

# Novel Electrified Sorption Enhanced Reforming Process for Blue Hydrogen Production

Abdelrahman Mostafa<sup>1\*</sup>, Alessandra Beretta<sup>1</sup>, Gianpiero Groppi<sup>1</sup>, Enrico Tronconi<sup>1</sup>, Matteo C. Romano<sup>2\*</sup>

<sup>1</sup> LCCP – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via la Masa 34, 20156, Milano, Italy.

<sup>2</sup> GECOS – Group of Energy Conversion Systems, Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy.

\*Corresponding authors: [abdelrahmanmohamed.mostafa@polimi.it](mailto:abdelrahmanmohamed.mostafa@polimi.it), [matteo.romano@polimi.it](mailto:matteo.romano@polimi.it)

## Section A: Modelling Methodology and Assumptions

**Table A1 Modelled reactor characteristics used in the 1D reactor model <sup>1</sup>**

Reactor diameter ( $d_t$ )	2.26	m
Reactor length ( $L_t$ )	5	m
Particle diameter ( $d_p$ )	1	mm
Sorbent to catalyst ratio	5/1	$\text{m}^3_{\text{CaO}} / \text{m}^3_{\text{Cat}}$
Catalyst particle density	1650	$\text{kg}/\text{m}^3$
Sorbent particle density	1650	$\text{kg}/\text{m}^3$
Max sorbent conversion ( $X_{\text{max}}$ )	0.4	$\text{mol}_{\text{CaCO}_3} / \text{mol}_{\text{CaO}}$
Catalyst activity factor ( $\eta$ )	0.3	-
Void fraction ( $\varepsilon$ )	0.4	-

## ASPEN Plus eSER reactor Modelling

The single eSER reactor is modelled assuming an input-output model that reproduces the time-average yields of all the species; these are computed by integrating the temporal flow profiles, predicted by the 1-D dynamic reactor model, of the species entering and exiting the reactor and ratioing them to the time on stream and by calculating the global heat demand for the eSER process (for the sorbent calcination and heating the reactor) by performing an enthalpy balance across the reactor. Except for the CO<sub>2</sub>, the specific yield of each component per mole of feed is calculated by integrating over time the outlet molar flow rate computed using the 1-D heterogenous model of from the start of feeding (time = 0) to the breakthrough time (time = BTt), Equation A1.

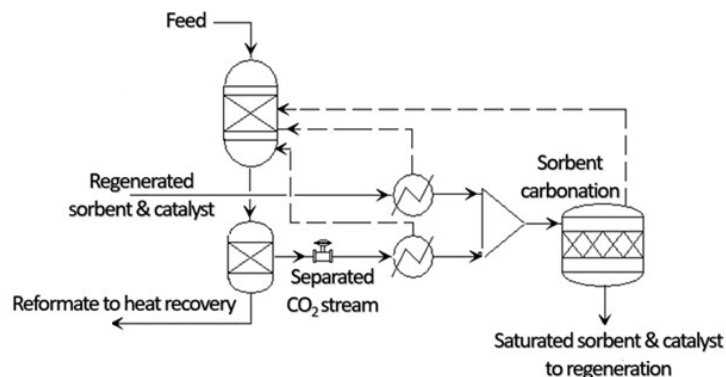
$$\text{Integral yield of species } i = \frac{\int_0^{BTt} \dot{n}_i^{gas\ out} dt}{\int_0^{BTt} \dot{m}_{total}^{gas\ in} dt} \quad i \neq CO_2 \quad (A1)$$

The specific yield of CO<sub>2</sub> of the SER reactor (Equation A2) is calculated by the summation of the integral of the CO<sub>2</sub> flow rate over the breakthrough time and the amount of CO<sub>2</sub> trapped in the reactor as converted CaO assuming that the SER stage begins with fully regenerated sorbent.

$$\text{Integral yield of } CO_2 = \frac{\int_0^{BTt} \dot{n}_{CO_2}^{gas\ out} dt + \int_0^L n_{CaCO_3}(BTt) dz}{\int_0^{BTt} \dot{m}_{total}^{gas\ in} dt} \quad (A2)$$

As presented in **Figure A1**, the solids (catalyst, fresh sorbent, and inerts) are modelled as virtual flows with a mass flowrate calculated as the mass of the reactor stock divided by the breakthrough time and a temperature assumed equal to the regeneration temperature. The virtual solid flows are then cooled down to the average bed temperature at the breakthrough time, calculated as shown in Equation A3, and then are mixed with a CO<sub>2</sub> stream that has a molar flow rate equivalent to the value of converted CaO moles in the 1D reactor model. The mixture is sent to stoichiometric reactor to ensure the carbonation reaction between the CO<sub>2</sub> and the sorbent. The heat of reaction from the stoichiometric reactor and the heat removed from the solids and the separated CO<sub>2</sub> stream are sent to the eSER yield reactor to close the enthalpy balance.

$$\text{Bed Temp} = \frac{\int_0^L m_{sorb}^{(BTt)} Cp_{sorb}^{(BTt)} T_{sorb}^{(BTt)} dz + \int_0^L m_{cat} Cp_{cat} T_{cat}^{(BTt)} dz}{\int_0^L (m_{sorb}^{(BTt)} Cp_{sorb}^{(BTt)} + m_{cat} Cp_{cat}) dz} \quad (A3)$$



**Figure A1 ASPEN eSER reactor model**

Table A2 shows an example of the errors generated in the material and the enthalpy balances. Regarding the material flows, an error of 0.34% is calculated comparing the reformat stream in the Aspen model to the outlet stream of the 1D reactor model. With except to the CO<sub>2</sub>, an error of 0.30% is calculated for all the species. It is worth mentioning that even though the relative difference of the amount of uncaptured CO<sub>2</sub> exiting the eSER reactor in the Aspen model reaches 5%, the absolute difference in terms of molar flow rate of CO<sub>2</sub> is small compared to the total carbon fed to the plant making the effect on the overall performance indicator negligible.

**Table A2 Example of the calculated variations in the material and enthalpy flows comparing the steady state ASPEN model and the 1D dynamic heterogeneous reactor model**

<b>Material Flows</b>					
		Inlet	1-D reactor model Outlet	Aspen Outlet	Error
CH <sub>4</sub>	[kmol/h]	287.58	8.60	8.62	0.30%
C <sub>2</sub> H <sub>6</sub>	[kmol/h]	22.22	0	0	-
C <sub>3</sub> H <sub>8</sub>	[kmol/h]	3.18	0	0	-
H <sub>2</sub> O	[kmol/h]	1646.26	997.91	1000.89	0.30%
H <sub>2</sub>	[kmol/h]	0.00	1276.74	1280.54	0.30%
CO	[kmol/h]	0.00	22.24	22.30	0.30%
CO <sub>2</sub>	[kmol/h]	7.60	15.98	16.93	5.94%
Total flows	[kmol/h]	1966.84	2321.47	2329.28	0.34%
<b>Overall Carbon Balance</b>			1-D reactor model	Aspen	
Inlet gas flow rate	[kmol C/h]		349.19	349.19	
Outlet gas flow rate	[kmol C/h]		46.81	47.85	
CaCO <sub>3</sub> equivalent flow rate	[kmol /h]		298.68	302.38	
Reactor stock at breakthrough time	[kmol C/h]		2.21	-	
Carbon Balance	[kmol C/h]		1.50	-1.04	
Error			0.43%	-0.30%	
<b>Enthalpy Flows</b>					
			1-D reactor model	Aspen	Error
Inlet	[MW]		-106.81	-106.91	0.10%

Outlet	[MW]	-52.42	-52.57	0.29%
--------	------	--------	--------	-------

---

### Economic Model:

The baseline equipment cost  $c_p^0$  is calculated as presented in Equation A4. Where, A is the scale parameter while k1, k2, and k3 are fitting parameters as reported in Table A3.

$$\log_{10} [c_p^0] = k_1 + k_2 \log_{10} A + k_3 [\log_{10} A]^2 \quad (\text{Equation A4})$$

The bare module equipment cost  $C_{BM}$  is calculated using Equation A5. Where,  $F_{BM}$  is the bare module factor that considers the equipment construction material and the direct and indirect project costs as reported in Table A3.

$$C_{BM} = F_{BM} \cdot c_p^0 \quad (\text{Equation A5})$$

The bare module equipment cost  $C_{BM}$  is further modified to take into account contingency and contractor fee, which are assumed to be 18% of the bare module cost <sup>2</sup>.

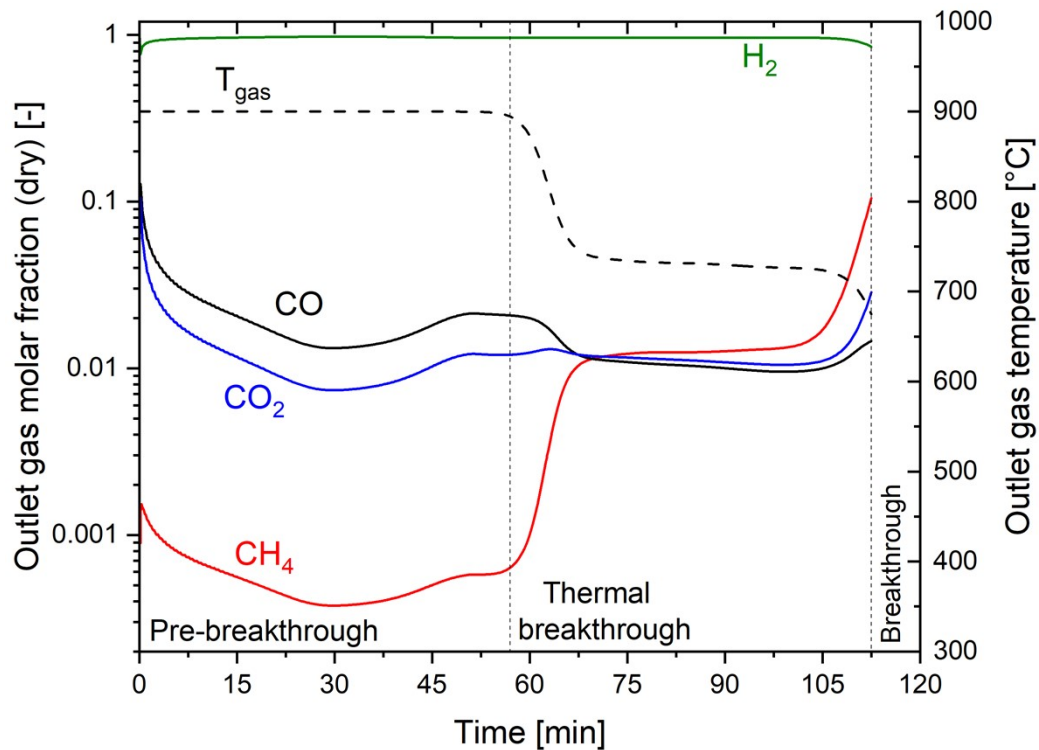
**Table A3 Cost function parameters for calculating the CAPEX of the eSER plants <sup>3</sup>**

Item	Type	Scale parameter	k <sub>1</sub>	k <sub>2</sub>	k <sub>3</sub>	F <sub>bm</sub>	Ref. CEPCI
Air blower	Centrifugal Fan	Flow rate	3.539	-0.353	0.448	2.7	397
Syngas/ CO <sub>2</sub> compressors	Centrifugal Compressor	Fluid power	2.290	1.360	-0.103	2.7	397
Water /CO <sub>2</sub> pumps	Centrifugal Pump	Shaft power	3.389	0.054	0.154	3.2	397
Electric driver	Explosion Proof Drive	Shaft power	2.460	1.419	-0.180	1.5	397
Heat exchangers	Fixed tube	Area	4.831	-0.851	0.319	3.9	397
Steam generators	Steam boiler	Heat duty	6.962	-1.480	0.316	5.8	397

**Table A4 Scaling function parameters for calculating the CAPEX of the eSER plants <sup>4</sup>**

Item	Scale parameter	Reference size	Reference Cost	Scaling exponent	Ref. CEPCI
Sulfur guard bed	Natural gas mass flow rate	17.7 kg/s	1.5 M€	0.67	709
Pressure Swing Adsorber	H <sub>2</sub> mass flow rate	5.6 k/s	22.7 M€	0.67	576.5

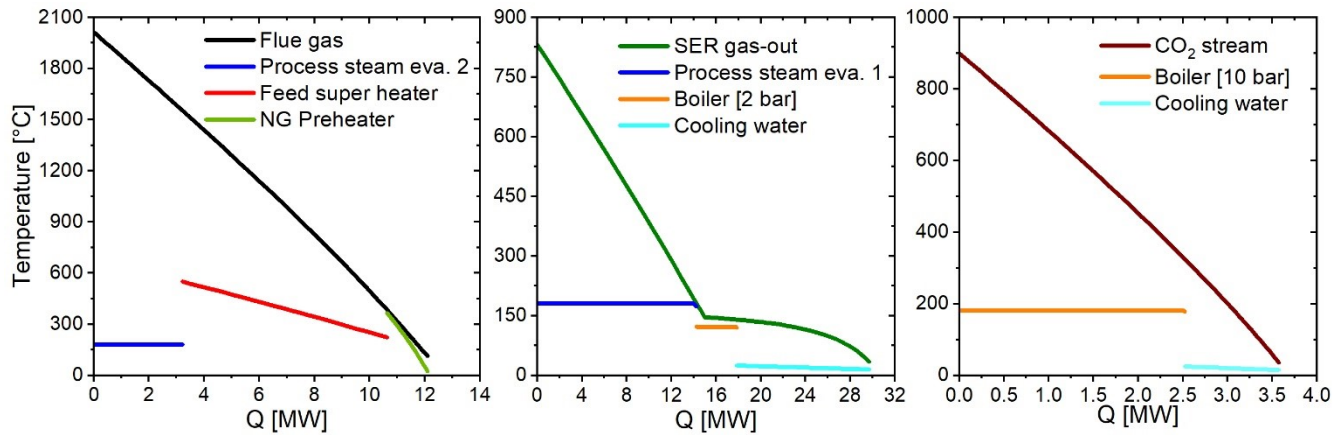
## Section B: Base case simulation results



**Figure B1 breakthrough curves of the SER step for the base case plant (Figure 3). Working conditions:  $P=10$  bar;  $S/C=4.8$ ;  $T_{\text{feed}}=550^{\circ}\text{C}$ ;  $T_{\text{bed,initial}}=900^{\circ}\text{C}$ . Left axis: solid lines: Reactor outlet species mole fractions (dry basis), Green:  $\text{H}_2$ , Red:  $\text{CH}_4$ , Blue:  $\text{CO}_2$ , and Black:  $\text{CO}$ . Right axis: Dashed line: Reactor outlet gas stream temperature.**

**Table B1 Base case plant (Figure 3) streams properties**

#	T [°C]	P [bar]	m [kg/s]	n [kmol/h]	Molar composition [%]									
					CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub> O	
1	25	10	1.60	330.2	89.0	7.0	1.0	0	0	2.0	0	1.0	0	
2	15	1	3.26	651.8	0	0	0	0	0	0	0	0	100	
3	30	10	4.98	994.5	0	0	0	0	0	0	0	0	100	
4	365	10	1.60	330.2	89.0	7.0	1.0	0	0	2.0	0	1.0	0	
5	182	10	8.24	1646.3	0	0	0	0	0	0	0	0	100	
6	550	10	9.84	1976.5	14.7	1.1	0.1	0	0	0.4	0	0.1	84.0	
7	831	10	6.14	2329.3	0.4	0	0	54.9	0.9	0.7	0	0.1	43.0	
8	35	10	1.17	1337.8	0.6	0	0	95.9	1.6	1.2	0	0.2	0.5	
9	107	30	0.65	1152.5	0	0	0	100	0	0	0	0	0	
10	107	1	0.51	181.6	4.8	0	0	70.0	12.2	9.2	0	1.8	2.0	
11	20	1	3.98	497.5	0	0	0	0	0	0	21.0	79.0	0	
12	2003	1	4.49	604.9	0	0	0	0	0	7.9	2.0	65.3	24.8	
13	104	1	4.49	604.9	0	0	0	0	0	7.9	2.0	65.3	24.8	
14	900	1	3.69	302.3	0	0	0	0	0	100	0	0	0	
15	38	110	3.69	302.3	0	0	0	0	0	100	0	0	0	
16	124	2	1.55	310.0	0	0	0	0	0	0	0	0	100	
17	182	10	1.20	240.0	0	0	0	0	0	0	0	0	100	



**Figure B2 TQ diagrams for Base case plant (Figure 3)**

## Section C: Equivalent CO<sub>2</sub> emissions

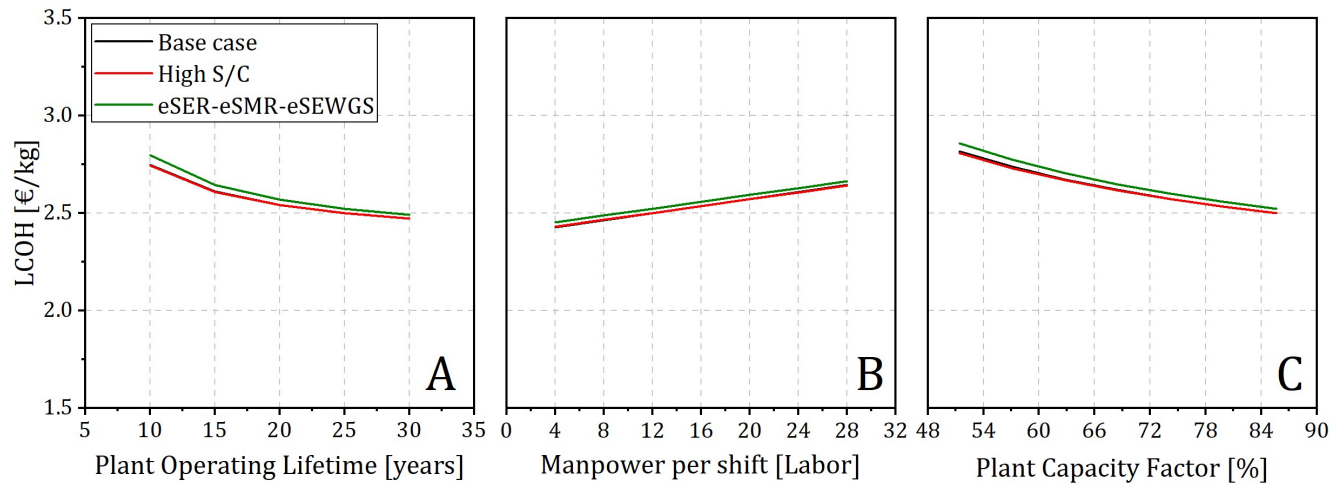
**Table C1 Equivalent CO<sub>2</sub> emissions (E<sub>CO<sub>2</sub>,eq</sub>) considering 50 kgCO<sub>2</sub>/MWh electric consumed**

		eSER Plants								Ref. Plants					
		Base case		High Pressure		Vaccum Regen.		High S/C		eSER-eSMR - eSEWGS		FTR		FTR Plus	
		GWP20	GWP100	GWP20	GWP100	GWP20	GWP100	GWP20	GWP100	GWP20	GWP100	GWP20	GWP100	GWP20	GWP100
Including no CH <sub>4</sub> leakage*	kg <sub>CO<sub>2</sub> eq</sub> /kg <sub>H<sub>2</sub></sub>	1.52		1.60		1.73		1.30		0.92		1.94		0.91	
Including 0.5% CH <sub>4</sub> leakage**	kg <sub>CO<sub>2</sub> eq</sub> /kg <sub>H<sub>2</sub></sub>	2.54	1.89	2.66	1.98	2.80	2.12	2.30	1.66	1.92	1.28	3.34	2.43	2.39	1.44
Including 1.5% CH <sub>4</sub> leakage**	kg <sub>CO<sub>2</sub> eq</sub> /kg <sub>H<sub>2</sub></sub>	4.60	2.63	4.79	2.86	4.93	2.89	4.32	2.39	3.92	2.00	6.17	3.45	5.35	2.51

\* Electrolysis with 65% H<sub>2</sub> production efficiency have a E<sub>CO<sub>2</sub>,eq</sub> of 2.56 kg<sub>CO<sub>2</sub> eq</sub>/kg<sub>H<sub>2</sub></sub> considering the same CIGrid.

\*\* Considering 82.5 kg<sub>CO<sub>2</sub> eq</sub>/kg<sub>CH<sub>4</sub></sub> estimated over 20 years (GWP20) and 29.8 kg<sub>CO<sub>2</sub> eq</sub>/kg<sub>CH<sub>4</sub></sub> estimated over 100 years (GWP100) <sup>5</sup>.

## Section D: Sensitivity of LCOH to Selected Assumptions



**Figure D1 Effect of A) plant operation lifetime, B) Manpower per shift, and C) Plant capacity factor on the levelized cost of hydrogen for the base case, high S/C, and eSER-eSMR-eSEWGS arrangement**



## References

- 1 A. Mostafa, I. Rapone, A. Bosetti, M. C. Romano, A. Beretta and G. Groppi, *Int. J. Hydrogen Energy*, 2023, **48**, 26475–26491.
- 2 R. Turton, *Analysis, Synthesis, and Design of Chemical Processes Fourth Edition*, 2013, vol. 53.
- 3 R. Turton, R. C. Bailie, W. B. Whiting, J. A. Shaeiwitz and D. Bhattacharyya, *Analysis, Synthesis, and Design of Chemical Processes*, 2001, vol. 40.
- 4 A. de Cataldo, M. Astolfi, P. Chiesa, S. Campanari, E. Martelli, P. Silva, S. Bedogni, L. Ottolina, M. Tappani and M. C. Romano, *J. Eng. Gas Turbines Power*, 2023, **145**, 1–9.
- 5 M. C. Romano, C. Antonini, A. Bardow, V. Bertsch, N. P. Brandon, J. Brouwer, S. Campanari, L. Crema, P. E. Dodds, S. Gardarsdottir, M. Gazzani, G. Jan Kramer, P. D. Lund, N. Mac Dowell, E. Martelli, L. Mastropasqua, R. C. McKenna, J. G. M. S. Monteiro, N. Paltrinieri, B. G. Pollet, J. G. Reed, T. J. Schmidt, J. Vente and D. Wiley, *Energy Sci. Eng.*, 2022, **10**, 1944–1954.