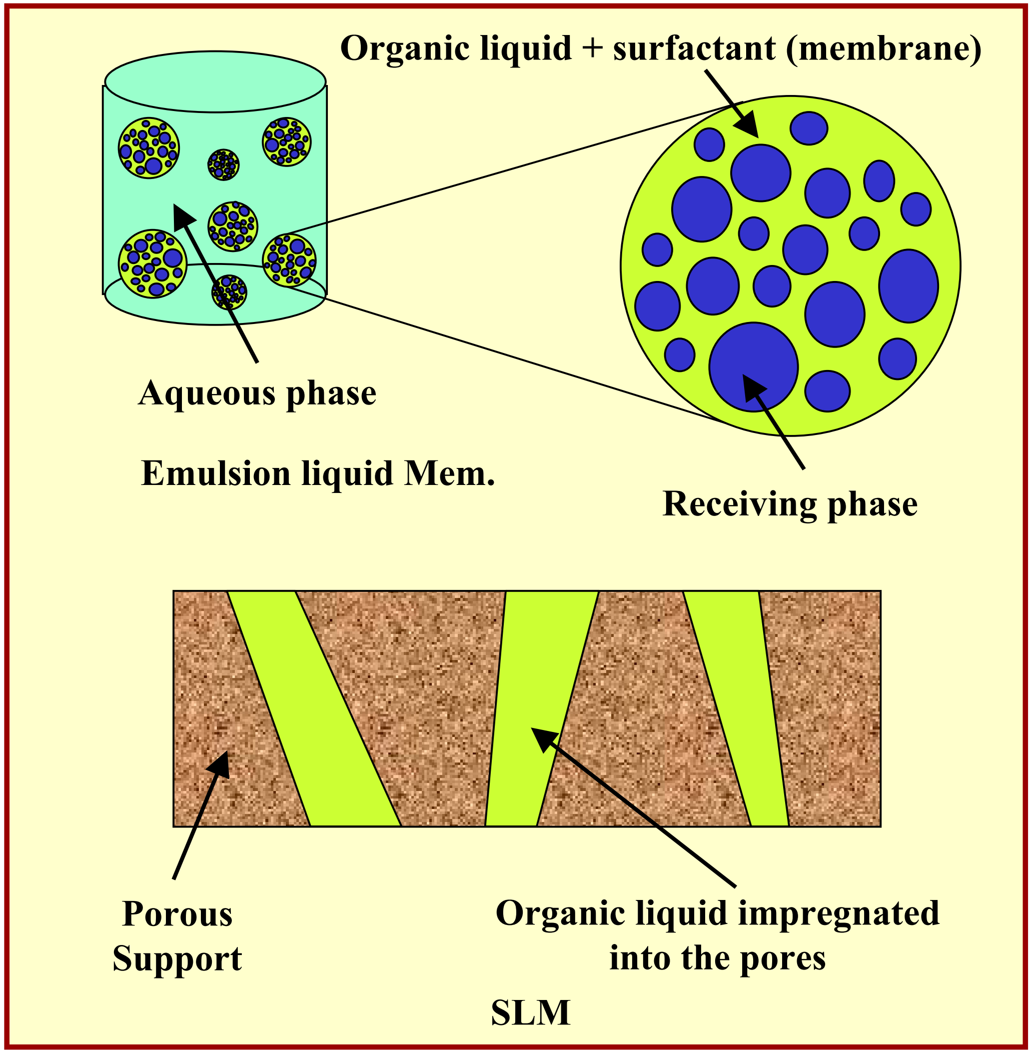
- Liquid Membranes

- A liquid barrier between to phases.

- Not yet industrial uses.
- Driving force: chemical potential, concentration.
- Two configurations:
  - Emulsion (ELM).
  - Supported Liquid Membranes (SLM).

• Liquid Membranes

Possible configuration for LM.



• Liquid Membranes

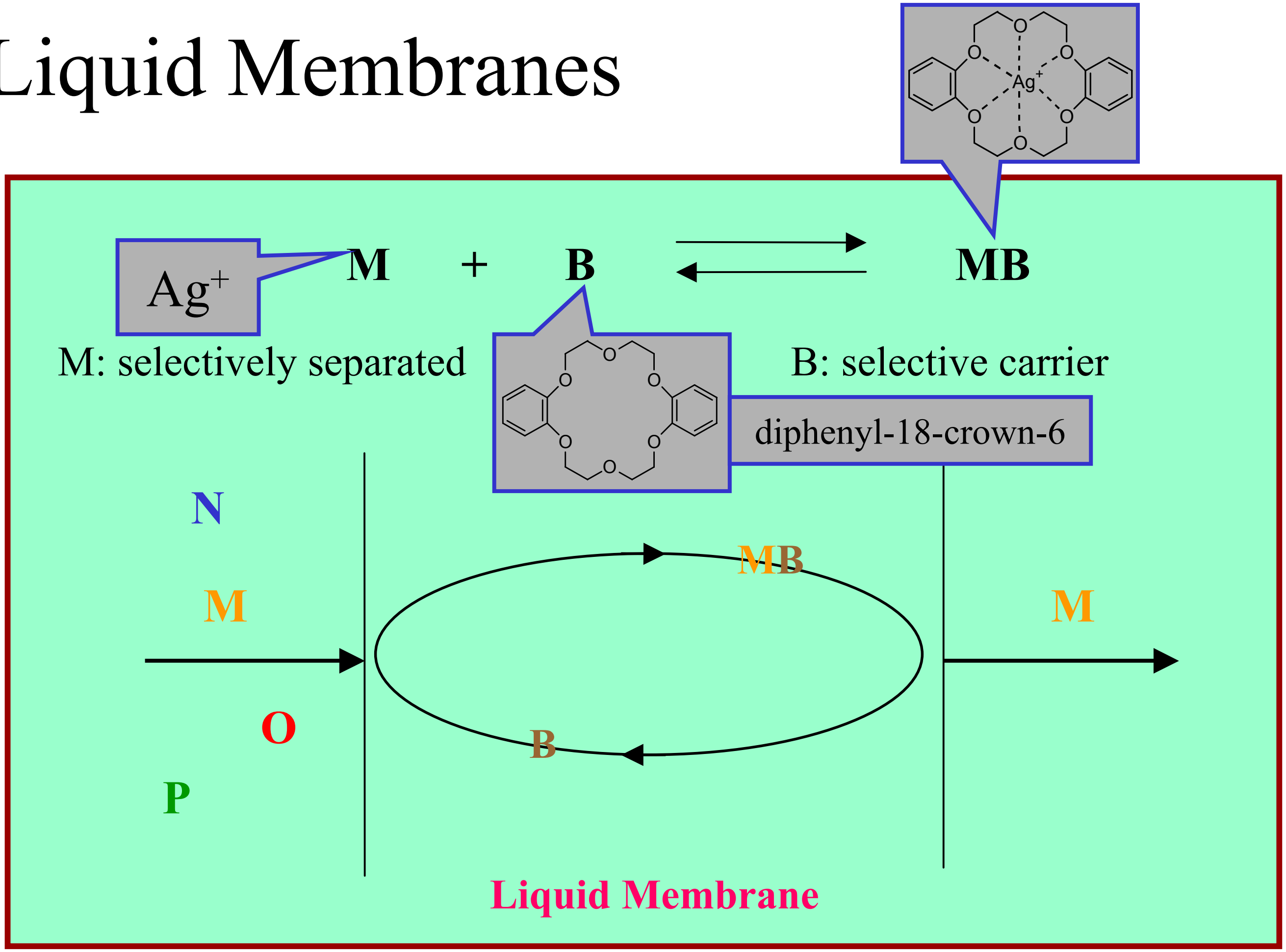
- Advantages:

- High flows due to the transport velocity in liquids.
- Selective separations due to the presence of specific reagents.
- Pumping effect (against the gradient) due to the carrier equilibrium.
- Small quantities of solvent lets to the application of expensive solvents.

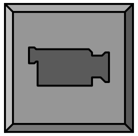
- Drawbacks:

- Low stability of emulsions in ELM.
- Leaching out of organic phase from the pores of a SLM .

- Liquid Membranes



Facilitated Transport in Liquid Membrane.



- Liquid Membranes

  - ELM: low practical interest
  - SLM: lab scale and few applications restricted high added value compounds.
  - Hydrophobic Membranes (PE, PP ...).
  - Hollow fibers.
  - Potential applications:

- Selective removal and concentration of cations in solution.
- Selective separation of gases.
- Recovery of acid or basic compounds.
- Organic compound separation in complex mixtures.

- Other Techniques

  - Membrane distillation.

- A hydrophobic membrane separates two aqueous phases.
- The volatile compounds cross the membrane and condensate.
- The hydrophobic membrane avoids the aqueous phases to get into the membrane.
- The driving force in the temperature gradient.

- Other techniques

- Membrane distillation.

- Driven by the phase equilibrium in both sides of the membrane.
- The membrane acts just like a physical barrier.
- Some applications:
  - ♦ Water demineralization.
  - ♦ Inorganic acid or salt concentration.
  - ♦ Ethanol extraction at the fermentation.

- Other techniques

  - Osmotic distillation.

- Similar to membrane distillation.
- Both phases at the same temperature.
- The partial pressure gradient due to the osmotic pressure is the driving force.

- The osmotic pressure is risen by adding appropriate compounds to the receiving phase.
- Attractive to the food industry provided it maintains the temperature.
  - ♦ Alcohol removal from wine and beer.
  - ♦ Fruit juice enrichment.

- Other techniques

  - Membrane extraction.

- The membrane acts as a barrier to separate immiscible phases.
- It has to assure immiscibility between phases.
- Hollow Fiber membranes have high area.
- It makes possible to avoid the separation at decanting of the phases at the end.
- Lab scale research.