Operation And Optimization Options Of Integrated System Of Reactor Modules For Solar Energy Conversion Into Chemicals

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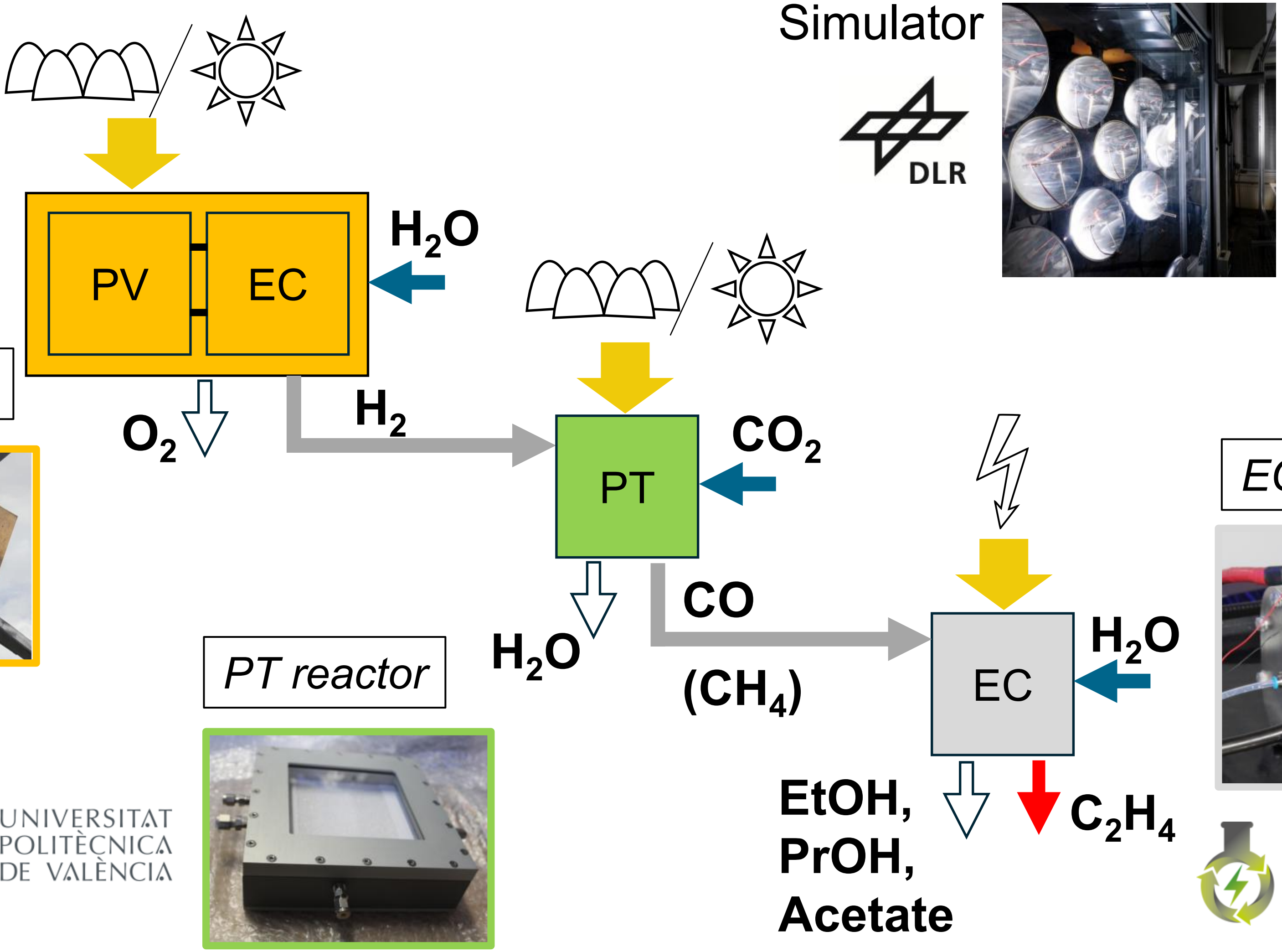
DLR

Outline

- Introduction of reactor modules & integrated system
- Experimental results
- Discussion on improvement options
- Summary

Integrated system demonstrator: Reactor modules and light source

High-Flux Solar Simulator



PEC reactor

EPFL

SoHHytec

PT reactor

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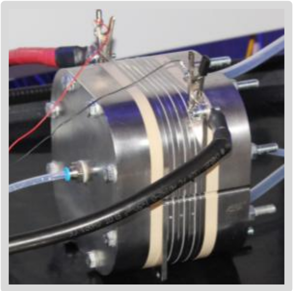
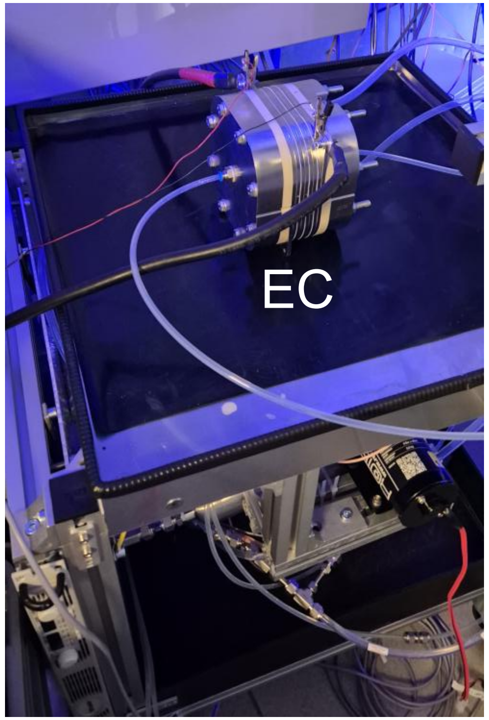
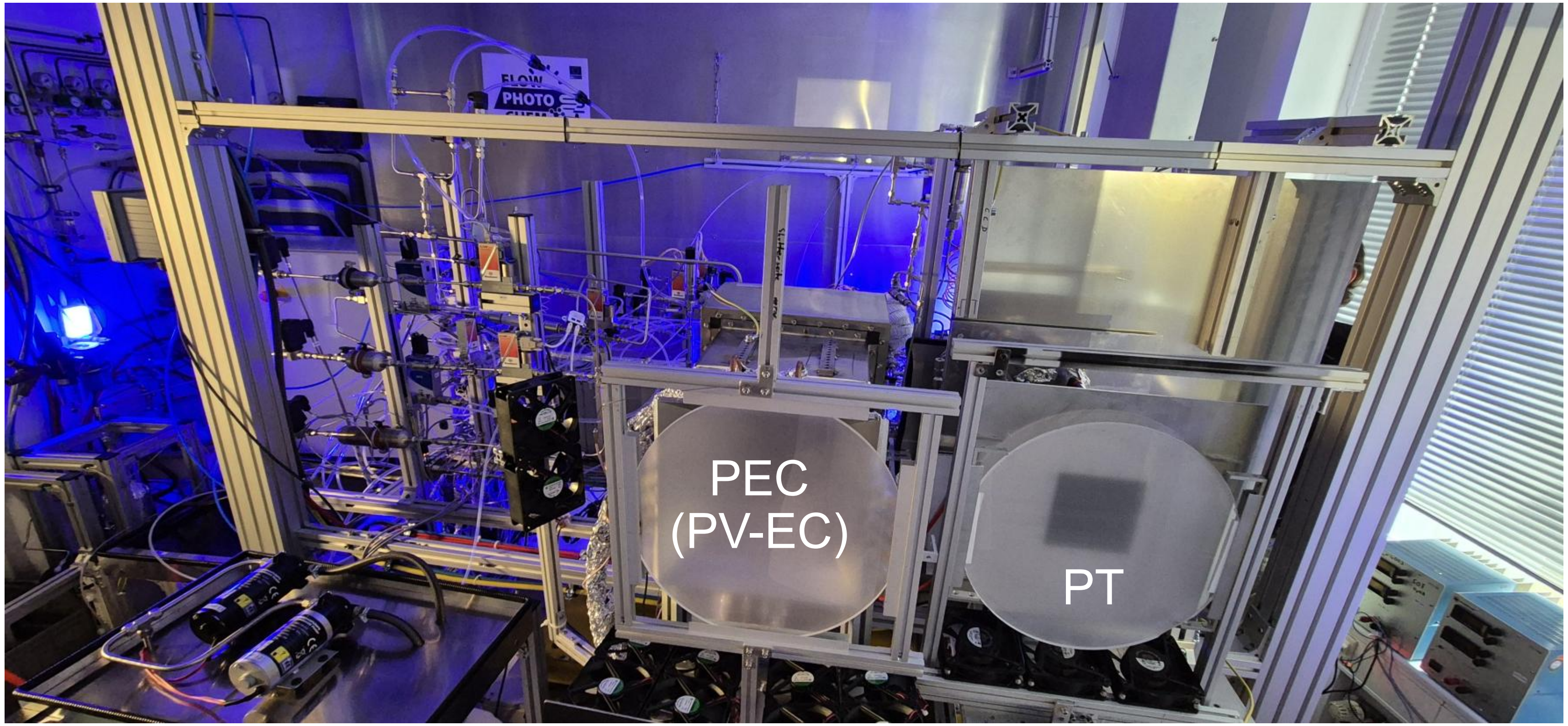
EC reactor



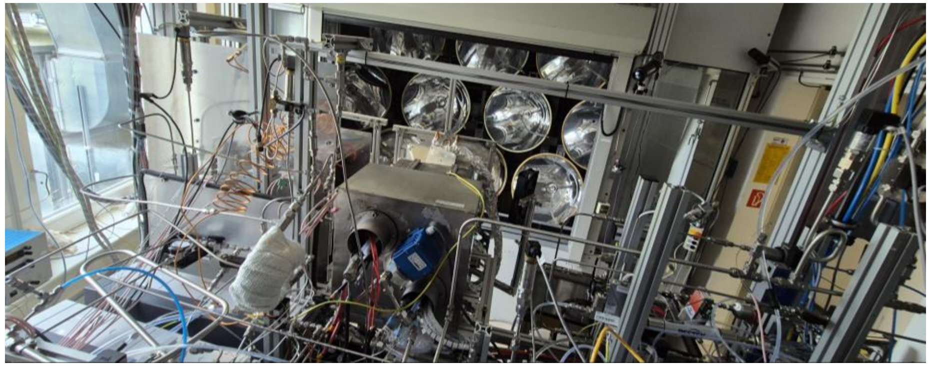
eChemicles

Reactor modules & test rig: Illustrations





Operating durations:
- PEC: 24.3 h
- PT: 21.8 h
- EC: 13.7 h



In DLR‘s High-Flux Solar Simulator

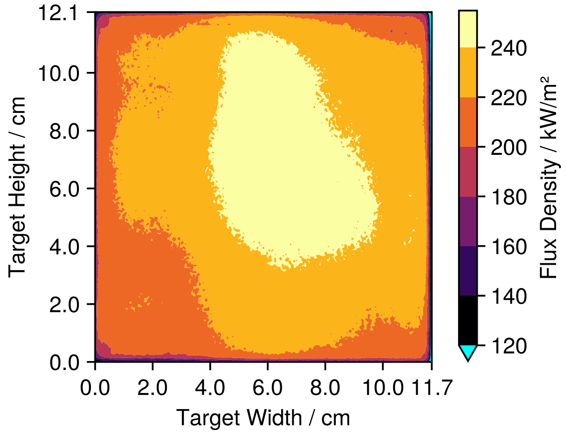
This material is part of an unpublished manuscript to be submitted for publication

Experimental results: Irradiation fluxes on active planes

PEC (8 lamps)

Total power: 3.21 kW
Mean flux: 226.6 kW/m²
Max: 254.9 kW/m²
Min: 67.4 kW/m²

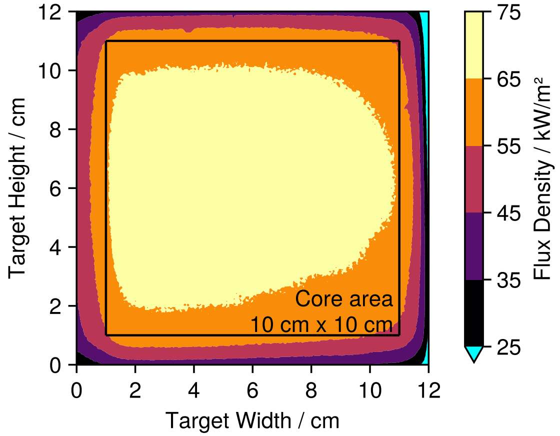
Std. dev.: 18.2 kW/m² / 8.0%

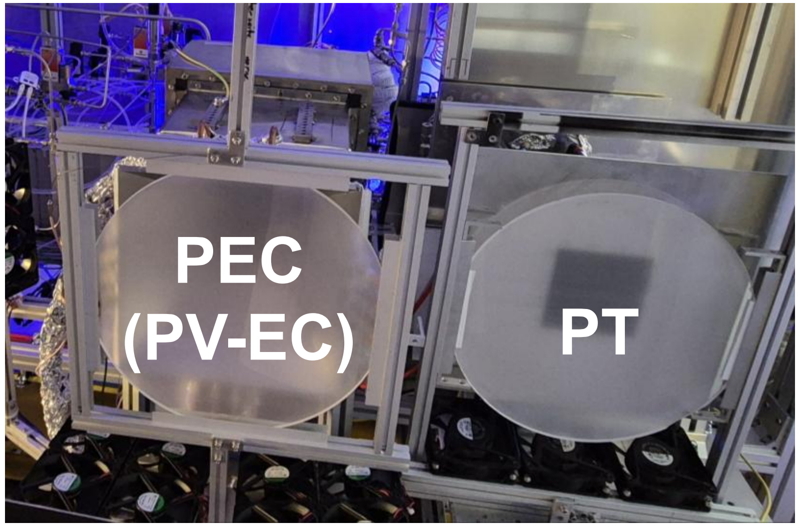


PT* (2 lamps)

Total power: 0.88 kW
Mean flux: 61.3 kW/m²
Max: 71.8 kW/m²
Min: 11.9 kW/m²

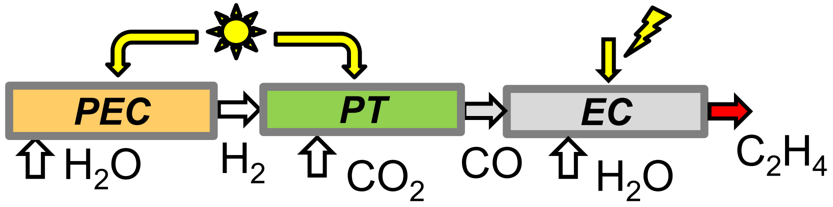
Std. dev.: 9.6 kW/m² / 15.6%





*PT reactor equipped with borosilicate window (transmissivity of 0.84), flux values obtained with window in place

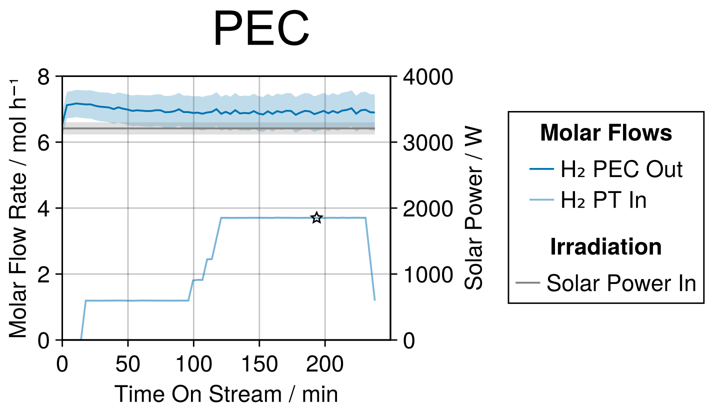
Experimental results: Integrated system

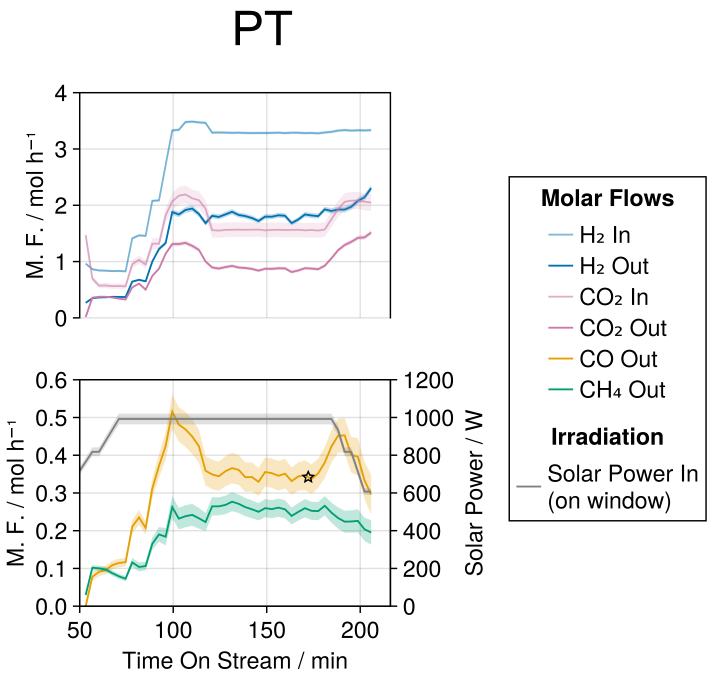


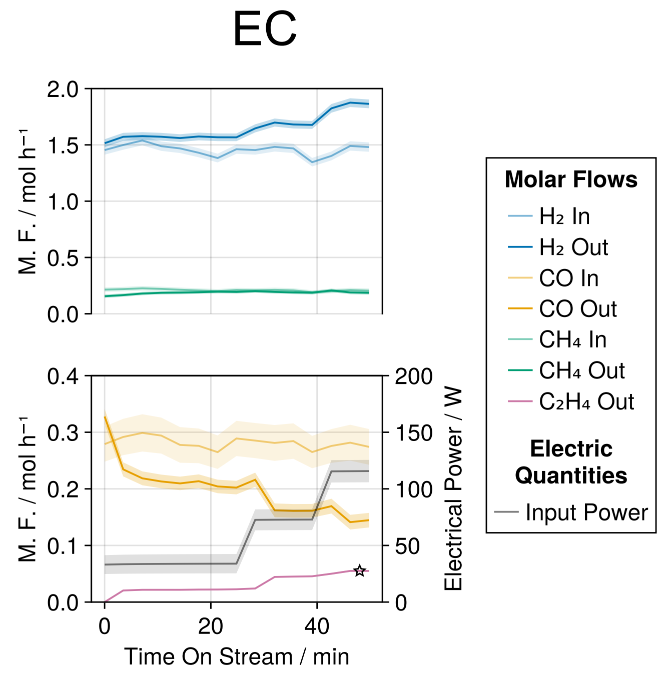
Max. 0.055 mol/h C_2H_4
(= 4.64 kg/a @ 8 h/d)

Efficiencies based on $\Delta h_{\mathrm{R}}^{0}$

- PEC: 17.0% STH
- PT: 0.39% STC (CO)
- EC:
  - 11.2% energetic efficiency (el.)
  - 26.2% FE (C_2H_4)
- STC (C_2H_4) = 0.64%
- STC (C_2H_4, interm.) = 6.8%
- STC (C_2H_4, interm.)* = 9.1%
  *(incl. gas analysis streams)



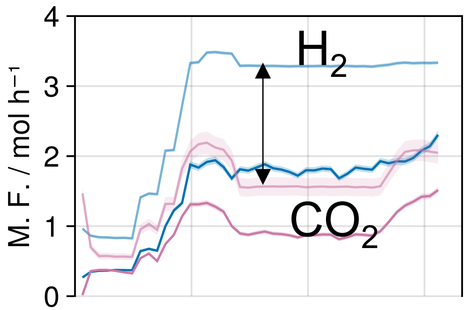


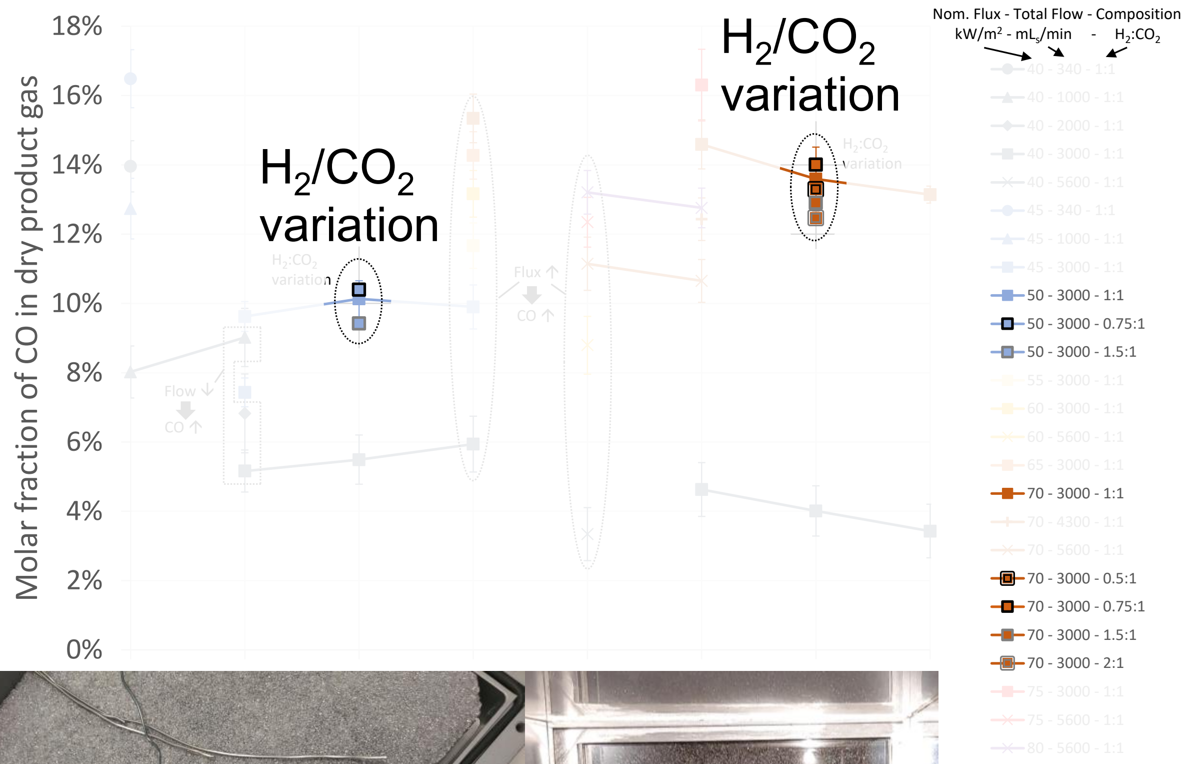


This material is part of an unpublished manuscript to be submitted for publication

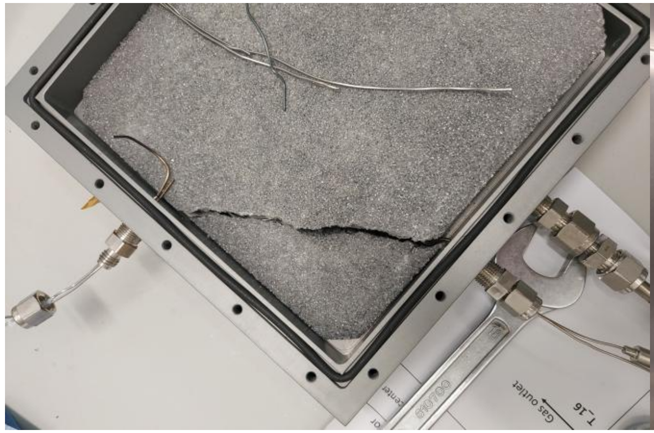
PT reactor: Operational challenges

- Deviation of feed composition
  - $H_2/CO_2 \approx 2/1$ (target: 1/1)
  - Caused by MFC malfunction





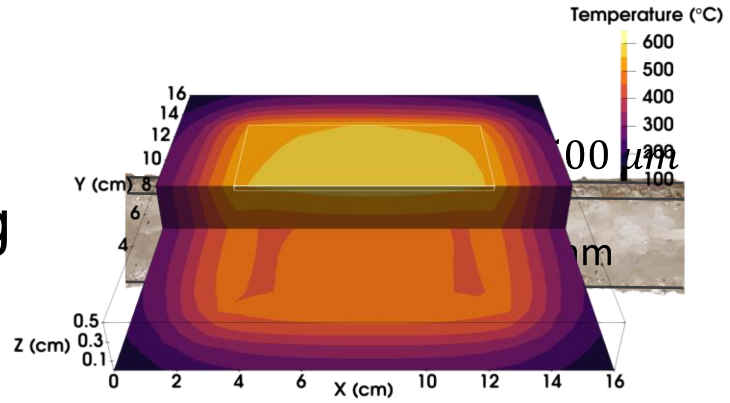
- Crack in catalyst frit
  - Bypass flow reduces conversion

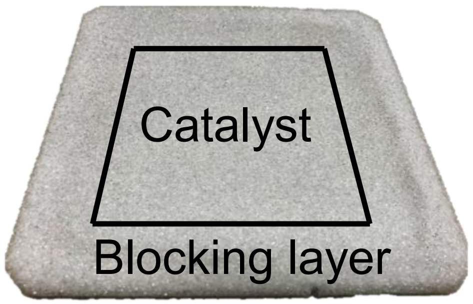


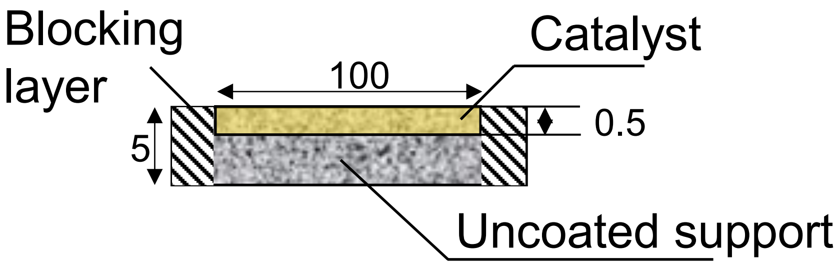
Brust, D. et. al. (2024), Journal of Environmental Chemical Engineering 12 (5), DOI: 10.1016/j.jece.2024.113372.

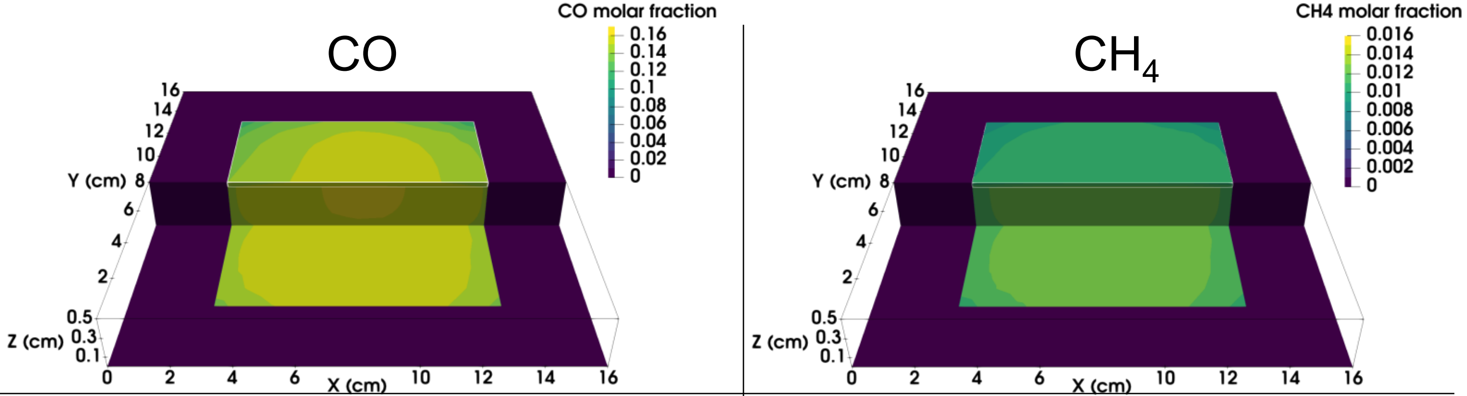
PT reactor: Design optimization

- Vary catalyst deposition depth at const. catalyst mass: 500 mg

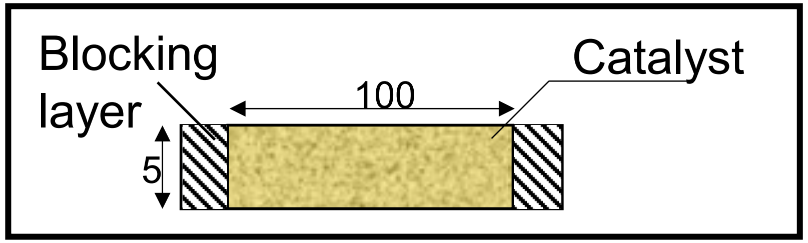


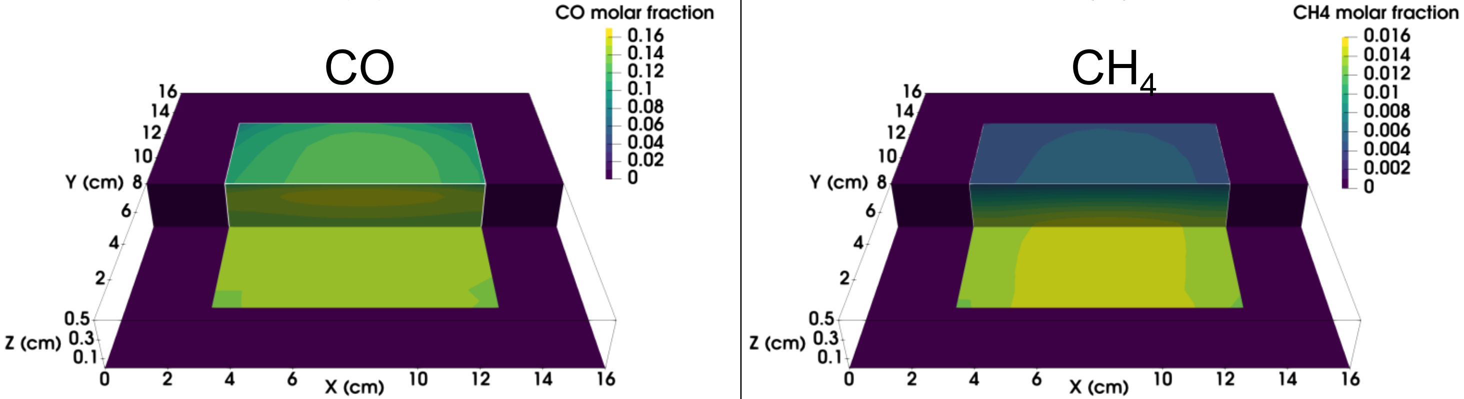






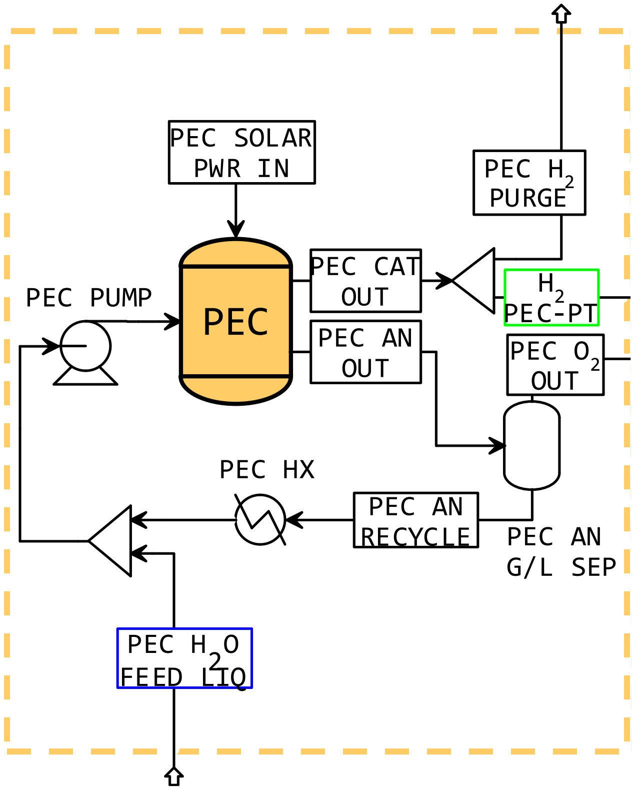
Installed configuration





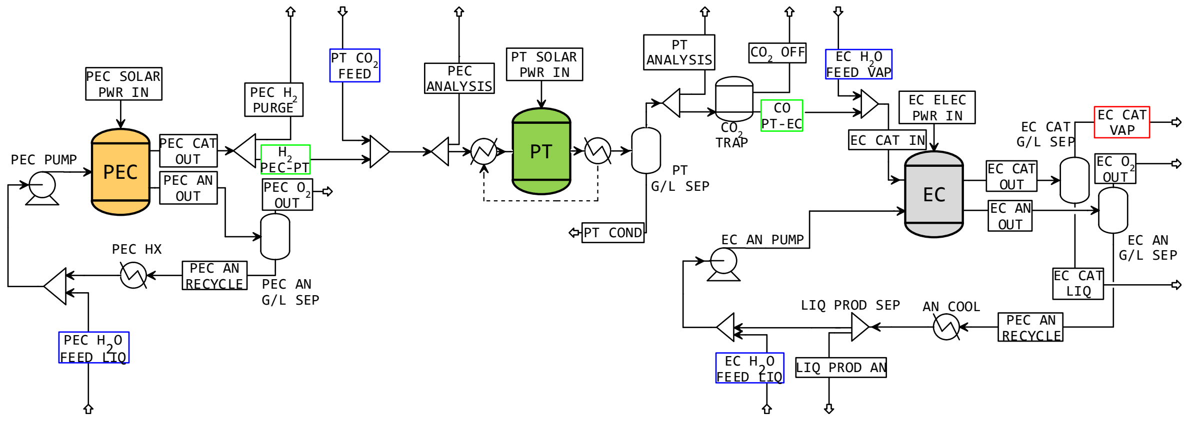
Brust, D. et. al. (2025), Chemical Engineering Journal 516, DOI: 10.1016/j.cej.2025.162027.

Process model on flowsheet level



System model on flowsheet level

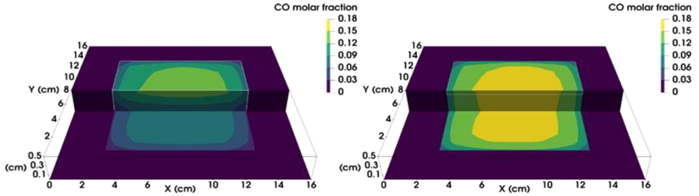
- Flowsheet Simulation implemented in Aspen Custom Modeler® (ACM)
- Custom models of physical reactors (PEC, PT & EC)
  - Model reactor performance as function of operation conditions

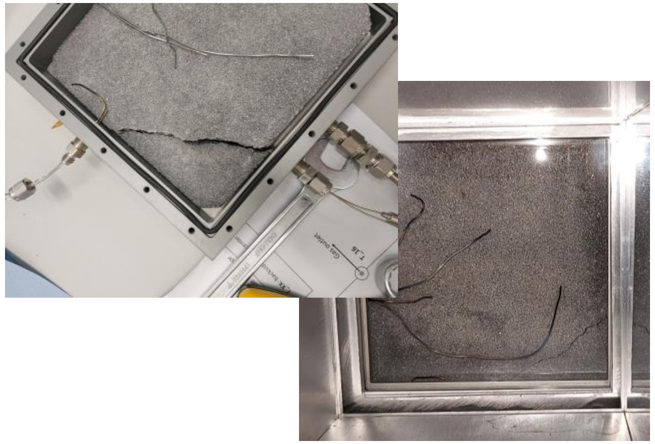


- Balance-of-plant component models (pumps, valves, phase separators, heat exchangers) from ACM database
- Simulate operation of cascade system → Optimize operating conditions for max. system efficiency

Discussion on improvements

- Strategy towards STC improvements





Cracked glass frit

<u>Prompt improvement options</u>

- PT
  - Apply H_2:CO_2 molar ratio of 1:1 in PT feed
  - Reduce thickness of catalyst layer to avoid back reaction of CO
  - No bypass flow through crack in frit (~ 20%)
- PEC
  - Operate at higher irradiation level
- System
  - No streams for gas analysis

System model

<u>Efficiencies</u> based on $\Delta h_{\mathrm{R}}^{0}$

- **STC (C_2H_4): 0.64% → 1.3%**
- **STC (C_2H_4, interm.): 6.8% → 8.7%**

Summary & Outlook

- Integrated cascade system for solar ethylene production demonstrated in a practical environment
- First-time operation of such a reactor cascade (PEC + PT + EC)
- General feasibility of approach confirmed, relevant amounts of ethylene produced at reasonable STC efficiency in a challenging context: 0.64% (C_2H_4) … 6.8% (C_2H_4, interm.)
- Modeling approaches elaborated as a basis to derive strategy towards STC (C_2H_4) efficiency improvements

→Technical refinement will help to increase the performance and stability of the PT reactor & EC reactor under conditions relevant for operation in the integrated system

→Comprehensive system model will be used to further explore system optimization potential (improved heat utilization, recycling of reactants, …)

Q&A

Project video:
https://vimeo.com/1008071679

www.flowphotochem.eu

@flowphotochem

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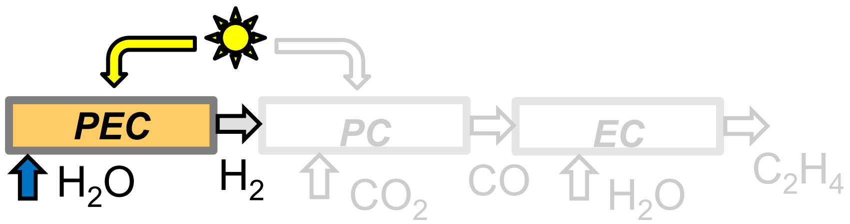
PEC reactor: Background



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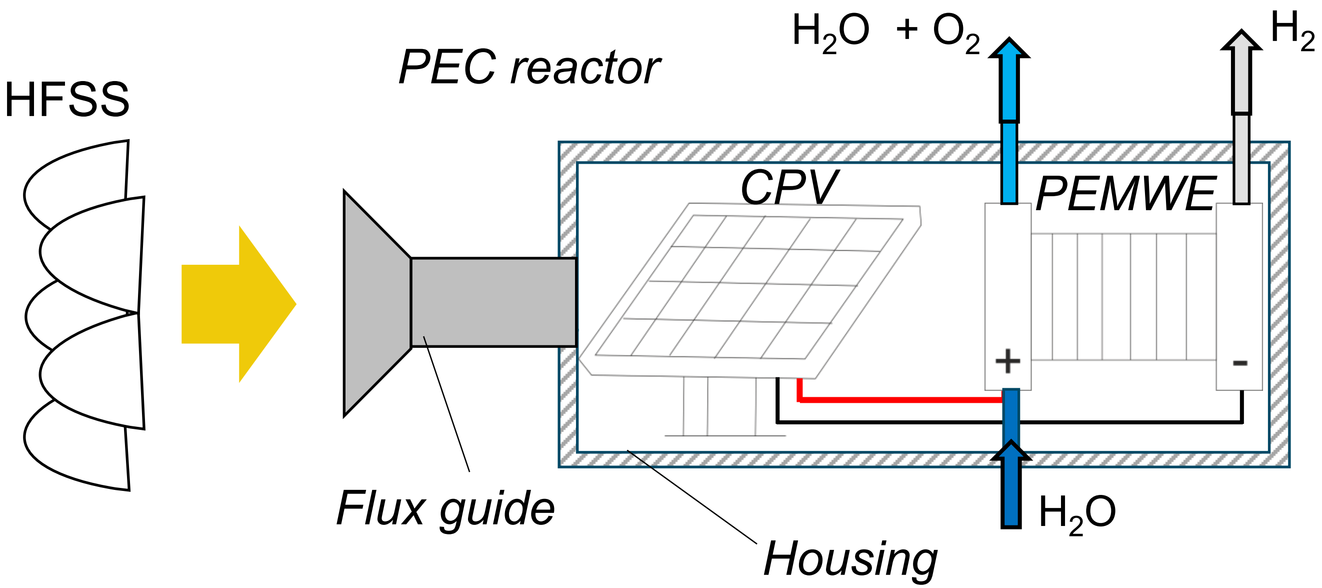
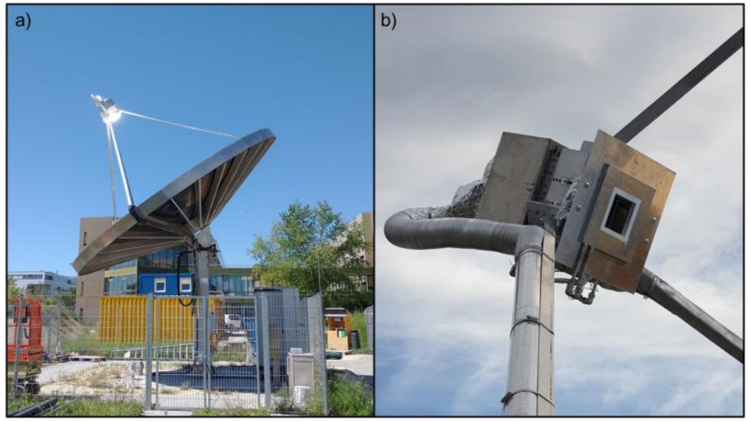
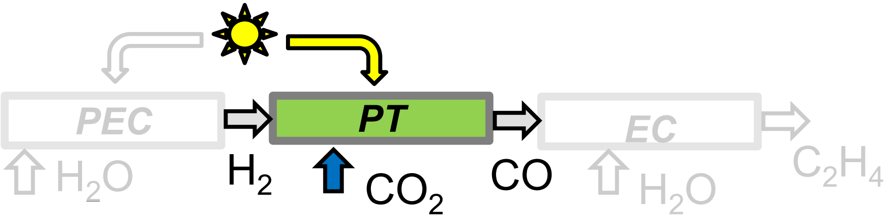




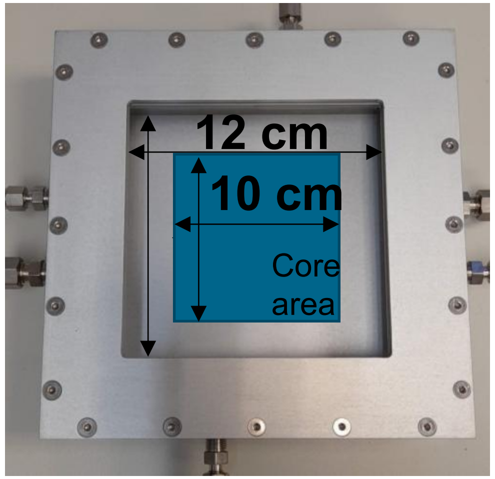
- CPV module
  - $A_{\mathrm{eff}} = 142.4\ \mathrm{cm}^2$
  - $P_{\mathrm{sol,max}} = 10\ \mathrm{kW}\ (C_{\max} = 700)$
- PEMWE stack
  - $A_{\mathrm{eff}} = 1600\ \mathrm{cm}^2$ (32 cells à $50\ \mathrm{cm}^2$)

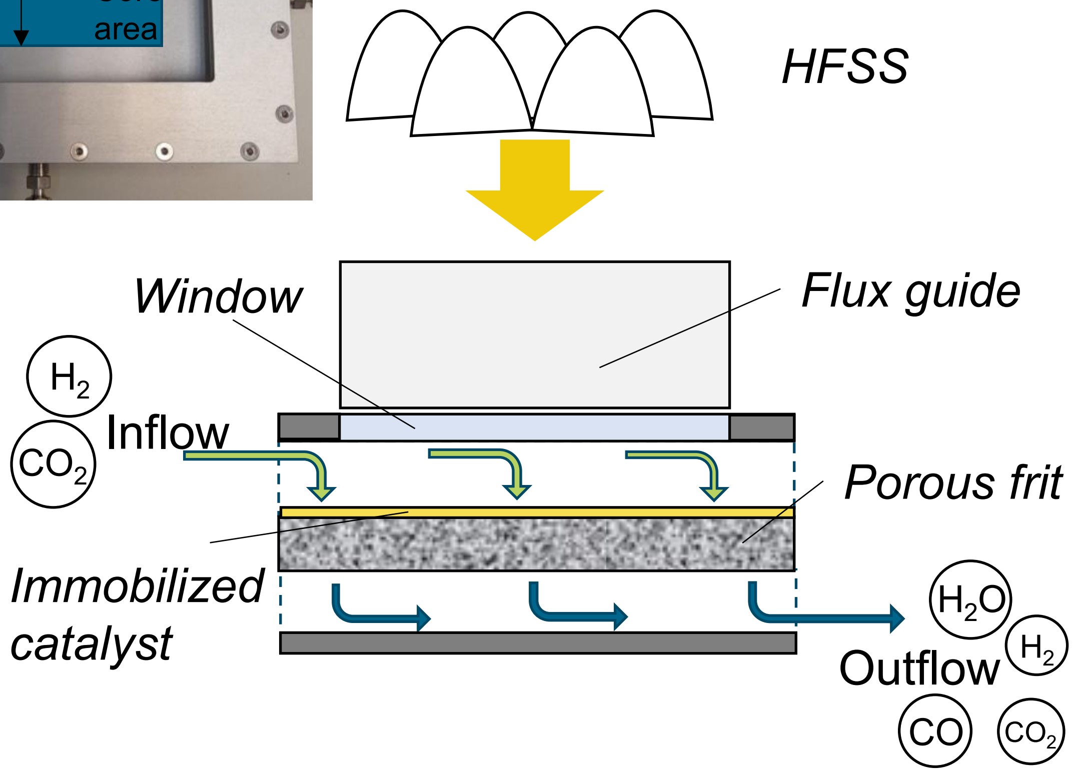
Haussener, S. et. al. (2023), Nature Energy 8 (6). DOI: 10.1038/s41560-023-01247-2.

PT reactor: Background



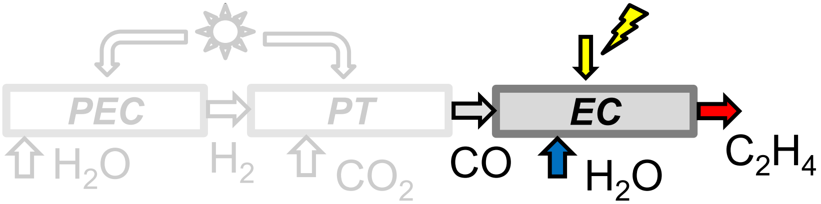
- Hydrogenation of CO_2
  - RWGS: $CO_2 + H_2 \leftrightarrow CO + H_2O$
  - Sabatier: $CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O$ (*unwanted side reaction)
- Heterogeneous Photo-thermal catalysis
  - RuO_2-$SrTiO_3$ catalyst immobilized on porous support, $m_{\mathrm{cat}} = 500\ \mathrm{mg}$
- Solar concentration: 40 – 80 Suns
  - $A_{\mathrm{irr}} = 144\ \mathrm{cm}^2$, (effective: $100\ \mathrm{cm}^2$)
  - $P_{\mathrm{sol,max}} = 1.16\ \mathrm{kW}$





Brust, D. et. al. (2024), Journal of Environmental Chemical Engineering 12 (5), DOI: 10.1016/j.jece.2024.113372.

EC reactor: Background



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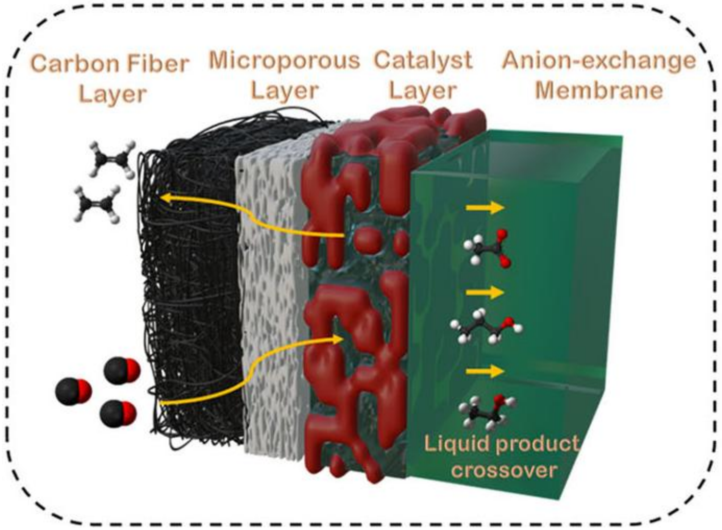
- Zero-gap electrolyser for CO reduction (COR):
  - 3 cell stack with $A_{\mathrm{cell}} = 100\ \mathrm{cm}^2,\ A_{\mathrm{stack}} = 300\ \mathrm{cm}^2$
- Cathode: Cu-based Gas diffusion electrode (GDE)
- Anion-exchange membrane (AEM)
- Anode: Ni-Foam, KOH circulation

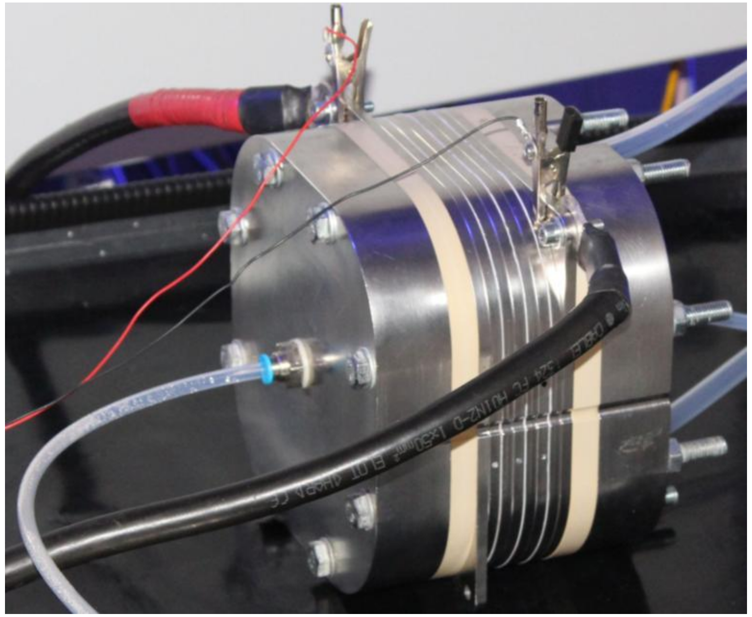


COR products:

FE_i

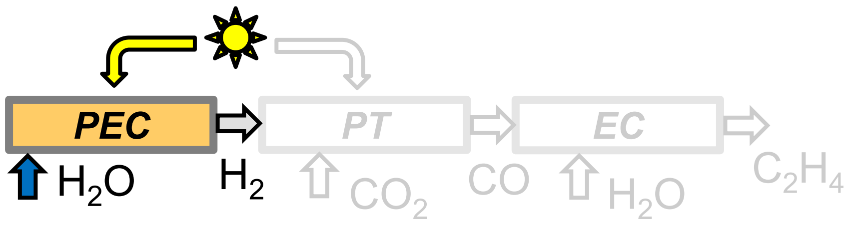
- Ethylene
- Ethanol
- Propanol
- Acetate

- Hydrogen

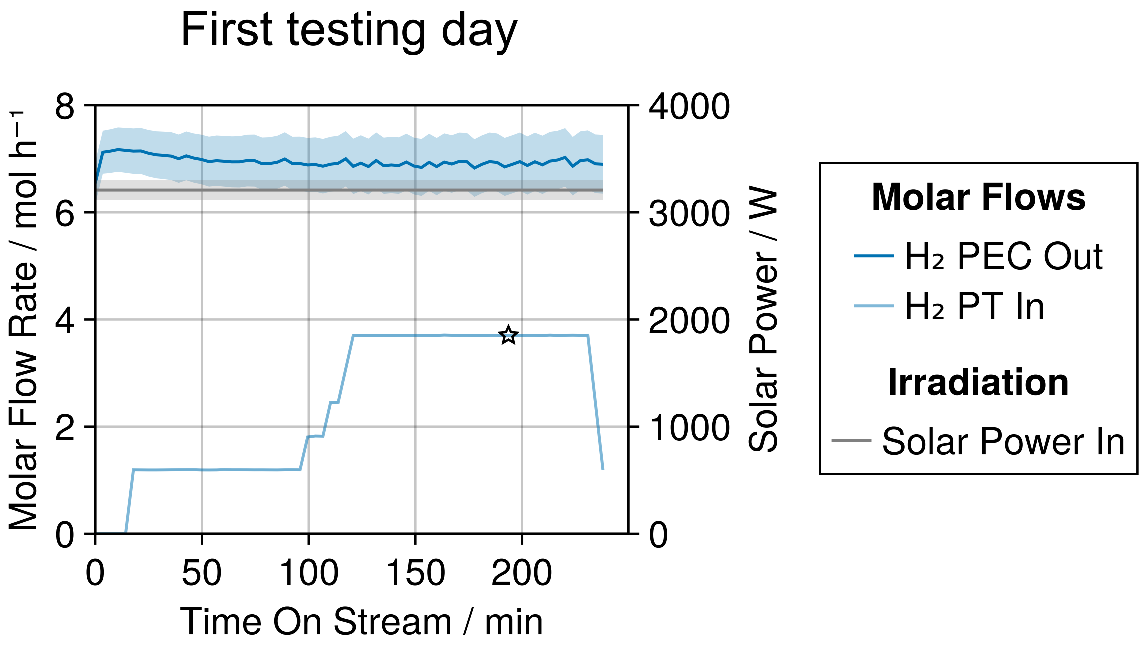


Janáky, C. et. al. (2025), Carbon Energy, DOI: 10.1002/cey2.674.

Experimental results: PEC reactor

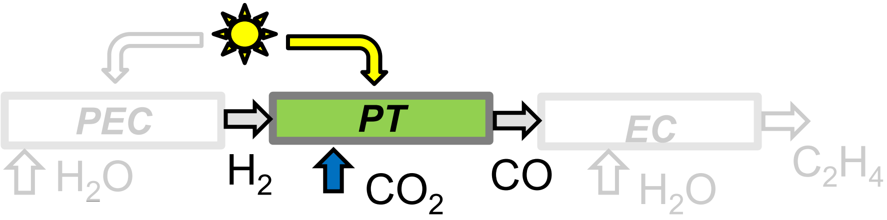


- Very stable operation (24.3 h total)
- $P_{\text{sol,in}} = 3.2\ \text{kW}$
- $\dot{n}_{\text{H2,PEC}} = \mathbf{6.9}\ (6.5 - 7.3)\ \frac{\text{mol}}{\text{h}}$
  $= 2400 - 2700\ \text{sccm}^*$
- $\text{STH}(\Delta h_R) = \mathbf{17.0}\ (16.1 - 18.0)\ \%$

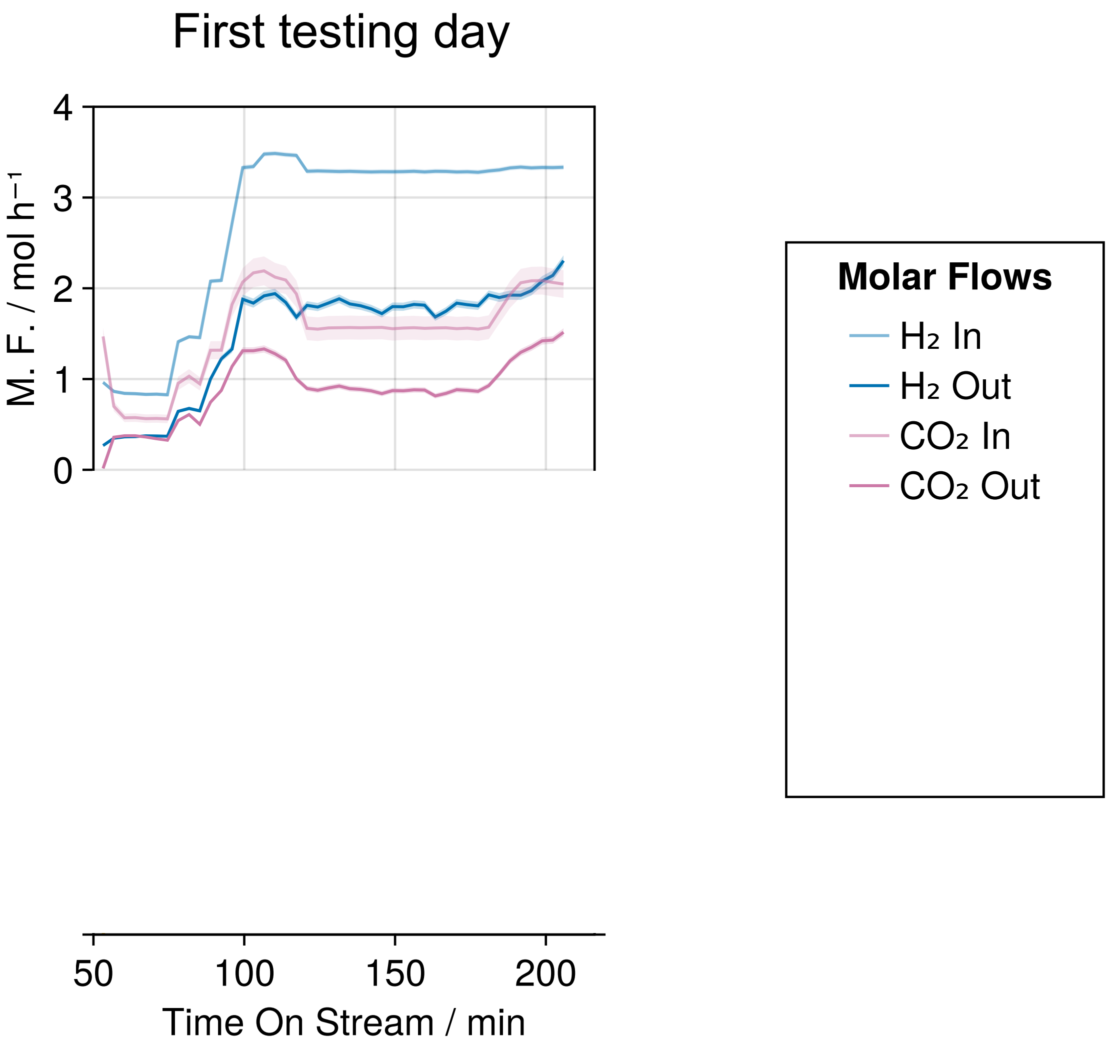


$^*T_n = 0°C$, $p_n = 1.01325\ \text{bar}_a$

Experimental results: PT reactor



- Mostly stable operation (21.8 h total)
- $\dot{n}_{\text{feed,total}} = \mathbf{4.4}\ (1.1 - 5.7)\ \frac{\text{mol}}{\text{h}}$
  $= \mathbf{1650}\ (400 - 2120)\ \text{sccm}\ ^*$
- Feed molar composition:
  $H_2/CO_2 = \mathbf{2.1}\ (1.5 - 6.3)^{\dagger}$
- $P_{\text{sol,in}} = \mathbf{1.0}\ (0.55 - 1.2)\ \text{kW}$
- $\dot{n}_{CO} = \mathbf{0.34}\ (0.11 - 0.52)\ \frac{\text{mol}}{\text{h}}\ ^{\dagger}$
- $\dot{n}_{CH_4} = \mathbf{0.26}\ (0.08 - 0.29)\ \frac{\text{mol}}{\text{h}}\ ^{\dagger}$
- $S_{CO} = \mathbf{57}\ (46 - 73)\%$
- $X_{CO_2} = \mathbf{44}\ (19 - 59)\%$
- $\text{STC}(CO, \Delta h_R^0) = \mathbf{0.39}\ (0.16 - 0.64)\%$

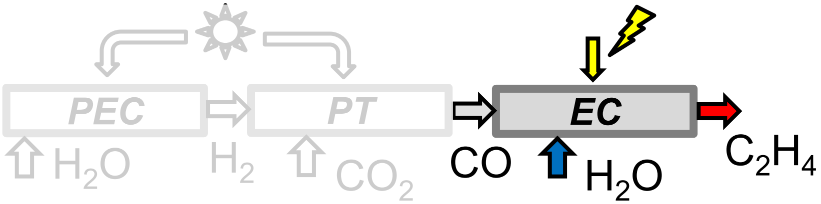


$^*T_n$=0°C, p_n=1.01325 bar_a

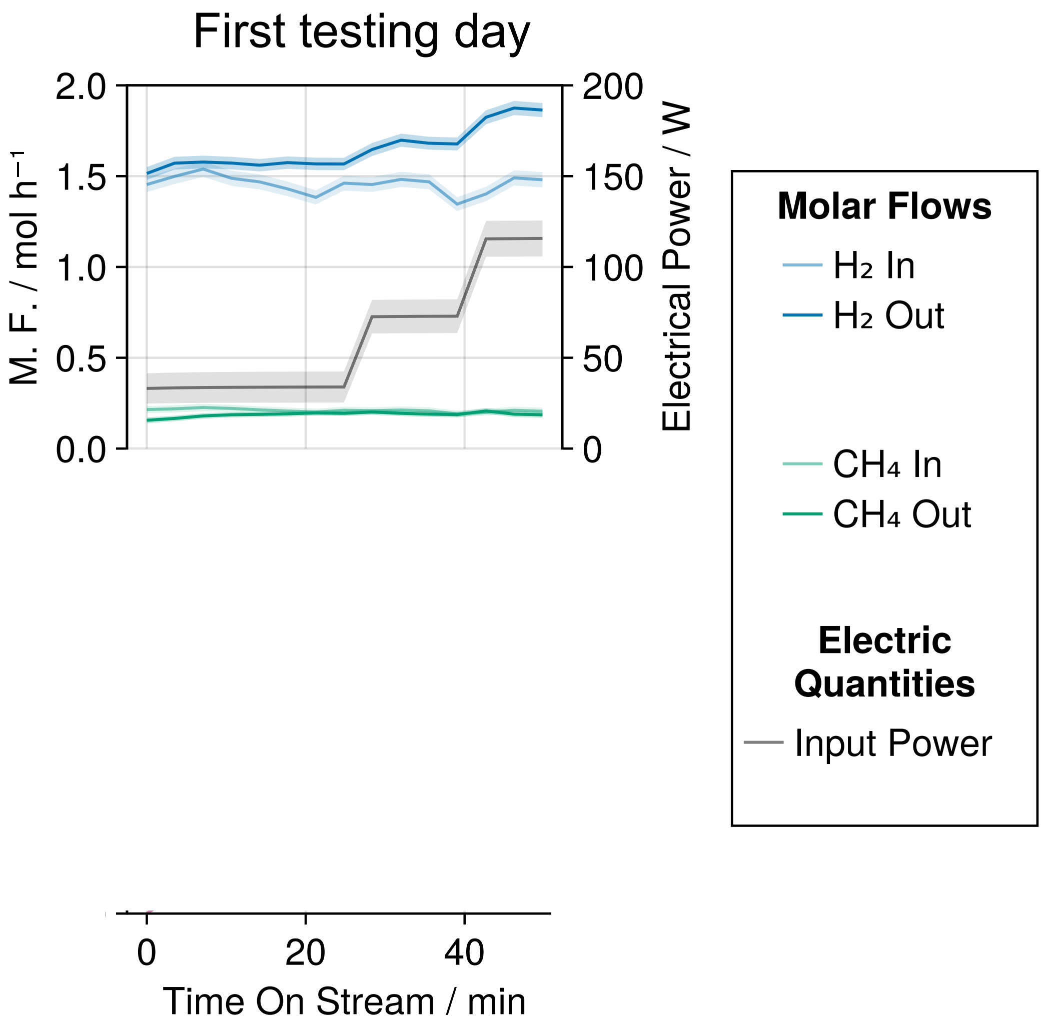
†Filtered for $\dot{n}_{\text{feed,total}} > 2.5\ \frac{\text{mol}}{\text{h}}$

This material is part of an unpublished manuscript to be submitted for publication

Experimental results: EC reactor



- Operation duration of 13.7 h total
- CO molar feed fraction: $\mathbf{14.1}\ (7.0 - 14.7)\%\ (\text{rest: } H_2 + CH_4)$
- $P_{\text{el}} = \mathbf{116}\ (33 - 163)\ \text{W}^{\dagger}$
- $\dot{n}_{C_2H_4} = \mathbf{0.055}\ (0.021 - 0.055)\ \frac{\text{mol}}{\text{h}}^{\dagger}$
- $\dot{n}_{\text{CO,feed}} = \mathbf{0.28}\ (0.08 - 0.32)\ \frac{\text{mol}}{\text{h}}$
- $\text{FE}(C_2H_4) = \mathbf{26}\ (16 - 33)\%^{\dagger}$
- $\text{EE}\left(C_2H_4, \Delta h_R^0\right) = \mathbf{11.2}\ (6.5 - 15.7)\%^{\dagger}$



† for Day 1 & 2

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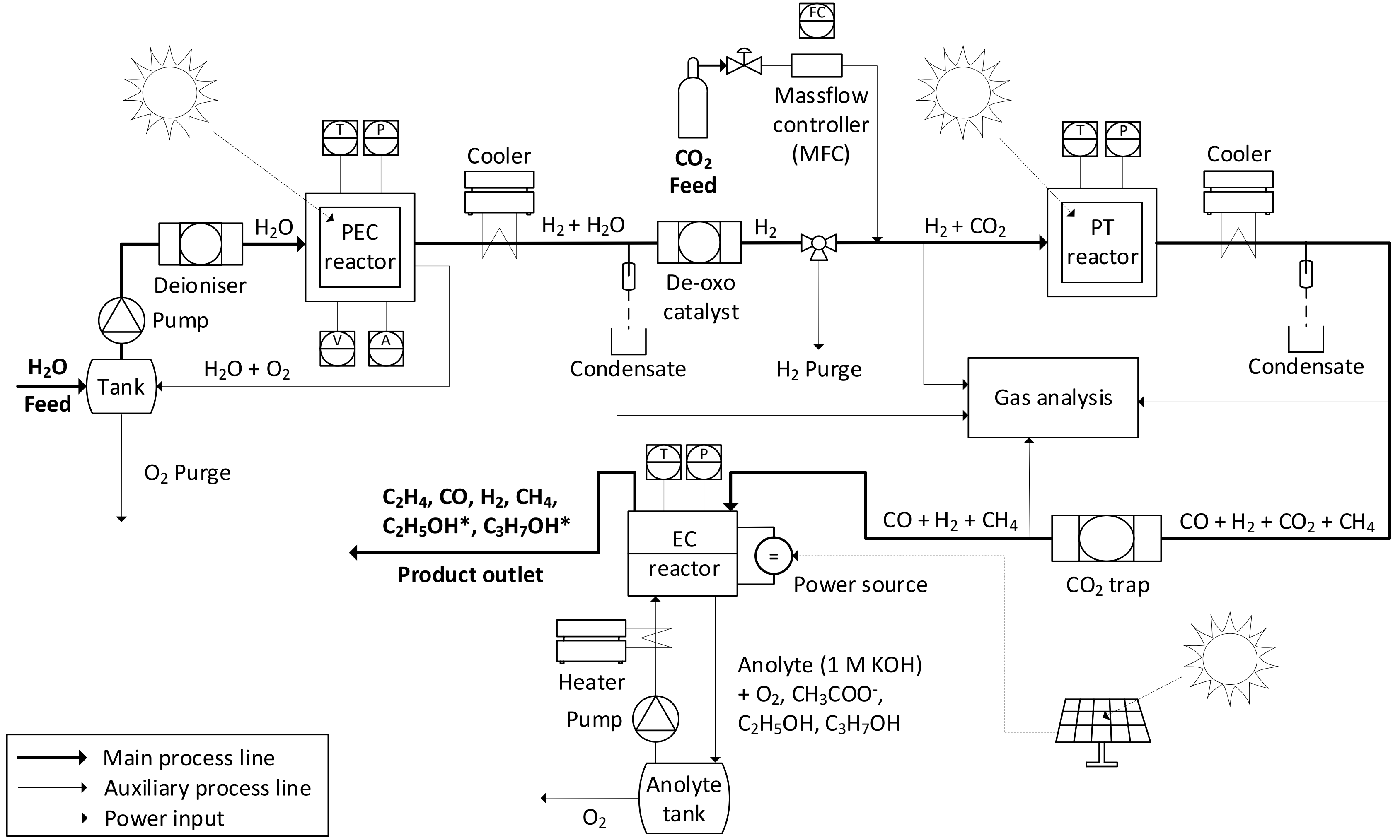
Scheme of integrated system



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Global reactions of relevance in integrated system

Reaction Name (Reaction Environment)	Main Product	Global Reaction Equation	$\Delta G^{R}_{298\ K}$ kJ/mol	$\Delta H^{R}_{298\ K}$ kJ/mol
Water splitting (PEC)	H_2	H_2O (l) → H_2 + ½ O_2	237.1	285.8
RWGS (PT)	CO	H_2 + CO_2 → CO + H_2O	28.6	41.2
Sabatier (PT)	CH_4	4 H_2 + CO_2 → CH_4 + 2 H_2O (g)	-113.3	-164.7
CO reduction to C_2H_4 (EC)	C_2H_4	2 CO + 2 H_2O (l) → C_2H_4 + 2 O_2	817.0	845.2
C_2H_4 synthesis (System)	C_2H_4	2 CO_2 + 2 H_2O (l) → C_2H_4 + 3 O_2	1331.5	1411.2
CH_3COO^- synthesis (System)	CH_3COO^-	2 CO_2 + 3 H_2O (l) → CH_3COO^- + H_3O^+ + 2 O_2	874.9	875.2
C_2H_5OH synthesis (System)	C_2H_5OH	2 CO_2 + 3 H_2O (l) → C_2H_5OH + 3 O_2	1327.4	1368.5
C_3H_7OH synthesis (System)	C_3H_7OH	3 CO_2 + 4 H_2O (l) → C_3H_7OH + 4.5 O_2	1963.3	2021.3
CO synthesis (System)	CO	CO_2 → CO + ½ O_2	257.2	283.0
CH_4 synthesis (System)	CH_4	CO_2 + 2 H_2O (l) → CH_4 + 2 O_2	818.2	890.6

Solar-to-chemical efficiency

- $$\mathrm{STC}_1(\Delta H^{\mathrm{R}}) = \frac{\dot{n}^{\mathrm{EC}}_{\mathrm{C_2H_4}} \Delta H^{\mathrm{R}}_{\mathrm{CO_2 \rightarrow C_2H_4}}}{P^{\mathrm{PEC}}_{\mathrm{sol}} + P^{\mathrm{PT}}_{\mathrm{sol}} + P^{\mathrm{EC}}_{\mathrm{el}} / \eta^{\mathrm{Si-PV}}}$$

- $$\mathrm{STC}_2(\Delta H^{\mathrm{R}}) = \frac{\dot{n}^{\mathrm{EC}}_{\mathrm{C_2H_4}} \Delta H^{\mathrm{R}}_{\mathrm{CO_2 \rightarrow C_2H_4}} + \dot{n}^{\mathrm{EC}}_{\mathrm{H_2}} \Delta H^{\mathrm{R}}_{\mathrm{WS}} + \dot{n}^{\mathrm{EC}}_{\mathrm{CO}} \Delta H^{\mathrm{R}}_{\mathrm{CO_2 \rightarrow CO}} + \dot{n}^{\mathrm{EC}}_{\mathrm{CH_4}} \Delta H^{\mathrm{R}}_{\mathrm{CO_2 \rightarrow CH_4}}}{P^{\mathrm{PEC}}_{\mathrm{sol}} + P^{\mathrm{PT}}_{\mathrm{sol}} + P^{\mathrm{EC}}_{\mathrm{el}} / \eta^{\mathrm{Si-PV}}}$$

- $$\mathrm{STC}^*_2(\Delta H^{\mathrm{R}}) = \frac{\dot{n}^{\mathrm{EC}}_{\mathrm{C_2H_4}} \Delta H^{\mathrm{R}}_{\mathrm{CO_2 \rightarrow C_2H_4}} + \left(\dot{n}^{\mathrm{EC}}_{\mathrm{H_2}} + \dot{n}^{\mathrm{AS}}_{\mathrm{H_2}}\right) \Delta H^{\mathrm{R}}_{\mathrm{WS}} + (\dot{n}^{\mathrm{EC}}_{\mathrm{CO}} + \dot{n}^{\mathrm{AS}}_{\mathrm{CO}}) \Delta H^{\mathrm{R}}_{\mathrm{CO_2 \rightarrow CO}} + (\dot{n}^{\mathrm{EC}}_{\mathrm{CH_4}} + \dot{n}^{\mathrm{AS}}_{\mathrm{CH_4}}) \Delta H^{\mathrm{R}}_{\mathrm{CO_2 \rightarrow CH_4}}}{P^{\mathrm{PEC}}_{\mathrm{sol}} + P^{\mathrm{PT}}_{\mathrm{sol}} + P^{\mathrm{EC}}_{\mathrm{el}} / \eta^{\mathrm{Si-PV}}}$$

Reactor efficiencies

- PEC reactor
- $\mathrm{STH}^{\mathrm{PEC}}\left(\Delta H^{\mathrm{R}}\right) = \dot{n}_{\mathrm{H_2}}^{\mathrm{PEC}} \Delta H_{\mathrm{WS}}^{\mathrm{R}} \Big/ P_{\mathrm{sol}}^{\mathrm{PEC}}$

- PT reactor
- $\mathrm{STC}^{\mathrm{PT}}\left(\mathrm{CO}, \Delta H^{\mathrm{R}}\right) = \dot{n}_{\mathrm{CO}}^{\mathrm{PT}} \Delta H_{\mathrm{RWGS}}^{\mathrm{R}} \Big/ P_{\mathrm{sol}}^{\mathrm{PT}}$

- EC reactor
- $\mathrm{FE}^{\mathrm{EC}}\left(\mathrm{C_2H_4}\right) = j_{\mathrm{C_2H_4}}^{\mathrm{EC}} \Big/ j^{\mathrm{EC}}$
- $\mathrm{EE}^{\mathrm{EC}}\left(\mathrm{C_2H_4}, \Delta H^{\mathrm{R}}\right) = \dot{n}_{\mathrm{C_2H_4}}^{\mathrm{EC}} \Delta H_{\mathrm{CO} \rightarrow \mathrm{C_2H_4}}^{\mathrm{R}} / P_{\mathrm{el}}^{\mathrm{EC}}$