DEMCAMER
Catalytic Membrane Reactors

SEVENTH FRAMEWORK PROGRAMME

Micro-structured membrane reactors for WGS reaction

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PIN21

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Newcastle University

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Where innovation starts

Outline

- DEMCAMER
- Objectives
- Strategy
- Result and discussion
- Lab-scale reactors

We all have a date with the planet

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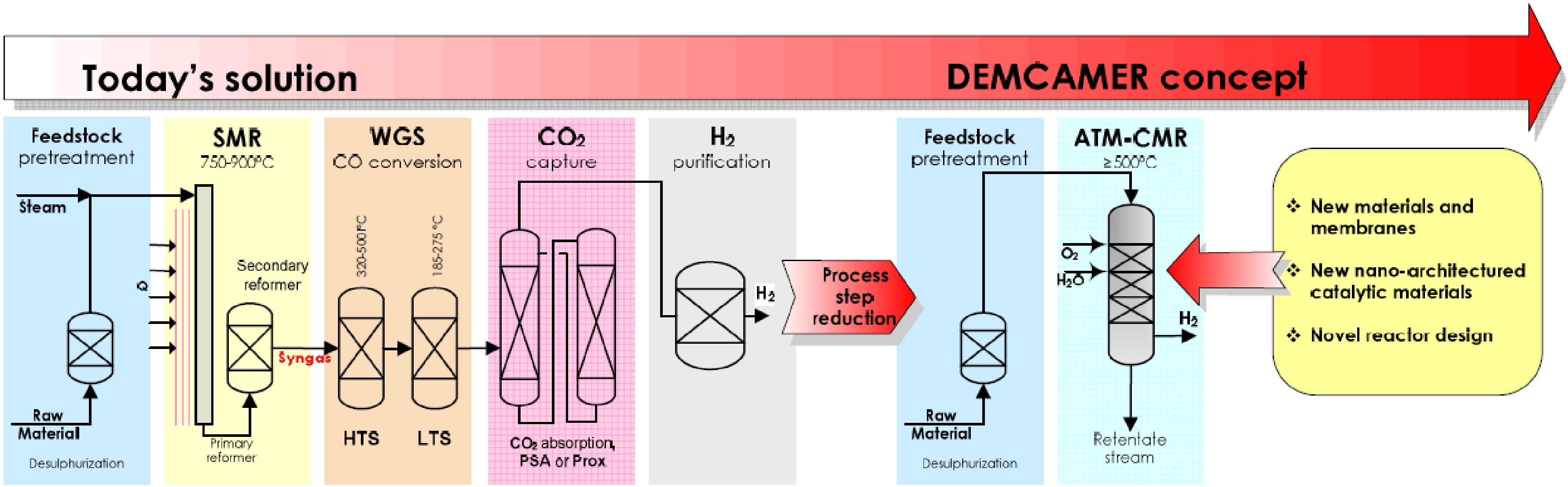
DEMCAMER

DESIGN AND MANUFACTURING OF CATALYTIC MEMBRANE REACTORS BY DEVELOPING NEW NANO-ARCHITECTURED CATALYTIC AND SELECTIVE MEMBRANE MATERIALS



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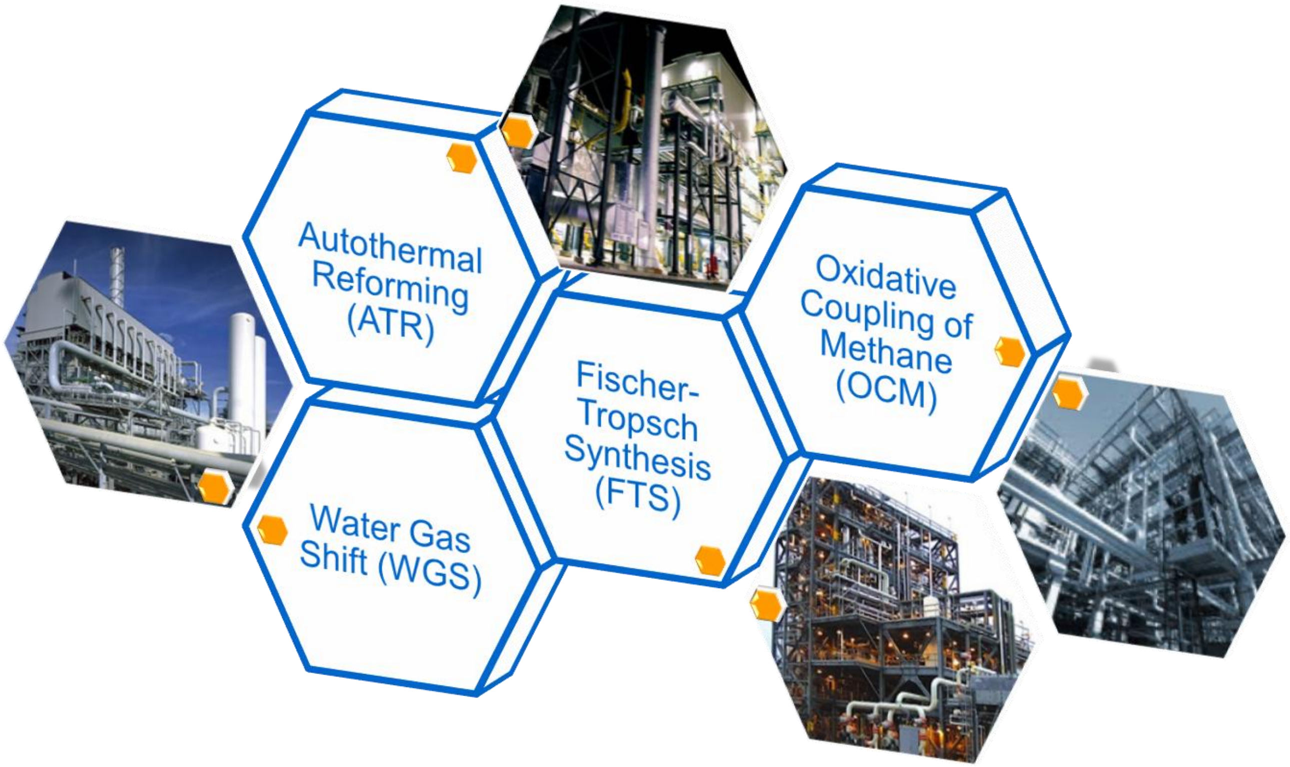
Selected chemical processes



Composition consortium

tecnalia Inspiring Business

ICP CSIC

University of Calabria

TU/e Technische Universiteit Eindhoven University of Technology

TOTAL

Fraunhofer IKTS

INERIS controlling risks for sustainable development

BIC SB RAS

CerPoTech Ceramic Powder Technology

vito vision on technology

Rauschert

Hybrid Catalysis

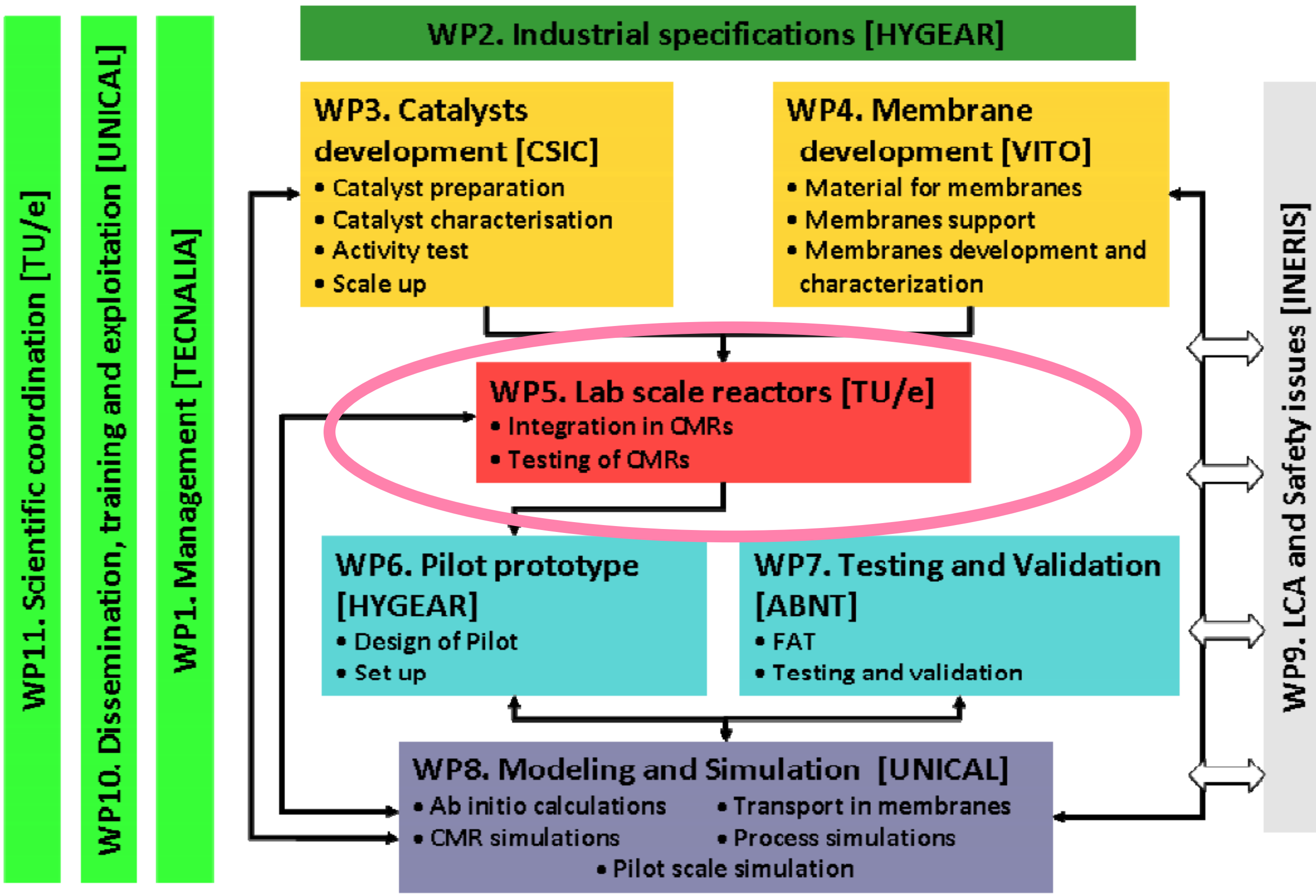
HYGEAR

ABENGOA BIOENERGIA NUEVAS TECNOLOGIAS

Höganäs

Quantis Sustainability counts

Work packages



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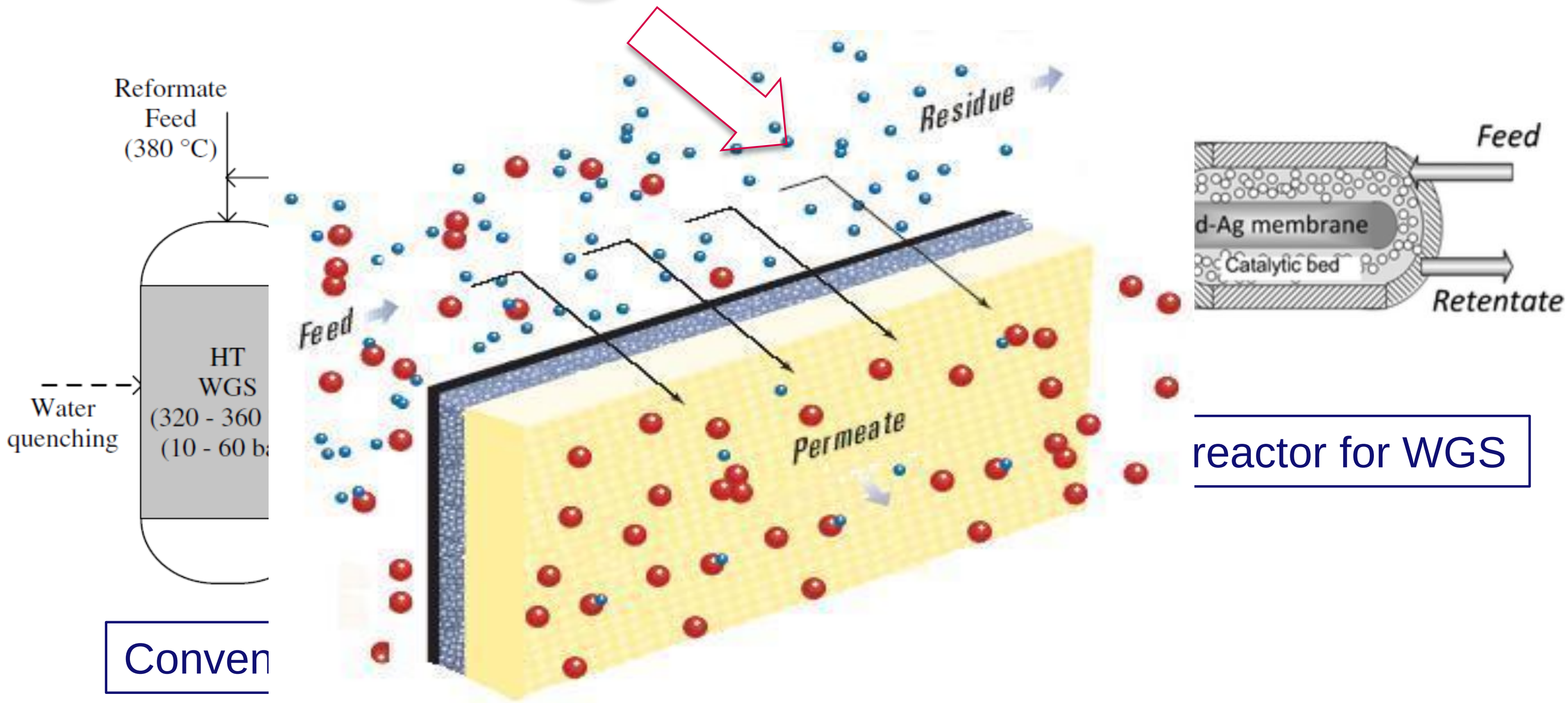
Water Gas Shift (WGS) reaction

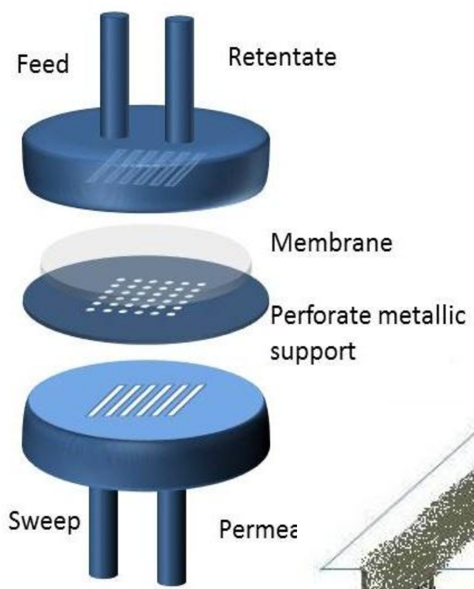
$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298}$=-41.09 kJ/mol



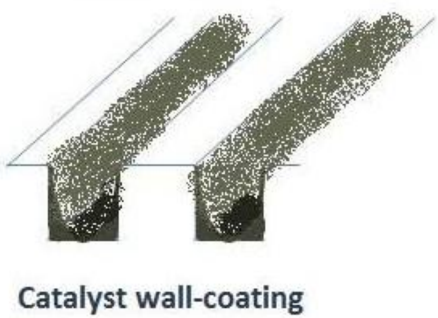
Micro-structured membrane reactors

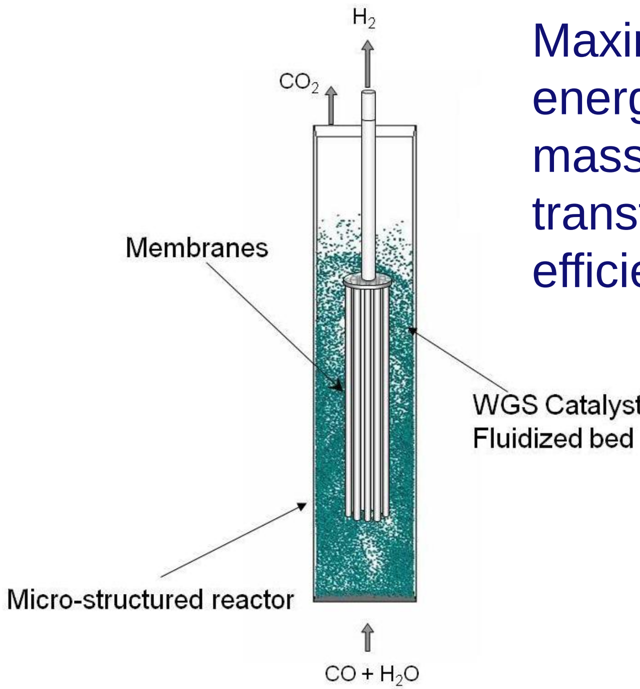
Maximization of membrane area

Complete process integration



Unique mass and heat transfer capabilities





Maximal energy & mass transfer efficiency

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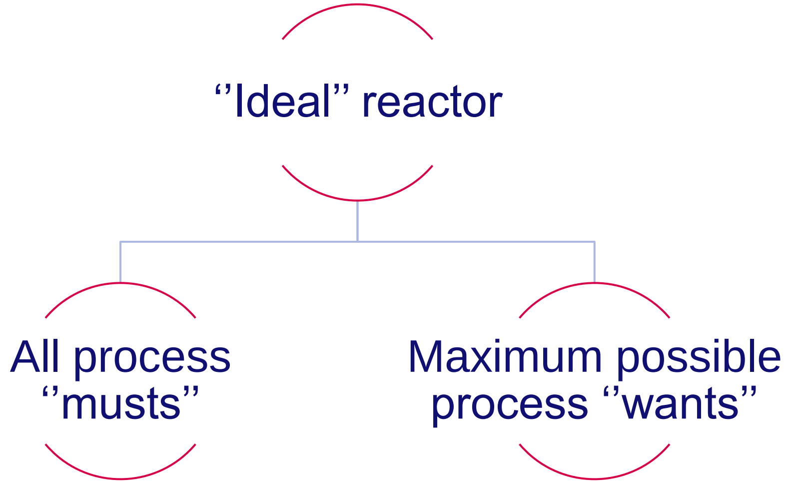
Objectives

- To evaluate different catalyst-membrane integration ways in order to optimize some reactor configurations (fluidized bed and packed bed micro-reactors)
- Test and validate the best designs based on the study of different concepts of membrane reactors at lab scale

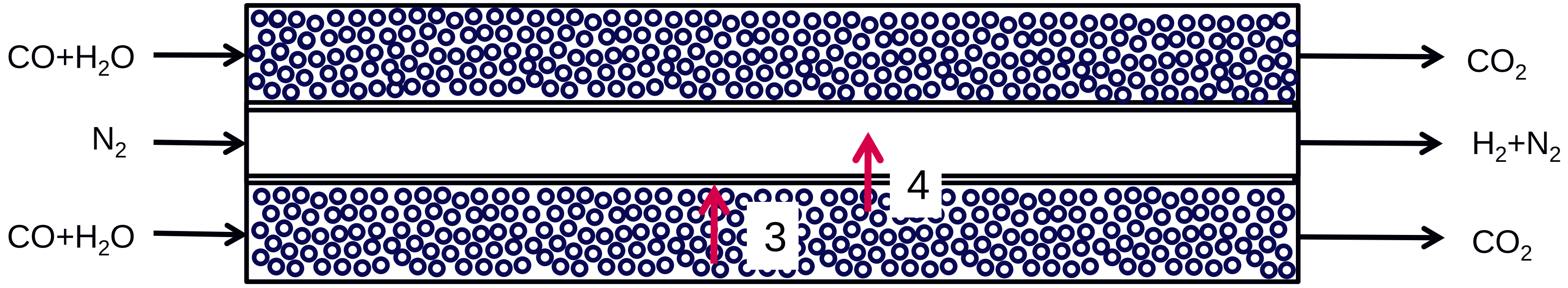
Strategy

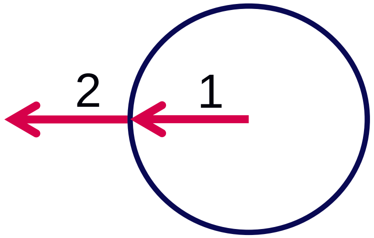
- **How do we arrive at the ideal multiphase reactor configuration meeting most closely with the process requirements?**
- **The problem is divided into three levels to be analyzed**



- ❑ **Reaction**
- ❑ **Separation**
- ❑ **Reactor type**

Mass transfer phenomena inside a PBMR





1) Internal mass transfer resistance
2) External mass transfer resistance
3) Resistance from bed to wall
4) Resistance through the membrane
5) Catalyst activity

Packed Bed Membrane reactor

1D pseudo-homogeneous

- **Continuity equation**

$$\frac{\partial}{\partial t}(\varepsilon\rho_g) + \frac{\partial}{\partial z}(\varepsilon\rho_g u) = 0$$

- **Total momentum balance**

$$\beta = 150\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu_g}{\rho_g d_\rho^2} + 1.75\frac{(1-\varepsilon)}{\varepsilon^3}\frac{\varepsilon u}{d\rho}$$

$$\frac{\partial}{\partial t}(\varepsilon\rho_g u) + \frac{\partial}{\partial z}(\varepsilon\rho_g u^2) = -\varepsilon\frac{\partial p}{\partial z} - \beta\varepsilon\rho_g u - \frac{\partial}{\partial z}(\varepsilon\tau_g) + \varepsilon\rho_g g$$

Friction coefficient

Packed Bed Membrane reactor

- **Component mass balance**

Trans membrane flux term depends on the membrane used

$$\frac{\partial}{\partial t}(\varepsilon\rho_g\omega_i) = -\frac{\partial}{\partial z}(\varepsilon\rho_g u\omega_i) + \frac{\partial}{\partial z}\left(\rho_g D_{ax,i}\frac{\partial\omega_i}{\partial z}\right) + S_{r,i} - J_i$$

$$S_{r,i} = (1-\varepsilon)\rho_g M_i \sum_{j=1}^{nr}\gamma_{ij}r_j$$

e.g. Richardson equation for permeation through thick Pd-based membranes

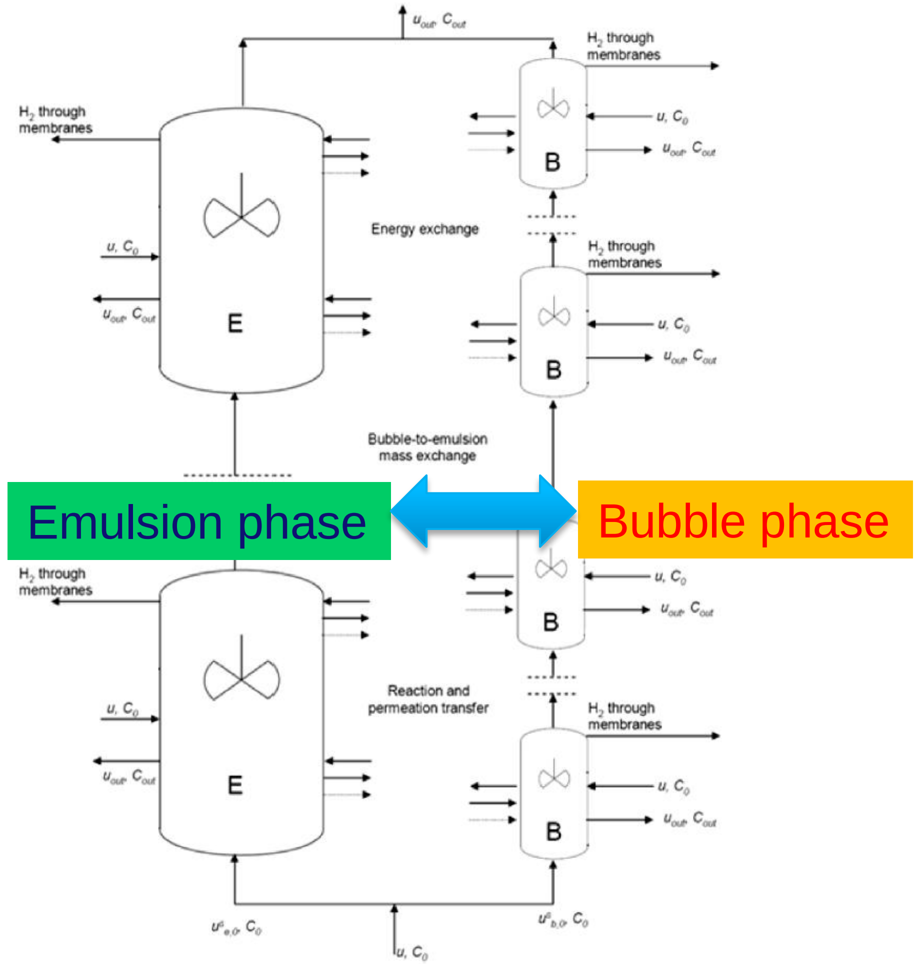
$$J_{H2} = \frac{Pe^0 \exp\left(\frac{Ea}{RT}\right)\left(\sqrt{P_{H_2,upstream}} - \sqrt{P_{H_2,downstream}}\right)}{\delta_m}$$

Fluidized bed Membrane reactor

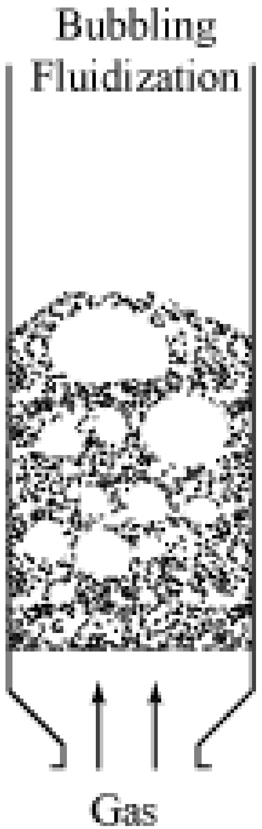
- **A typical two-phase model for a membrane assisted fluidized bed reactor can be used for simulation**

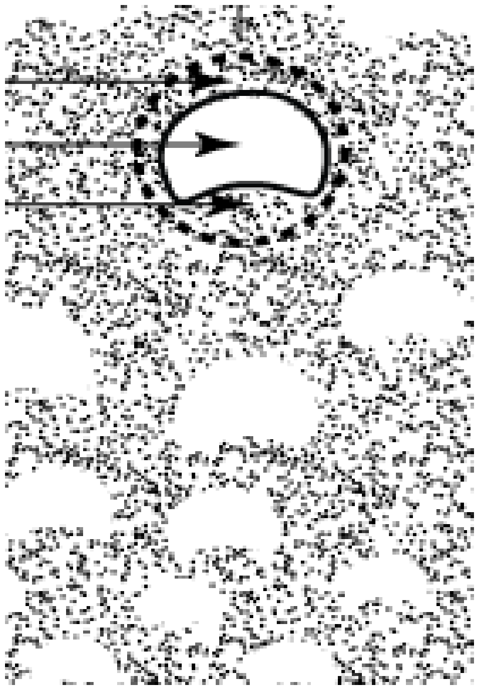
- **Membranes are immersed in the reactor**

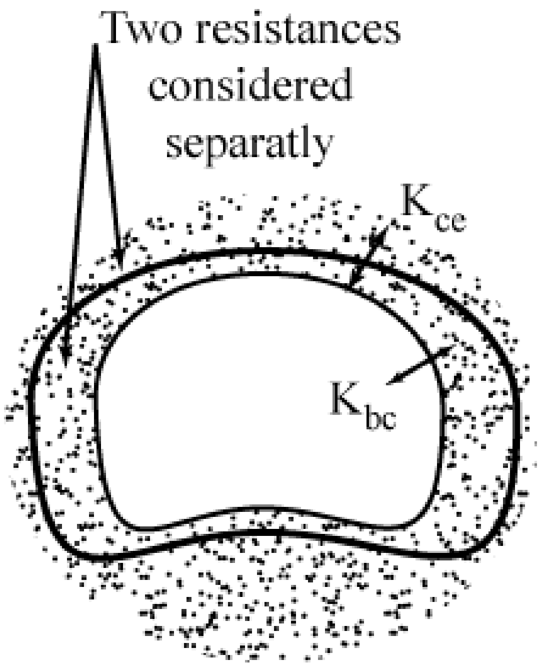
- **Reactor consists of two phase. The bubble and the emulsion phase**



Mass transfer phenomena inside a FBMR

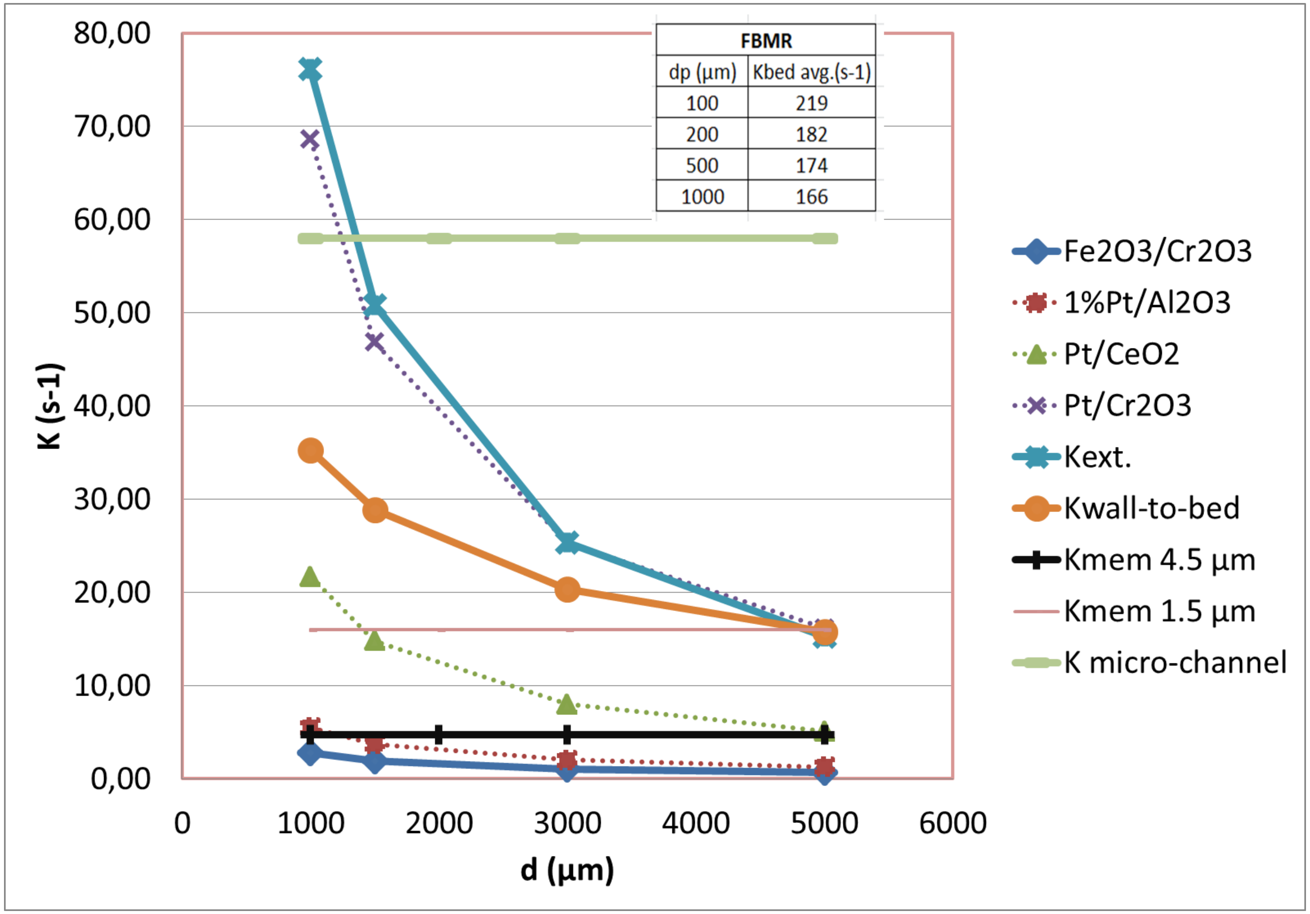






$$\frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}}$$

General maps



DEMCAMER target for membrane

Membrane code	Selective layer material / thickness	Black resin in the interphase	Temperature (ºC)	Permeance H_2 [10^{-8} (mol/m2 s Pa)]*	H_2/N_2 ideal selectivity
DEMCAMER/REFORCELL Projects target	*Pd alloy / <3 µm*	*N/A*	*400*	***260***	***10.000***
P19	Pd PVD / not measured	Yes	300	**85**	**26.100**
P20	Pd PVD / 4.0-4.2 µm	No	400	**175**	**3.288**
P44	Pd-Ag PVD / not measured	Yes	300	**162**	**8.972**
P47	Pd-Ag PVD / not measured	Yes	300	**71**	**8.662**
AIST (Pacheco et al. 2006)	Pd pore filling / 5 µm	N/A	300	**170**	**1.000**
AIST (Pacheco et al. 2008)	Pd pore filling / 5 µm	N/A	425	**210**	**300**
CSM (Hatlevik et al. 2010)	Pd-Au ELP / 2.3 µm	N/A	400	**710**	**82.000**
DICP (Goldbach and Xu 2011)	Pd-Au ELP / 2-3 µm	N/A	500	**620**	**1.400**
SINTEF (Peters et al. 2011a)**	Pd-Ag PVD / 2.8 µm	N/A	400	**1.500**	**2.900**
WPI (Ma 2009)	Pd ELP / 7 µm	N/A	450	**96**	**4.500**
REB (2003)	Pd-Ag / (4-5 µm)	N/A	400	**8,12**	**-**

Gallucci, F., Fernandez, E., Corengia, P., van Sint Annaland, M, Chemical Engineering Science 92 , (2013) 40-66.

DEMCAMER target for catalyst

Catalyst type	BET area (m2/g)	Rate at 450 °C (mmol/g cat. s)	Ea (KJ/mol)
DEMCAMER catalyst	75.2	1.864	52±1
Pt/Cr2O3	22	0.174	41±2
Pt/Cr2O3-Fe3O4	63	0.149	50±3
Pt/U3O8	2.3	0.142	59±3
Pt/CeO2-ZrO2	67	0.079	28±1
Pt/CeO2	122	0.055	52±1
Pt/MgO	77	0.034	41±1
Pt/V2O5	6	0.032	52±3
Pt/Fe3O4	29	0.022	55±3
Pt/MoO3	1.6	0.02	49±3
Pt/Al2O3	272	0.014	47±1

Ratnasamy C. , Wagner J. P. , Catalysis reviews: Science and Engineering, 51:3, 325-440

According to general maps:

- ✓ **At the presence of enough active catalyst and highly permeable membrane, extent of wall-to-bed mass transfer is the limiting phenomenon**

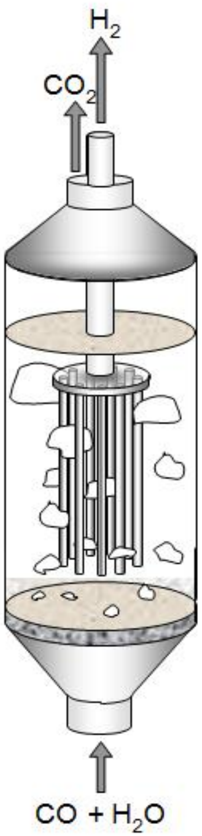
- ✓ **With the micro-structured membrane reactor large reduction in bed-to-membrane mass transfer limitations can be achieved**

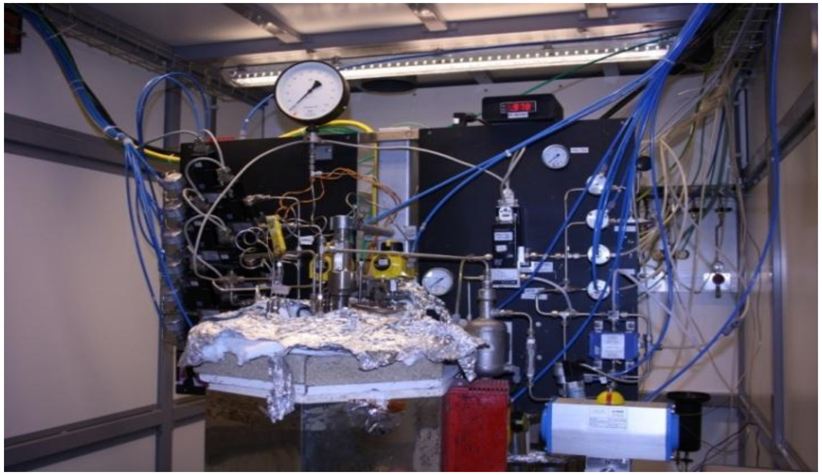
Lab scale membrane reactors

- **Testing & Validation of Membrane Reactors at Lab-scale:**

1. **Packed bed membrane reactor (PBMR)**
2. **Fluidized bed membrane reactor (FBMR)**
3. **Micro-channel membrane reactor**

FBMR





Two options will be compared:

1) Small flat channels where the walls are the (flat) membranes confining a fluidized suspension

2) Small membrane tubes positioned closely together submerged into a fluidized bed

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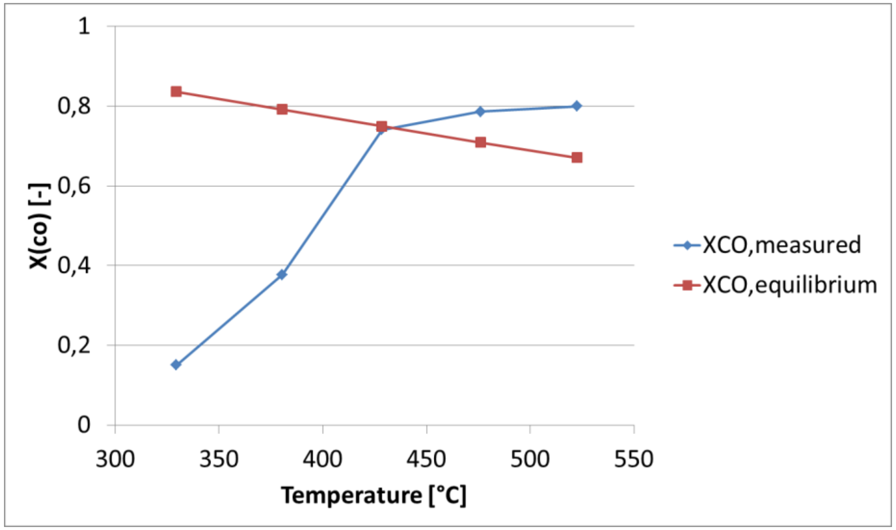
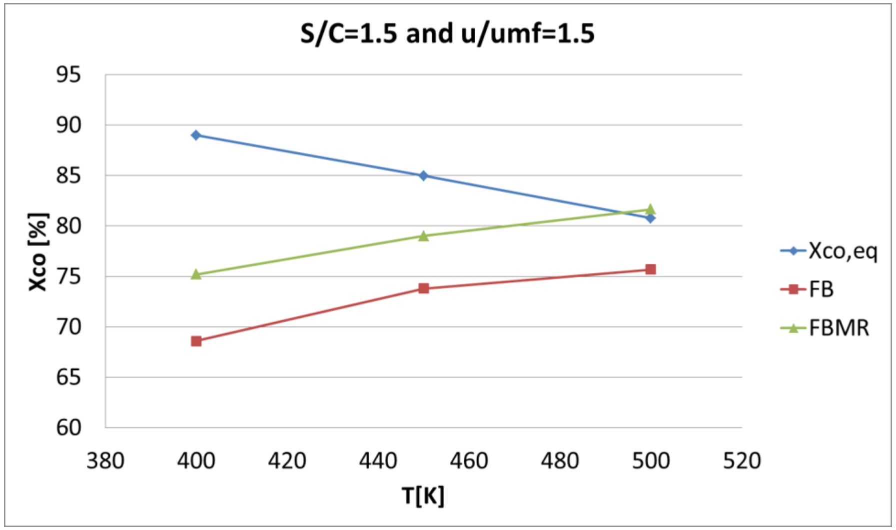
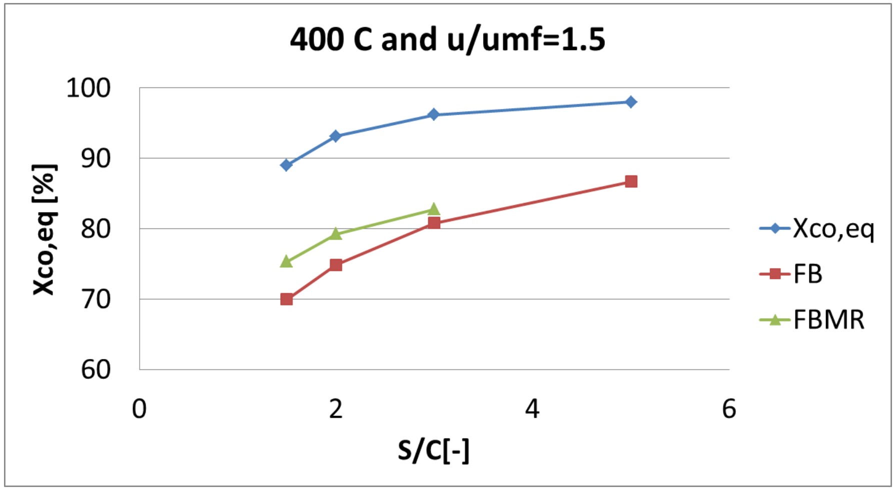
Results for FBMR

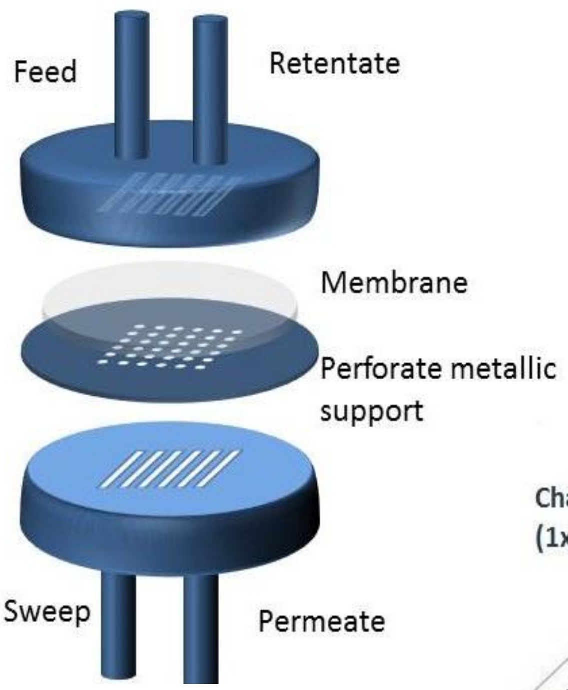


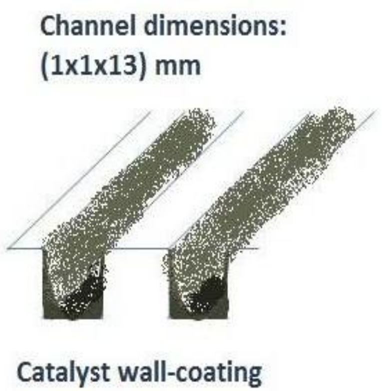


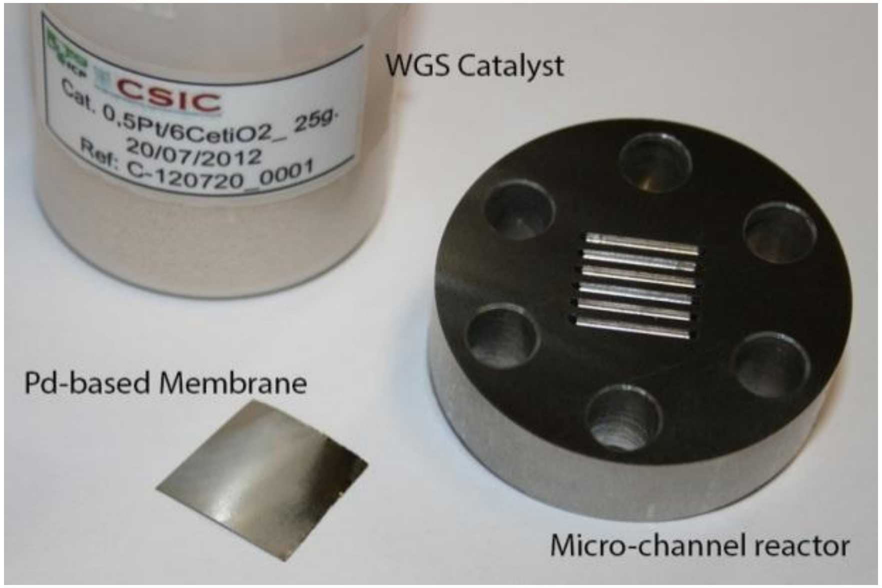


- Pd-based membranes can markedly enhance the fluidized bed reactor performance
- CO conversions higher than equilibrium value can be reached at high temperatures

Micro-channel membrane reactor

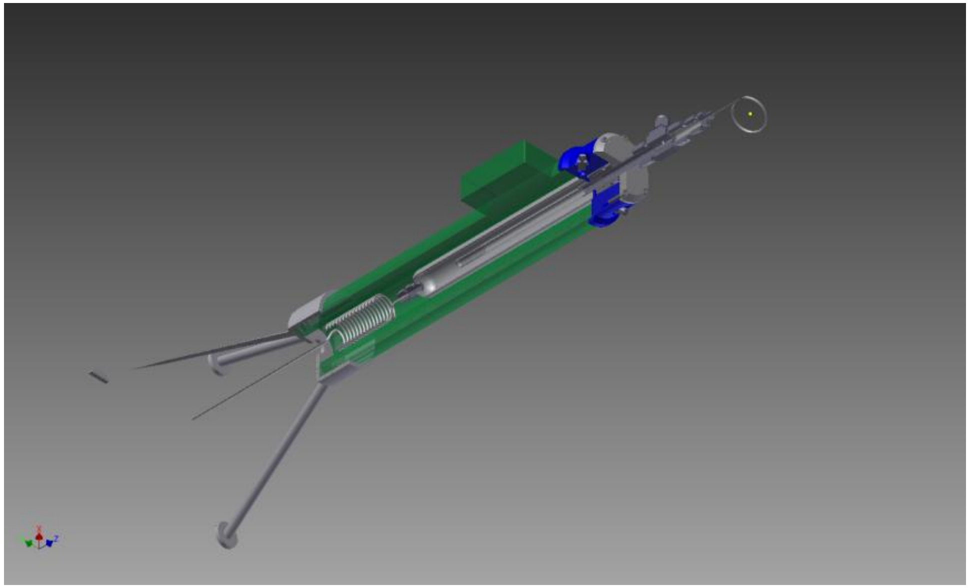






PBMR (backup solution)

- 1 membrane tube inside the bed
- Highly active Pt based catalyst and highly permeable Pd based membrane



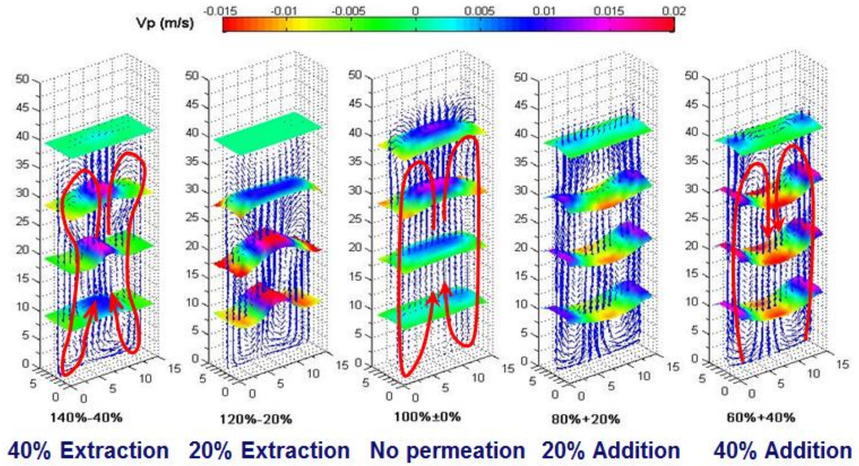
Summary & future work

- ✓ At the presence of enough active catalyst and highly permeable membrane, extent of wall-to-bed mass transfer is the limiting phenomenon
- ✓ With the micro-structured membrane reactor large reduction in bed-to-membrane mass transfer limitations can be achieved
- ✓ Membrane reactor concepts have been already developed for model validation and study the performance of the reactor concepts at lab scale

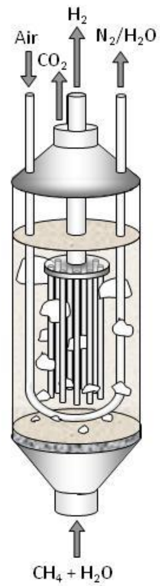
Ongoing projects on Micro FBMR

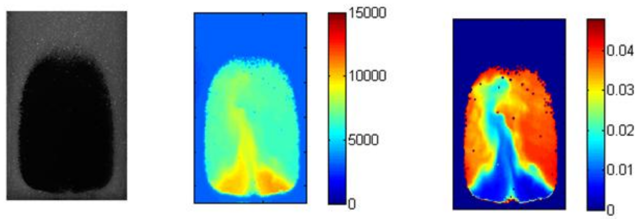
- **Effect of gas permeation on hydrodynamics and heat & mass transfer (Tan, L.)**

Solids circulation pattern



- **Design of Micro FBMR for H2 production (Dang T.Y.N.)**





Visual image

IR image

Concentration profile

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Thank you for your attention

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