WP3
Membrane Based Technologies

Marc Pfister & May-Britt Hägg

PhD-student CNRS Professsor NTNU

Partners:

- NTNU Norway (WP-Leader)
- Sintef M&C Norway
- TNO. The Netherlands
- TIPS, Russia
- CNRS, France
- EDF, France1
- CSIRO, Australia

Membrane based technologies

Task 3.1 Hybrid membrane development (NTNU, SINTEF, TNO) - OBJECTIVES

- Develop high flux mixed matrix membrane based on incorporation of nanoparticles in polymer.
  - Target: CO_2 permeance of 2.5 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100.
  - Membrane fabrication and study on transport phenomena.

Task 3.2 Supported ionic liquid membranes (SILM) (NTNU, TIPS) - OBJECTIVES

- Develop contained supported ionic liquid ceramic membranes (CILM)
  - Target: CO_2 permeance above 4 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100
- Develop nanoporous polymer/ILs membranes
  - Target: CO_2 permeance 12-15 m^3(STP)/ m^2 h bar, selectivity CO_2/ N_2 = 20-30
- Temperature stability >100°C.

Task 3.3 Process modelling and simulation (CNRS, EDF, NTNU) - OBJECTIVES

- Develop membrane module simulation model for nanocomposite and SILM membranes.
  - Evaluate the energy requirement & membrane area for different set of operating conditions
- Develop concepts for utilizing the membranes in a post-combustion process.

Task 3.1: Hybrid Membrane Development

Objectives

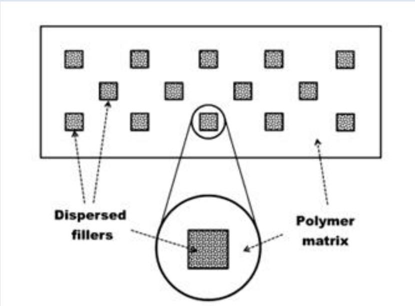
- Develop a high flux mixed matrix membrane based on incorporation of functionalized SiO-particles and nano TiO2-particles in a polymer.
  - Target: CO_2 permeance of 2.5 m^3(STP)/ m^2 h bar
    selectivity CO_2/N_2 above 100.
  - Membrane fabrication and study on transport phenomena.

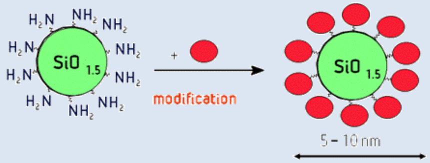
Research Activities

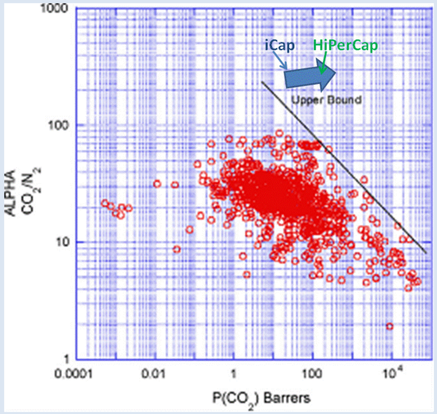
- Study of the transport mechanism and role of the nano-sized particles.
- Tailoring nanoparticles to tune the desired membrane properties such as selectivity and flux.
  - Nanosized particles prepared and characterized (SINTEF & TNO)
  - Hybrid membranes prepared and performance tested at NTNU
- Optimization in different iteration steps for the hybrid membrane.

Expected outcome

- Hybrid membranes with targeted performance
- Dedicated permeability model based on experimental flux data over a wide range of operating conditions







Task 3.1 Hybrid membrane development
Status on Work

1. **Study of the transport mechanism and role of the nano-sized particles: (report delivered)**

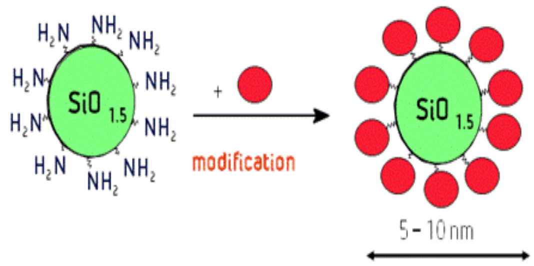
$$J_A = -D_A \frac{dC_A}{dx} = \frac{D_A}{dx}(C_{A,f} - C_{A,p}) + \frac{D_{AC}}{dx}(C_{AC,f} - C_{AC,p})$$

2. **The mechanism of gas transport in Facilitated Transport Membranes (FTM) most complicated** The total transport flux is the sum of both the Fickian diffusion and the carrier mediated diffusion.

Hence: The gas stream has to be humid for the facilitated transport to take place

→ CO_2 reacts and forms bicarbonate (fast reaction) and is released again as CO_2 on permeate side

→ The functionalized SiO-particles (HAPS) must not be protonised in order to promote facilitated transport (hence pH must be high)



HAPS Nanoparticles

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$$

$$H_2CO_3^- + NH_2 - R + H_2O \Leftrightarrow R - NH_3^+\, HCO_3 + OH^-$$

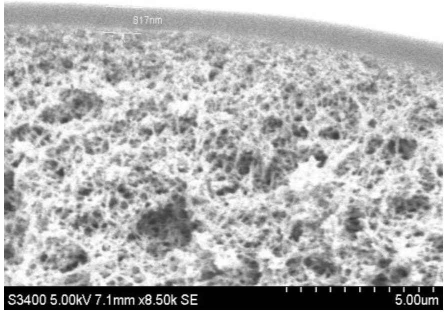
$$R - NH_3^+\, HCO_3 \rightarrow R - NH_2 + H_2O$$

3. Two types of hybrid membranes will be tested:

HAPS embedded in PVA (facilitated transport)

TiO2 nanoparticles in PVA (Maxwell adapted transport)

(PVA is hydrophilic by nature and has good film forming properties)



SEM: 2%PVA on PSF Membrane support

Task 3.1 Hybrid Membrane Development Status on Work

At NTNU-Sintef: Facilitated transport : Initial focus is on reproducing good results obtained

- New PVA-HAPS-1 membrane samples are manufactured
  - PPO-supported PVA/HAPS asymmetric membrane
  - PSf-supported PVA/HAPS asymmetric membrane

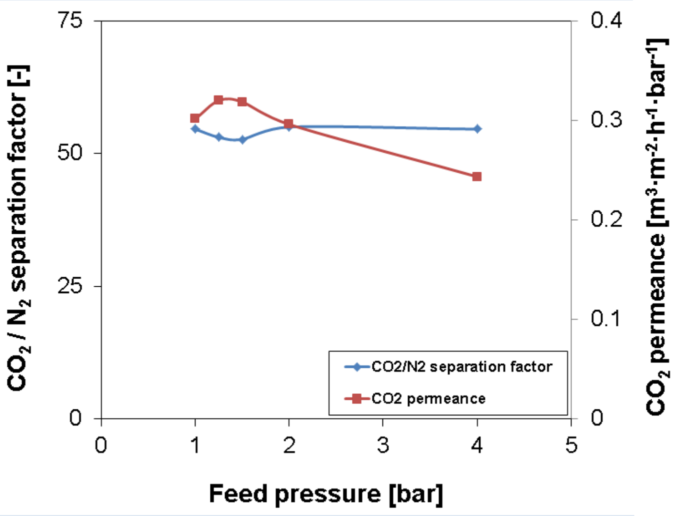
  (PPO = Hollow fibers; PSf = flat sheets)

Results to date

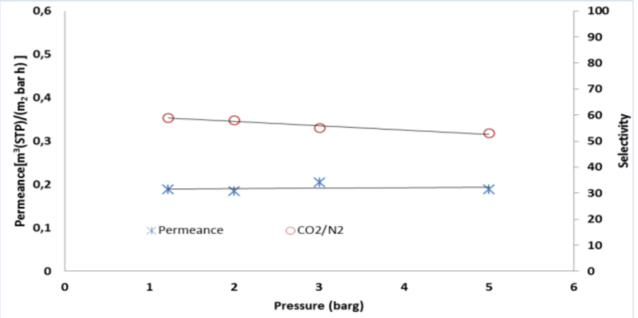
- First permeance measurements using PPO HF support, indicated CO_2 no success in facilitated transport

Conclusion

- The various parameters and variables which may influence the preparation of these membranes containing the functionalized nanoparticles are currently being systematically investigated
- Aim is to establish a reproducible manufacturing, and prepare a somewhat larger module for flux evaluation providing task 3.3 and WP4 with the required input



Performance of PVA-HAPS on PPO



Performance of 2% PVA Membrane on PSf

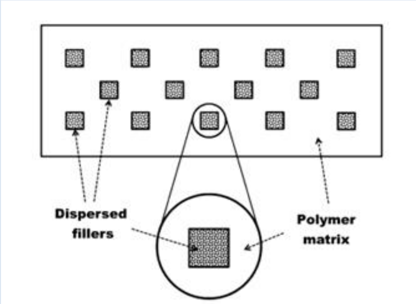
Task 3.1: Hybrid Membrane Development Status on Work

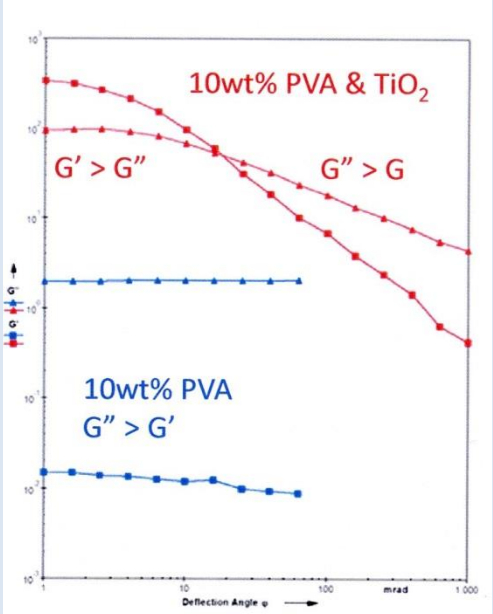
Ongoing Research Activities at TNO

- Synthesis of Nano-TiO2 particles seams successful (first indication
  d < 20 nm)
- Well soluble/dispersible in water
- Study on interaction between PVA and nano-TiO2 to indicates physical network is formed (see figure). More solid-like behaviour at low deformation and more liquid-like behaviour at high deformation.
- Factors affecting interaction under study.

Further:

- Nanoparticles will be sent to NTNU to be prepared as hybrid membranes; embedded in PVA on PSf flat sheet support
- Performance will be measured with and without humid gas





Task 3.2 Ionic Liquid Membranes

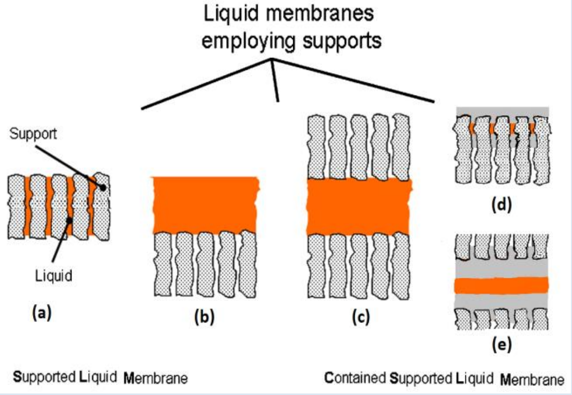
Objectives

- Develop contained supported ionic liquid membranes (CILM)
  - Target: CO_2 permeance above 4 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100
- Develop nanoporous polymer/ILs membranes
  - Target: CO_2 permeance 12-15 m^3(STP)/ m^2 h bar, selectivity CO_2/ N_2 = 20-30
- Temperature stability >100°C.

Research activities

- Selection, synthesis & evaluation of ILs for CO_2 facilitated transport membranes (NTNU).
- Selection and synthesis of high free volume polymers and advanced porous ceramic membranes (TIPS, NTNU).
- SILMs preparation, with focus on polymeric thin film composite support (TIPS).
- SILMs preparation, with focus on ceramic supports (NTNU).
- Separation performance testing (NTNU).

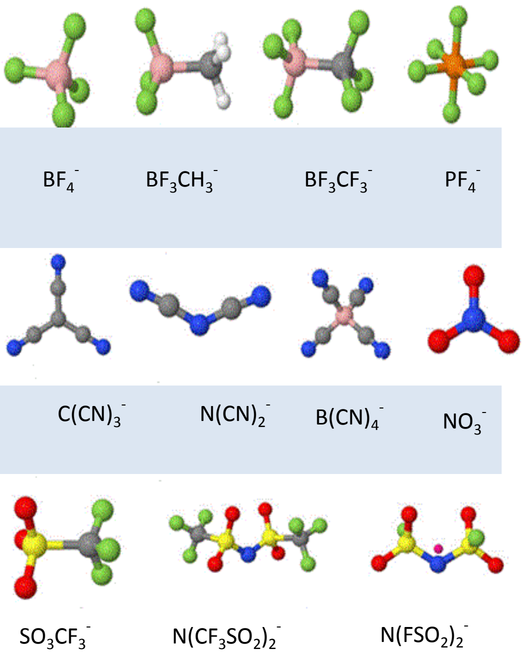
Type of SLM membranes



Task3.2 Ionic Liquid Membranes
Status on Work at NTNU – screening; OK ☺

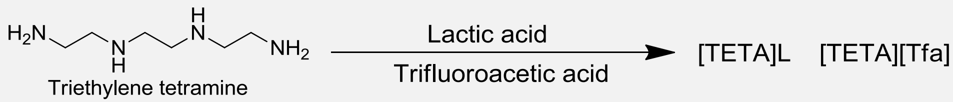
ILs	T_d °C	Types of absoption	CO_2 absorption capcity		Conditions bar/°C
			mol CO_2/IL	g CO_2/g IL	
[bmim][PF_6]	622.15	physisorption	0.295	0.0459	15.79/60
[C_8mim][PF_6]	647.15	physisorption	0.330	0.0428	17.38/60
[bmim][NO_3]	243	physisorption	0.224	0.0492	15.61/60
[bmim][Tf_2N]		physisorption	0.213	0.0224	13.64/60
[TETA]L	——	chemisorption	0.944	0.176	/110
[aP_{4443}][Ala]-SiO_2	283	chemisorption	~1.0	0.126	/25
[aP_{4443}][Gly]-SiO_2	281	chemisorption	~1.0	0.132	/25
[P_{66614}][Im]	252	chemisorption	1.0	0.0799	/23
[Li(DOBA)][Tf_2N]	319	chemisorption	0.71	0.072	/100

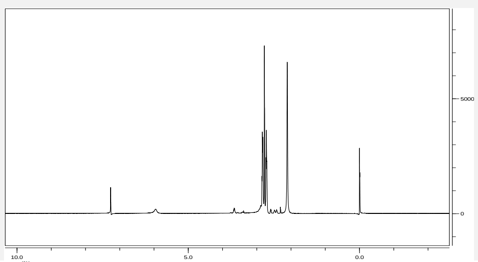
Common anions in ILs



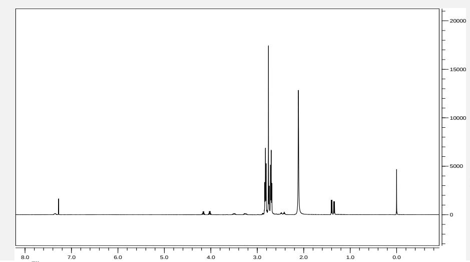
Task3.2 Ionic Liquid Membranes
Status on Work at NTNU – synthesis and charact.; OK ☺

- **Polyamine-based ILs**



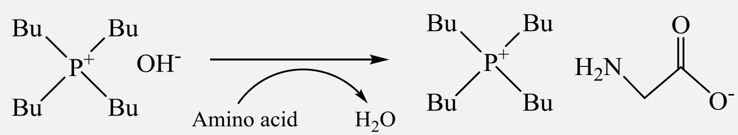


^{1}HNMR of [TETA]Tfa

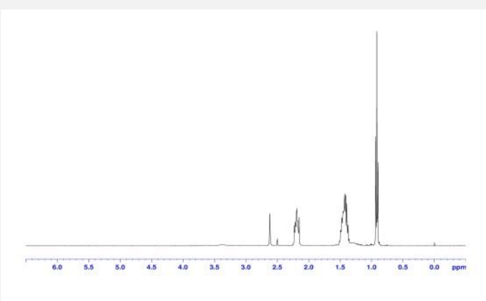


^{1}HNMR of [TETA]L

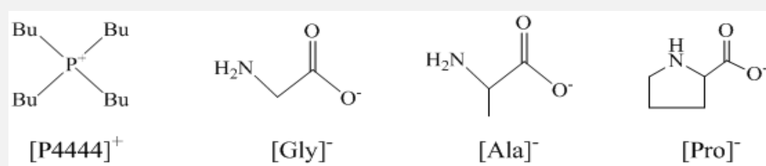
- **Amino acid ILs**



P4444[Gly]



^{1}HNMR of P444[Gly]



Structures of the cation and anions of AAILs

Task3.2 Ionic Liquid Membranes
Status on Work at NTNU – evaluation of synthesized IL; OK ☺

- **CO_2 sorption**

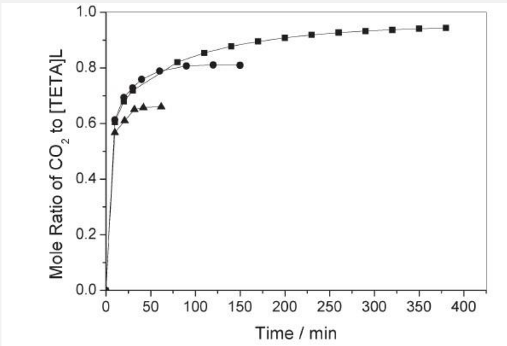
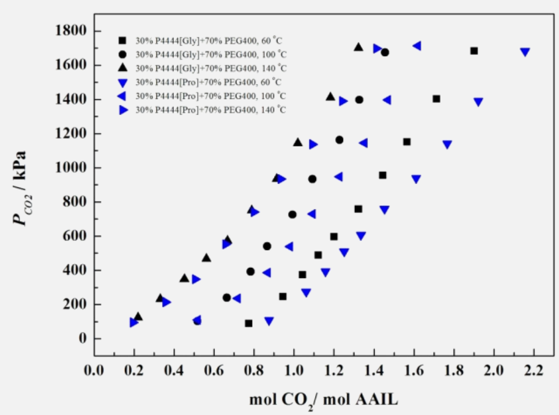
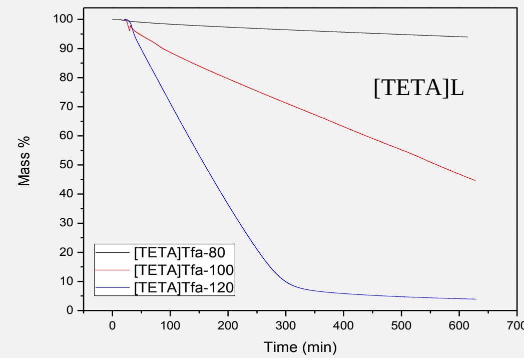


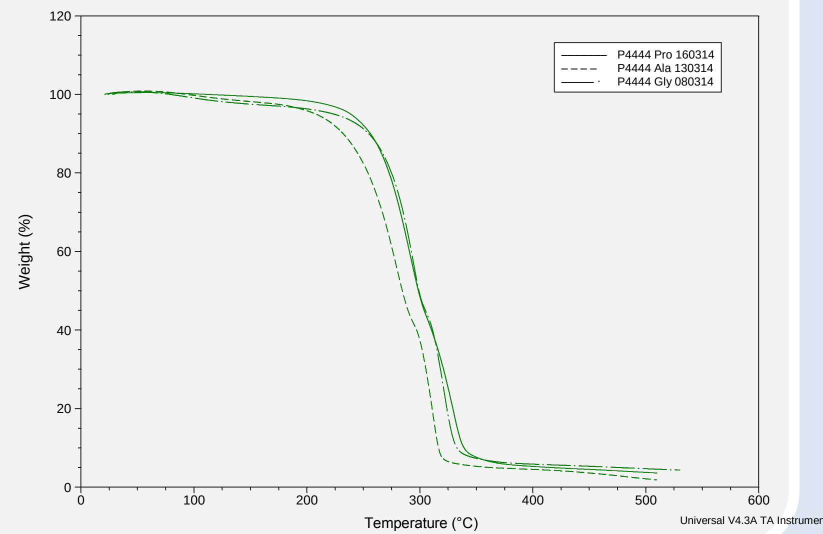
Fig. 2 Absorption of CO_2 in [TETA]L with pure CO_2 at different temperatures: ■, 110 °C; ●, 120 °C; ▲, 130 °C.

Ref: Ren, S., Y. Hou, et al. (2012). Rsc Advances **2**(6): 2504-2507



- **Thermal stability**





Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS

TIPS RAS

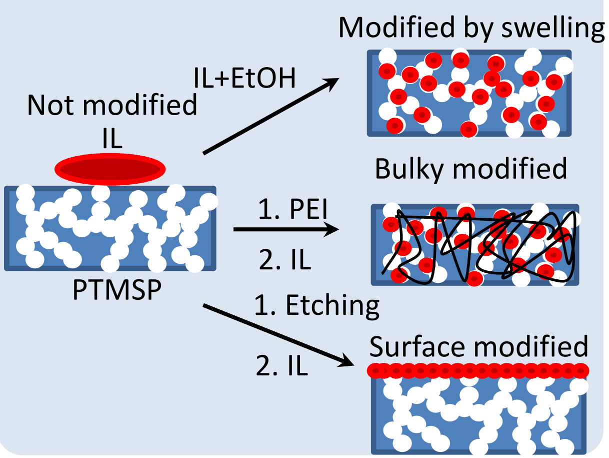
Objectives

- Develop nanoporous polymer/ILs membranes
  - Target: CO_2 permeance 12-15 m^3(STP)/ m^2 h bar, selectivity CO_2/ N_2 = 20-30
- Temperature stability >100°C.

Research activities at TIPS

- ✓ The two samples of high free volume glassy polymer - poly[1-trimethylsilyl-1-propyne] (PTMSP) were synthesized.
- ✓ Two ionic liquids (ILs) based on imidazolium cation with high solubility selectivity for gas pair CO_2/N_2 were selected.
- ✓ Three methods of incorporation of selected ILs into the PTMSP dense membranes were developed: modification by swelling in IL/EtOH mixture, bulky hydrophilization by X-linked PEI and IL incorporation, surface hydrophilization by chemical etching and IL incorporation.

Methods of IL incorporation in PTMSP

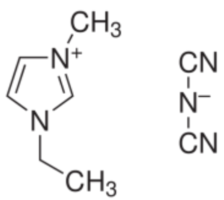


Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS – the Concept

TIPS RAS

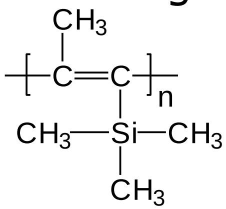
Imidazolium-based IL (EmimDCA)

- ✓ High CO_2/N_2 selectivity – 50
- ✓ Low vapor pressure
- ✓ High thermal stability
- ✓ High tunability
- ✓ Relatively high CO_2 solubility



Nanoporous glassy polymers (PTMSP)

- ✓ Extra high CO_2 permeability coefficient 29000 Barrer
- ✓ High thermal stability
- ✓ High film-forming ability



Bara J. E. , et al. Guide to CO2 separations in imidazolium-based room-temperature ionic liquids *Ind. & Eng. Chem. Res.* 48.6 (2009): 2739-2751.

Robeson L. M. The upper bound revisited. J. Membr. Sci. 320.1 (2008): 390-400.

Hybrid PTMSP/EmimDCA membrane material with improved CO_2/N_2 selectivity

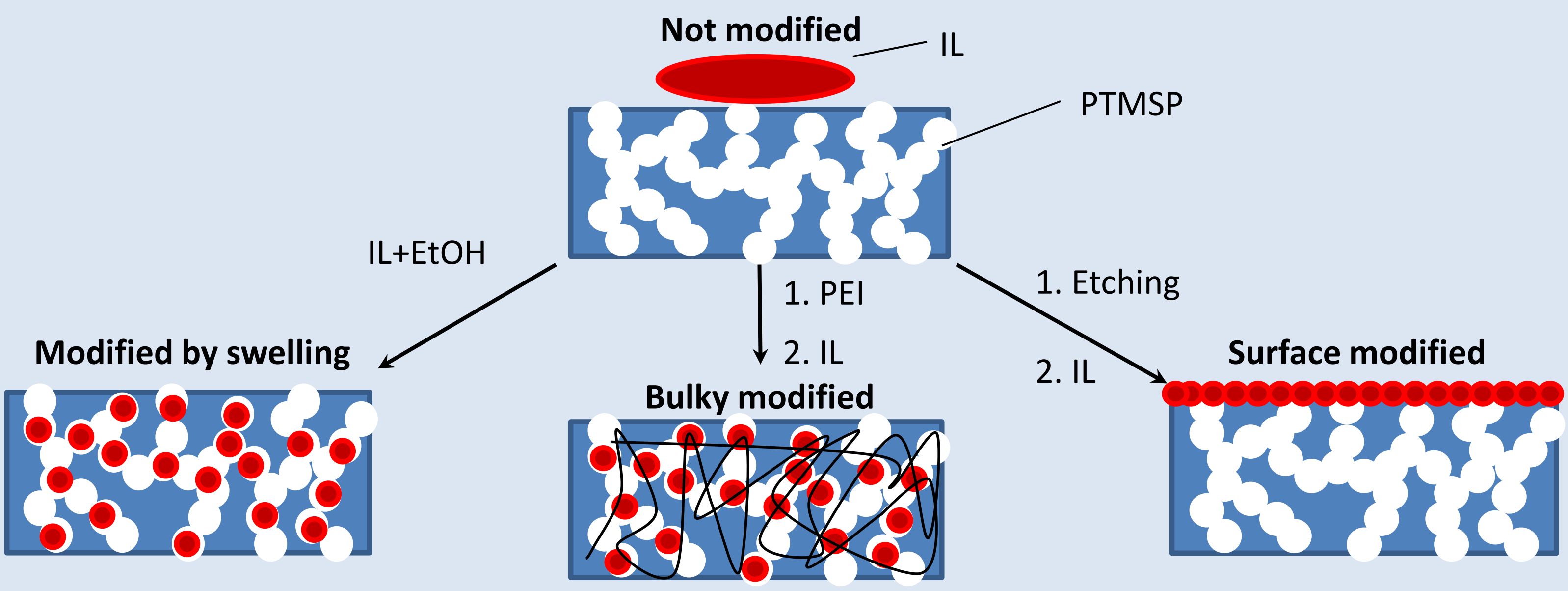
Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS

TIPS RAS

Research activities at TIPS

- ✓ The two samples of high free volume glassy polymer - poly[1-trimethylsilyl-1-propyne] (PTMSP) were synthesized.
- ✓ Two ionic liquids (ILs) based on imidazolium cation with high solubility selectivity (50 – 80) for gas pair CO_2/N_2 were selected.
- ✓ Three methods of incorporation of selected ILs into the PTMSP dense membranes were developed: modification by swelling in IL/EtOH mixture, bulky hydrophilization and IL incorporation, surface hydrophilization and IL incorporation

Methods of membranes modification



Task3.2 Supported Ionic Liquid Membranes Status on Work at TIPS

TIPS RAS

Gas permeation results

Membrane	CO_2 permeance, l(STP)/m²h bar	N_2 permeance, l(STP)/m²h bar	CO_2/N_2 selectivity	Membrane thickness, µm	Gas pressure, bar
PTMSP unmodified	2700	670	4	30	1
	2900	770	3.8		5
PTMSP / IL	6.8	0.43	16	42	1
	20.7	0.42	47		5
Bulky modified PTMSP + IL	110	8	14	25	1
	120	8	15		5
Surface modified PTMSP + IL	240	20	12	45	1
	240	18	13		5

Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS

TIPS RAS

PTMSP modified by swelling in alcohol/IL

Membrane	Sorption, vol.%	CO_2 permeance, l(STP)/m²h bar	N_2 permeance, l(STP)/m²h bar	CO_2/N_2 selectivity
PTMSP unmodified	-	2900	770	3.8
PTMSP + (1% EmimDCA in EtOH)	0.2	2930	660	4.4
PTMSP + (5% EmimDCA in EtOH)	3.1	1060	230	4.6

- **Relatively low CO_2 permeance loss and gradual increase during incorporation of IL in PTMSP**
- **Optimization of swelling method is in progress**

Task 3.3 Process modelling and simulations

Task 3.3 Process modelling and simulation (NTNU, CNRS, EDF)

Objectives

- Develop membrane module simulation model for nanocomposite and SILM membranes.
    - Evaluate the energy requirement & membrane area for different set of operating conditions
- Develop concepts for utilizing the membranes in a post-combustion process.

Research Activities

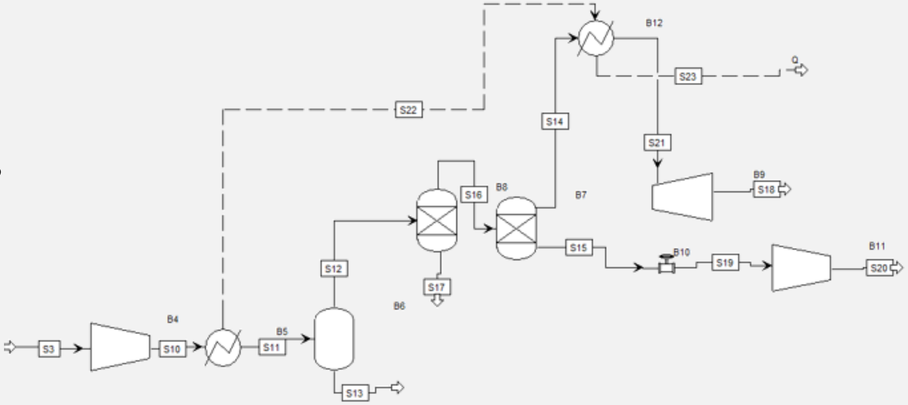
- Development of permeability models based on the experimental results obtained in tasks 3.1 and 3.2 :
    - Analysis of the mass transfer characteristics (constant or variable permeability, coupling phenomena, role of temperature)
    - Modelling of the mass transfer performances for the different compounds through a general permeability relationship.
- Parametric simulation study of the performances for the two types of membranes
    - Review of the different modelling approaches
    - Influence of feed mixture composition (i.e. CO2 content)
    - Parametric study for a target CO2 purity and capture ratio
    - Analysis of the energy (pressure ratio) / membrane area trade-off
- Modelling framework in a process simulation environment with energy integration aspects

Task 3.3 Process Modelling and simulations
Status on Work at CNRS

Objectives

- Develop membrane module simulation model for hybrid membranes.
  - Model mass transfer with a reaction diffusion mechanism
  - Enquire about possible disturbances of process modelling (temperature, water impact, competing reaction…)
  - Evaluate the impact of inlet conditions variations

- Develop concepts for utilizing the membranes in a post-combustion process (Aspen Plus software)



Task 3.3 Process Modelling and simulations
Status on Work at CNRS

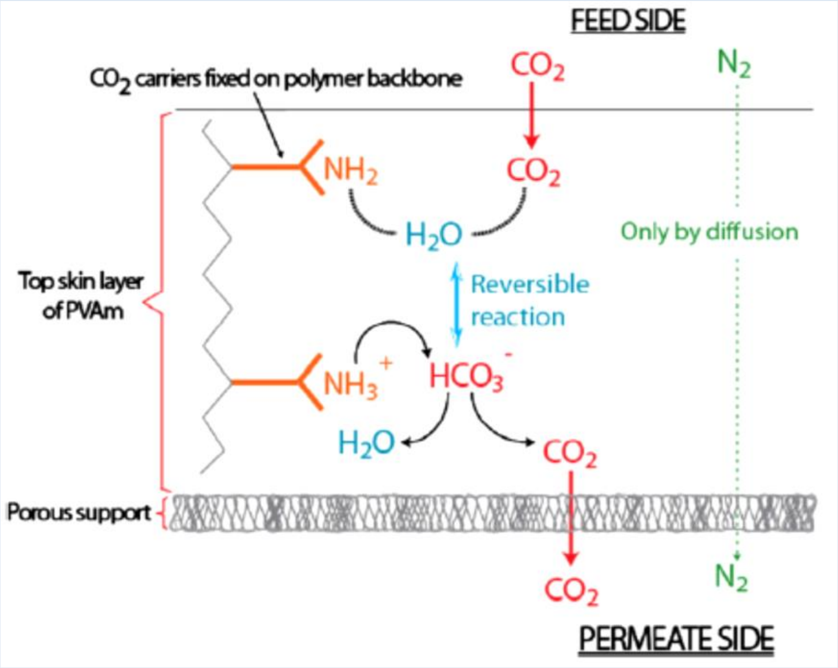
- Two transport mechanisms:
  - Sorption diffusion for N2 compound
  - Reaction diffusion for CO2 compound

- Main reversible chemical reaction:

$$CO_2 + H_2O \xleftrightarrow{+NH_2} HCO_3^- + H^+$$

- Water in the feed flow is a requirement

- Competing reactions between amine fixed sites and CO2 occur



Task 3.3 Process Modelling and simulations Status on Work at CNRS

- Two Transport mechanisms but only one equation:

$$J_A = -D_A \frac{dC_A}{dx} = \boxed{\frac{D_A}{dx}(C_{A,f} - C_{A,p})} + \boxed{\frac{D_{AC}}{dx}(C_{AC,f} - C_{AC,p})}$$

Sorption diffusion mechanism

Reaction diffusion mechanism

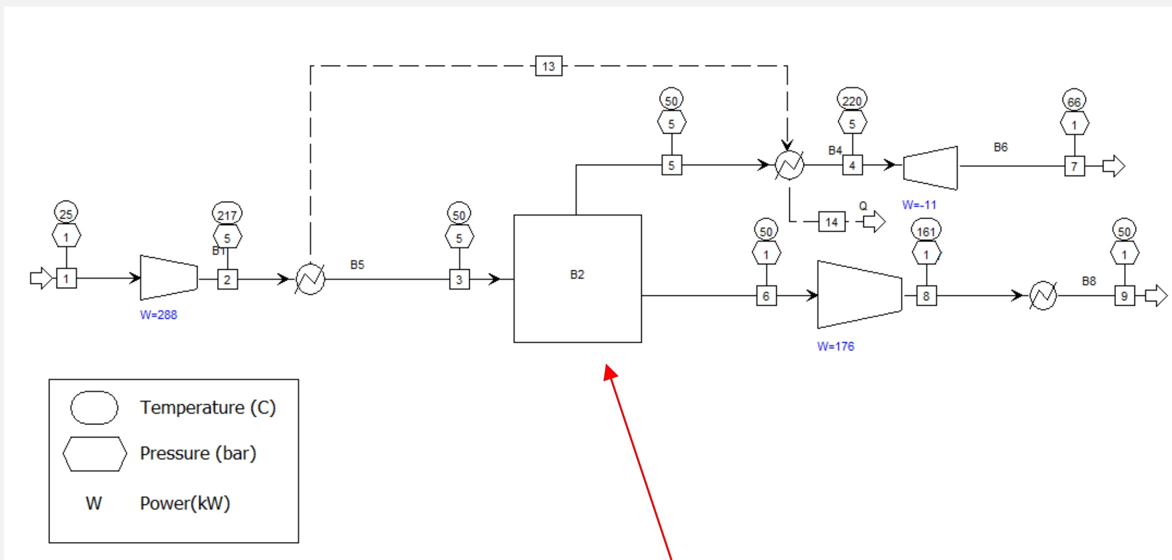
$$C_{AC,f} = \frac{K C_{A,f} C_T}{1 + K C_{Af}}$$

$$C_{AC,p} = \frac{K C_{A,p} C_T}{1 + K C_{A,p}}$$

- Important parameters :
  - K (equilibrium constant of the reaction) depends on temperature
  - C_T (Total carrier concentration) depends on nanoparticles volume fraction (5, 10, 25 wt%)
  - Carrier diffusion coefficient is considered as constant

Task 3.3 Process Modelling and simulations Status on Work at CNRS

- Membranes in a post-combustion process:
  - Aspen Plus software



Retentate Flow

Permeate Flow

Membrane unit

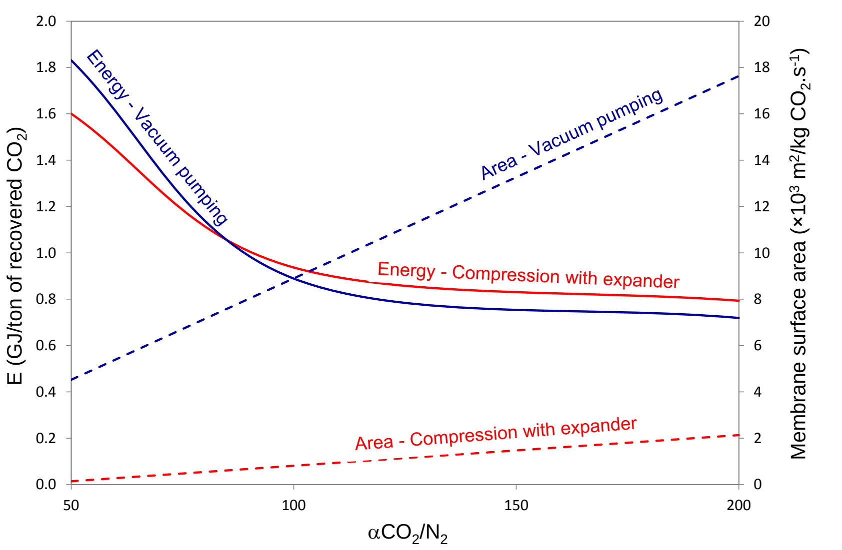
Task 3.3 Process Modelling and simulations
Status on Work at CNRS

- Variation of the Input conditions:
  - ➢ Temperature
  - ➢ Pressure in the upside part of the membrane
  - ➢ Pressure in the downside part of the membrane
  - ➢ CO2 volume fraction in the feed flow

- Membrane area estimation

- Energy requirement evaluation (compressor, expender, vacuum pumping)

- Technical economical estimation (in collaboration with EDF)



Task 3.3 Process Modeling and simulations Status on Work at NTNU

NTNU will contribute with:

- Details on the facilitated transport model for the functionalized nanocomposite hybrid membranes.
- Providing experimental data to check the model at given conditions
- Compare the simulation results with their own in-house model, and discuss the impact of inlet conditions variations

- Contribute in discussions with respect to utilizing the hybrid

membranes in a post-combustion process.