instituto imdea energía

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Advances and challenges in the development of redox materials for thermochemical solar fuels production

MATSUS | Materials for Sustainable Development Conference
MATSUS Fall 2024 Lausanne, Switzerland · 12th - 15th November, 2024 #MATSUS24

Manuel Romero[1], José González-Aguilar[1], Aldo Steinfeld[2]

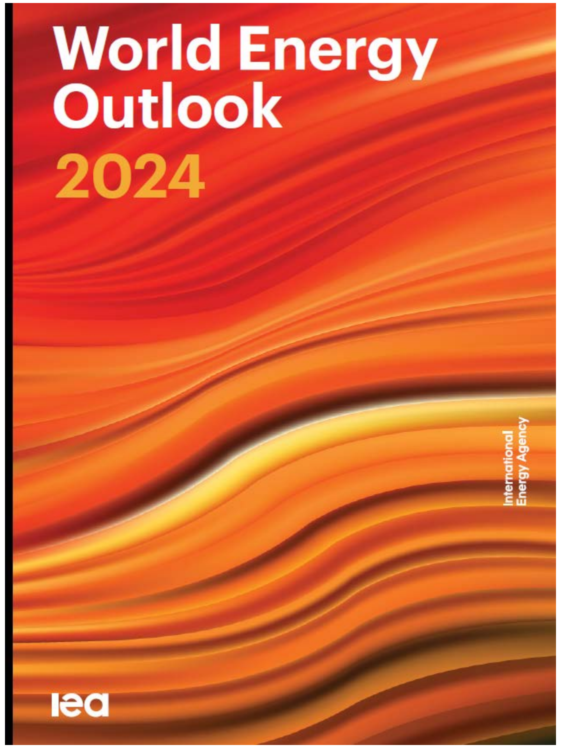
[1]High-Temperature Processes Unit,
IMDEA Energy, E-28935 Móstoles, Spain

[2]Department of Mechanical and Process Engineering.
ETH Zurich, 8092 Zurich, Switzerland

Index

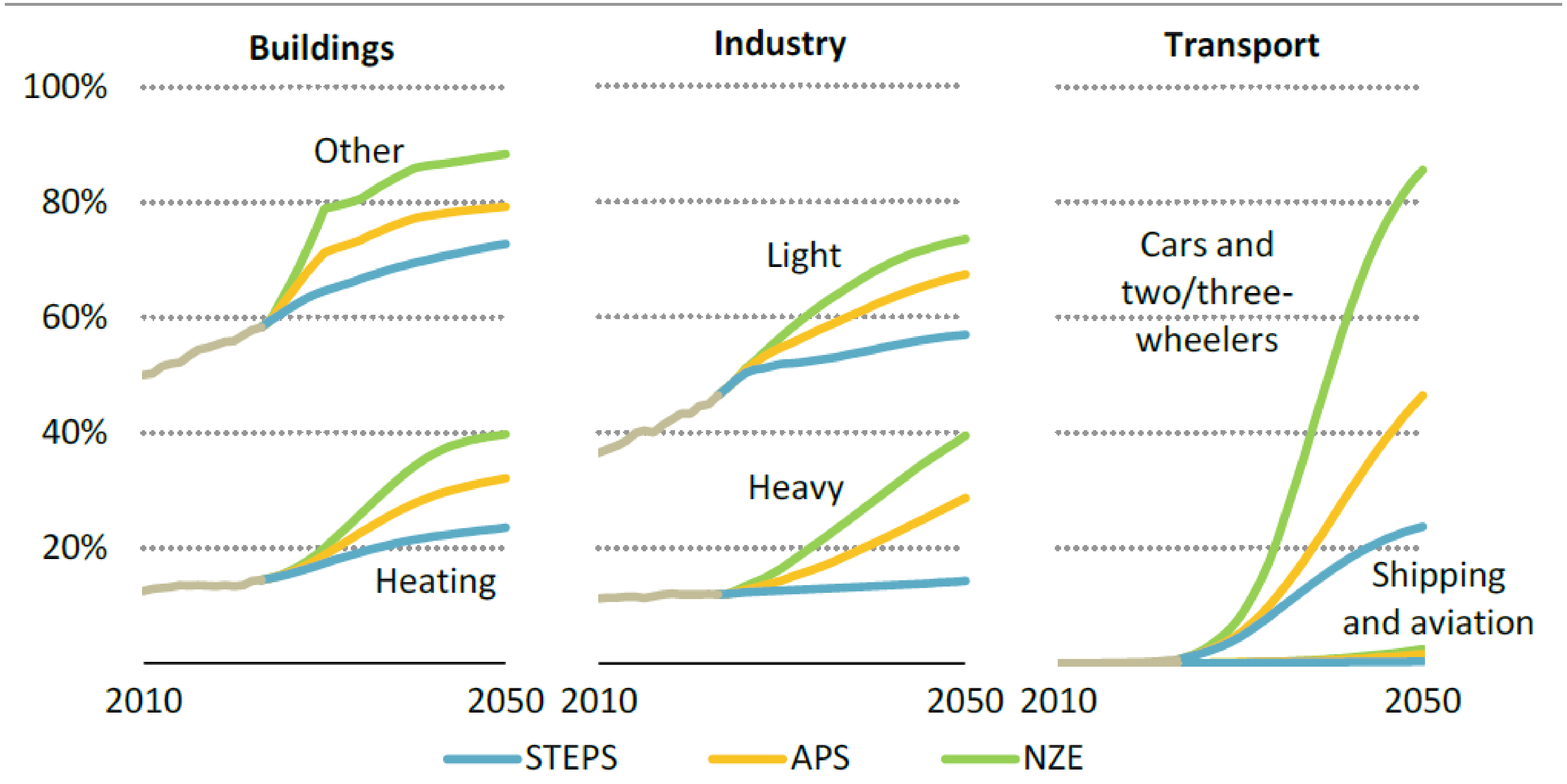
Advances and challenges in the development of redox materials for thermochemical solar fuels production

The challenge of sectors hard to electrify in the NZE scenario



http://www.iea.org/weo

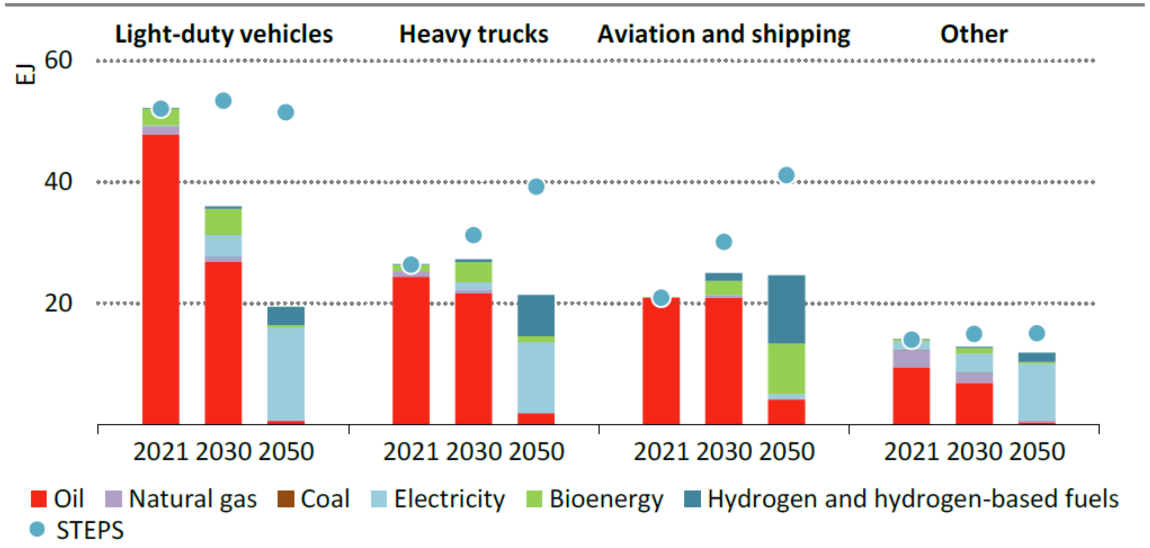
Share of electricity in total final consumption by end-use sector and scenario, 2010-2050



Stated Policies Scenario (STEPS).
Announced Pledges Scenario (APS)
Net Zero Emissions by 2050 (NZE)

Decarbonizing Aviation: “3-S” criteria, a driver to develop StL path

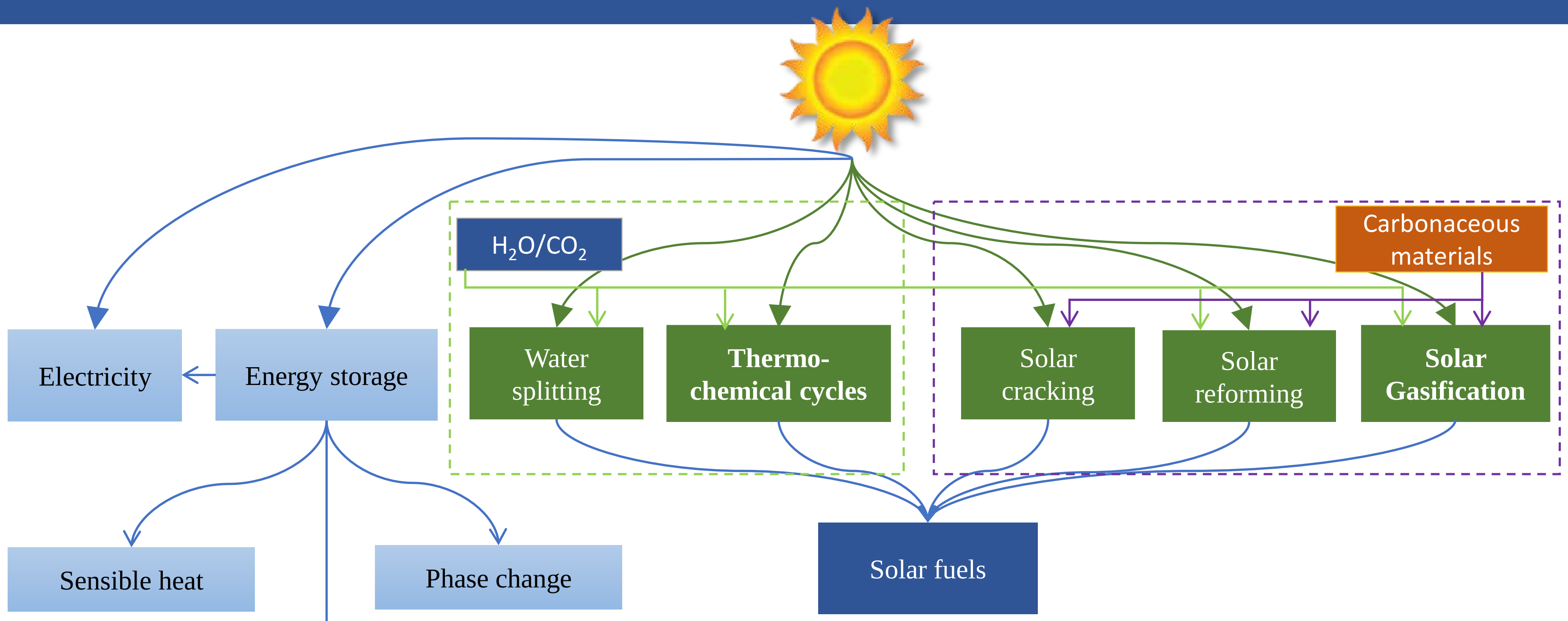
- Aviation will rely on liquid hydrocarbons that are suitable, sustainable an scalable



Final energy consumption in transport by source and mode in the NZE Scenario, 2021-2050
IEA World Energy Outlook 2022, www.iea.org/weo

Energy carrier	Suitability	Sustainability	Scalability
GTL, CTL	Drop-in capable blend	Fossil carbon release	Commercial scale implementation
BTL		Potentially low carbon emission	Feedstock development, logistics and competition for bio-mass
HEFA			
New bio-fuels			
STL, PTL			Large-scale production less restrictive than for biofuels
LNG	Non-drop-in solution	Fossil carbon release	Existing infrastructure
LH_2		Potentially zero carbon emission	Distribution and storage
Electric power	Low specific energy in storage		Scalable through diversity and large-scale plants

STL: Sun to Liquid Concentrated Solar Radiation



H_2O/CO_2

Carbonaceous materials

Electricity

Energy storage

Water splitting

Thermo-chemical cycles

Solar cracking

Solar reforming

Solar Gasification

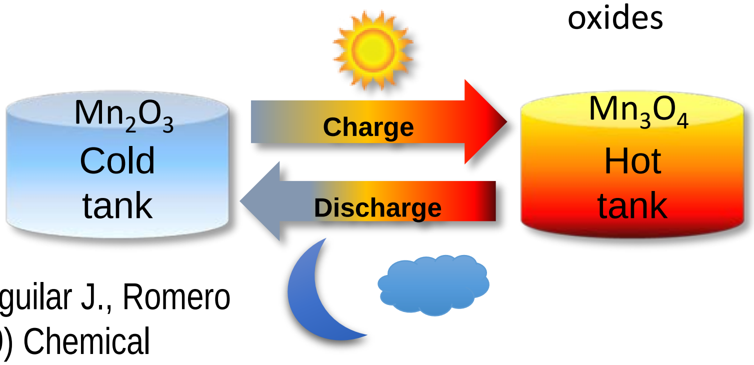
Sensible heat

Phase change

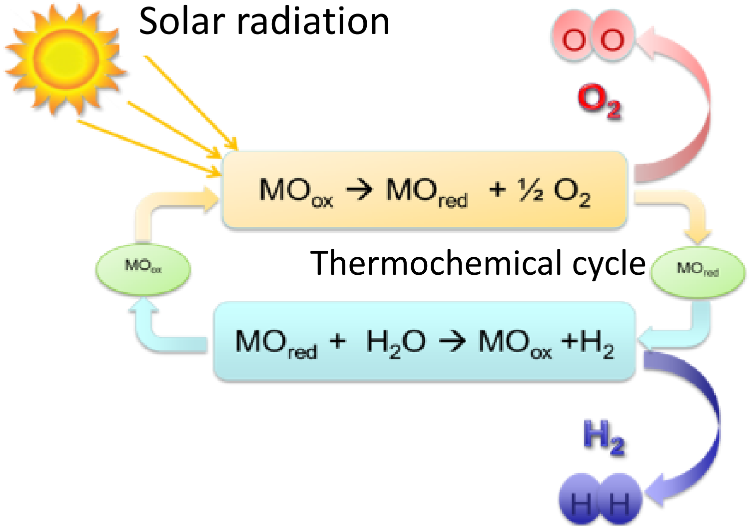
Solar fuels

Thermochemical

Reduction-oxidation metal oxides

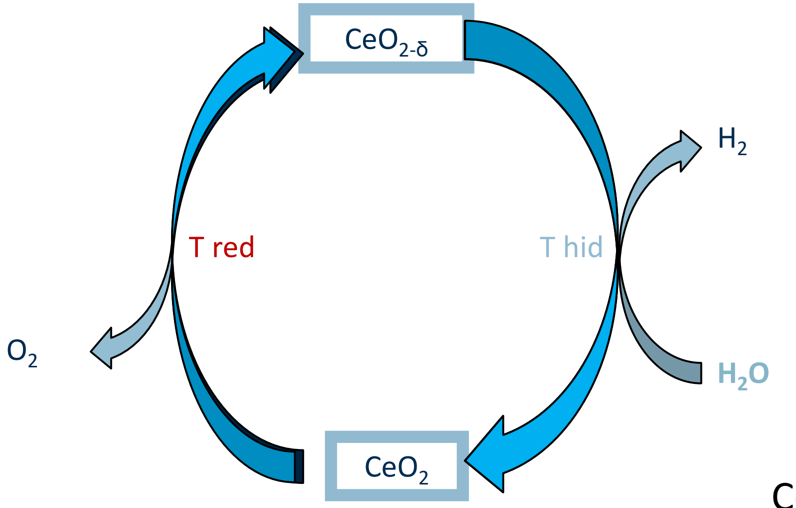


Carrillo A.J., González-Aguilar J., Romero M., Coronado J.M. (2019) Chemical Reviews, 119 (7), pp. 4777 – 4816



J.R. Scheffe, A. Steinfeld, Mater. Today 17 (7) (2014) 341–348 .

Production of hydrogen with non-stoichiometric metal oxides



Thermodynamic analysis should pay attention to system pressure, oxygen partial pressure, reduction temperature, oxidation temperature, heat recovery, and irradiation concentration ratio

$$\Delta G^{\circ}_{\mathrm{red}}(T) = \Delta H^{\circ}_{\mathrm{red}} + T\Delta S^{\circ}_{\mathrm{red}} \qquad \Delta G_{\mathrm{ox}} = \Delta G^{\circ}_{\mathrm{ox}}(T) + RT\ln\left(\frac{p_{\mathrm{H_2}}}{p_{\mathrm{H_2O}}}\right)$$

$$\Delta G^{\circ}_{\mathrm{ox}}(T) = 0 \text{ when } \Delta G^{\circ}_{\mathrm{ws}}(T) = \Delta G^{\circ}_{\mathrm{red}}(T) \qquad p_{\mathrm{H_2}} = p_{\mathrm{H_2O}}$$

Max. Conversion → 50%

Lidor A., Bulfin, B. Solar Compass, 11 (2024) 100077

Ceria is the main benchmark redox material used in such processes because it provides very good oxidation reaction kinetics, reactions reversibility and thermal cycling stability

$$CeO_2 \rightleftarrows CeO_{2-\delta} + {}^{\delta}/_{2}\, O_2$$

$$CeO_{2-\delta} + \delta H_2O \rightleftarrows CeO_2 + \delta\, H_2$$

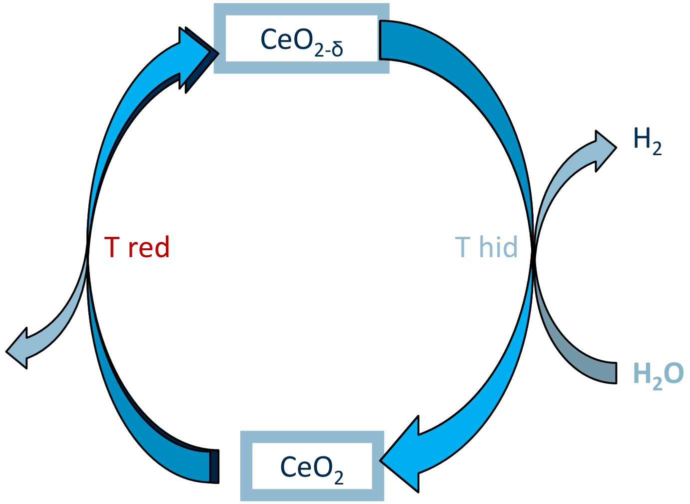
$$\delta = \frac{mol\ vacancies}{mol\ CeO_2}$$

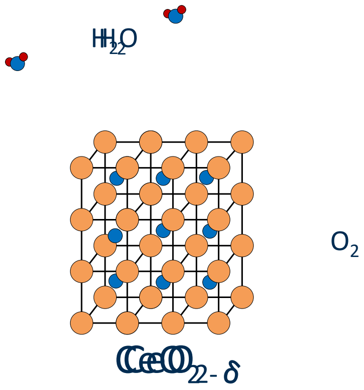
Panlener, R. J., Blumenthal, R. N. & Garnier, J. E. A thermodynamic study of nonstoichiometric cerium dioxide. J. Phys. Chem. Solids 36, 1213–1222 (1975)

Nonstoichiometric oxides like $CeO_{2-\delta}$, are stable and present high disorder (entropy) due lattice defects oxygen release

Activity properties have a dependence on δ

Production of hydrogen with non-stoichiometric metal oxides

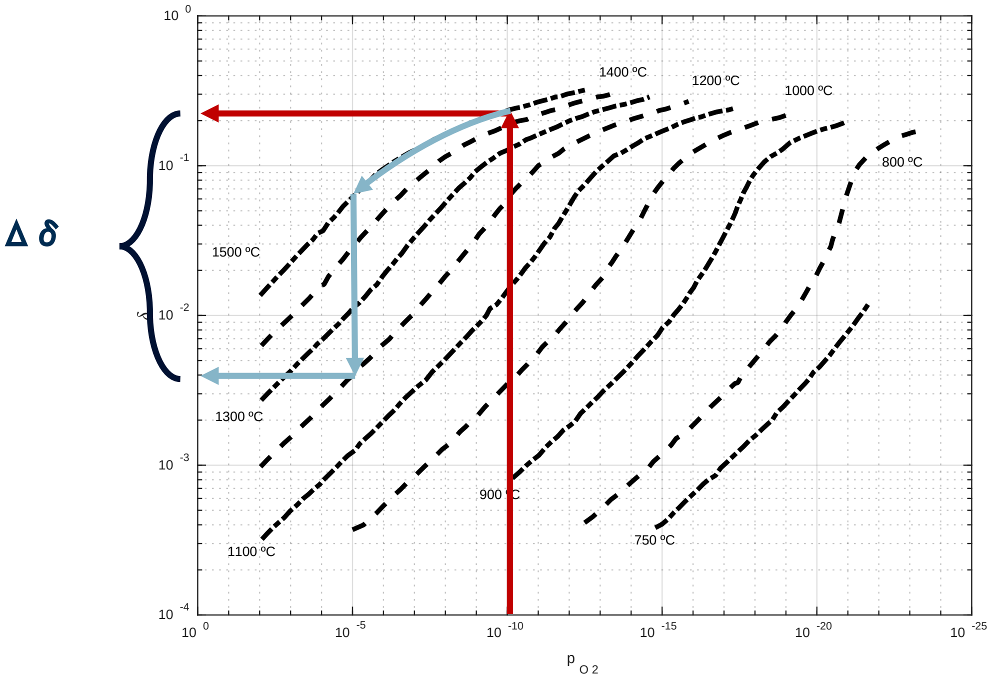


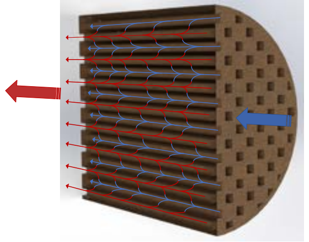


$$CeO_{2-\delta} + \delta H_2O \rightleftarrows CeO_2 + \delta\ H_2$$

$$CeO_2 \rightleftarrows CeO_{2-\delta} + {}^{\delta}/_{2}\,O_2$$

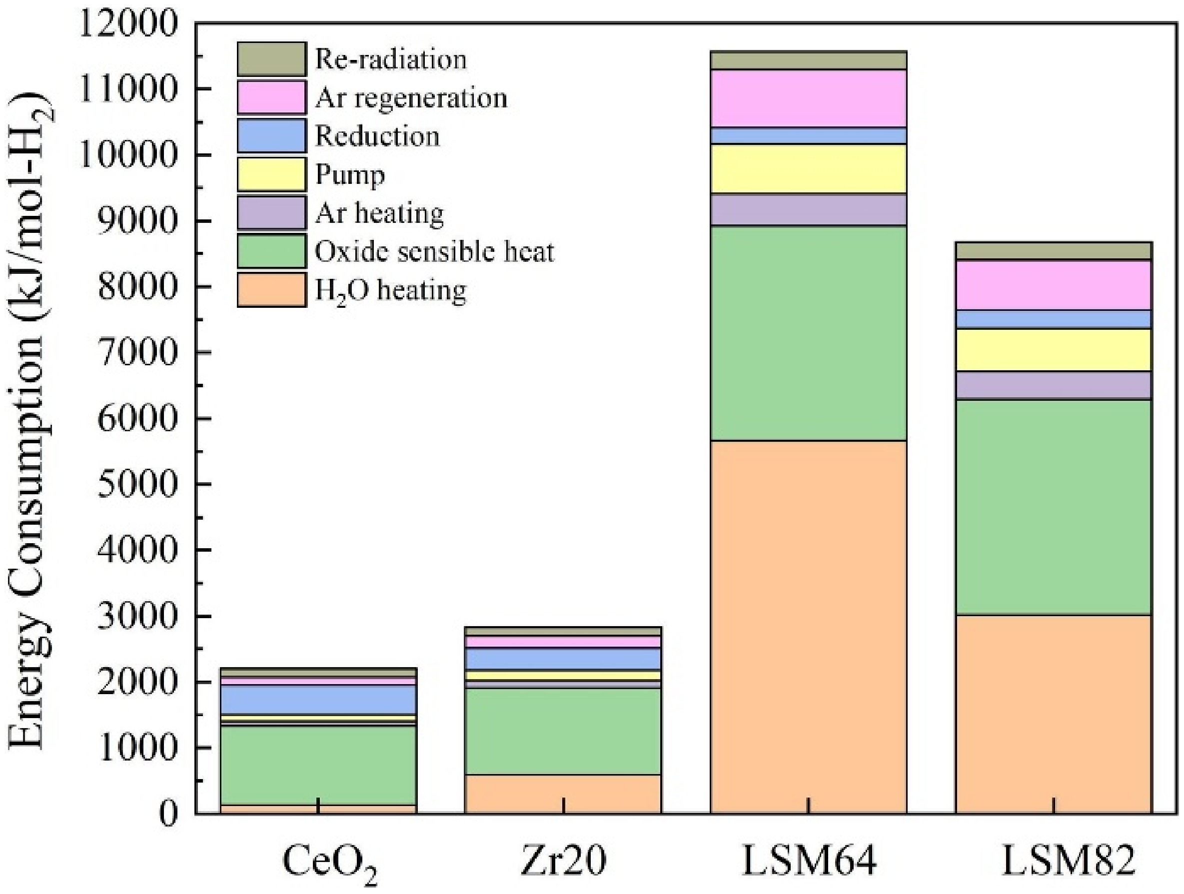
$$\delta = \frac{mol\ vacancies}{mol\ CeO_2}$$

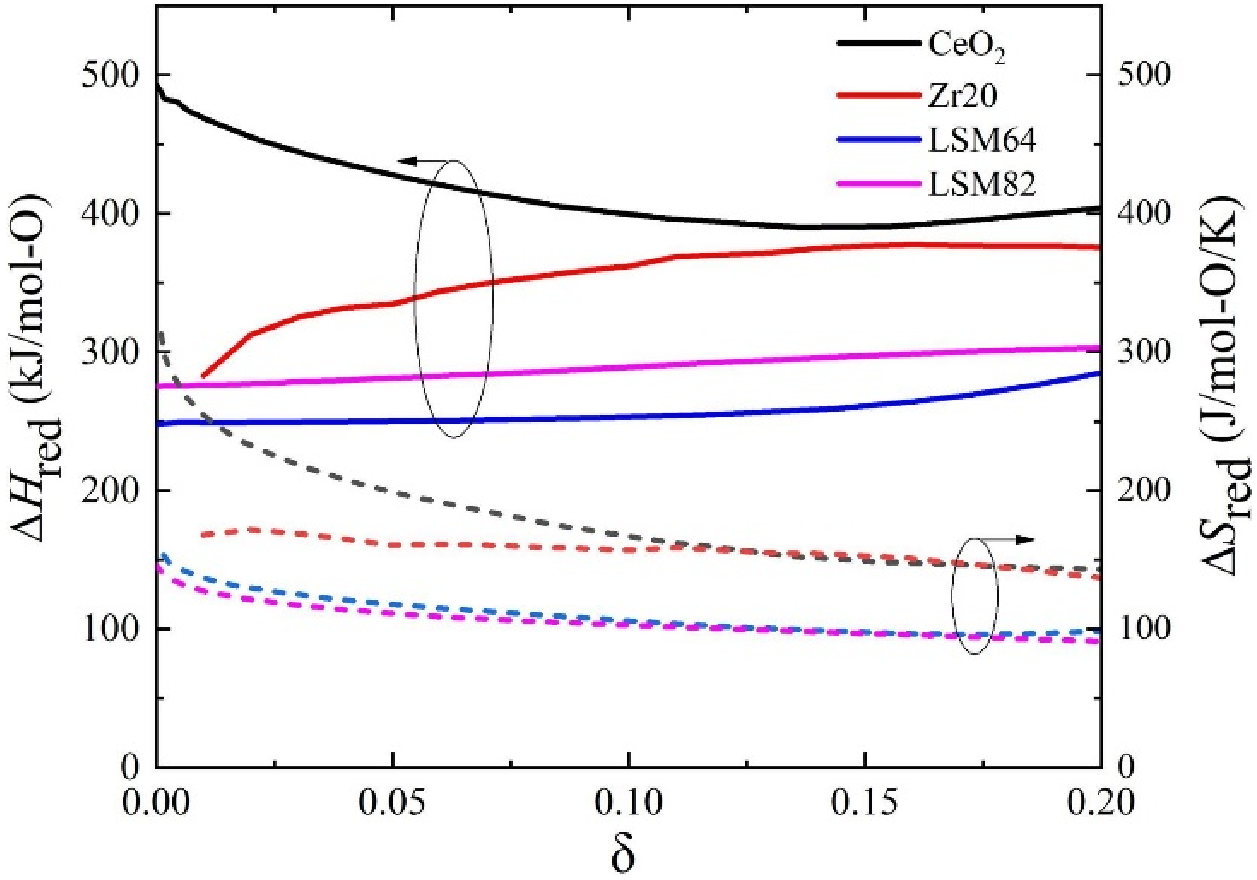




Panlener, R. J., Blumenthal, R. N. & Garnier, J. E. A thermodynamic study of nonstoichiometric cerium dioxide. J. Phys. Chem. Solids 36, 1213–1222 (1975)

Efficiency under material optimum conditions

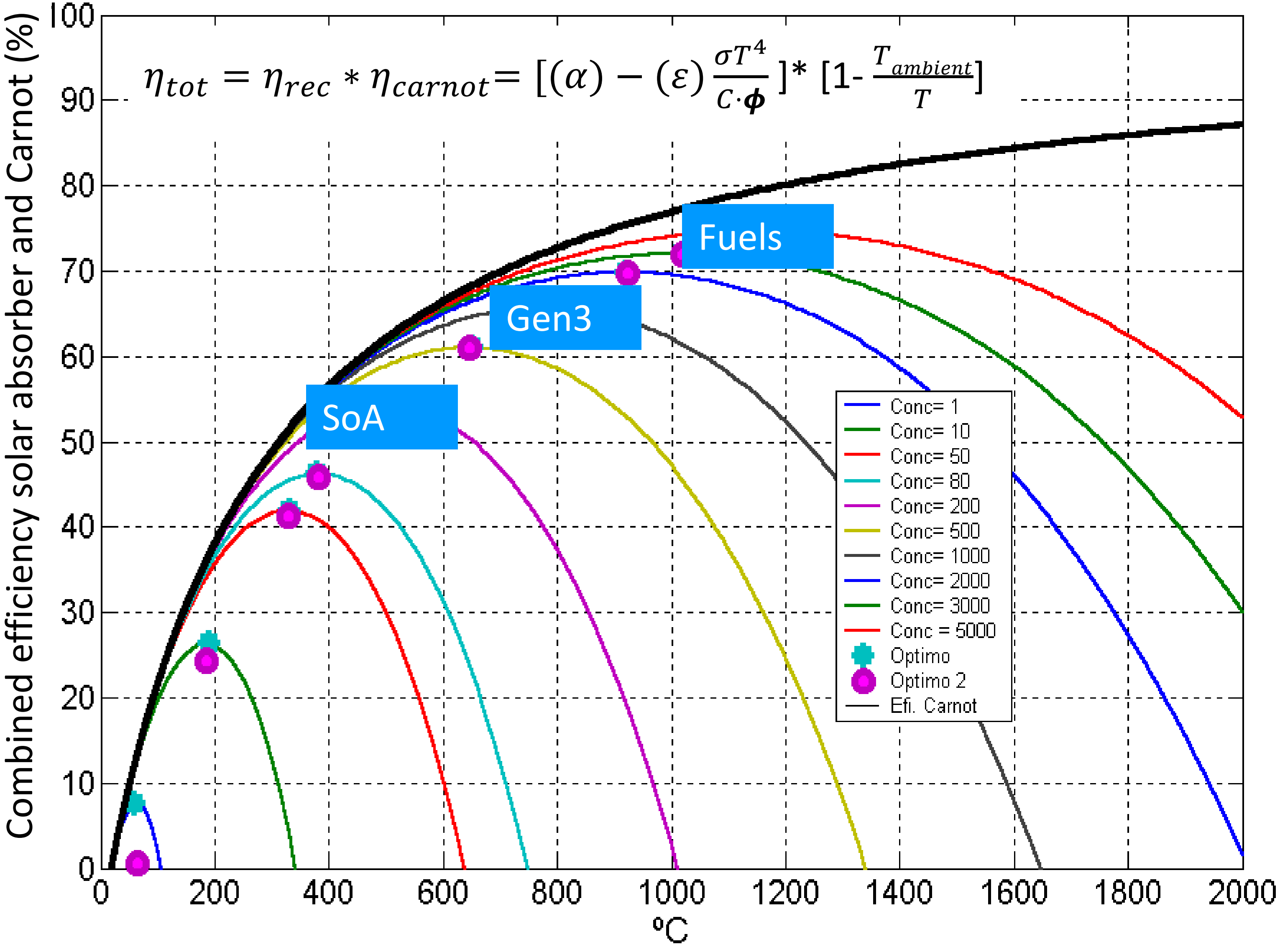




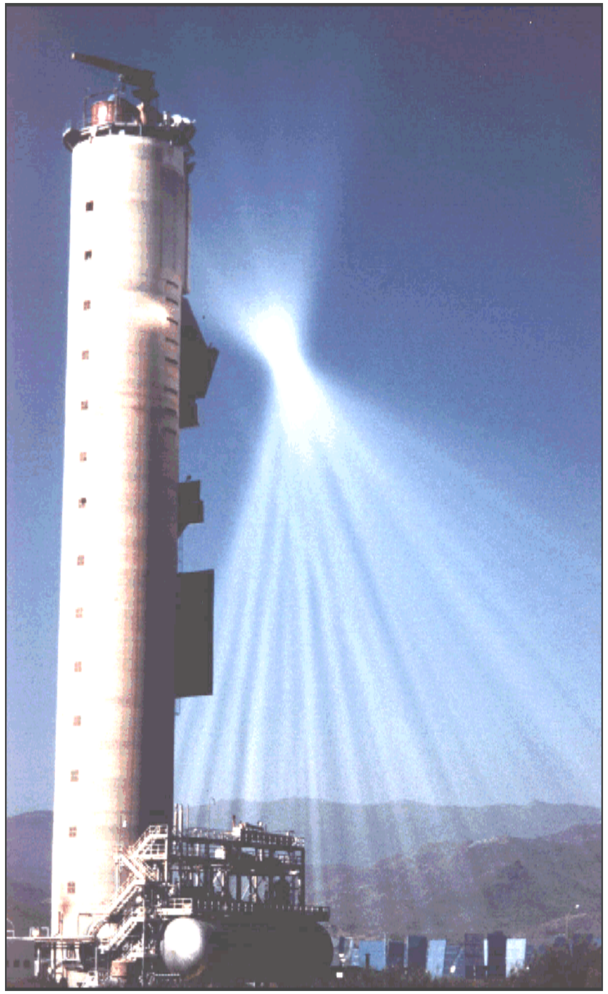
Lou J, Tian Z, Wu Y, Li X, Qian X, Haile S.M.,Hao Y, Solar Energy 241 (2022) 504–514

Challenge 1: Solar fuels, beyond SoA of solar towers

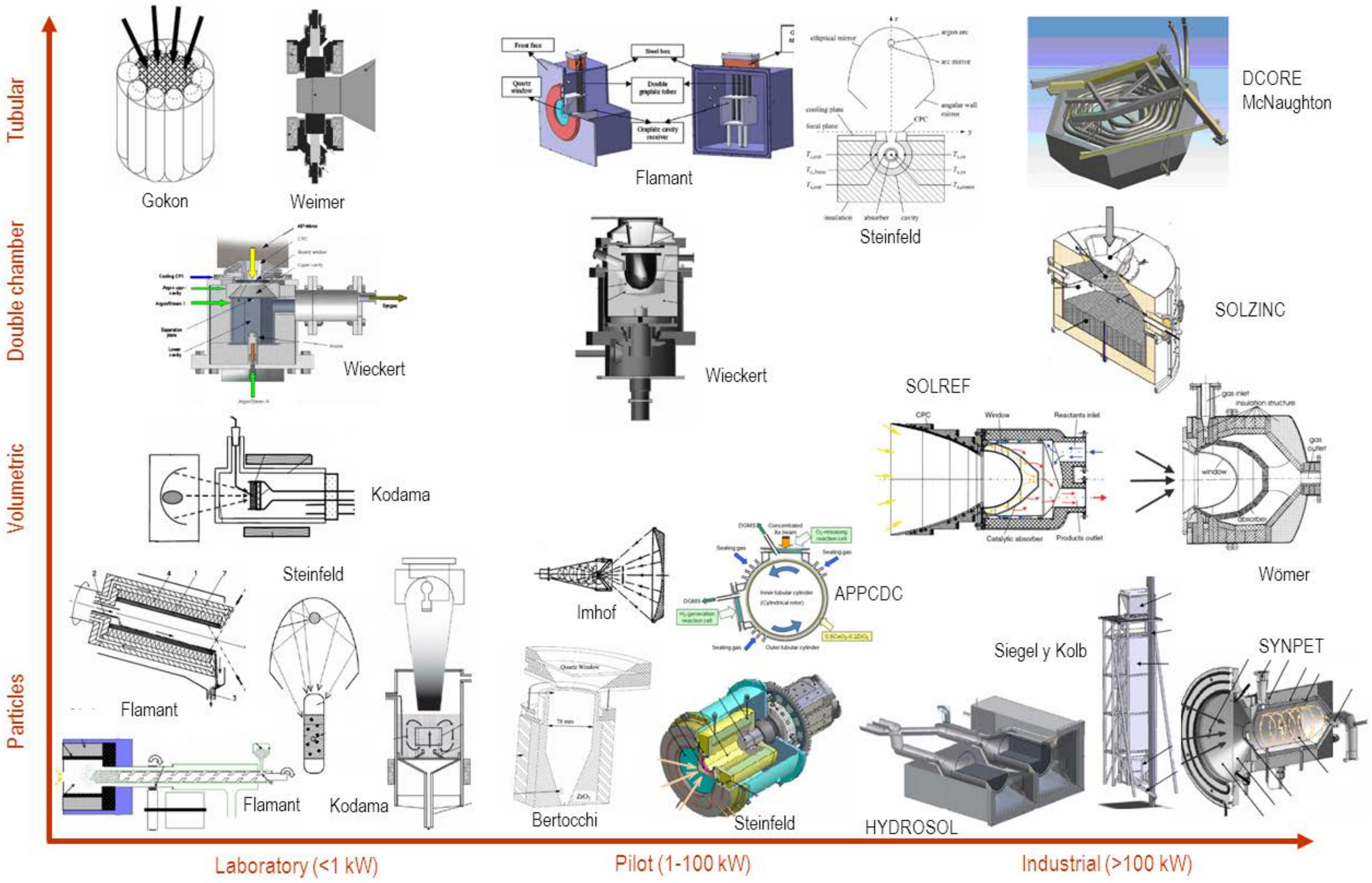
T_{amb}=20ºC, ϕ = 770 W/m^2 and $\alpha=\varepsilon=0.95$



$$\eta_{tot} = \eta_{rec} * \eta_{carnot} = [(\alpha) - (\varepsilon)\frac{\sigma T^4}{C \cdot \boldsymbol{\phi}}]* [1- \frac{T_{ambient}}{T}]$$

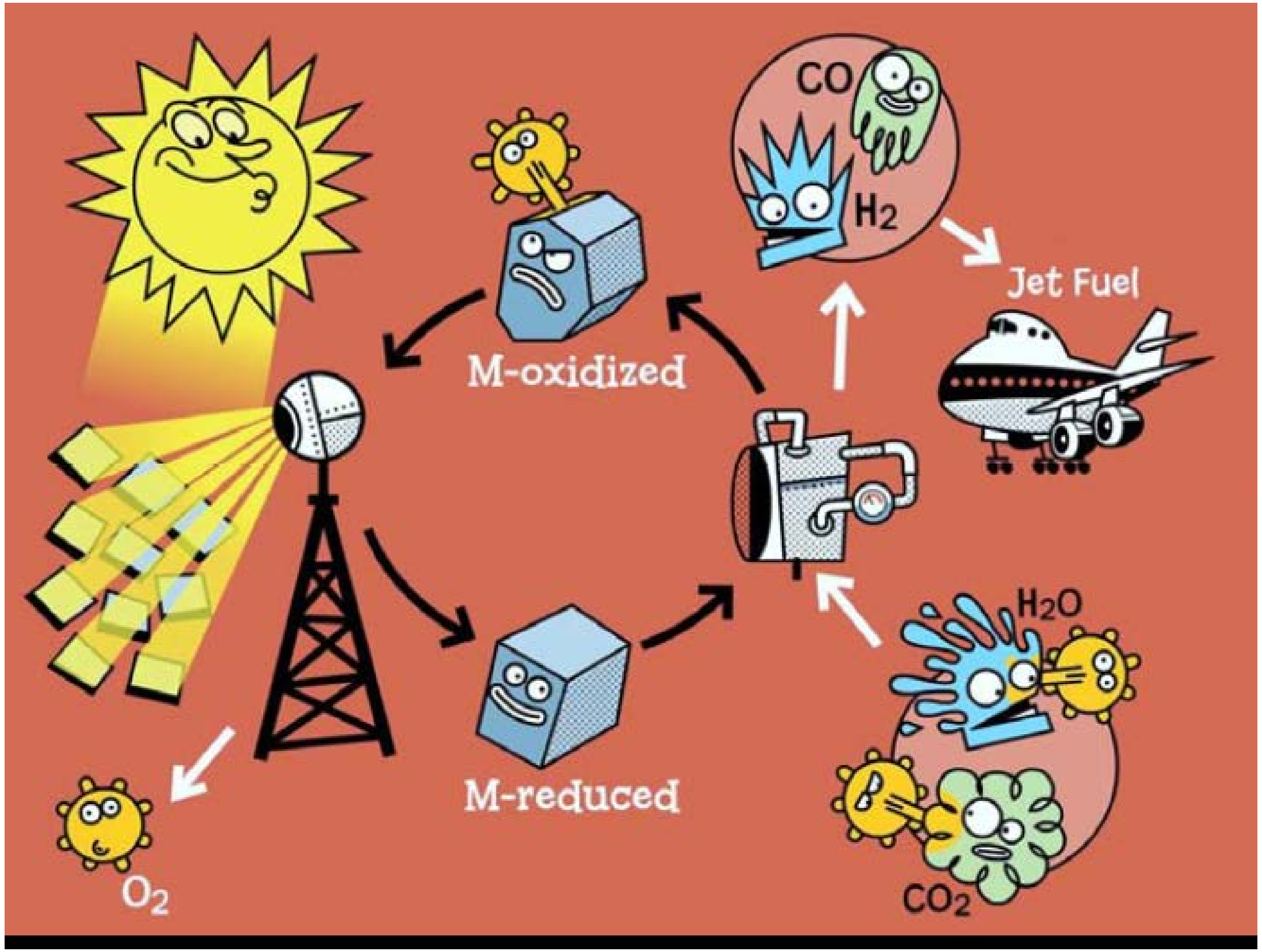


Challenge 2: Materials and solar reactors for high flux/high temperature



- **Very high concentration optics ($>2000\ kW/m^2$ average)**
- **High flux/high T materials**
- **New concepts of solar reactors (volumetric, particles)**
- **Scaling up issues**
- **Heat recovery (a must)**

The good coupling of solar tower technology and termochemical redox reactors



Romero and Steinfeld, Energy Environ. Sci., 2012, 5, 9234

SolarPACES Lifetime Achievement Award, Rome, October 11th, 2024

SUN to LIQUID (2016-2019)

Fuels from concentrated sunlight

Contact:
Dr. Andreas Sizmann

Tel:
+49 (0)89 307 4849-38

Email:
andreas.sizmann@bauhaus-luftfahrt.net
valentin.batteiger@bauhaus-luftfahrt.net Web: **www.sun-to-liquid.eu**

Address:
Bauhaus Luftfahrt e.V.
Willy-Messerschmitt-Str. 1 82024
Taufkirchen
Germany

● A project gathering **7 partners** from **5 European countries:**

ABENGOA

Bauhaus Luftfahrt
Neue Wege.

DLR Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center

ETH zürich

HYGEAR
COST-EFFECTIVE GAS SUPPLY

institute imdea energy

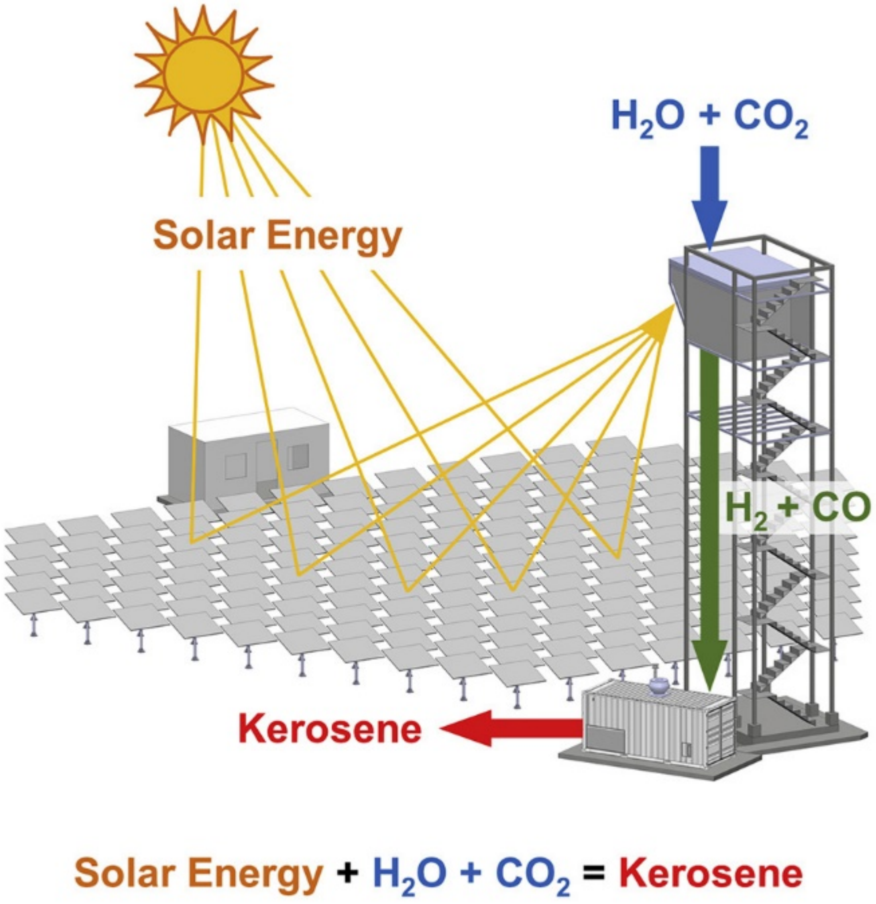
ARTTIC
INTERNATIONAL MANAGEMENT SERVICES

SUN-to-LIQUID
http://www.sun-to-liquid.eu

This work was supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0330

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 654408

Solar field ACES / VHCST



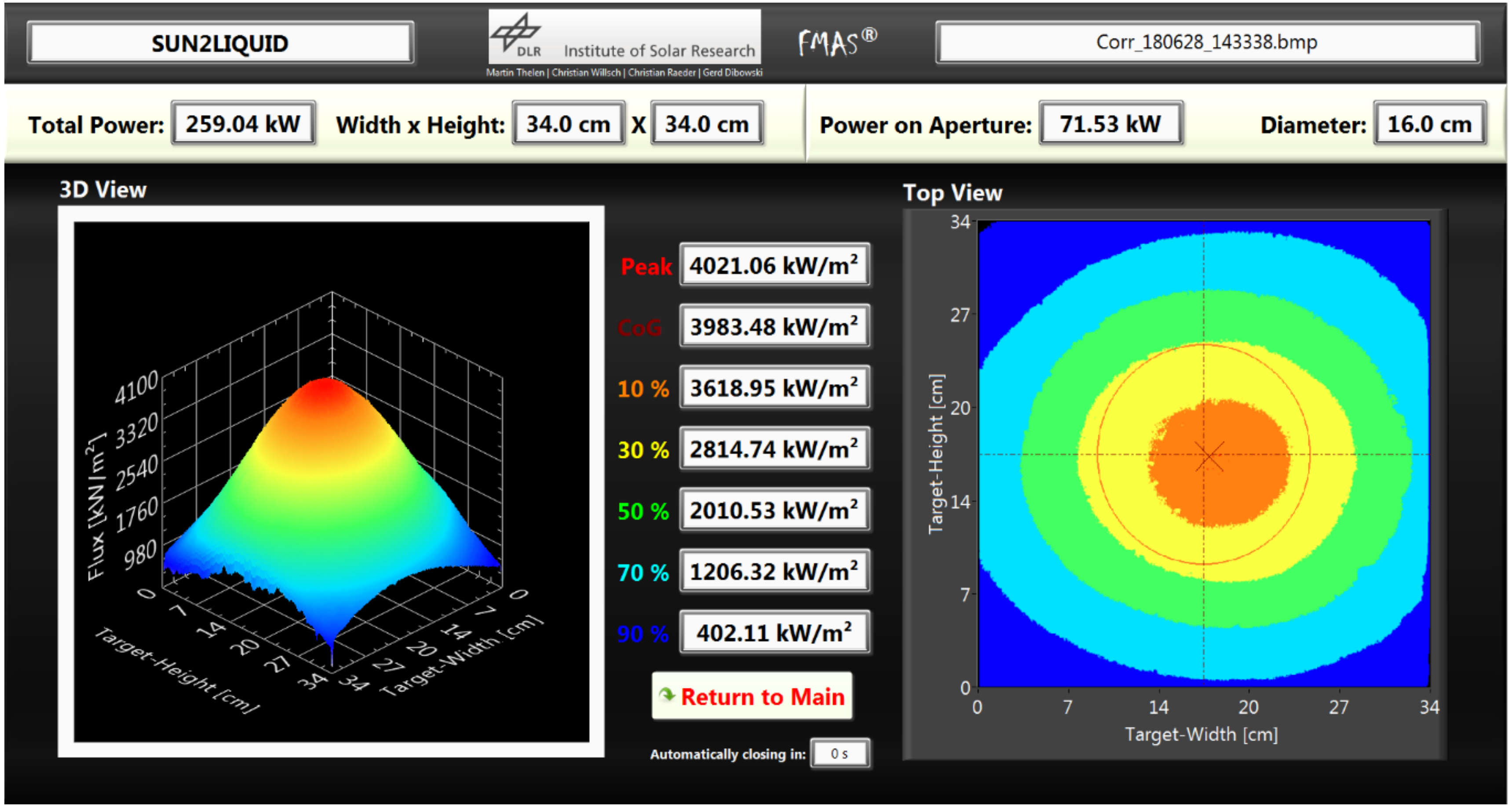
Nominal thermal power, 250 kW

169 heliostats (3 m^2)

2 testing platforms

Testing and characterization of high-flux solar concentration system

- Highest measured power ever achieved: 71.5 kW onto 16-cm aperture (new calorimeter on site), solar noon on 28th June 2018, for a DNI of 800 W/m^2



SUN2LIQUID

DLR Institute of Solar Research

Martin Thelen | Christian Willsch | Christian Raeder | Gerd Dibowski

FMAS®

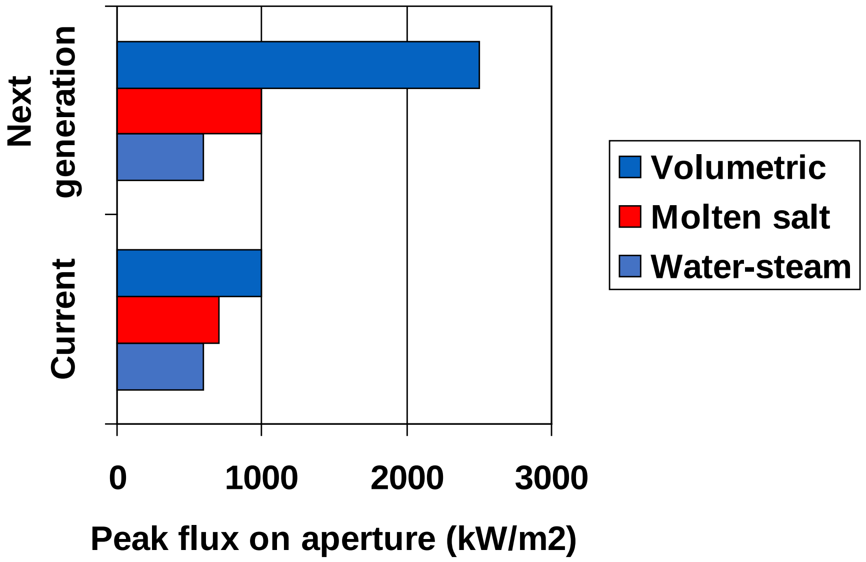
Corr_180628_143338.bmp

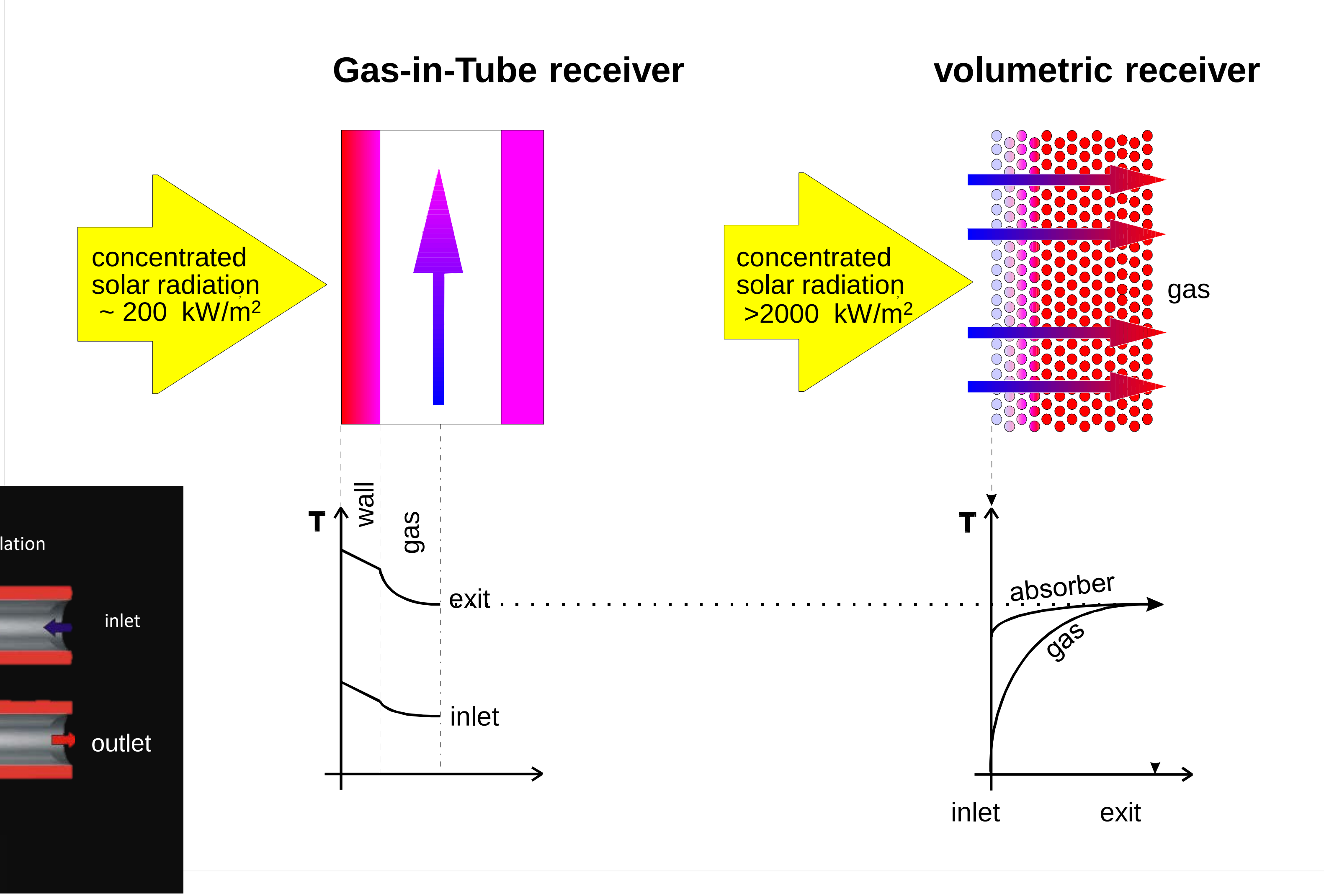
Total Power: 259.04 kW **Width x Height:** 34.0 cm X 34.0 cm **Power on Aperture:** 71.53 kW **Diameter:** 16.0 cm

Peak	4021.06 kW/m²
CoG	3983.48 kW/m²
10 %	3618.95 kW/m²
30 %	2814.74 kW/m²
50 %	2010.53 kW/m²
70 %	1206.32 kW/m²
90 %	402.11 kW/m²

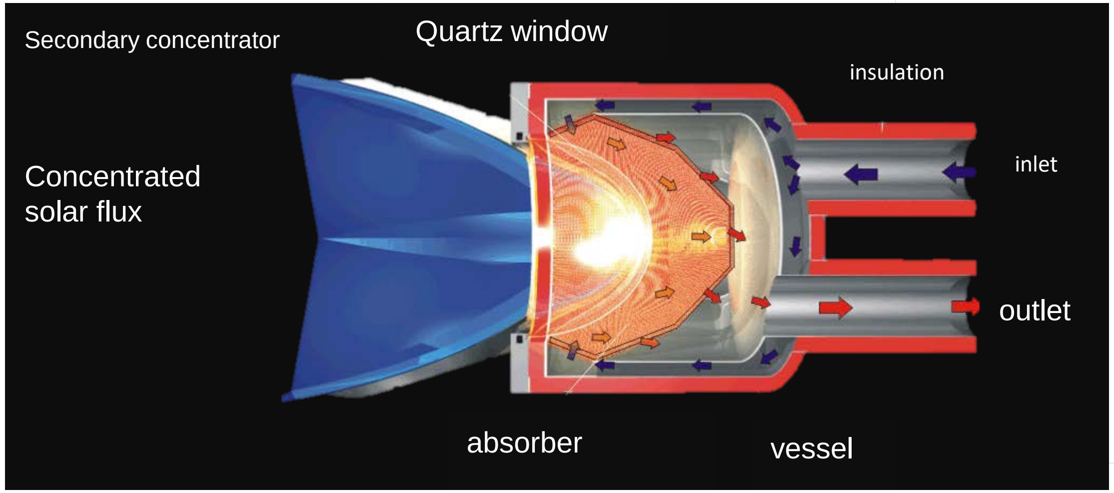
Automatically closing in: 0 s

Fundamentals of a volumetric solar receiver

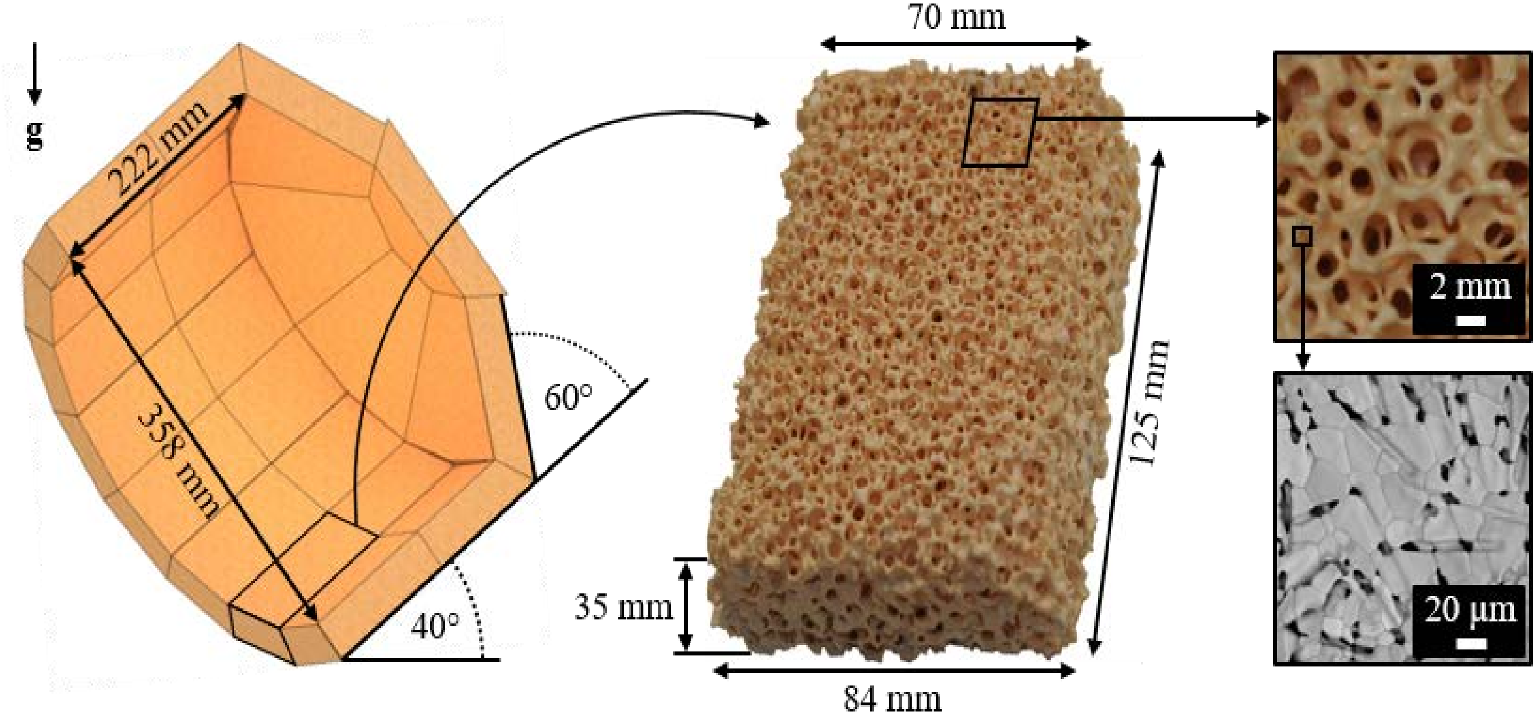



Gas-in-Tube receiver

volumetric receiver



Internal distribution of Ceria RPC bricks



Details on the self-supporting, interlocking ceria structure assembled out of 41 separate RPC bricks, including the center-back keystone. The RPC features dual-scale porosity: millimeter-scale pores made by struts which contain micrometer-scale pores.

Operation of the Solar Reactor

1st step: **Reduction**

$$\mathrm{CeO_2} \rightarrow \mathrm{CeO_{2-\delta}} + \frac{\delta}{2}\mathrm{O_2}$$

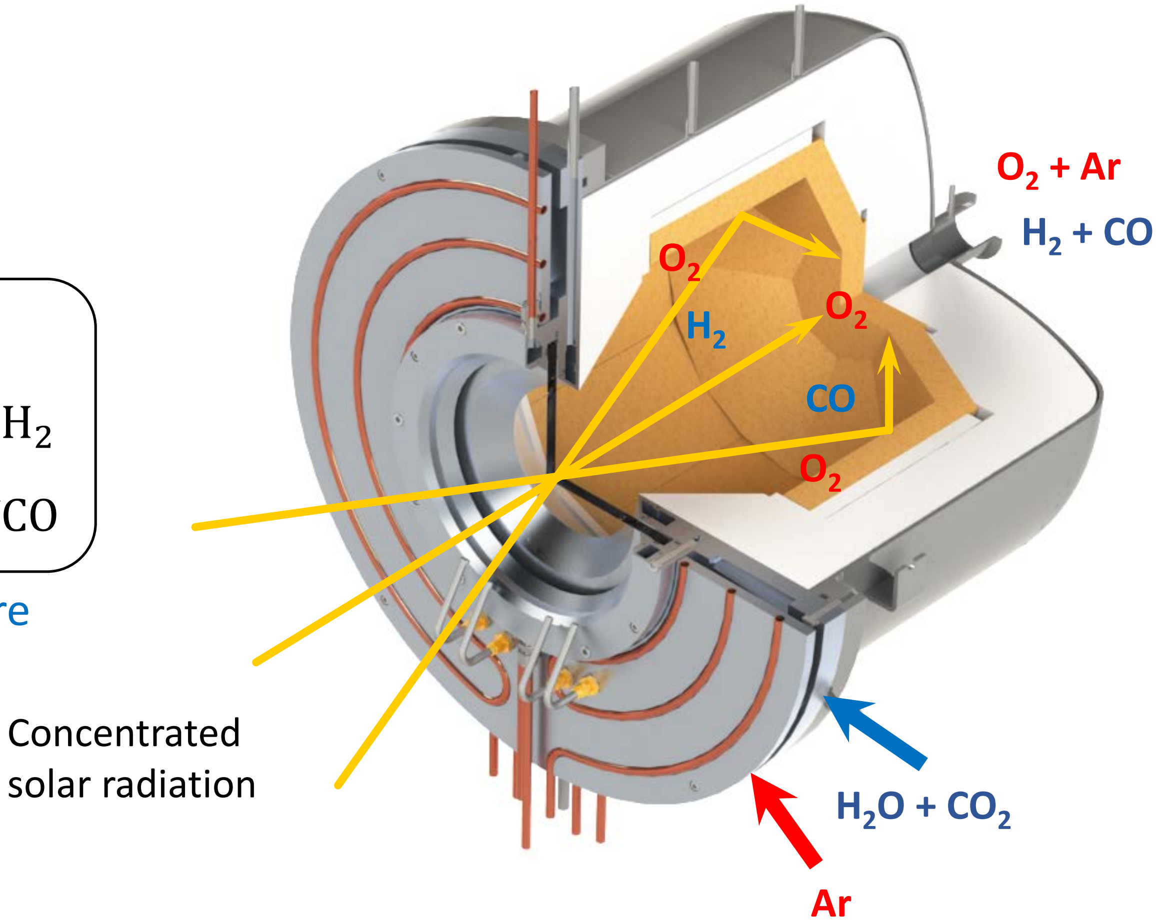
1500 °C, vacuum

2nd step: **Oxidation**

$$\mathrm{CeO_{2-\delta}} + \delta\mathrm{H_2O} \rightarrow \mathrm{CeO_2} + \delta\mathrm{H_2}$$

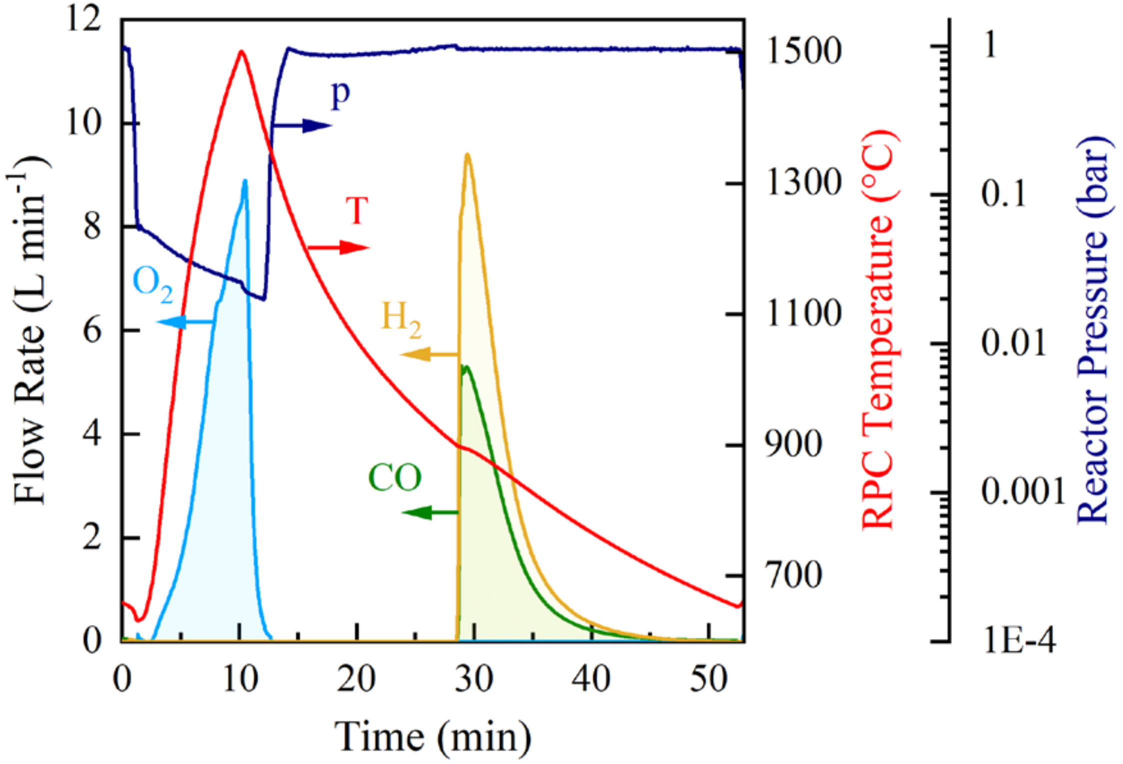
$$\mathrm{CeO_{2-\delta}} + \delta\mathrm{CO_2} \rightarrow \mathrm{CeO_2} + \delta\mathrm{CO}$$

900 °C, atmospheric pressure



Zoller S., Koepf E., Nizamian D., Stephan M., Patané A., Haueter Ph., Romero M., Gonzalez-Aguilar J., Lieftink D., de Wit E., Brendelberger S., Sizmann A., Steinfeld A. Joule 6, 1606–1616, July 20, 2022

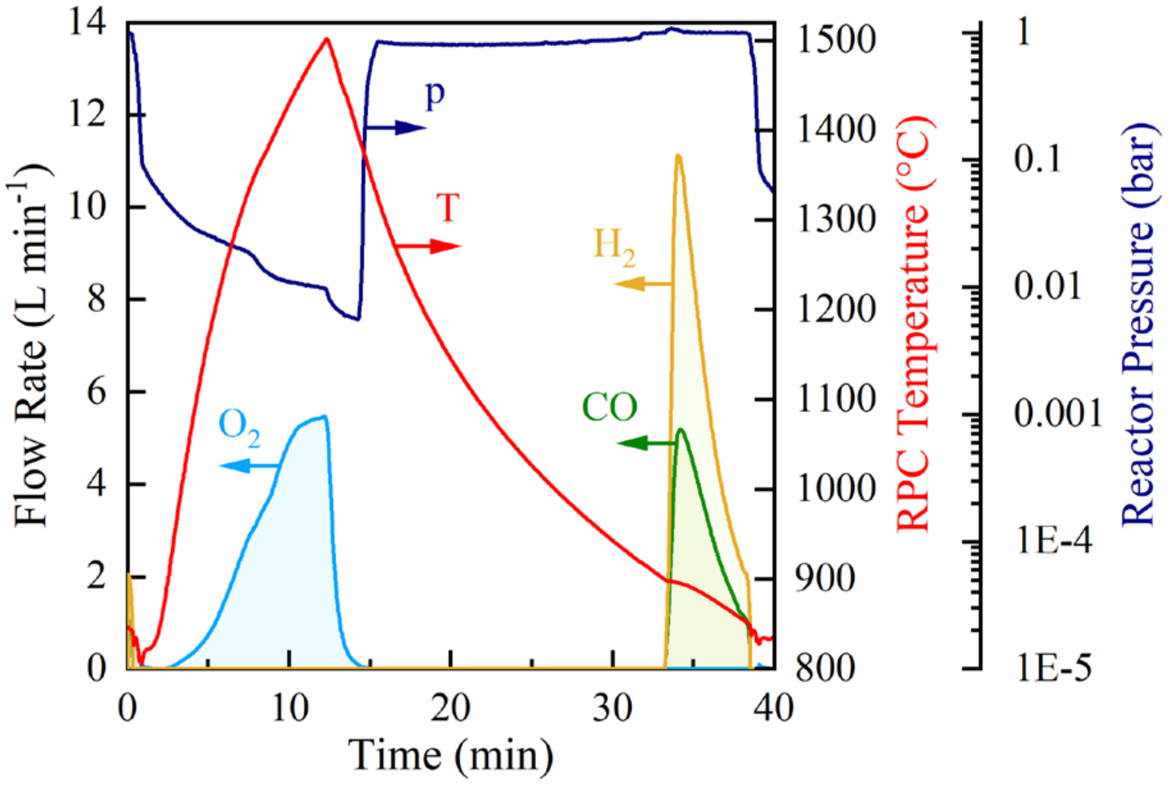
Co-Splitting of H_2O and CO_2 at mean solar flux concentration of 2,500 kW/m^2



$$\eta_{solar-to-syngas} = \frac{Q_{syngas}}{Q_{input}} = \frac{Q_{syngas}}{Q_{solar}+Q_{pump}+Q_{inert}}$$

Variable	Symbol	Value	Unit
Ceria RPC mass	m_{RPC}	18.1	kg
Average solar power input during reduction	P_{solar}	42.0±6.2	kW
Reduction start-end temperature	$T_{reduction,start}$	632-1502	°C
Oxidation start-end temperature	$T_{oxidation,start}$	900-654	°C
Ar flow rate during reduction	$\dot{V}_{Ar}$	5.0	L min^{-1}
H_2O flow rate during oxidation	$\dot{n}_{H2O}$	0.033	mol s^{-1}
CO_2 flow rate during oxidation	$\dot{n}_{CO2}$	0.0074	mol s^{-1}
Reactor pressure during reduction		26-70	mbar
Reactor pressure during oxidation		atmospheric	
Reduction duration		8.8	min
Duration of cooling-down		18.3	min
Oxidation duration		24.0	min
Cycle duration		51.1	min
Total amount of O_2 released		36.2±0.7	L
Avg. nonstoichiometry of ceria after reduction	δ	0.031±0.001	
Total amount of H_2O produced		48.9±3.9	L
Total amount of CO produced		24.4±2.0	L
Molar ratio H_2/CO		2.01±0.35	
Solar-to-syngas energy efficiency	$\eta_{solar-to-syngas}$	4.1±0.8	%

Typical Cycle with Optimized Oxidation

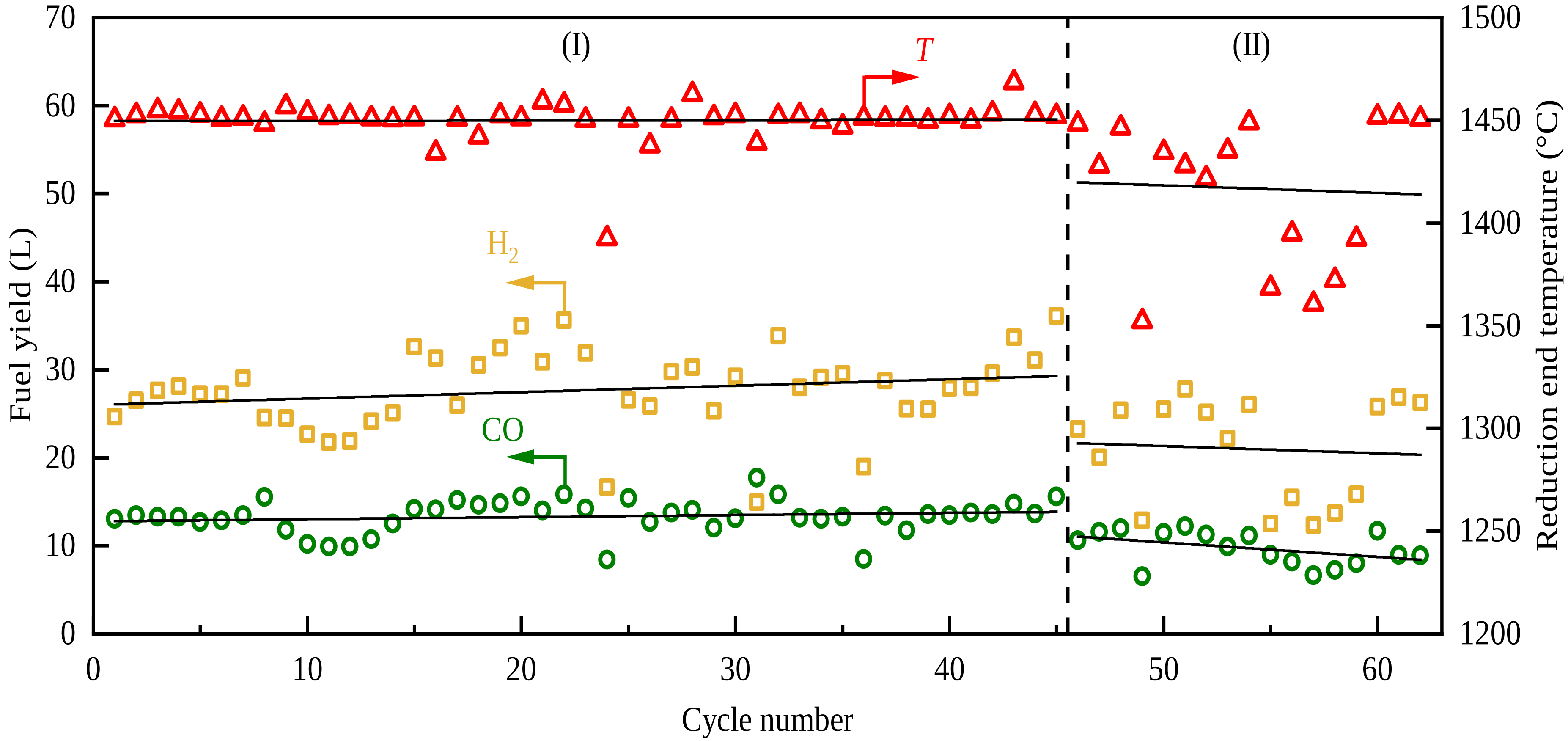


Strategy to reduce unreacted CO_2 and increment daily production

Experimental Conditions	
$T_{start,oxidation}$	900 °C
$\dot{V}_{H_2O} + \dot{V}_{CO_2}$	81 L/min
Molar ratio H_2O:CO_2	5.5
Oxidation end	x_{CO_2} = 80 %
Ox. duration	6.8 min

Experimental Results	
V_{H_2}	15 L
V_{CO}	30 L
Molar ratio H_2:CO	2.0

Total amounts of produced H2 and CO per cycle for 62 consecutive redox cycles



Nominal ceria RPC temperature at the end of the reduction step and total amounts of produced H2 and CO per cycle for 62 consecutive redox cycles, yielding 5,191 G 364 L of syngas with a composition 31.8% G 3.2% H2, 15.2% G 2.4% CO, and 53.0% G 3.6% CO2 (H2O condensed).

Zoller S., Koepf E., Nizamian D., Stephan M., Patané A., Haueter Ph., Romero M., Gonzalez-Aguilar J., Lieftink D., de Wit E., Brendelberger S., Sizmann A., Steinfeld A. Joule 6, 1606–1616, July 20, 2022

Specific test validation

SUNtoLIQUID II

FUELS FROM CONCENTRATED SUNLIGHT

(2023-2027)

Efficient solar thermochemical synthesis of liquid hydrocarbon fuels using tailored porous-structured materials and heat recuperation

HORIZON-CL5-2022-D3-03-07 - Development of algal and renewable fuels of non-biological origin

Bauhaus Luftfahrt *The Aviation Think Tank*

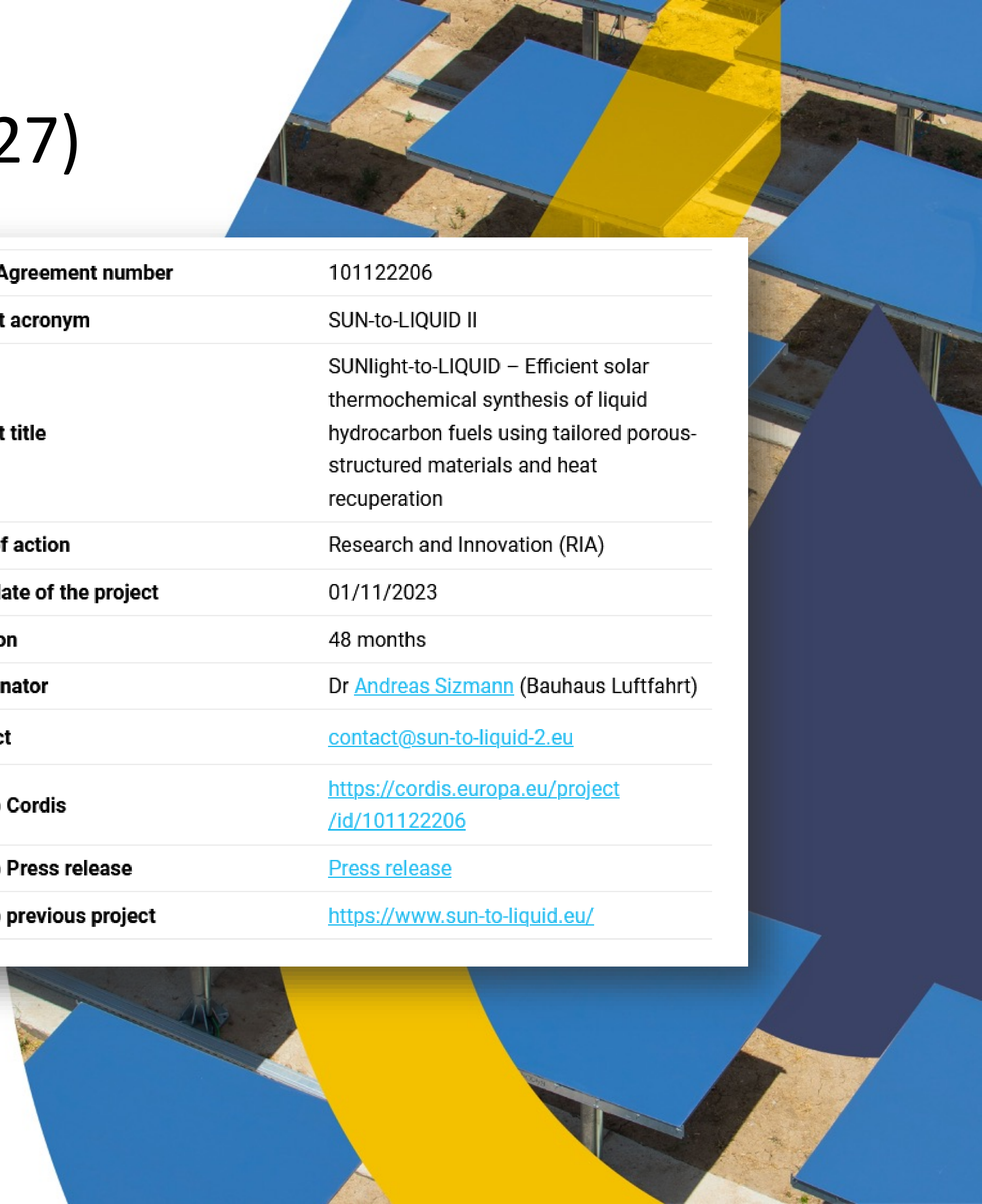
instituto imdea energía

DLR

HYGEAR THE GLOBAL HYDROGEN SOURCE

UPL

Synhelion



Grant Agreement number	101122206
Project acronym	SUN-to-LIQUID II
Project title	SUNlight-to-LIQUID – Efficient solar thermochemical synthesis of liquid hydrocarbon fuels using tailored porous-structured materials and heat recuperation
Type of action	Research and Innovation (RIA)
Start date of the project	01/11/2023
Duration	48 months
Coordinator	Dr Andreas Sizmann (Bauhaus Luftfahrt)
Contact	contact@sun-to-liquid-2.eu
Link to Cordis	https://cordis.europa.eu/project/id/101122206
Link to Press release	Press release
Link to previous project	https://www.sun-to-liquid.eu/

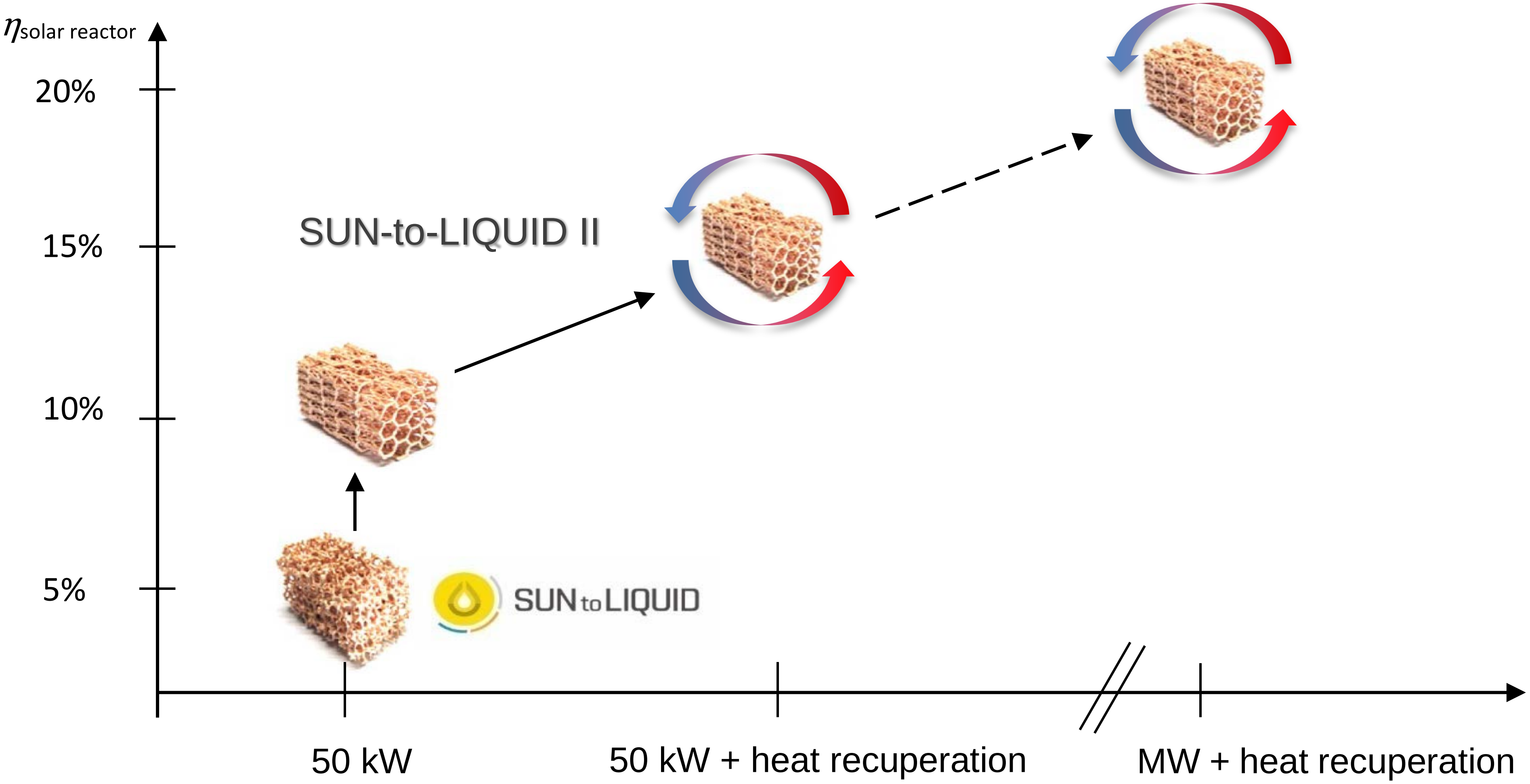
Project funded by

Schweizerische Eidgenossenschaft
Confédération Suisse
Condederazione Svizzera
Confedeaziun svizraSwiss confederation

Federal Department of Economic Affairs, Education and Research EAER
State Secretariat for Education, Research and innovation SERI

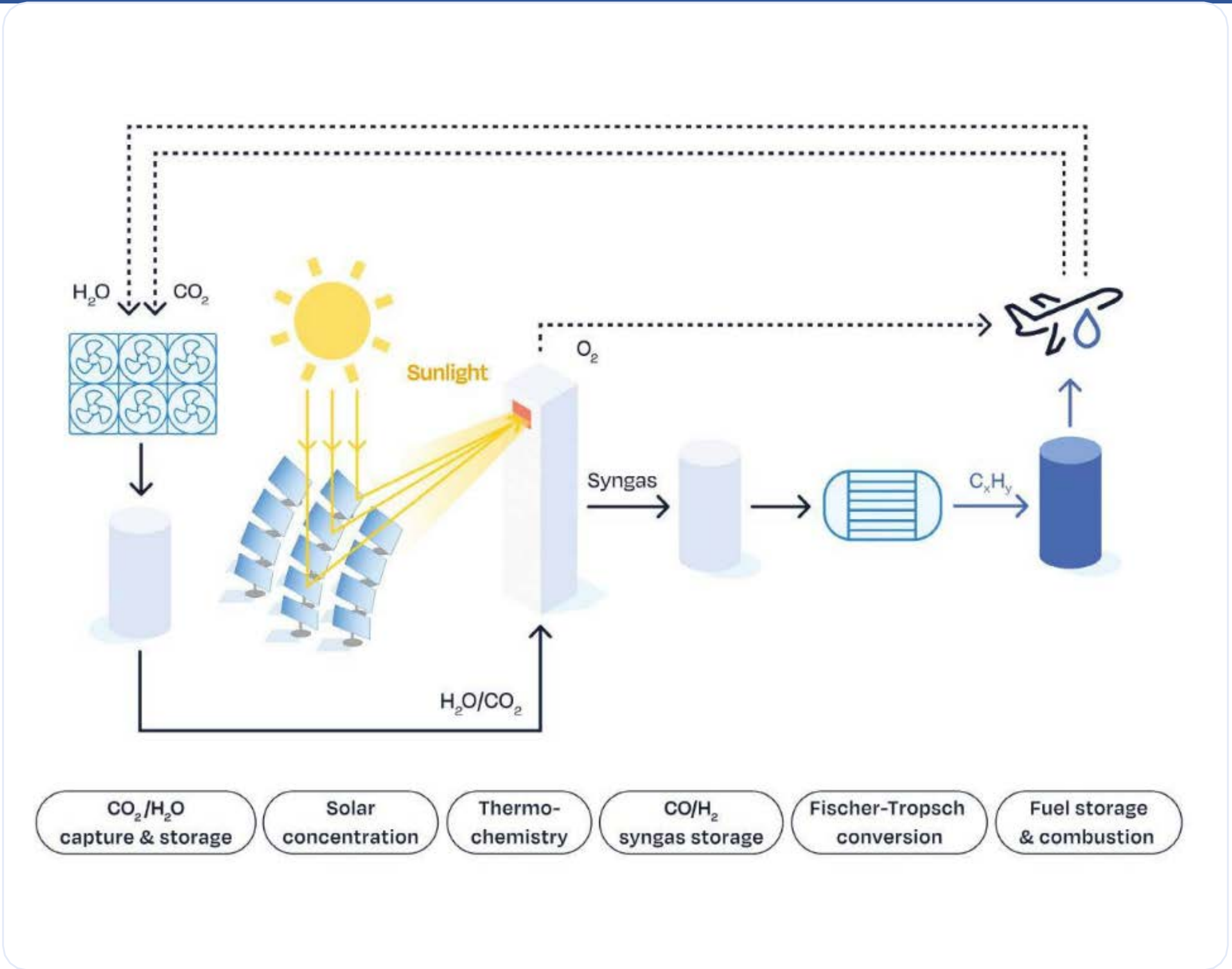
Funded by
the European Union

Ambition


$\eta_{\text{solar reactor}}$
20%
15%
10%
5%
SUN-to-LIQUID II
SUN to LIQUID
50 kW
50 kW + heat recuperation
MW + heat recuperation

Thank you for your attention!

SUN to LIQUID
Fuels from concentrated sunlight



SUNtoLIQUID II
FUELS FROM CONCENTRATED SUNLIGHT

Results presented originating from educational cooperation between Dr. Manuel Romero and Dr. José González-Aguilar, IMDEA Energía and Prof. Steinfeld’s PREC-ETHZ and from partnerships at H2020 EU project Sun-to-Liquid (EU GA 654408), HE Sun to Liquid II (EU GA 101122206) and Swiss SERI.