University of Santiago de Chile
Department of Chemical Engineering

Membrane Technologies and Supercritical Fluids: Chemical Engineering for coupled processes

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CONTENTS

- Presentation of the Membrane Processes Team (USACH)

- SCF and Membrane Technology: State of the art

- Separation of mixtures containing supercritical solvents through microporous membranes

- Coupling SCF and no conventional membrane processes: modeling and simulation of the extraction by membrane contactors using supercritical solvents

Laboratory of Membrane Processes

Dr. Aldo Saavedra, Dr. Julio Romero, Dr. Valeri Bubnovich

14 under graduate y graduate students

Participation in 10 Research Projects (FONDECYT, FONDEF, USACH and UNESCO) from 1995

Research Subjects

✓ Applications of MF, UF, NF and RO to food industry and wastewater treatment
✓ ED and polyelectrolyte enhanced ultrafiltration (PEUF) for treatment of drinking water
✓ Membrane contactor operations (OD, MD, VMD and liquid-liquid extraction)
✓ Processes coupling SCF and Membrane Technology (separation by microporous membranes and porocritical extraction)

International cooperation

European Institute of Membranes (CNRS, Montpellier, France), **University of San Luis** (Argentine), **Joint Research Team "Supercritical Fluids and Porous Media"** (CEA/CNRS/UM2/ENSCM)

STATE OF THE ART

From 1992: Several membrane applications connected to SC CO_2

Improvement of membrane preparations in term of chemical resistance

→

Fractionation of SC CO_2/EtOH and SC CO_2/iso-octane using asymmetric Kapton® membrane (*Semenova and Ohya, 1992*)

Fractionation of water/EtOH mixtures in presence of SC CO_2 using a RO membrane (*Hsu and Tan, 1993*)

When SC CO_2 is used as a solvent for extraction, it is interesting to recover CO_2, without performing a pressure drop

→

A membrane process is proposed within the SCF cycle reducing drastically the energy losses.
80-90% of low volatile compounds (LVC) discharged from SC CO_2 using a NF membrane
(*Birtigh, 1995; Sartorelli and Brunner, 2000*)

STATE OF THE ART

Nanofiltration coupled to SFE *(Sarrade, 1994)*

NF and SFE are intended to act on the same chemical species (i.e. low molecular weight compounds up to 1500 Dalton)

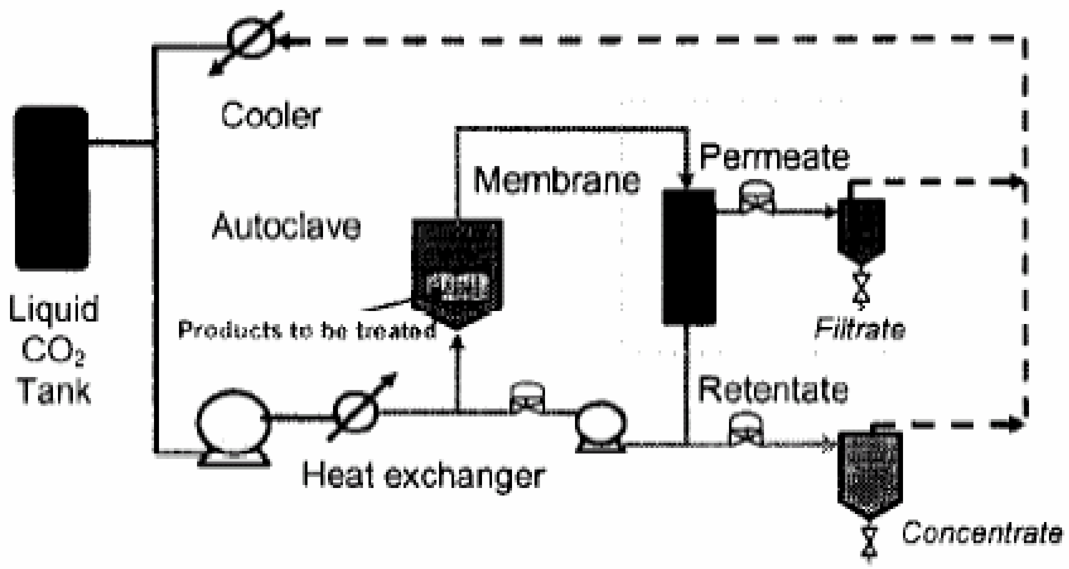
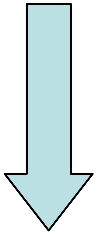


Fig. 1. Nanofiltration plus supercritical fluid extraction process. Flow rate: 0.5–3 $m^3.h^{-1}$; T_{max} = 423 K; P_{max} = 35 MPa.

Hybrid membranes:
Nafion® layer supported on a TiO_2 with a mean pore diameter of about 10 nm)



Mass transfer mechanism proposed:

CONVECTION ?

STATE OF THE ART

Nanofiltration coupled to SFE *(Sarrade, 1994)*

ADVANTAGES

✓ High permeate flux (low viscosity of SC CO_2, ten times lower than for water)

✓ Good control of the whole extraction/separation process. In the conventional SFE the choice of optimal extraction conditions is often blocked by a preoccupation with a good final fractionating of extracts

✓ Two functions (extraction and separation) may be optimised separately

STUDIED SYSTEMS

- Separation of model solutions constituted of small PEGs-SC CO_2
- Extraction/separation of EPA and DHA from fish oils
- Extraction/separation of β-carotene (Provitamin A) and yellow-orange colorants of agro-food industries

SCF assisted ultrafiltration *(Rodriguez et al., 2002)*

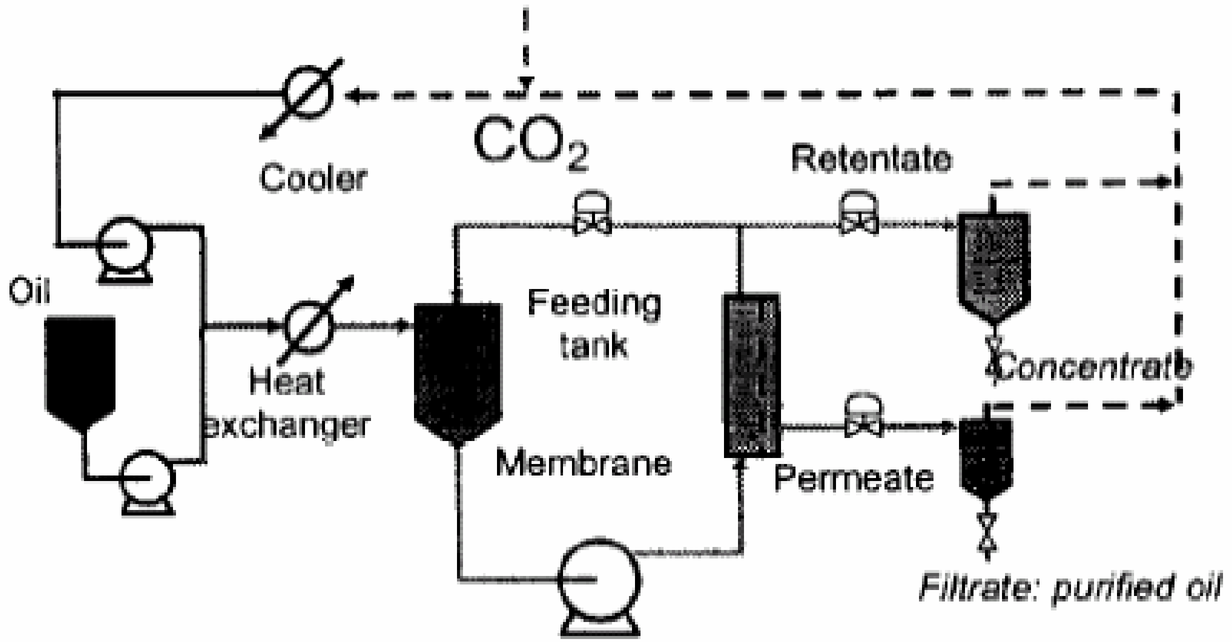


Fig. 2. Pilot-plant for SCF assisted ultrafiltration. Flow rate: 0.5–3 $m^3.h^{-1}$; $T_{max} = 423$ K; $P_{max} = 35$ MPa.

STATE OF THE ART

SCF assisted ultrafiltration *(Rodriguez et al., 2002)*

UF of highly viscous liquids (particulary oils) is an uneasy and expensive operation (up to 350ºC, adding chemicals, improved equipment security)

Low permeate flux and high energy consumption

Cross-flow UF: profiting the properties of SC CO_2 (20 MPa and 150ºC)
- *low viscosity*
- *low surface tension*
- *“tunable” solvent power*

PEGs solutions + SC CO_2: viscosity reduced 6 times
Used motor oil + SC CO_2: viscosity reduced 9 times

UF of SC CO_2-used oils
Flow increasing higher than 300%; P_{opt}= 15 MPa
Inorganic membrane: ZrO_2 (MWCO = 50-300 kD)

Excelent rejection of metals (Fe, Zn, Cu): 96% and 99% depending on species for a mass concentration factor of about 27

SCF assisted ultrafiltration *(Rodriguez et al., 2002)*

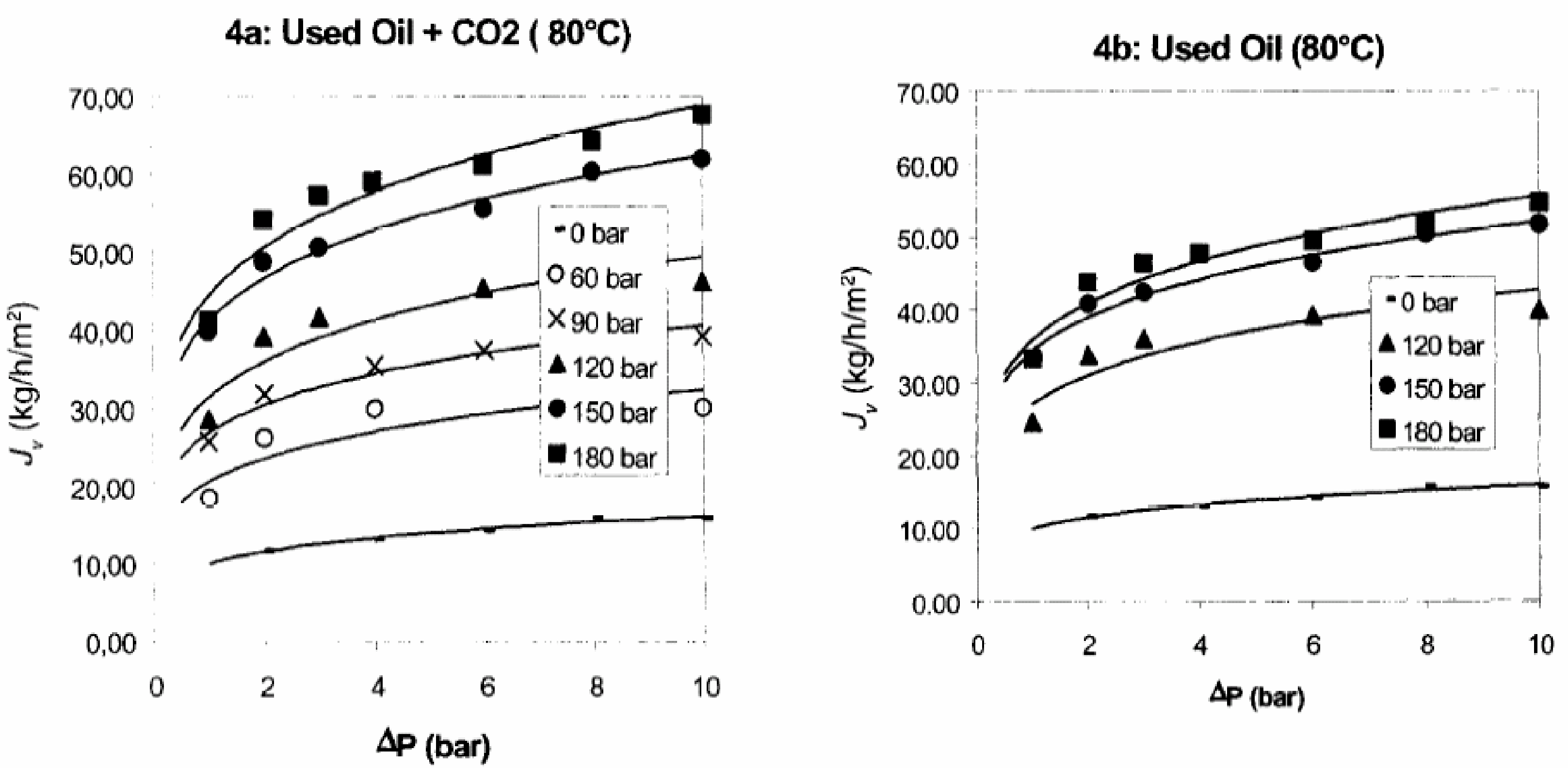


Fig. 4. Influence of transmembrane and CO_2 pressures on oil permeate flux (a): Jv = mixture flux; (b): Jv = net flux in oil).

RESEARCH ACTIVITIES IN USACH

Subject 1: Permeability and selectivity determination of SCF through microporous membranes (Project FONDECYT 1040240)

Subject 2: Modeling of the extraction by membrane contactors using supercritical solvents: simulations of porocritical extraction

S1: PERMEATION OF SCF THROUGH MICROPOROUS MEMBRANES

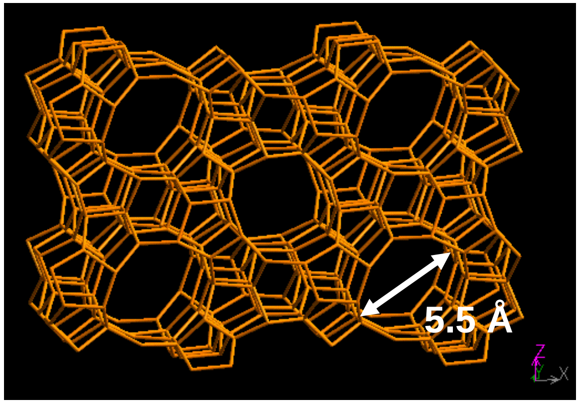
Many questions and few answers:

How SCF flow through a microporous membrane?

What is the selectivity mechanism within micropores (d_p < 2 nm)?

How is the permeation behavior of SCF compared to gas and liquid phases?

CHOSEN SYSTEM:
Permeation of SC CO_2 through a supported MFI zeolite membrane



Thin layer (10-50 μm) of MFI zeolite (d_p = 5.5 Å) deposed on a macroporous α-Al_2O_3 support

Previous works / Technical limitations

Sarrade, 1994: Permeability and selectivity values for PEG-SC CO2 mixtures using Nafion-TiO_2 membranes / Proposed mechanism: convection? (presence of defaults?)

Romero et al., 2001: Permeability values of SC CO_2 and SC N_2O through zeolites membranes / Variability in the permeance measurements with a continuous flow apparatus (G_{CO2} = 1.8*10^{-7} mol m^{-2} s^{-1} Pa^{-1}), adsorption effect is observed

Kulcke, 2002: Permeability of SC CO2 through several mesoporous membranes / Problems in the flow determination using microporous membranes (small values, non-reported)

Romero et al., 2004: Unified approach for liquid, gas an SC mass transfer through microporous membranes / Adsorption effect taking into account a Langmuir isotherm

how is the adsorption within micropores at high pressure conditions?

High pressure adsorption isotherms in microporous materials

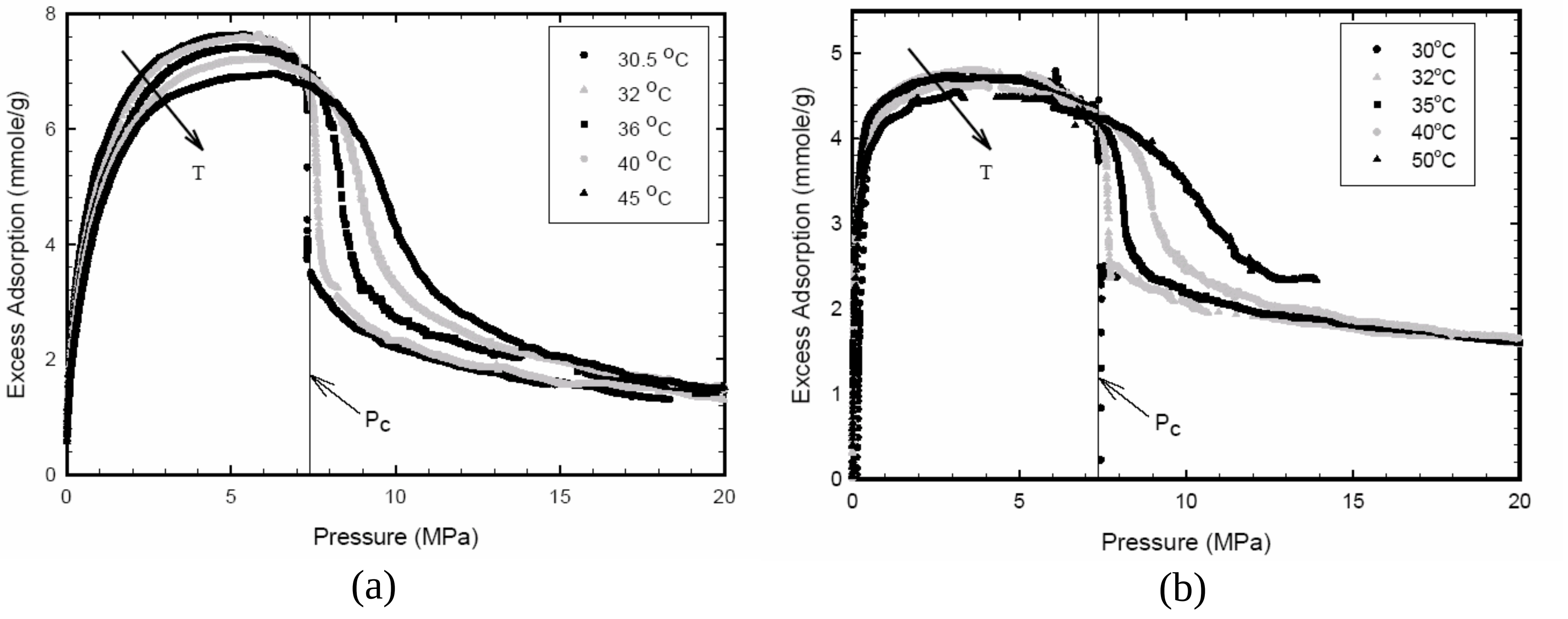
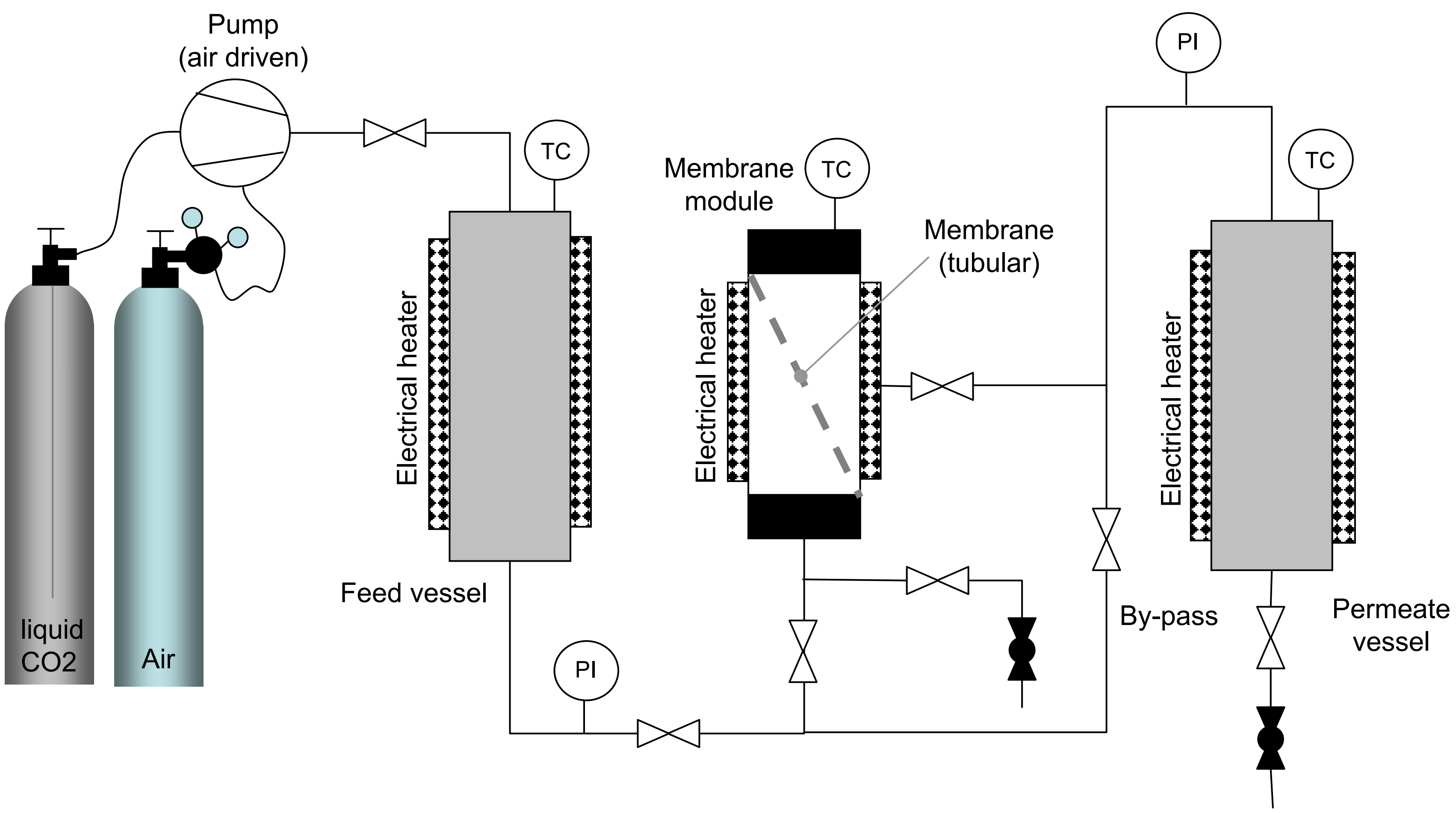


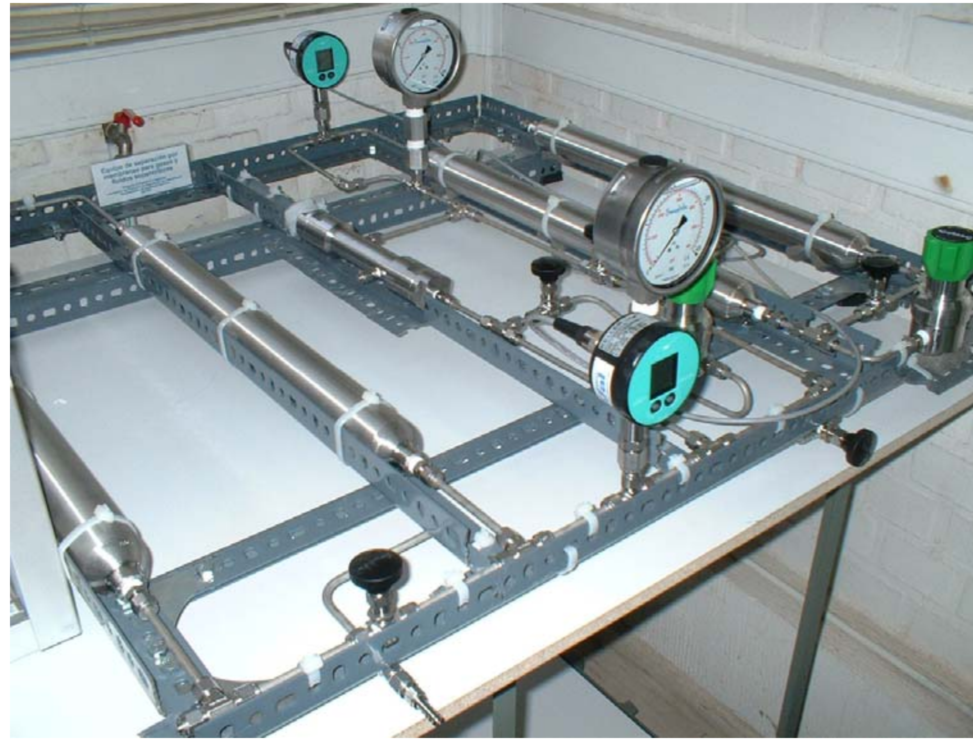
Figure 2. Adsorption of CO_2 on GAC (a) and NaY zeolite (b) showing the crossover behavior

Simplified flow sheet: equipment for SCF permeability through membranes by transient method



S1: PERMEATION OF SCF THROUGH MICROPOROUS MEMBRANES

Equipment for permeability determination of gases and supercritical fluids



Project FONDECYT 1040240

Compression unit:

- **Liquid CO_2 pump (5 L/h, 250 bar)**

Air driven

Permeation unit:

- **Pressure (700 bar)**
- **Temperature (25-250°C)**
- **Feed and permeate vessels (0.5-1.0 L)**
- **Inorganic membrane module**
- **zeolite membrane (L = 15 cm, D = 1 cm)**

S1: PERMEATION OF SCF THROUGH MICROPOROUS MEMBRANES

Modeling SC CO_2 permeation through MFI zeolite membrane

(Navarrete and Romero, 2004)
Mechanism proposed: Surface diffusion *(Krishna, 1993)*
Mass transfer model proposed: Darken equation *(Burggraaf and Cot, 1996)*

$$J_i = -\varphi \cdot D_{0,i} \cdot \frac{\delta Ln(P)}{\delta Ln(q_i)} \cdot \frac{dq_i}{dz}$$

$$\int J_i . dz = -\int_{q_{f,i}}^{q_{p,i}} \varphi \cdot D_{0,i}(q_i) . \Gamma . dq$$

Γ = Thermodynamic factor

Modeling carrying out numerical resolution of the integral with the Thermodynamic Factor using adsorption experimental data

S1: CONCLUSIONS AND CHALLENGES

SCF/Inorganic membranes: possibility of proposing several processes and configurations (separation, membrane reactor = reaction + separation)

The microporous membrane gives a particular thermodynamic condition of the fluid within the pore (liquid = gas = SCF)

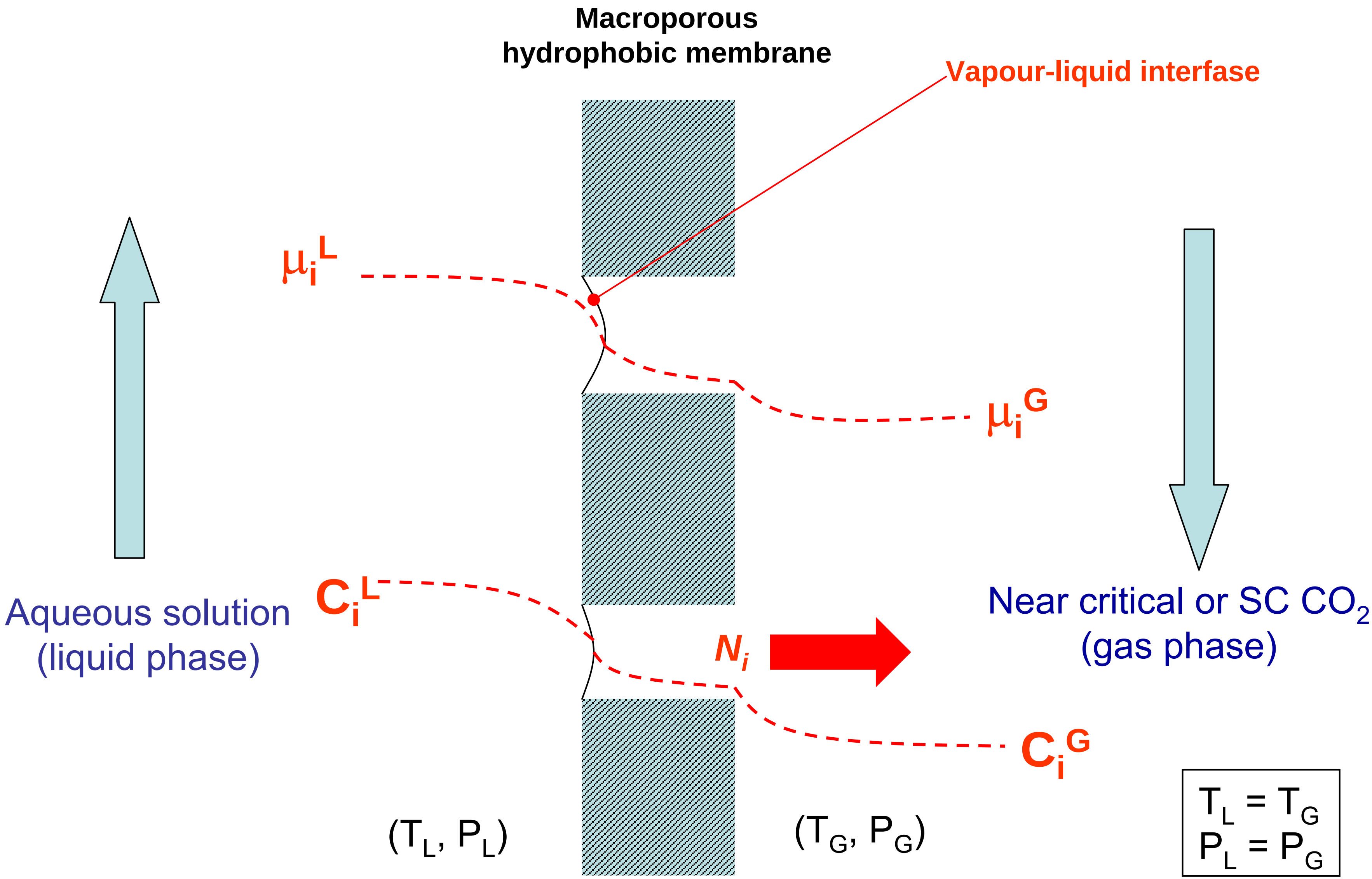
Can different mechanisms be observed (sorption, diffusion, etc….)?

Adsorption effects observed: new model incorporates these aspects for SCF

RESEARCH ACTIVITIES IN USACH

Subject 1: Permeability and selectivity determination of SCF through microporous membranes

Subject 2: Modeling of the extraction by membrane contactors using supercritical solvents: simulations of porocritical extraction



Macroporous
hydrophobic membrane
Vapour-liquid interfase
μ_i^L
μ_i^G
C_i^L
N_i
C_i^G
Aqueous solution
(liquid phase)
Near critical or SC CO_2
(gas phase)
(T_L, P_L)
(T_G, P_G)
$T_L = T_G$
$P_L = P_G$

Why to carry out SFE using a membrane contactor?

- Porocritical fluid extraction is a efficient alternative to conventional contacting columns which disperse one fluid phase in another

- Advantages include high throughput capacity without column flooding or emulsion formation, independence of density between solvent and feed, and modularity of design (There are no large expensive vessels in a typical PoroCrit application, just pipes and pumps)

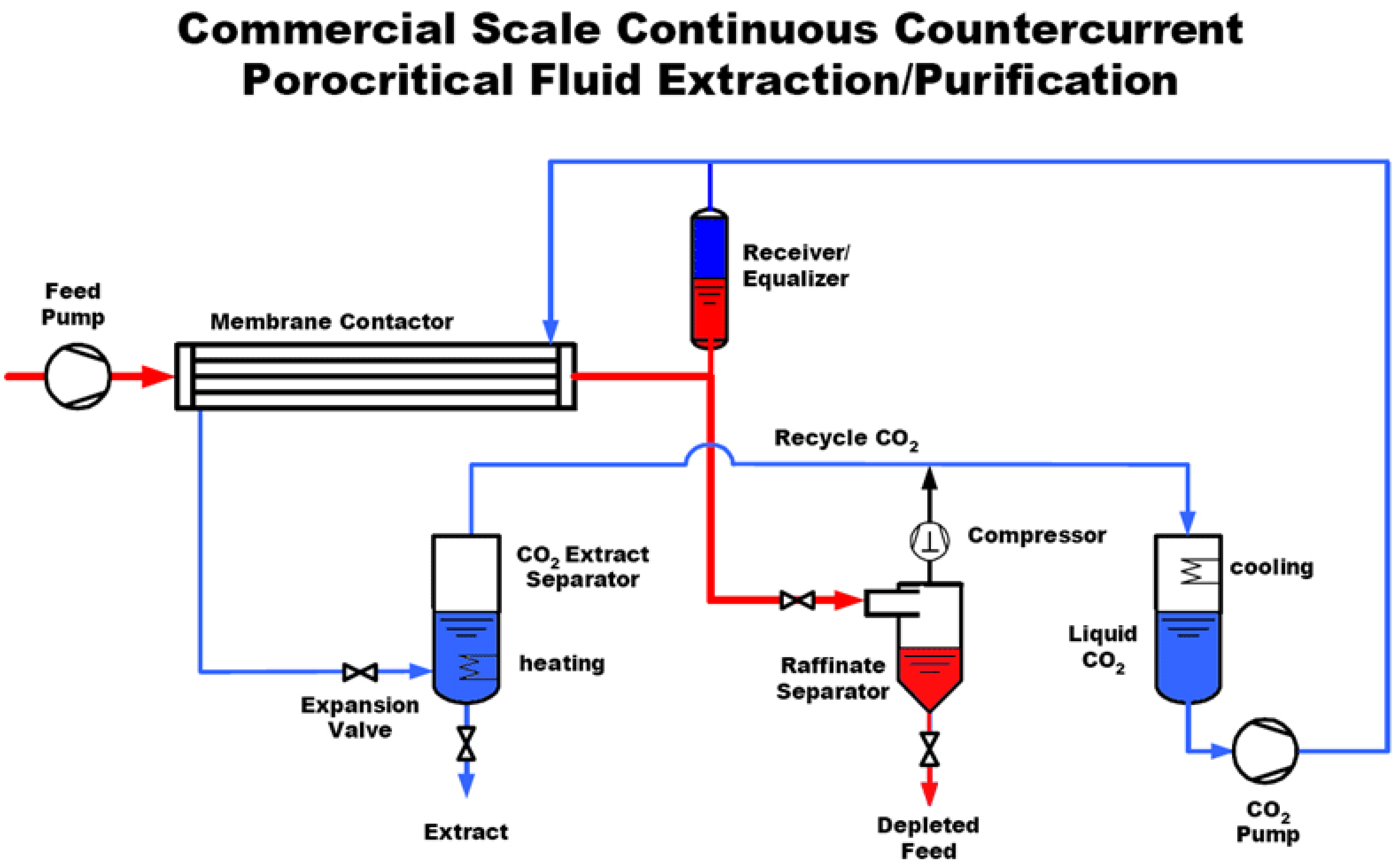
- The reduced process complexity and expense can enable a broader industrial use of carbon dioxide's attributes as a non-toxic, environmentally benign extraction solvent.

- A hollow fiber membrane contactor is usually 100 times more efficient on a volumetric basis (m^2/m^3) than a conventional contactor.

Comparison of Contactors in Solvent Extraction

CHARACTERISTIC	CONVENTIONAL	MEMBRANE CONTACTOR
Can form emulsion	yes	no
Requires fluid density differences	yes	no
Contact area per volume (efficiency)	1	10-100
Modular design	no	yes
Limited throughput and velocity	yes	no
Maintain sterility	no	yes
Cleans without dismantling	no	yes
Handles suspensions	no	yes
Breaks emulsions	no	yes

S2: MEMBRANE CONTACTORS USING SC SOLVENTS



Modeling PoroCrit® extraction

Model based on a system constituted by three mass transfer resistances in series:

1) Liquid boundary layer
2) Stagnant gas layer within the membrane porosity (and VLE)
3) Gas boundary layer

$$\frac{1}{K_W} = \frac{1}{k_W} + \frac{d_i}{d_{ML} k_m m_i} + \frac{d_i}{d_o k_o m_i}$$

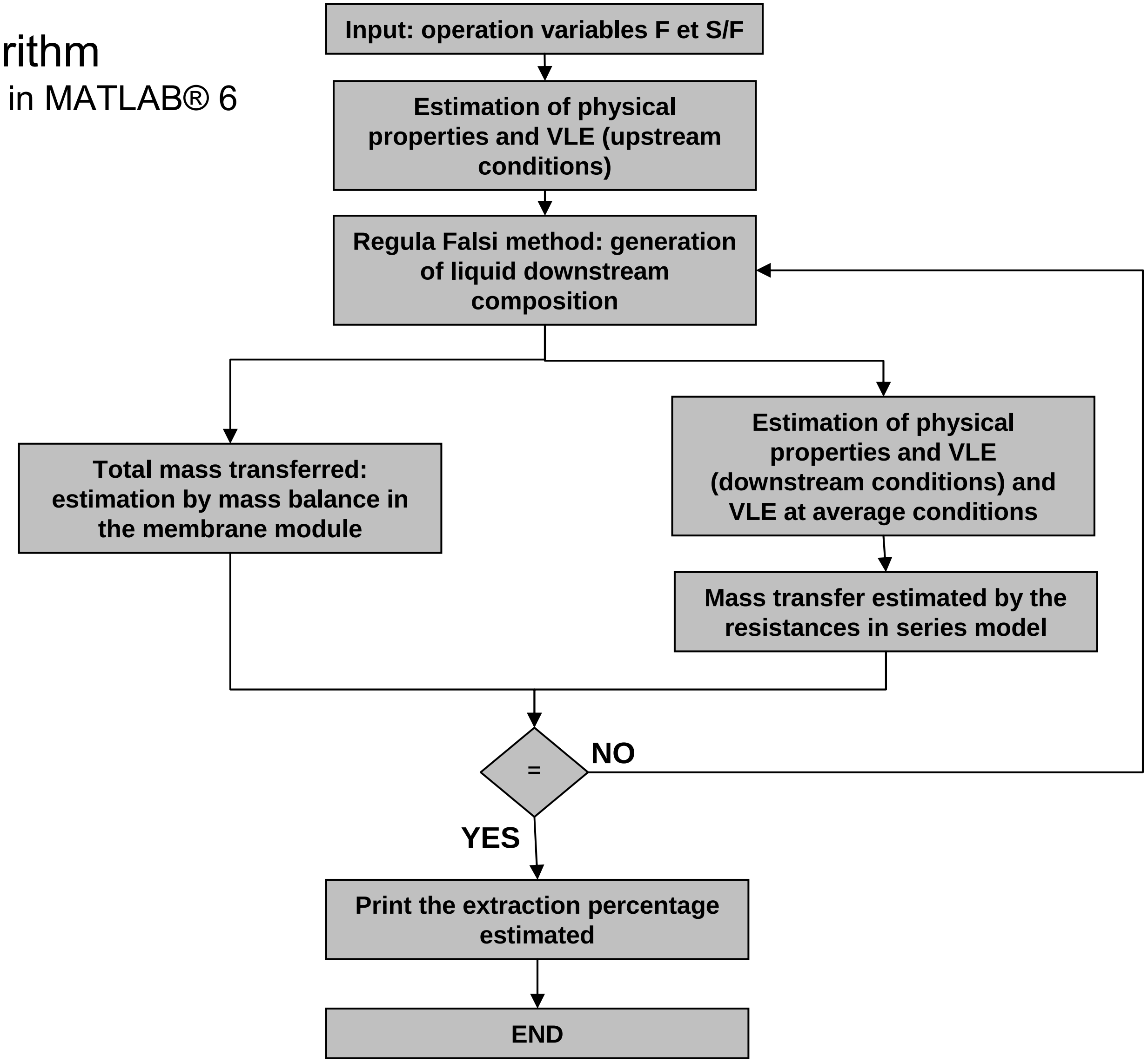
$$\Delta C_{ML} = \frac{(C_l - C_{sc}/m_i)_1 - (C_l - C_{sc}/m_i)_2}{\ln\left[\frac{(C_l - C_{sc}/m_i)_1}{(C_l - C_{sc}/m_i)_2}\right]}$$

$$m_i = \frac{C_{sc}}{C_l}$$ **: Partition coefficient**

S2: MEMBRANE CONTACTORS USING SC SOLVENTS

Simulation algorithm

Program developed in MATLAB® 6



Equations for prediction of properties in liquid phase (water-ethanol)

Property	System	Equation	Authors
Density	water-ethanol	$\rho = a \exp\left[-\frac{(X-b)^2}{2c^2}\right]$	Perry et al., 2000 Estay and Romero, 2004
Viscosity	water -ethanol		Estay and Romero, 2004
Diffusion coefficient	water -ethanol		Reid et al., 1977 Perry et al., 2000

S2: MEMBRANE CONTACTORS USING SC SOLVENTS

Equations for prediction of properties in gas phase (CO2-ethanol)

Property	System	Equation	Authors
Density	CO_2-ethanol	PR EOS	Brunner, 1994
Viscosity	CO_2-ethanol	Chung et al	Chung et al:, 1988
Diffusion coefficient	CO_2-ethanol	Catchpole et al	Catchpole and King, 1994

S2: MEMBRANE CONTACTORS USING SC SOLVENTS

Conditions used for the simulations

Operation conditions of experiments (Bothum et al., 2003)	
Pressure (liquid and gas)	69 bar
Temperature	298 K
Composition of liquid feed (X_{EtOH}, $X_{acetone}$)	10 % w/w
Structural parameters of the membrane contactor	
Membrane material	Polypropylene
Number of fibers, n	1
Length, L	1.07 m
Internal diameter, d_{in}	0.6 mm
External diameter, d_{out}	1.02 mm
Pore diameter, d_p	0.2 μm
Porosity, ε	75 %

S2: MEMBRANE CONTACTORS USING SC SOLVENTS

Extraction percentage (**EX**) of **ethanol** from the aqueous solution through porocritical extraction in function of the liquid flow (**F**) and the molar flow ratio sweep gas/liquid (**S/F**)

F (mL/min)	S/F	EX_{EXP} (%)	EX_{EST} (%)
0.15	3	15.2 ± 0.5	16.17
0.25	3	10.4 ± 0.5	13.31
0.5	3	4.7 ± 1.8	13.61
1.0	3	9.9 ± 0.5	9.67
0.1	10	31.9 ± 1.4	34.00

Extraction percentage (**EX**) of **acetone** from the aqueous solution through porocritical extraction in function of the liquid flow (**F**) and the molar flow ratio sweep gas/liquid (**S/F**)

F (mL/min)	S/F	EX_{EXP} (%)	EX_{EST} (%)
0.15	3	96.1 ± 1.8	95.04
0.25	3	89.6 ± 1.8	88.31
0.5	3	68.9 ± 1.8	75.56
1.0	3	67.9 ± 1.8	58.12

S2: CONCLUSIONS AND CHALLENGES

Coupled processes = coupled effects

Vapour-liquid equilibrium (VLE)

Mass transfer resistances in series
(gas and liquid boudary layers and membrane pores)

Stability of the interfaces: good control of operation variables and easy scale-up

Potential applications:

- ✓ Foods
- ✓ Biotechnolgy
- ✓ Chemicals
- ✓ Cosmetics
- ✓ Pharmaceuticals
- ✓ Polution remediation
- ✓ Chemical analysis
- ✓ Polymers
- ✓ Pasteurización
- ✓ Solvent recovery

Monofiber membrane module for porocritical extraction (LPSM, USACH)

GENERAL CONCLUSIONS

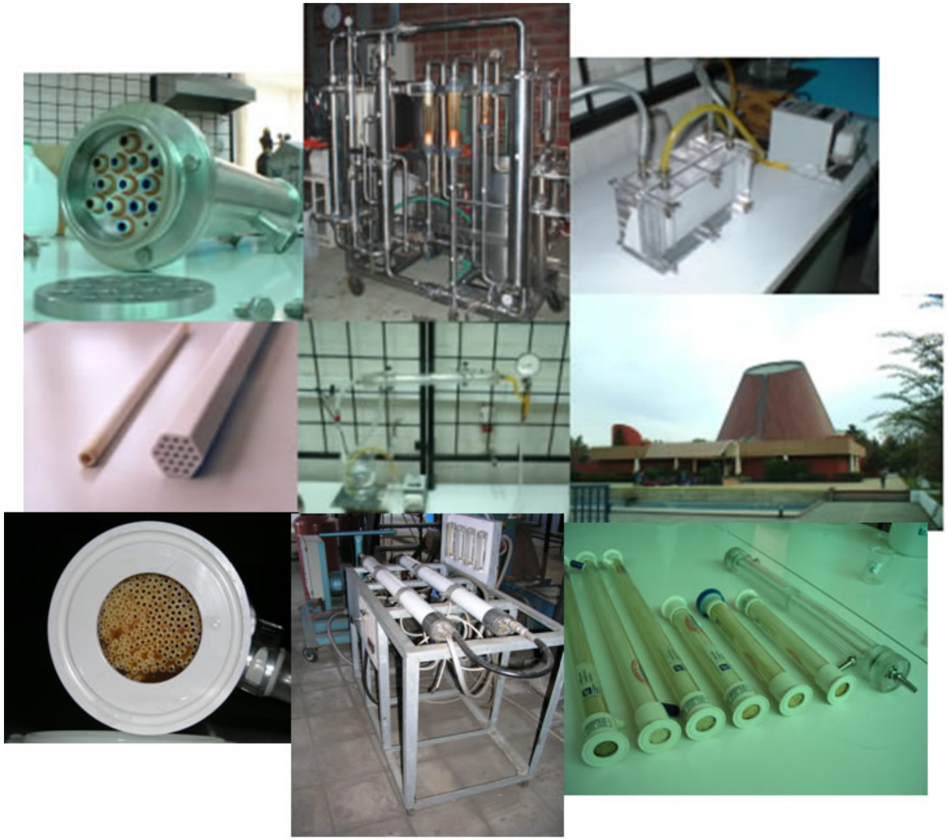
The use of a membrane in presence of a supercritical fluid makes possible the design of very attractive and powerful processes

Several processes and configurations: improve transfer or reaction, to set in contact phases, to fluidify highly viscous liquids

Overall the major interest of all the processes thus created is to be safeguarding for environment and products, which is in particular essential when these ones are of biological nature

The principal effort requested from the researcher is a whole effort of imagination, and serious in further investigation with appropiate knowlwdge of membranes and supercritical fluid technologies

Thank you for your attention



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