Energy analysis of membrane reactors

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POLITECNICO MILANO 1863

ERGO Energy Technology Group

GECOS Group of Energy COnversion Systems

MACBETH Membranes And Catalysts Beyond Economic and Technological Hurdles

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Introduction: Hydrogen application

Small scale (< 5 Nm^3/h)

- Micro-CHP system for distributed or off-grid generation

Medium scale (< 50-100 Nm^3/h)

- Automotive, Fuelling stations
- Industrial applications (Glass or Steel industry)

Large scale (>100 Nm^3/h)

- Chemicals
- Oil Refinery
- Ammonia Production

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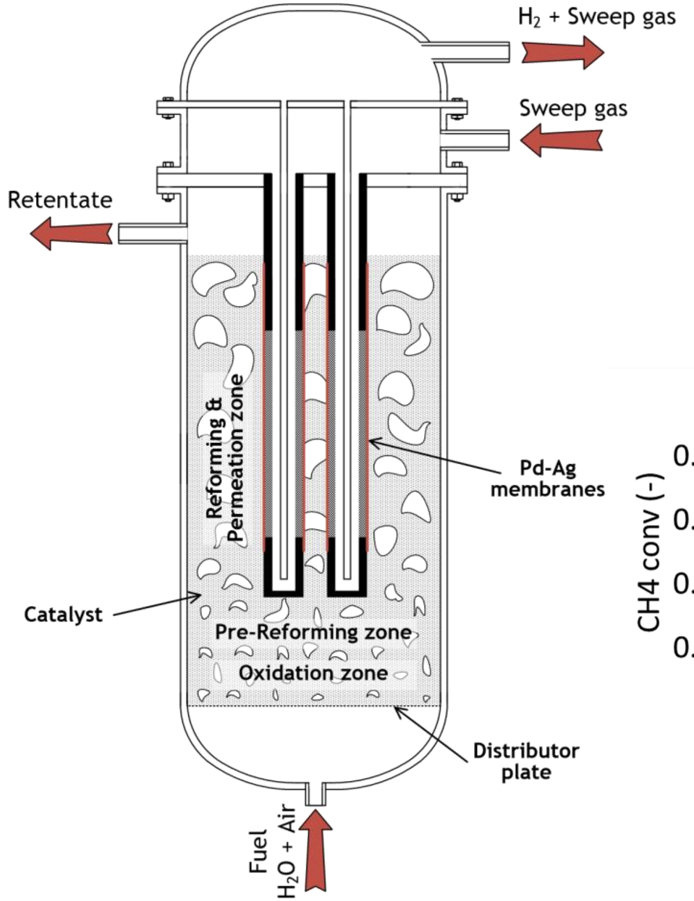
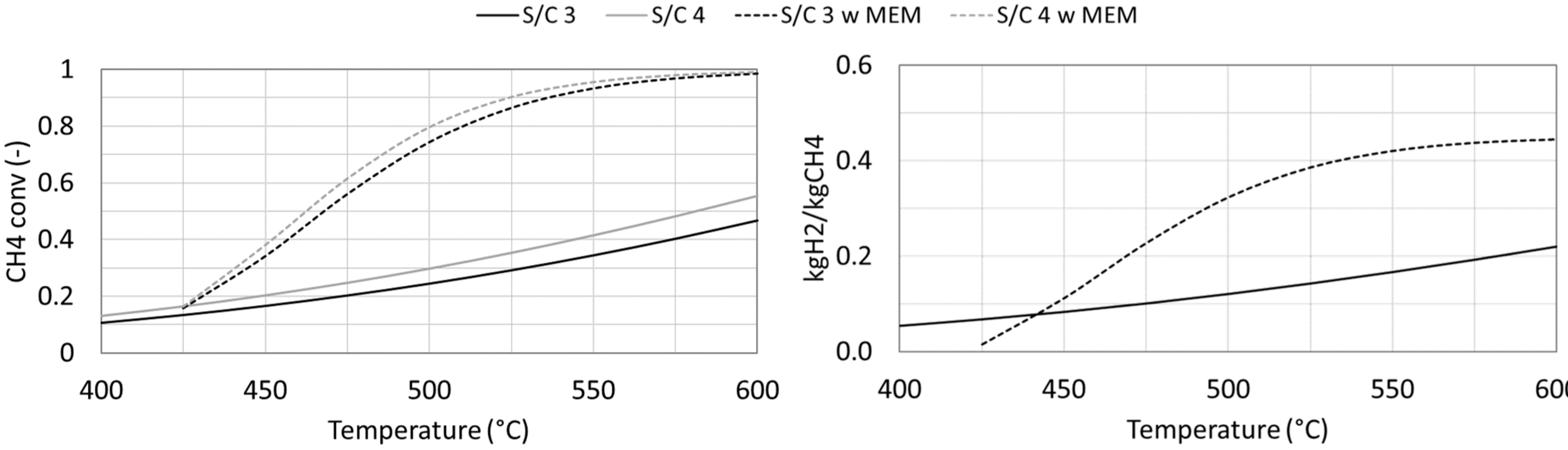
Membrane Reactor for hydrogen production



SR: $CH_4 + H_2O \rightleftarrows CO + 3H_2$ endo↑↑

WGS: $CO + H_2O \rightleftarrows CO_2 + H_2$ exo↑

Ox: $CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O$ exo↑↑



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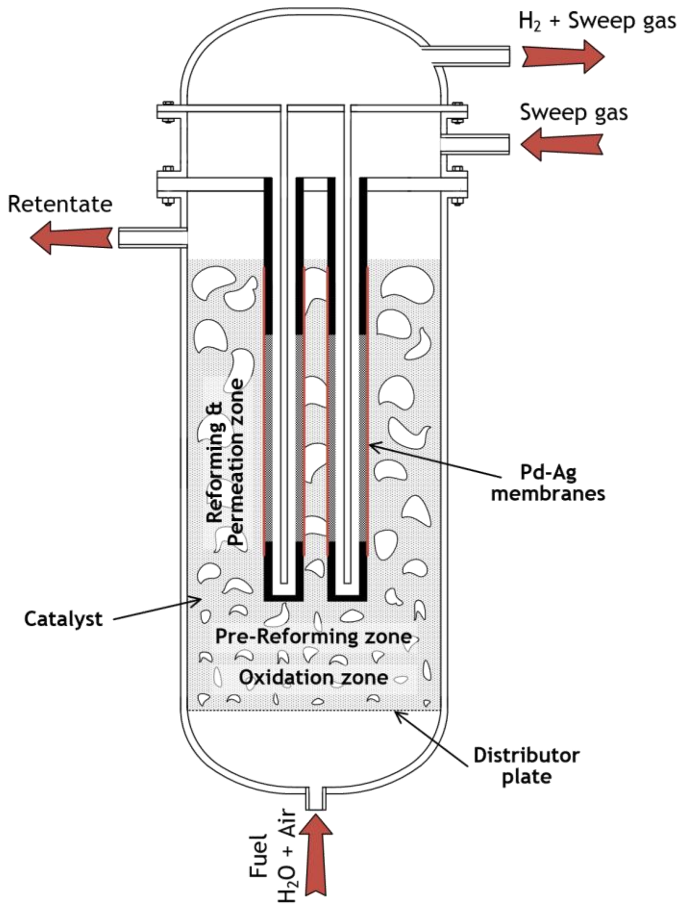

SR: $CH_4 + H_2O \leftrightarrows CO + 3H_2$ endo⮅

WGS: $CO + H_2O \leftrightarrows CO_2 + H_2$ exo↑

Ox: $CH_4 + 2O_2 \leftrightarrows CO_2 + 2H_2O$ exo⮅

- **Structure: Fixed bed vs Fluidized bed**

<u>Fixed bed</u>

▲ Semplicity
▲ Structured Catalyst
▼ Pressure drop not negligible
▼ Temperature profile
▼ Difference between bulk and wall

<u>Fluidized bed</u>

▲ Reduce concentration polarization losses
▲ Reduce temperature and concentration gradients
▲ Improve heat transfer
▼ Gas velocity (control) and particle size

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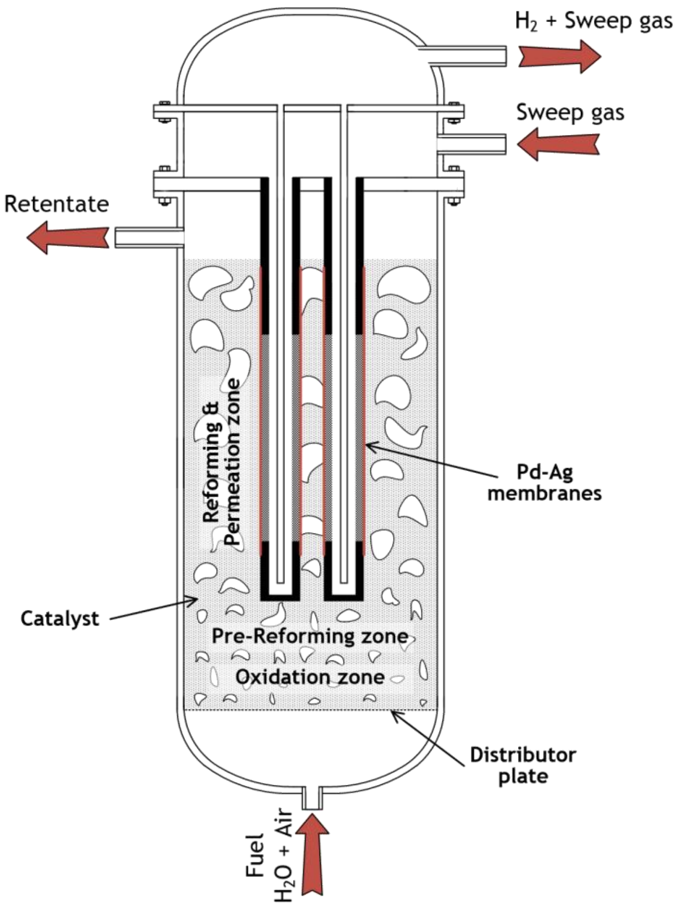
Membrane Reactor for hydrogen production



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Ox: $CH_4 + 2O_2 \leftrightarrows CO_2 + 2H_2O$ exo↑↑

- **Heat supply: ATR vs SR**

ATR-MR

▲ Smaller (compact) and cheaper unit

▼ High H_2 dilution in the products

SR-MR

▲ Less H_2 dilution in the products

▼ Heat transfer section arrangement and source (see next slides)

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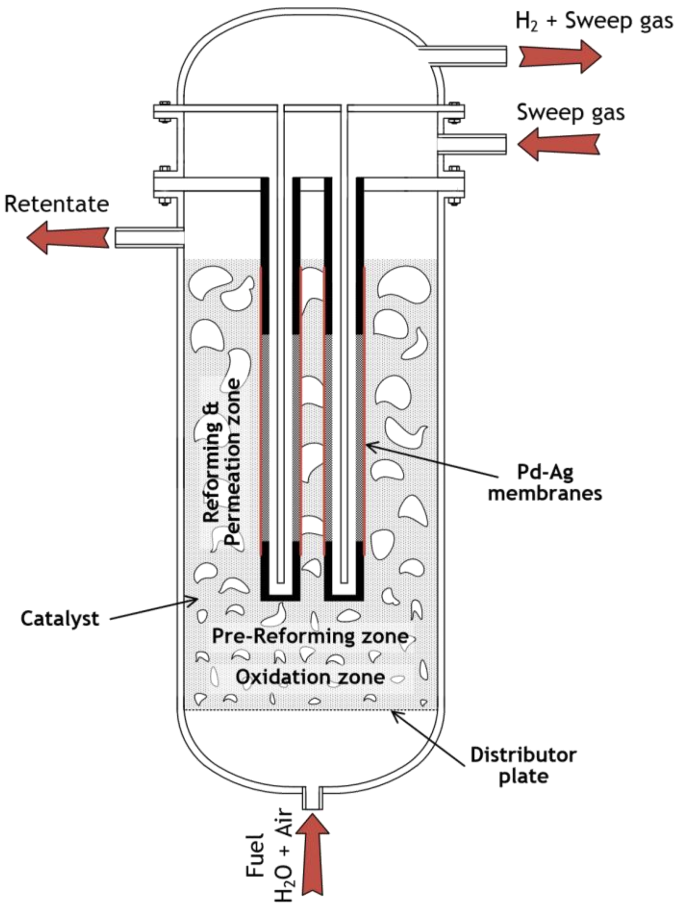
Membrane Reactor for hydrogen production



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- **Permeate Side configurations**

→ H_2 partial pressure reduction

Parameter	Vacuum pump	Sweep gas
Reactor Design	++	--
System complexity	++	-
Auxiliaries	--	++
System efficiency	-	+

In MACBETH project a fluidized bed ATR-MR with vacuum pump is selected!

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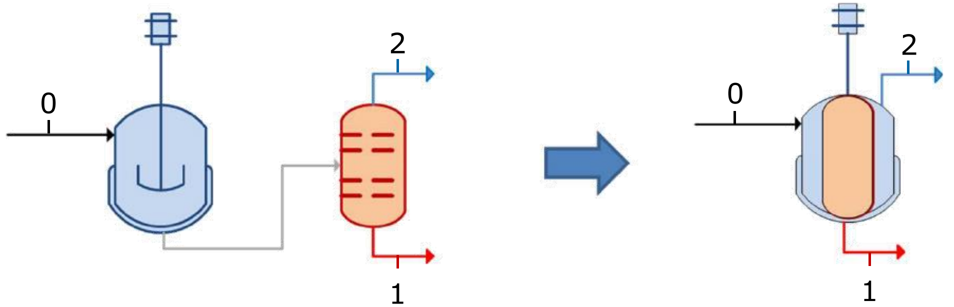
MR-based system: performance

- Key Performance Indicators (KPIs) for MR-based system and benchmark comparison
- Reference case models implemented in Aspen Plus/retrieved from literature



Reactor level

KPI	units	Definition
Conversion	-	$X_R = \frac{F_{R,0} - F_{R,1/2}}{F_{R,0}}$
Yield	-	$Y_{R,P} = \frac{F_{P,1} + F_{P,2} - F_{P,0}}{F_{R,0} + \nu_{R,\beta} F_{R,0}} \cdot \frac{\lvert \nu_{R,\alpha} \rvert}{\lvert \nu_{P,\alpha} \rvert}$
Selectivity	-	$S_{R,P} = \frac{Y_{R,P}}{X_R}$
Space Time Yield	kg/m³s	$STY_P = \frac{\dot{M}_{P,1}}{V_{reactor}}$

α (Main reaction) $\nu_{R,\alpha} R \leftrightarrow \nu_{P,\alpha} P$

β (Side reaction) $\nu_{R,\beta} R \leftrightarrow \nu_{Q,\beta} Q$

System level

KPI	units	Definition
Specific primary energy consumption	kWh/kg	$SEC_P = \frac{Q_{in} + W_{aux}/\eta_{el,ref}}{\dot{m}_P}$
Specific GHG emissions	kg_{CO2eq}/kg	$GHG = \frac{\sum \dot{m}_i GWP_i}{\dot{m}_P}$
Purity	-	$PUR_P = \frac{F_1 - \sum_{i \neq P} F_{i,1}}{F_1}$
Cost of product	€/kg	$COP_P = \frac{CAPEX + OPEX \cdot h_{eq}}{M_P}$

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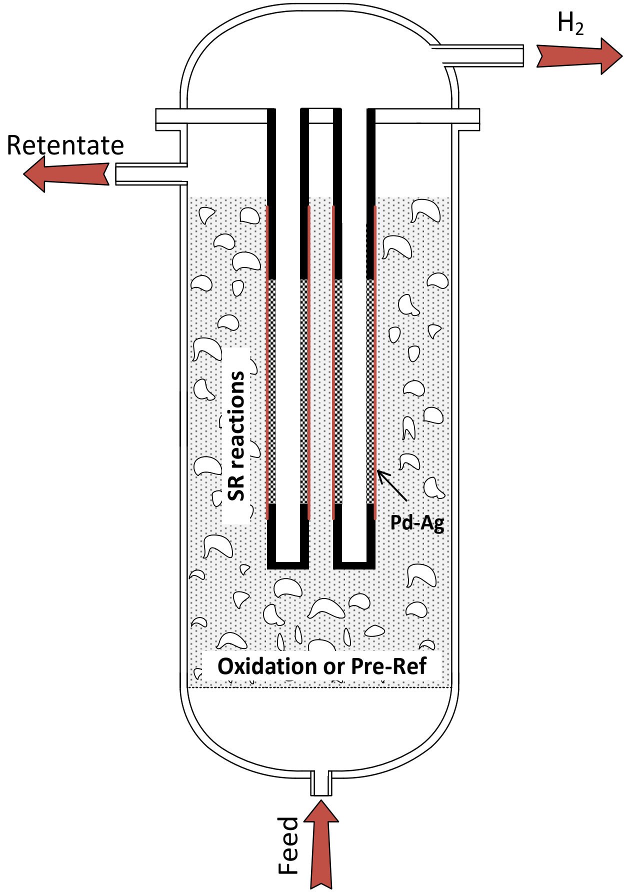
MR integration in the overall system



- To define the proper system layout and set of simulations
  → It is important to understand

  - Reactor requirements (operating conditions)
  - Reactor inputs/outputs
  - Relation between the streams

Stream	Flow		T (°C)	p (bar)	Composition (% molar basis)						
	Molar (mol/s)	Mass (g/s)			CH_4	H_2	CO	CO_2	H_2O	O_2	N_2
1	0.359	9.401	15	1	58.10	0	0	33.90	3.10	1.10	3.80
2	0.709	19.511	308.45	12	29.39	0	0	17.15	1.57	10.93	40.96
3	1.104	26.620	444.46	12	18.88	0	0	11.02	36.77	7.02	26.32
4	0.833	25.462	500	12	2.11	3.00	1.02	36.48	22.53	0	34.86
5	1.223	39.058	40	1	0	0	0	26.97	6.30	5.68	61.05
6	0.575	1.158	500	0.1	0	100	0	-	0	0	0

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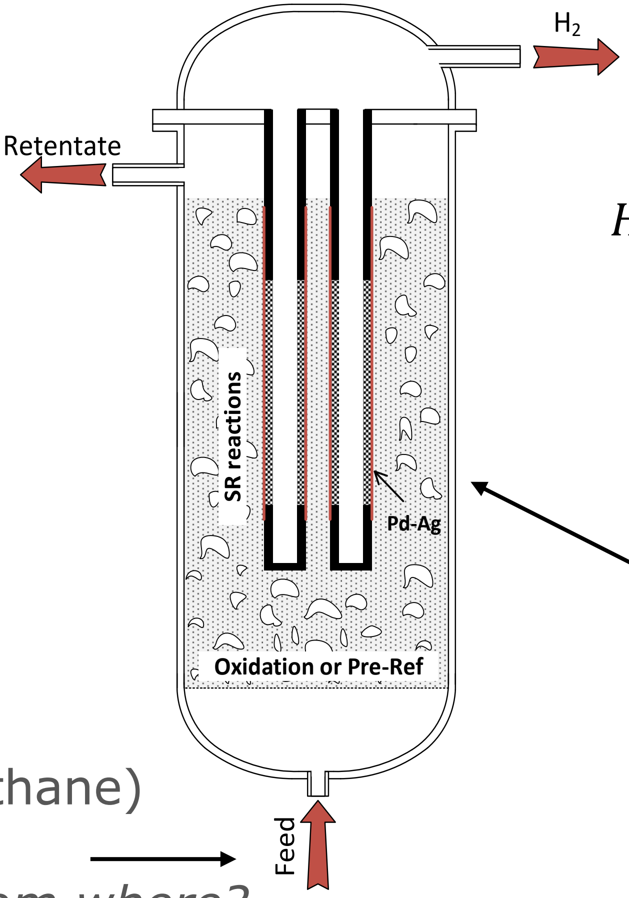
MR integration in the overall system

How much?
What is its energy content?
Any implications?

$$\eta_{sys} = \frac{\dot{m}_{H_2} \cdot LHV_{H_2}}{\dot{m}_{feed} \cdot LHV_{feed} + \frac{W_{aux}}{\eta_{el,ref}}}$$



How much?
At which conditions?

$$HRF = \frac{\dot{n}_{H_2,permeated}}{4 \cdot (\dot{n}_{CH_4,in} - 2 \cdot \dot{n}_{O_2,in})}$$

How the building blocks can affect the reactor behaviour?

How to handle theFluidization regime?

1. NG or BG (methane)
2. Steam
3. Air T,p? From where?

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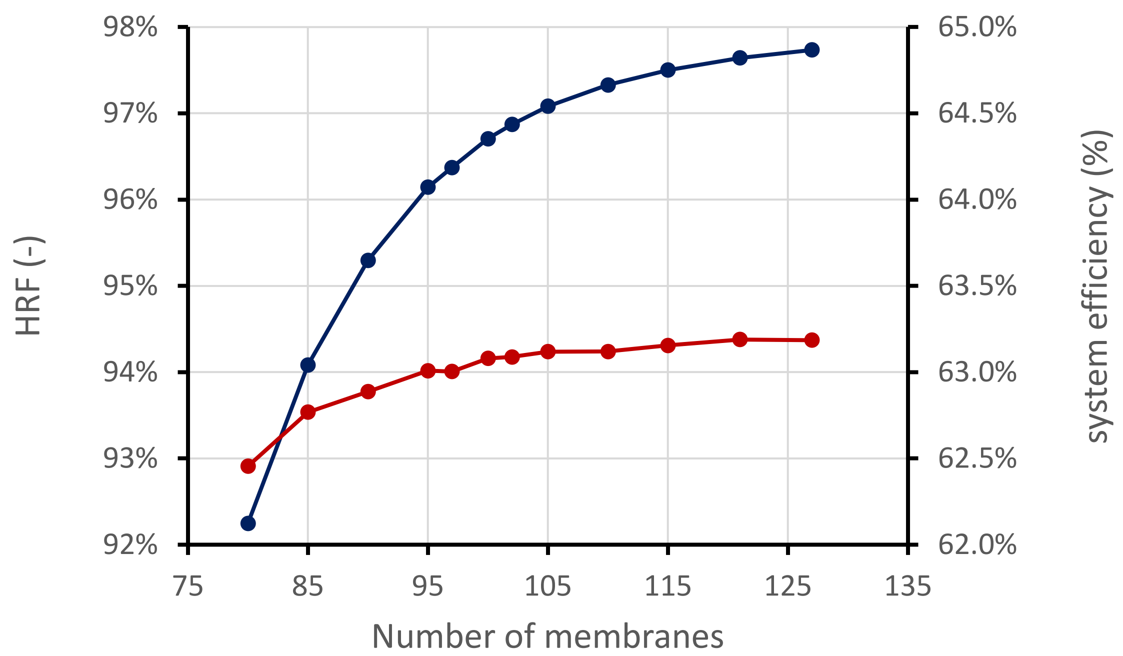
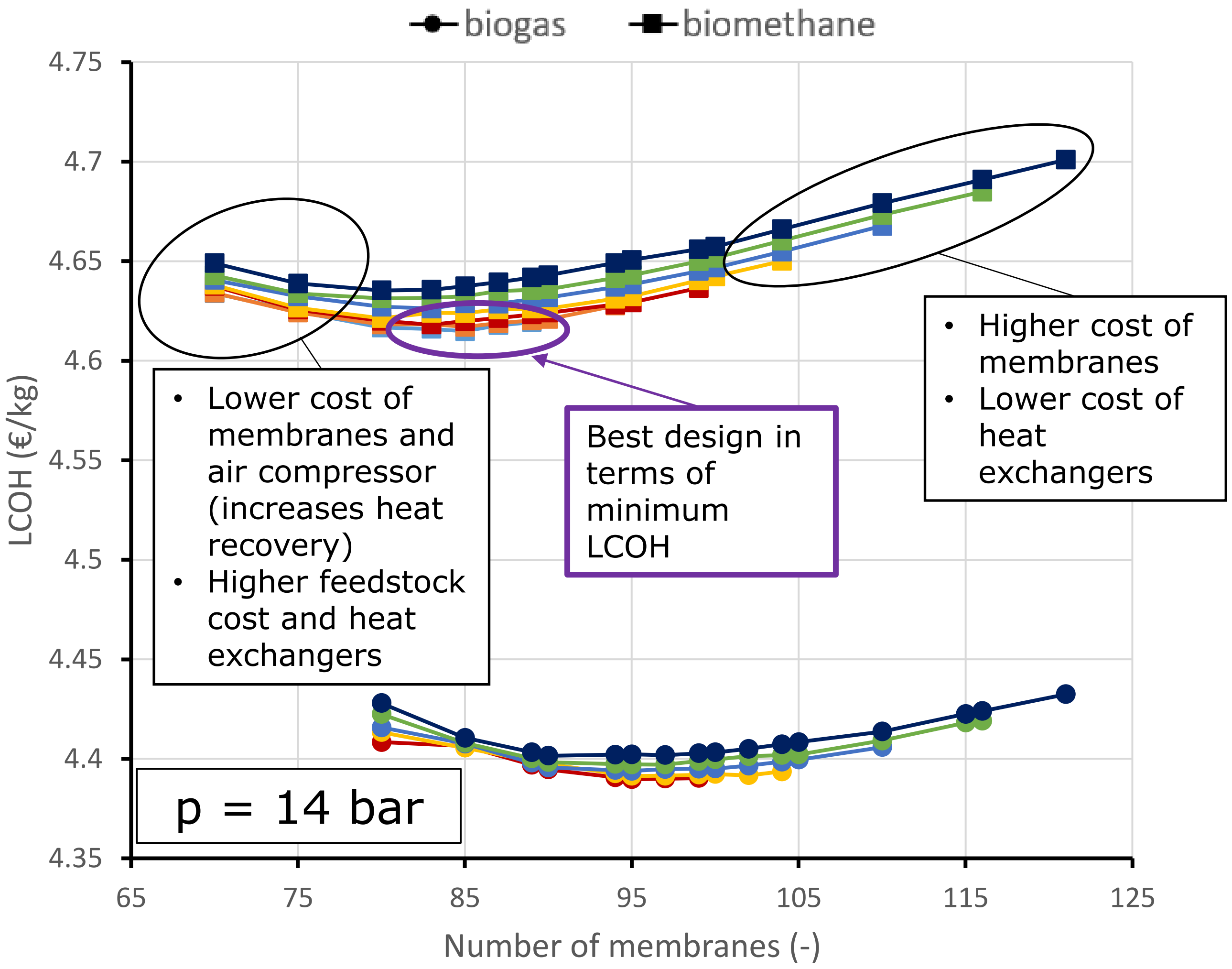
MR integration in the overall system





- System efficiency follows the trend of the HRF
- BUT the plateau is reached at a lower number of membranes since lower HRF is counterbalanced by an increase of heat recovery from the retentate
- Moreover minimum LCOH does not correspond to the maximum efficiency

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MR integration in the overall system

➢ <u>Thermal integration (HX arrangement)</u>

- ❑ Tfeed lower than Treactor
- ❑ Right matching between exchanged thermal power and temperature levels
- ❑ Check HX area
- ❑ Better to avoid HX between H2 and air

$$\dot{Q} = \dot{m} c_p \Delta T$$

To calculate stream energy content

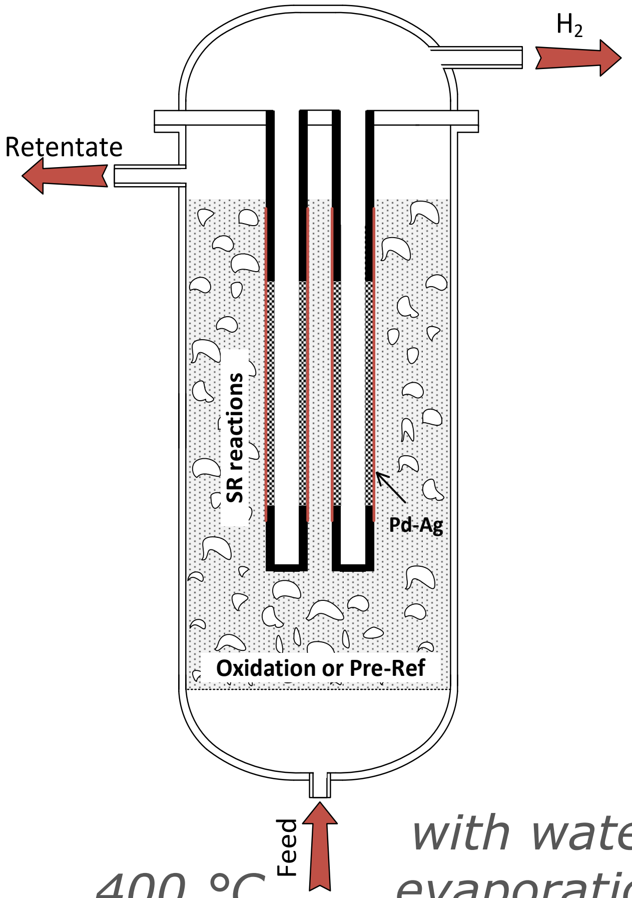
$$\dot{Q} = UA\Delta T_{ml}$$

To calculate HX area

HOW

- ❖ User defined solutions
- ❖ PINCH analysis? (can be performed by Aspen tools)

500 °C 10 bar → *25 °C 1 bar BUT…*



500 °C 1 bar → *25 °C 1 bar*

*25 °C** 1 bar* → *400 °C 10 bar*

with water evaporation
*** compression*

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MR integration in the overall system

➢ Thermal integration (HX arrangement)

- ❑ Tfeed lower than Treactor
- ❑ Right matching between exchanged thermal power and temperature levels
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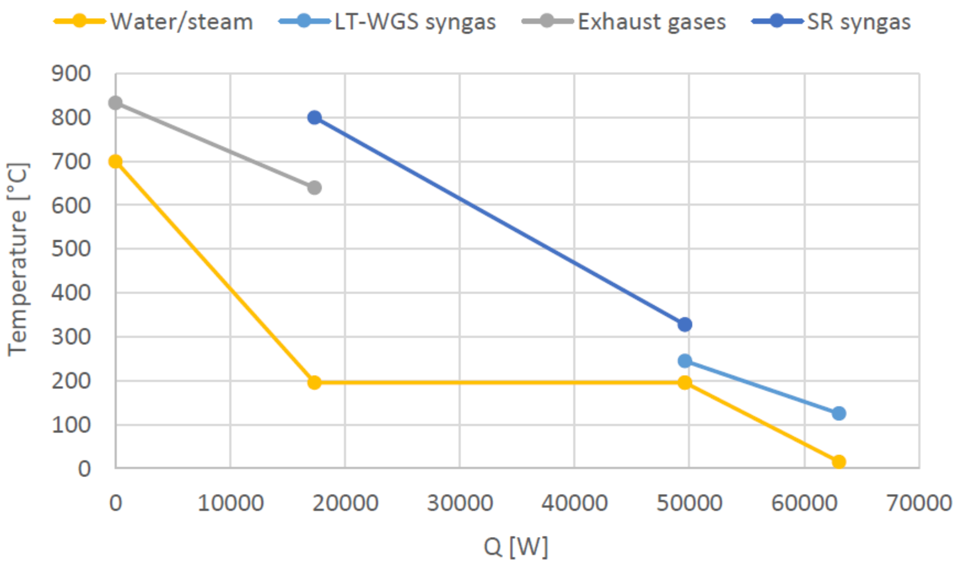

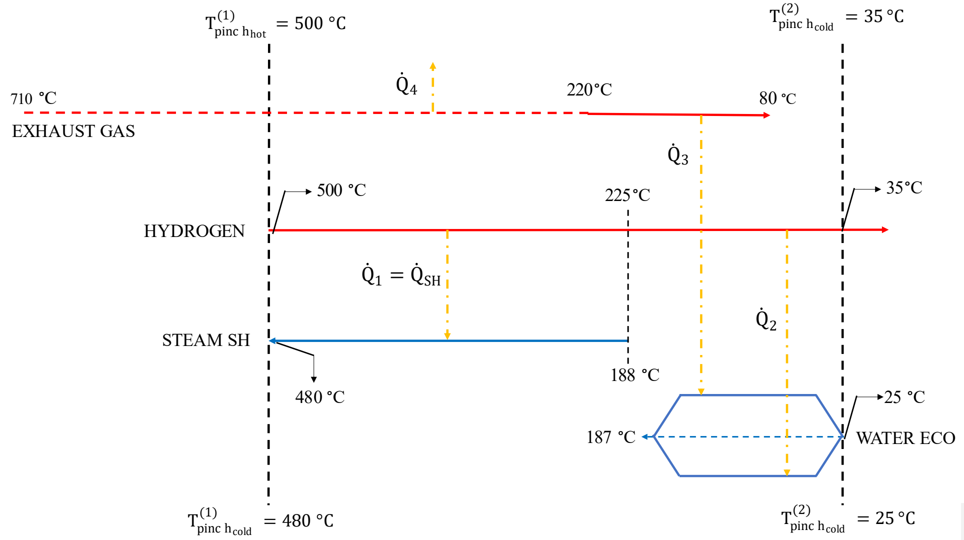

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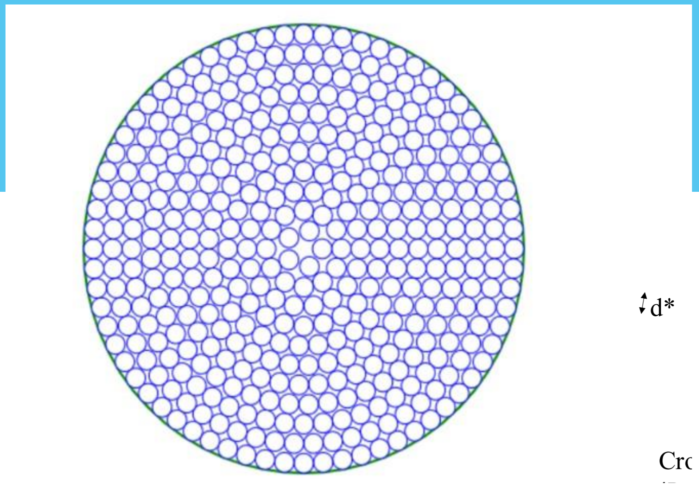
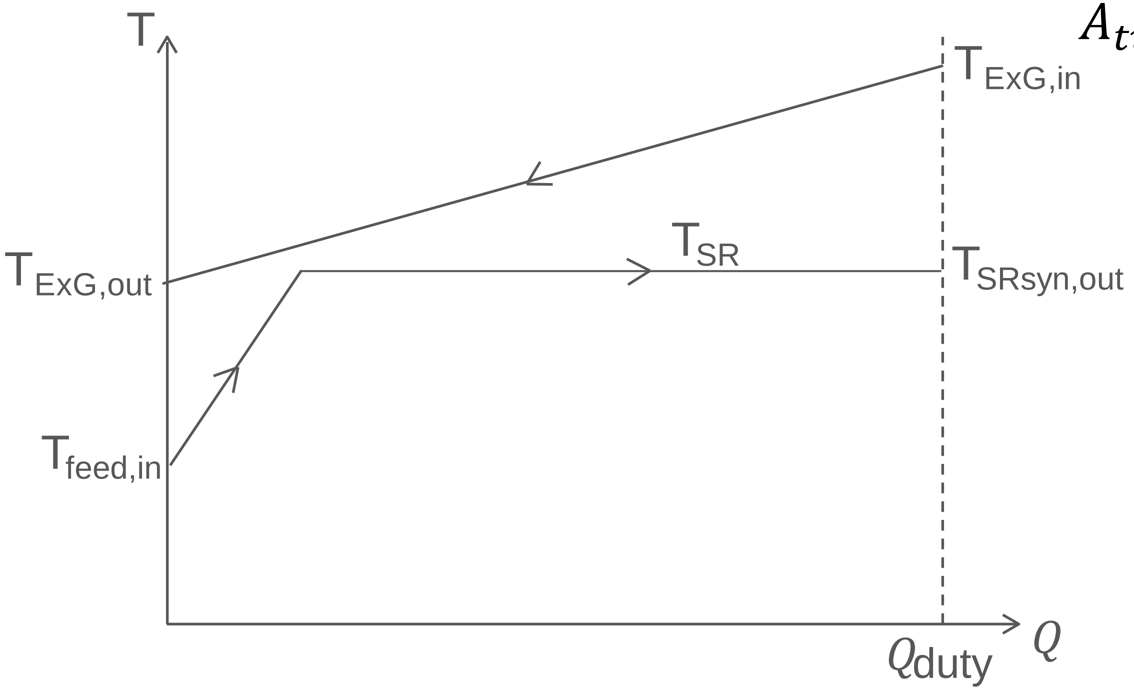
MR integration in the overall system: SR-MR



- Tube bandles inside the reactor

Exhaust gases from the combustion of the retentate (and aux fuel)



$$A_{tubes} = \frac{Q_{duty,FBMR}}{U \cdot \frac{\left(T_{in,fg} - T_{SR}(or\ T_{feed})\right) - \left(T_{out,fg} - T_{SR}(or\ T_{feed})\right)}{\ln\left(\frac{T_{in,fg} - T_{SR}(or\ T_{feed})}{T_{out,fg} - T_{SR}(or\ T_{feed})}\right)}}$$

the convective coefficient of the fluidized bed is lower than the one of the flue gases, then the global heat transfer coefficient is set equal to the heat transfer coefficient of the fluidized bed ($U \approx h_{bed}$=200 W/m²K)

$$U = \frac{1}{\frac{1}{h_0} + \frac{d_0 \ln\left(\frac{d_0}{d_i}\right)}{2k_w} + \frac{d_0}{d_i h_i}}$$

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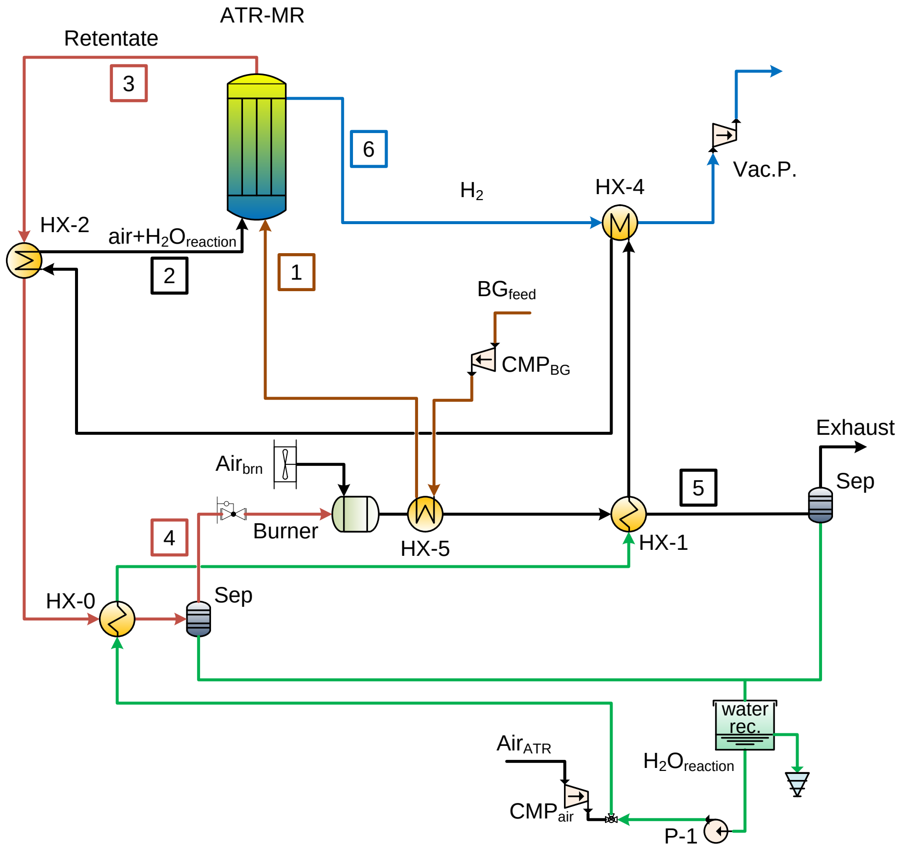
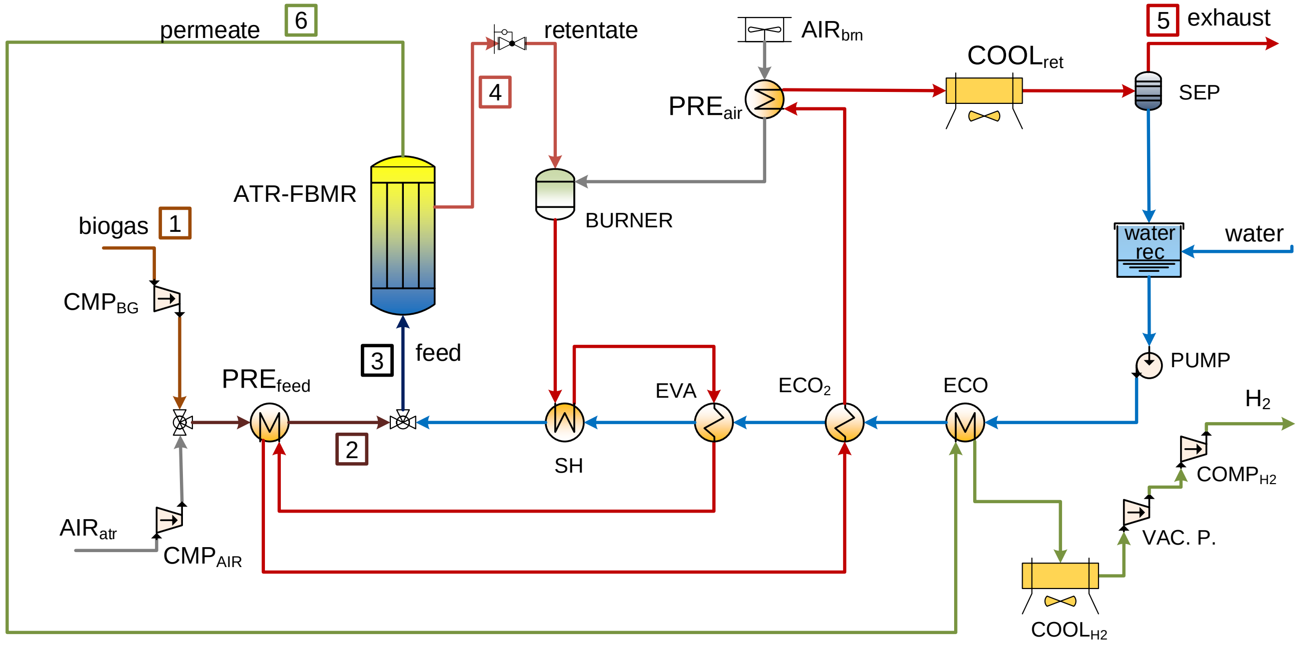
MR-based system: examples of layout

➤ Small scale BIOGAS Autothermal reforming (ATR-MR): 100 kg_{H2}/day





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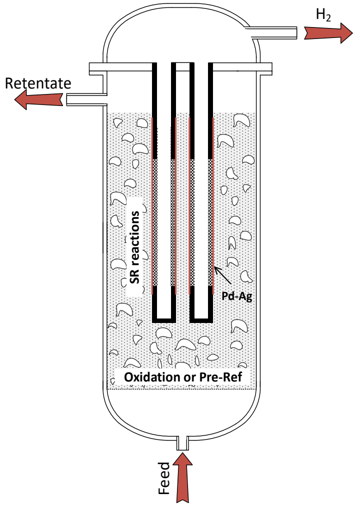
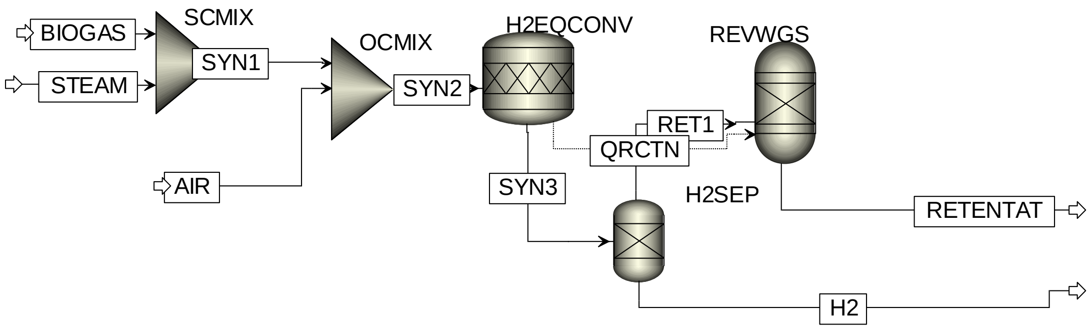
MR modelling: approach / level of detail



- Why is membrane reactor modelling important?
- CAPEX calculation
- Definition of membrane area and catalyst amount (& their reliability)
- Improve accuracy on Opex (BG cost and electric consumptions, membrane and catalyst cost)

- DIFFERENT LEVELs for a process simulation

  - 0D model to check MR potentiality



- 2 reactors and 1 separator
- Membrane model can be included for Area calculation

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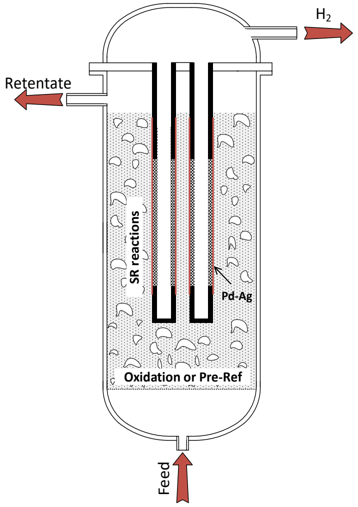
MR modelling: approach / level of detail



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- • CAPEX calculation
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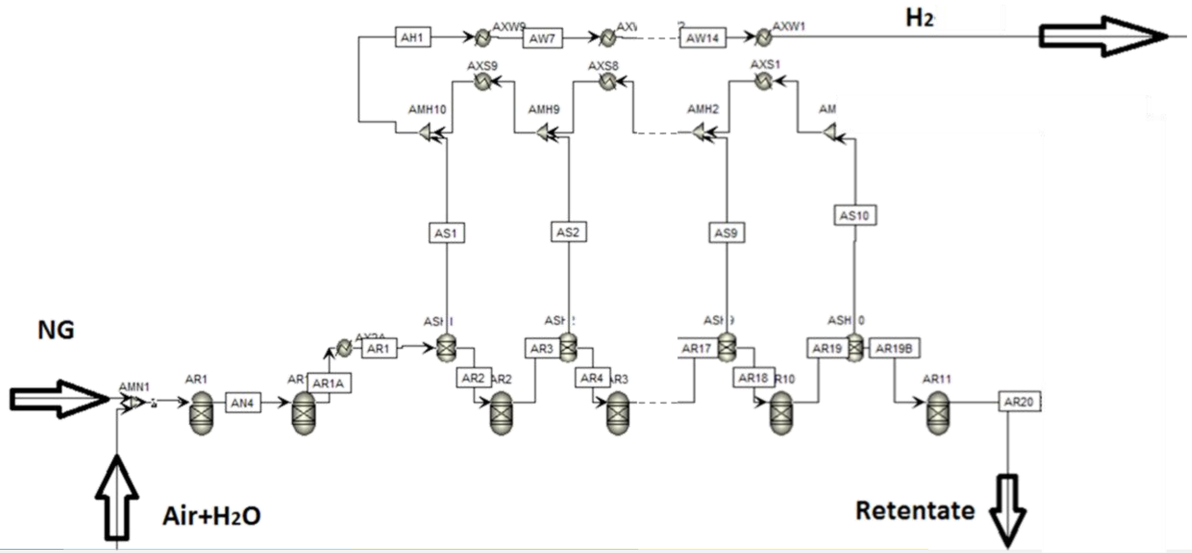
- ➢ DIFFERENT LEVELs for a process simulation
  - ➢ 1D simplified model to check the concentration profile and required duty



- ❖ MR is discretized in a series of 10 reactors and separators
- ❖ Each reactor is set to equilibrium conversion by Gibbs free energy minimization
- ❖ In the separators, hydrogen is extracted (infinite perm-selectivity is assumed) according to the permeation expression
- ❖ Membrana area calculation

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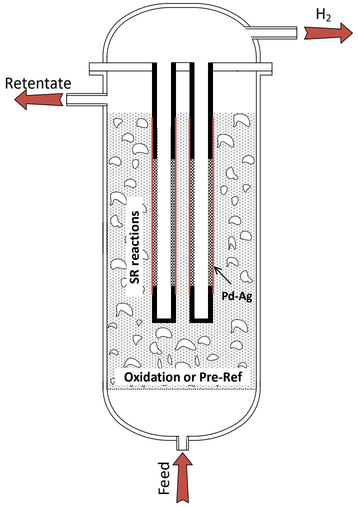

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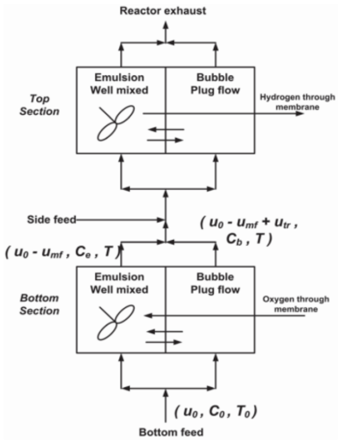
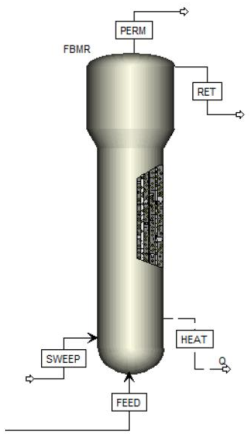
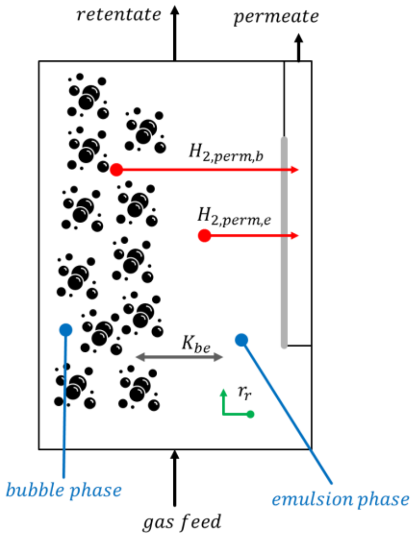
  - 1D model to design the reactor and its building blocks (in ACM)







The steady state overall (bubble and emulsion phases) component mass conservation equations and the total volume balance (to calculate the excess velocity) have been formulated, taking chemical transformations in the emulsion phase and a net gas production due to the chemical reactions and gas removal via membranes into account.

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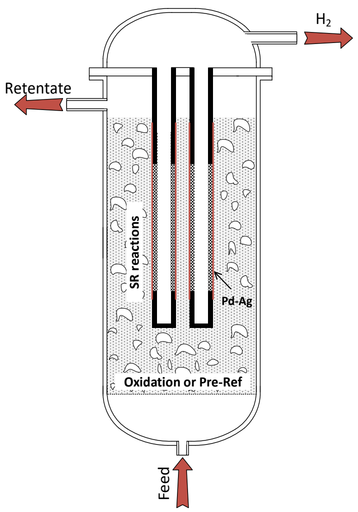

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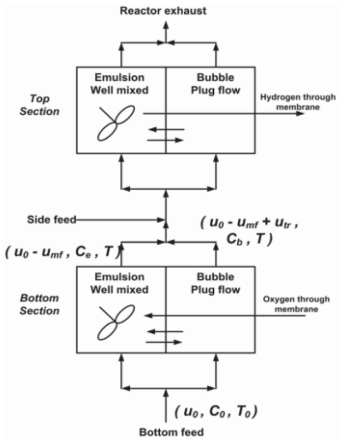

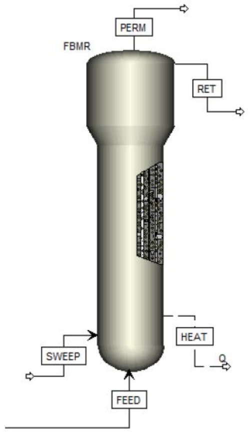

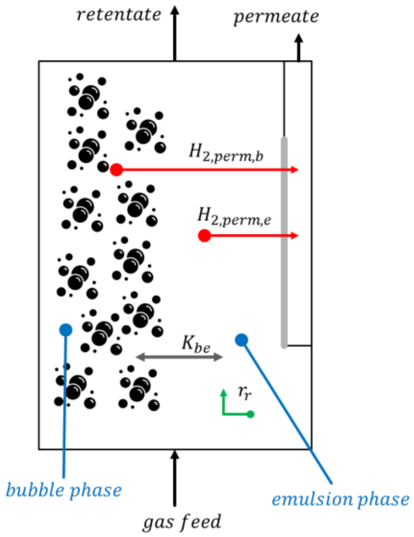

- ❖ Reactor geometry
- ❖ Reaction kinetics
- ❖ Film layer model for concentration polarization losses
- ❖ Both sweep gas and vacuum configuration
- ❖ Wake description
- ❖ Both steam reforming and autothermal reforming
- ❖ Dusty Gas Model for permeation in membrane support

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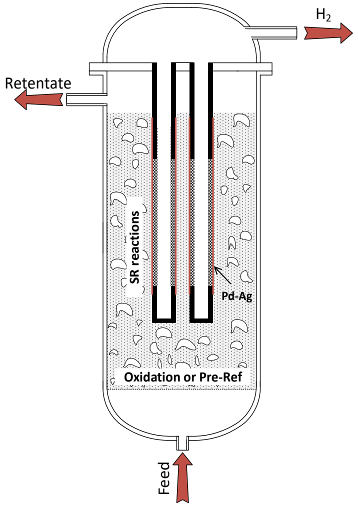
MR modelling: approach / level of detail



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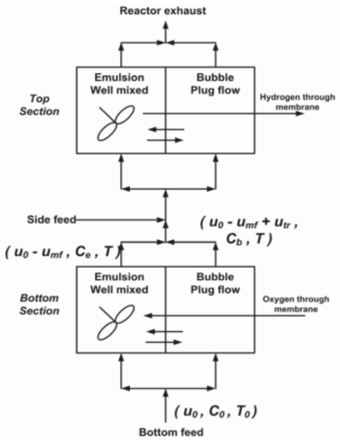

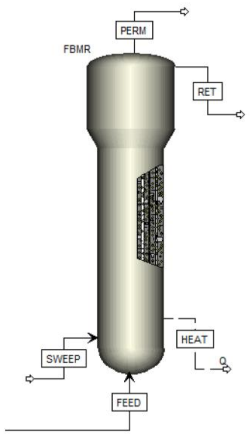

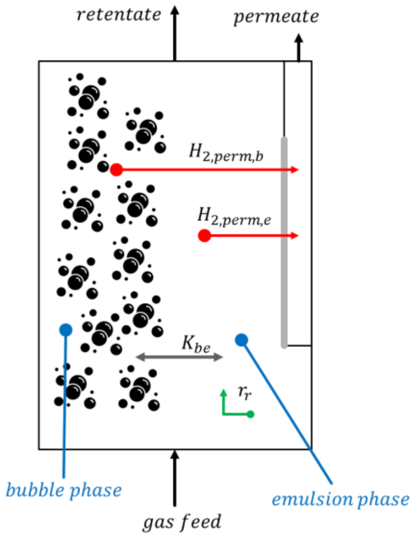

Integration of the ACM model in the overall system Aspen Plus model has two significant effects:

(i) evaluation of the influence of kinetic and transport phenomena in fluidization on hydrogen recovery factor (or reactor efficiency)

(ii) definition of the main reactor design parameters such as reactor diameter (D reactor), average membrane distance (Mem. Dist.) or required membrane area

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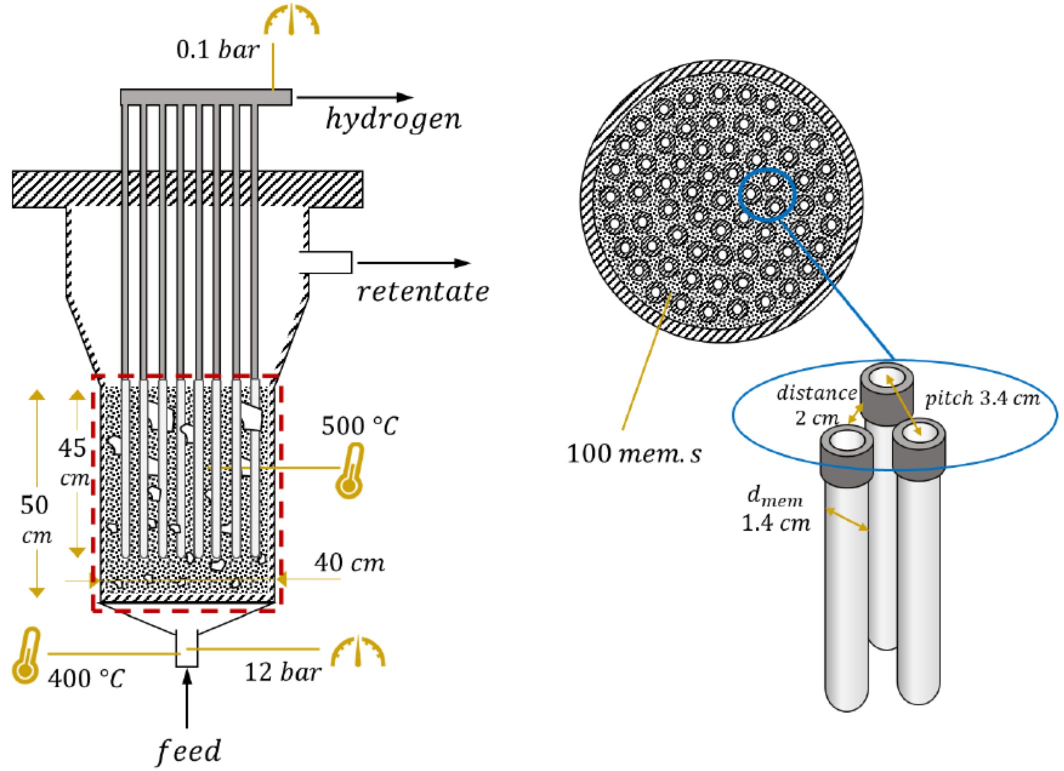
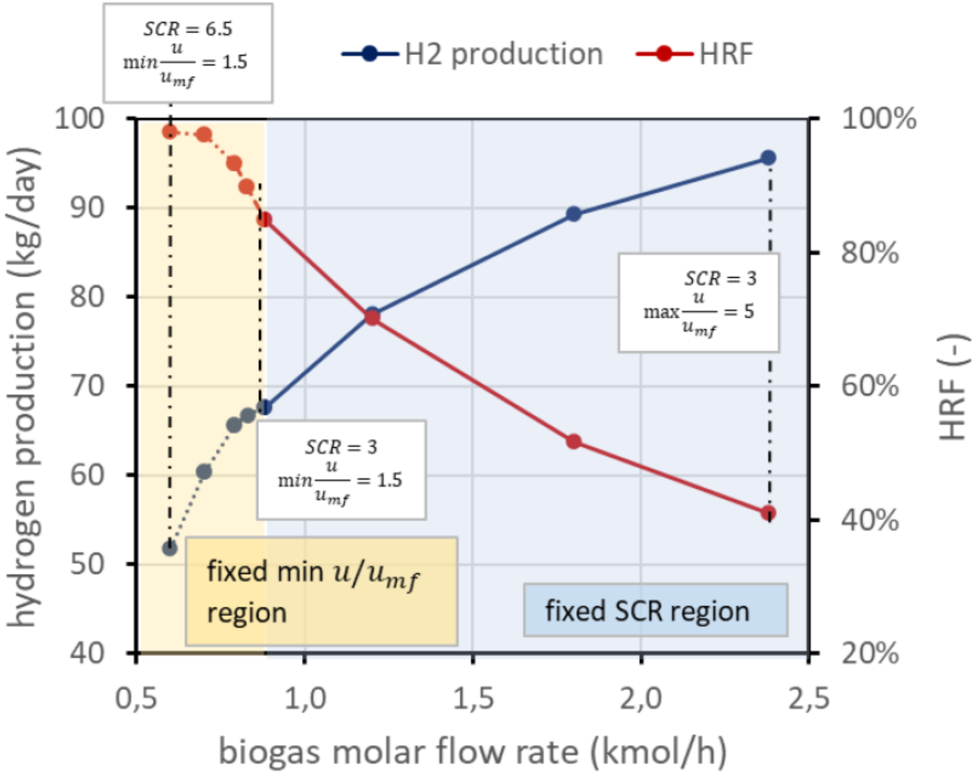
MR modelling: preliminary results

- Analysis at fixed geometry and fixed operating conditions





- *Increasing the H2 production (BG↑) leads to a HRF reduction*

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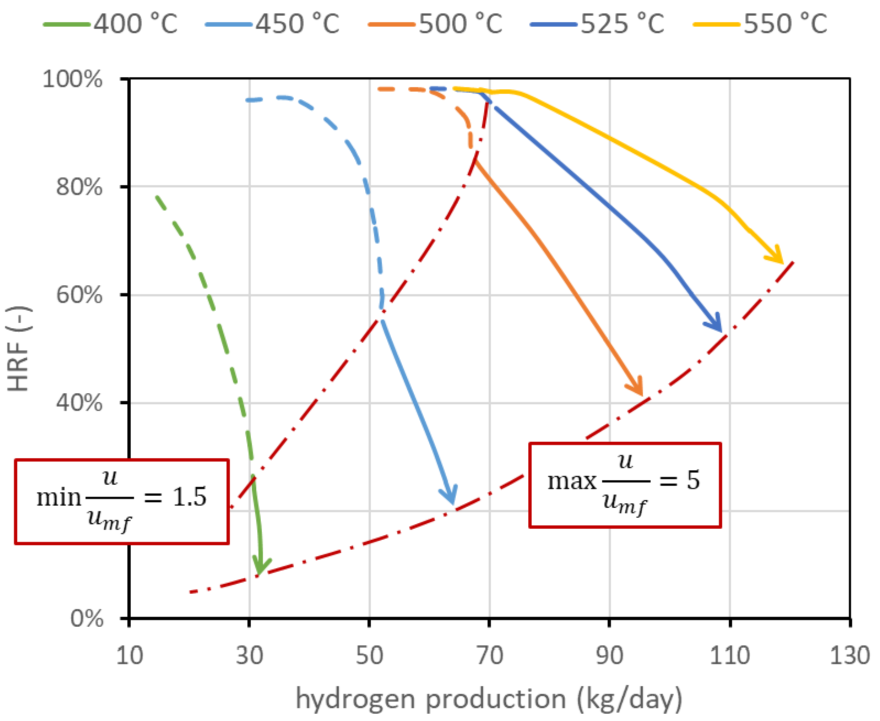
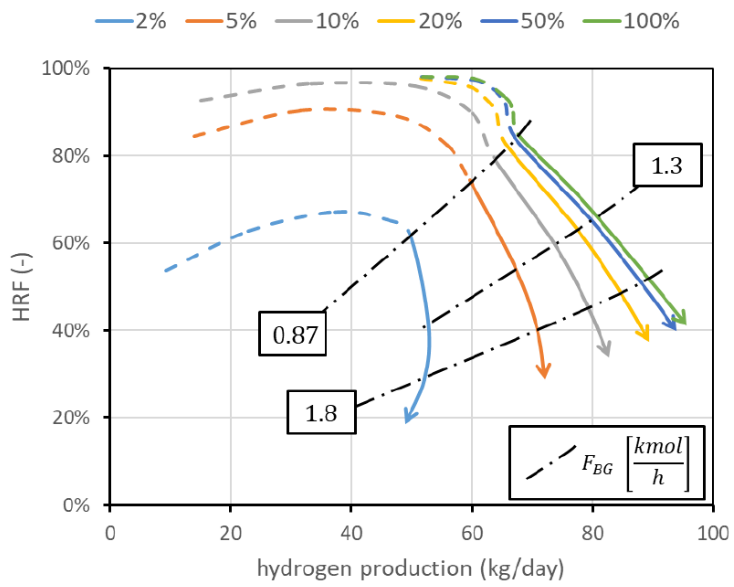
MR modelling: preliminary results

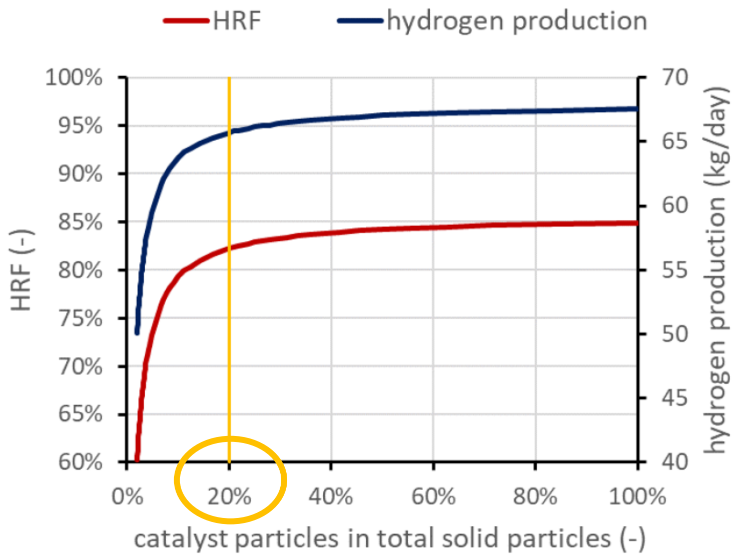
- Analysis at fixed geometry and fixed operating conditions

- *Reactor temperature effect*



- *Loading effect: catalyst over total solid particles*





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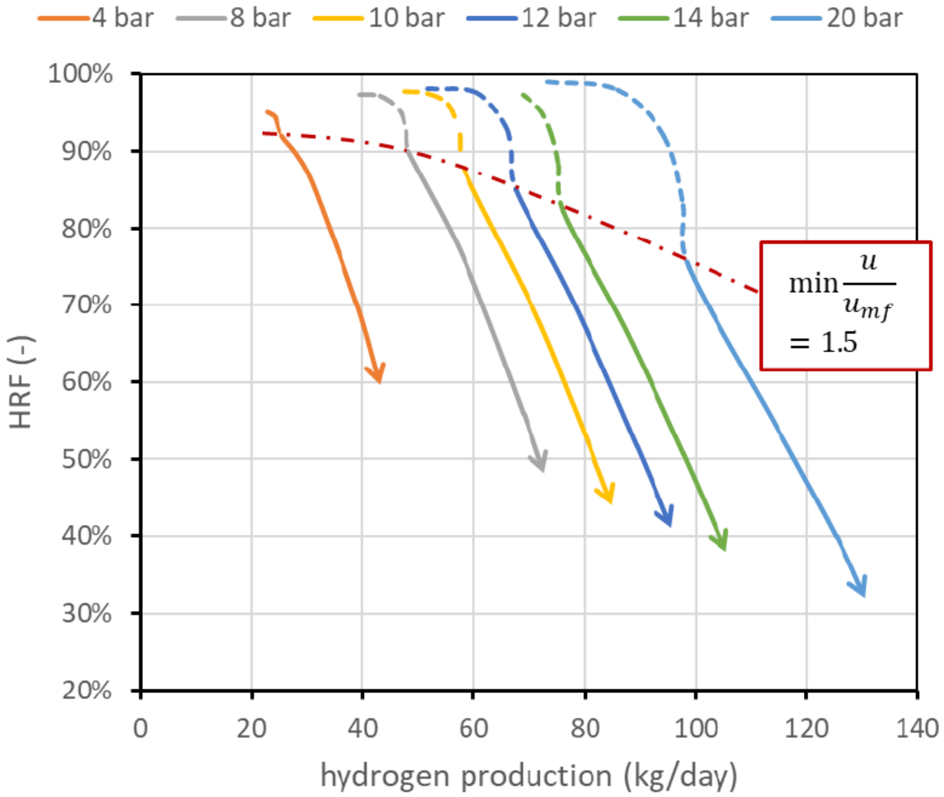
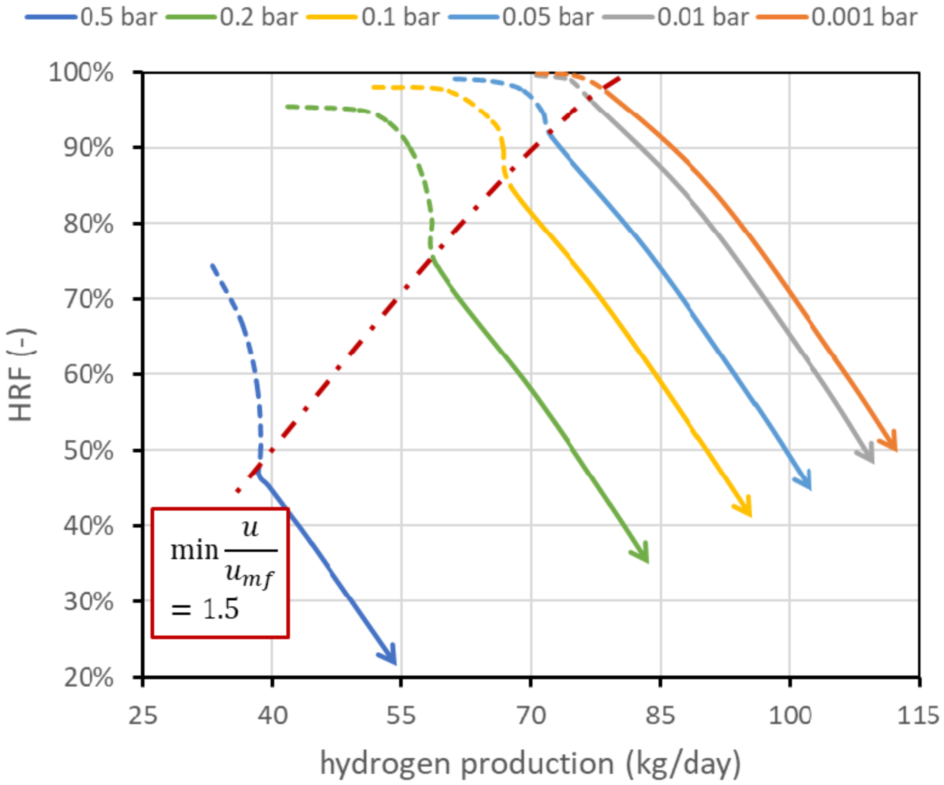
MR modelling: preliminary results

- Analysis at fixed geometry and fixed operating conditions

- *Pressure effect: retentate side*



- *Pressure effect: permeate side*



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

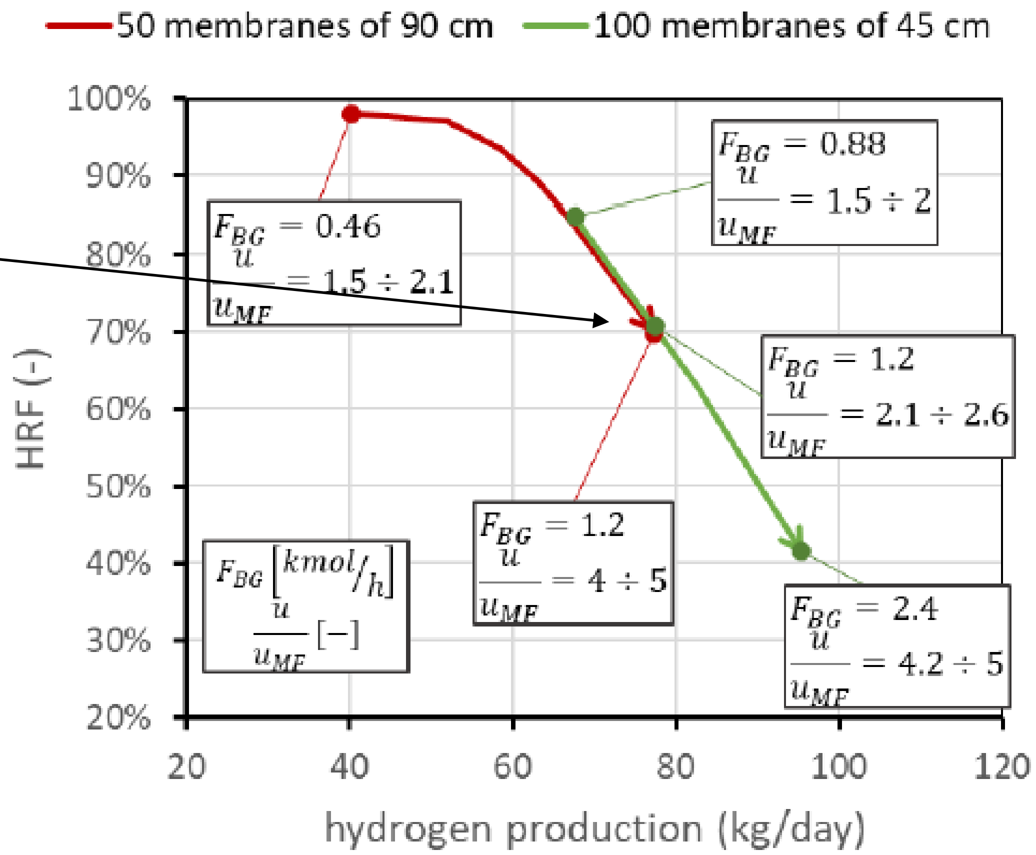
MR modelling: preliminary results

- Membrane installation (Total Membrane Area Fixed)

  - Reactor with longer membranes and lower Diameter

  →Higher gas velocity with the same reactants amount

  →Increase HRF with lower H_2 production with the same trend of the reactor with 100 membranes



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MR-based system: methodology

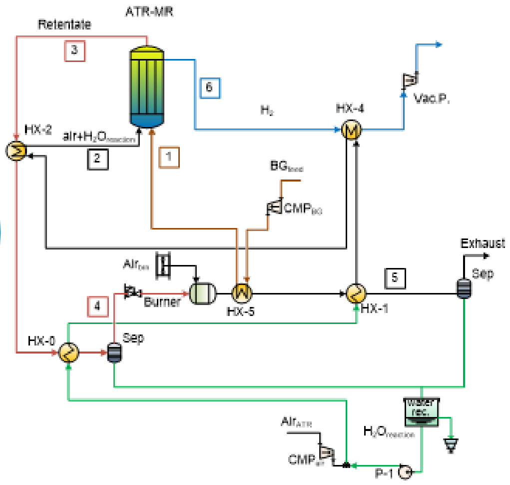
MAIN INPUT

- *BG comp.*
- *T,p reactors*
- *Convent. systems*
- *Main components parameters*

Literature

Components SoA

Aspen Tools



OUTPUT (I)

- *T,p,flows of all streams*
- *System efficiency*
- *Aux. cons.*
- *CMR design*

Literature

Economic Analysis

GHG emissions

Literature

OUTPUT (II)

H_2 cost

Preliminary environ-mental indicator

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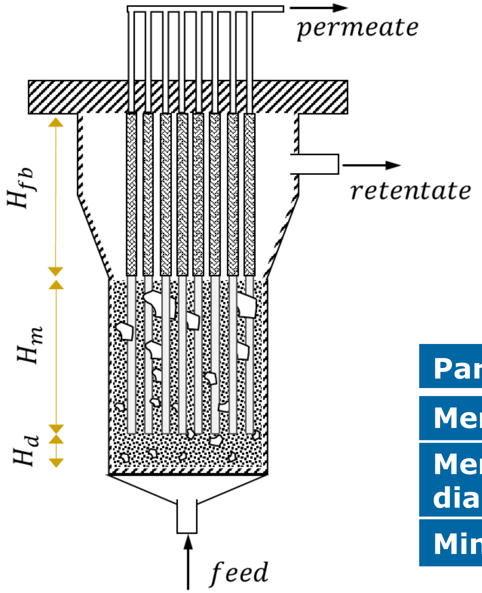
MR-based system: methodology

➢ Assumptions

Parameter	Value	Units
SCR	3 (Macbeth) 4 (Reference)	-
Hydrogen production	100	kg/day
Hydrogen delivery pressure	20	bar
Ambient temperature	15	°C
Controller consumption (% of total auxiliary consumption)	10	%
Average electric efficiency of the power generating park	45	%
Water pump hydraulic / mechanical efficiency	0.7/0.9	-
Compressors isentropic / mechanical efficiency	0.7/0.85	-
Vacuum pump isentropic / mechanical efficiency	0.7/0.85	-
Minimum ΔT in heat exchangers	25	°C
Heat transfer coefficient gas/gas	60	W/(m²K)
Heat transfer coefficient gas/liquid-two phase	70	W/(m²K)



Parameter	Value	Units
Membrane length	45	cm
Membrane external diameter	1.4	cm
Minimum pitch	3.4	cm

Parameter	Value	Units
Distance distributor to membranes (H_d)	5	cm
Reactor active height (with membranes) (H_m)	45	cm
Reactor freeboard height (H_{fb})	50	cm
Reactor total height	1	m
Fluidization (u/u_{mf}) range	1.5 ÷ 2	-

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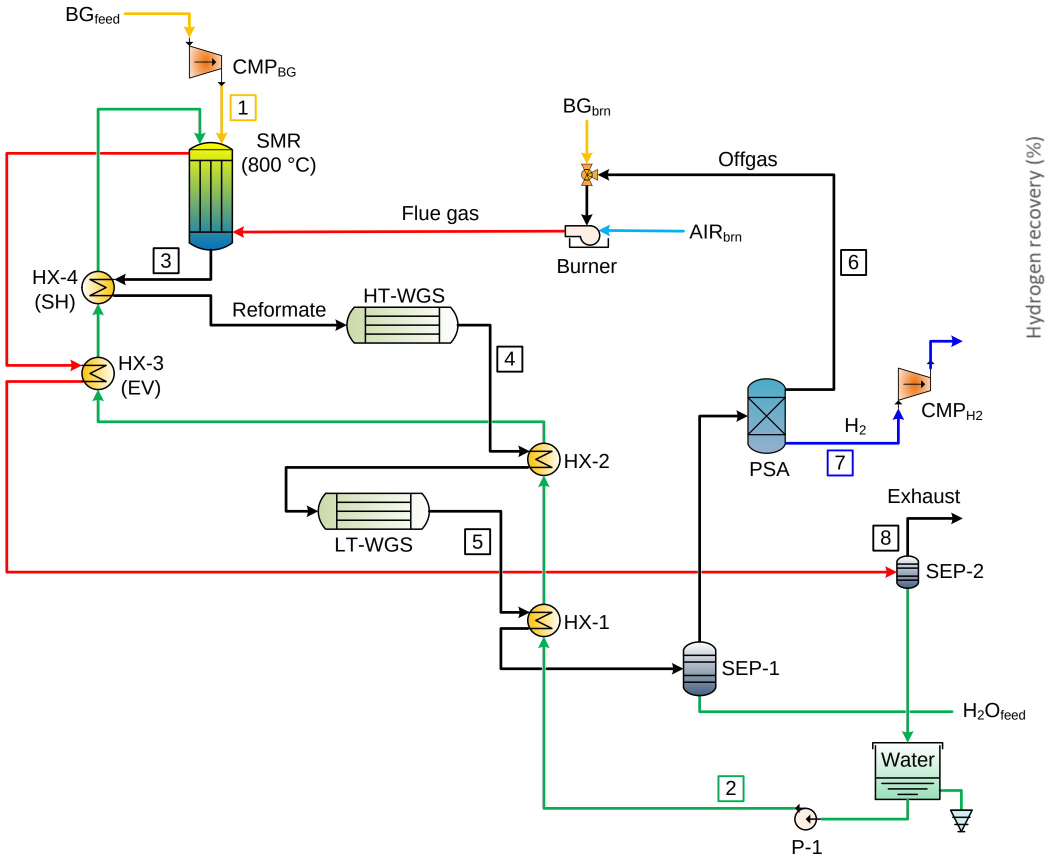
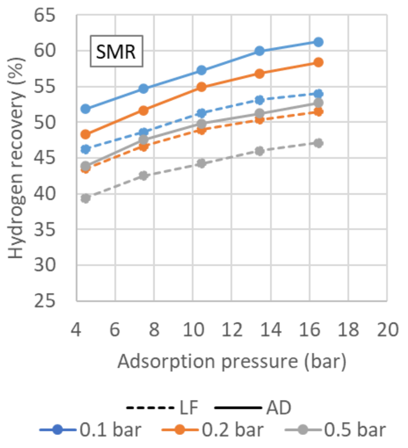
H_2 from biogas: benchmark

- Steam reforming of Biogas modelled in Aspen Plus (100 kg_{H2}/day)
- SMR+2WGS steps and separation with VPSA system





Parameter	units	
Reforming temperature	°C	800
Reforming pressure	bar	14
HT/LT WGS temperature	°C	350/200
H2 delivery pressure	bar	20
KPIs reactor Refcase		
Reactor Conversion	%	92.63
Reactor Yield	%	83.65
Reactor Selectivity	%	90.30
KPIs system Refcase		
System efficiency	%	51.92
Specific Energy Consumption	kWh/kg_{H2}	63.61
GHG specific emissions (direct)[a]	kg_{CO2eq}/kg_{H2}	17.03
GHG specific production (total)[b]	kg_{CO2eq}/kg_{H2}	18.19
COP	€/kg_{H2}	6.011

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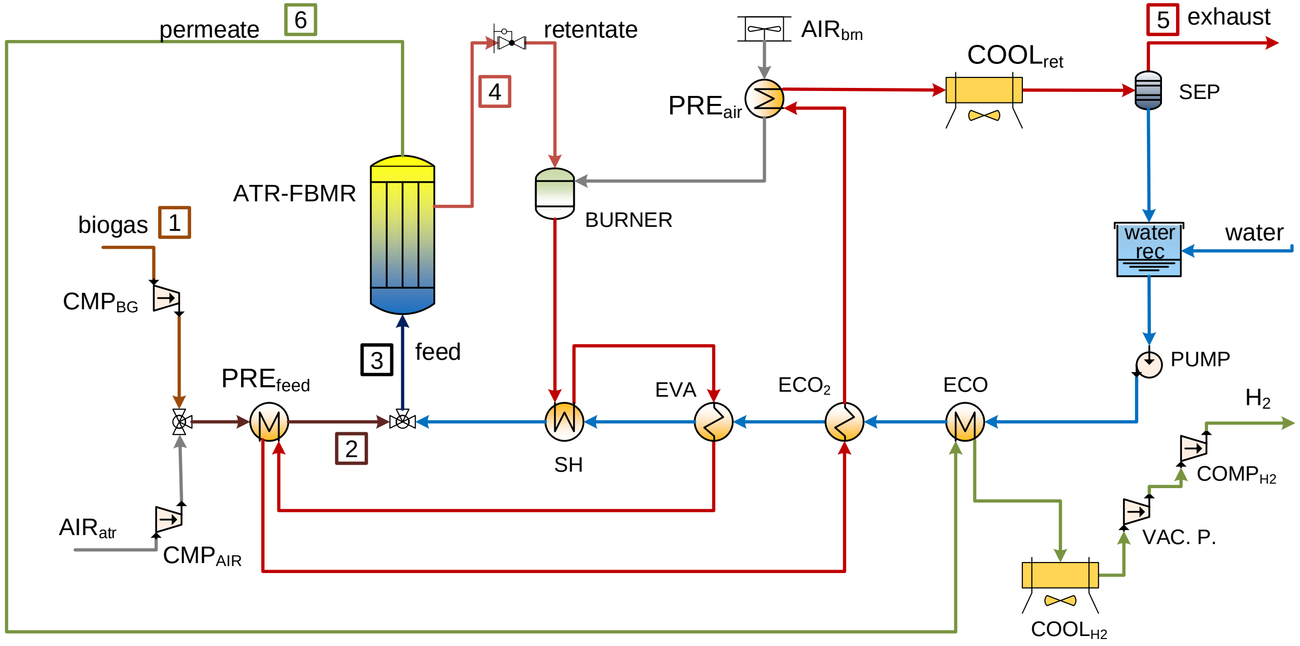
H_2 from biogas: ATR-MR-based system



Stream	Flow		T (°C)	p (bar)	Composition (% molar basis)						
	Molar (mol/s)	Mass (g/s)			CH_4	H_2	CO	CO_2	H_2O	O_2	N_2
1	0.359	9.401	15	1	58.10	0	0	33.90	3.10	1.10	3.80
2	0.709	19.511	308.45	12	29.39	0	0	17.15	1.57	10.93	40.96
3	1.104	26.620	444.46	12	18.88	0	0	11.02	36.77	7.02	26.32
4	0.833	25.462	500	12	2.11	3.00	1.02	36.48	22.53	0	34.86
5	1.223	39.058	40	1	0	0	0	26.97	6.30	5.68	61.05
6	0.575	1.158	500	0.1	0	100	0	-	0	0	0

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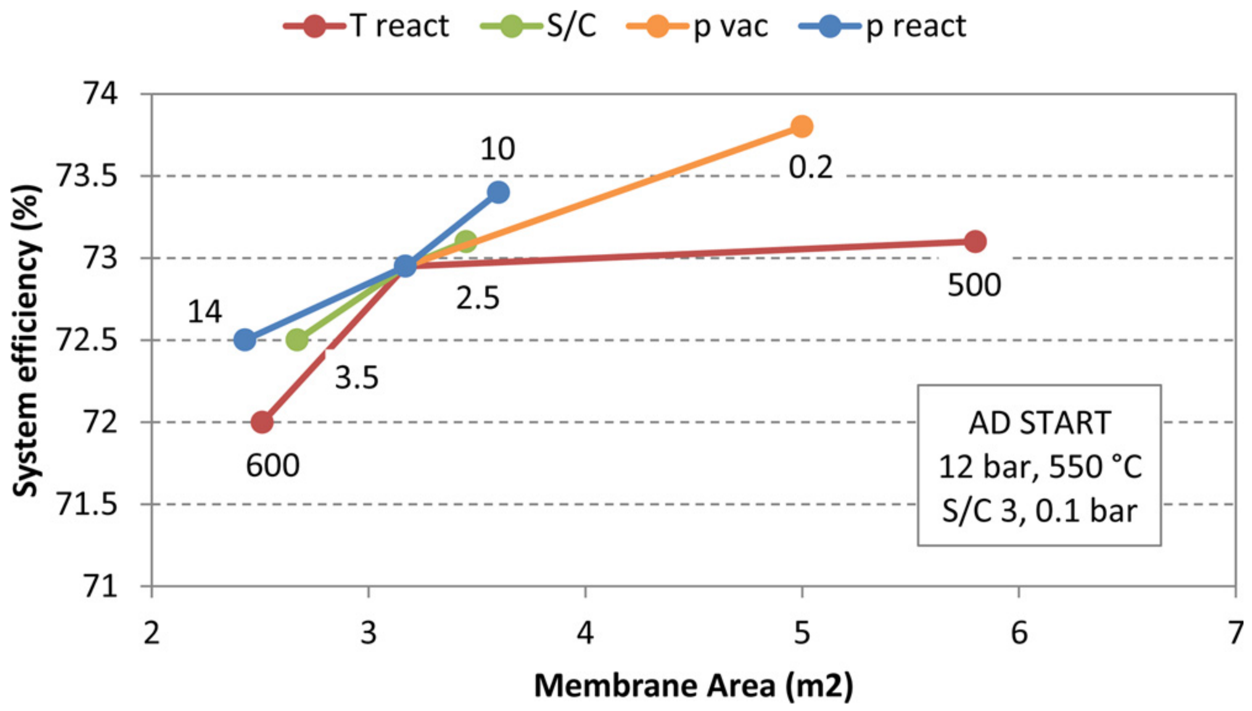
H_2 from biogas: ATR-MR-based system

- Preliminary results



molar fractions (%)	Biogas
CH_4	58.1
CO_2	33.9
N_2	3.8
O_2	1.1
H_2O	3.1
LHV (MJ/kg)	17.8
MM (kg/kmol)	26.215

$$\eta_{sys} = \frac{\dot{m}_{H_2} LHV_{H_2}}{\left(\dot{m}_{BG_f} + \dot{m}_{BG_{aux}}\right) LHV_{BG} + {W_{aux}}/{\eta_{el,rif}}}$$

- LHV_{H2} is equal to 120 MJ/kg
- W_{aux} is the sum of the electric consumptions of the system auxiliaries (i.e. compressors, pumps, control system)
- $\eta_{el,rif}$ is set equal to 45%, as the average electric efficiency of the power generating park

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H_2 from biogas: ATR-MR-based system

- 36 combinations with different reactor operating conditions are simulated
  - Sensitivity analysis on relevant parameters
    - Reactor temperature
    - Feed pressure
    - Permeate pressure
    - Steam-carbon-ratio
    - Number of membranes

Parameter	Units	Base case	Range
Reactor temperature, T_R	°C	500	475-500-525
Feed pressure, P_{feed}	bar	12	9-12-15
Permeate pressure, P_{perm}	bar	0.1	0.1-0.3
S/C ratio at the beginning of the membranes	-	3	3-4
N membranes	-	147	100-200

For each combination,

Nmem has been varied taking into account few constraints:

i) minimum membrane diameter pitch

ii) fluidization regime

iii) maximum temperature for BG and air mixture and reactor feed streams and

iv) minimum ΔT in the heat exchangers

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Winter school - Eindhoven

Membrane Reactors in Chemical Industry

Thank you for your attention!

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