EU- Australian workshop, Oslo, Norway
13th- 14TH september 2017

Modelling of membrane based CO_2 capture processes

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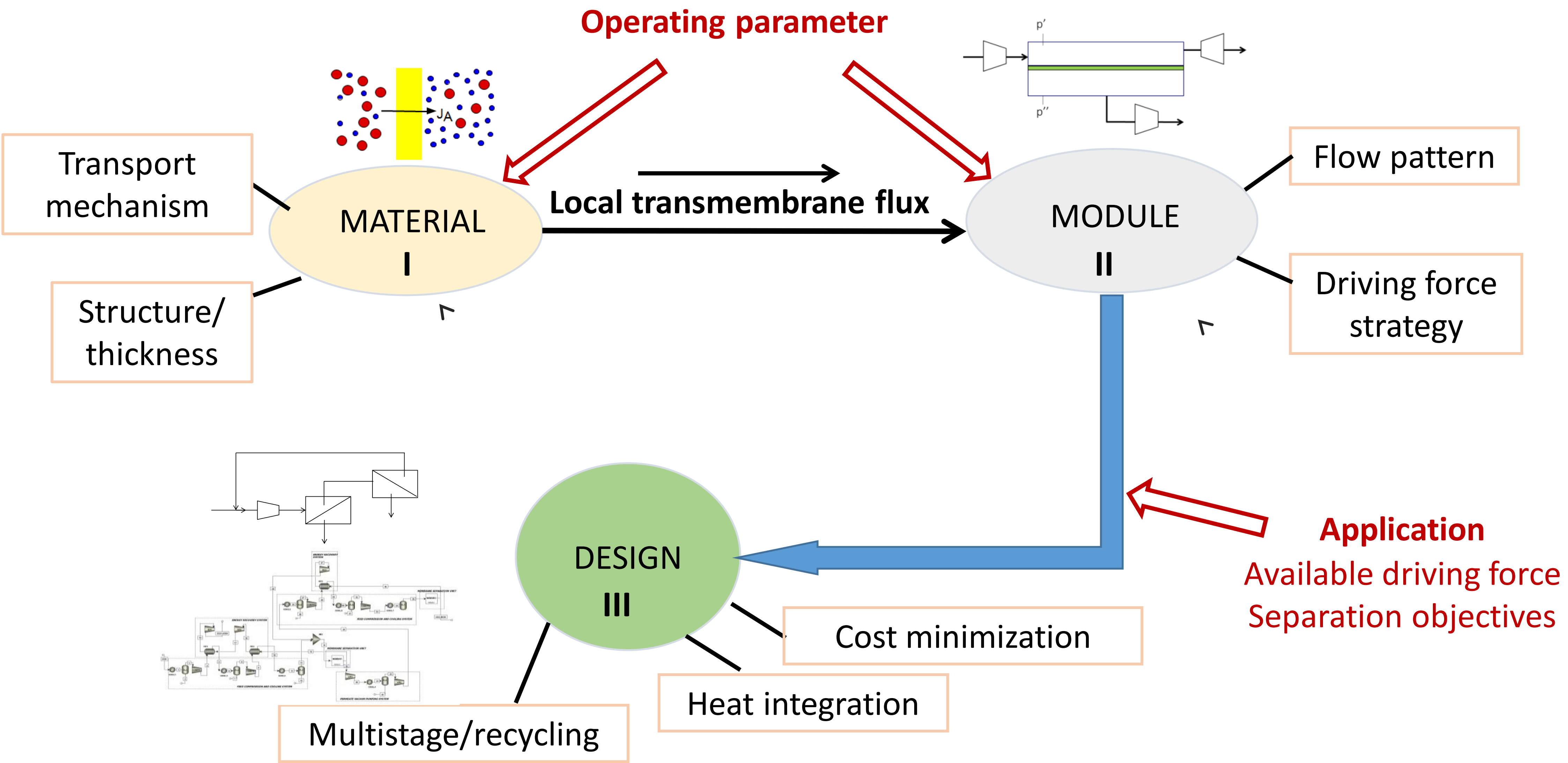
From material to process design



Operating parameter

Transport mechanism

Structure/ thickness

MATERIAL
I

Local transmembrane flux

MODULE
II

Flow pattern

Driving force strategy

DESIGN
III

Cost minimization

Heat integration

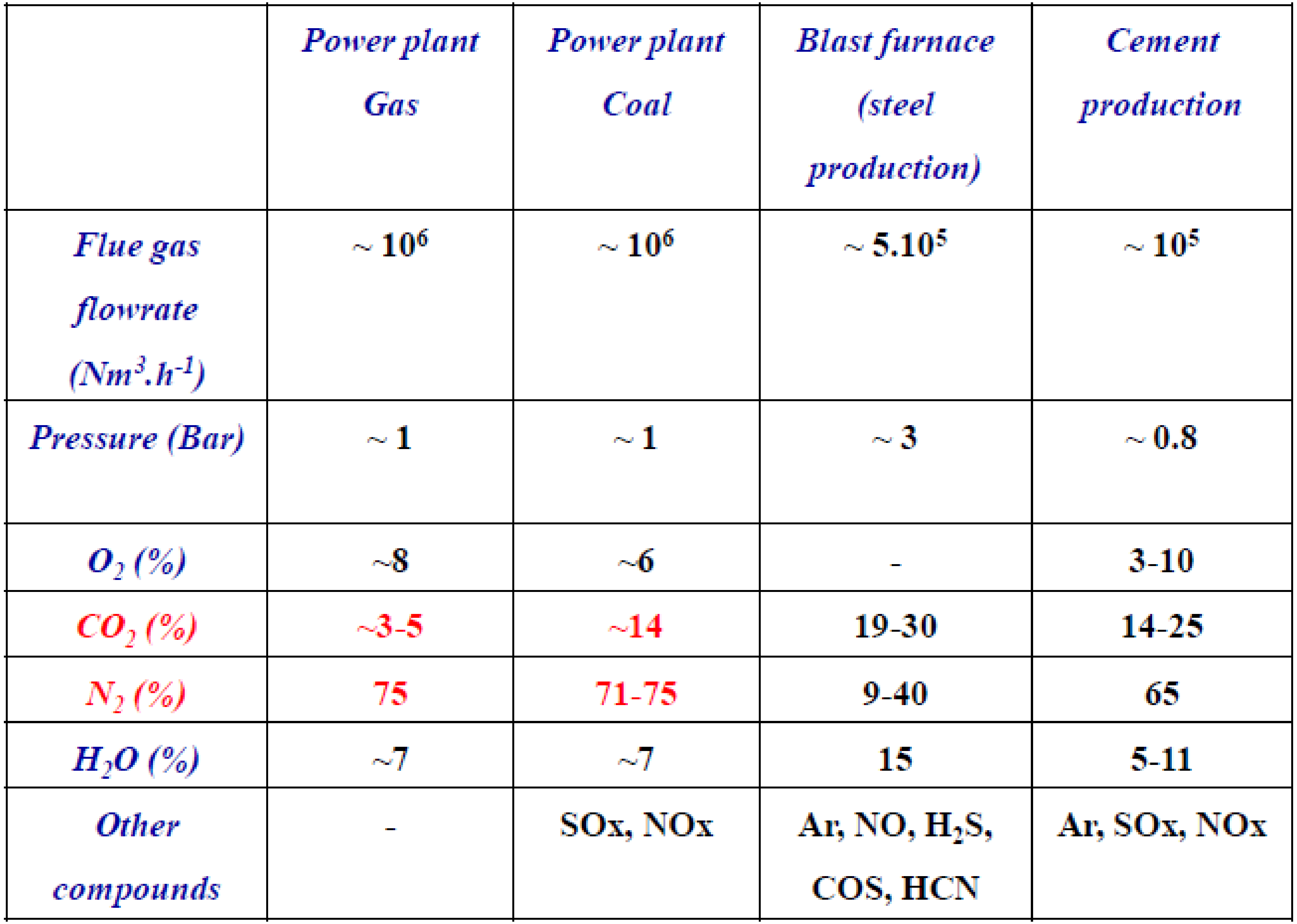
Multistage/recycling

Application
Available driving force
Separation objectives

Composition of emission points (Post-combustion)

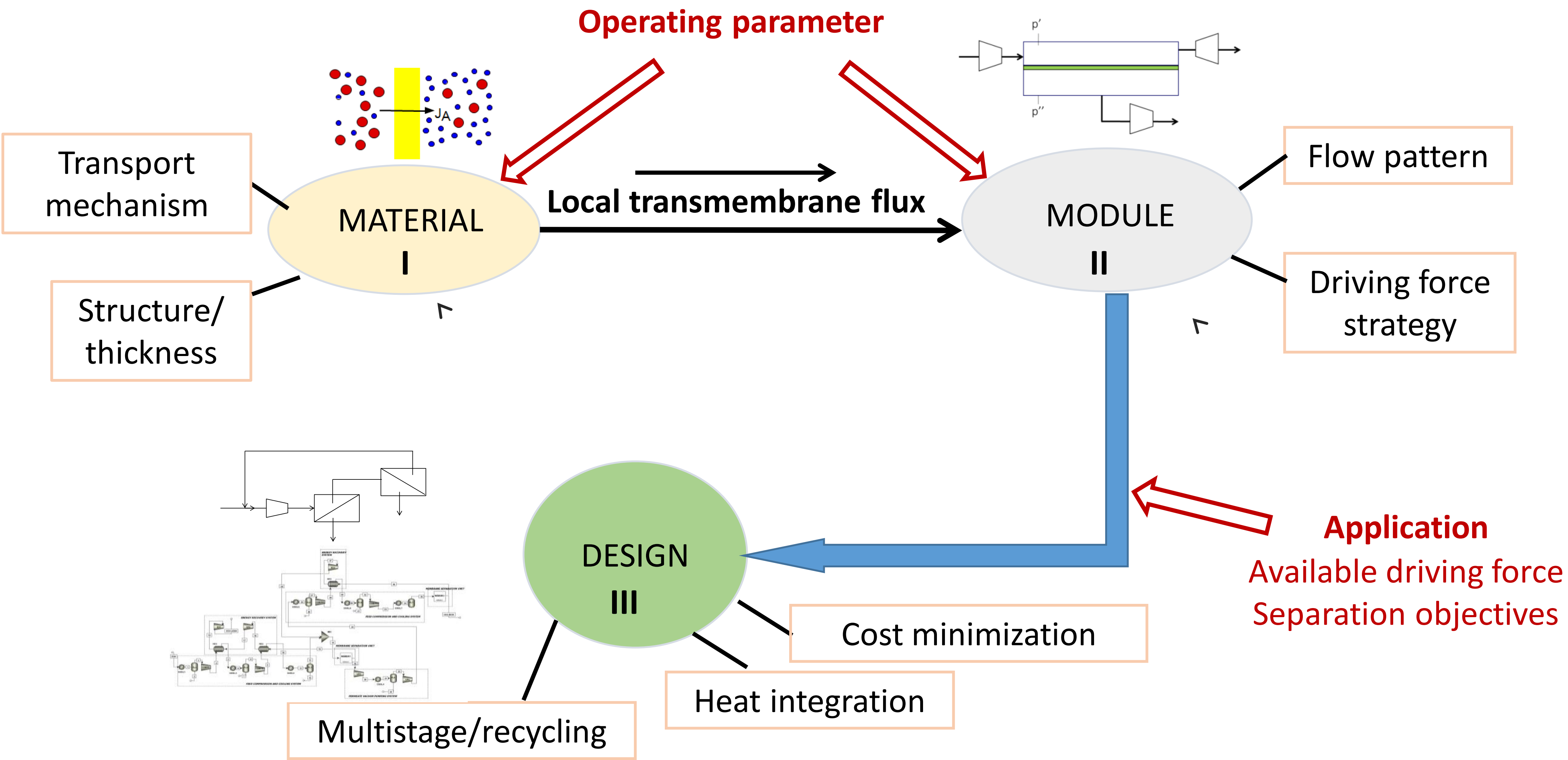
Low CO_2 partial pressures

Multicompnent mixtures



	Power plant Gas	*Power plant Coal*	*Blast furnace (steel production)*	*Cement production*
Flue gas flowrate ($Nm^3.h^{-1}$)	~ 10^6	~ 10^6	~ 5.10^5	~ 10^5
Pressure (Bar)	~ 1	~ 1	~ 3	~ 0.8
O_2 (%)	~8	~6	-	3-10
CO_2 (%)	~3-5	~14	19-30	14-25
N_2 (%)	75	71-75	9-40	65
H_2O (%)	~7	~7	15	5-11
Other compounds	-	SOx, NOx	Ar, NO, H_2S, COS, HCN	Ar, SOx, NOx

From material to process design



Operating parameter

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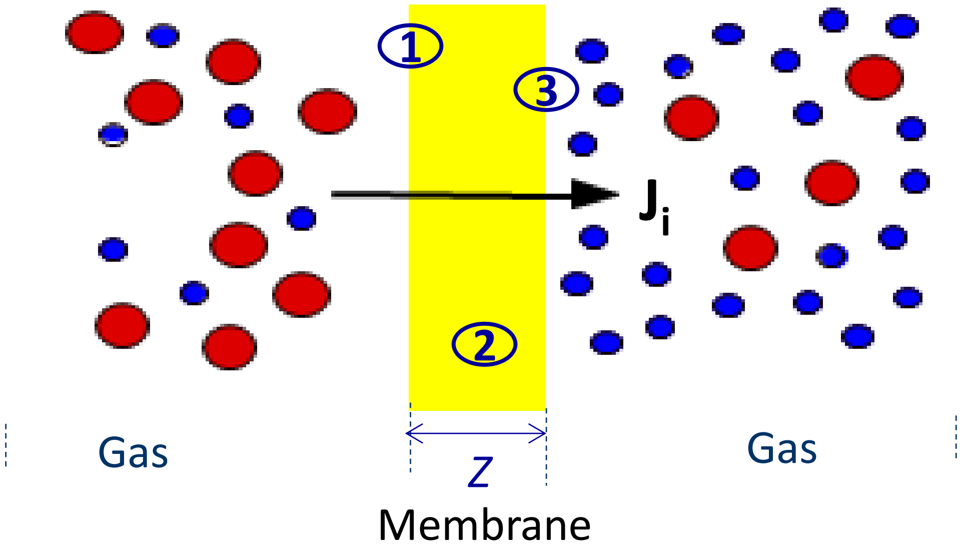
Application
Available driving force
Separation objectives

Partial transmembrane flux prediction



① Sorption
② Diffusion
③ Desorption

Solution-diffusion model

The simplest case: constant permeability (S and D constant)

When permeability is constant, steady state flux prediction based on transmembrane pressure (ΔP) and membrane dry thickness (z) is straightforward

Constant $\wp_i$

$$J_i = \frac{\wp_i}{Z}\left(p_i^{'} - p_i^{''}\right) = \frac{\wp_i}{Z}\Delta p_i \quad , \qquad \wp_i = D_i \times S_i$$

Some material performances for post-combustion carbone capture

Membrane type	*Material and/or carrier*	*CO_2/N_2 selectivity*	*CO_2 permeability (Barrer) or permeance (GPU)*
Gas separation membrane (dense polymers)	PEO-PBT PEG/Pebax© PEG-DME/ Pebax© PEGDA/PEGMEA **Polaris™**	70 47 43 41 **50**	120 Barrer 151 Barrer 600 Barrer 570 Barrer **1000 GPU**
Facilated transport membrane (FTM	PAAM-PVA / PS **PVAm/PS*** PEI / PVA PDMA/PS PDMAMA	80 **145** 230 53 80	24 GPU **212 GPU** 1 GPU 30 GPU 5 GPU
Liquid Membrane (LM)	PVAm-PVA/PS PVAm/PVA Amines/PVA Carbonic anhydrase Amines / PVA	90 90 500 250 493	22 GPU 15 GPU 250 GPU 80 GPU 693 Barrer

← ***MTR***

← ***NTNU***

Tested at pilot scale with real gas

*M.-B. Hägg's group

Variable permeability

S and/or D non constant, permeability is concentration(partial pressure) dependent

Steady state flux prediction requires an explicit knowledge of upstream and downstream pressure

$$J_i = f(p_i', p_i'', T)$$

Extrapolation based on transmembrane pressure (ΔP) can lead to significant error*….

$$\xcancel{J_i = \frac{\wp_i}{Z}\Delta p_i}$$

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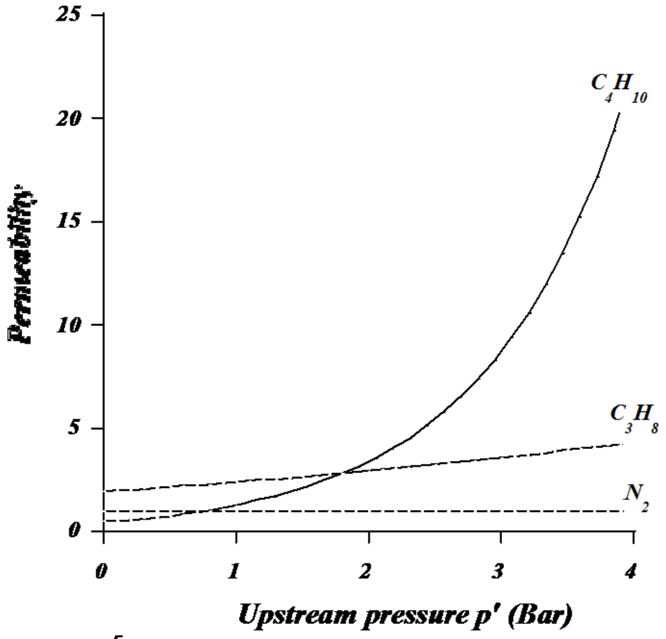
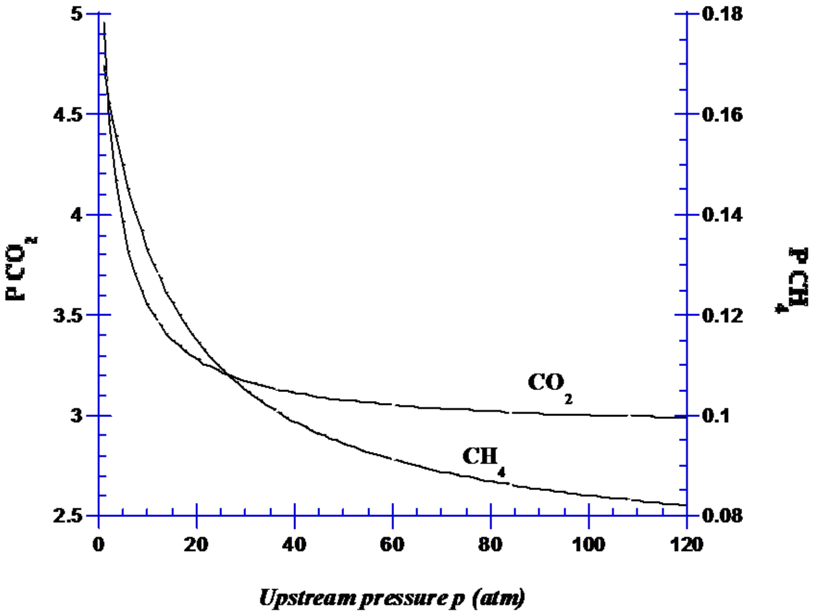
*Mauviel, G. et al. *J. Membr. Sci.* (2005) 266, 62-67.

Variable permeability

S and/or D non constant, permeability is concentration(partial pressure) dependent

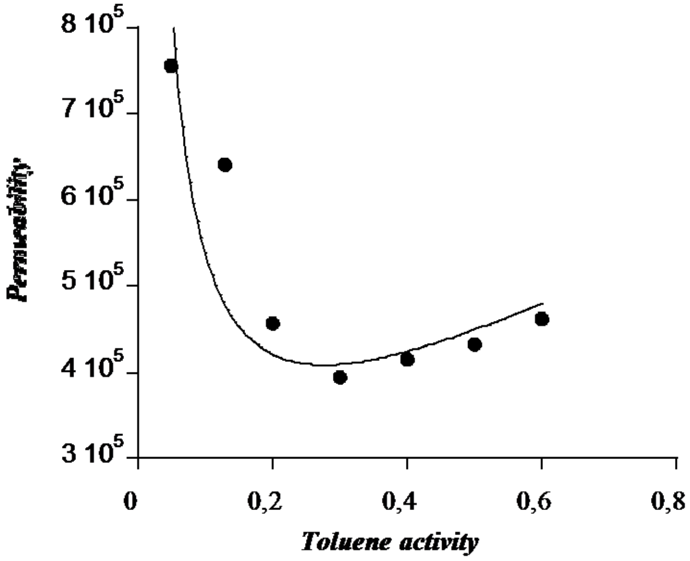
Rubbery (PDMS)





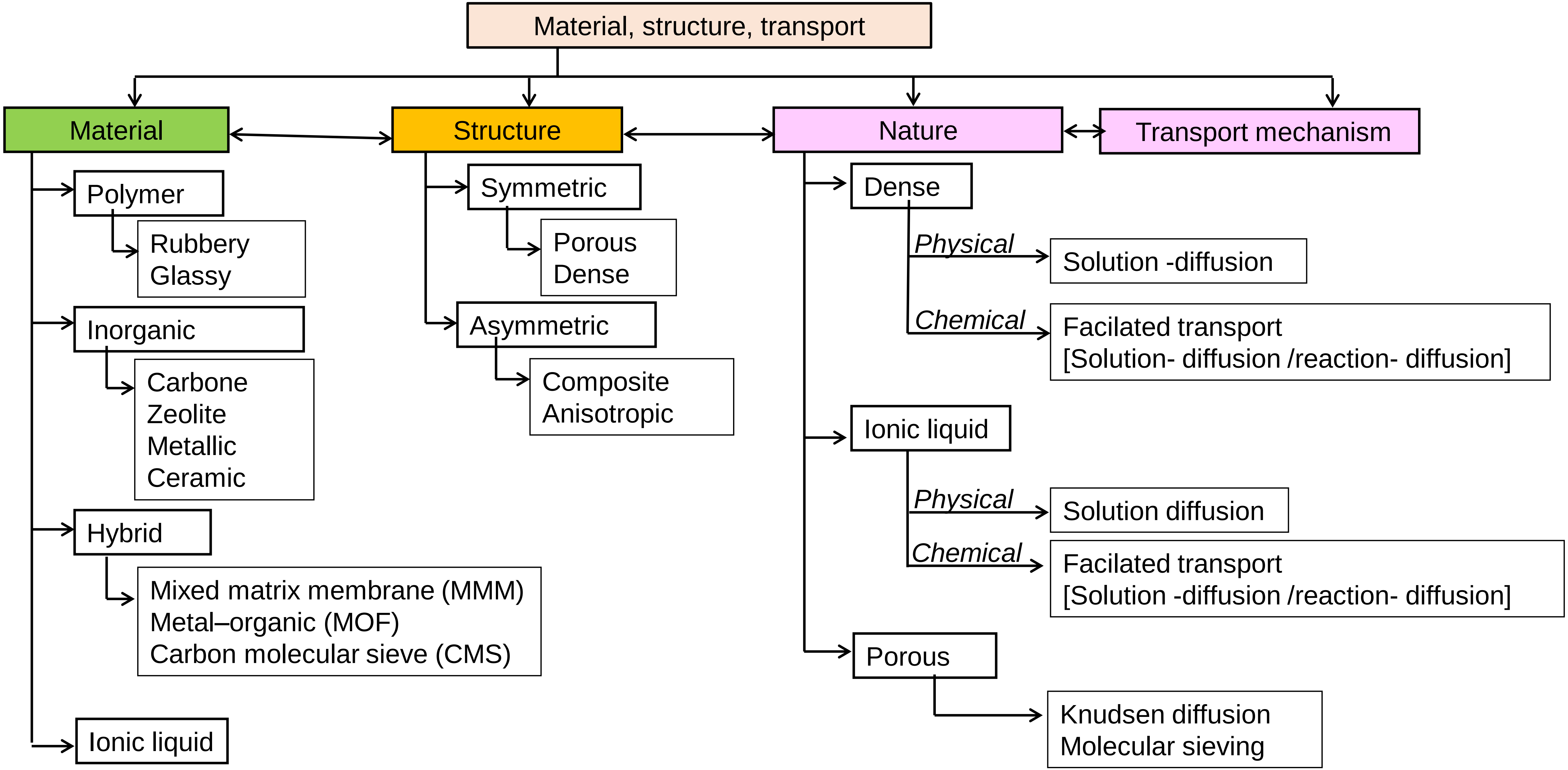
Glassy (PSf)

Superglassy (PTMSP)



Permeability is not always constant…

Material landscape



Material, structure, transport

Material

Polymer

Rubbery
Glassy

Inorganic

Carbone
Zeolite
Metallic
Ceramic

Hybrid

Mixed matrix membrane (MMM)
Metal–organic (MOF)
Carbon molecular sieve (CMS)

Ionic liquid

Structure

Symmetric

Porous
Dense

Asymmetric

Composite
Anisotropic

Nature

Transport mechanism

Dense

Physical → Solution -diffusion

Chemical → Facilated transport
[Solution- diffusion /reaction- diffusion]

Ionic liquid

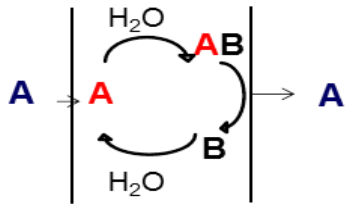
Physical → Solution diffusion

Chemical → Facilated transport
[Solution -diffusion /reaction- diffusion]

Porous

Knudsen diffusion
Molecular sieving

Transport model- partial transmembrane flux (*illustration*)

Glassy polymers ***Dual mode***	$J_i = -D_{D,i}\frac{dc_i}{dx} - D_{H,i}\frac{dc_i}{dx}$ with : $C_i = C_{D,i} + C_{H,i} = k_{D,i}p_i + \frac{C'_{H,i}b_i\ p_i}{1+\sum_{k=1}^{N} b_k\ p_k}$ $J_i = D_{D,i}\underbrace{\frac{k_{D,i}}{Z}\left(p'_i - p''_i\right)}_{\text{Henry's sorption}} + D_{H,i}\underbrace{\frac{C'_{H,i}b_i}{Z}\left(\frac{p'_i}{1+\sum_{k=1}^{N} b_k x_k p'} - \frac{p''_i}{\sum_{k=1}^{N} b_k x_k p''}\right)}_{\text{Langmuir's sorption}}$
Facilated transport membrane  	$J_A = -D_A\frac{dc_A}{dx} - D_{AB}\frac{dc_{AB}}{dx}$ ⇒ $J_{i\neq A} = D_i\frac{k_{D,i}}{l}\left(p'_i - p''_i\right)$ $J_A = D_A\underbrace{\frac{k_{D,A}}{l}\left(p'_A - p''_A\right)}_{\text{SD mechanism}} + \underbrace{D_{AB}KC_Tk_{D,A}\left(\frac{p'_A}{1+Kk_{D,A}p'_A} - \frac{p''_A}{1+Kk_{D,A}p''_A}\right)}_{\text{RD mechanism}}$ Instantaneous reaction
Rubbery membrane (vapor permeation)	$J_i = D_i\frac{\phi'_i - \phi''_i}{Z\ V_{mi}}$ **Florry Huggin :** $\ln(a_i) = \ln(\phi_i) + (1-\phi_i) + \chi_i(1-\phi_i)^2$ $a_i = \frac{p_i}{p_i^{sat}}$ **ENSIC model :** $\phi_i = \frac{\exp((K_{Si}-K_{Pi})a_i)-1}{\frac{K_{Si}-K_{Pi}}{K_{Pi}}}$ $\phi_i = C_i Vm_i$

Transport model parameters

Type de membrane	Mechanism	Transport model	Model parameter
Rubbery (vapor permeation)	SD	Florry Huggin/ENSIC	KPi, KSi
Glassy	SD	Dual Mode	$D_{Di}, D_{Hi,}\ k_{Di},$ $C'_{Hi}\ et\ b_i$
Fixed site carrier membrane	SD et RD	Facilated transport	$D_i, k_{Di}, D_{HCO_3^-}, K\ et\ C_T$

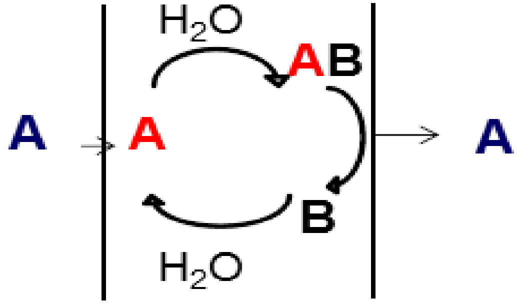
D: diffusion
S: sorption
R : reaction

Need for experimental data for model parameter determination

Transport model parameter

Type de membrane	Mechanism	Transport model	Model parameter
Rubbery (vapor permeation)	SD	Florry Huggin/ENSIC	KPi, KSi
Glassy	SD	Dual Mode	$D_{Di}, D_{Hi,}\ k_{Di},$ $C'_{Hi}\ et\ b_i$
Fixed site carrier membrane	SD et RD	Facilated transport	$D_i, k_{Di}, D_{HCO_3^-}, K\ et\ C_T,$ **Z, k_{-1}**

$A{=}CO_2$
$\mathrm{B} = \mathrm{R} - \mathrm{NH}_3^+$
$\mathrm{AB} = HCO_3^-$



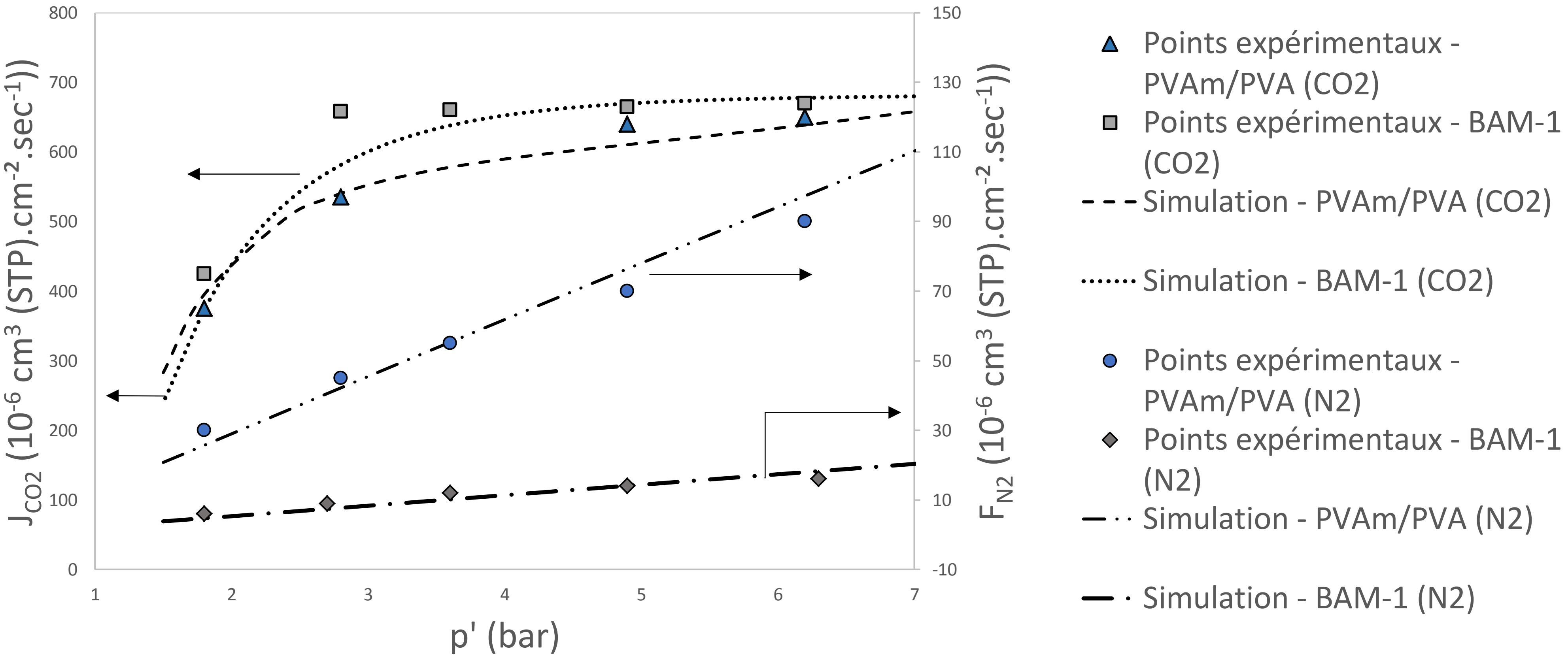
Kinetically controlled reaction

$$Da = \frac{k_{-1}z^2}{D_{AB}}$$

Damköhler number

Facilated transport membrane - Model /experiment

M. Pfister's PhD



Data from literature

Experimental results from :

- A. Mondal et al., *Int. J. Greenh. Gas Control*, 2015.
- M. Wang et al., *Energy Environ. Sci.*, 2011.
- Y. Cai, *J. Membr. Sci.*, 2008.

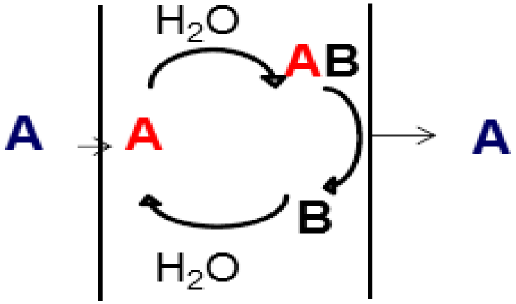
Material-process design interaction

$A = CO_2$

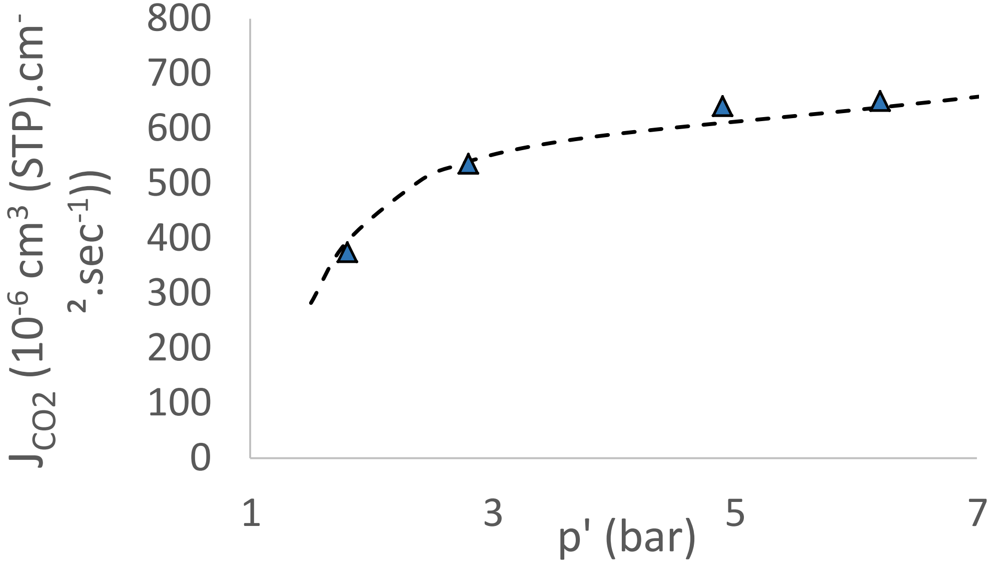
$B = R - NH_3^+$

$AB = HCO_3^-$

Fixed site carrier membrane



PVAm/PVA Binary dry basis CO_2/N_2 (20%/80%) (Mondal et al.)



- Need humidity (near saturation) (need to avoid gas drying)
- Active site carrier saturation at high CO_2 partial pressure

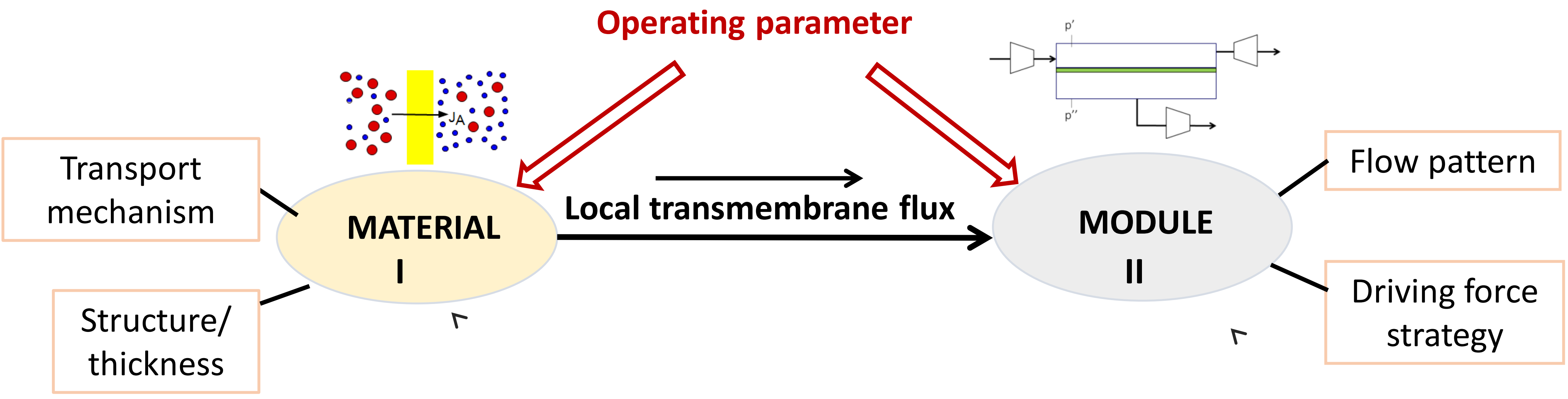
This impacts module driving force strategy :

- **Upstream pressure : limited to avoid active site saturation**
- **Downstream pressure : limited to avoid membrane drying**

+

Need to avoid gas drying humidity control

Material-Module design interactions



Operating parameter

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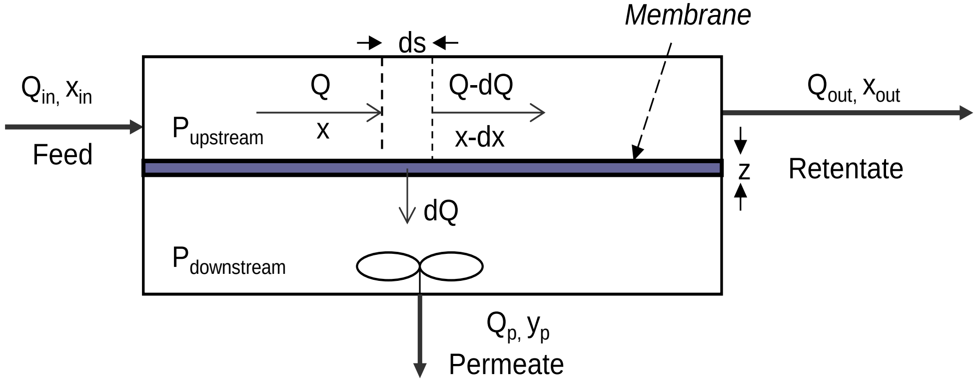
MODULE
II

Flow pattern

Driving force strategy

Membrane gas separation process simulation
Baseline approach



Key variables

Selectivity $$\alpha^* = \frac{\Pi_A}{\Pi_B}$$

Pressure ratio $$\psi = \frac{P''}{P'}$$

Stage cut $$\theta = \frac{Q_p}{Q_{in}}$$

Key assumptions

Binary mixture

Well defined hydrodynamics (CPF, CC, Co)

Constant P', P'', T

Constant permeability

Mass transfer resistance = membrane (no polarisation effect)

No flux coupling

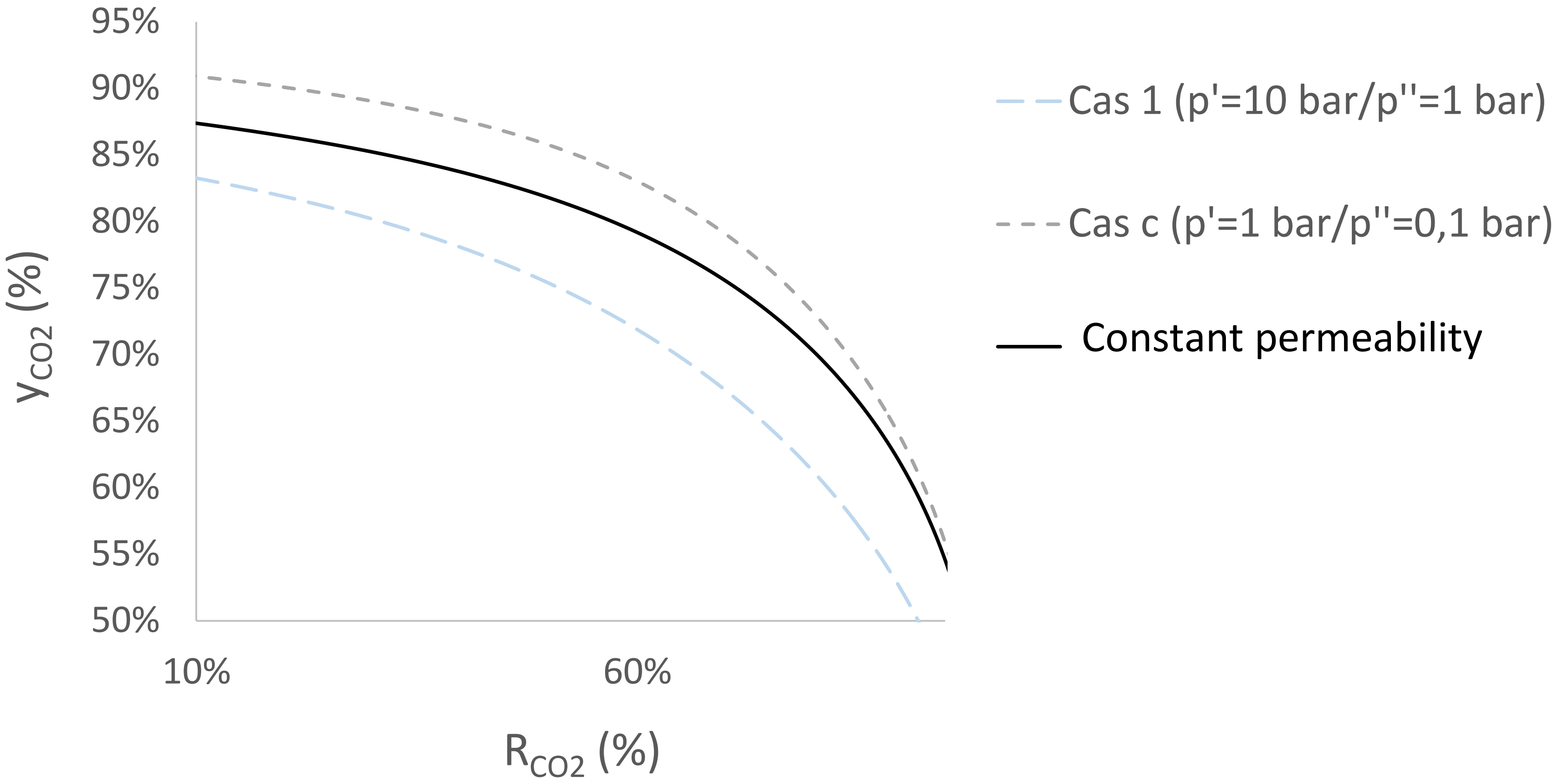
Process modeling studies : a complex landscape

		ΔP’’	**ΔP’**	**Concentration polarization**	**Joule Thompson cooling**	**Real gas behavior**	**$\mathscr{P}$= f(T)**	**$\mathscr{P}$=f(P)**
Alpers et al. 1999		-	-	+	-	+	-	-
Coker et al. 1999					+			
Kaldis et al. 1998 and 2000		+	-	-	-	-	+	-
Marriott et al. 2001		+	+	+				
Esteves et Motta 2002		-	-	-	-	-	-	-
Makaruk et Harasek 2009		-	-	-	-	-	-	-
Katoh et al. 2011		+	-	-	-	-	-	-

M. Scholz, T. Harlacher, T. Melin, and M. Wessling, “Modeling Gas Permeation by Linking Nonideal Effects,” *Ind. Eng. Chem. Res.*, vol. 52, no. 3, pp. 1079–1088, Jan. 2013.

Variable permeability behavior can impact module design…

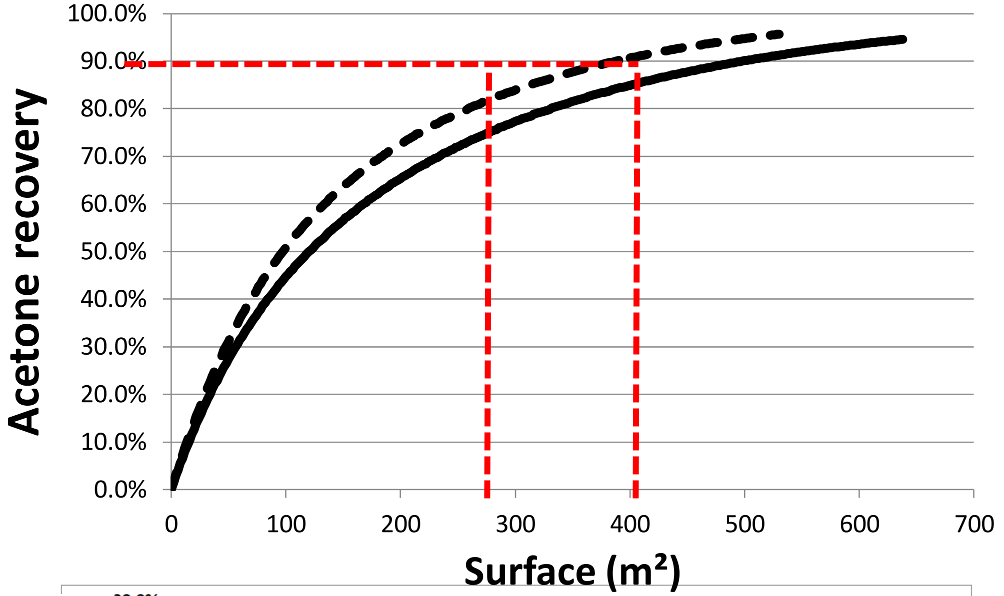
*Glassy membrane **
Dual mode transport model
CO_2/ CH4 : 20%/80%



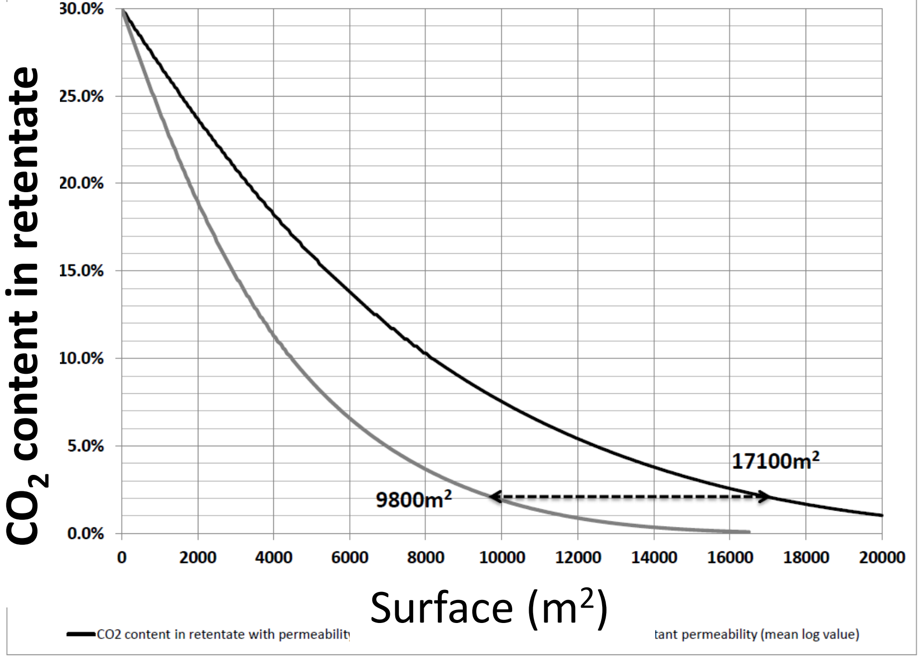
* 6FDA-TAPDO

Variable permeability behavior can impact module design

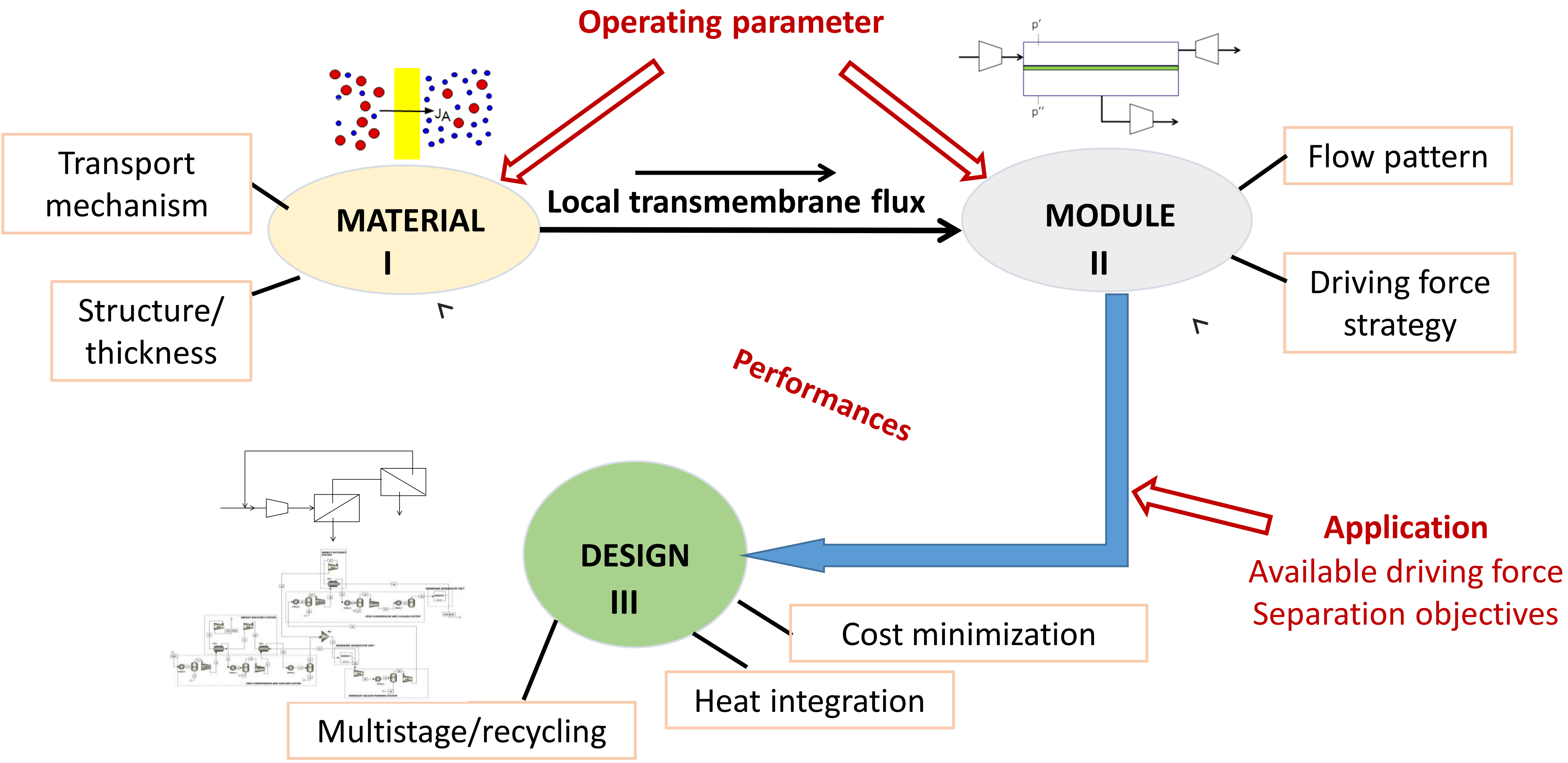
Acetone recovery from air
Elastomeric membrane (PDMS)
Flory Huggins transport model



Natural gas treatment
Glassy membrane (CA)
Dual mode transport model



From material to process design



Operating parameter

Transport mechanism

Structure/ thickness

MATERIAL I

Local transmembrane flux

MODULE II

Flow pattern

Driving force strategy

Performances

Application
Available driving force
Separation objectives

DESIGN III

Cost minimization

Heat integration

Multistage/recycling

MEMSIC* : a user friendly CAPE OPEN simulation tool

Tailor made multicomponent module simulation for PSE

Characteristics:

Multicomponent mixtures compatibility (> 50)

Constant or variable permeability behavior

Transport models (S-D mechanism):
Flory-Huggins, Dual mode, ENSIC, faciltated transport membrane

Multistages with recycling loops

Sucessfully tested on PSE softwares
(Aspen, Hysis, ProII, G Prom's…)

***: © R. Bounaceur (2015)**

MEMSIC : a user friendly CAPE OPEN simulation tool

❑ Operating inlet data

- Temperature, T
- Pressure, P_{in}
- Composition, x_{in}
- Flow rate, Q_{in}

❑ Material data

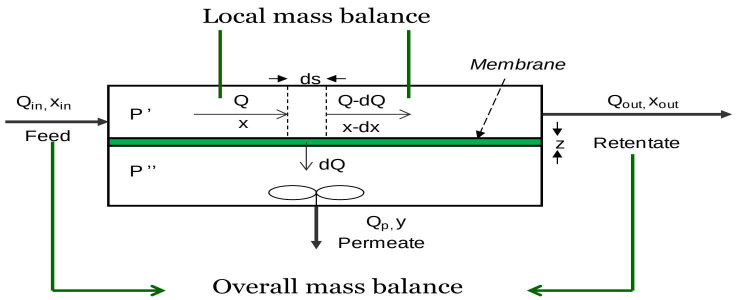
- Transport model + parameters

Or Constant permeability model and active layer thickness

- Membrane surface area (design option)

❑ Specifications/ Objectives

Purity, recovery ratio



$$\frac{dq'}{dS} = -\sum_i J_i(x_i, y_i, p', p'') \quad , \quad y_i = \frac{\alpha_i(x_i - \psi y_i)}{\sum_i \alpha_i(x_i - \psi y_i)}$$

$$\frac{dx_i}{dS} = \frac{x_i \sum_i J_i(x_i, yi, p', p'') - J_i(x_i, y_i, p', p'')}{q'}$$

$$\text{à } \; S = 0, \; q' = 0 \; \text{ et } x_i = x_{in,i}$$

❑Driving force

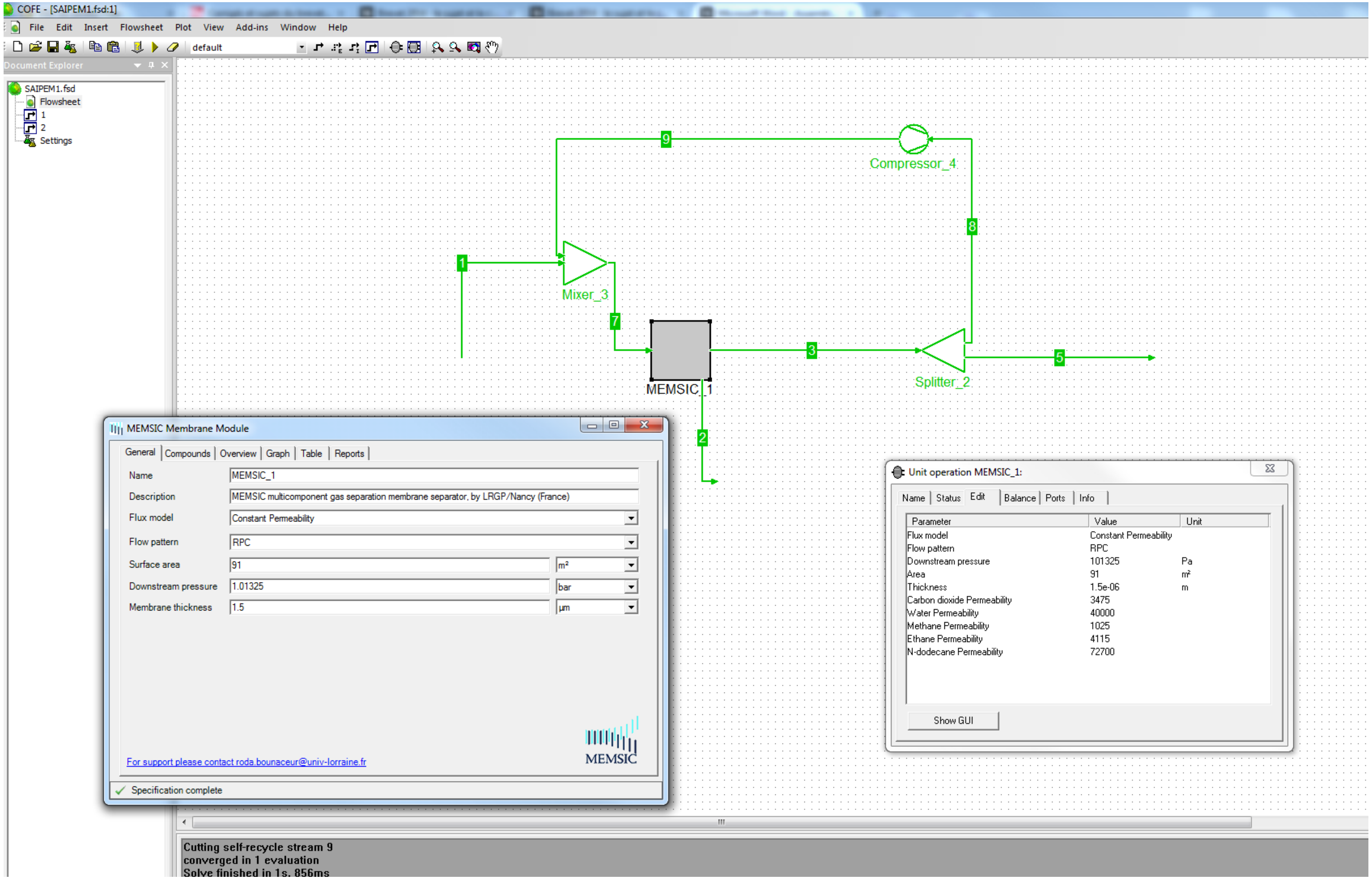
- Feed compression /vacuum/ turbo-expander on the retentate.

❑Flow configuration

- Co-current
- Counter current
- Cross-plug flow

Energy consumption
Required membrane surface area

MEMSIC* : a user friendly CAPE OPEN simulation tool



MEMSIC Membrane Module

Name	MEMSIC_1	
Description	MEMSIC multicomponent gas separation membrane separator, by LRGP/Nancy (France)	
Flux model	Constant Permeability	
Flow pattern	RPC	
Surface area	91	m²
Downstream pressure	1.01325	bar
Membrane thickness	1.5	µm

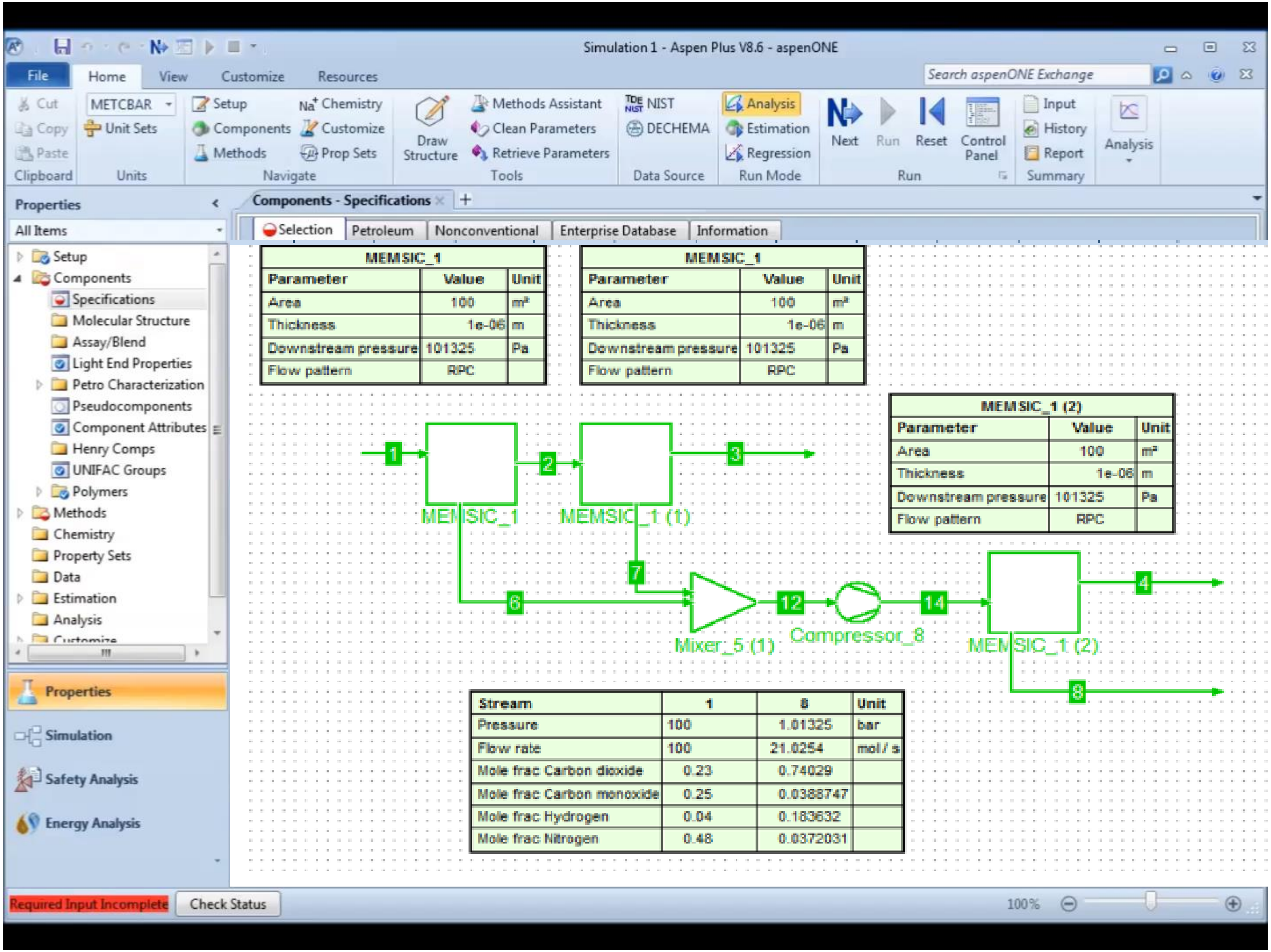
For support please contact roda.bounaceur@univ-lorraine.fr

✓ Specification complete

Unit operation MEMSIC_1:

Parameter	Value	Unit
Flux model	Constant Permeability	
Flow pattern	RPC	
Downstream pressure	101325	Pa
Area	91	m²
Thickness	1.5e-06	m
Carbon dioxide Permeability	3475	
Water Permeability	40000	
Methane Permeability	1025	
Ethane Permeability	4115	
N-dodecane Permeability	72700	

```
Cutting self-recycle stream 9
converged in 1 evaluation
Solve finished in 1s, 856ms
```



MEMSIC_1		
Parameter	Value	Unit
Area	100	m²
Thickness	1e-06	m
Downstream pressure	101325	Pa
Flow pattern	RPC	

MEMSIC_1		
Parameter	Value	Unit
Area	100	m²
Thickness	1e-06	m
Downstream pressure	101325	Pa
Flow pattern	RPC	

MEMSIC_1 (2)		
Parameter	Value	Unit
Area	100	m²
Thickness	1e-06	m
Downstream pressure	101325	Pa
Flow pattern	RPC	

Stream	1	8	Unit
Pressure	100	1.01325	bar
Flow rate	100	21.0254	mol / s
Mole frac Carbon dioxide	0.23	0.74029	
Mole frac Carbon monoxide	0.25	0.0388747	
Mole frac Hydrogen	0.04	0.183632	
Mole frac Nitrogen	0.48	0.0372031	

Concluding remarks

- *Post combustion carbon capture (CO_2, H_2O, N_2, O_2) : multicomponent problem*
  - *Compression changes water content*
  - *Water decreases surface (internal sweep)*
- *Simulation based on the sole pressure difference dependency of permeability are not able to correctly predict separation performance*
- *Rigorous steady state flux prediction requires an explicit knowledge of upstream and downstream pressure*
- *Taking into account variable permeability generates a large effort in terms of inputs data (such effort might be not necessary but it can be of major importance in some cases (*glassy, reactive membranes, vapor permeation in rubbery*)*

EU- Australian workshop, Oslo, Norway
13th- 14TH september 2017

Thank you for your attention

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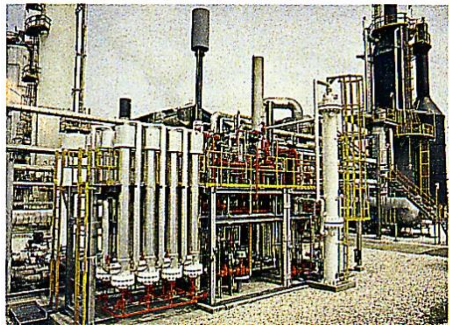
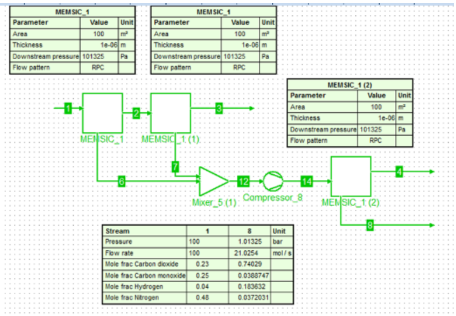
eric.favre@univ-lorraine.fr





MEMSIC_1

Parameter	Value	Unit
Area	100	m²
Thickness	1e-06	m
Downstream pressure	101325	Pa
Flow pattern	RPC	

MEMSIC_1

Parameter	Value	Unit
Area	100	m²
Thickness	1e-06	m
Downstream pressure	101325	Pa
Flow pattern	RPC	

MEMSIC_1 (2)

Parameter	Value	Unit
Area	100	m²
Thickness	1e-06	m
Downstream pressure	101325	Pa
Flow pattern	RPC	

Stream	1	8	Unit
Pressure	100	1.01325	bar
Flow rate	100	21.0254	mol / s
Mole frac Carbon dioxide	0.23	0.74029	
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