Chemical looping membrane reformer concept for H_2 production and CO_2 capture

J.A. Medrano, V. Spallina, M. van Sint Annaland, F. Gallucci

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XXII PIN Meeting

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Where innovation starts

OUTLINE

- *Introduction*
- *Novel reactor concept*
- *Some results*
- *Conclusions*

H_2 PRODUCTION…

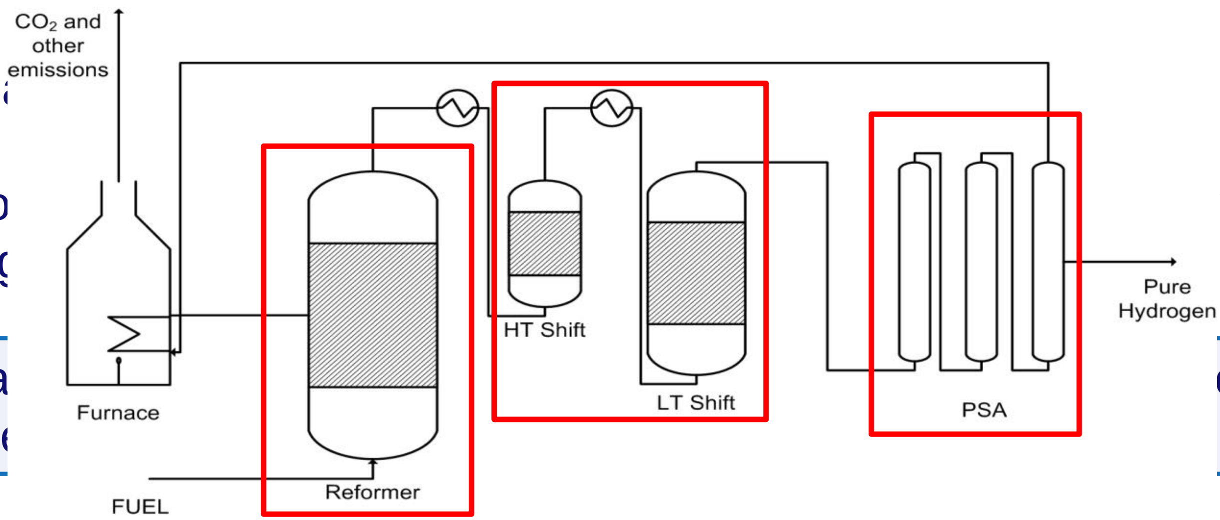
… is continuously increasing for both chemical and energy industries, and it is considered an ideal energy carrier for the foreseeable future.

Fossil fuels represent the main source for hydrogen production. More than **80%** is produced by Steam Reforming **(SR)** of natural gas/methane in multi-tubular fixed-bed reactors.

Main drawba

→ Reactio … y penalty
→ The larg

Moreover, a … onmental impact if ade



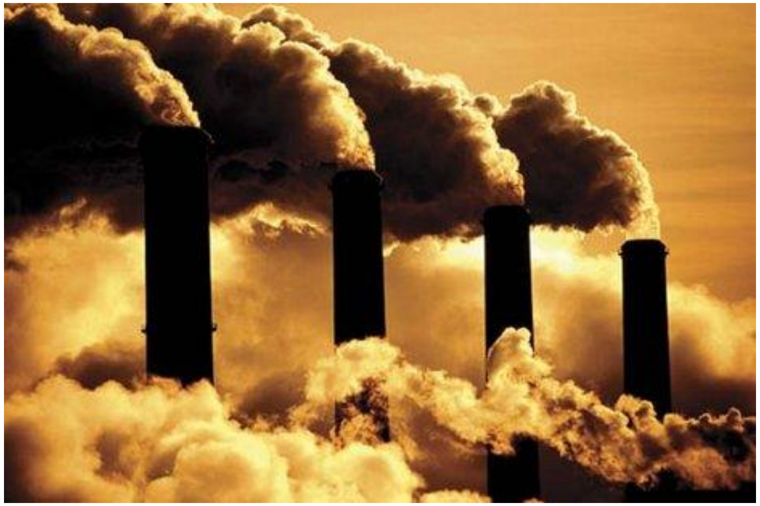
$CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H°_{298K} = +206$ kJ/mol $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H°_{298K} = -41$ kJ/mol

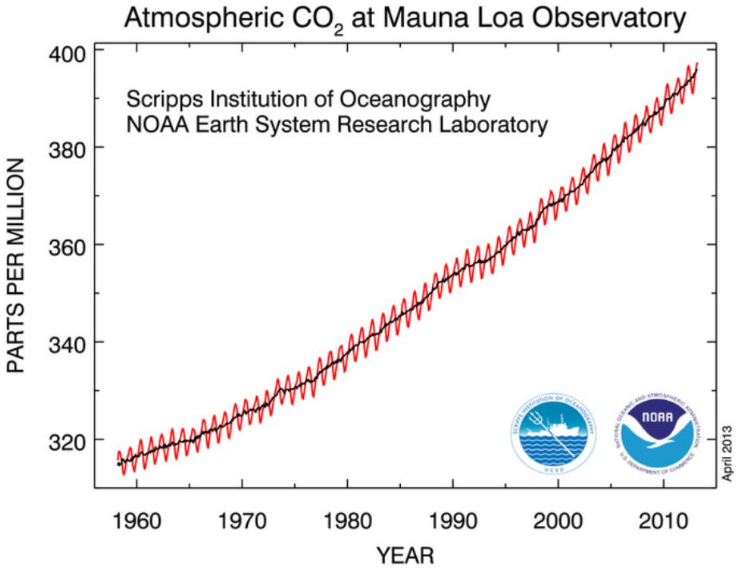
800-1000 °C
20-35 atm

200-400 °C

THE CO_2 PROBLEM

CO_2 is the main gas affecting the climate change. CO_2 concentration in the atmosphere has increased from about 280 ppm in pre-industrial period till 390 ppm in 2010.



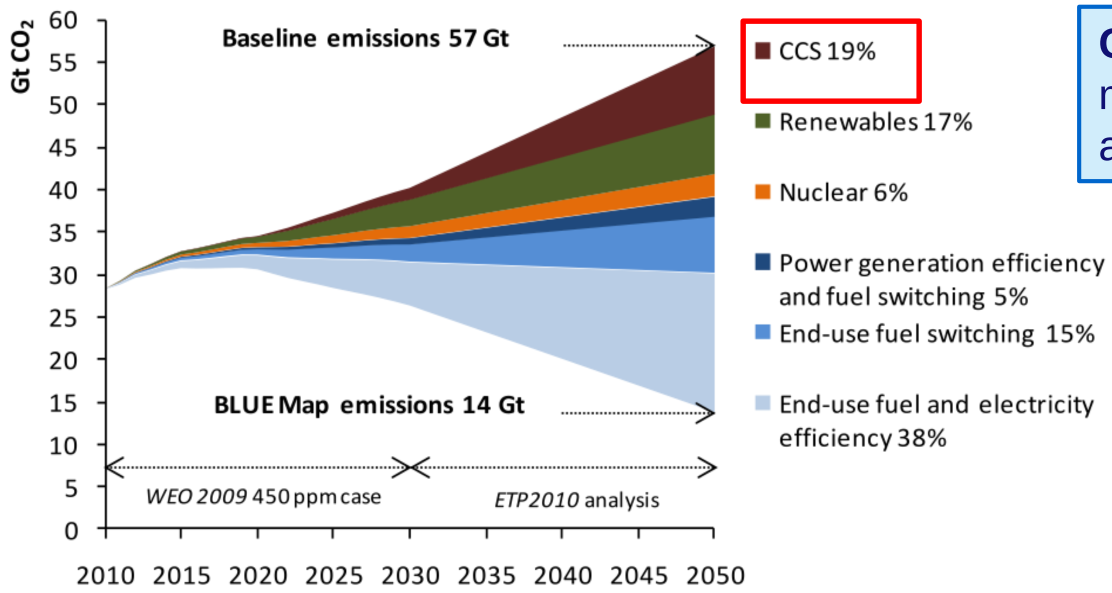


REDUCTION IN EMISSIONS IS NECESSARY TO PREVENT CATASTROPHIC VARIATIONS IN THE EARTH

THE CO_2 PROBLEM

CO_2 is the main gas affecting the climate change. CO_2 concentration in the atmosphere has increased from about 280 ppm in pre-industrial period till 390 ppm in 2010.

The IPCC summarized in a report different mitigation strategies:



Chemical looping is one of the most promising technology among CCS strategies.

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H_2 PRODUCTION WITH CO_2 CAPTURE

The goal is to develop an efficient process for hydrogen production with integrated CO_2 capture

Efficient: ***reduction*** *in the number of steps in the steam reforming and the achievement of* ***auto-thermal*** *operation.*

CCS system: *a* ***pure*** $\boldsymbol{CO_2}$ *stream provides an important contribution in the* ***reduction*** *of* CO_2 *emissions and thus climate change*

Different systems have been proposed under this consideration

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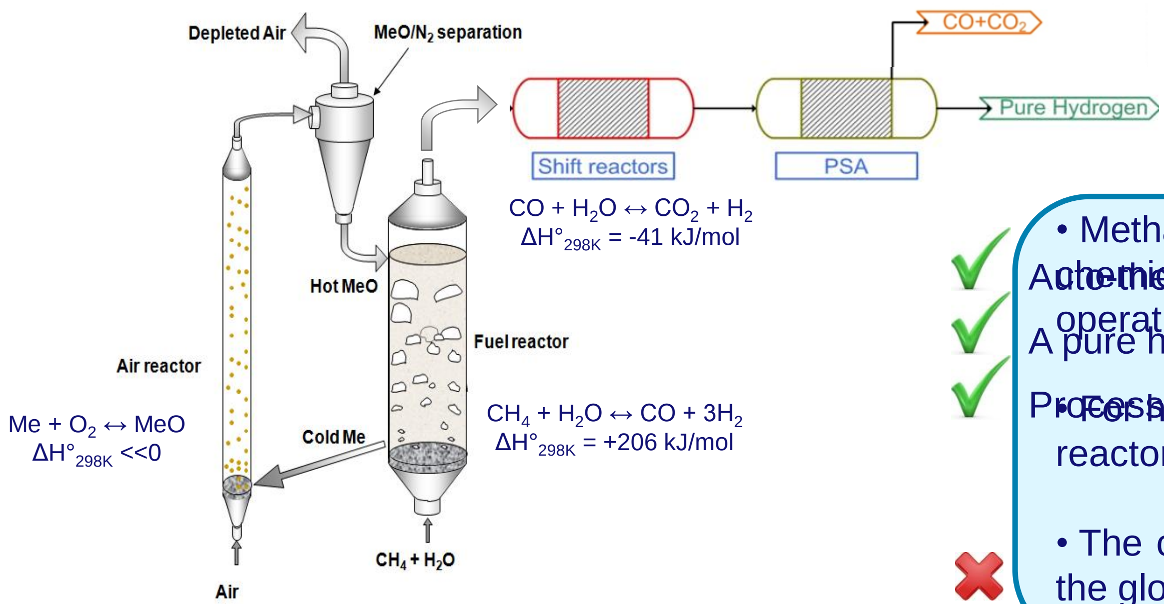
H_2 PRODUCTION WITH CO_2 CAPTURE

“The goal is to develop an efficient process for hydrogen production with integrated CO_2 capture”

Other systems: *Chemical looping concept*



M. Ortiz, et al. Int J Hydrogen Energy 36 (2011) 9663-9672

- ✓ Auto-thermal process is achieved
- ✓ A pure hydrogen stream is produced
- ✓ Process efficiency is improved
- ✗
- ✗ An external purification system is needed (penalty)

- Methane reforming takes place in a chemical looping reactor → auto-thermal operation
- For higher yields to hydrogen recovery, shift reactors and PSA step are needed.
- The concept represents an improvement in the global process efficiency.

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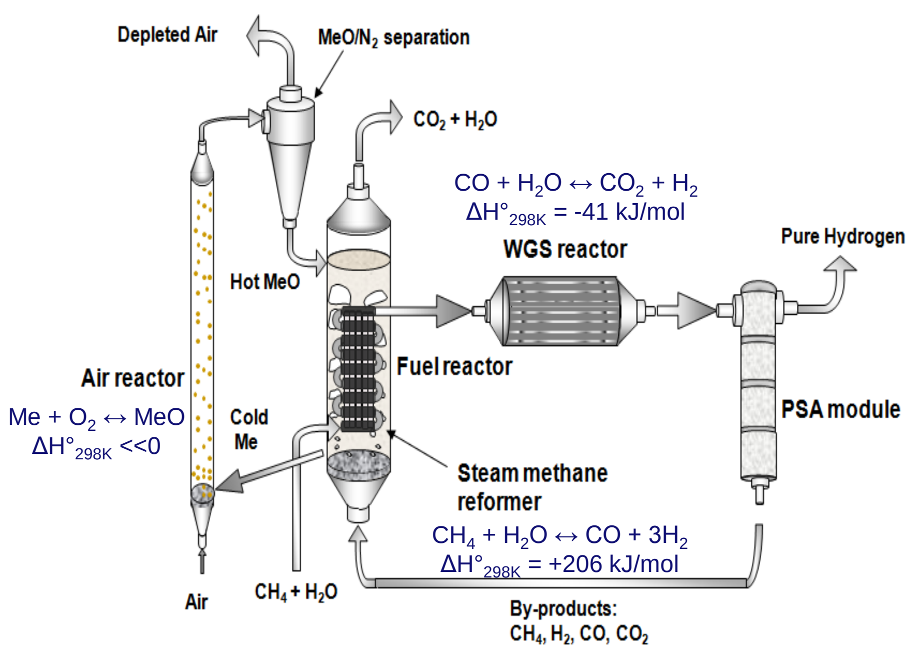
H_2 PRODUCTION WITH CO_2 CAPTURE

"The goal is to develop an efficient process for hydrogen production with integrated CO_2 capture"

Other systems: *Steam Methane Reforming – Chemical Looping Combustion*



M. Ryden, et al. Int J Hydrogen Energy 31 (2006) 1271-1283

- Steam reformer is placed inside a fuel reactor of a CLC → auto-thermal operation
- For higher yields to hydrogen recovery, shift reactors and PSA step are needed.
- CO_2 can be easily separated

✓ Auto-thermal process is achieved

✓ A pure hydrogen stream is produced at high pressure

✓ Process efficiency is improved

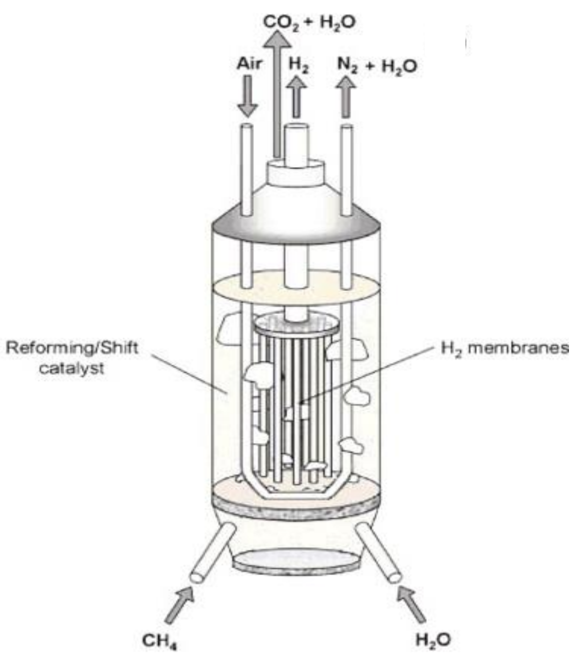
✗ There is no reduction in the number of steps

✗ CO_2 is produced at atmospheric conditions

H_2 PRODUCTION WITH CO_2 CAPTURE

“The goal is to develop an efficient process for hydrogen production with integrated CO_2 capture”

<u>Other systems:</u> *Fluidized bed membrane reactors*



F. Gallucci, et al. Top Catal 51 (2008) 133-145

- Reforming and water gas-shift reactions are carried out in the same unit.
- H_2 extraction through the membranes displaces the thermodynamic equilibrium towards products.
- Heat is supplied by hydrogen combustion inside the U-shaped membrane → Auto-thermal operation

✖ Up to 30% of extra Pd membrane surface is needed
✖ Part of the hydrogen produced is consumed in-situ

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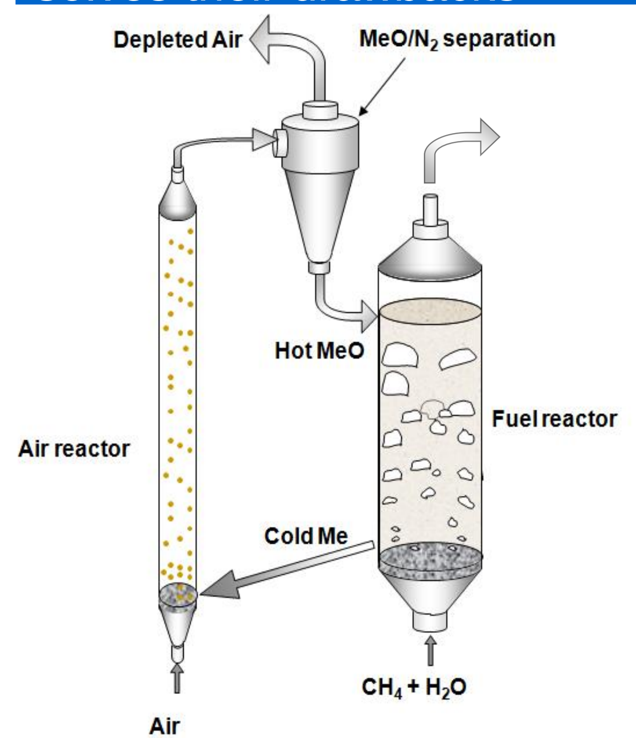
The novel reactor combines the advantages of the other systems and solves their drawbacks



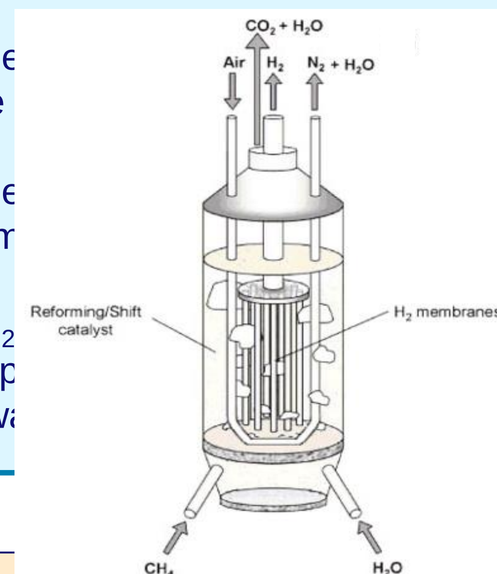
Me + O$_2$
ΔH°$_{29\ldots}$

…elective
…es

… CO$_2$ + H$_2$
…41 kJ/mol

… CO + 3H$_2$
…206 kJ/mol

- Re… …t reactions are
- He… …gen carrier com…
…ion
- H$_2$ … …membranes disp… …equilibrium towa…



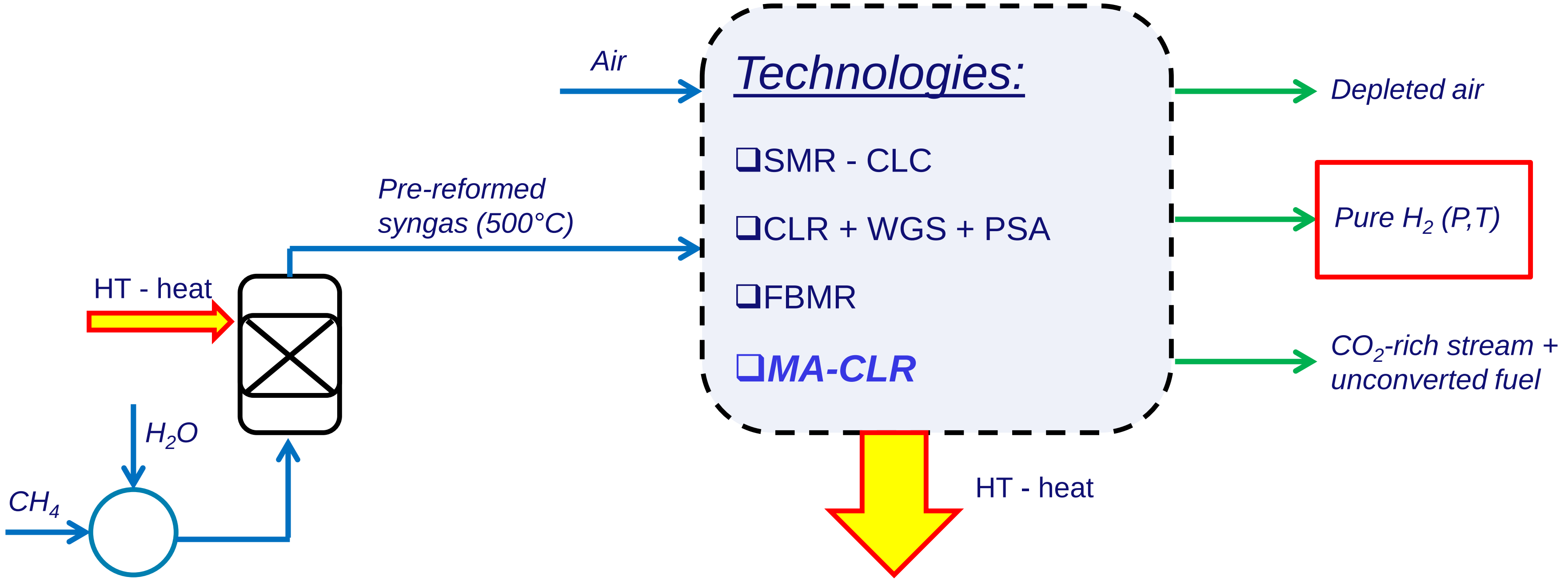
THE SYSTEM PROVIDES A HIGH DEGREE OF PROCESS INTENSIFICATION

VIDI project ClingCO$_2$ – project number 12365

THERMODYNAMICS

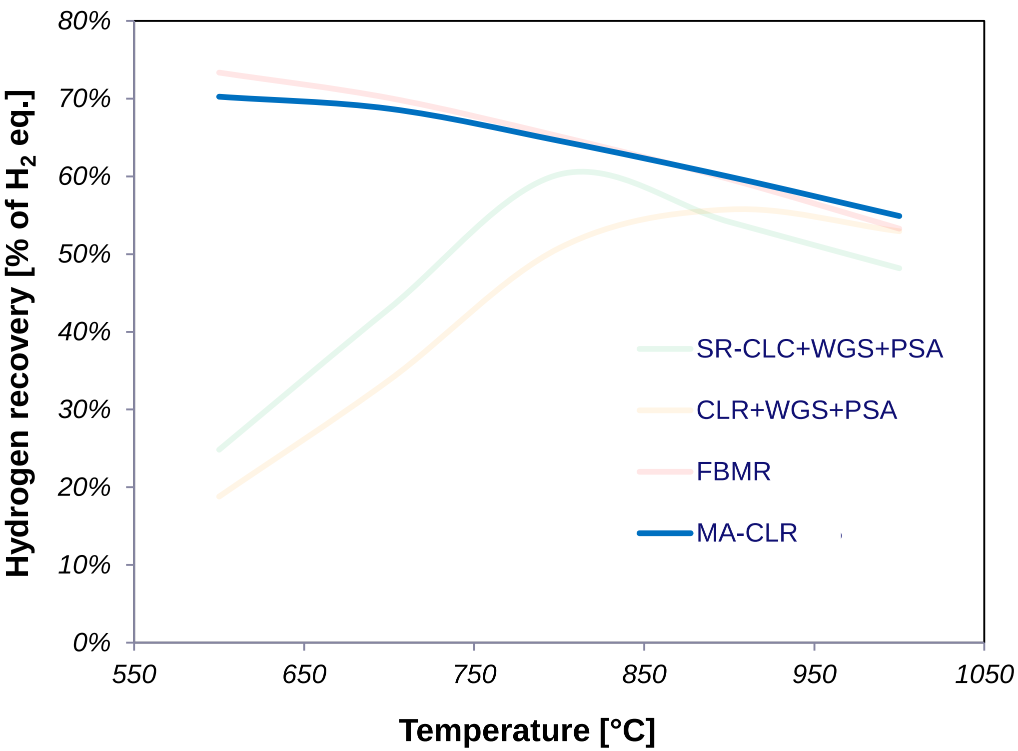
All reactor concepts previously depicted have been analyzed with ***Aspen Plus*** and the calculations are carried out at *chemical equilibrium*

General **scheme** of the different cases studied:



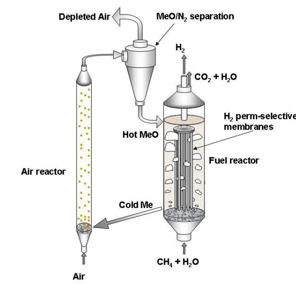
THERMODYNAMICS

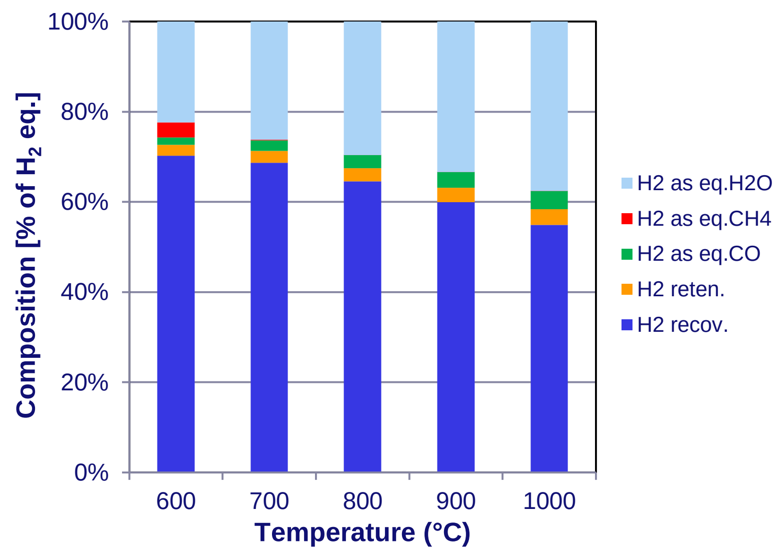
MA-CLR



Assumptions

- MeO in solid (wt%)= 20%
- Min ΔP_{H2} : 0.2 bar
- Pressure permeate side: 1 bar
- Pressure feed side: 20 bar
- S/C=1.5 & O/C=variable
- H_2 selectivity membrane: infinite
- Max solid T = 1200°C





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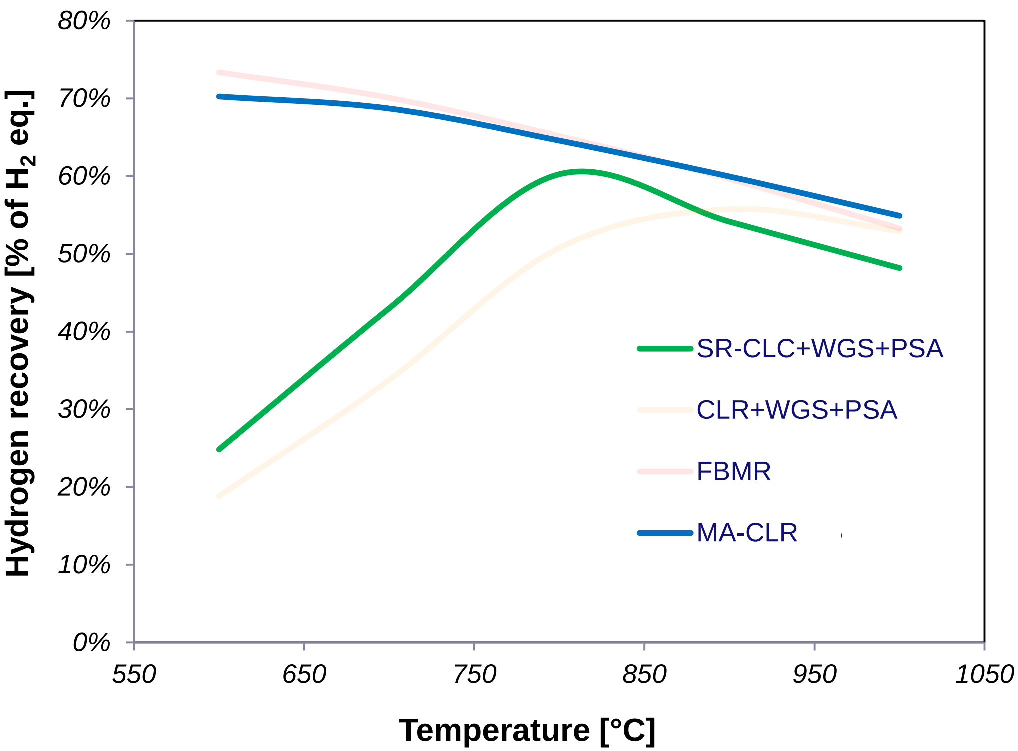
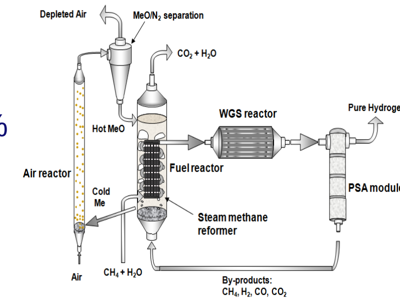
THERMODYNAMICS

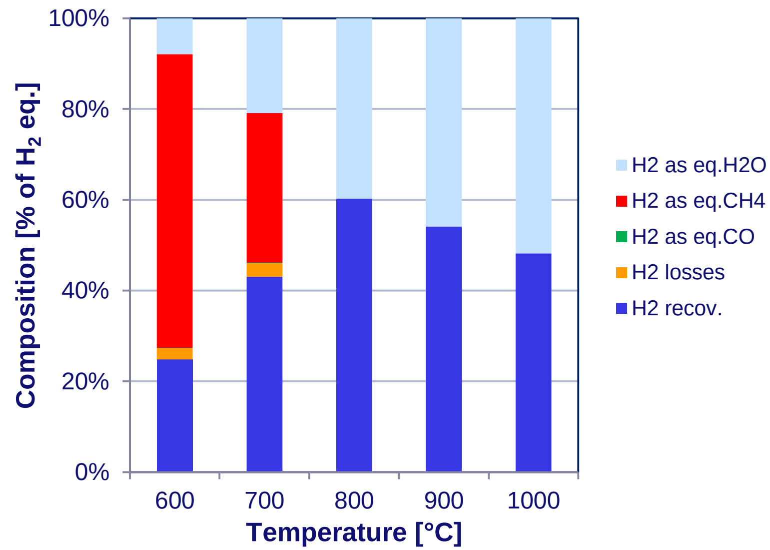
SMR - CLC



Assumptions

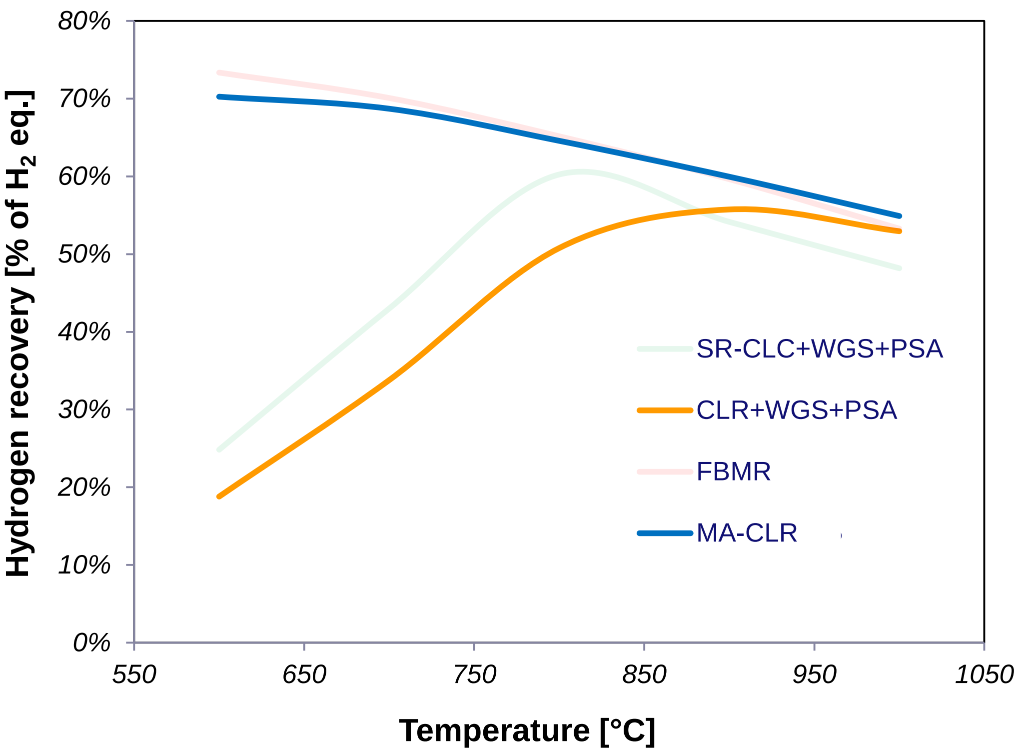
- WGS eq T = 250°C
- PSA eff: 90%
- MeO in solid (wt%)= 40%
- S/C=3.0 & O/C=variable
- Max solid T = 1200°C
- Pressure : 20 bar





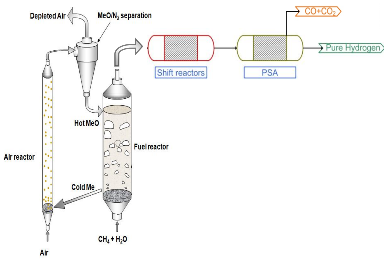
THERMODYNAMICS

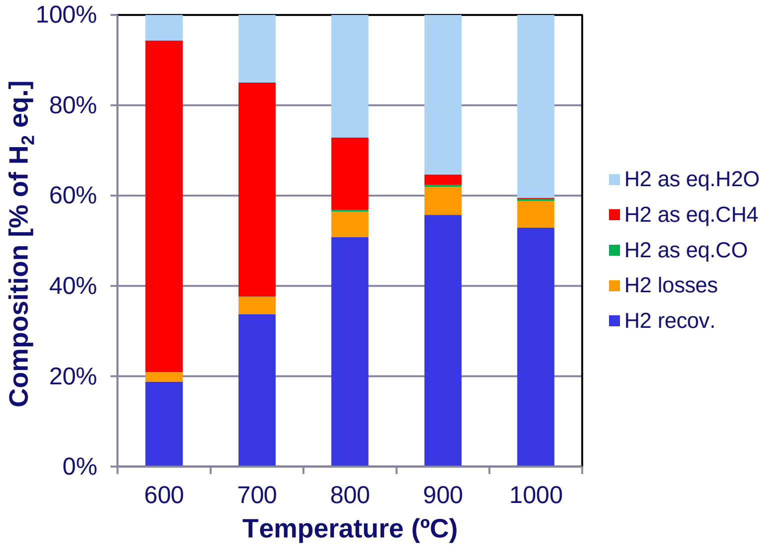
CLR + WGS +PSA



Assumptions

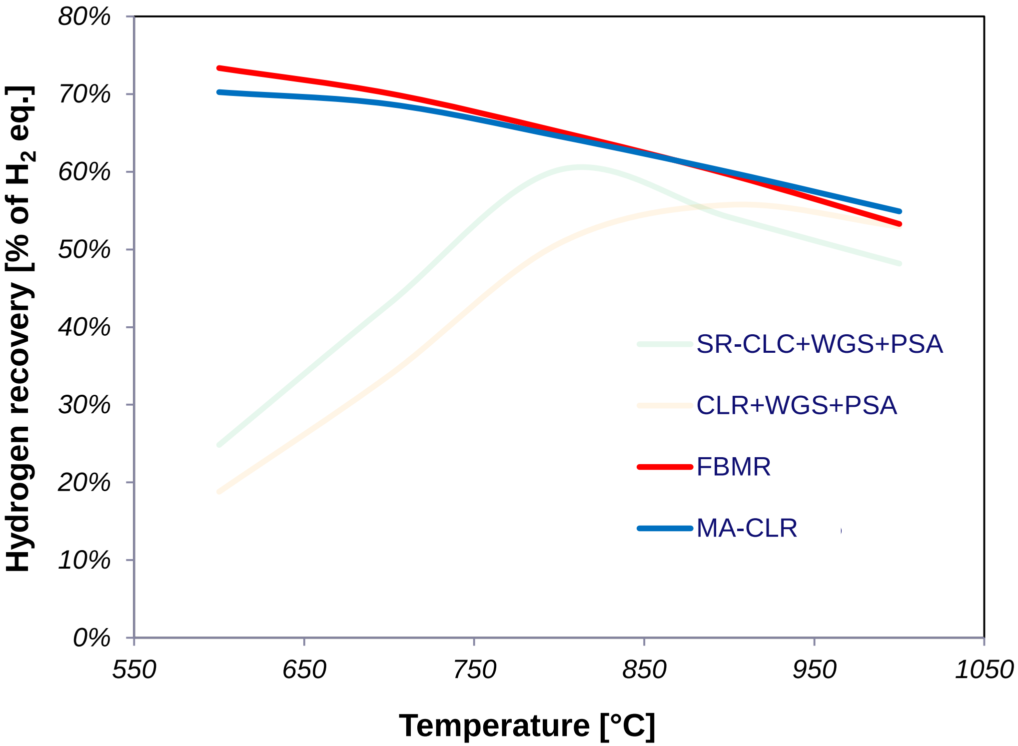
- WGS eq T = 250°C
- PSA eff: 90%
- MeO in solid (wt%)= 20%
- S/C=2.0 & O/C=variable
- Max solid T = 1200°C
- Pressure : 20 bar





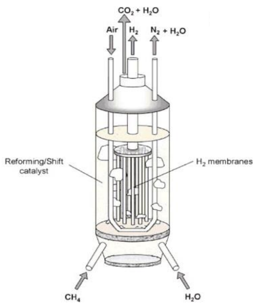
THERMODYNAMICS

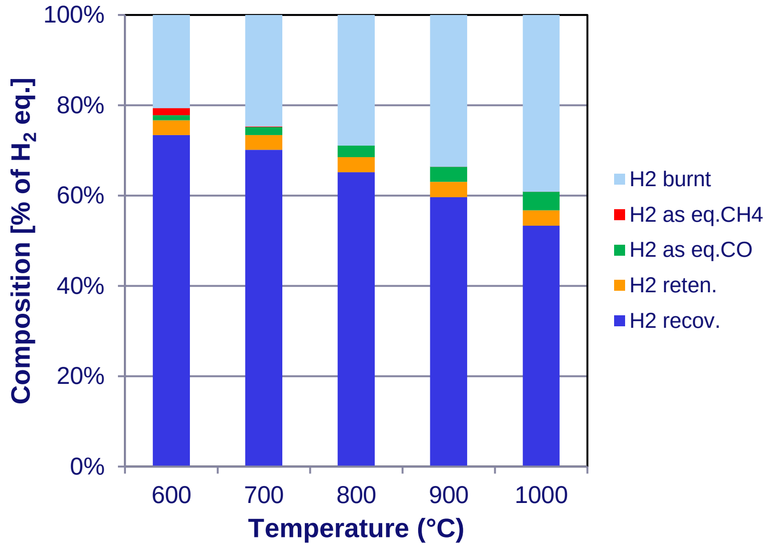
FBMR



Assumptions

- MeO in solid (wt%)= 20%
- Min ΔP_{H2}: 0.2 bar
- Pressure permeate side: 1 bar
- Pressure feed side: 20 bar
- S/C = 3.0
- $\%O_2$ in the vitiated air: 5%
- H_2 selectivity membrane: infinite





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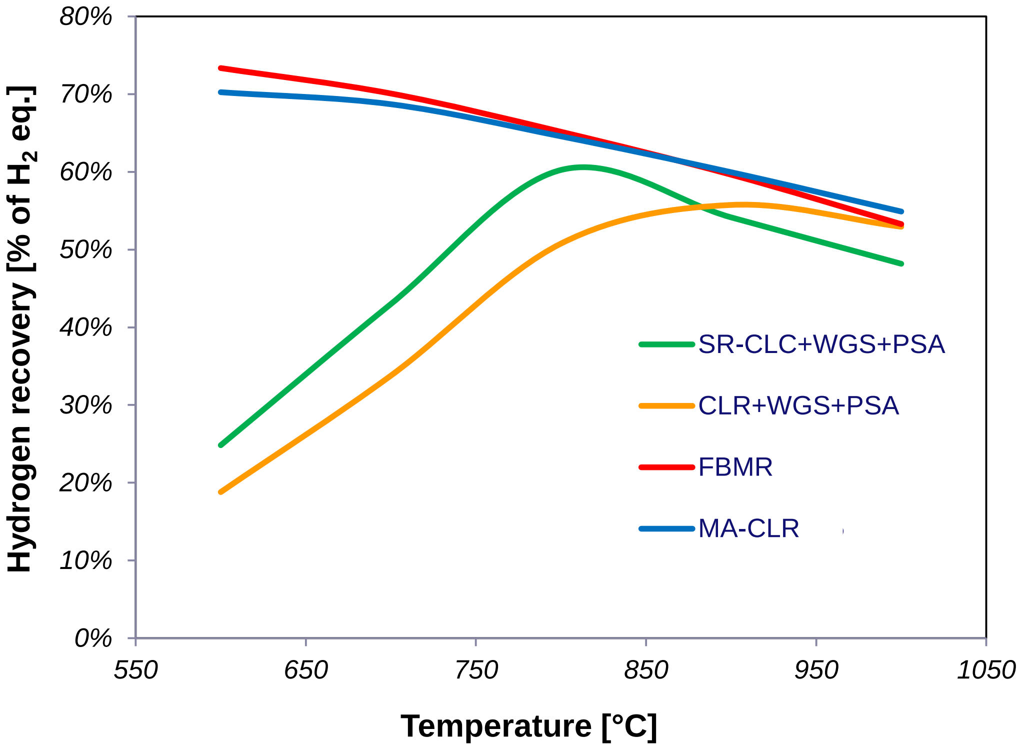
THERMODYNAMICS

Hydrogen recovery with the different reactor concepts



Conclusions

- SMR-CLC has an optimum around 800°C and provides pure CO_2
- CLR+WGS+PSA concept is only interesting at very high temperatures.
- Processes with membrane reactors would provide higher hydrogen recoveries.
- MA-CLR presents identical results as FBMR by working with lower S/C ratios and initial investment costs.

RESULTS. Thermodynamics

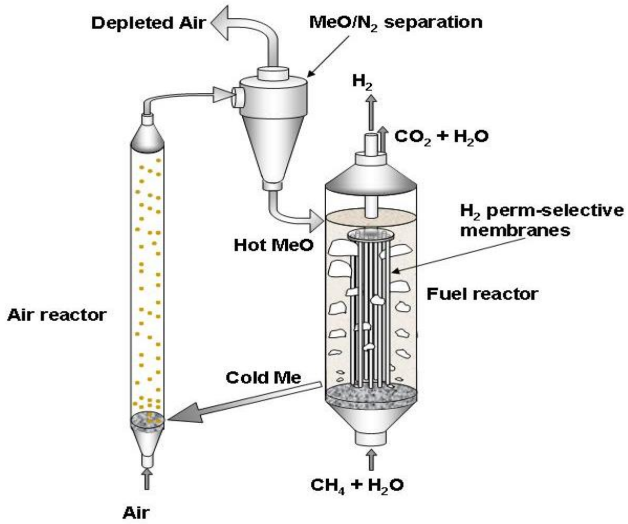
Technology	Advantages	Disadvantages
CLR	▪ The CLR **downstream technologies are developed** and commercialized ▪ Possibility of retrofitting the existing plant ▪ H_2 and CO_2 are produced and separated at high pressure	▪ CLR reactors under pressurized conditions (Solid circulation, HT/HP cyclones, etc…) ▪ **H_2 losses** in the PSA process ▪ **High T or very high S/C ratio** are required for high performance (CH_4 conversion)
SMR-CLC	▪ The **downstream technologies are developed** ▪ Possibility of retrofitting the existing plant ▪ H_2 is produced and separated at high pressure	▪ **H_2 losses** in the PSA process ▪ **High S/C ratio** (typical of tubular SMR) are required for high performance ▪ CO_2 is produced at atmospheric pressure ▪ Very high solid circulation is required to operate the FR-SR at high temperature
FBMR	▪ Possibility to operate at the high pressure ▪ High methane conversion at 600-700°C ▪ High purity H_2 separation ▪ **Conversion and Separation in only one unit**	▪ Part of the permeated **H_2 is burnt** – High **membrane area** is required (≈30% extra) ▪ **Very high S/C ratio** is required to guarantee high H_2 production
MA - CLR	▪ High performance at intermediate temperature ▪ Adiabatic reactors ▪ **High S/C is NOT required** ▪ High purity H_2 separation ▪ **Conversion and Separation in only one unit**	▪ The reactors are operated under pressurized conditions ▪ **Technology complexity and challenge** for the reactor design ▪ Permeated side pressure is limited to the membrane area and the reactor pressure

GENERAL CONCLUSIONS ABOUT THE CONCEPT

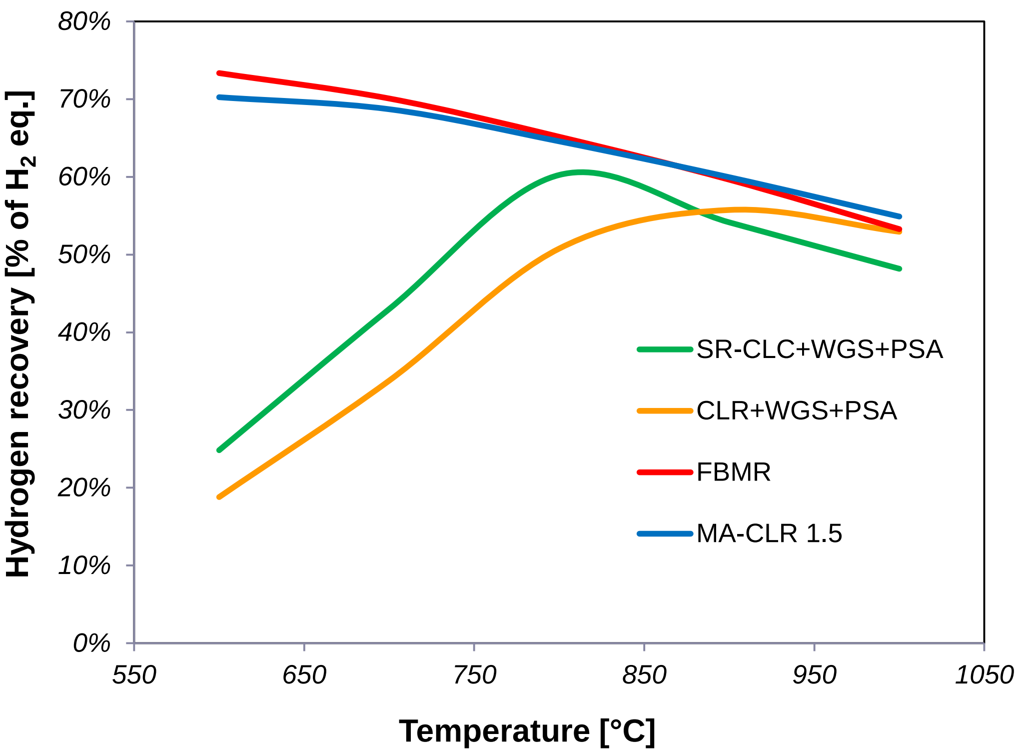
- The novel MA-CLR could provide a solution of several disadvantages of the conventional technology for SMR, with some technological challenge
- Hydrogen recovery in concepts with integrated membrane reactors is higher than in traditional processes.
- Auto-thermal reaction with integrated hydrogen production and CO_2 capture could be achieved in only one unit.
- Lower S/C values (reducing energy penalty) and low membrane surfaces (reducing cost) are needed with the novel concept proposed compared with FBMR.
- The system represents a high degree of process intensification.

MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR

Preliminary study:
Thermodynamics



MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR



It has been demonstrated the potential of the MA-CLR concept compared to other novel reactor concepts

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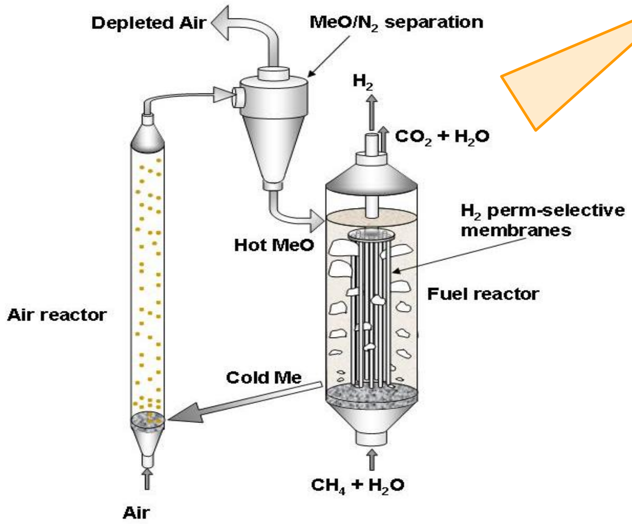
Preliminary study: Thermodynamics

Oxygen carrier evaluation



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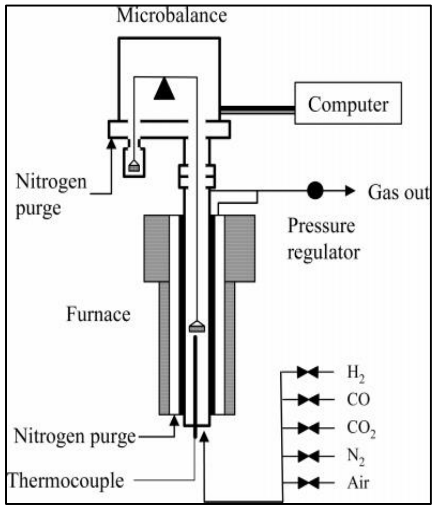
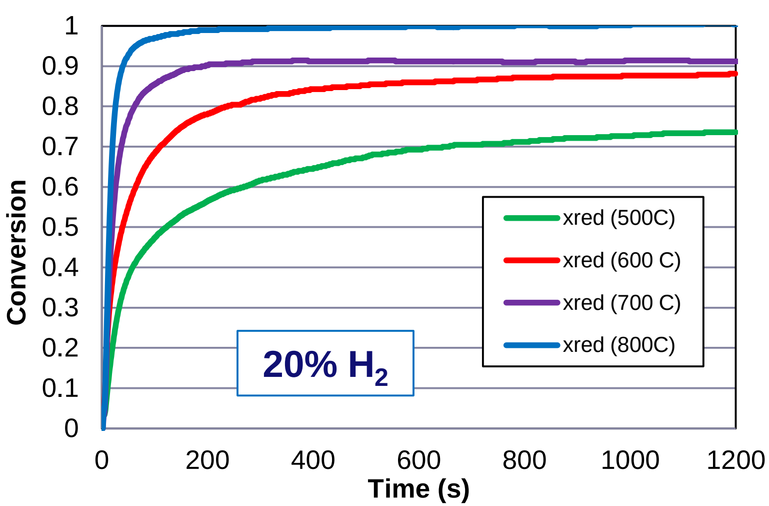
TGA experiments

- Oxygen carrier conversion



$NiO + H_2 \rightarrow Ni + H_2O$

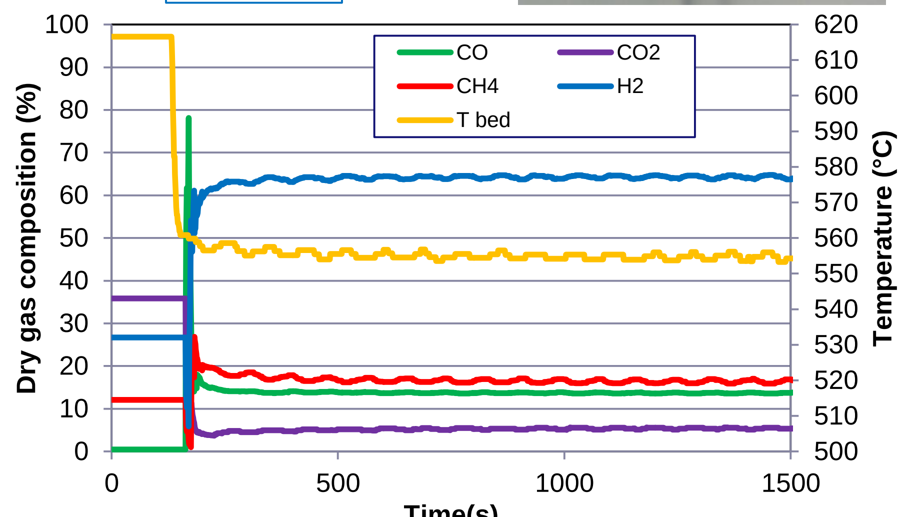
$2Ni + O_2 \rightarrow 2NiO$



Packed bed

-Fuel conversion
-Selectivity to products

600°C
S/C = 3



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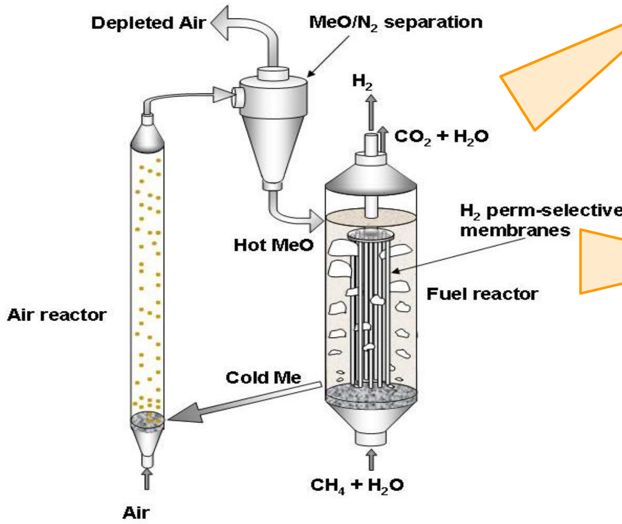
Preliminary study: Thermodynamics

Oxygen carrier evaluation

Hydrodynamic study in the membrane reactor



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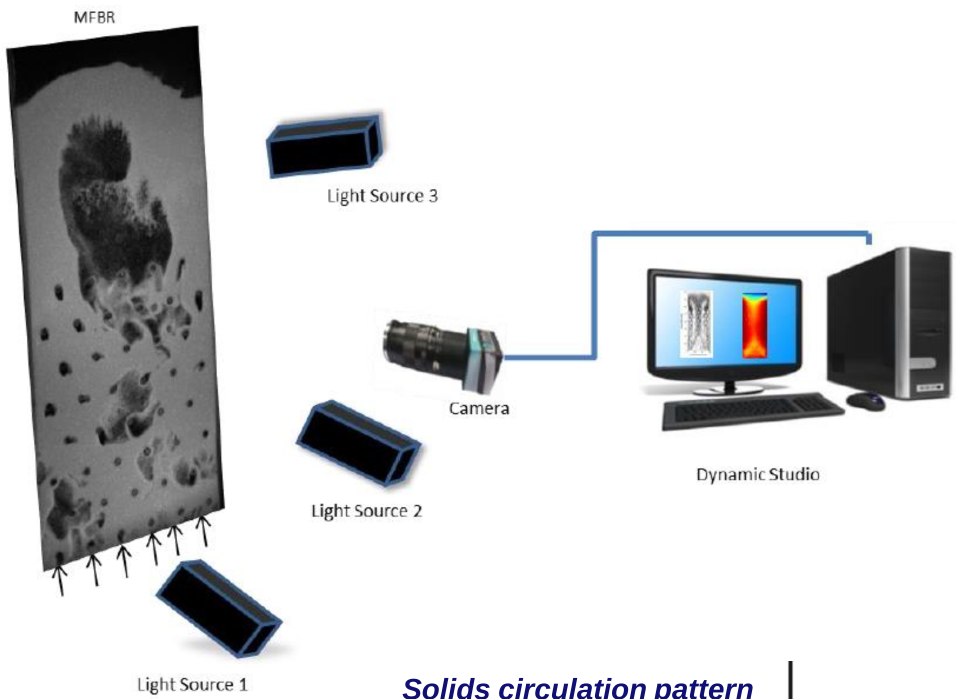
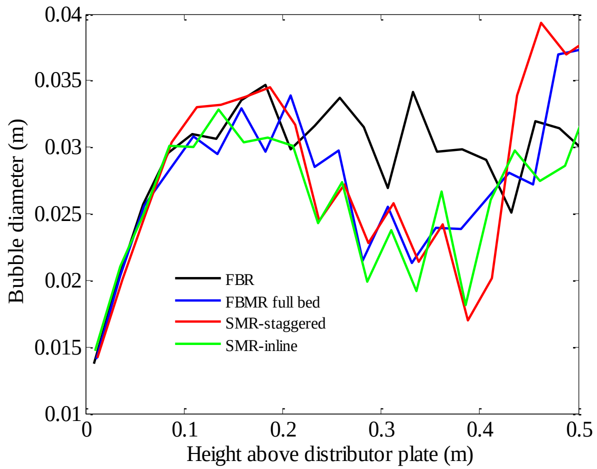
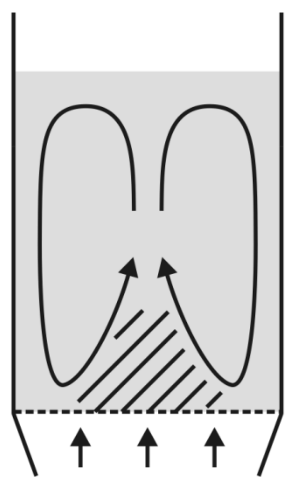
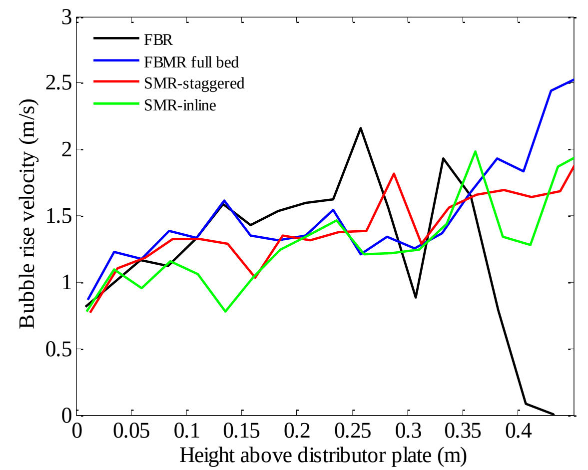




Solids circulation pattern





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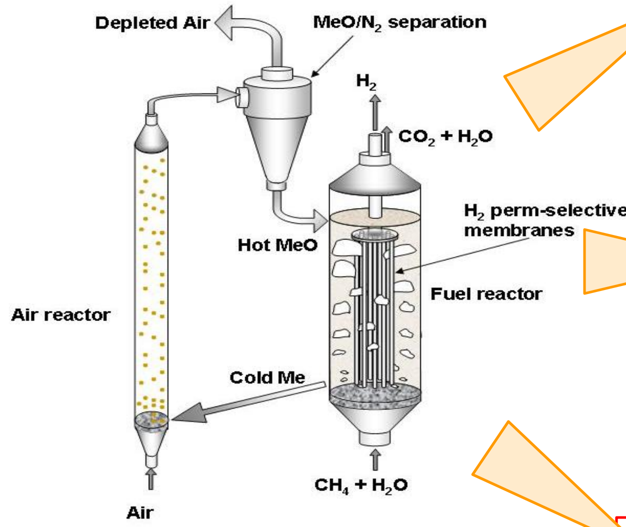

Hydrodynamic study in the membrane reactor

Phenomenological model

MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR

Combination of mass and heat balances with hydrodynamics.

- Kinetics from the oxygen carrier evaluation
- Permeation from membranes evaluation
- Hydrodynamics from experimental findings

Bubble-wake phase

$$\frac{\partial (f^B + f^W \varepsilon_e) C_i^{BW(g)}}{\partial t} = -\frac{\partial}{\partial z}\left[u^{b(g)}(f^B+f^W\varepsilon_e)C_i^{BW(g)}\right] + K_i^{BW-CE(g)}(f^B+f^W\varepsilon_e)\left(C_i^{CE(g)} - C_i^{BW(g)}\right) + \left(\lambda_1 C_i^{BW(g)} + \lambda_2 C_i^{CE(g)}\right)\frac{\partial}{\partial z}\left[u^{b(g)}(f^B+f^W\varepsilon_e)\right] \pm R_j^{W(g)}\rho_p f^W(1-\varepsilon_e)$$

Cloud-emulsion phase

$$\frac{\partial (f^C+f^E)\varepsilon_e C_i^{CE(g)}}{\partial t} = -\frac{\partial}{\partial z}\left[u^{e(g)}(f^C+f^E)\varepsilon_e C_i^{CE(g)}\right] - K_i^{BW-CE(g)}(f^B+f^W\varepsilon_e)\left(C_i^{CE(g)}-C_i^{BW(g)}\right) - \left(\lambda_1 C_i^{BW(g)} + \lambda_2 C_i^{CE(g)}\right)\frac{\partial}{\partial z}\left[u^{b(g)}(f^B+f^W\varepsilon_e)\right] \pm R_j^{CE(g)}\rho_p(f^C+f^E)(1-\varepsilon_e)$$

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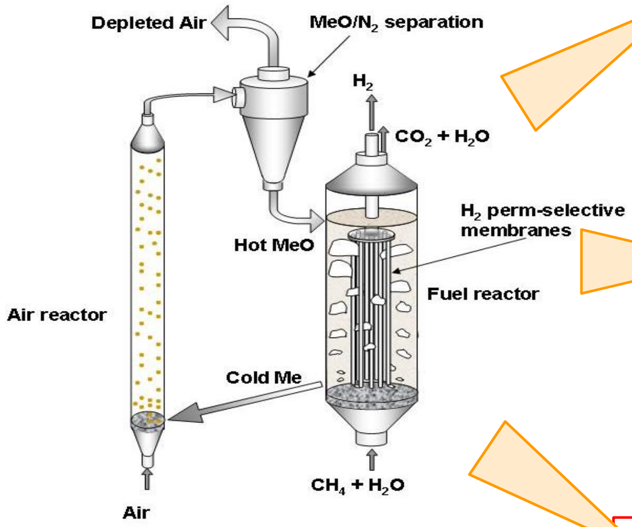

Hydrodynamic study in the membrane reactor

Phenomenological model

Detailed model of the reactor

MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR

Two Fluid Modeling

Gas and solid phase modeled as inter-penetrating continua

- OpenFOAM model
- Kinetic Theory of Granular Flow (KTGF) is included
- Added immersed membranes
- Gas pockets

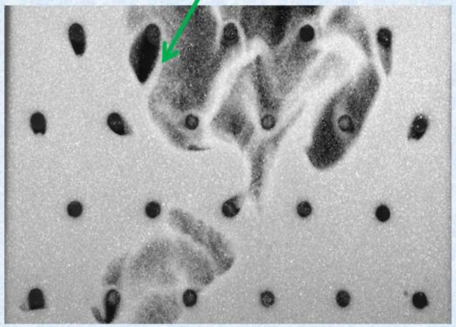

Figure 2: *Fluidization with immersed membranes (courtesy: J.A. Medrano Jimenez)*

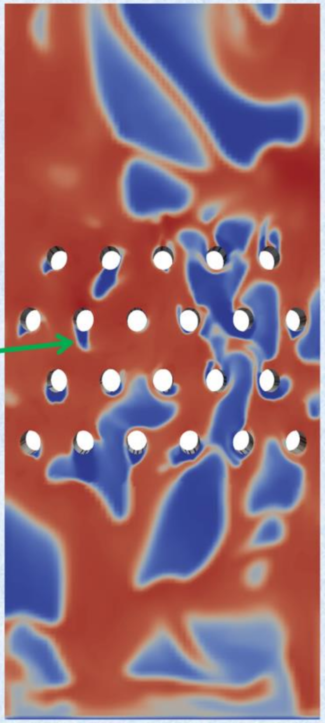

Figure 3: *OpenFOAM TFM simulation*

Discrete Particle Modeling

Particles: Newton's law of motion; Gas: Navier-Stokes

- Three DPM models available:
  - In-house code
  - LIGGGHTS/CFDEM
  - OpenFOAM
- Gas extraction via walls
- Densified zones

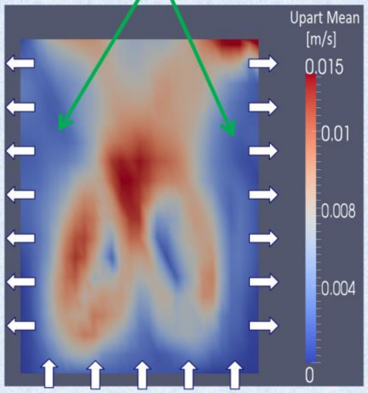

Figure 4: *Gas extraction via walls, time-averaged particle velocities (LIGGGHTS/CFDEM)*

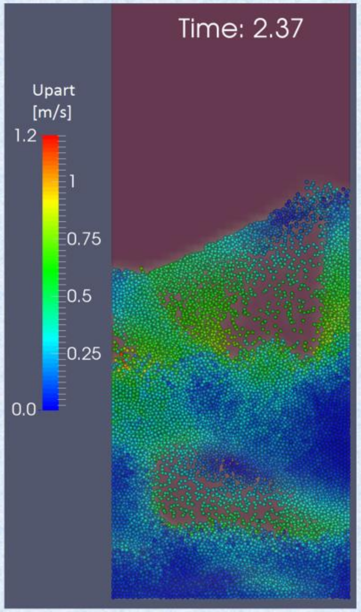

Figure 5: *OpenFOAM DPM simulation of gas-solid fluidized bed*

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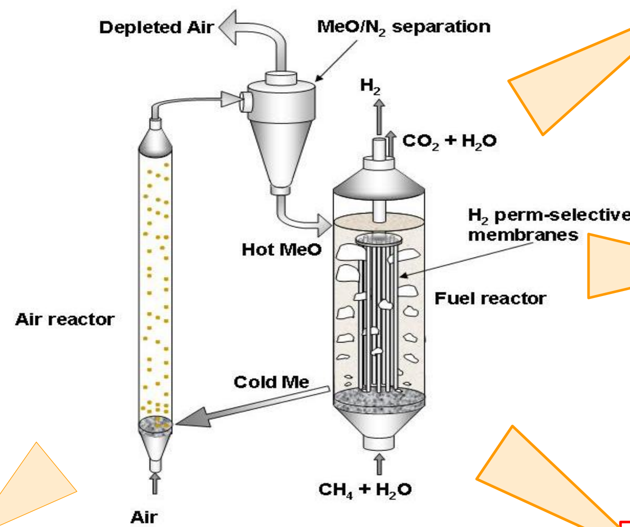
Oxygen carrier evaluation



Hydrodynamic study in the membrane reactor

Techno-economical analysis

Phenomenological model

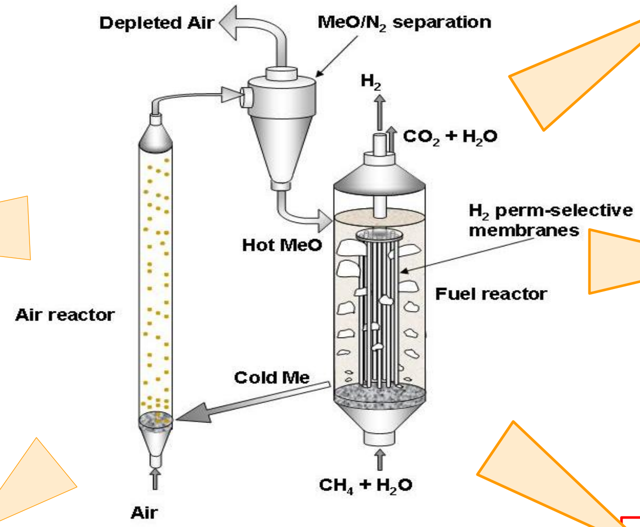
Detailed model of the reactor

MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR

Preliminary study: Thermodynamics

Oxygen carrier evaluation

Lab scale demonstration



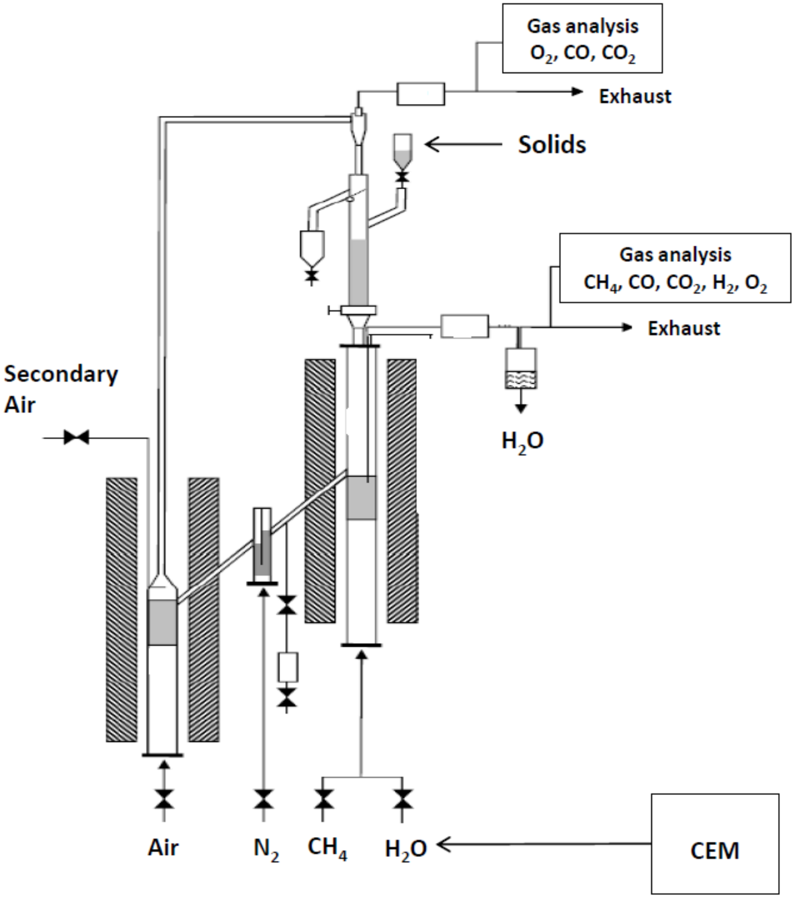
Hydrodynamic study in the membrane reactor

Techno-economical analysis

Phenomenological model

Detailed model of the reactor

MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR



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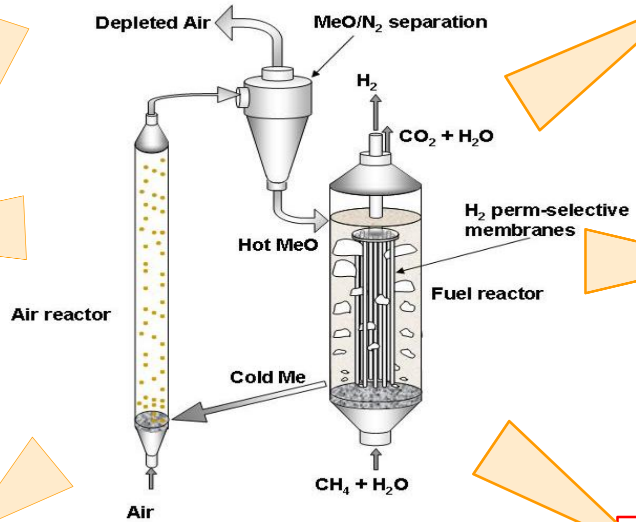

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Department of Chemical Engineering & Chemistry

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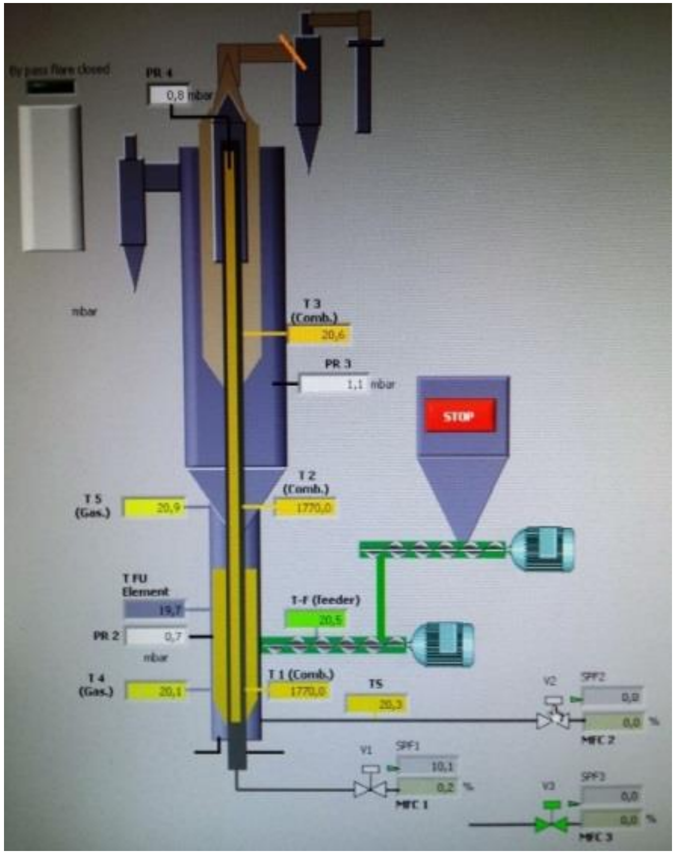

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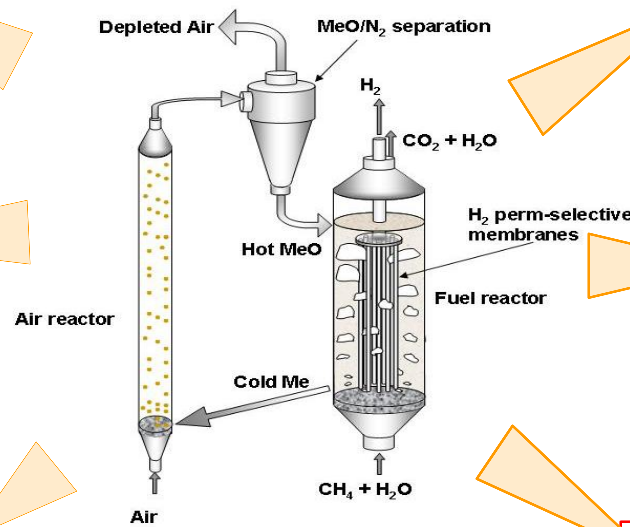

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Thank you for your attention

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