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Protocols and performance indicators for reporting on and benchmarking solar thermochemical fuel production reactors

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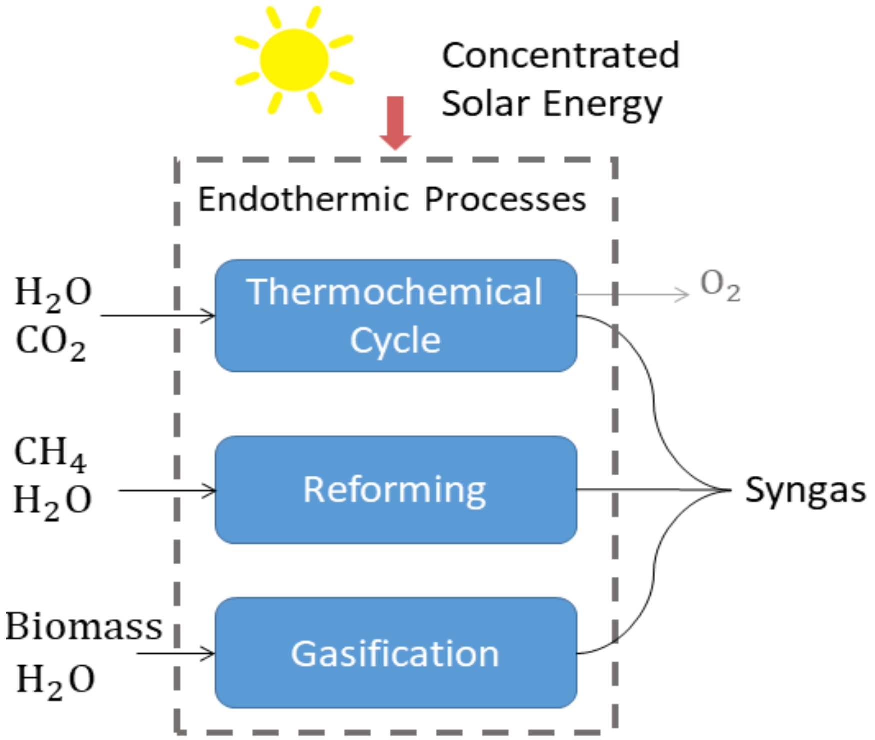
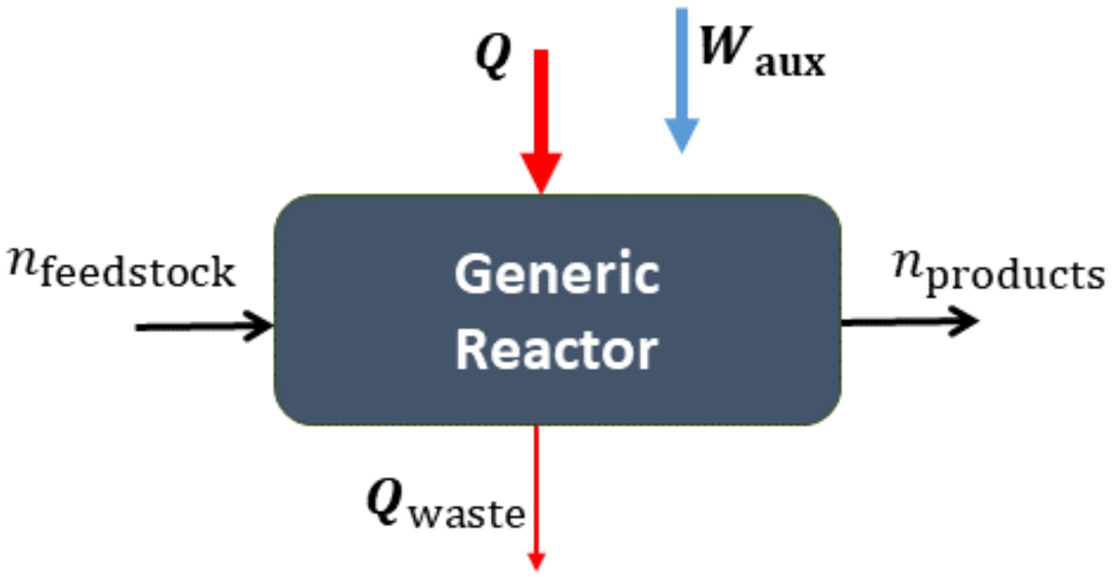
Solar fuel production processes



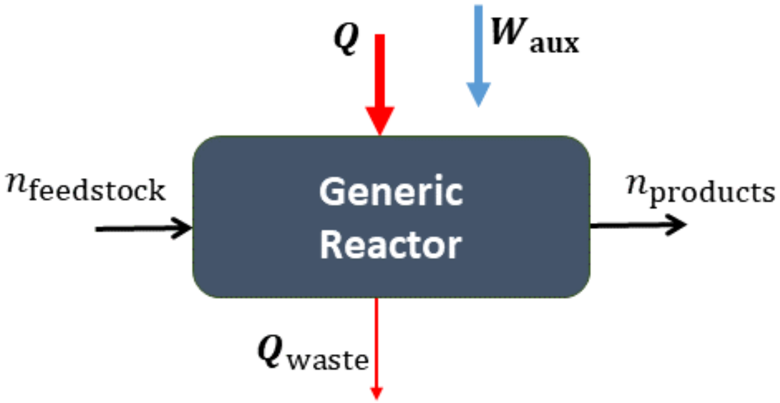
SFERA III: task 8.2 – propose standard protocols and performance indicators for reporting on and benchmarking solar fuel production reactors.

Generic fuel production reactor



The system has an energy and mass flow, and we need performance indicators for both.

Energy balance – Efficiency

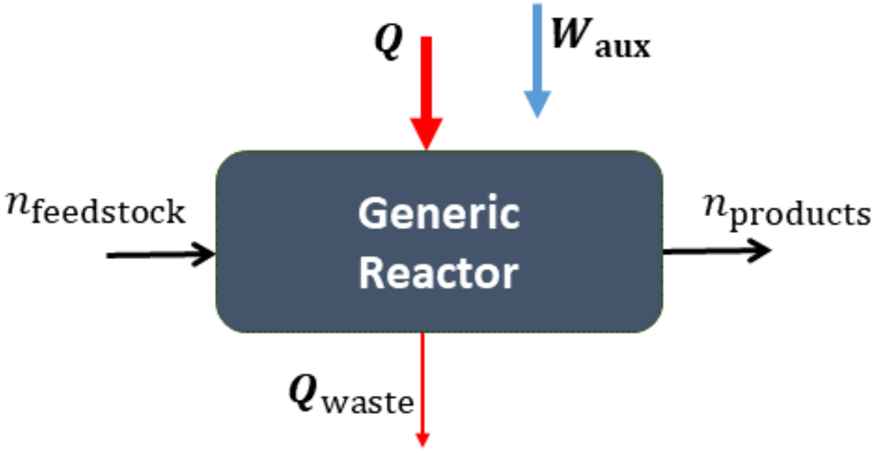


$$\eta = 1 - \frac{Q_{\text{waste}}}{E_{\text{total}}} \tag{1}$$

$$E_{\text{total}} = Q + Q_{\text{aux}} \;\text{ and }\; Q_{\text{aux}} = \frac{W_{\text{aux}}}{\eta_{\text{heat-to-work}}}$$

A generic energy efficiency, but in experiments we rarely measure Q_{waist} directly.

Efficiency – Second Law Definition



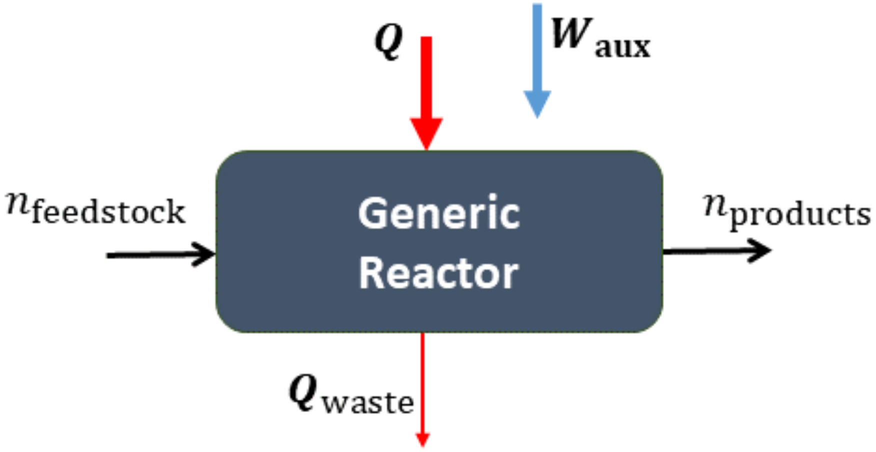
$$\eta = \frac{\sum_i^{\text{products}} \mathrm{n_i} G_\mathrm{i} - \sum_i^{\text{feedstock}} \mathrm{n_i} G_\mathrm{i}}{E_\text{total}} \quad (3)$$

$$\eta_\text{max} = \left(1 - \frac{\sigma T_\mathrm{H}^4}{IC}\right)\left(1 - \frac{T_\mathrm{L}}{T_\mathrm{H}}\right)$$

This equation was often used by Fletcher. ΔG_process is the chemical work done.

Noring, J. E., & Fletcher, E. A. (1982). High temperature solar thermochemical processing—hydrogen and sulfur from hydrogen sulfide. Energy, 7(8), 651-666.

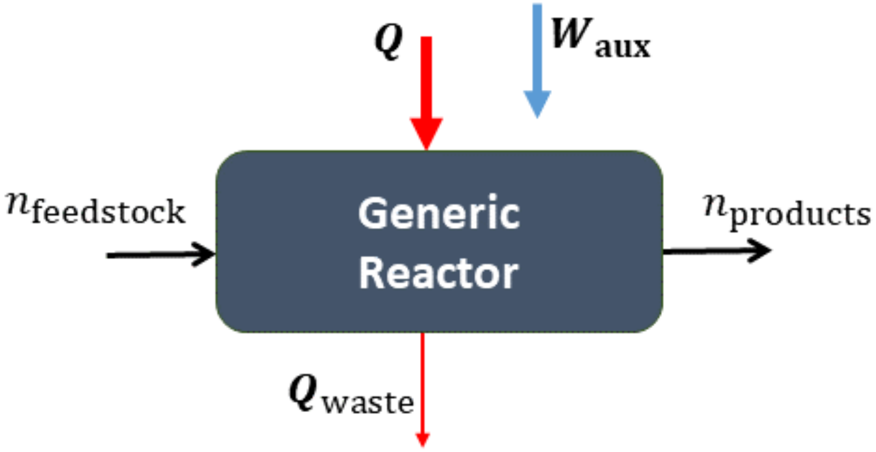
Efficiency – First Law Definition



$$\eta = \frac{\sum_i^{products} n_i HHV_i - \sum_i^{feedstock} n_i HHV_i}{E_{total}} \quad (5)$$

$$\eta_{max} = \left(1 - \frac{\sigma T_H^4}{IC}\right)\left(1 - \frac{T_L}{T_H}\right)$$

Efficiency – First Law Definition number 2



$$\eta = \frac{\sum_i^{\text{products}} \mathrm{n_i HHV_i}}{E_{\text{total}}} \qquad (6)$$

$$E_{\text{total}} = Q + Q_{\text{aux}} + \sum_i^{\text{reactants}} \dot{n}_{\mathrm{i}} \mathrm{HHV_i}$$

Efficiency definitions in the literature

Reference	Process	Equation*	LHV/HHV	W_{aux}/Q_{aux}
Bhosale et. al. 2017	Thermochemical cycle	(5) or (6)	HHV	Q
Bhosale 2019	Thermochemical cycle	(5) or (6)	HHV	Q
Binnoti et. al. 2017	Thermochemical cycle	(5) or (6)	HHV	Q
Bulfin et. al. 2016	Thermochemical cycle	(5) or (6)	HHV	Q
Chuayboon et. al. 2019 July	Gasification	(6)	LHV	-
Chuayboon et. al. 2019	Reforming	other	LHV	-
Falter 2017	Thermochemical cycle	(5) or (6)	HHV	Q
Falter et. al. 2017	Thermochemical cycle	(5) or (6)	HHV	Q
Fletcher & Moen 1977	Thermolysis	(3)	-	-
Gokon et. al. 2014	Gasification	(5)	-	-
Hathaway et. al. 2017	Gasification	(6)	LHV	-
Hathaway et. al. 2016	Thermochemical cycle	(5) or (6)	HHV	Q
Jin et. al. 2015	Reforming	(5)	-	-
Koepf et. al. 2016	Thermochemical cycle	(5) or (6)	-	W
Kong et. al. 2016	Reforming	(5)	HHV	-
Kong et. al. 2018	Thermochemical cycle	(5) or (6)	HHV	Q
Lapp et. al. 2012	Thermochemical cycle	(5) or (6)	HHV	Q
Marxer et. al. 2017	Thermochemical cycle	(5) or (6)	HHV	Q
Müller et. al. 2017	Gasification	(6)	LHV	-
Müller et. al. 2018	Gasification	(6)	LHV	-
Muroyama et. al. 2018	Gasification	(6)	LHV	-
Palumbo et. al. 2015	Reforming/Gasification	(6)	LHV	-
Piatowski et. al. 2011	Gasification	(6)	LHV	-
Yuan et. al. 2015	Thermochemical cycle	(5) or (6)	HHV	W
Z'Graggen et. al. 2006	Gasification	(5)	-	-
Z'Graggen et. al. 2008	Gasification	(5)	-	-
Zheng et. al. 2015	Reforming	(5)	HHV	-
Zhu et. al. 2016	Membrane reactor	other	HHV	-
Zoller et. al. 2019	Thermochemical cycle	(5) or (6)	HHV	Q

Mass balance – Conversion extent

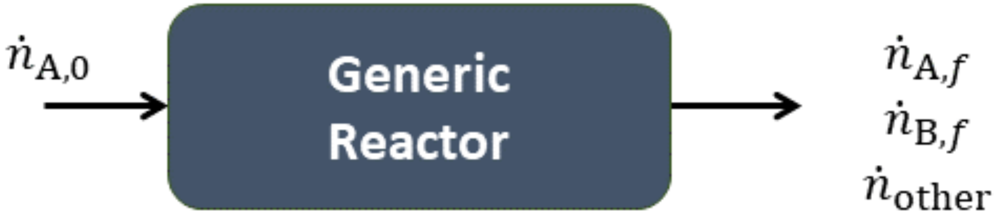
$$A \rightarrow B \qquad (1)$$

$$X_{\mathrm{A}} = 1 - \frac{\dot{n}_{\mathrm{A},f}}{\dot{n}_{\mathrm{A},0}}$$

For mass balance we can use the standard definitions from chemical engineering.

Levenspiel, O. (2001). Chemical Reaction Engineering 3rd edition John Willey and Sons.

Mass balance – Selectivity



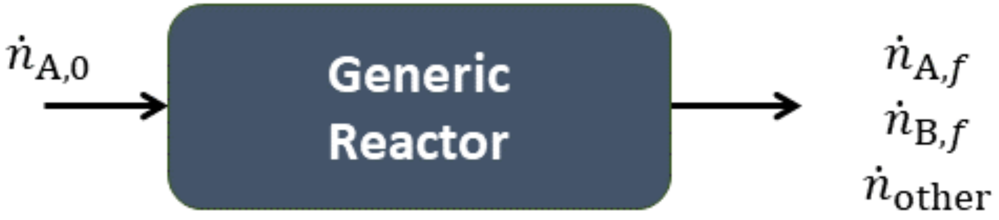
$$A \rightarrow B \qquad (1)$$

$$S_{\mathrm{B}} = \frac{\dot{n}_{\mathrm{B},f}}{\dot{n}_{\mathrm{A},0} - \dot{n}_{\mathrm{A},f}}$$

For mass balance we can use the standard definitions from the literature.

Levenspiel, O. (2001). Chemical Reaction Engineering 3rd edition John Willey and Sons.

Mass balance – Yeild



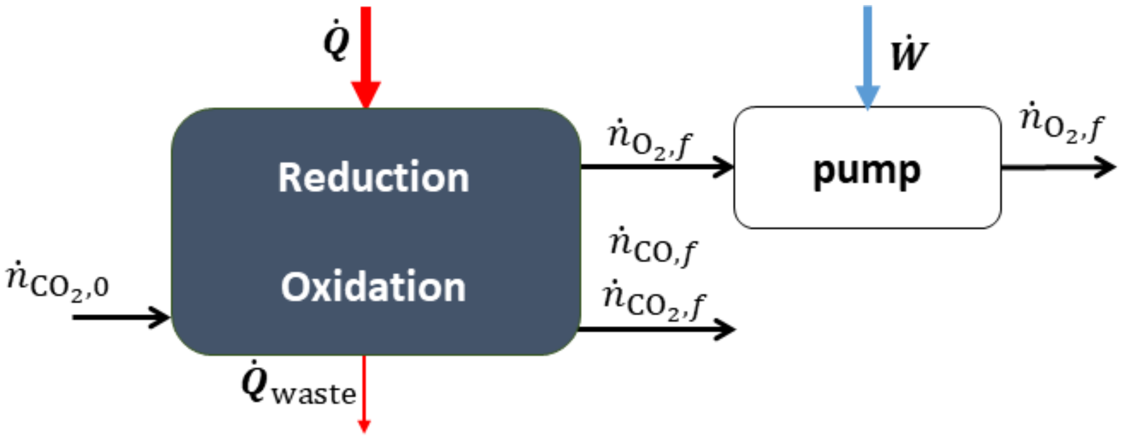
$$A \rightarrow B \qquad (1)$$

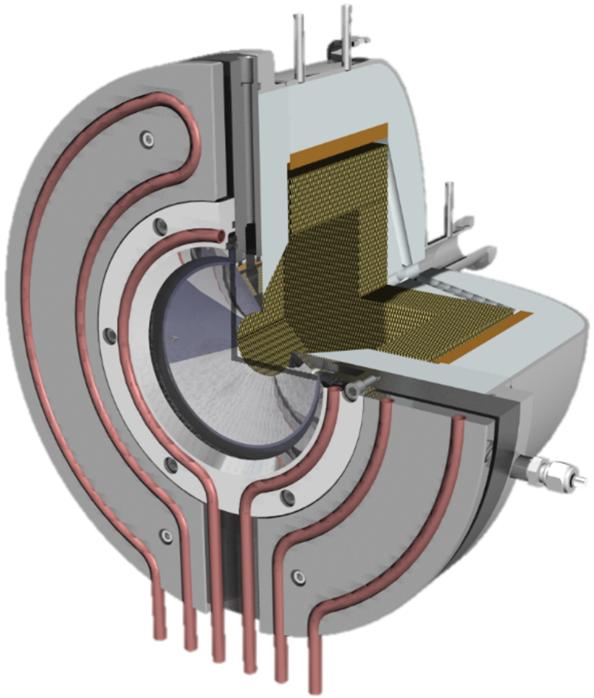
$$Y_B = X_A S_B = \frac{\dot{n}_{B,f}}{\dot{n}_{A,0}}$$

For mass balance we can use the standard definitions from the literature.

Levenspiel, O. (2001). Chemical Reaction Engineering 3rd edition John Willey and Sons.

Thermochemical redox cycles - STCH



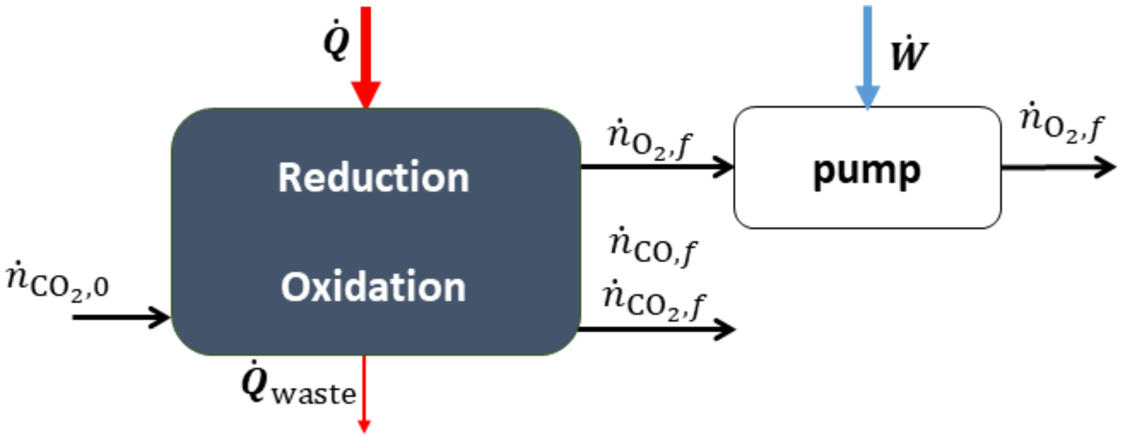


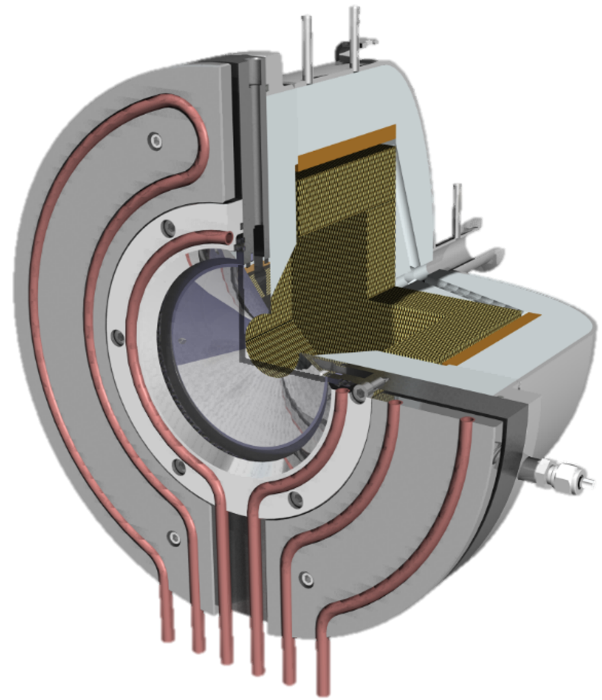
$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2$$

$$MO_{x-\delta} + CO_2 \rightarrow MO_x + CO$$

$$MO_{x-\delta} + H_2O \rightarrow MO_x + H_2$$

Thermochemical redox cycles - STCH



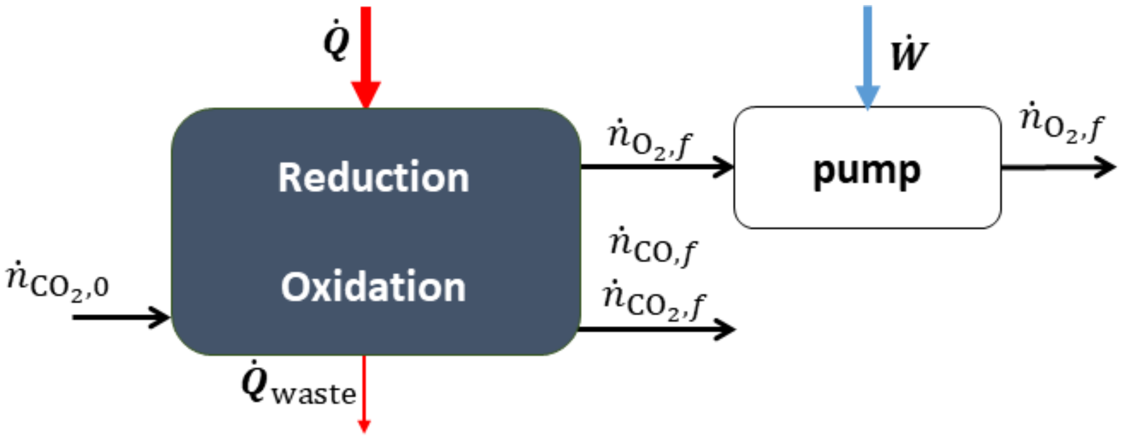


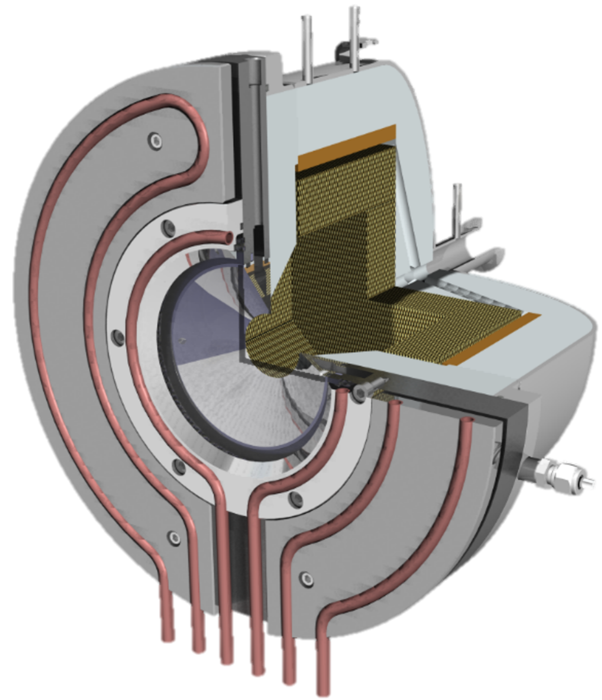
$$\eta = \frac{\mathrm{HHV_{CO}} \int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO}}(t)\,\mathrm{d}t}{\int_0^{t_{\mathrm{cycle}}} \dot{Q}(\mathrm{t}) + \dot{Q}_{\mathrm{aux}}(t)\ \ \mathrm{d}t}$$

$$X_{\mathrm{CO_2}} = 1 - \frac{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO_2},f}\,\mathrm{d}t}{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO_2},0}\,\mathrm{d}t}$$

$$\mathrm{S_{CO}} = \frac{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO},f}\,\mathrm{d}t}{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO_2},0} - \dot{n}_{\mathrm{CO_2},f}\,\mathrm{d}t}$$

Thermochemical redox cycles - STCH



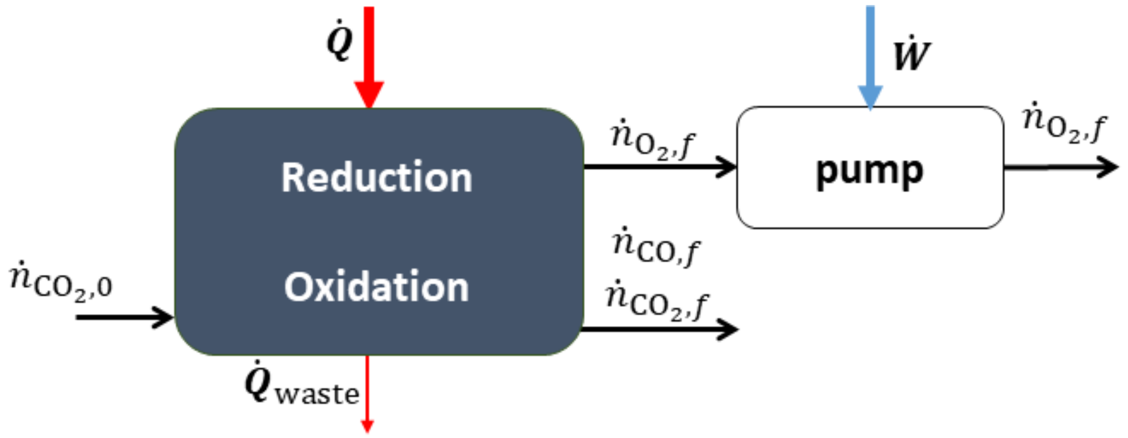


$$\eta = \frac{\mathrm{HHV_{CO}} \int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO}}(t)\,\mathrm{d}t}{\int_0^{t_{\mathrm{cycle}}} \dot{Q}(\mathrm{t}) + \dot{Q}_{\mathrm{aux}}(t)\ \mathrm{d}t}$$

$$X_{\mathrm{CO_2}} = 1 - \frac{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO_2},f}\,\mathrm{d}t}{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO_2},0}\,\mathrm{d}t}$$

$$\mathrm{S_{CO}} = \frac{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO},f}\,\mathrm{d}t}{\int_0^{t_{\mathrm{cycle}}} \dot{n}_{\mathrm{CO_2},0} - \dot{n}_{\mathrm{CO_2},f}\,\mathrm{d}t}$$

The importance of conversion extent



STCH
$X \approx 0.01$

- Want 10 MW output $\dot{n}_{H_2} \approx 35 \text{ mol s}^{-1}$.
- $\dot{n}_{H_2O} \approx 3500 \text{ mol s}^{-1}$
- If reactor is at 1 bar and 1173 K, $\dot{v} = \frac{\dot{n}_{H_2O} RT}{p} = 341.4 \text{ m}^3 \text{ s}^{-1}$
- Residence time 1 second $\Rightarrow V_{reactor} = 340 \text{ m}^3$

Summary of proposed reporting protocols

The dimensioned parameters required to described the reactor system are:

1. The reactor volume and free volume.
2. Mass loading of any catalyst or cycled redox material.
3. The operating conditions of the reactor (e.g. temperature, pressure, *etc.)*.
4. The molar/mass flow rates of feedstock into the reactor.
5. The total heat supply to the reactor, Q (e.g. solar heat, etc.)
6. Auxiliary work demands, W_{aux}, (e.g. pumping work, inert gas production, *etc.)*

Summary of proposed reporting protocols and performance indicators

Performance indicators:

1. The energy efficiency $\eta = \frac{\mathrm{HHV_{products}}}{\mathrm{HHV_{reactants}}+Q+Q_{\mathrm{aux}}}$

2. The conversion extent of the feedstock, $X_{\mathrm{A}} = 1 - \frac{\dot{n}_{\mathrm{A},f}}{\dot{n}_{\mathrm{A},0}}$.

3. The selectivity towards the desired product $S_{\mathrm{B}} = \frac{\dot{n}_{\mathrm{B},f}}{\dot{n}_{\mathrm{A},0}-\dot{n}_{\mathrm{A},f}}$, and the yield of the desired product $Y_{\mathrm{B}} = \frac{\dot{n}_{\mathrm{B},f}}{\dot{n}_{\mathrm{A},0}}$ if the selectivity is not reported.

4. Performance stability, *i.e.* report the above indicators over time during a test campaign.

Summary of proposed reporting protocols and performance indicators

Reactor type	Efficiency η	Conversion extent X_i	Selectivity (or Yield) S (or Y)
Thermochemical redox CO_2 splitting	$\frac{\mathrm{HHV_{CO}} \int_0^{t_\mathrm{cycle}} \dot{n}_\mathrm{CO}(t)\,\mathrm{d}t}{\int_0^{t_\mathrm{cycle}} \dot{Q}(\mathrm{t}) + \dot{Q}_\mathrm{aux}(t)\,\mathrm{d}t}$	$1 - \frac{\int_0^{t_\mathrm{cycle}} \dot{n}_{\mathrm{CO_2},f}\,\mathrm{d}t}{\int_0^{t_\mathrm{cycle}} \dot{n}_{\mathrm{CO_2},0}\,\mathrm{d}t}$	$\frac{\int_0^{t_\mathrm{cycle}} \dot{n}_{\mathrm{CO},f}\,\mathrm{d}t}{\int_0^{t_\mathrm{cycle}} \dot{n}_{\mathrm{CO_2},0} - \dot{n}_{\mathrm{CO_2},f}\,\mathrm{d}t}$
Solar methane reforming	$\frac{\sum_i^{\mathrm{products}} \dot{n}_\mathrm{i}\mathrm{HHV_i}}{\dot{n}_{\mathrm{CH_4},0}\mathrm{HHV_{CH_4}} + \dot{Q}}$	$1 - \frac{\dot{n}_{\mathrm{CH_4},f}}{\dot{n}_{\mathrm{CH_4},0}}$	$\frac{\dot{n}_{\mathrm{CO},f}}{\dot{n}_{\mathrm{CH_4},0} - \dot{n}_{\mathrm{CH_4},f}}$
Biomass gasification	$\frac{\sum_i^{\mathrm{gas-products}} \dot{m}_\mathrm{i}\mathrm{HHV_i}}{\dot{m}_\mathrm{biomass}\,\mathrm{HHV_{biomass}} + \dot{Q}}$	$1 - \frac{\dot{m}_\mathrm{C-residue}}{\dot{m}_\mathrm{C,0}}$	$(Y_\mathrm{syngas} = \frac{\sum_i^{\mathrm{gases}} \nu_{i,C}\dot{n}_\mathrm{i,gas}}{\dot{n}_\mathrm{C,0}})$
Generic A → B	$\frac{\dot{n}_\mathrm{B}\mathrm{HHV_B}}{\dot{n}_\mathrm{A}\mathrm{HHV_A} + \dot{Q} + \dot{Q}_\mathrm{aux}}$	$1 - \frac{\dot{n}_{A,f}}{\dot{n}_\mathrm{A,0}}$	$\frac{\dot{n}_{\mathrm{B},f}}{\dot{n}_\mathrm{A,0} - \dot{n}_{\mathrm{A},f}}$

Acknowledments

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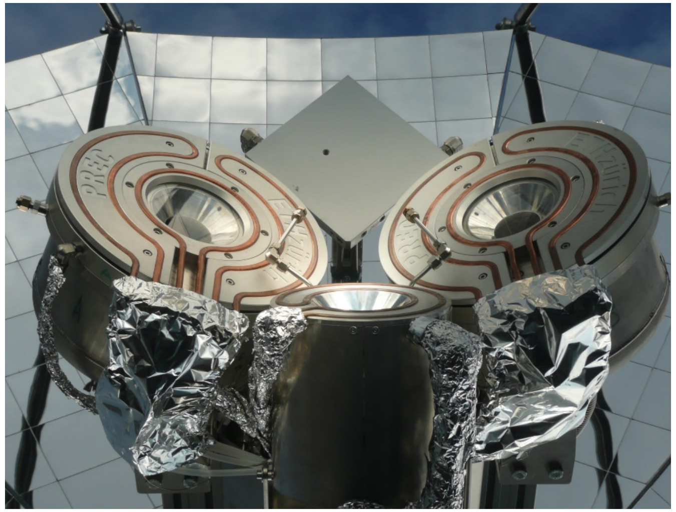
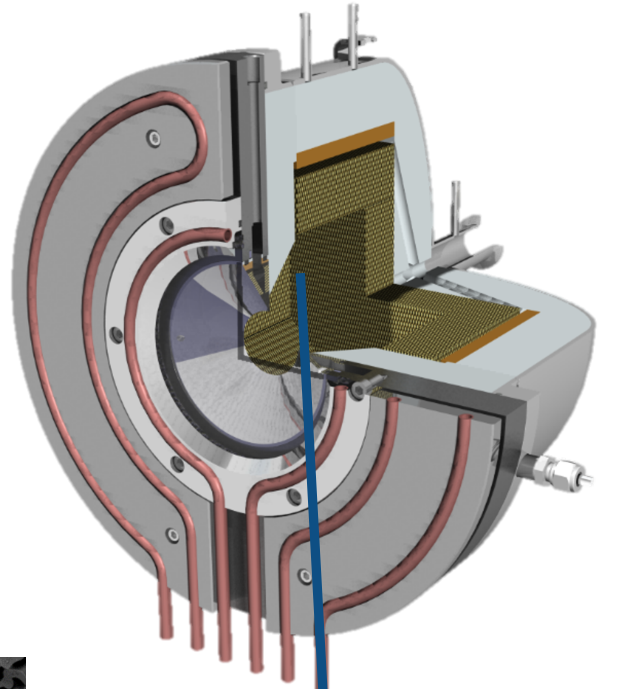
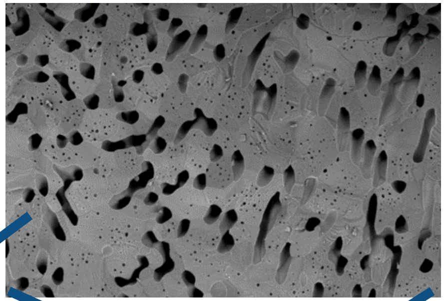
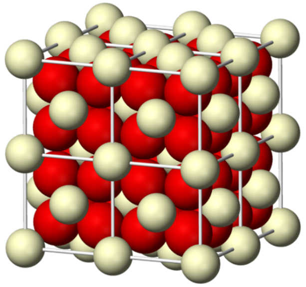
Application – Thermochemical Fuel Production – $CeO_{2-\delta}$

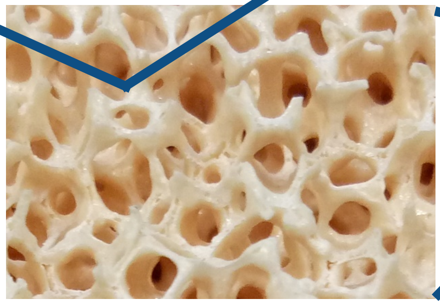


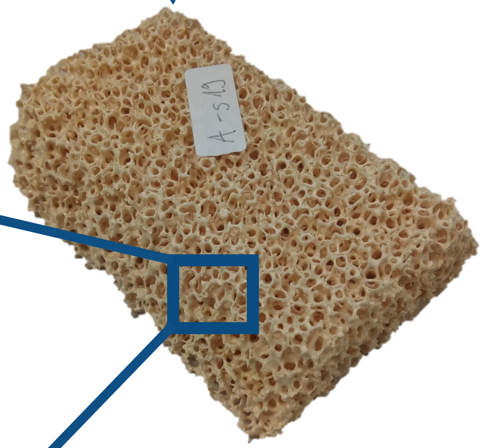




CeO_2







Process chain to solar fuels