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Chemical Looping Reforming with Packed Bed Reactor for Bulk Chemical Production with near-zero CO_2 emissions

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Summary

- About me
- Chemical Looping in brief
- The Concept
- Testing and Modelling
- Techno-Economic Assessment
- Conclusions
- Future works @University of Manchester

About me

- Born in Sicily the 18/04/1983 and grow up in Geraci Siculo (Pa) until the end of the High School and then moved to Milan
- July 2005: **BSc in Energy Engineering** – Politecnico di Milano
- Dec 2008: **MSc in Energy Engineering** – Politecnico di Milano
- Mar. 2013: **PhD (with honour) in Energy and Nuclear Science and Technology** – Politecnico di Milano: *mid-long term solutions for coal power plant with CCS*
- Apr. 2013 – Apr. 2017: **Postdoc position at the TU Eindhoven**: *Chemical looping technologies & Membrane reactor*
- May 2017 – Nov. 2017 : **Postdoc position at Tecnalia (Spain)**: *Membrane reactor design and scale-up*
- *From Jan 2018* **Lecturer in Chemical Engineering at the University of Manchester**

About me

Research Interests

- Gas-Solid reactions: chemical looping, sorption technologies
- Membrane and membrane reactors
- High temperature fuel cells
- Low-carbon technologies applied to industry (Refineries, Iron&Steel, bulk Chemicals, etc..)

Research Approach

- From particle to complete process modelling
- Material and Reactor testing

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Chemical Looping in Brief

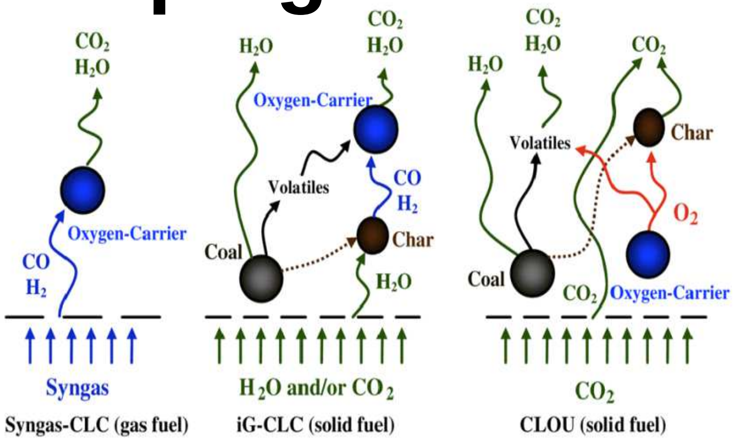
$$MeO_{\alpha-1} + \frac{1}{2}O_2 \rightarrow MeO_{\alpha}$$

$$MeO_{\alpha} + H_2 \rightarrow MeO_{\alpha-1} + H_2O$$

$$MeO_{\alpha} + CO \rightarrow MeO_{\alpha-1} + CO_2$$

$$\left(2x+\frac{y}{2}\right)MeO_{\alpha} + C_xH_y \rightarrow \left(2x+\frac{y}{2}\right)MeO_{\alpha-1} + xCO_2 + \frac{y}{2}H_2O$$

$\Delta H^0_{ox} << 0$ (always exothermic)
$\Delta H^0_{red} \approx$variable (depends on the fuel)



- Very high selectivity toward CO_2 and H_2O (CLC)
- High oxygen capacity
- High stability under repeated cycles (support use):
  - thermal
  - chemical
  - mechanical

- Low Toxicity
- High melting point
- Low Cost
- High resistance to contaminants
- Attrition resistance (in case of FBR application)
- Catalytic properties (WGS/SMR)

Spallina, V., Hamers, H.P., Gallucci, F., Sint Annaland, Chemical Looping Combustion for Power Production, Process intensification for sustainable energy conversion. Chichester: Wiley, 416 pp, 2015.

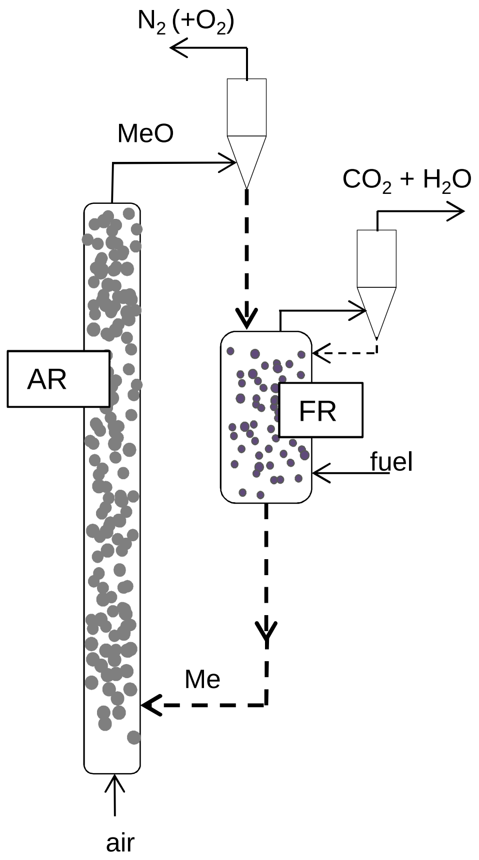
Chemical Looping in Brief

material type	support type	Oxygen Carrier pair considered	Melting points °C	Oxygen ratio, R_0 (not considering support)	Reaction enthalpy at 1000°C** (kJ/mol reactant gas					Metal cost ($/ton metal)
					CO	H_2	CH_4	C	O_2	
Ni based	α-Al_2O_3,γ-Al_2O_3, Al_2O_3, $NiAl_2O_4$, $NiAl_2O_4$-MgO, $MgAl_2O_4$, Bentonite, ZrO_2-MgO	NiO/Ni	1455°C	0.214	-47	-15	134	75	-468	15'000
Cu based	α-Al_2O_3,γ-Al_2O, $MgAl_2O_4$	CuO/Cu	1085°C	0.201	-134	-101	-212	-99	-296	7'000
Cu based	Al_2O_3,γ-Al_2O, Sepiolite, $MgAl_2O_4$, Bentonite, ZrO_2, TiO_2, SiO_2	CuO/Cu_2O	1235°C	0.112	-151	-119	-283	-135	-260	7'000
Fe based	Al_2O_3, Bentonite	Fe_2O_3/Fe_3O_4	1565°C	0.033	-42	-10	154	84	-479	200
Ilmenite ($FeTiO_3$)	-	Fe_2O_3/FeO	1565°C	0.100	-4.7	27.5	304	158	-554	<200
Mn based	ZrO_2-MgO	Mn_2O_3/MnO	1347°C	0.101	-102	-70	-85	-36	-359	<200
Mn based	SiO_2	Mn_2O_3/Mn_3O_4	1347°C	0.034	-192	-160	-446	-217	-179	<200

Spallina, V., Hamers, H.P., Gallucci, F., Sint Annaland, Chemical Looping Combustion for Power Production, Process intensification for sustainable energy conversion. Chichester: Wiley, 416 pp, 2015.

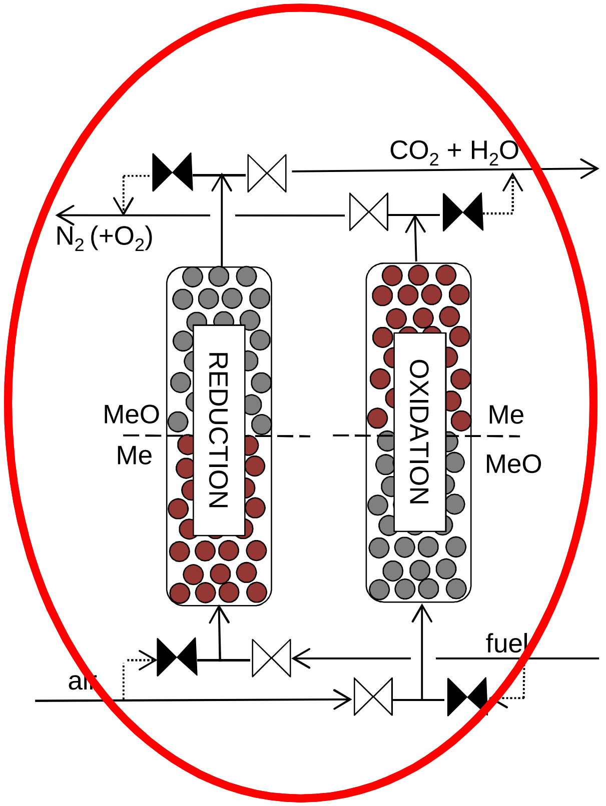
Chemical Looping in Brief

Fluidized Bed



FBR	*comparison*	**PBR**
😐	Fuel Flexibility	☹
☺	Oxygen Carriers Design	😐
😐	Operation in a plant	☹
☹	High pressure operation	☺
😐	Gas/solid separation	☺
☹	Solid circulation	☺
☺	System complexity (valves, piping, cyclones, loop seal etc..)	☹

Packed Bed



Chemical Looping in PBR

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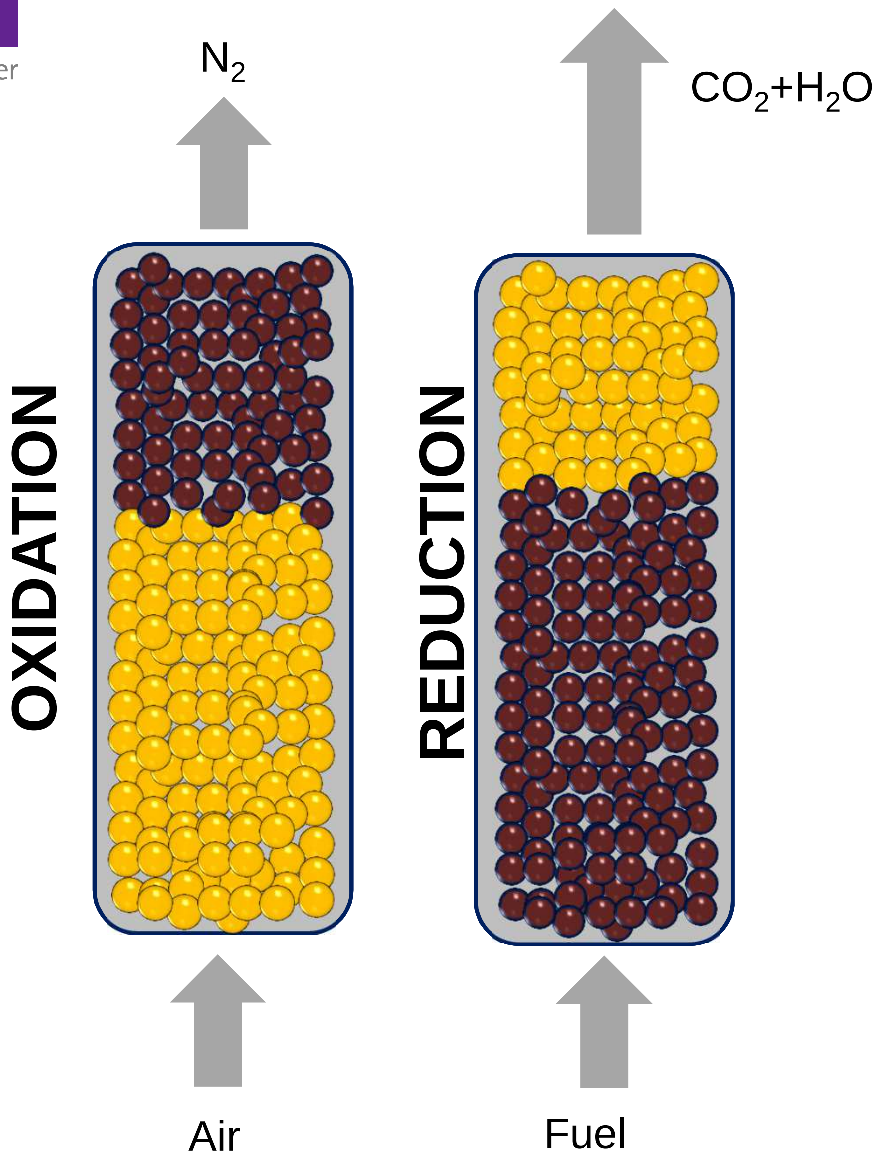
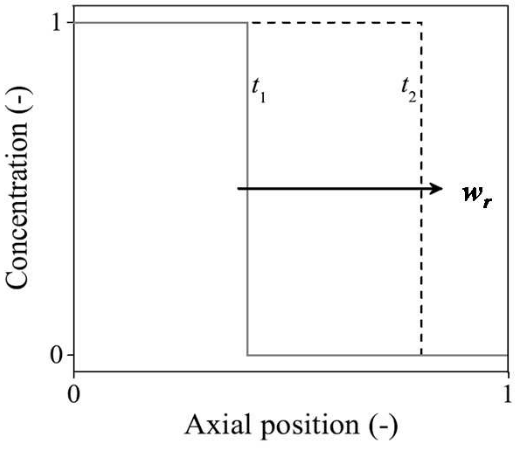
$\Delta H^0_{ox} << 0$
always highly
exothermic

$\Delta H^0_{red} \approx 0$ (variable)
depends on the fuel
depends on the OCs

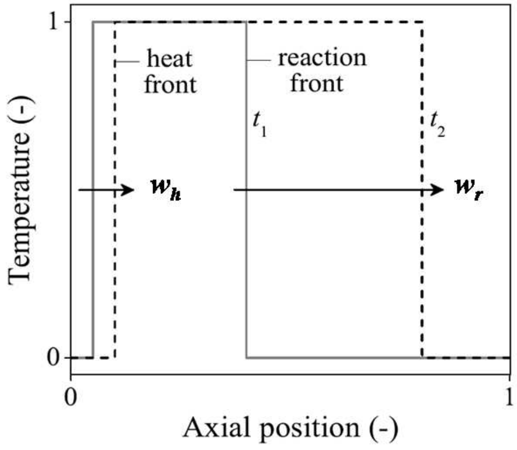
$\Delta H^0_{red} + \Delta H^0_{ox} = \Delta H^0_{comb}$
Overall Heat
is generated



● Me
● MeO

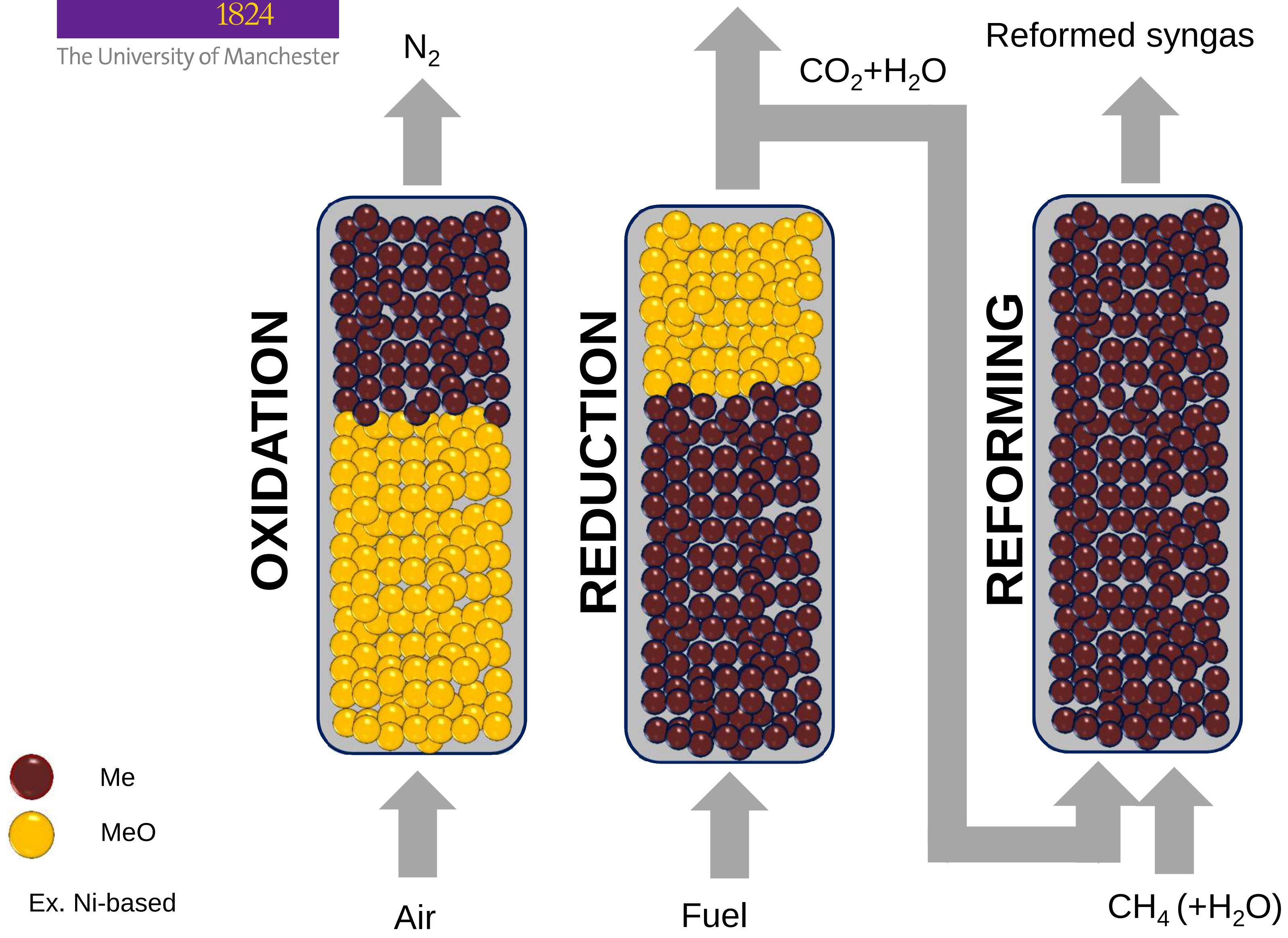


(a) Concentration profile

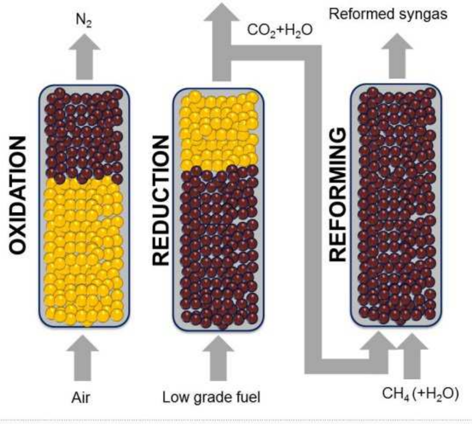


(b) Temperature profile

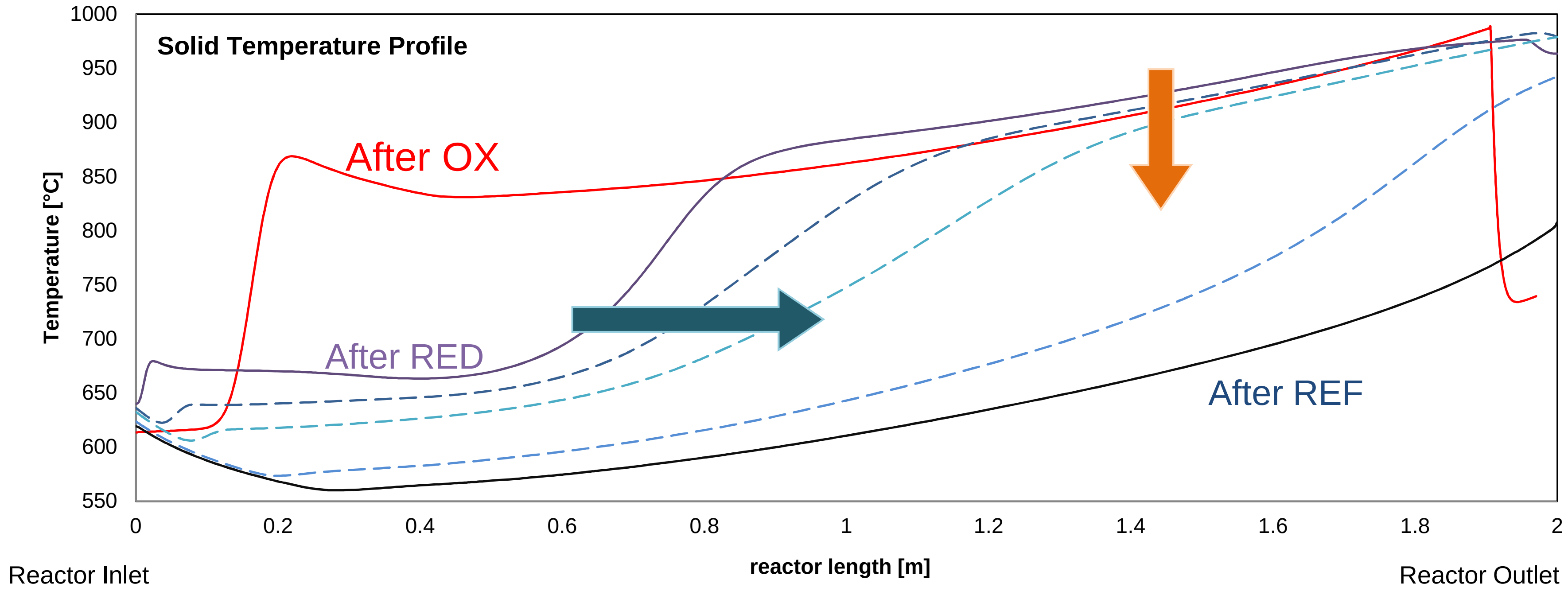
The Concept


N$_2$
CO_2+H_2O
Reformed syngas
OXIDATION
REDUCTION
REFORMING
Me
MeO
Ex. Ni-based
Air
Fuel
CH_4 (+H_2O)

CLR in PBR – how does it work?



- The OXIDATION step heats up the bed (850-900˚C)
- The REDUCTION with a fuel moves the heat front to the reactor outlet (cooling less than 30% of the bed)
- The REFORMING acts as heat removal:
  - ✓ the heat front cools down the reactor 'from left to right'
  - ✓ the reaction front cools down the reactor 'from top to down'



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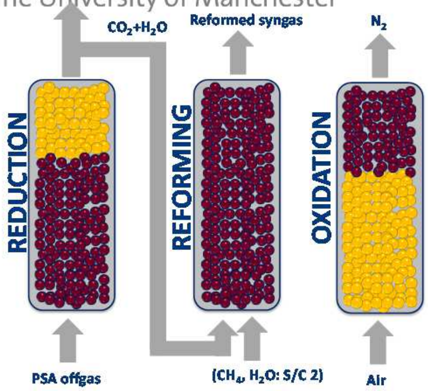
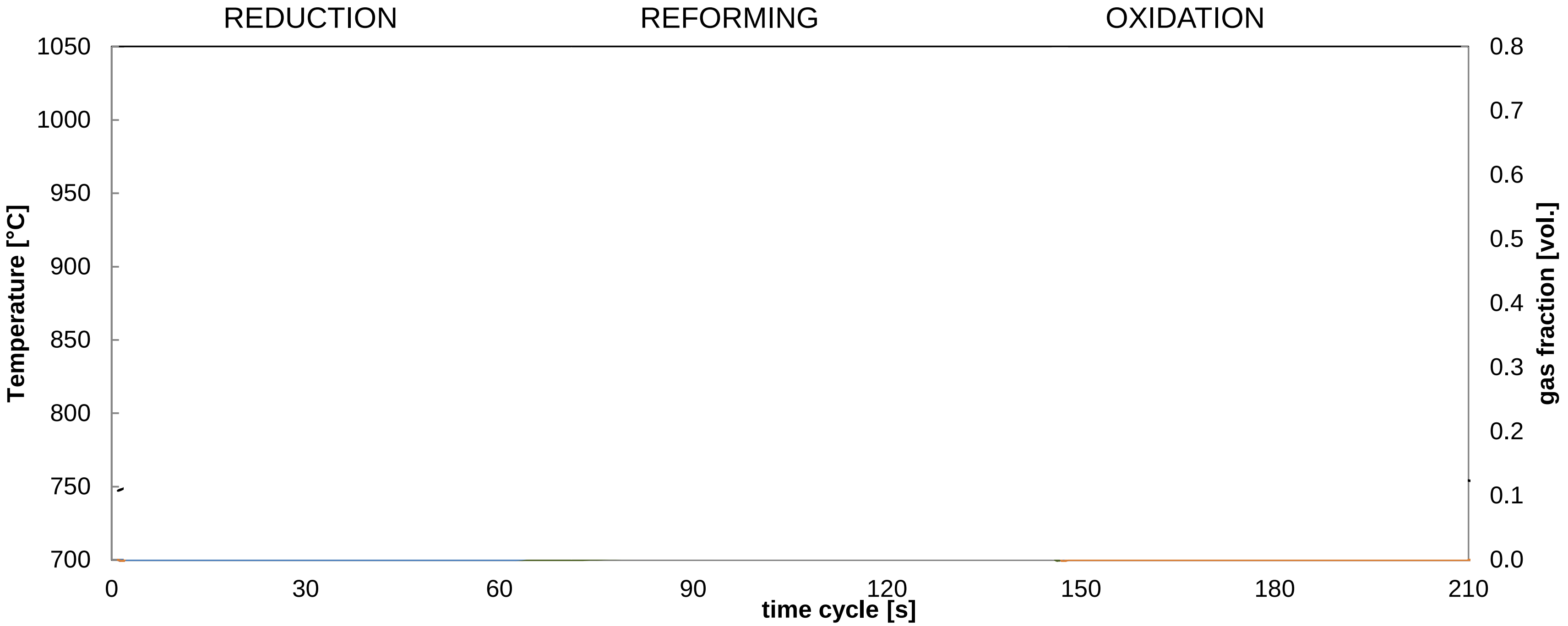
CLR in PBR – how does it work?



- Reduction with PSA off-gas leads to full gas conversion and the gas is delivered at high temperature
- The reforming step is providing H_2-rich gas at the equilibrium conditions. Due to the lower temperature, the CH_4 conversion decreases at the end of reforming.
- During Oxidation the Gas temperature is in the range of 770-800˚C



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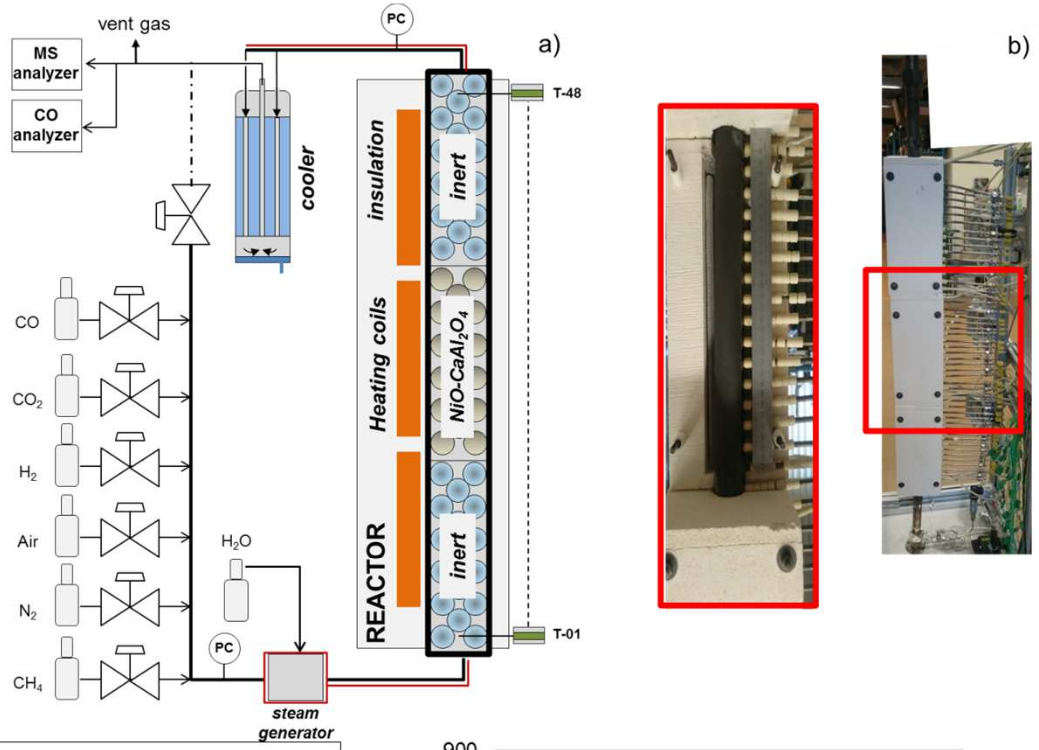
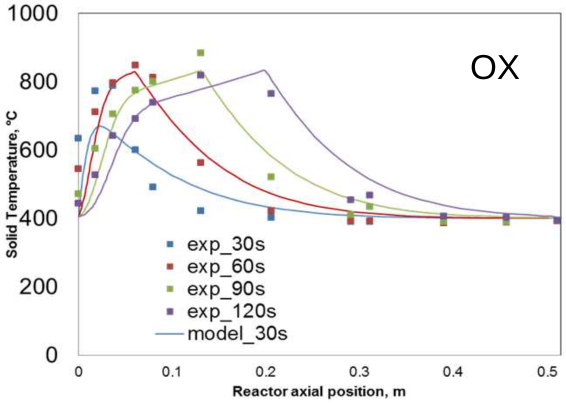
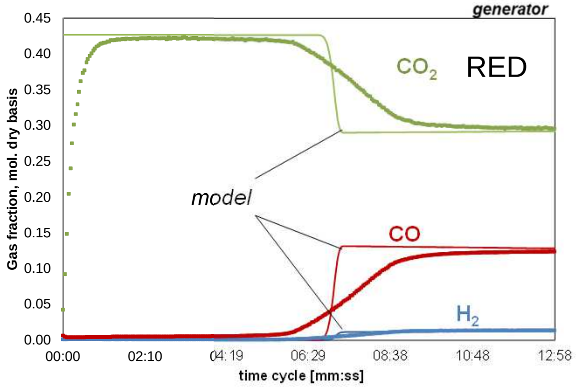
Testing & Validation

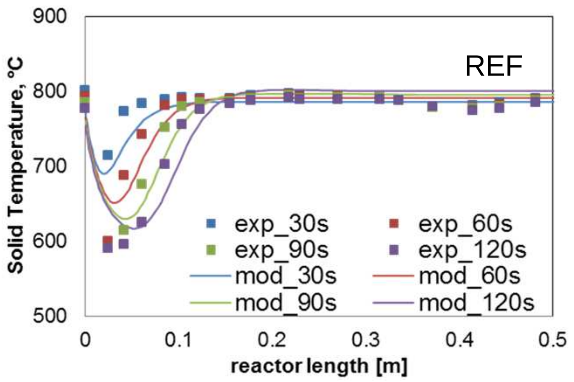
Tests have been carried out:

- ✓ 1 $_n$L/min of CH_4 (500 W_{th} input)
- ✓ 60 cm of reactive length
- ✓ H_2O/CH_4 and CO_2/CH_4 = 4-5
- ✓ Temperature 800-900 °C
- ✓ Pressure = atmospheric
- ✓ (500 g) Ni supported on $CaAl_2O_4$ (JM catalyst)



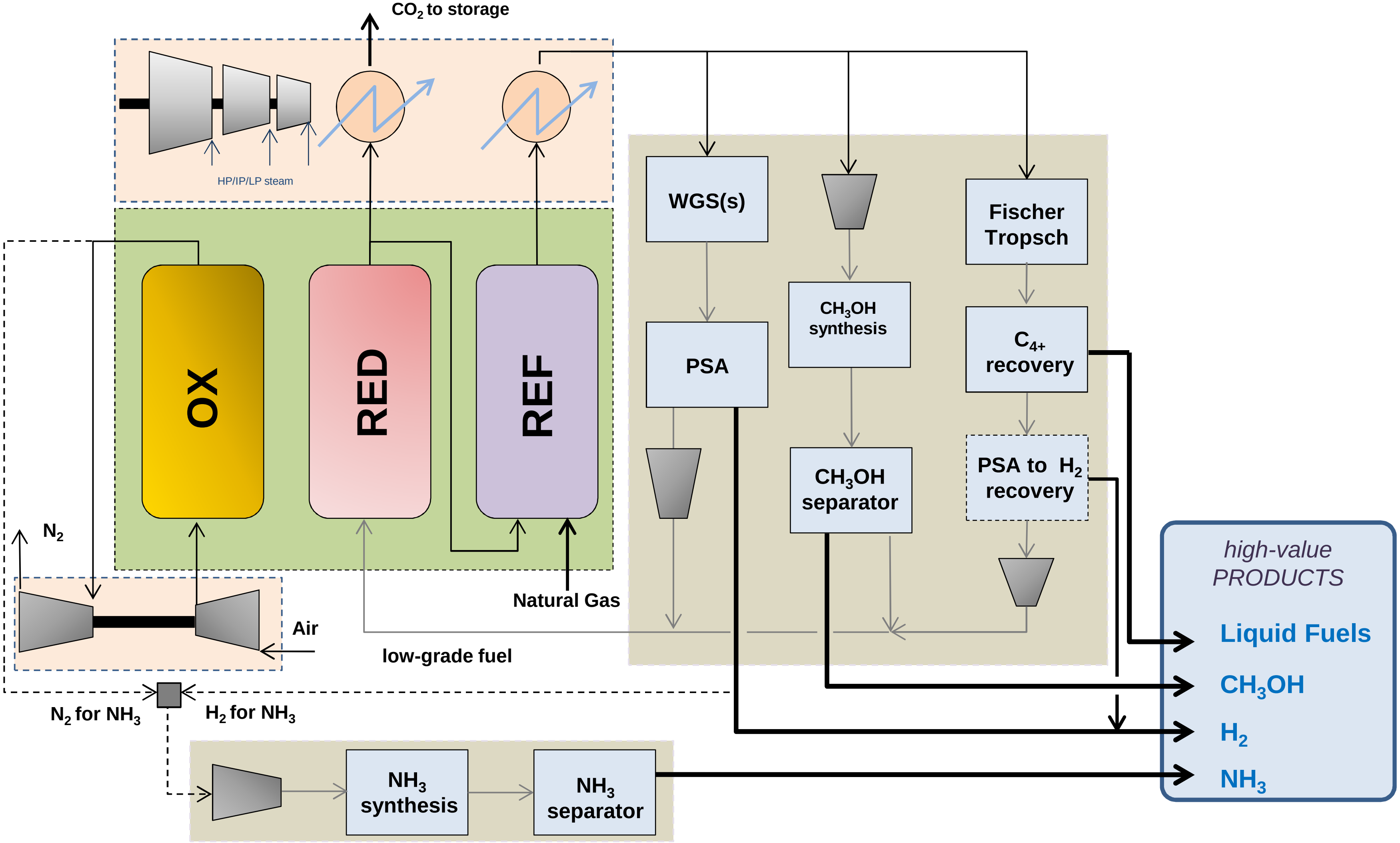






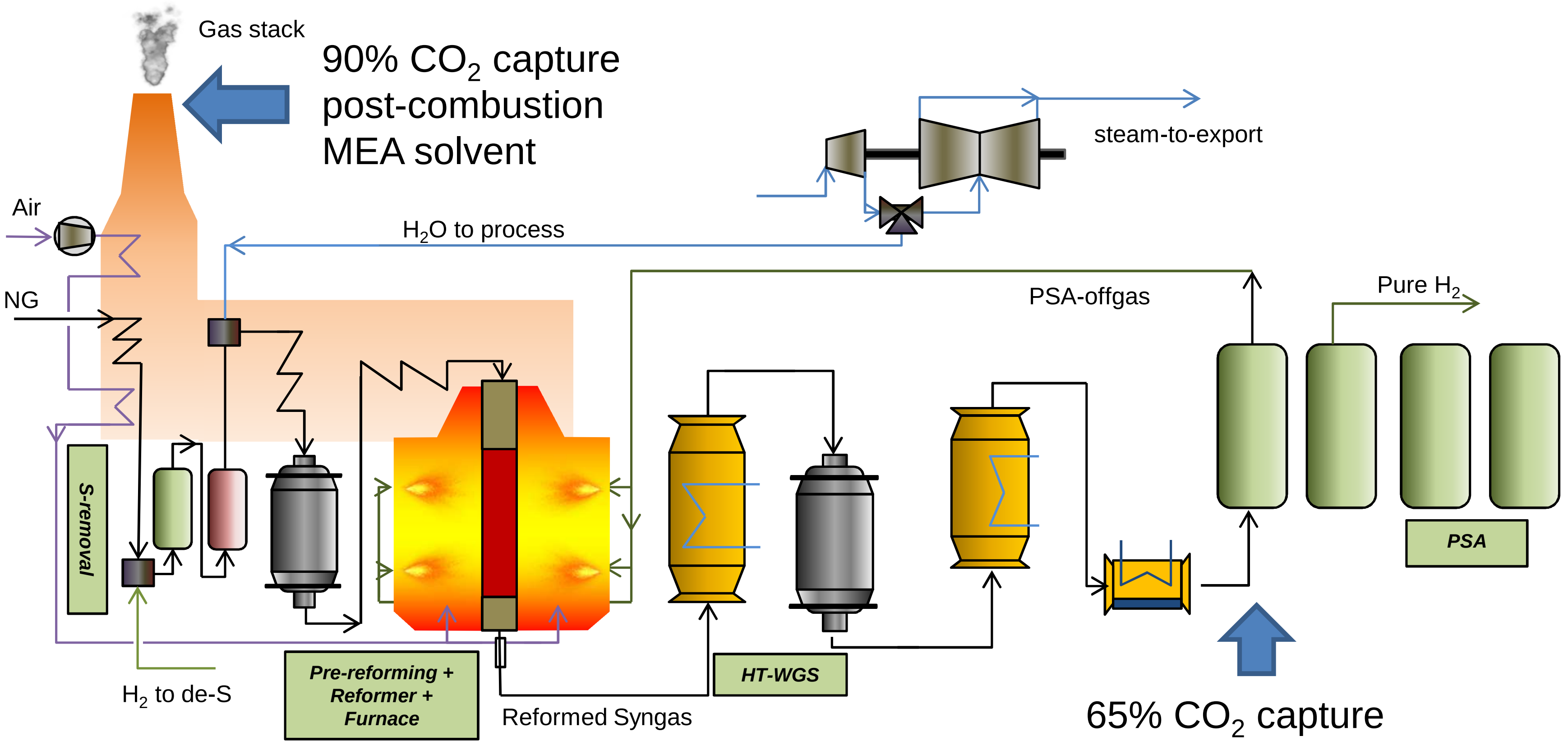
Spallina, V., Marinello B., Gallucci, F., Romano M.C., Sint Annaland, M. van. (2017). Chemical Looping Reforming in packed bed reactors: experimental validation and large scale reactor design. Fuel Processing Technology,156, 156-170.

Integration



Integration H_2

(Fired Tubular Reforming)

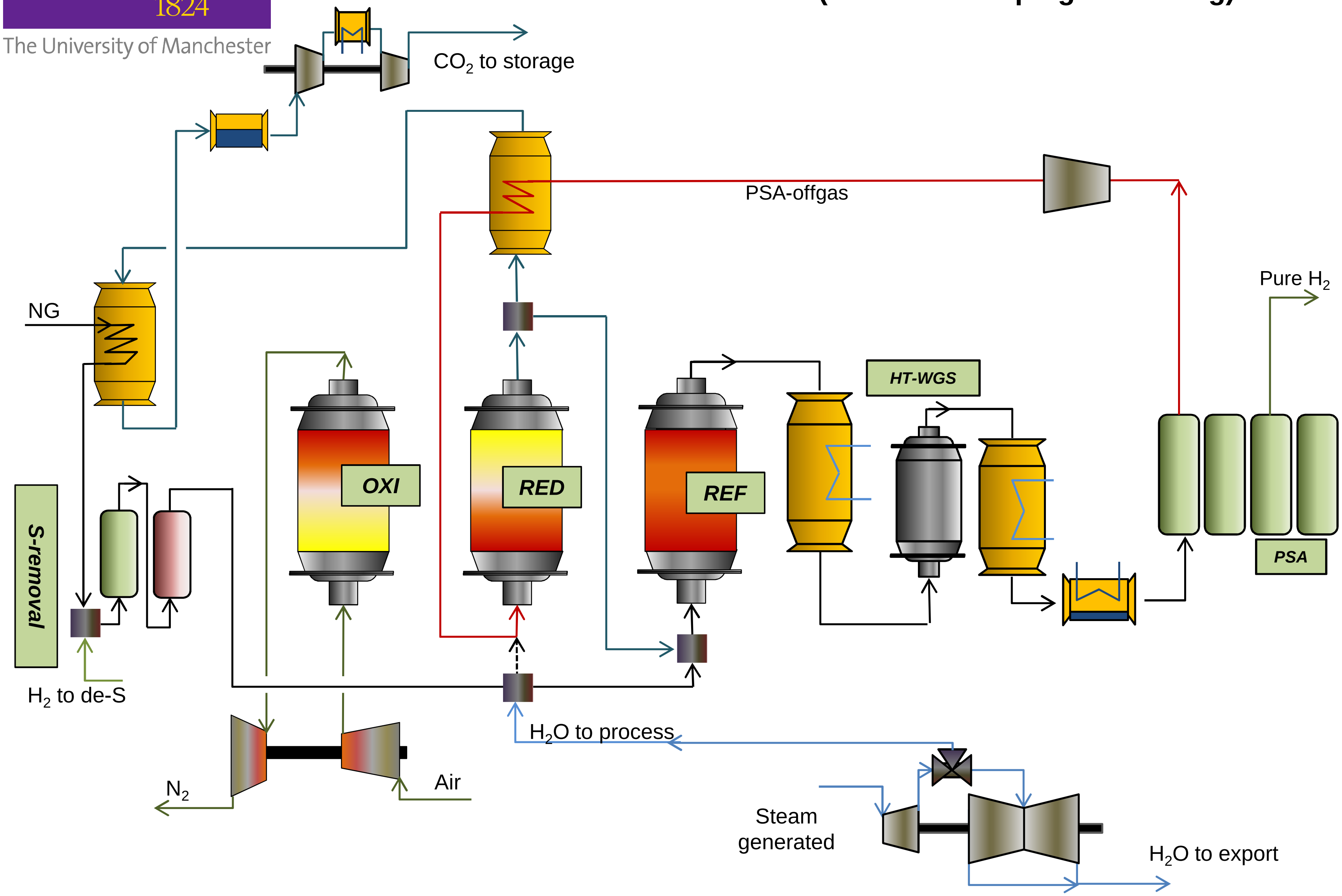


90% CO_2 capture
post-combustion
MEA solvent

65% CO_2 capture
with MDEA solvent

Integration H_2

(Chemical Looping Reforming)



results

Hydrogen Production		SMR	SMR	SMR	CLR - PBR
			Ready technologies		
		N/A	MEA flue gas	MDEA syngas	oxy-CLC
NG flow rate	kg/s	2.62	2.62	2.62	2.62
H_2 flow rate	Nm^3/h	29490	29494	29199	29222
net electric power	MW_{el}	2.11	-0.48	0.34	-0.66
steam export (160°C, 6 bar)	kg/s	4.58	-6.70	1.17	5.34
H_2 yield	mol_{H2}/mol_{NG}	2.49	2.49	2.48	2.46
Eq. Ref. efficiency $\eta_{H2,eq}$	**$H_{2,LHV}/NG_{eq,\ LHV}$**	**81.3%**	**63.4%**	**73.7%**	**78.4%**
Heat Rate	$Gcal/kNm^3_{H2}$	3.25	4.02	3.52	3.31
CO_2 specific emissions, E_{CO2}	g_{CO2}/Nm^3_{H2}	856.78	85.66	313.20	0.00
CO_2 avoidance	**%**	-	**90.0%**	**63.4%**	**100.0%**
CAPEX	**€ × 10^6**	**50.13**	**84.06**	**58.40**	**54.61**
CCA cost	**€/ton_{CO2}**	-	**49.90**	**16.90**	**10.00**

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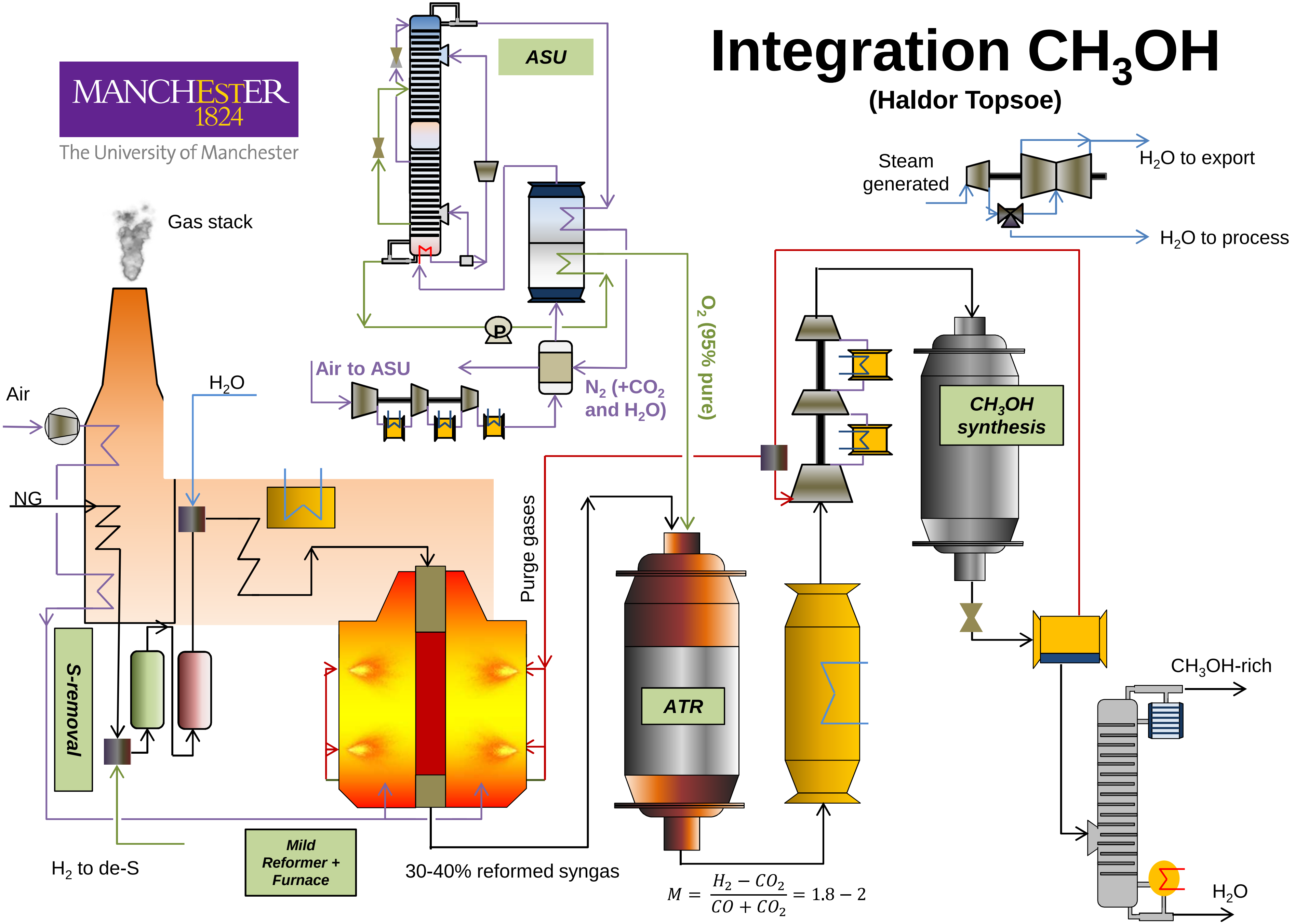
Integration CH_3OH

(Haldor Topsoe)



$$M = \frac{H_2 - CO_2}{CO + CO_2} = 1.8 - 2$$

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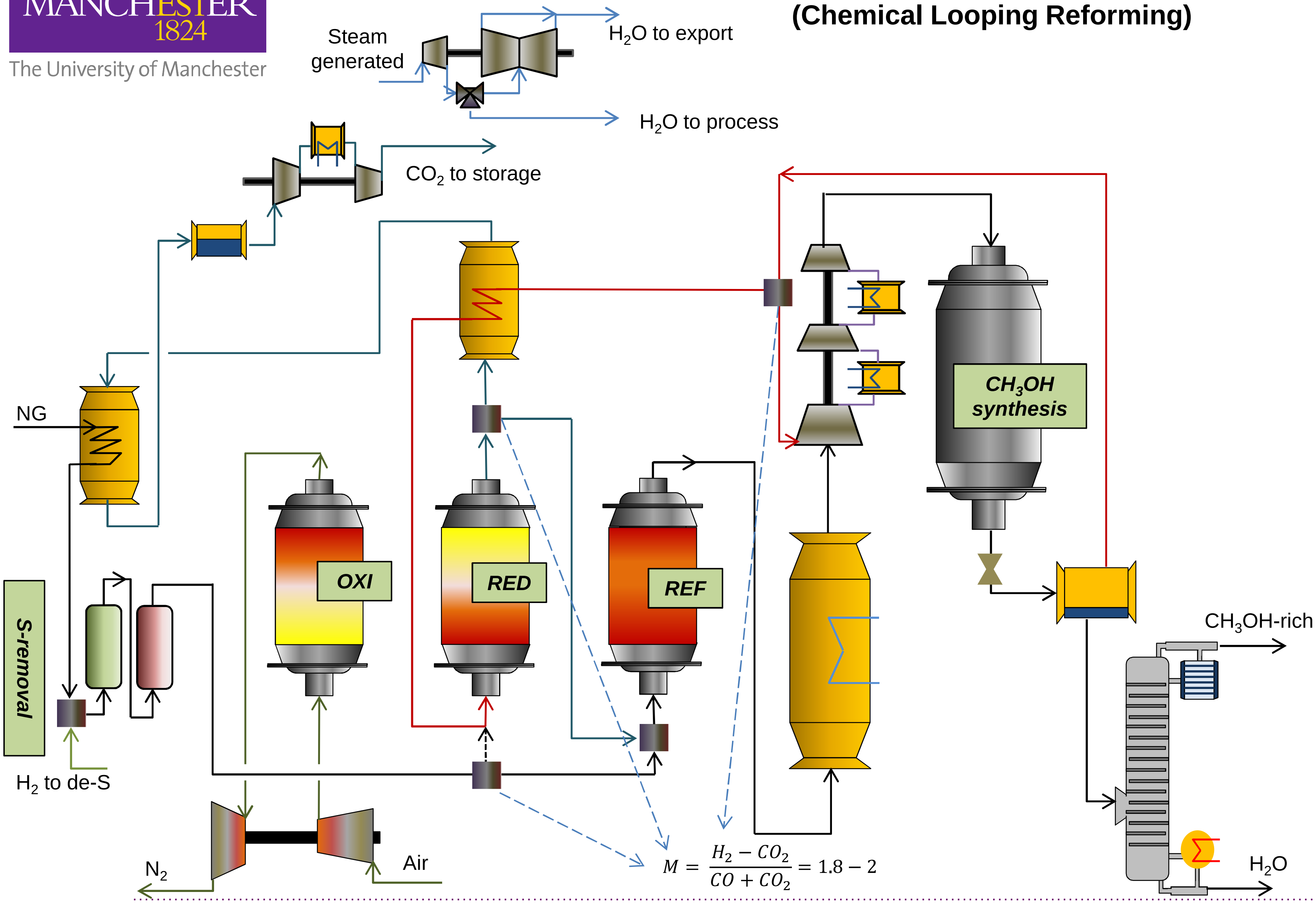
Integration CH_3OH

(Chemical Looping Reforming)



$$M = \frac{H_2 - CO_2}{CO + CO_2} = 1.8 - 2$$

results

Methanol Production		two stage reforming +ASU	CLR - PBR
		Haldor Tropsoe	**oxy-CLC**
NG flow rate	kg/s	73.55	73.55
NG thermal Input	$MW_{LHV, NG}$	3489.86	3489.95
MeOH flow rate	tonn/d	10230	10117
net electric power	MW_{el}	-30.59	26.14
steam export (160°C, 6 bar)	kg/s	45.16	69.20
carbon efficiency	$mol_{CH3OH}/mol_{NG,carb}$	83.7%	82.7%
Eq. Ref. efficiency	**$MeOH_{,LHV}/NG_{eq, LHV}$**	**77.0%**	**78.9%**
Heat Rate	$GJ_{LHV,NG}/ton_{MeOH}$	28.94	28.35
CO_2 specific emissions, E_{CO2}	kg_{CO2}/ton_{MeOH}	273.84	4.95
CO_2 avoidance	**%**	-	**98%**
CAPEX	**€ × 10^6**	**705.83**	**441.73**

Conclusions

- The yield of products is not affected
- The heat recovery increases (more steam-to-export)
- The electricity consumption reduces (especially for MeOH)
- Higher CO_2 avoidance
- Reduced CAPEX: no absorption processes (H_2/NH_3 production) neither cryogenic ASU (MeOH, FT-process)
- Adiabatic vessels instead of furnace for the reforming process
- Synergy and flexibility in the products

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Conclusions

- Chemical Looping technologies can be also efficiently integrated in other processes

→ Packed Bed Reactor for Chemicals

- **Proof of concepts** have been carried out already for steam/dry chemical looping reforming

→ Chemical Looping exploitation in industrially relevant processes

- **Fuel-to-chemicals conversion** is less demanding in terms of heat management than fuel-to-heat/power: the overall heat of reaction is lower when compared to fuel combustion; and the operating conditions are less severe

→ CLR vs CLC

- Exploiting **chemical looping technology** in other industrially relevant processes

→ chemical looping convenient without CO_2 capture policies

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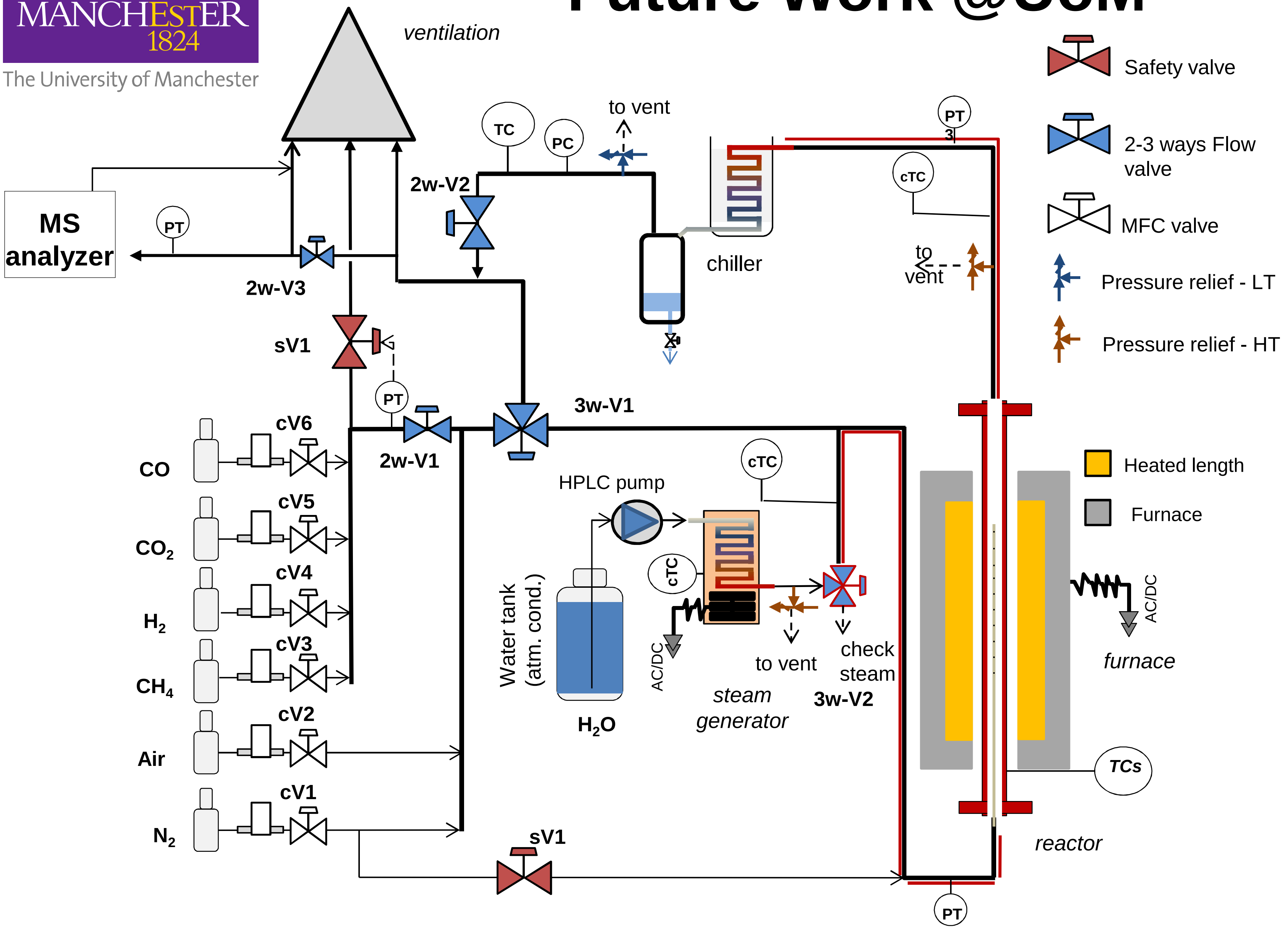
Future Work @UoM



Future Work @UoM

- **Large particle diameter** (typically higher than 1 mm in packed bed reactor)
- **Heterogeneous catalysis** of Oxygen Carriers
- Combination of **different OC formulations**
- **1,2-D dynamically operated reactor modelling** and **model validation** in the *new gas-solid reaction lab* at high pressure/high temperature reactions (up to 1 kg of active bed material).
- Combination of **Steam-Iron and Chemical Looping Reforming** reactions to enhance the H_2-rich streams and asses the feasibility use at small-scale
- Combination of Chemical Looping and **Paraffin de-hydrogenation and oxy-de-hydrogenation** due to the synergies in terms of exothermic and endothermic reactions

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Thank you for your attention!

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