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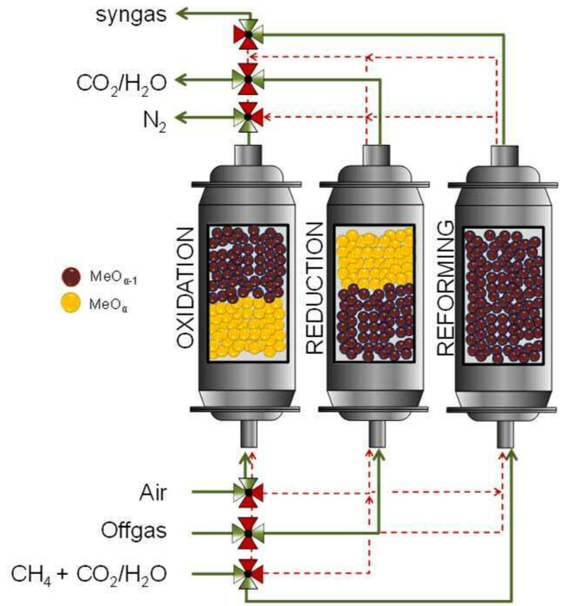
CLean h***Y***drogen and ***CH***emicals production via chemical loop***ING***



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Outline of the presentation

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- The concept
- Experimental results
- Reactor Modelling and Integration
- Conclusion
- Next steps

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The concept

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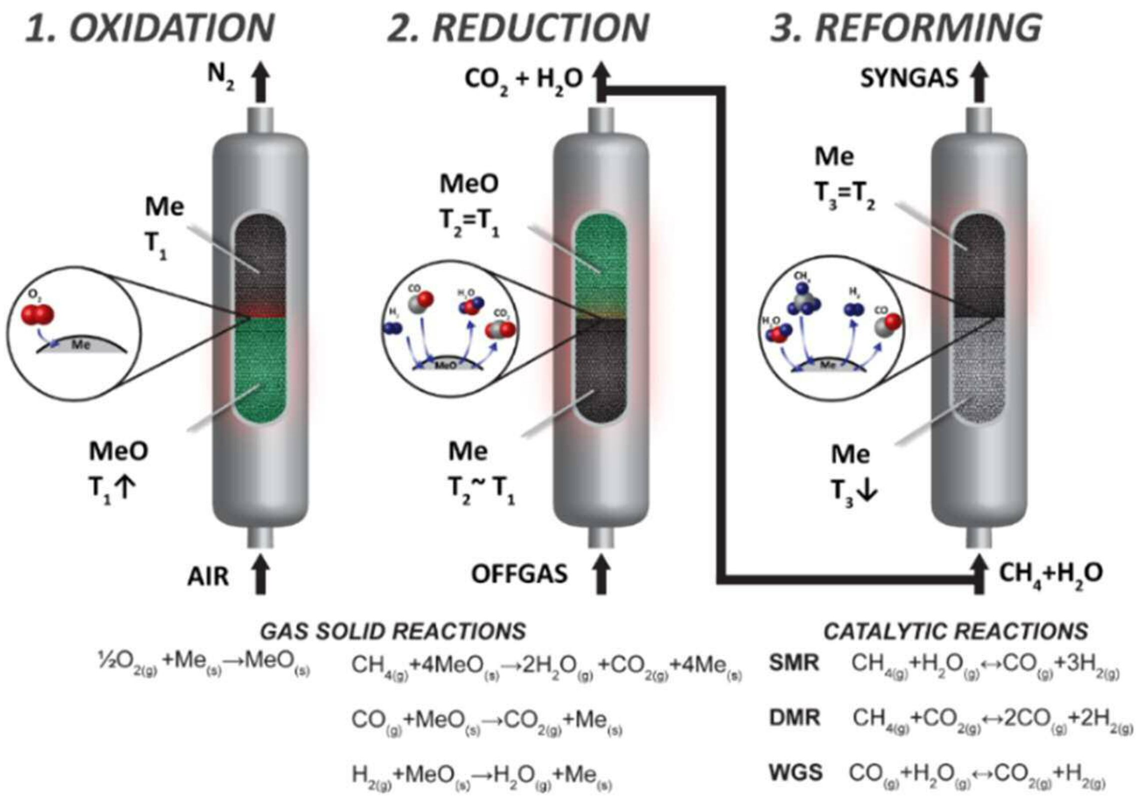

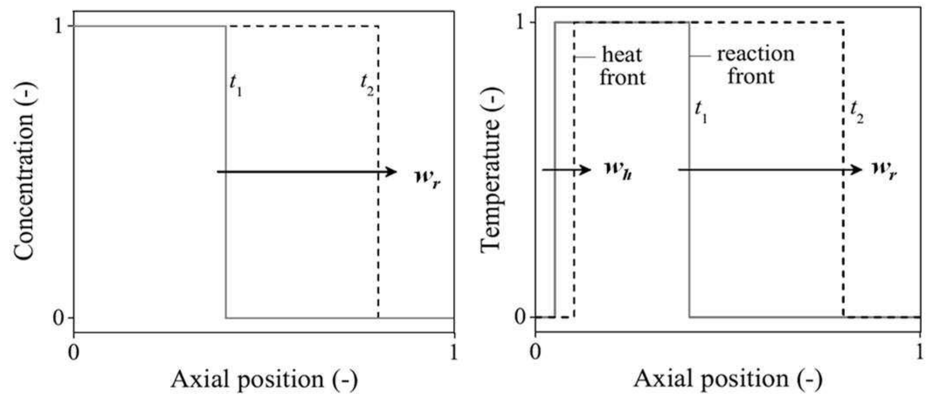

(a) Concentration profile (b) Temperature profile

$\Delta H^0_{ox} << 0$
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

Metal oxide: Ni, Fe, Cu, Mn, mixed oxides, etc…. In general synthetic material and natural ore are possible

Support material: Al_2O_3, $MgAl_2O_4$, $CaAl_2O_4$, TiO_2, ZrO_2, perovskite materials, etc….

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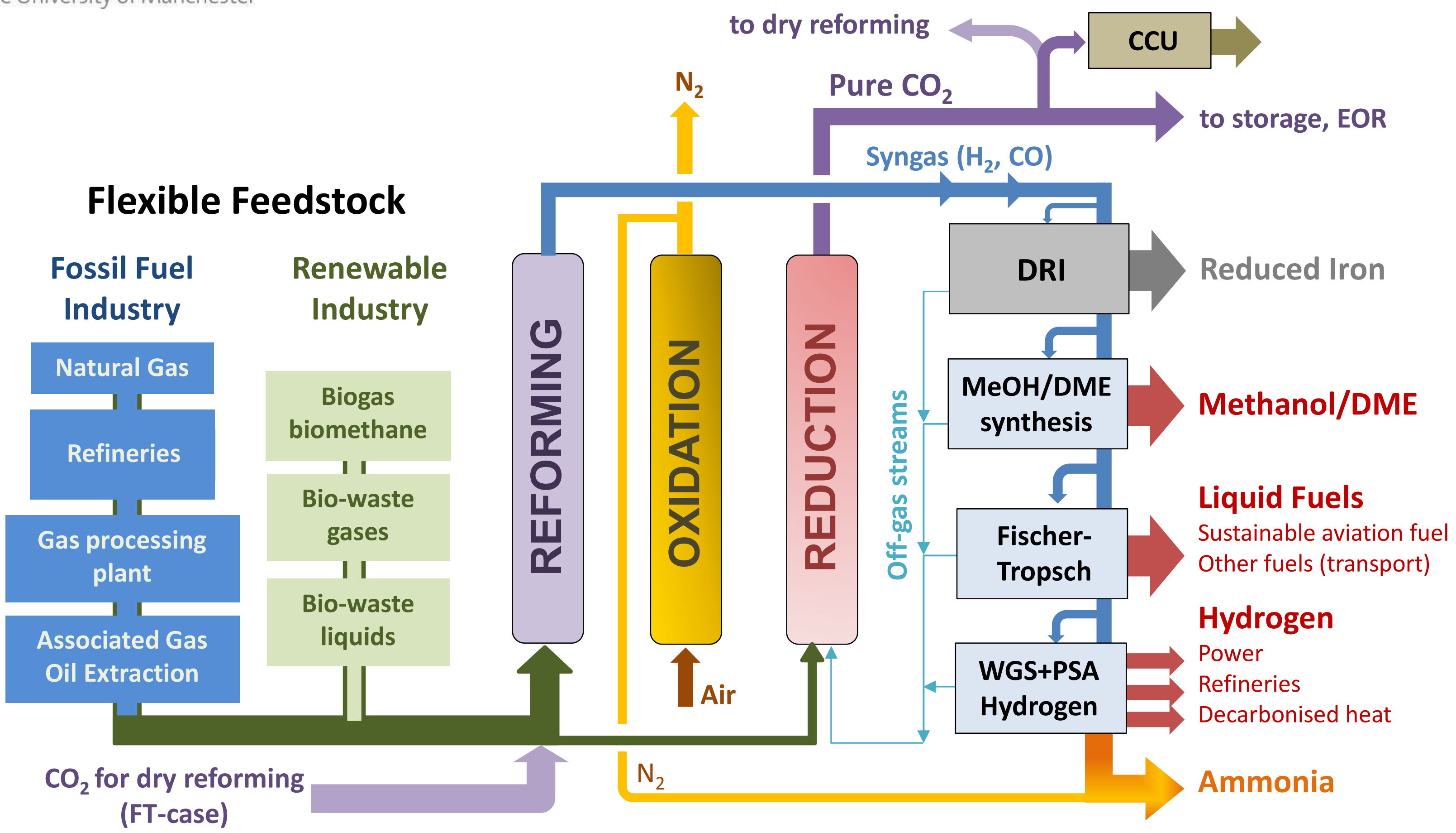
The Integration



Potential IMPACT

8% global CO_2 emissions from Iron manufacturing [1] | DRI is 5% of global production

340 $MTPA_{MeOH}$ capacity and 211 $MTPA_{CO2}$ [2]

75 $MTPA_{H2}$ with 800 MTPA $_{CO2}$ (≈ 500 $MTPA_{H2}$ in 2050, 40% from blue H_2) [2]

180 $MTPA_{NH3}$ capacity and 406 $MTPA_{CO2}$ [2]

[1] Energy Transition Commission, sectorial focus Steel, (2020) source
[2] IEA (2020), CCUS in Clean Energy Transitions, IEA, Paris source

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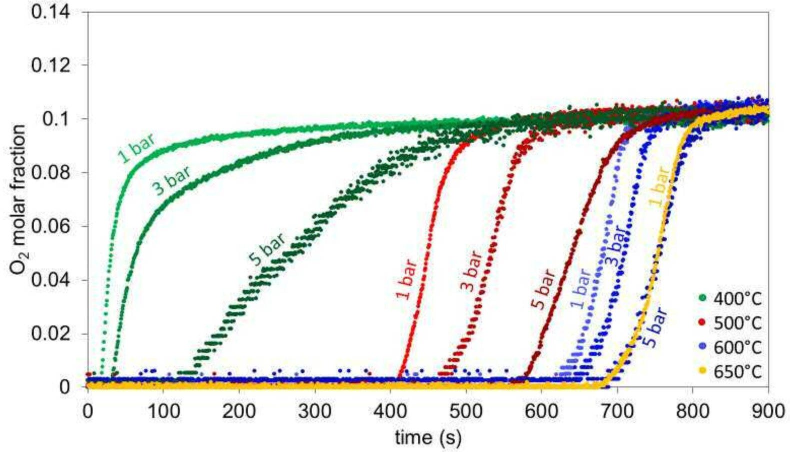
The experimental results

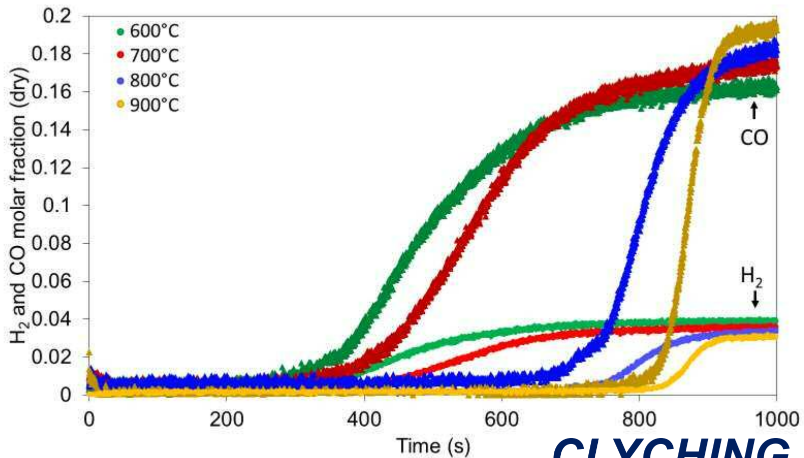
Effect of initial solid Temperature limited > 500°C (oxidation) and >800°C (reduction) [3]

Flowrates 10 - 40 NLPM has been tested showing the impact of superficial gas velocity up to 1 m·s^{-1} [3]

Higher pressure (up to 5 bar) gives better results do to lower gas velocity/higher residence time[3]

The max temperature rise recorded by the multipoint thermowell during oxidation is 400°C [3], however the actual max ΔT is >500°C as detailed 1D model and 2D model [4]





[3] Argyris et al., Chem. Eng. J., 2022, 435, 134883.
[4] Argyris et al., accepted for publication to Sustain. Energy Fuels., 2022

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The experimental results

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Chemical looping reforming [3]

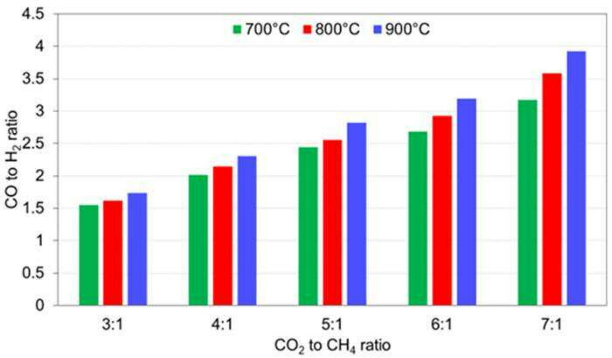
Catalytic process occurs at TDN equilibrium → controlled composition (by heat management)

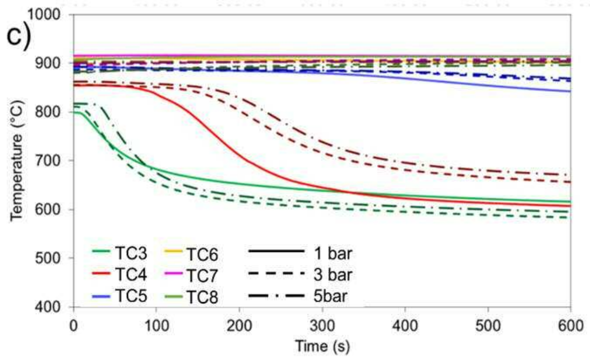
Temperature drop demonstrates the cooling effect and thermal balance of the process

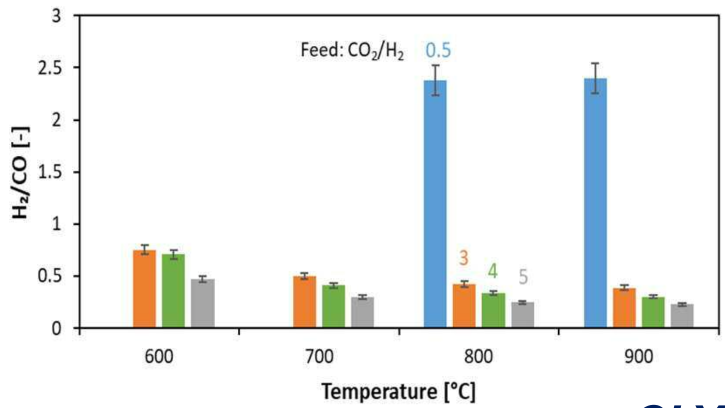
Chemical looping Reverse WGS [5]

RWGS is also endothermic and requires (>800°C)

This has been demonstrated also as process for CO_2 utilisation and green H_2 to syngas for FT liquids (by producing $H_2/CO \approx 2$)







[3] Argyris et al., Chem. Eng. J., 2022, 435, 134883.
[5] de Leeuwe et al., to be submitted, 2022.

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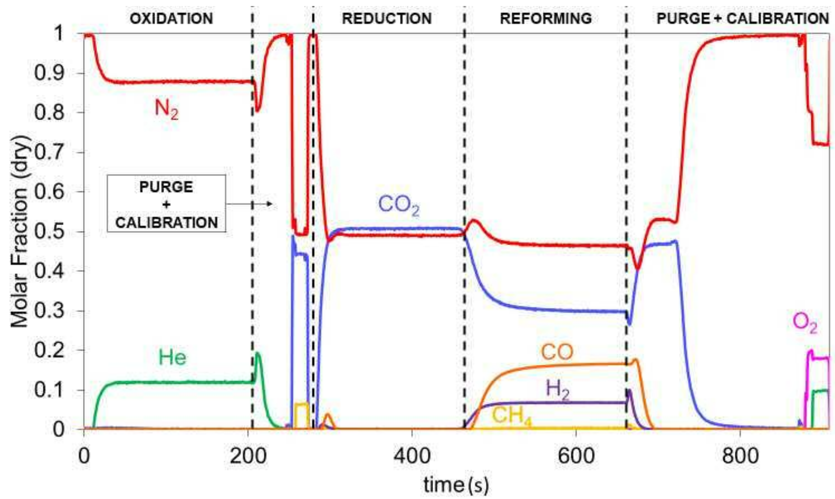
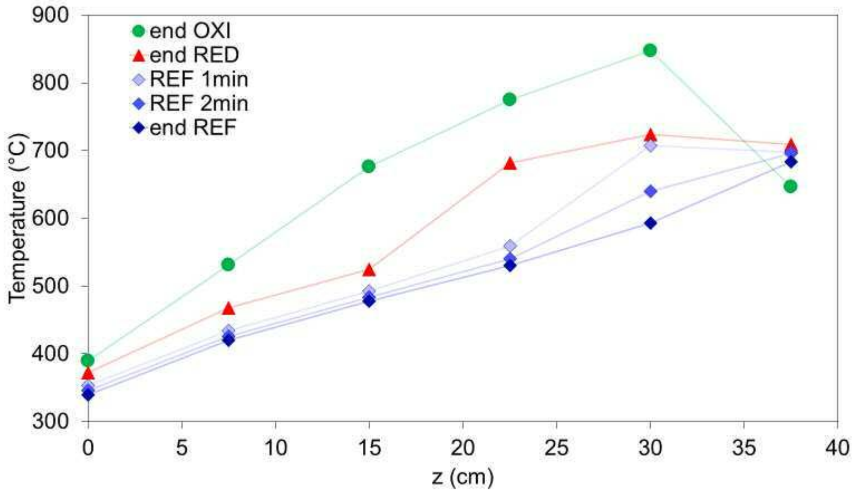
The experimental results

- Full cycle operation has been achieved at pseudo-adiabatic conditions (Furnace temperature at 600°C)
- Clear breakthrough and distinctive phases: overall 4 complete cycles were operated continuously
- Thermal management acheived with heat of dry reforming reaction provided during oxidation/reduction

Inlet conditions	Oxidation	Purge	Reduction	Reforming	Purge	Purge
Flow Rate (NLPM)	10	7	14	14	13	7
Feed time (s)	180	60	190	180	40	150
Molar Fraction %						
N_2	71.1	100.0	50.0		53.8	100
O_2	18.9	-	-		-	-
He	10.0	-	-		-	-
CO_2	-	-	42.9		46.2	-
CH_4	-	-	7.1		-	-





[3] Argyris et al., Chem. Eng. J., 2022, 435, 134883.

Process Performance

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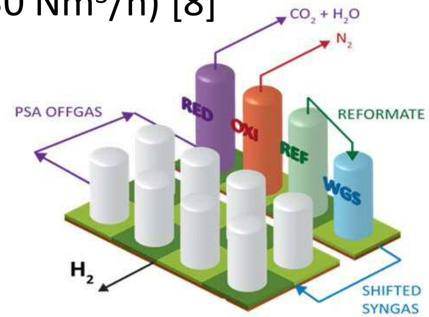
Process	Plant size	CO_2 emissions (CCR) kg_{CO2}/ton_i (%)		CAPEX (TPC) M€		Cost of product €/ton_i		Cost of CO_2 avoidance €/ton_{CO2}	
		Bench.	CLYCHING	Bench.	CLYCHING	Bench.	CLYCHING	Bench.	CLYCHING
Hydrogen [6]	30 kNm³/h	3470 (64%) 950 (90%)	**190 (98%)**	73.4 107	**61.8**	2006 2450	**2190**	70.6 95.6	**59.8**
Methanol [6]	10 kTPD	220 (-)	**6 (>98%)**	2000	**1150**	368.9	**304**	-	**-303**
Ammonia [7]	500 kTPY	440 (>73%)	**3 (>99%)**	680	**593.6**	556	**527.6**	17.6	**-5**
FT- liquids	52 kbbl/d	47 (>95%)	**23 (>97%)**	3051	**2423**	430	**415**	13.6	**-1**

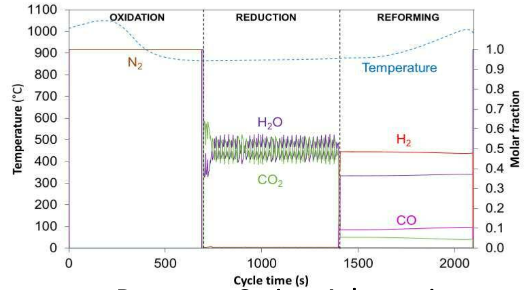
- CCR > 97-98% for all processes (all carbon components not converted goes to CO_2-rich streams)
- Cost of the product >20% lower and CO_2 avoidance cost significantly lower (even negative for GTL)

The process has been simulated also for small scale stand-alone unit, on-site generator, single skid [8]

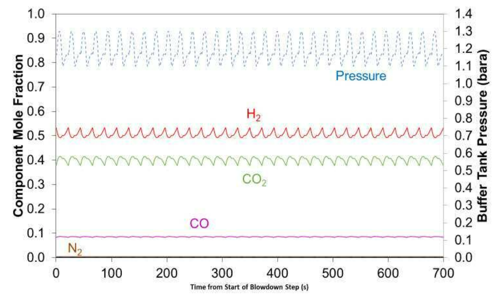
Small scale H_2 production (130 Nm³/h) [8]



Chemcial Looping Reforming



Pressure Swing Adsorption



[6] Spallina et al., Int. J. Greenh. Gas Control, 2019, 88, 71-84.
[7] Pereira Lee R. et al., Appl. Energy, 2020, 280,115874.
[8] Argyris et al., Chem. Eng. J., 2022, 428, 132606.

Conclusions

There is a momentum for hydrogen generation and CCUS as key enabling technology to achieve the ambitious net zero targets (in Europe and UK)

Blue hydrogen or Renewable hydrogen is not the ONLY solution but **is PART OF the solution and imperative for energy-intensive industry**

Chemical looping at high pressure **has been demonstrated** up to 5 bar and successfully operated now for > 1000 hours using 400/500 grams batch material up to 50 NLPM

The techno-economic studies and feasibility design show **very favourable performance** in terms of reduction of CO_2 emissions (>95% CCR) and costs (CO_2 avoidance 30% lower) for large scale applications

Notably, The technology **is modular, and flexible (feedstocks and products) → small/medium scale** processes with inherent pure CO_2 production are possible → we are looking to develop a business case for possible stakeholders, e.g. glass, food industry, small industrial boilers

Networks and joint collaborations are required to move the technology towards **pilot and demonstration stage**

Follow – up

April 2020: Manchester is collaborating in the scale-up of gas-solid chemical looping reactor technology applied to steel decarbonisation in **H2020 C4U project**

https://c4u-project.eu/

May 2020: Manchester is leading a € 5M **H2020 GLAMOUR project**, where a TRL5 process for chemical looping reforming of glycerol to produce SAF

https://www.glamour-project.eu/

Nov 2021: a **new PhD project co-funded** by TotalEnergies has started to develop a 2D industrial scale reactor modelling and design of the technology

Jan 2022: **follow-up feasibility study project** in collaboration with industrial partners publicly funded in UK (more info to be released in May 2022)

the next stage has to demonstrate at pilot scale the feasibility of the process

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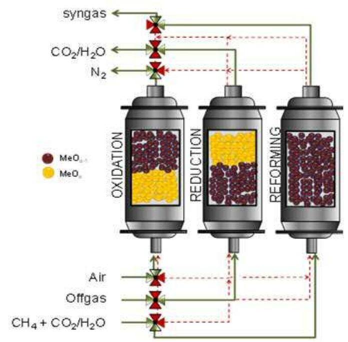

Thank you for your attention

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