ASME ES 2023

17th International Conference on Energy Sustainability

THE MADISON HOTEL
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Solar hydrogen production with a membrane reactor: Process description and reactor design

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Agenda

- Introduction: Mesowas project and membrane reactors for WS
- Thermodynamic assessment of concept
- Design of solar membrane reactor
- FEM simulations of solar flux distribution on membrane reactor

Introduction: The MESOWAS project

Membrane-based solar thermal cycles for the synthesis of green hydrogen

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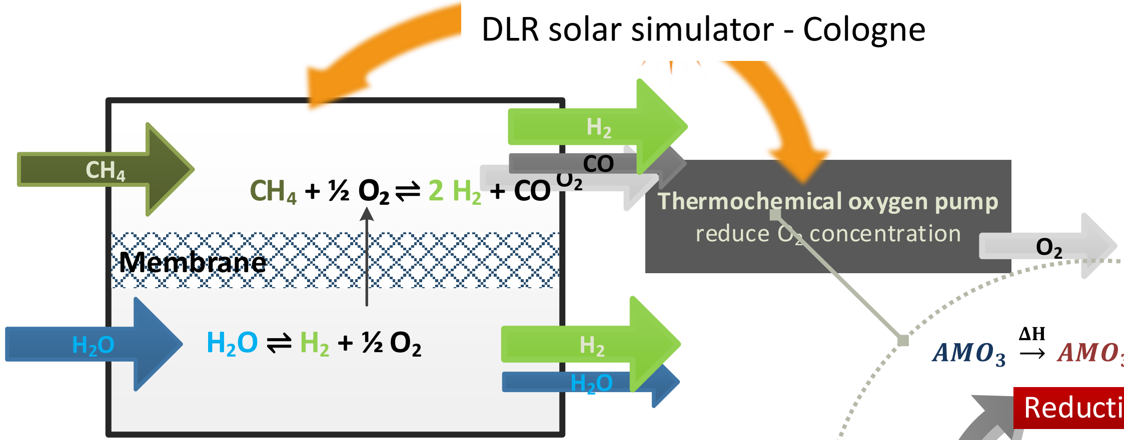
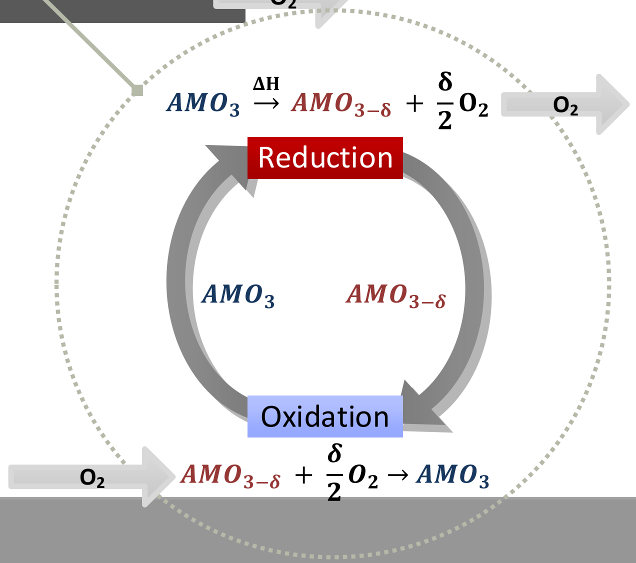
DLR solar simulator - Cologne





- ✓ no electricity required for H_2O splitting
- ✓ continuous operation possible
- ✓ direct separation of oxygen from H_2

Option A: Sweep gas or thermochemical O_2 pump
Option B: partial oxidation of biomethane or biogas

Aim of project:

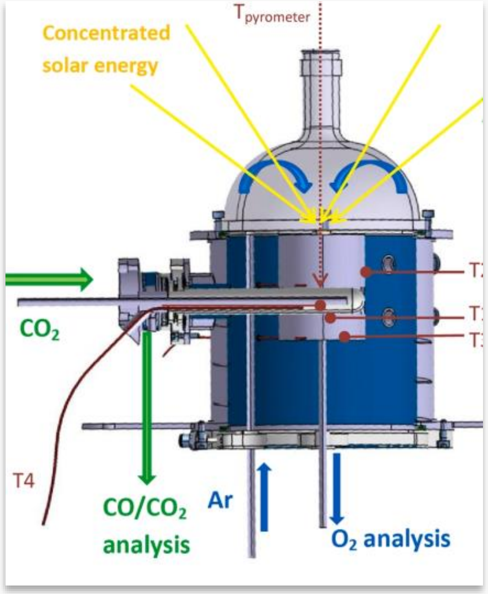
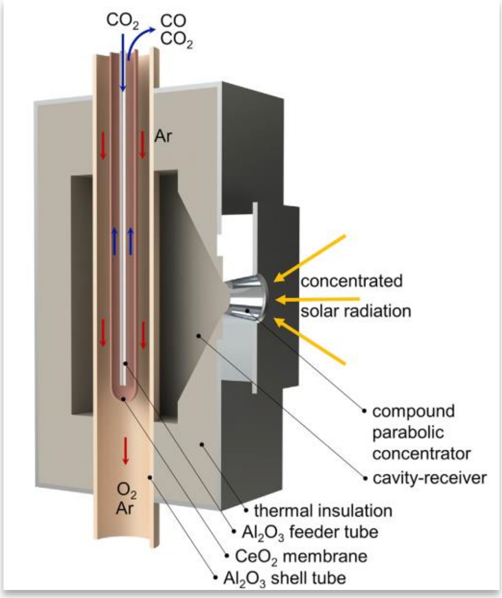
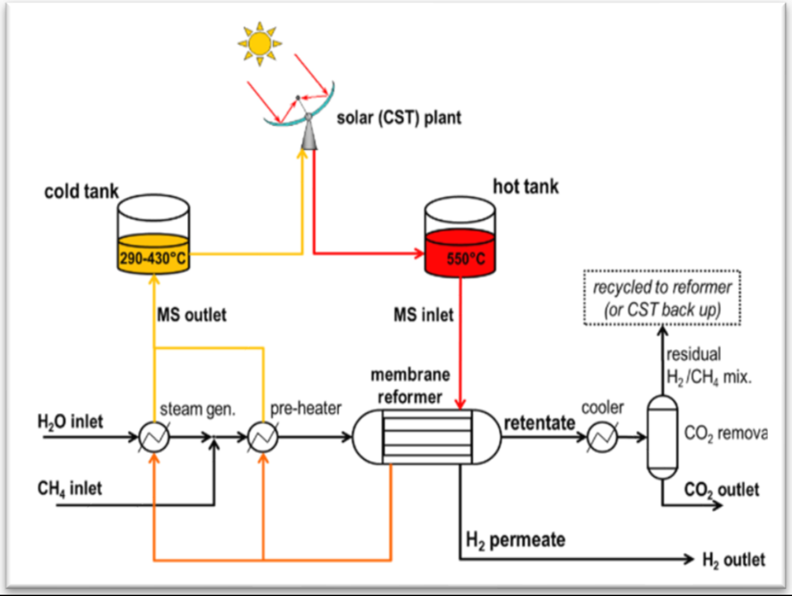
1. Experimental proof-of-concept of a solar membrane reactor for water splitting
2. Development of membrane
3. Investigation of different approaches to reduce the oxygen concentration on permeate side
4. Potential analysis of membrane technology

Consortium:

Synhelion JÜLICH Forschungszentrum DLR

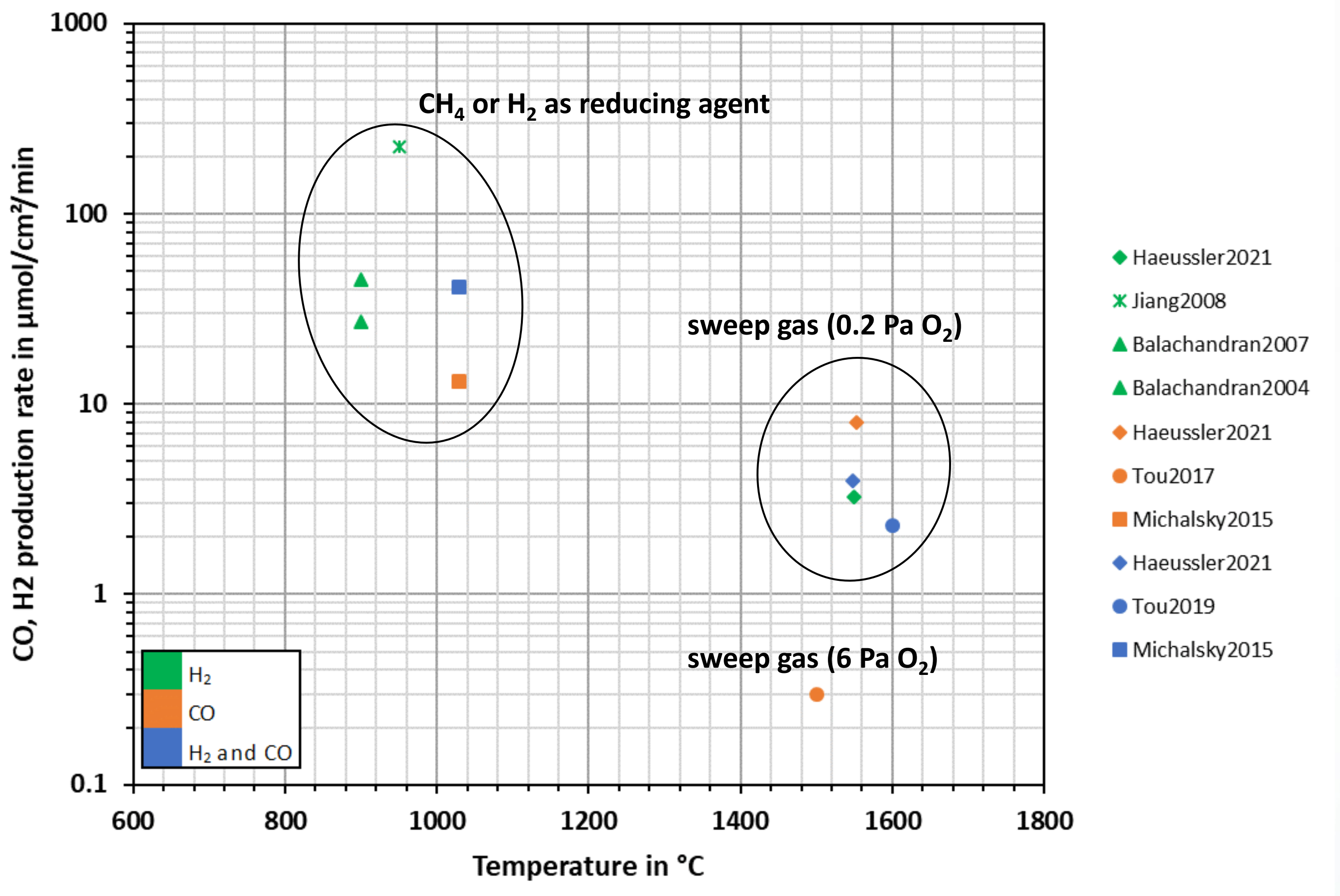
MESOWAS: Membranbasierte solarthermische Kreisläufe für die Synthese von grünem Wasserstoff

Solar membrane reactors – state-of-the-art

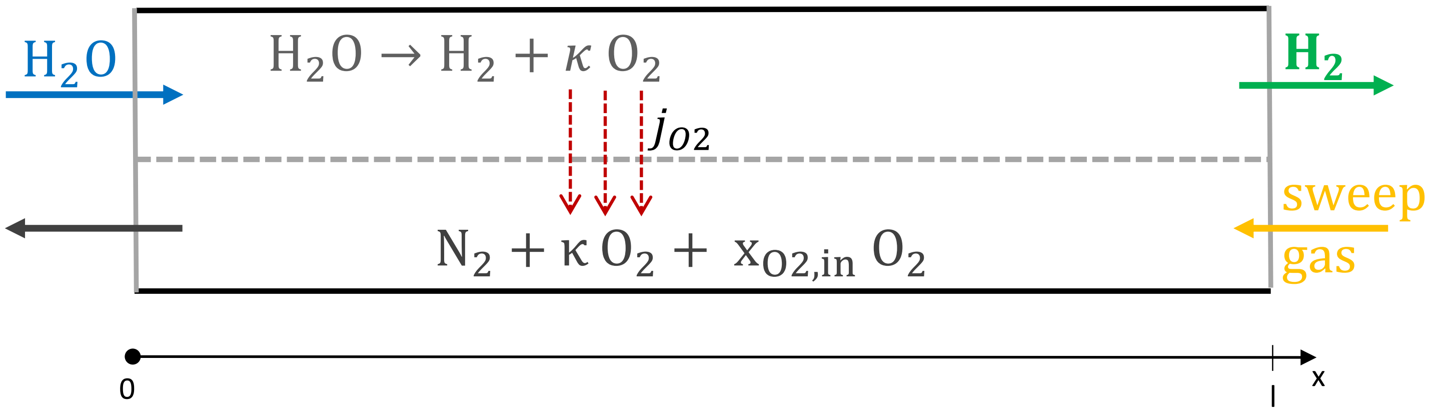
<table>
<tr><th rowspan="2">membrane directly irradiated</th><th colspan="2">membrane indirectly irradiated</th></tr>
<tr><th>irradiation of external tube/plate</th><th>Using external HTF</th></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>Tubular CeO_2-based solar membrane reactor.
1450 °C – 1550 °C
Sweep gas: Ar with < 0.2 Pa O_2.
Feed gas: CO_2 (H_2O)
Solar irradiation from parabolic dish.</td><td>Tubular CeO_2-based membrane reactor.
1300 °C – 1600 °C
Sweep gas: Ar with 0.3 – 6 Pa O_2.
Feed gas: CO_2, H_2O in Ar, CO_2 and H_2O.
Solar radiation from solar simulator: 2 – 3 kW.</td><td>Membrane reformer heated with molten salt
T < 550 °C
Methane
Feed gas: H_2O
Solar thermal heat for molten salt: $NaNO_3/KNO_3$</td></tr>
</table>

Abanades et. al 2021 | **Tou et. al 2017; Tou et. al 2019** | **Giaconia et. al 2020**

Performance of membrane reactors in literature



Thermodynamic assessment of concept



$$\kappa = \frac{\int_0^l |j_{O2}(x)|\ dx}{\dot{n}_{H2O}}, \qquad \kappa_{total} = 0.5$$

$$p_{O2,\,feed}(\kappa) \geq p_{O2,sweep}(\kappa)\ \forall\ \kappa \in [0, \kappa_{total}]$$

- κ → O_2 transport through membrane
- Feed and sweep gas flows definition → Gri30 solution (Cantera)
- Definition of parameters to represent oxygen impurities; ratio of sweep and feed gas flows
- Calculations performed for T: 800 °C – 1500 °C; pO_2: 10^{-5} – 10^{-14} bar

Based on work by Brendan Bulfin 2019: Thermodynamic limits of countercurrent reactor systems, with examples in membrane reactors and the ceria redox cycle *https://pubs.rsc.org/en/content/articlehtml/2019/cp/c8cp07077f*

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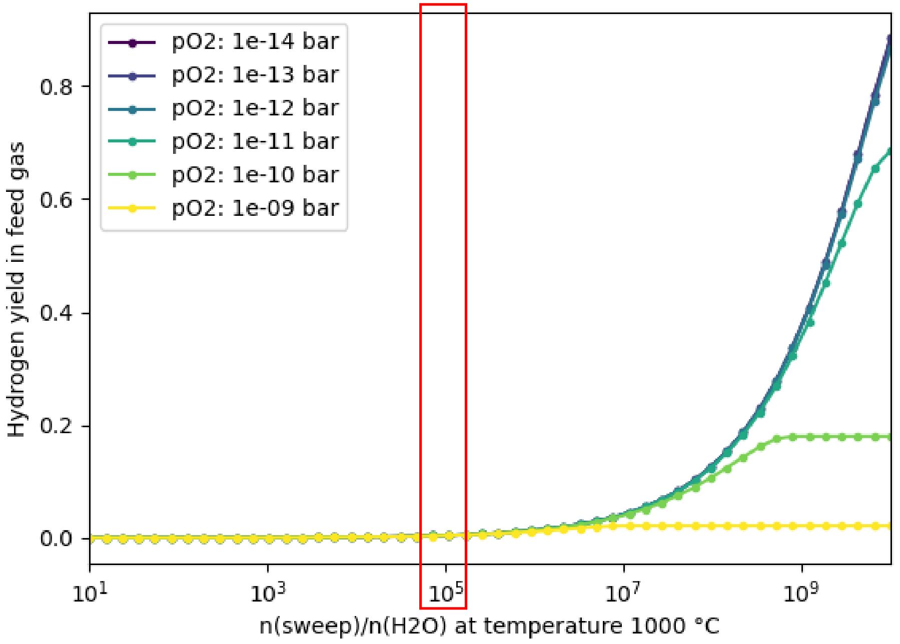
Thermodynamic assessment: H_2O thermolysis with sweep gas

in principle feasible with thermochemical „oxygen pump“

1000 °C operation



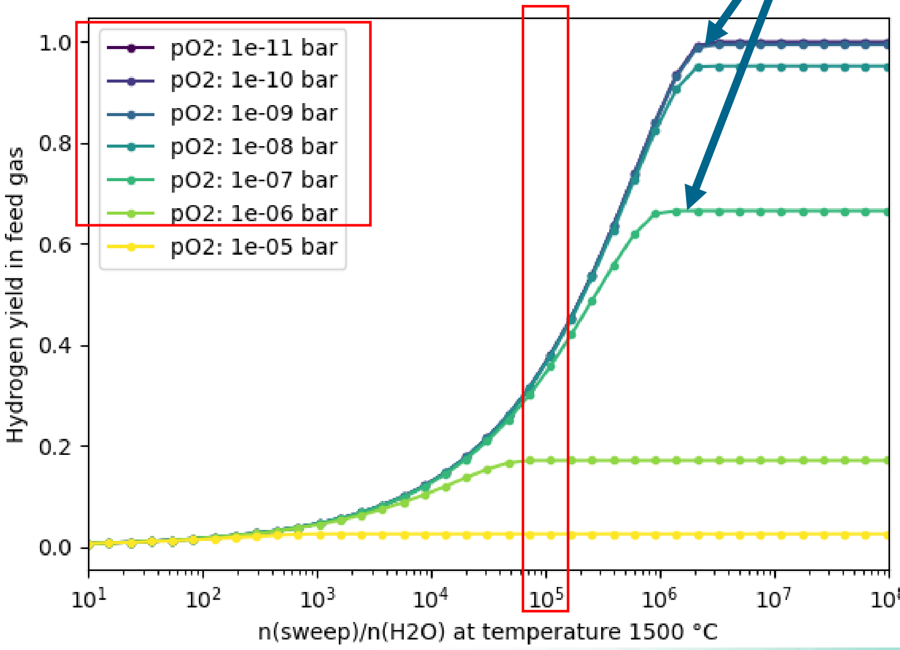
Molar flow ratio of sweep/feed gas:

$$\omega = \frac{\dot{n}_{sweep}}{\dot{n}_{H2O}}$$

Oxygen impurity in sweep gas:

$$\phi = \frac{\dot{n}_{O2,in}}{\dot{n}_{sweep}} = \frac{p_{O2,in}}{p_{sweep}}$$

1500 °C operation



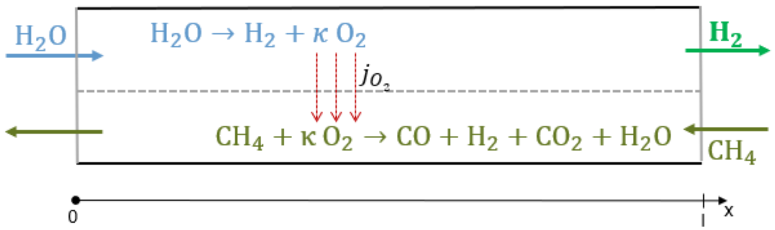
→ Sweep gas for operation at 1000 °C not viable

→ High demand on sweep gas flow rate 1500 °C, but high hydrogen yields (thermodynamically) possible

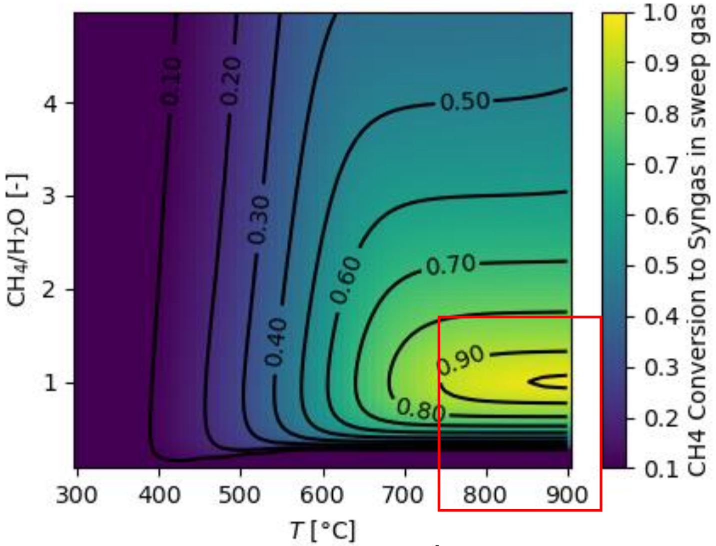
→ Higher H_2 yield due to lower oxygen impurities only relevant if flow rate ratio ca. 10^5 to 10^7 (in case of an ideal membrane)

Based on work by Brendan Bulfin 2019: Thermodynamic limits of countercurrent reactor systems, with examples in membrane reactors and the ceria redox cycle *https://pubs.rsc.org/en/content/articlehtml/2019/cp/c8cp07077f*

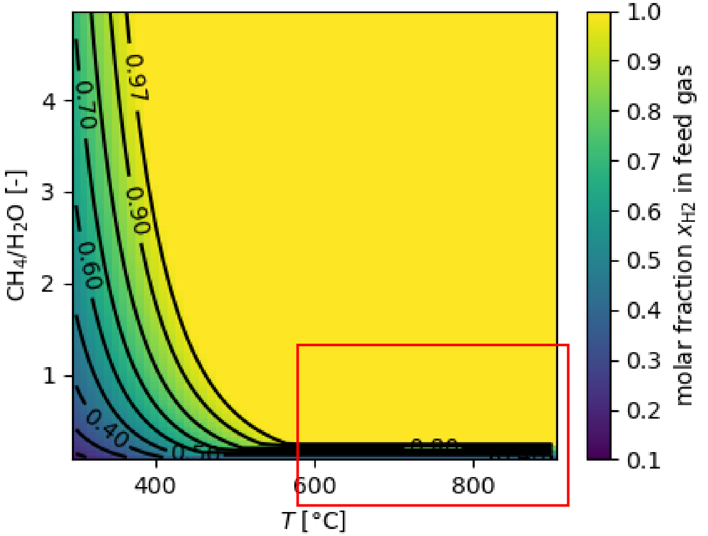
Thermodynamic assessment: H_2O thermolysis with CH_4 as reducing agent



- ratio of $n(CH_4)/n(H_2O)$ = 1 full conversion of H_2O to H_2 and CH_4 to CO/H_2
- Temperature of operation for reactor > 750 °C



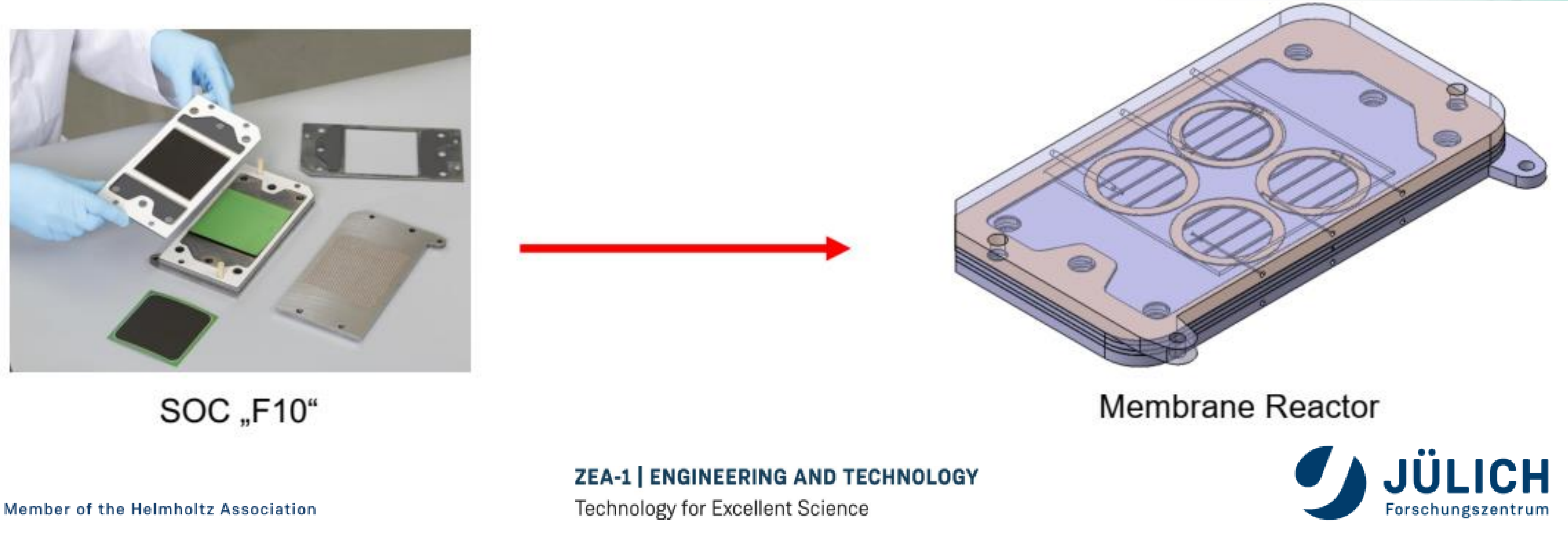
Permeate side



Retentate side

Based on work by Brendan Bulfin 2019: Thermodynamic limits of countercurrent reactor systems, with examples in membrane reactors and the ceria redox cycle ***https://pubs.rsc.org/en/content/articlehtml/2019/cp/c8cp07077f***

Design of reactor: From F10 Jülich Solid Oxide Electrolysis design to membrane reactor



Feasibility of the design:

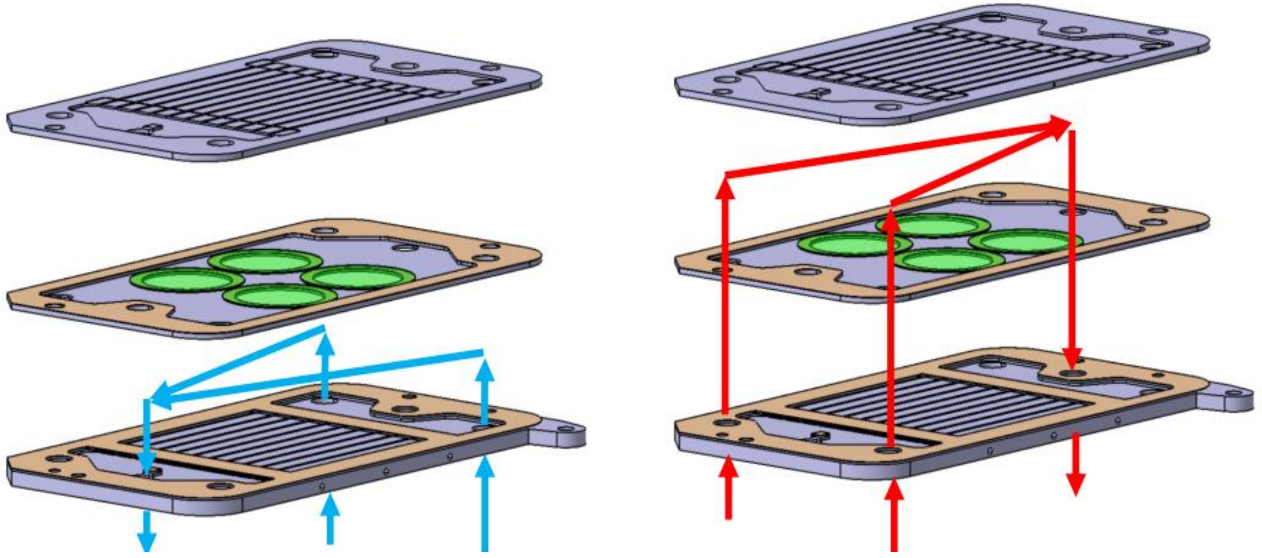
→ Similar outer envelope can be used; X layer stack footprint: 220 mm x 120 mm **x scalable**

→ Different membrane shapes can be adapted (e.g. circular or rectangular)

→ Shape and type of glass solders can be adapted to membrane and metals of the design

→ Stacks allow scalability of system

Design of membrane reactor



Repeatable layer - partially assembled

proof-of-concept of the solar membrane reactor (using stacks):

- Membrane material determines 1) joining technique (e.g. glass sealant or metallic braze) and 2) frame material
- Different materials for the membrane are considered (e.g. Fe-doped $SrTiO_3$)
- Gas distribution in each stack-layer possible due to orientation of the frame plates (brown)
- All components are joined into a stack
- Stack heated with solar energy (800-900 °C)

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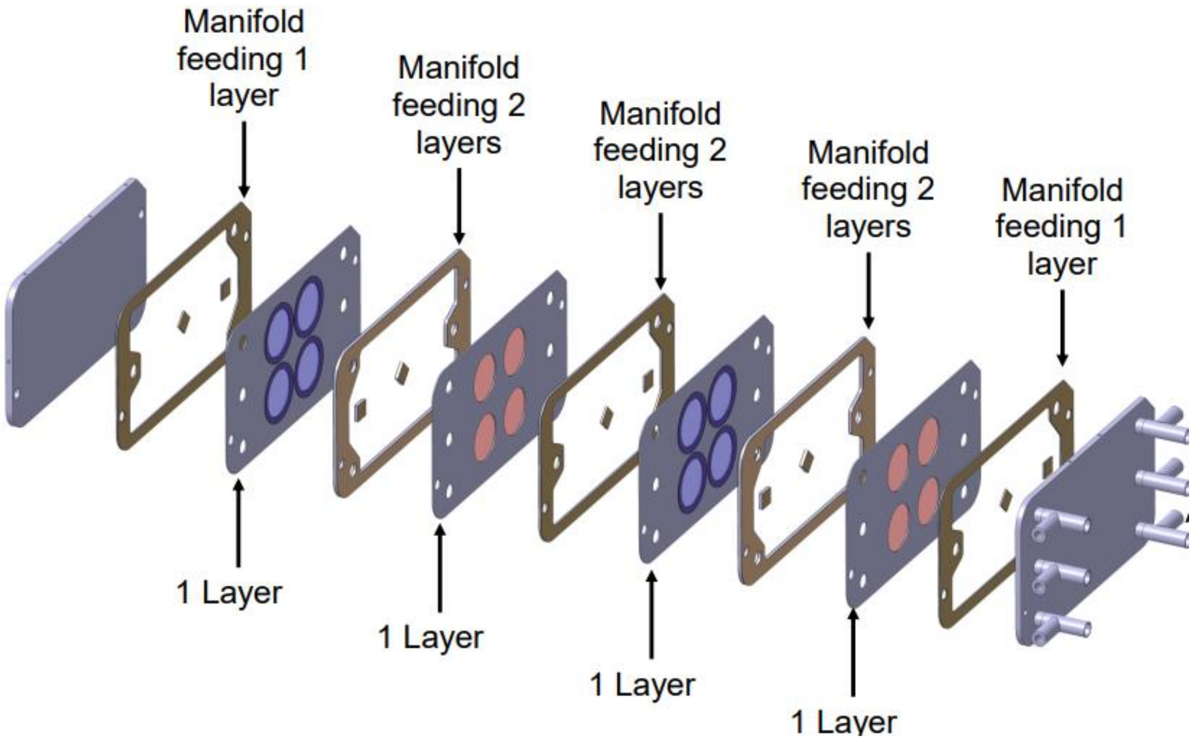
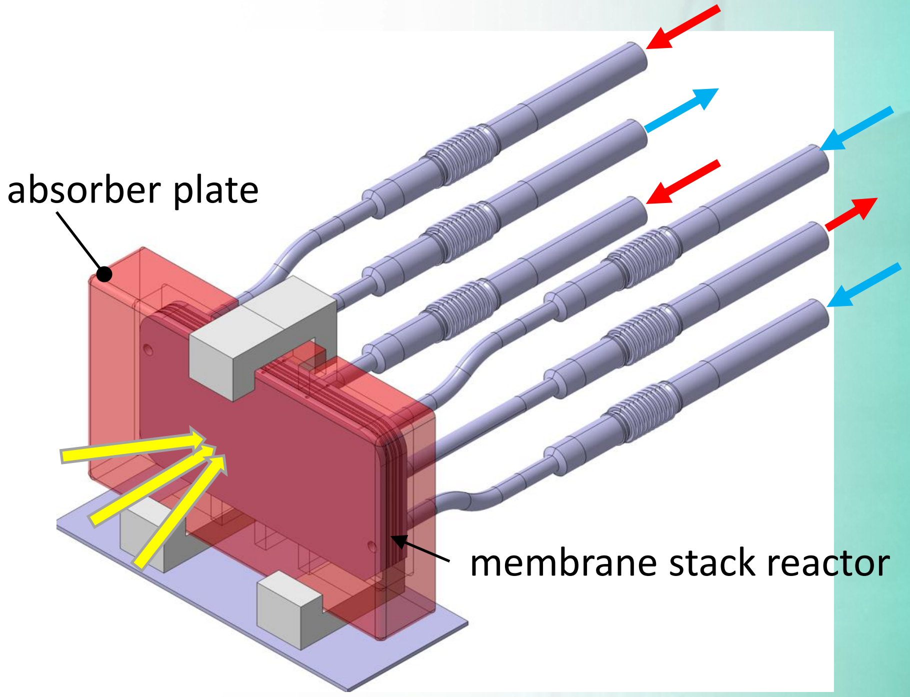
Current state of design





Considerations for experimental demonstration of solar membrane reactor

Operation at ambient pressure

Gas flow rates defined:

- Steam: 30 – 130 g/h
- Reducing agent flow: 0.05 – 1 L/min (STP)

Different reducing agent

- Methane
- Biogas (CH_4 – CO_2 mixture)

Homogeneous T distribution on membrane reactor

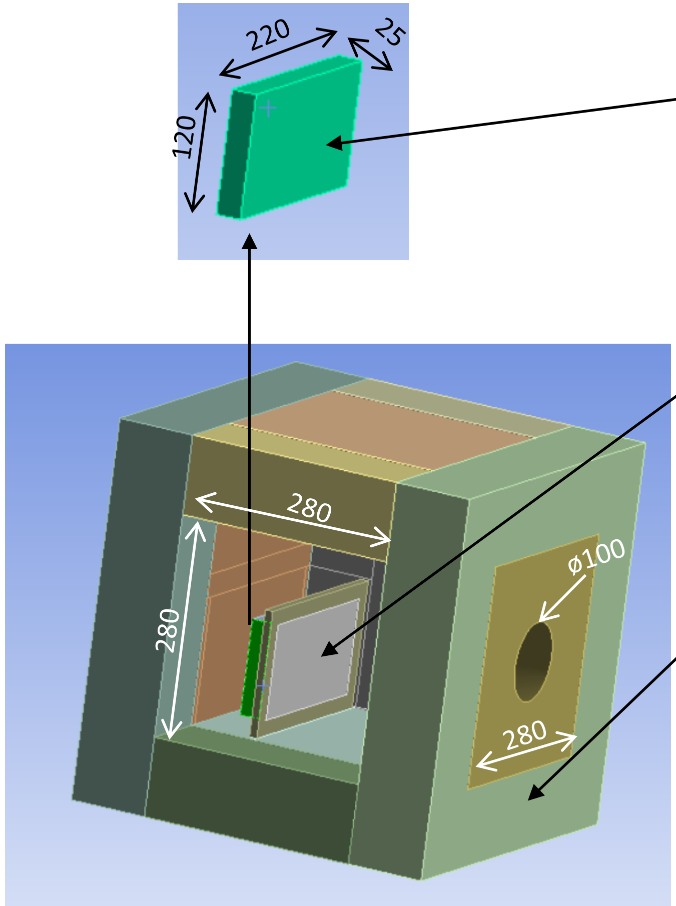
- Temperature for experiments: **(800 – 900 °C)**
- Max. allowable T gradient: **50 K**

Integration of solar energy

Using intermediate Heat Transfer Fluid (scale up concept analysis)

Using indirect irradiation of stack (experiments)

Simulations of solar flux distribution on membrane reactor



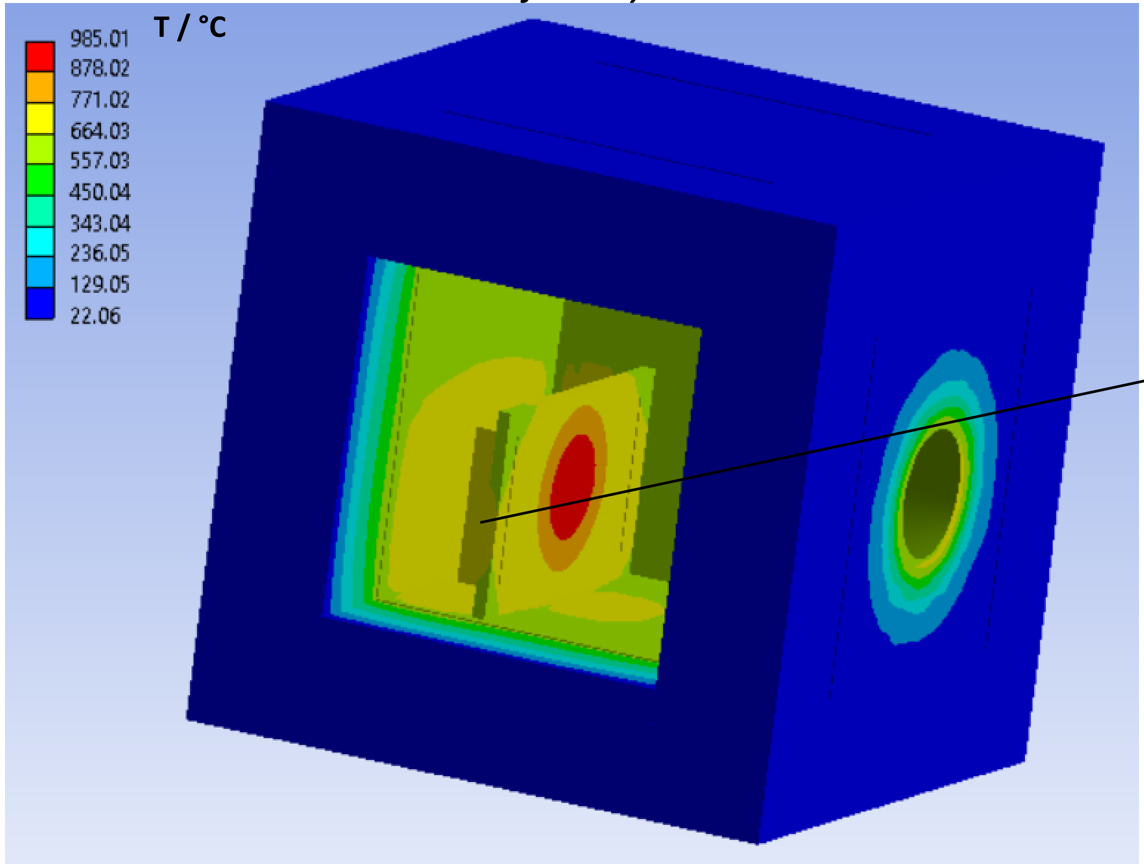
dimensions in mm

- Simulation with Ansys: **Thermal steady state**
- Membrane reactor: steel; ε = 0.8
- Irradiated plate placed in front of reactor to reduce T gradient: steel / copper; ε = 0.8
- Cavity walls: Calcium silicate; ε = 0.5
- Integration of energy flux density from DLR solar simulator using Ray-tracing: SPRAY/FEMRAY tools (1 Lamp: ≈ 1.8 kW)
- Heat of reaction: 100 W
- Convection losses inside the cavity calculated using model of Clausing

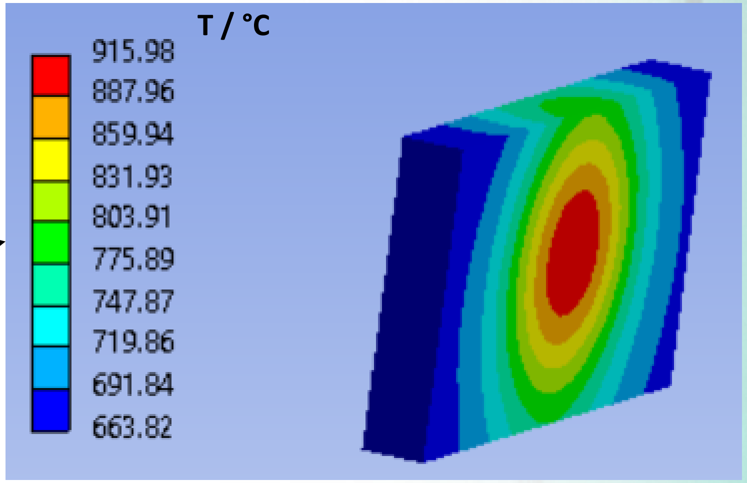
Simulations performed with Ansys® Academic Research Workbench 2022 R1

Material of irradiated plate: steel

T distribution of cavity



T distribution membrane reactor



Hot spot in central part; temperature gradient too large!

Simulations performed with Ansys® Academic Research Workbench 2022 R1

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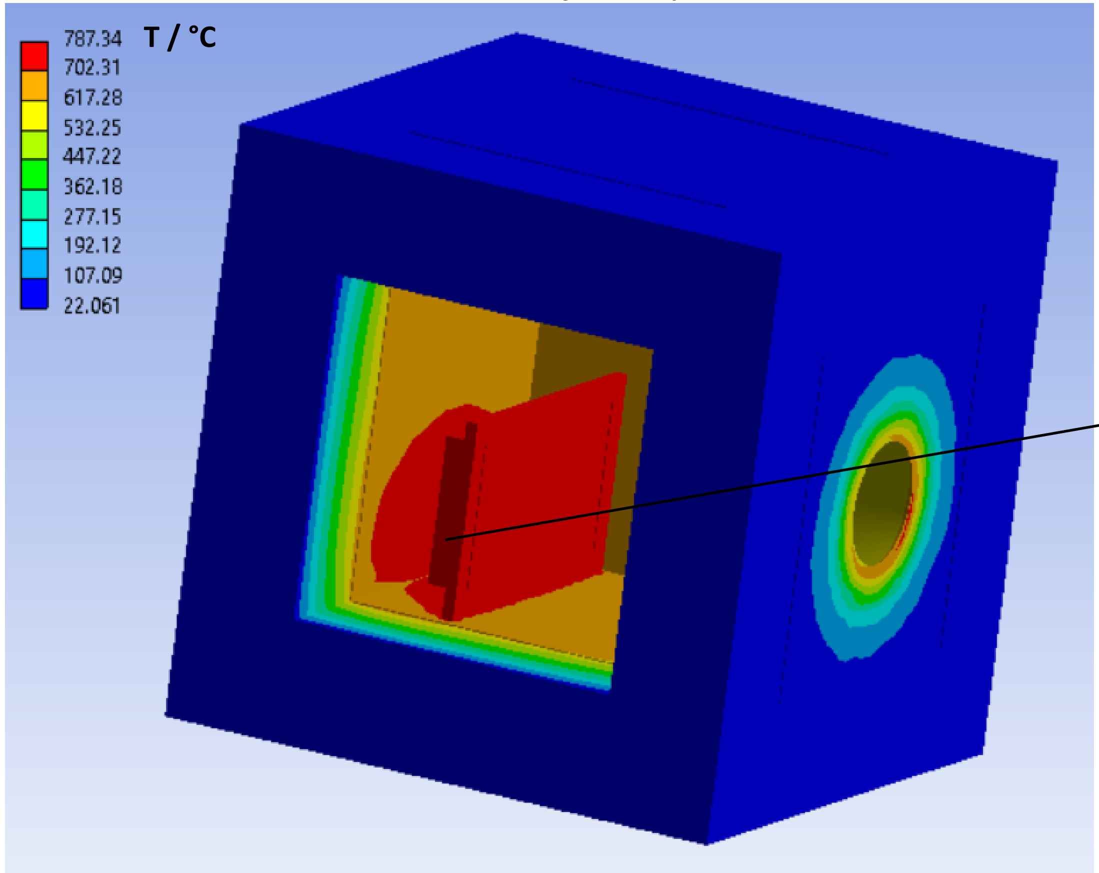
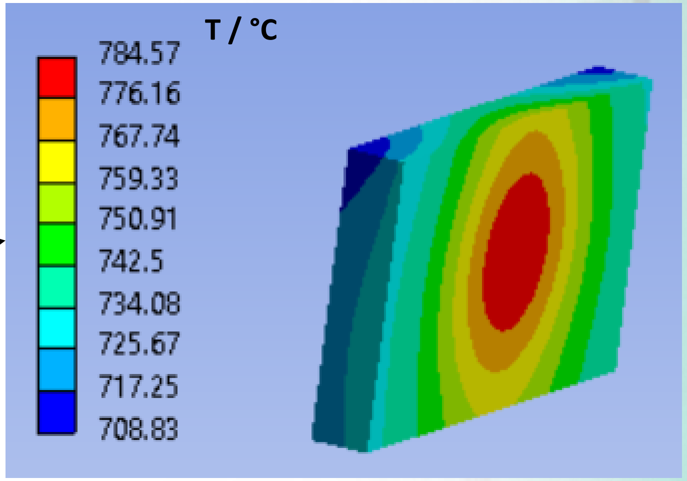
Material of irradiated plate: copper

T distribution of cavity



T distribution membrane reactor

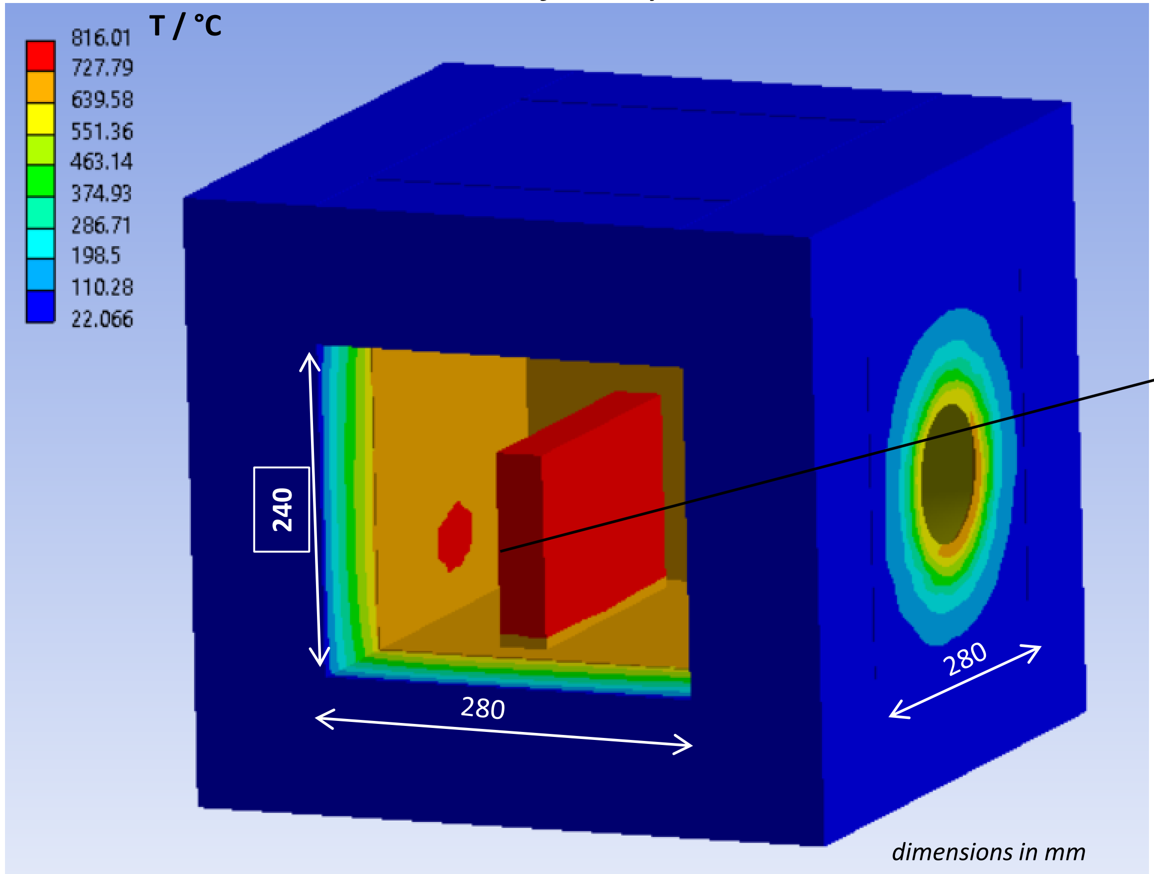


Thermal conductivity of copper (330-350 W/mK) → better heat distribution on membrane reactor → lower T gradient, but T < 800 °C

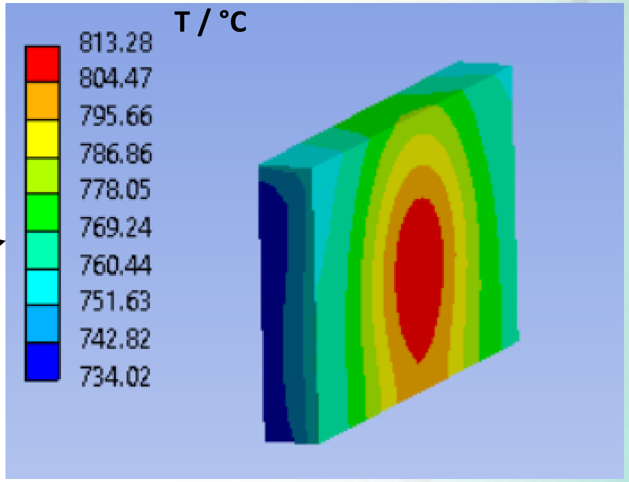
Simulations performed with Ansys® Academic Research Workbench 2022 R1

Modification of volume of cavity to reach higher temperatures

T distribution of cavity



T distribution membrane reactor



High temperature achieved, but T gradient still > 50 K

Simulations performed with Ansys® Academic Research Workbench 2022 R1

Outlook

- Reactor concept design ✓
- Boundary conditions for the experimental demonstration of proof-of-concept reactor ✓
- Definition of the solar integration concept (cavity + irradiated plate) ✓
- Experimental campaign planned for the second part of 2024
- Plans to publish our project results in the ASME journal

Thanks for your attention!
Questions?

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DLR - Institute of Future Fuels

Department of Solar Chemical Process Development

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