

Chemical looping membrane reformer concept for H₂ production and CO₂ capture

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The Membrane-Assisted Chemical Looping Reforming concept as efficient reactor for H₂ production and CO₂ capture: a comparison to benchmark technology.

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Fundamentally Innovative



OUTLINE

- *Introduction*
- *Description of different systems*
- *Results*
- *Conclusions*

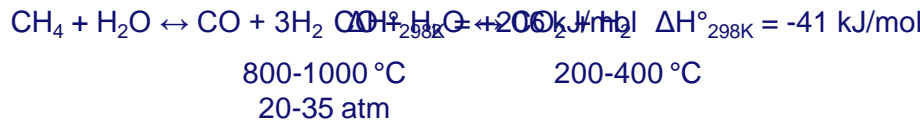
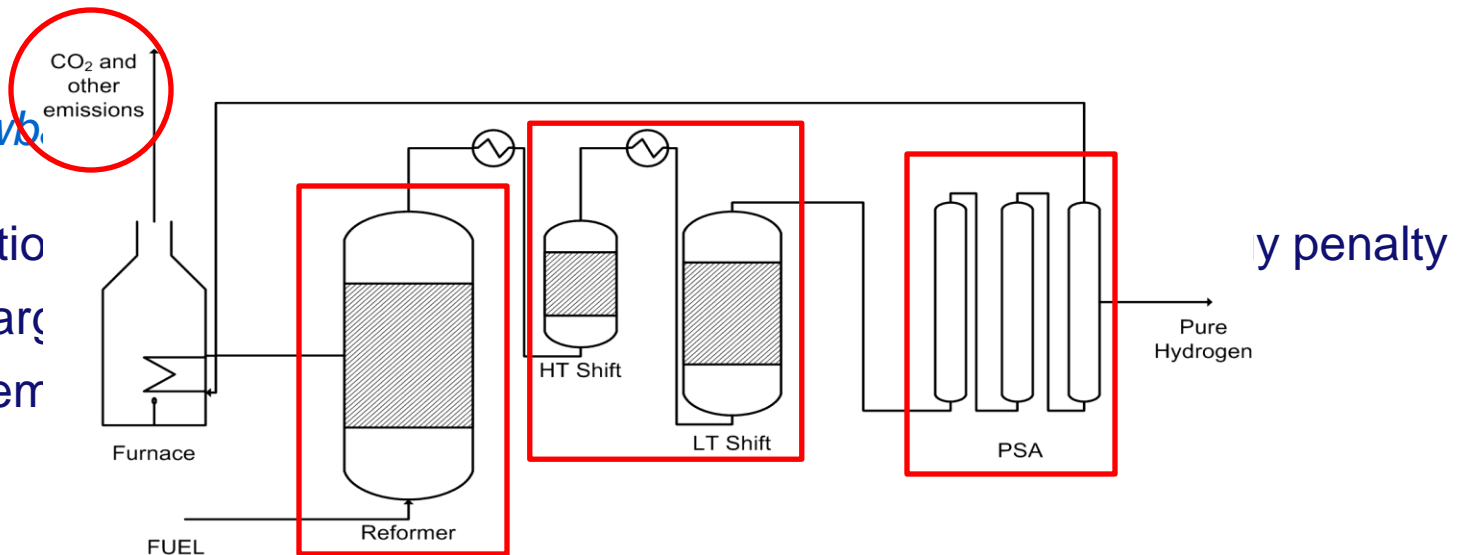


H₂ PRODUCTION...

- Is continuously increasing
- 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 drawbacks

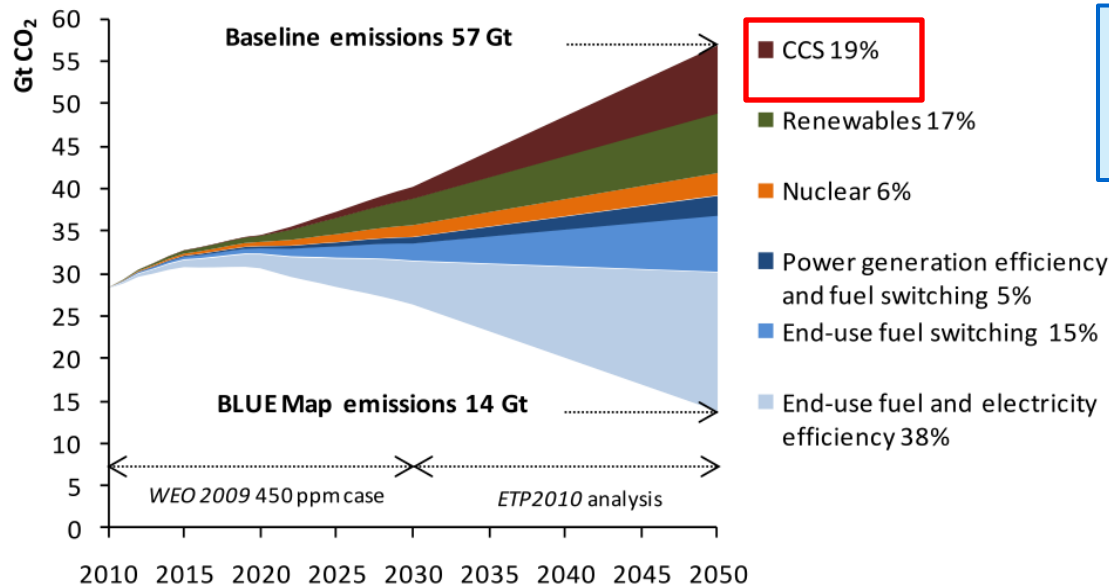
- Reaction
- The large
- CO₂ emissions



THE CO₂ PROBLEM

CO₂ is the main gas affecting the climate change. CO₂ 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.

H₂ PRODUCTION WITH CO₂ CAPTURE

Introduction

Reactor concept

Results

Conclusions

The goal is to develop an efficient process for hydrogen production with integrated CO₂ capture

- Efficient: **reduction** in the number of steps in the steam reforming and the achievement of **auto-thermal** operation.
- CCS system: a **pure CO₂** stream provides an important contribution in the **reduction** of CO₂ emissions and thus climate change

A novel reactor concept might be the solution...

MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR

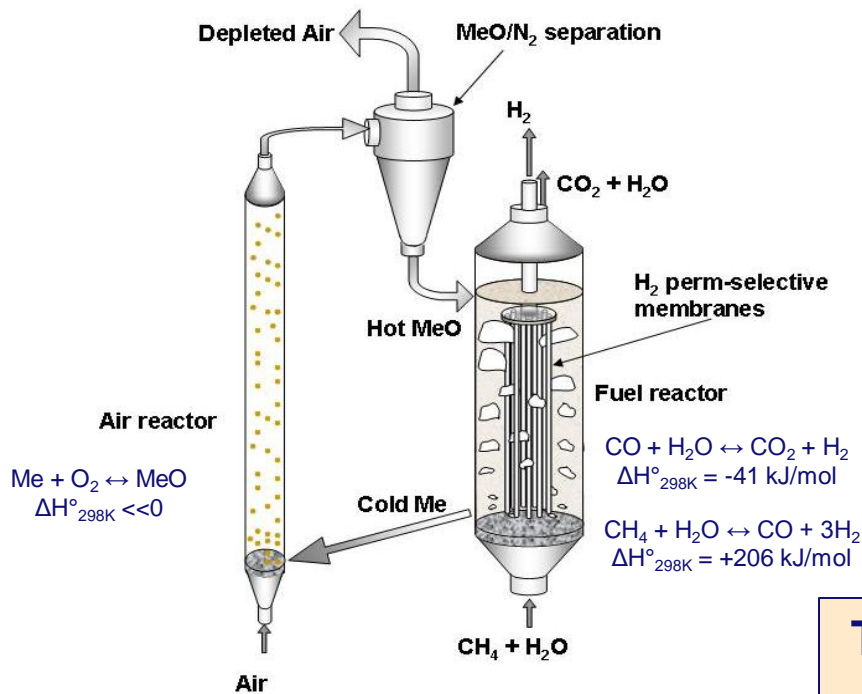
Introduction

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Conclusions

The novel reactor combines the advantages of chemical looping and membranes reactors and solves drawbacks of benchmark technology



- Reforming and water gas-shift reactions are carried out in the same unit.
- Heat is supplied by a warm oxygen carrier coming from the air reactor.
- H₂ extraction through the membranes displaces the thermodynamic equilibrium towards products.

THE SYSTEM PROVIDES A HIGH DEGREE OF PROCESS INTENSIFICATION

VIDI project *ClingCO₂* – project number 12365

THERMODYNAMICS

Introduction

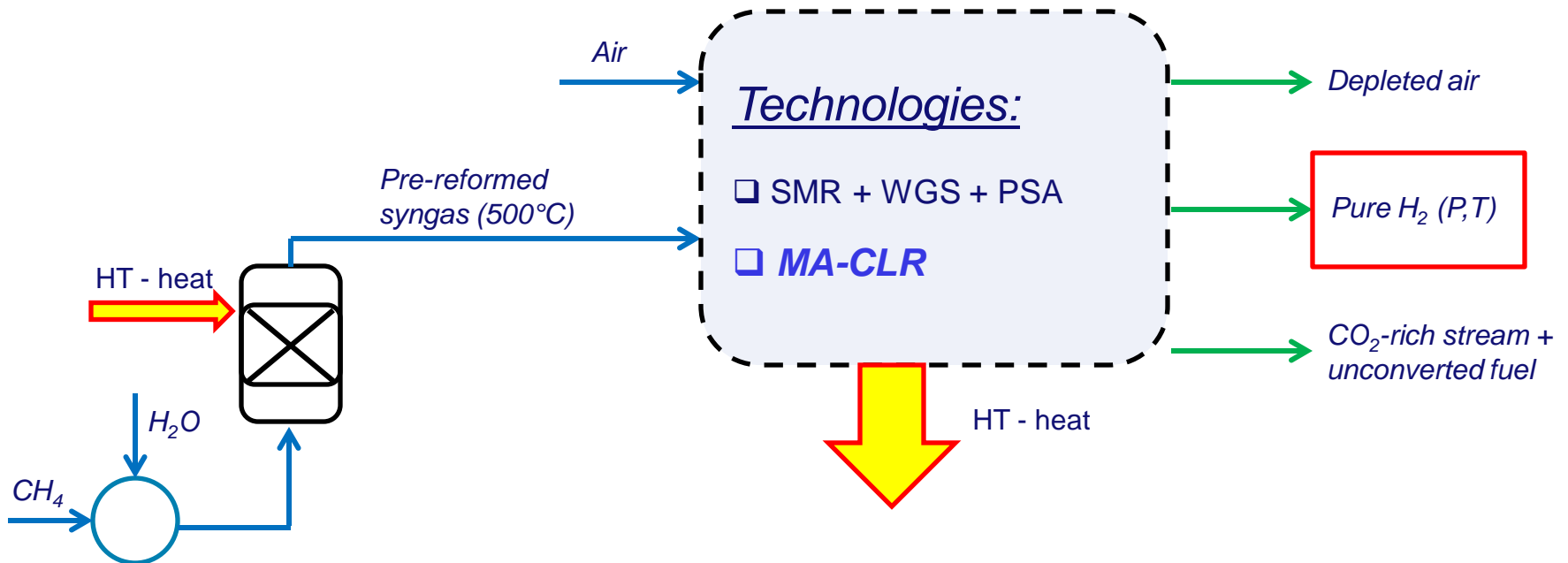
Reactor concept

Results

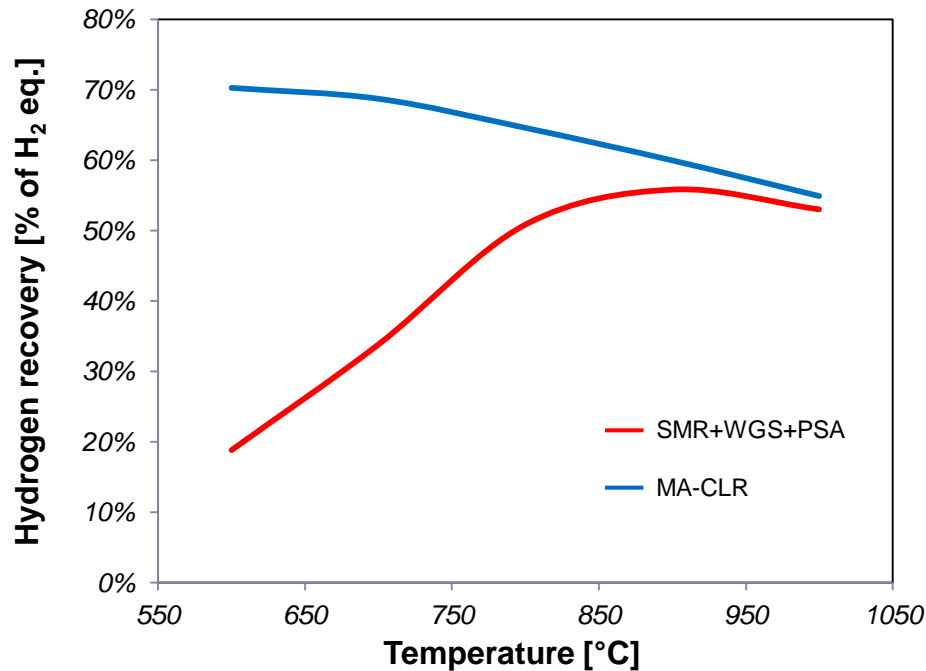
Conclusions

The reactor concept has been analyzed with *Aspen Plus* and the calculations are carried out at *chemical equilibrium*

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



Hydrogen recovery with the different reactor concepts



J.A. Medrano, et al. *Int J. Hydrogen Energy* 39 (2014) 4725-4738

Conclusions

- ❖ SMR+WGS+PSA concept is only interesting at very high temperatures. At low temperatures CH₄ conversion is low
- ❖ Processes with membrane reactors achieve higher hydrogen recoveries.

GENERAL CONCLUSIONS ABOUT THE CONCEPT

Introduction

Reactor concept

Results

Conclusions

- ★ 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 CO₂ capture could be achieved in only **one unit**.

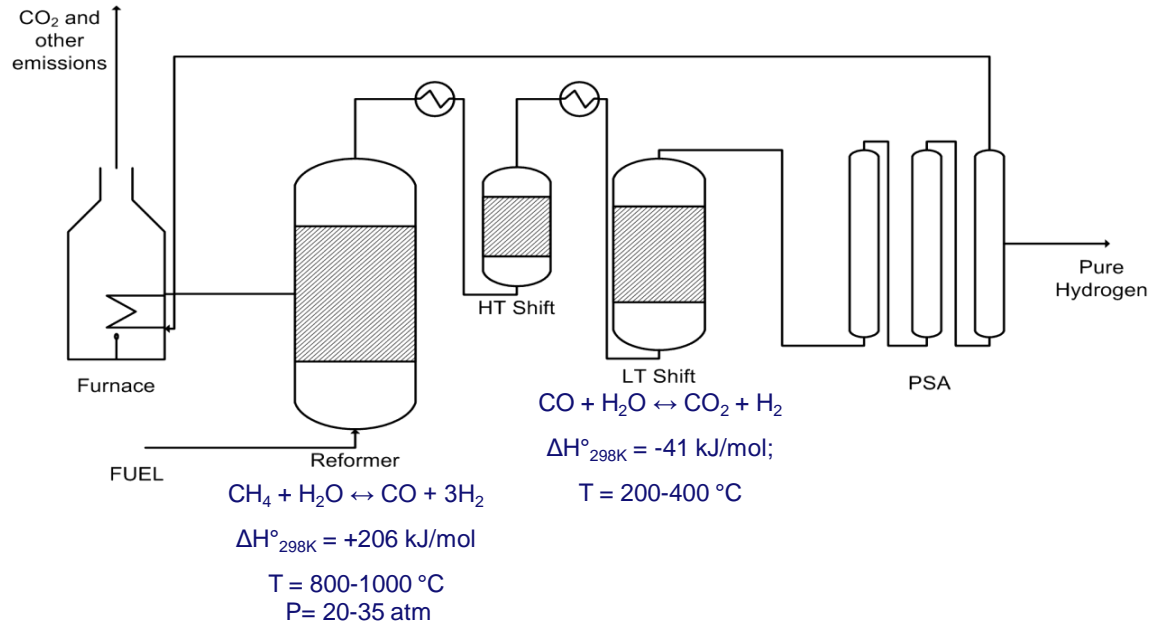
Question:

What happens when we consider **NOT ONLY** the reactor **BUT THE WHOLE PLANT?**

CONVENTIONAL PLANT OF SMR

The scheme presented below does not represent the real plant for H₂ production.

It is much more complicated !!



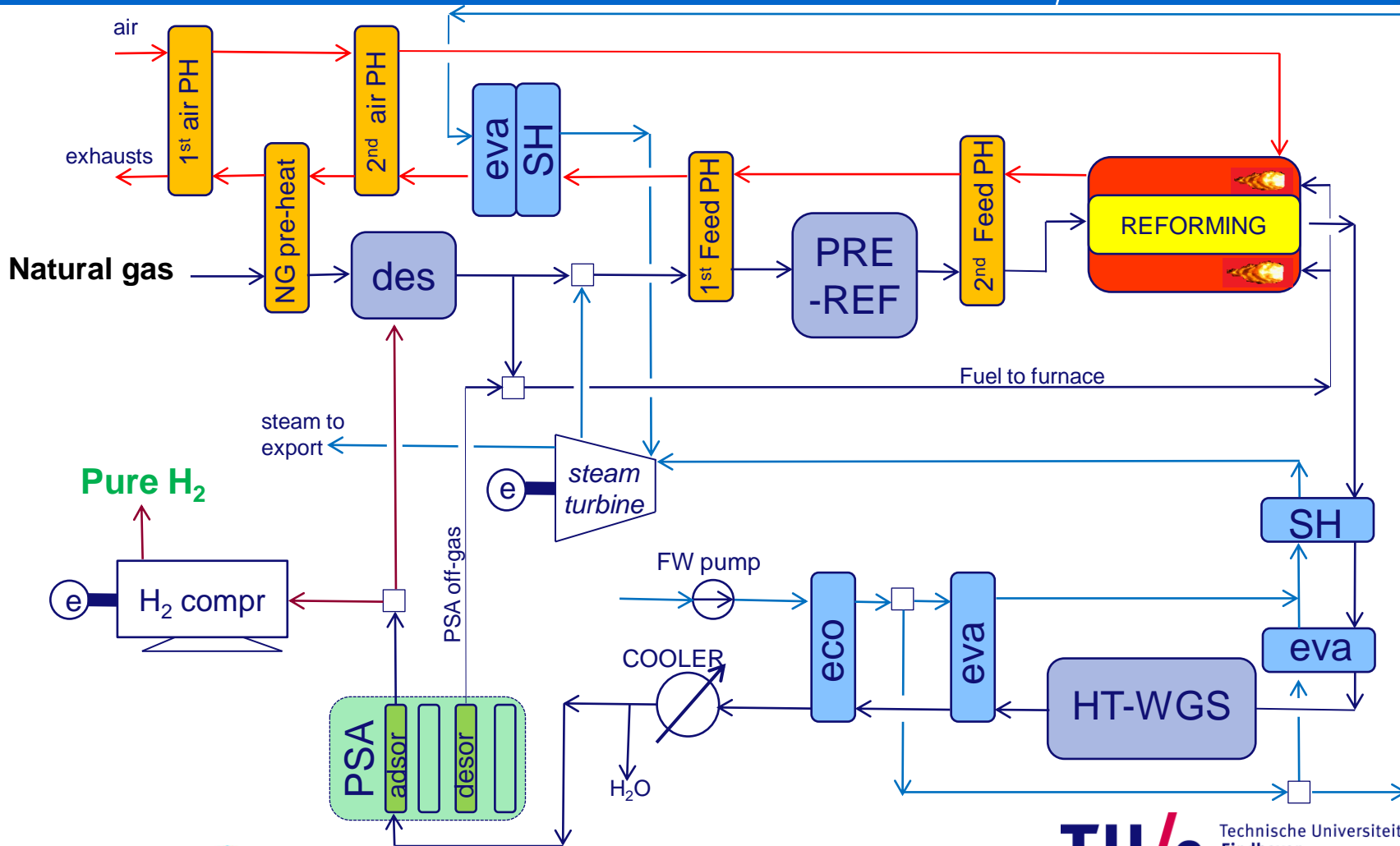
The objective is to compare the efficiency of the benchmark technology for SMR with the whole plant including a MA-CLR concept

CONVENTIONAL PLANT

Introduction
Reactor concept

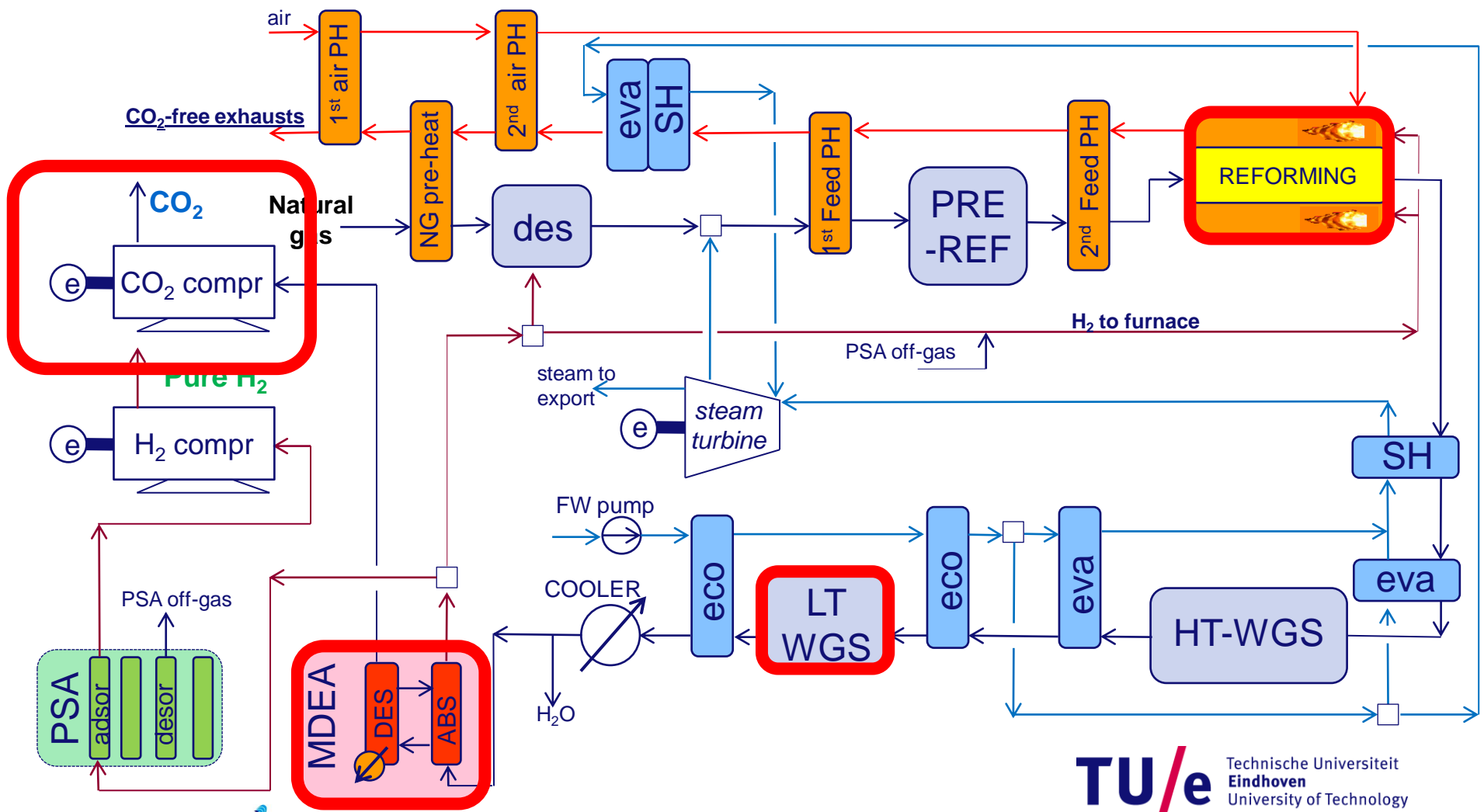
Results

Conclusions



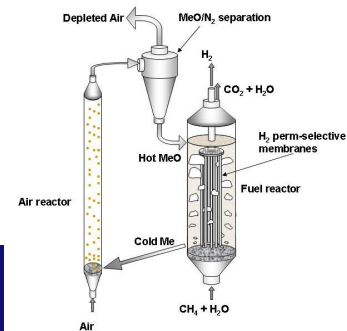
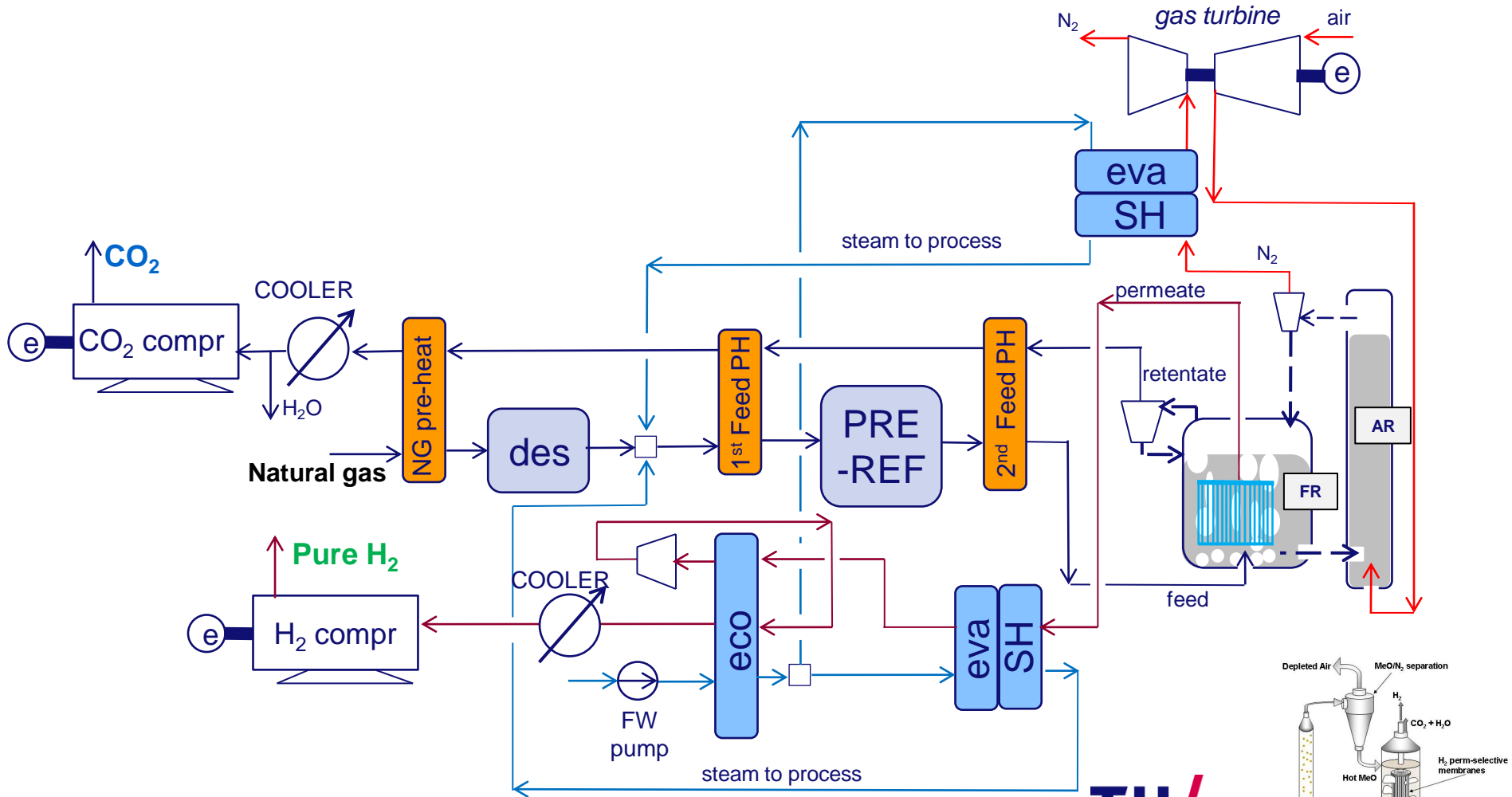
CONVENTIONAL PLANT WITH CO₂ CAPTURE

Introduction
 Reactor concept
Results
 Conclusions



MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING

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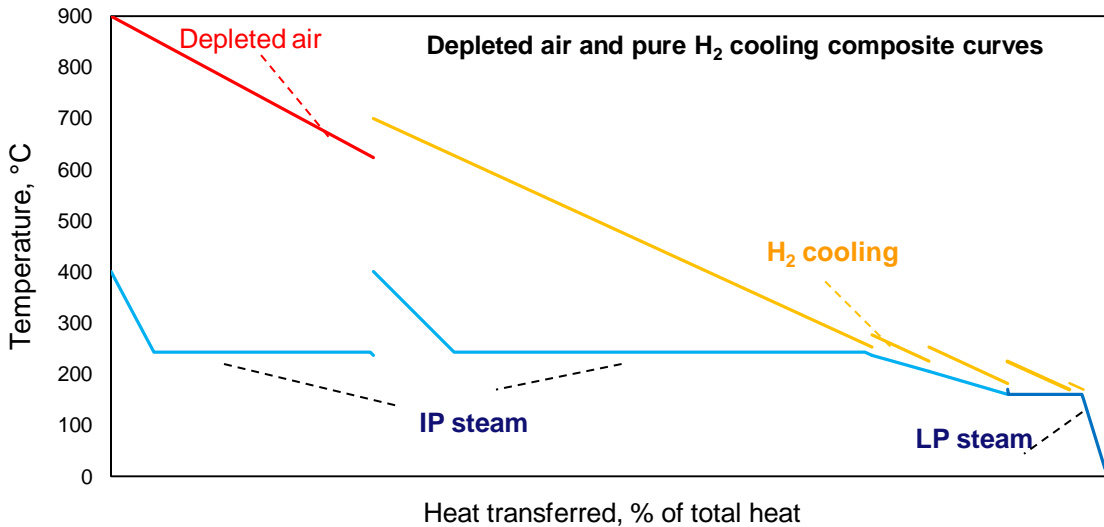
HEAT INTEGRATION MA-CLR

Introduction

Reactor concept

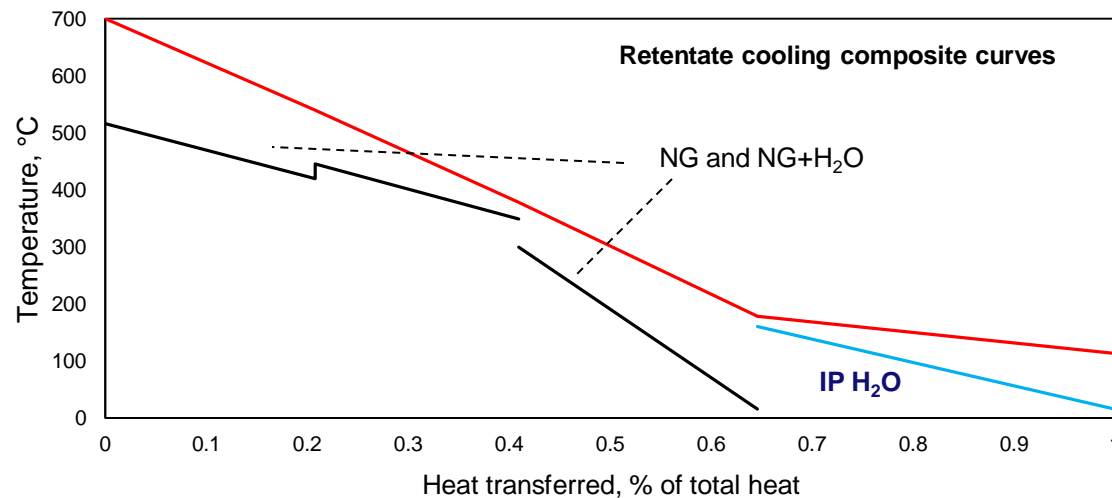
Results

Conclusions



The HT N₂-rich stream is first cooled down to produce the required steam for the process (steam cycle is not present). After that, N₂ is expanded and released to the atmosphere

Most of the H₂O required for the process is produced by cooling the ultra-pure H₂.



The retentate is only CO₂ and H₂O:

- the system can be designed properly
- No additional processes are required for high purity CO₂

MAIN ASSUMPTIONS (1/2)

DATA	Conventional	Conventional	MA-CLR
CO ₂ capture	-	MDEA	H ₂ O condensation
T _{REF} , °C	890	890	600-700
p _{REF} , bar	32.7	32.7	32-50
S/C, mol/mol	2.7	4	1.5-2
T _{WGS} , °C	400	400/270	-
η _{H₂, PSA} , %	89%	89%	-
H ₂ pressure (after separation), bar	29.7	29.7	P _{permeate}
p _{H₂,del} , bar	150	150	150
CO ₂ pressure, bar	-	110	110
Minimum CO ₂ purity, %	-	>95%	>95%

MAIN ASSUMPTIONS (2/2)

DATA	Conventional	Conventional	MA-CLR
CO ₂ capture	-	MDEA	H ₂ O condensation
CHEMICAL LOOPING			
Oxygen Carriers, %vol			20% NiO, 80%MgAl ₂ O ₄
T _{FR} , °C			600-700
ΔT _{AR-FR} , °C			200
H₂ MEMBRANE			
Minimum Δp _{H₂} , bar			0.2
Permeate pressure, bar			1-5
H ₂ selectivity			infinite
Max temperature, °C			700

COMPARISON THERMAL BALANCE

Introduction
Reactor concept

Results

Conclusions

COMPARISON		SMR+WGS+PSA	SMR+WGS+PSA	MA-CLR
CO ₂ capture		-	MDEA	H ₂ O cond
<i>THERMAL BALANCE</i>	UNITS			
NG mass flow rate	kg/s	2.62	2.81	2.62
H ₂ mass flow rate	kg/s	0.75	0.75	0.91
Electricity prod/cons				
Air Compressor/Air Fan	MW _{el}	-0.68	-0.91	-5.73
Gas turbine expander	MW _{el}	-	-	4.07
H ₂ , compressors	MW _{el}	-2.27	-2.28	-9.03
CO ₂ compressors	MW _{el}	0.00	-2.23	-0.60
Steam Turbine	MW _{el}	3.23	3.80	-
LP/HP pumps	MW _{el}	-0.21	-0.29	-0.04
Other Auxiliaries	MW _{el}	-0.05	-0.11	-0.12
Net electric power	MW _{el}	0.03	-2.03	-11.44
Heat export/import				
Steam (160°C, 6 bar)	kg/s	3.94	1.94	0.47
Steam heat content	MW _{th}	8.57	4.29	1.03

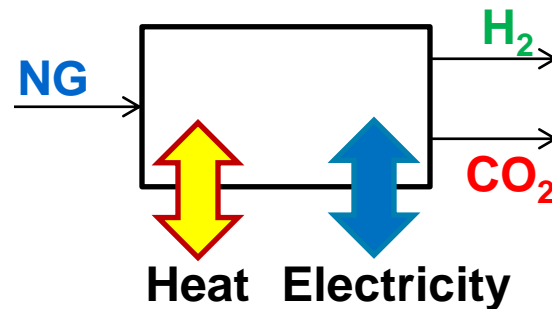
HOW TO COMPARE THE PERFORMANCE?

Introduction

Reactor concept

Results

Conclusions



$$\eta_{el} = 58.3\%$$

$$E_{el} = 351.7 \frac{kg_{CO_2}}{kWh_{el}}$$

$$\eta_{th} = 90\%$$

$$E_{th} = 227.9 \frac{kg_{CO_2}}{kWh_{th}}$$

- **Reforming Efficiency :** $\eta_{H_2} = \frac{\dot{m}_{H_2} * LHV_{H_2}}{\dot{m}_{NG} * LHV_{NG}}$
- **Heat Output:** $Q_{th} = \dot{m}_{steam,imp/exp} * (h_{steam@6bar} - h_{liqsat@6bar})$
- **Equivalent NG mass:** $\dot{m}_{NG,eq} = \dot{m}_{NG} - \frac{Q_{th}}{LHV_{NG} * \eta_{th}} - \frac{W_{el}}{LHV_{NG} * \eta_{el}}$
- **Equivalent H₂ production efficiency :** $\eta_{EQ,H_2} = \frac{\dot{m}_{H_2} * LHV_{H_2}}{\dot{m}_{NG,eq} * LHV_{NG}}$
- **Specific CO₂ emissions:** $E = \frac{\dot{m}_{CO_2,vent}}{\dot{m}_{H_2} * LHV_{H_2}}$
- **Equivalent specific CO₂ emissions per unit of heat and electricity :**

$$E_{eq} = \frac{\dot{m}_{CO_2,vent} - E_{el} * W_{el} - E_{th} * Q_{th}}{\dot{m}_{H_2} * LHV_{H_2}}$$

COMPARISON PERFORMANCE

Introduction
Reactor concept

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<i>COMPARISON</i>		SMR+WGS+PSA	SMR+WGS+PSA	MA-CLR
<i>PERFORMANCE</i>	CO ₂ capture UNITS	-	MDEA	H ₂ O cond.
Ref. efficiency η_{H_2}	MW _{H₂,LHV} /MW _{NG,LHV}	0.74	0.69	0.89
Equivalent NG $m_{NG,eq}$	kg/s	2.42	2.88	3.02
H ₂ yield	kmol _{H₂} /kmol _{eq,CH₄}	2.47	2.29	2.98
Eq. Ref. efficiency $\eta_{H_2,eq}$	MW _{H₂,LHV} /MW _{NGeq,LHV}	0.80	0.67	0.78
CO ₂ specific emissions, E_{CO_2}	kg _{CO₂} /MWh _{NG,LHV}	76.91	12.70	0.00
Eq. CO ₂ spec. em., $E_{CO_2,eq}$	kg _{CO₂} /MWh _{NG,LHV}	70.88	11.88	9.64
CO ₂ avoided, eq	-	-	0.83	0.86

MA-CLR concept converts mostly NG into H₂ → the system is designed to maximize the H₂ flow through the membrane

Due to the high power consumptions (mainly H₂ compressors) of the MA-CLR concept the reforming efficiency drops → $\uparrow p_{permeate}$ and $\uparrow p_{retentate}$

Carbon avoidance is accounted also for the equivalent CO₂ required for the production of electricity (membrane systems)

FINAL CONCLUSIONS

Introduction

Reactor concept

Results

Conclusions

- CO₂ capture in the benchmark technology: the main efficiency decay (14 pp) is represented by the **CO₂ consumptions** and the **less steam export** (higher S/C and AGR reboiler)
- Membrane reactor: **high process intensification** + very low efficiency decay (≈ 1 pp).
 - ❖ High electric consumptions: especially because of the low pressure of the H₂ at the permeate side
 - ❖ Low cost CO₂ separation technology
 - ❖ Possible scale-down to medium-small applications

FINAL CONCLUSIONS

Introduction

Reactor concept

Results

Conclusions

- **Challenge:** In MA-CLR a **HP circulating FBRs** is required for the chemical looping process

TECHNO-ECONOMIC DECISION

- H₂ production: higher membrane area or higher pressure difference across the membrane is necessary. However, the system already produces **between 13-20% more H₂ than conventional plant.**
- **Power consumption is the main issue** of the membrane-assisted plant: optimization is required also according to the economics of the systems. In case of MA-CLR the higher pressure affects the GT selection and operation

ACKNOWLEDGMENTS



Enabling new technology

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*Thank you for your
attention*



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