Chemical looping membrane reformer concept for H2 production and CO2 capture

Enabling new technology

The Membrane-Assisted Chemical Looping Reforming concept as efficient reactor for H_2 production and CO_2 capture: a comparison to benchmark technology.

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NPS14

fundamentally innovative

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Where innovation starts

OUTLINE

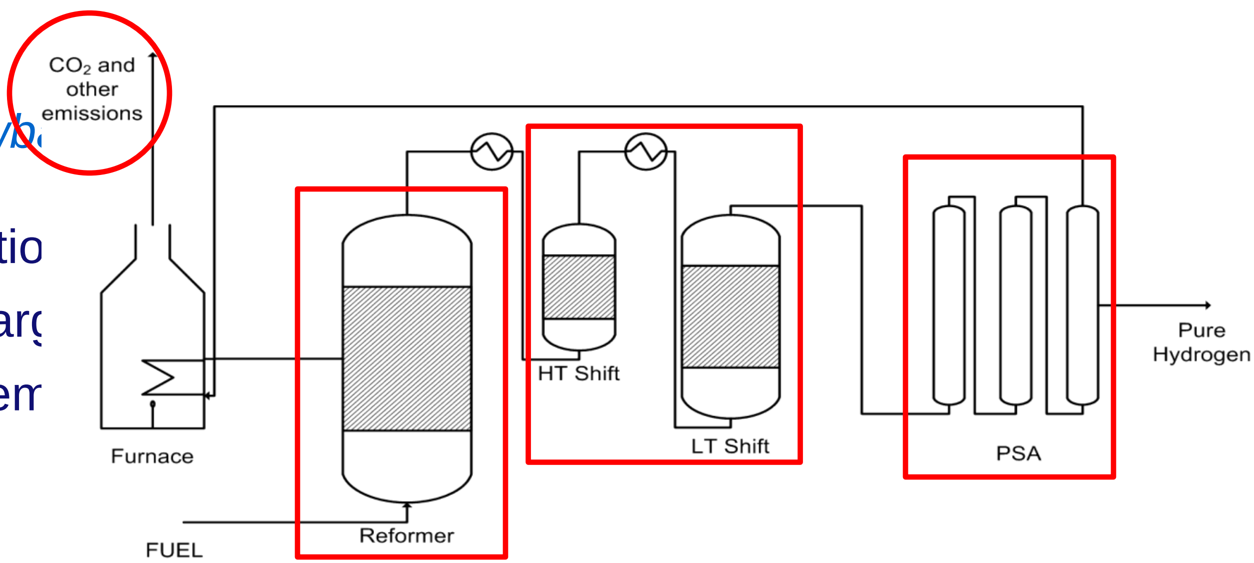
- Introduction
- Description of different systems
- Results
- Conclusions

H_2 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 drawb

→ Reactio … y penalty
→ The larg
→ CO_2 em



$CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H°_{298K} = +206$ 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

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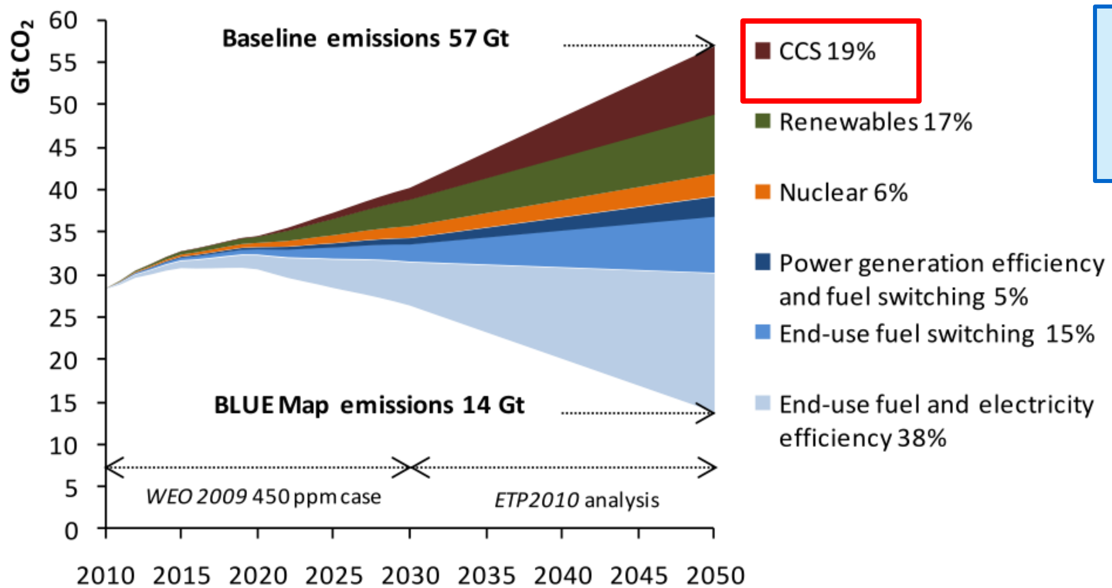
THE CO_2 PROBLEM

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.

H_2 PRODUCTION WITH CO_2 CAPTURE

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

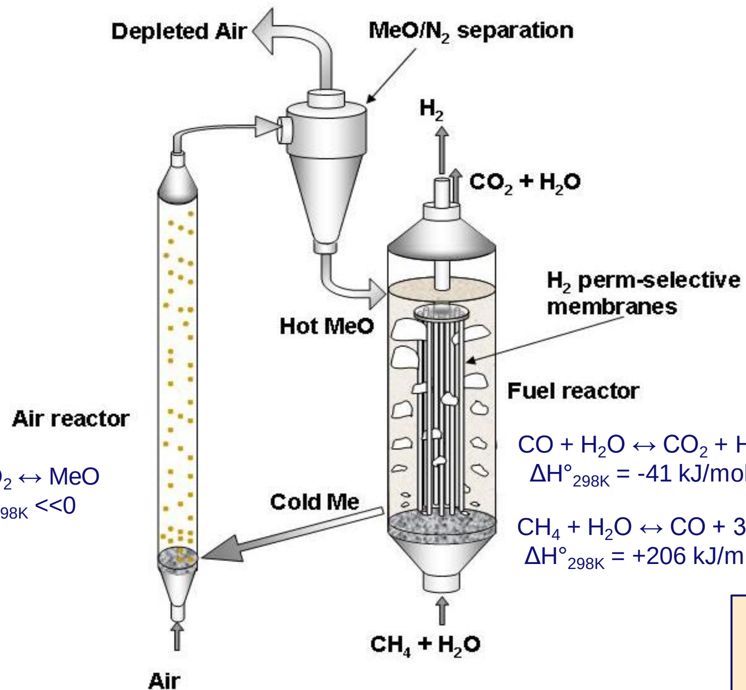
- Efficient: ***reduction*** *in the number of steps in the steam reforming and the achievement of* ***auto-thermal*** *operation.*

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

A novel reactor concept might be the solution…

MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING REACTOR

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



$Me + O_2 \leftrightarrow MeO$
$\Delta H^\circ_{298K} << 0$

$CO + H_2O \leftrightarrow CO_2 + H_2$
$\Delta H^\circ_{298K} = -41$ kJ/mol

$CH_4 + H_2O \leftrightarrow CO + 3H_2$
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VIDI project ClingCO$_2$ – project number 12365

- 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.
- H_2 extraction through the membranes displaces the thermodynamic equilibrium towards products.

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THE SYSTEM PROVIDES A HIGH DEGREE OF PROCESS INTENSIFICATION

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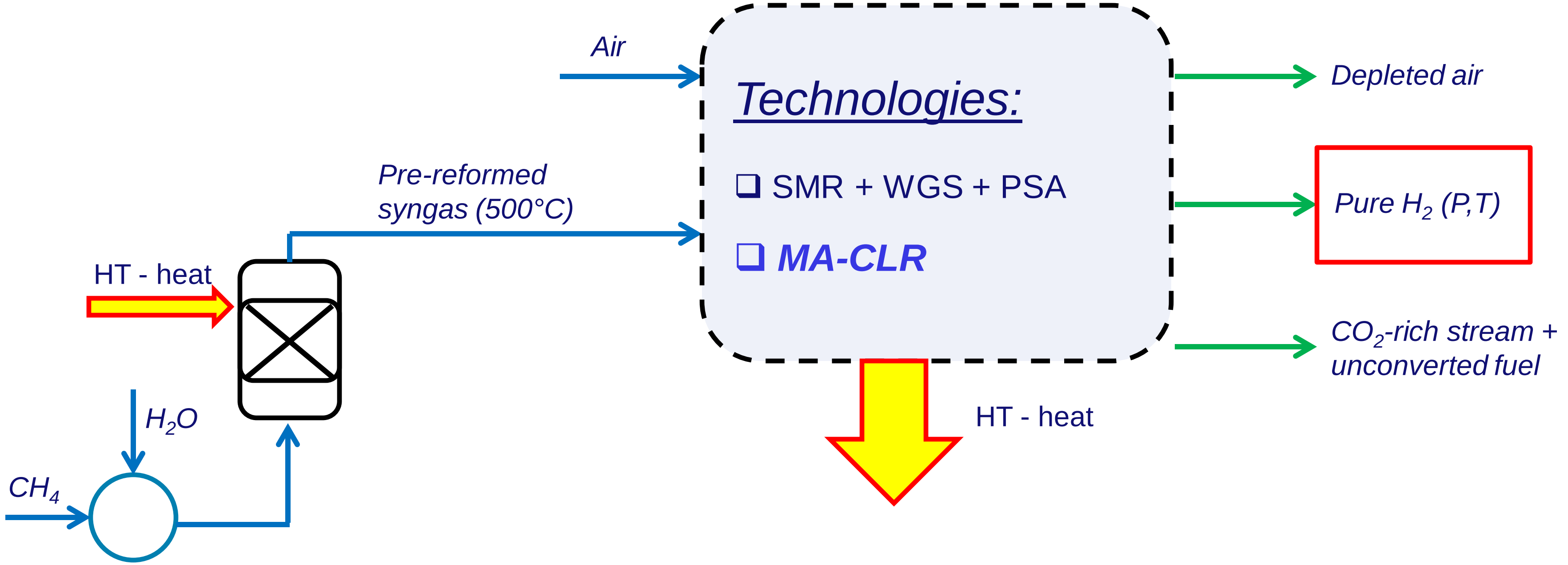
THERMODYNAMICS

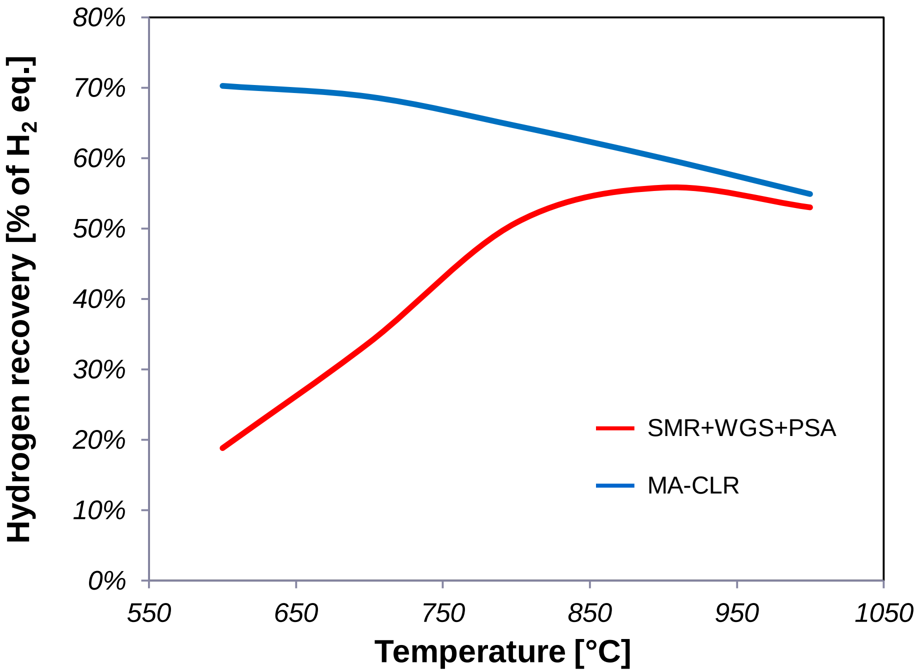
The reactor concept has been analyzed with ***Aspen Plus*** and the calculations are carried out at *chemical equilibrium*

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



THERMODYNAMICS

Hydrogen recovery with the different reactor concepts



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Conclusions

- SMR+WGS+PSA concept is only interesting at very high temperatures. At low temperatures CH_4 conversion is low
- Processes with membrane reactors achieve higher hydrogen recoveries.

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**.

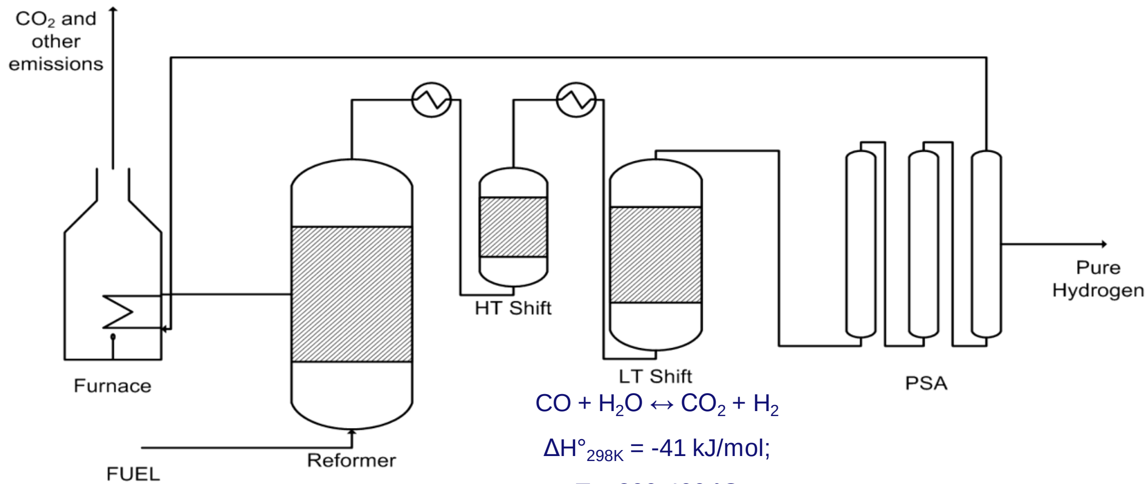
Question:

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 H_2 production.

It is much more complicated !!



$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$\Delta H°_{298K}$ = +206 kJ/mol

T = 800-1000 °C
P= 20-35 atm

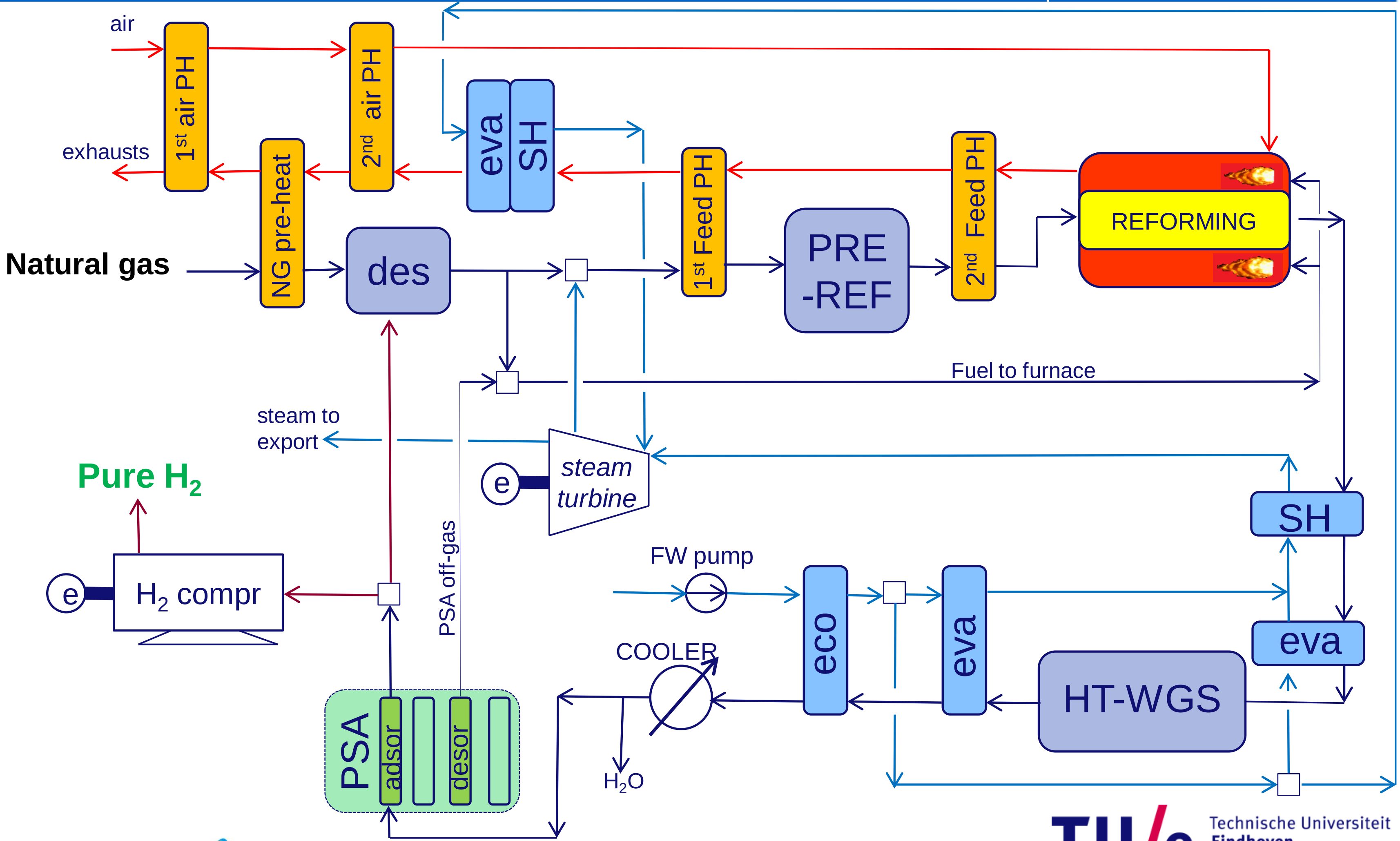
$CO + H_2O \leftrightarrow CO_2 + H_2$

$\Delta H°_{298K}$ = -41 kJ/mol;

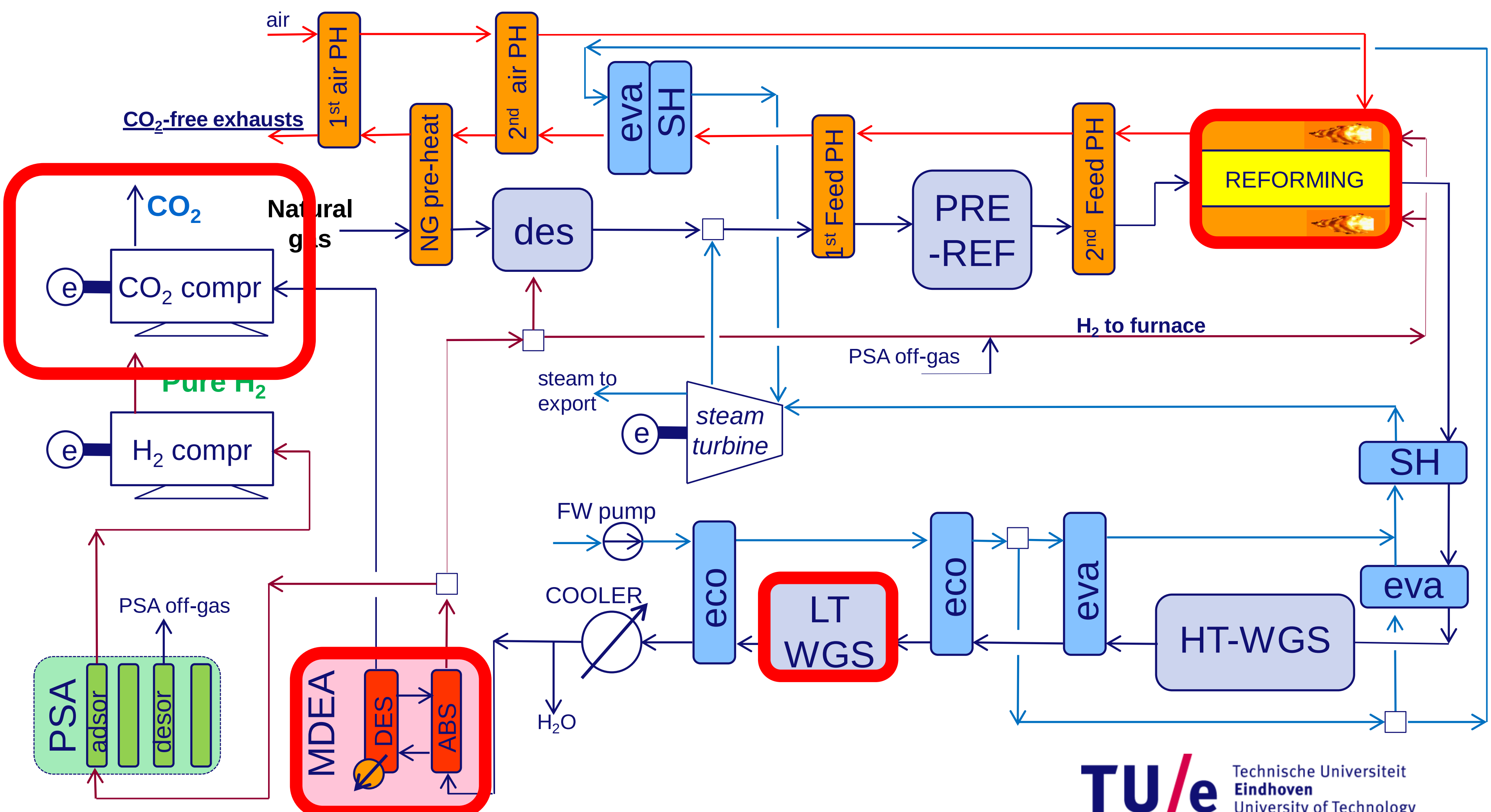
T = 200-400 °C

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

CONVENTIONAL PLANT



CONVENTIONAL PLANT WITH CO_2 CAPTURE



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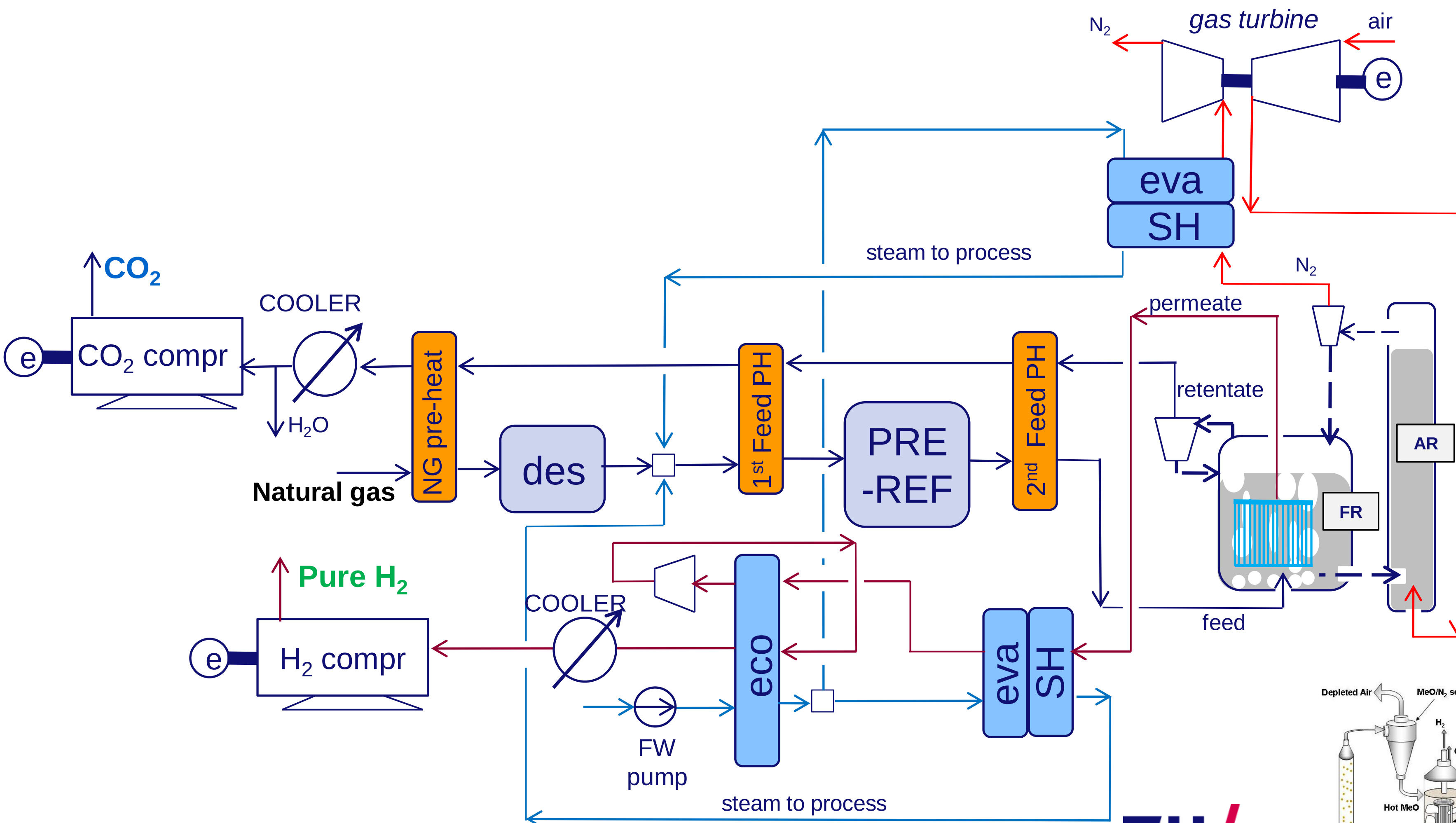
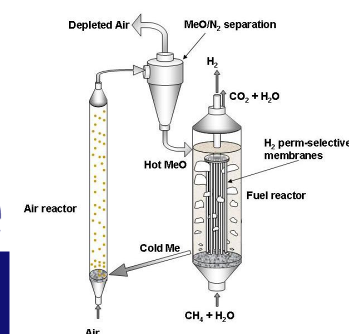
MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING





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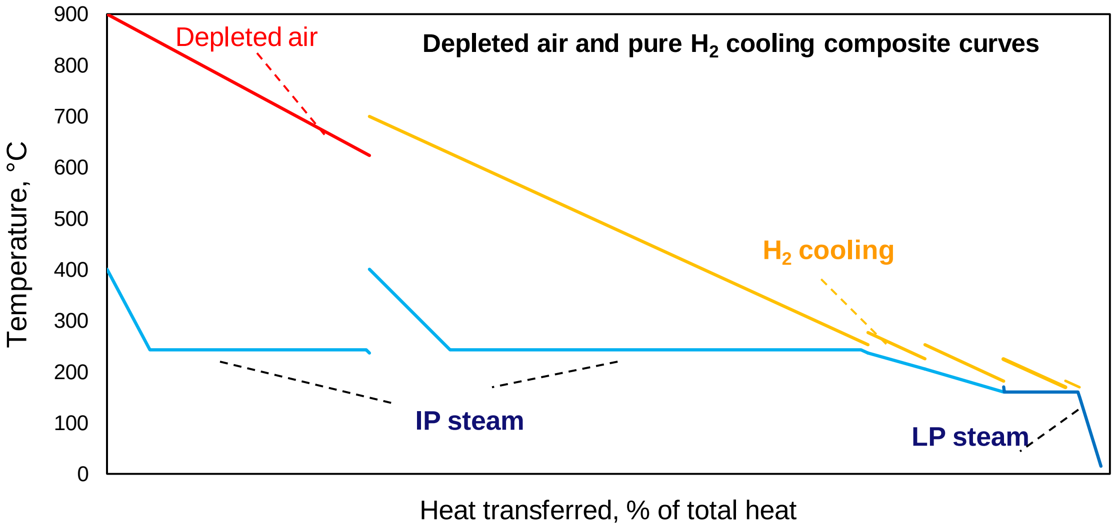
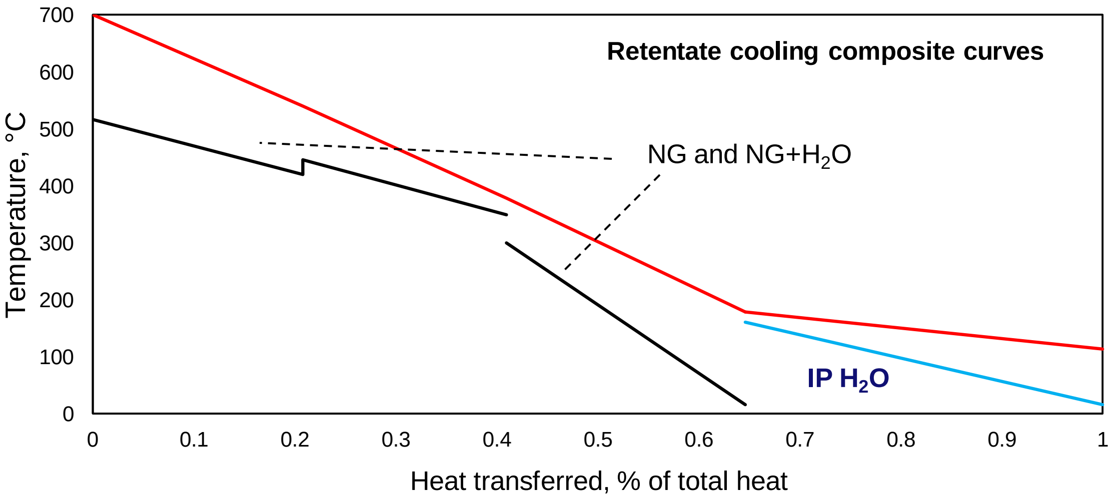
HEAT INTEGRATION MA-CLR





The HT N_2-rich stream is first cooled down to produce the required steam for the process (steam cycle is not present). After that, N_2 is expanded and released to the atmosphere

Most of the H_2O required for the process is produced by cooling the ultra-pure H_2.

The retentate is only CO_2 and H_2O:
- the system can be designed properly
- No additional processes are required for high purity CO_2

MAIN ASSUMPTIONS (1/2)

DATA	Conventional	Conventional	MA-CLR
CO_2 capture	**-**	**MDEA**	**H_2O 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	-
$\eta_{H2, PSA}$, %	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%

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MAIN ASSUMPTIONS (2/2)

DATA	Conventional	Conventional	MA-CLR
CO_2 capture	**-**	**MDEA**	**H_2O condensation**
CHEMICAL LOOPING			
Oxygen Carriers, %vol			20% NiO, 80%$MgAl_2O_4$
T_{FR}, °C			*600-700*
ΔT_{AR-FR}, °C			200
H_2 MEMBRANE			
Minimum Δp_{H2} , bar			0.2
Permeate pressure, bar			*1-5*
H_2 selectivity			infinite
Max temperature, °C			700

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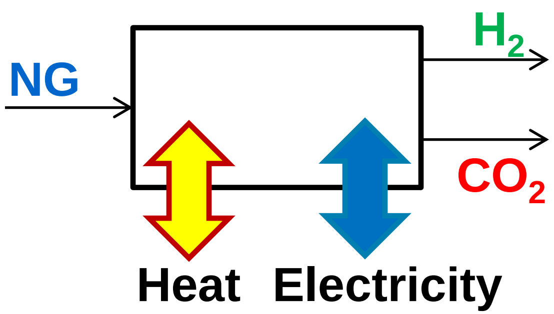
COMPARISON THERMAL BALANCE

COMPARISON		SMR+WGS+PSA	SMR+WGS+PSA	MA-CLR
	CO_2 capture	-	MDEA	H_2O cond
THERMAL BALANCE	*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?



$$\eta_{el} = 58.3\%$$
$$E_{el} = 351.7\frac{kg_{CO2}}{kWhel_{el}}$$

$$\eta_{th} = 90\%$$
$$E_{th} = 227.9\frac{kg_{CO2}}{kWh_{th}}$$

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

$$E_{eq} = \frac{\dot{m}_{CO2,vent} - E_{el} * W_{el} - E_{th} * Q_{th}}{\dot{m}_{H_2} * LHV_{H_2}}$$

COMPARISON PERFORMANCE

COMPARISON		SMR+WGS+PSA	SMR+WGS+PSA	MA-CLR
	CO_2 capture	-	MDEA	H_2O cond.
PERFORMANCE	*UNITS*			
Ref. efficiency η_{H2}	$MW_{H2,LHV}/MW_{NG,LHV}$	0.74	0.69	0.89
Equivalent NG $m_{NG.eq}$	kg/s	2.42	2.88	3.02
H_2 yield	$knmol_{H2}/kmol_{eq,CH4}$	2.47	2.29	2.98
Eq. Ref. efficiency $\eta_{H2,eq}$	$MW_{H2,LHV}/MW_{NGeq,LHV}$	0.80	0.67	0.78
CO_2 specific emissions, E_{CO2}	$kg_{CO2}/MWh_{NG,LHV}$	76.91	12.70	0.00
Eq. CO_2 spec. em., $E_{CO2,eq}$	$kg_{CO2}/MWh_{NG,LHV}$	70.88	11.88	9.64
CO_2 avoided, $_{eq}$	-	-	0.83	0.86

MA-CLR concept converts mostly NG into H_2 → the system is designed to maximize the H_2 flow through the membrane

Due to the high power consumptions (mainly H_2 compressors) of the MA-CLR concept the reforming efficiency drops → ↑$p_{permeate}$ and ↑$p_{retentate}$

Carbon avoidance is accounted also for the equivalent CO_2 required for the production of electricity (membrane systems)

FINAL CONCLUSIONS

- <u>CO_2 capture in the benchmark technology</u>: the main efficiency decay (14 pp) is represented by the **CO_2 consumptions** and the **less steam export** (higher S/C and AGR reboiler)

- <u>Membrane reactor</u>: **high process intensification** + very low efficiency decay (≈ 1 pp).
  - High electric consumptions: especially because of the low pressure of the H_2 at the permeate side
  - Low cost CO_2 separation technology
  - Possible scale-down to medium-small applications

FINAL CONCLUSIONS

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

TECHNO-ECONOMIC DECISION

- H_2 production: higher membrane area or higher pressure difference across the membrane is necessary. However, the system already produces **between 13-20% more H_2 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

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Thank you for your attention

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