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

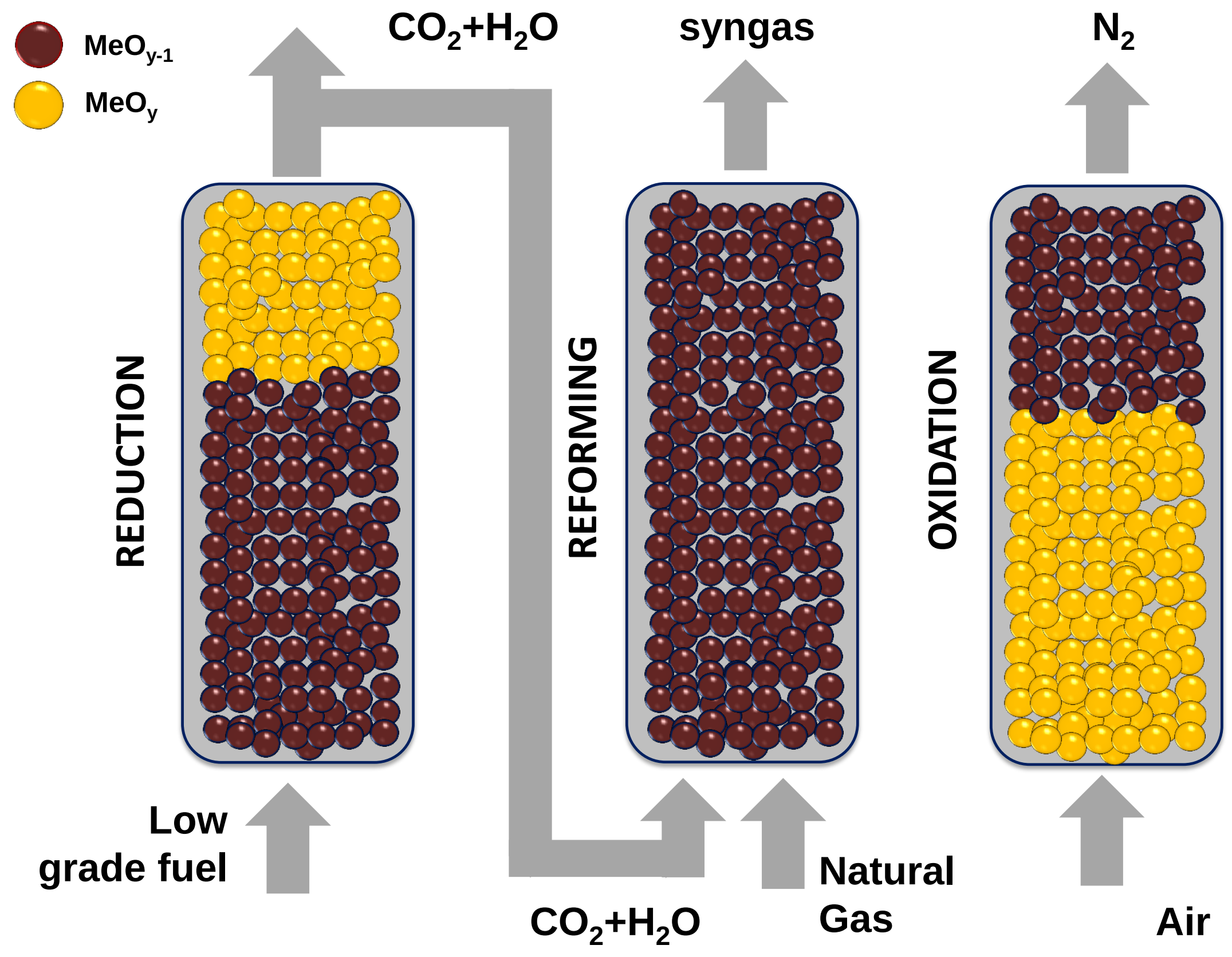
Vincenzo Spallina

School of Chemical Engineering and Analytical Science

Contacts:
Vincenzo Spallina
Lecturer in Chemical Engineering
Group of Catalysis and Porous Materials

email: vincenzo.spallina@manchester.ac.uk
tel: +44 (0) 161 306 9339

The Process Concept



The chemical looping reforming with packed bed reactors occurs in three steps [1]:

i) **Oxidation** with air

ii) **Reduction** with a low grade fuel available in the plant

iii) **Steam/Dry Reforming**

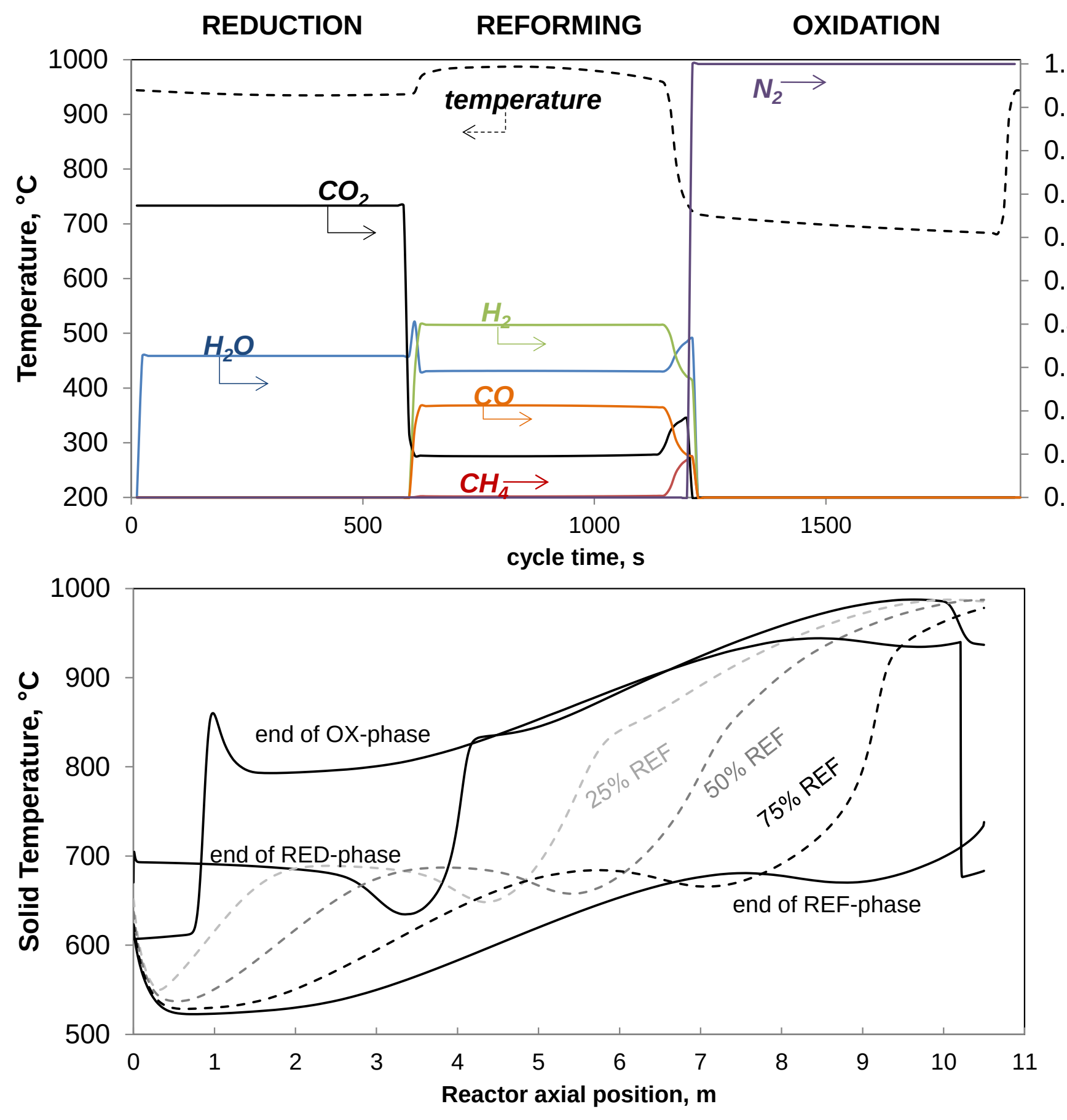
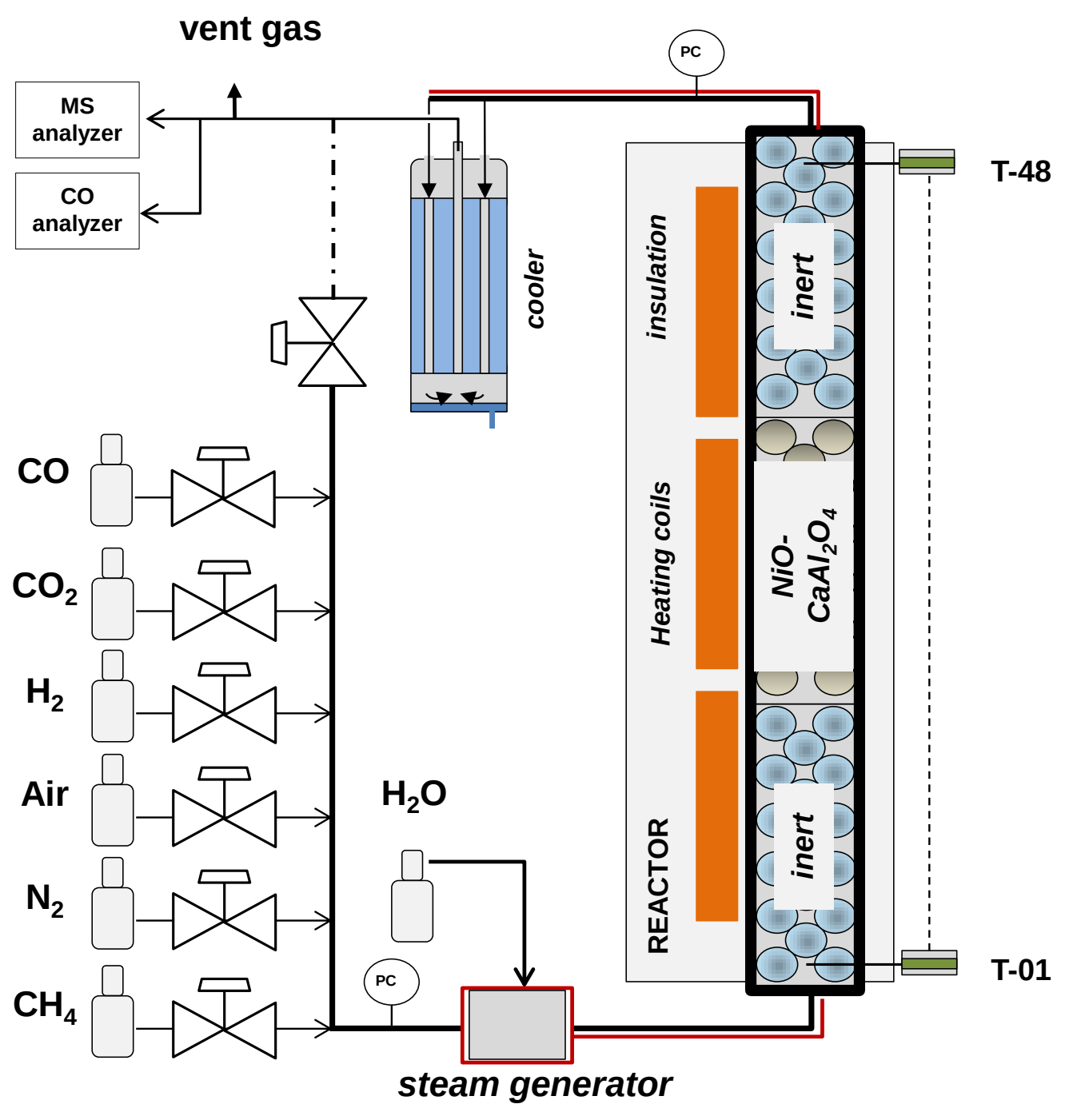


Fig 1: dynamically operated reactor modelling

The heat stored inside the reactor during oxidation (**exothermic**) is removed during the reforming (**endothermic**).

Proof-of-Concept



The concept has been already demonstrated at lab scale using **500 g** of a commercial catalyst ($NiCaAl_2O_4$), at atmospheric pressure and temperature about 800-900°C.using 1 l_n/min of CH_4 at different steam or carbon dioxide to methane ratio [1].

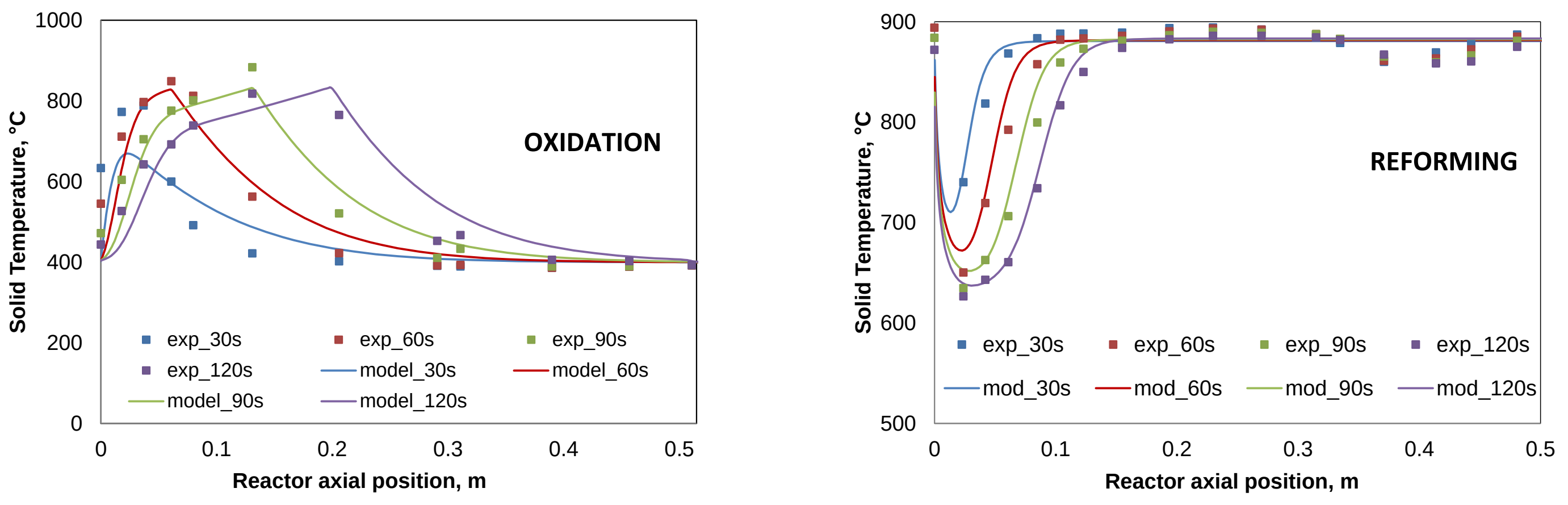


Fig 2: experimental proof-of-concept and model validation

Performance

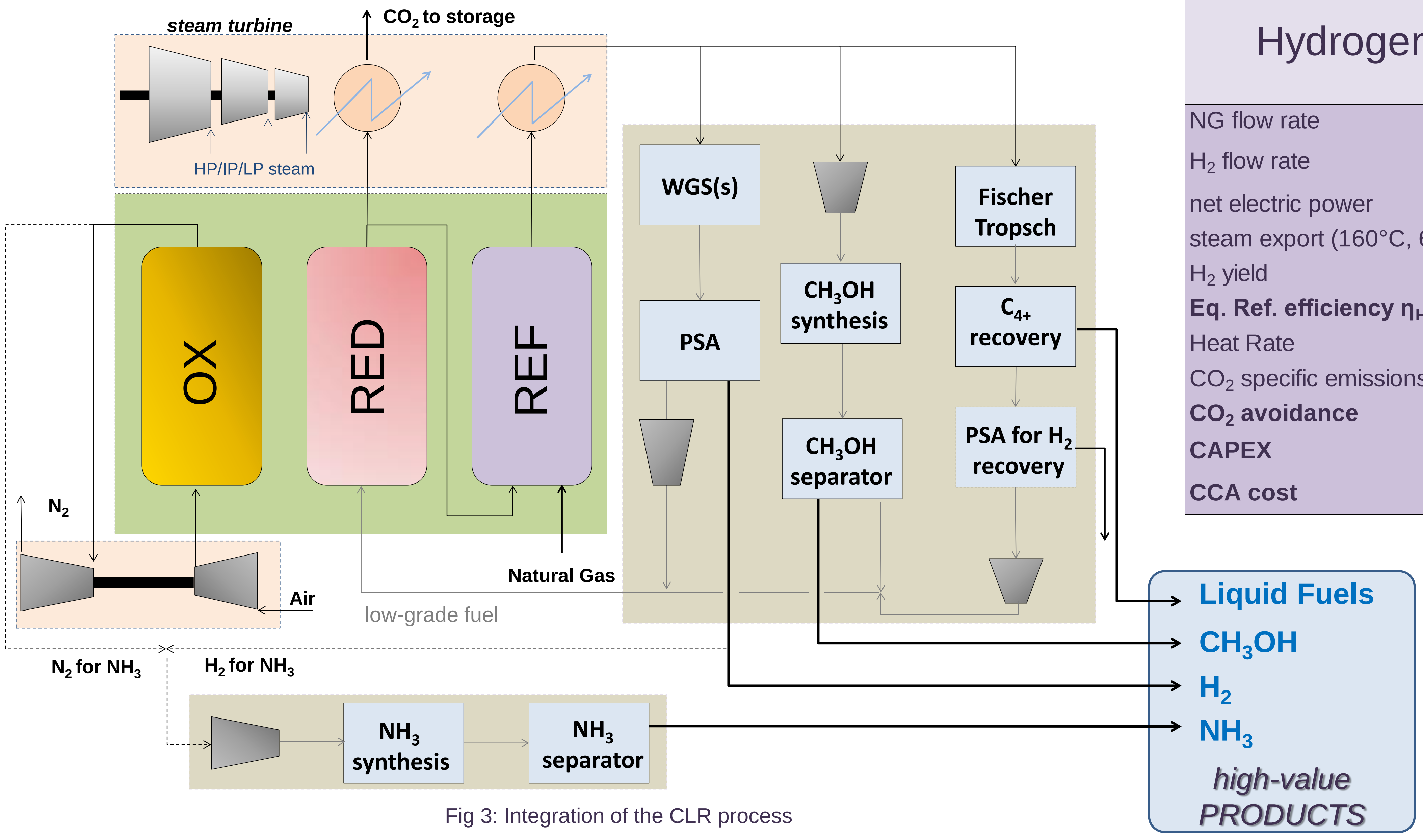


Fig 3: Integration of the CLR process

- The **yield** of products is not affected
- The **heat** recovery increases (more steam-to-export)
- The **electricity** consumptions 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

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**

Methanol Production		two stage reforming +ASU Haldor Tropsoe	CLR - PBR 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**

Particle and Reactor Development

- **Large particle diameter** (typically higher than 1 mm in packed bed reactor) **Heterogeneous catalysis** of Oxygen Carriers
- Combination of **different OCs** (e.g. Fe, Cu, Ni-based)
- Effect of **pressure** and type of **support**
- **1,2-D dynamically operated reactor model** is going to be developed solving partial differential equations of M&H balances with an effective time/space discretization
- The **model validation** will be carried out in the *new establish gas-solid reaction lab* where high pressure/high temperature reactions will be performed up to 1 kg of active bed material.

Follow up research

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

Conclusions

Chemical Looping reforming with Packed Bed Reactors is a promising technology to be used for the production of different relevant bulk chemicals. The proof-of-concept has been already achieved and the fully integrated plants show significant reduction in the CCA compared to other existing technologies without any relevant performance decays.

Future works will focus on the optimization of the oxygen carrier formulation(s) and reactor design as well as the assessment of similar concept in other relevant chemical processes such as olefins production.

Acknowledgements

The author is grateful to the **Chemical Process Intensification Group from Eindhoven University of Technology** (The NL) for the great help and relevant effort which have made possible to start this research in the past years and to the **School of Chemical Engineering and Analytical Science of the University of Manchester** for the current technical and economical support

References

[1] V. Spallina, B. Marinello, F. Gallucci, M. C. Romano, and M. Van Sint Annaland, "Chemical looping reforming in packed-bed reactors: Modelling, experimental validation and large-scale reactor design," Fuel Process. Technol., vol. 156, pp. 156–170, 2017.

[2] V. Spallina, D. Pandolfo, A. Battistella, M. C. Romano, M. Van Sint Annaland, and F.Gallucci, Techno-economic assessment of membrane assisted fluidized bed reactors for pure H2 production with CO_2 capture, Energy Convers. Manag., vol. 120, pp. 257–273, 2016.

[3] Haldor-Topsoe, C. S. N. Kim Aasberg-Petersen, I. Dybkjær, and J. Perregaard, "Large Scale Methanol Production from Natural Gas," Haldor Topsoe, pp. 1–14, 2016.

[4] Cost Estimation Methodology for NETL Assessments of Power Plant Performance DOE/NETL-2011/1455," p. 26, 2011

[5] L. Mancuso, S. Cloete, P. Chiesa, S. Amini, Economic assessment of packed bed chemical looping combustion and suitable benchmarks, Int. J. Greenh. Gas Control, 64, pp 223-233, 2017