Hydrogen Production using Membrane-Assisted Autothermal Reforming Integrated with Chemical Looping Air Separation

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Outline

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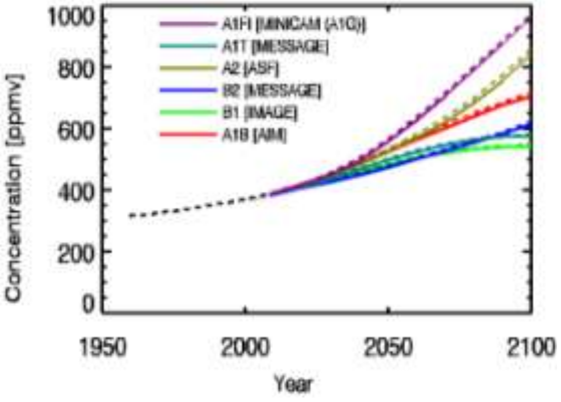
Why CCS is important?

- For global average temperature increases to not exceed pre-industrial levels by more than **2°C**, then global carbon dioxide emissions must be reduced by at least **50 – 85 %** by **2050**.
- This requires the application of all available low-carbon technologies and negative emissions at a scale and rate far greater than current efforts (Paris Agreement: “net-zero GHG emissions in the second half of the century”).
- Next 40 years the world population will increase from **7 to 9 billion people**
- By 2030 the energy demand may increase by **50%**
- Today fossil fuel provides **80%** of energy need. In 2040, **44%** of energy will still need to come from fossil fuels (IEA’s 2˚C scenario).
- CCS can capture **90%** of emissions from power, heavy industry and petrochemicals (50% of global CO_2)

Introduction

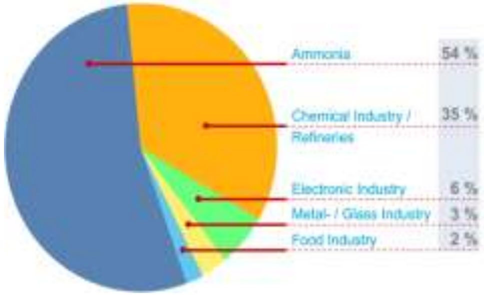
- Increase in fossil fuel consumption – CO_2 concentration rising
- Development of new energy utilization technologies and new energy carriers
- Hydrogen is a clean and green fuel with high energy density
- Future hydrogen demand
  - More strict environmental standards
  - Applications in automobiles and fuel cells
  - Use as an energy storage medium for renewable energy sources

CO_2 concentration



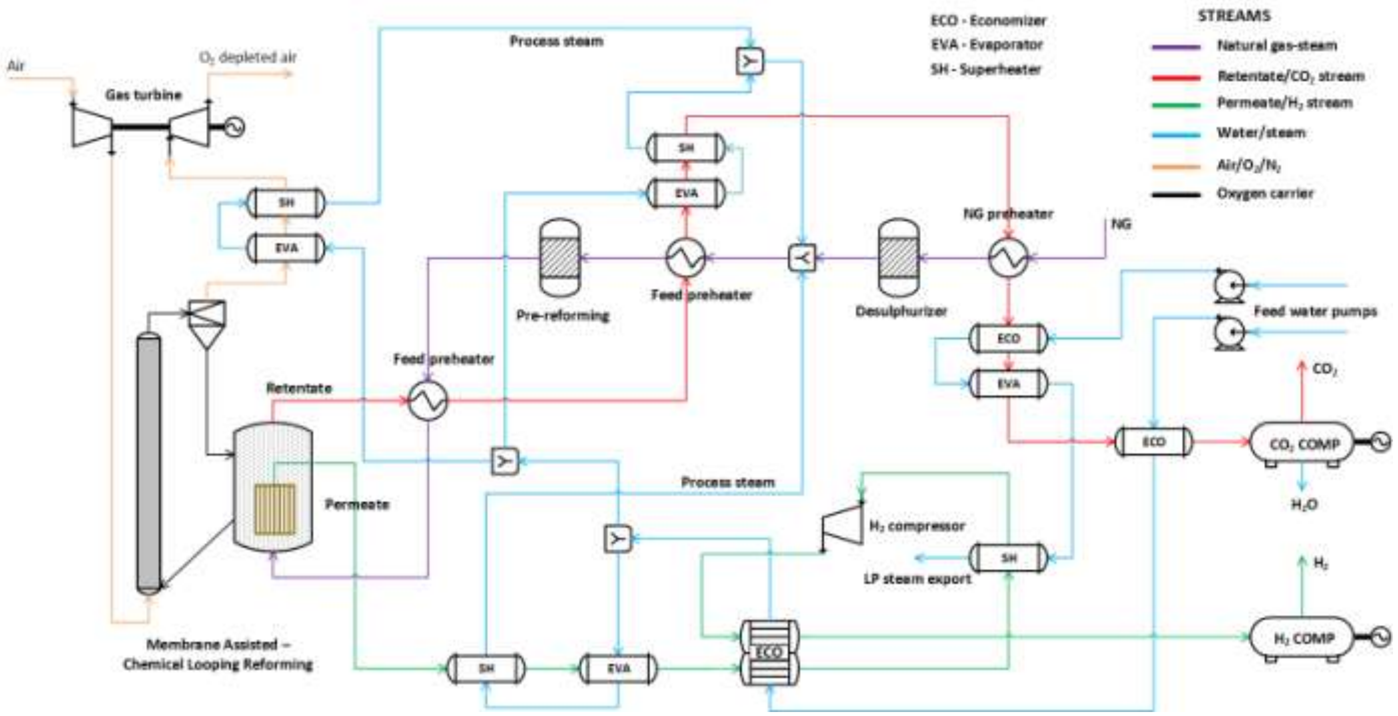
Source: IPCC

Hydrogen Consumers



Source: Linde Engineering

Membrane-assisted chemical looping reforming



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Membrane-assisted autothermal reforming (MA-ATR)

- Challenges with MA-CLR include steady oxygen carrier circulation under high pressures (≥ 50 bar)
- High pressures maximize hydrogen permeation flux and minimize the required membrane surface area
- MA-ATR consists of single reactor without solids circulation
- Oxygen carrier is oxidized above the membranes with high purity oxygen
- Role of oxygen carrier is to ensure complete conversion of fuel that slips past the membranes
- Transport the produced heat down to the membrane region to drive the reforming reaction
- Gentle bubbling fluidized bed reactor in MA-ATR will have much lower particle attrition and elutriation

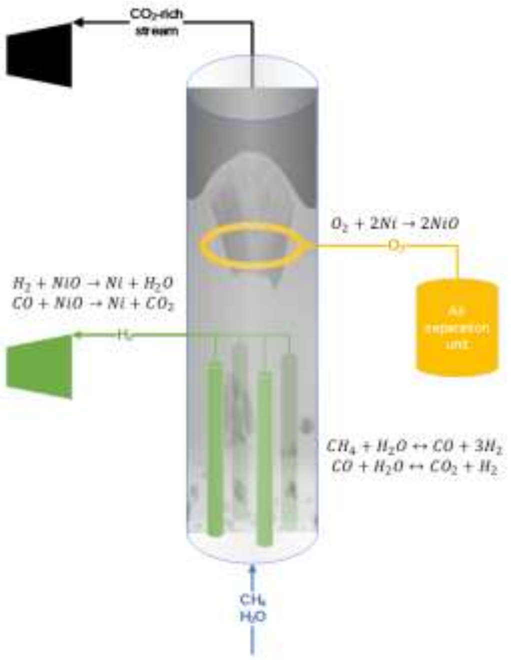
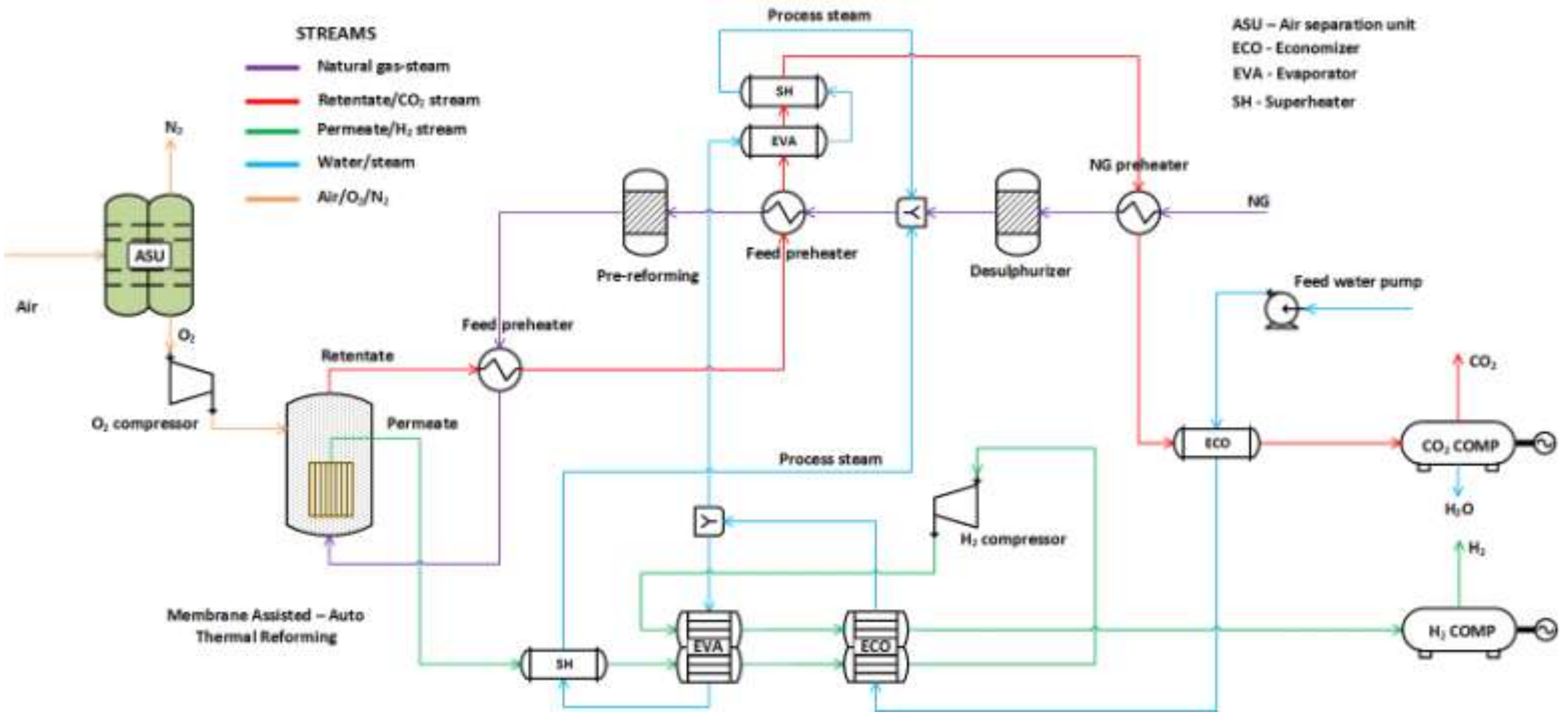


Illustration of MA-ATR concept

Membrane-assisted autothermal reforming with air separation unit



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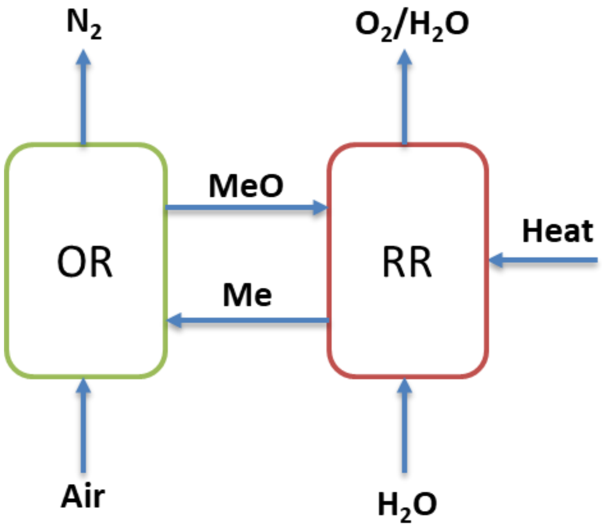
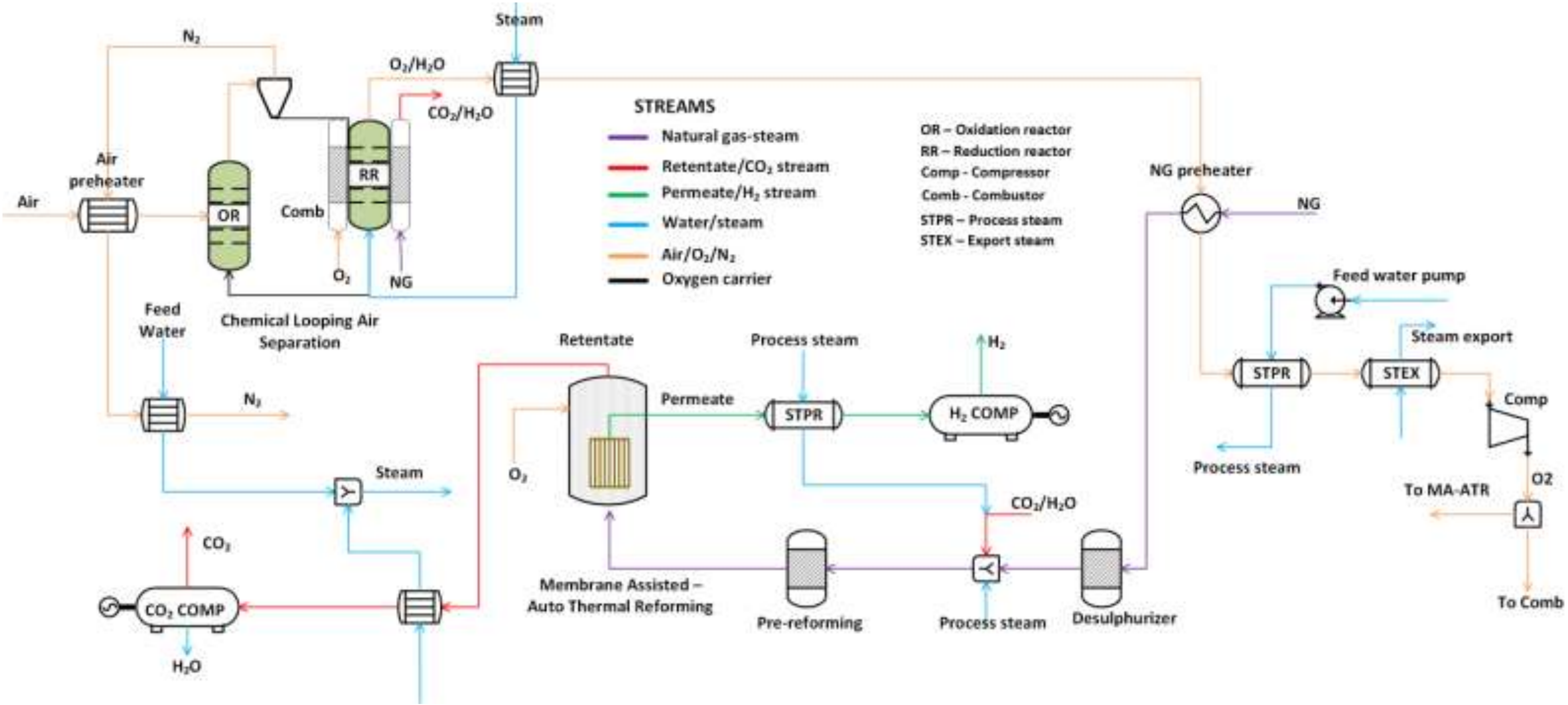
Chemical looping air separation (CLAS)

- Air separation method relies on chemical looping principle similar to chemical looping combustion
- Two step redox reactions by circulating metal oxide particles between two connected reactors
- CLAS incorporates concept of oxygen decoupling into a two-step redox reaction mechanism
- Oxygen decoupling occurs in the presence of steam
- Product oxygen can be compressed for storage or directly fed to another process



Schematic of chemical looping air separation

MA-ATR integrated with CLAS



Process modeling assumptions

- A simple 0D mass and energy balance model was used to describe the reactor behaviour for coupling to the process simulations
- Steam-to-carbon ratio of 1.75 is assumed
- Reactor is operated at 50 bar while the H_2 is permeated at 2 bar
- Reforming occurs at a temperature of 700 °C
- Oxygen purity – 96%
- Final H_2 conditions – 30 °C and 150 bar
- Final CO_2 conditions - 30 °C and 110 bar

Plant performance

H_2 production efficiency

$$\eta_{H_2} = \frac{\dot{m}_{H_2} LHV_{H_2}}{\dot{m}_{NG} LHV_{NG}}$$

Equivalent H_2 production efficiency

$$\eta_{H_2,eq} = \frac{\dot{m}_{H_2} LHV_{H_2}}{\dot{m}_{NG,eq} LHV_{NG}}$$

$$\dot{m}_{NG,eq} = \dot{m}_{NG} - \frac{\dot{m}_{steam} h_{evap}}{\eta_{th} LHV_{NG}} - \frac{W_{el}}{\eta_{el} LHV_{NG}}$$

NG flow rate	kg/s	3.55
H_2 mass flow rate	kg/s	1.31
O_2 compression	MW_{el}	-4.96
H_2 compression	MW_{el}	-10.83
CO_2 compression	MW_{el}	-0.30
Pumps	MW_{el}	-0.39
Net electric power	MW_{el}	-16.48
Steam export (160°C, 3bar)	kg/s	2.30
H_2 production efficiency, η_{H2}	$H_{2,LHV}/NG_{LHV}$	0.95
Equivalent NG input, $m_{NG,eq}$	kg/s	5.24
Eq. H_2 production efficiency, $\eta_{H2,eq}$	$H_{2,LHV}/NG_{eq, LHV}$	0.644
Equivalent CO_2 avoided	%	82.71

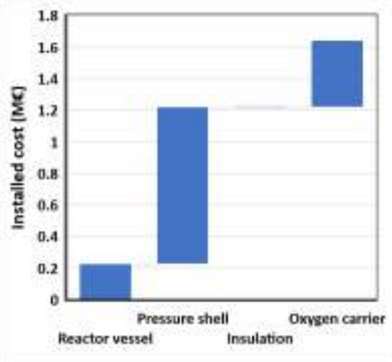
Economic assumptions

- Installed cost of the components from Aspen are considered as bare erected costs
- All bare module costs are adjusted for inflation to the year 2019 by a CEPCI factor
- Reactor costs are estimated by assuming that the reactor is composed of two process vessels: a thick outer pressure shell and a inner reactor vessel separated by an insulation material
- Membrane costs are taken as $1000 /ft^2
- Cost of NiO is $15 /kg and Mn_2O_3 is $2 /kg
- Natural gas price considered is € 9.15 /GJ
- Electricity price considered is € 76.36 /MWh
- Discount rate of 10% is assumed
- Capacity of 85% with lifetime of 25 years
- CO_2 T&S = €11 /ton-CO_2

Capital cost estimation

Bare erected cost	Installed cost
EPC contractor services	10% of BEC
Engineering, procurement and construction cost	
Process contingency	40% of BEC
Project contingency	15% of (BEC+EPCC+PC)
Total plant cost	BEC + EPCC + Contingencies
Owners cost	20% of TPC
Total overnight cost	TPC + Owners cost
Total capital requirement	1.14*TOC

Economic assessment



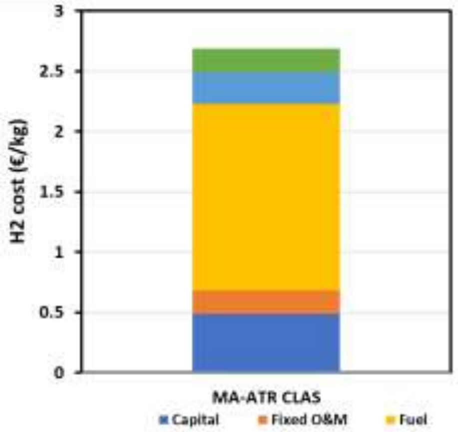
MA-ATR reactor cost

Capital cost breakdown (M€)

Air reactor	0.94
Reduction reactor	0.98
Combustor	1.13
Desulphurizer	0.49
Pre-reformer	4.86
Pumps	0.71
H2 compressor	11.11
CO2 compressor	1.82
CO2 Flash	0.21
Air/O2 compressor	4.14
Heat exchangers	17.63
Coolers	1.17
Cooling tower	0.79
Reactor	2.55
Membrane	15.43
Contingency and fees	11.51
Bare module cost	63.95
Total capital requirement	154.93

Overall costs breakdown

Fixed costs		
Capital	17.1	M€/year
O&M	7	M€/year
Labour	1.5	M€/year
Variable costs		
Oxygen carrier	0.08	M€/year
OR OC cost	0.02	M€/year
RR OC cost	0.02	M€/year
Membranes	1.54	M€/year
Cooling water	0.18	M€/year
Process water	0.14	M€/year
Natural gas	54.22	M€/year
Steam export	-0.11	M€/year
Electricity	9.92	M€/year
CO2 T&S	3.73	M€/year
H2 production	35.12	Mkg/year
Total annual cost	94.73	M€/year
H2 cost	2.7	€/kg

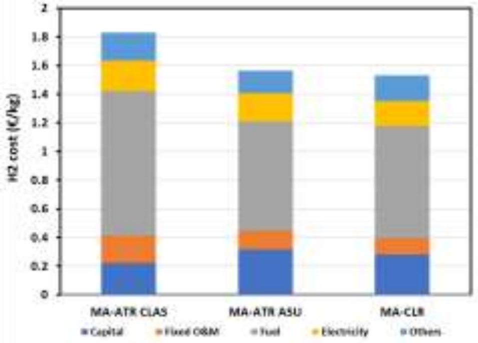


H_2 cost breakdown

H_2 cost comparison

	Eq. H_2 efficiency (%)	Cost (€/kg)
**Steam methane reforming	81	2.58
**Steam methane reforming with MDEA	67	3.37
**Fluidized bed membrane reactor	76	2.63
**Membrane assisted chemical looping reforming	82	2.29
**Membrane assisted autothermal reforming with CLAS	64.4	2.7

***Spallina, V., Pandolfo, D., Battistella, A., Romano, M. C., Annaland, M. V. S., & Gallucci, F. (2016). Techno-economic assessment of membrane assisted fluidized bed reactors for pure H2 production with CO2 capture. Energy conversion and management, 120, 257-273.*



Assumptions: Fuel - €6 /GJ; Electricity - €60 /MWh; Capacity factor = 0.9

Cost components

	MA-ATR (ASU)	MA-ATR (CLAS)
Power consumption (MW_{el})	11.31	16.48
Major CAPEX component (M€)	ASU – 17.5	HX – 17.63
Annualized capital cost (M€/year)	8.64	8.3
Natural gas (M€/year)	20.77	37.65
Total annual cost (M€/year)	42.59	68.05
Hydrogen production (Mkg/year)	27.23	37.19

**Cloete, S., Khan, M. N., & Amini, S. (2019). Economic assessment of membrane-assisted autothermal reforming for cost effective hydrogen production with CO2 capture. International Journal of Hydrogen Energy, 44(7), 3492-3510.*

Conclusions

- A techno-economic assessment of a membrane-assisted autothermal reforming plant integrated with chemical looping air separation is conducted
- H_2 production efficiency of 95% is observed
- Equivalent H_2 production efficiency of 64.4% is observed
- Cost of H_2 production is estimated as €2.7 /kg which is higher than steam-methane reforming without capture (€2.58 /kg)
- Compared to MA-CLR and MA-ATR ASU, the cost of H_2 production is 16.3% and 14.5% more, respectively
- Future work should focus on testing the long-term performance and reliability of membranes under industrially relevant pressures and temperatures
- Actual and operating partial pressures of oxygen and the operation temperature are the major controlling parameters
- Heat management in CLAS is the main challenge

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Thank you