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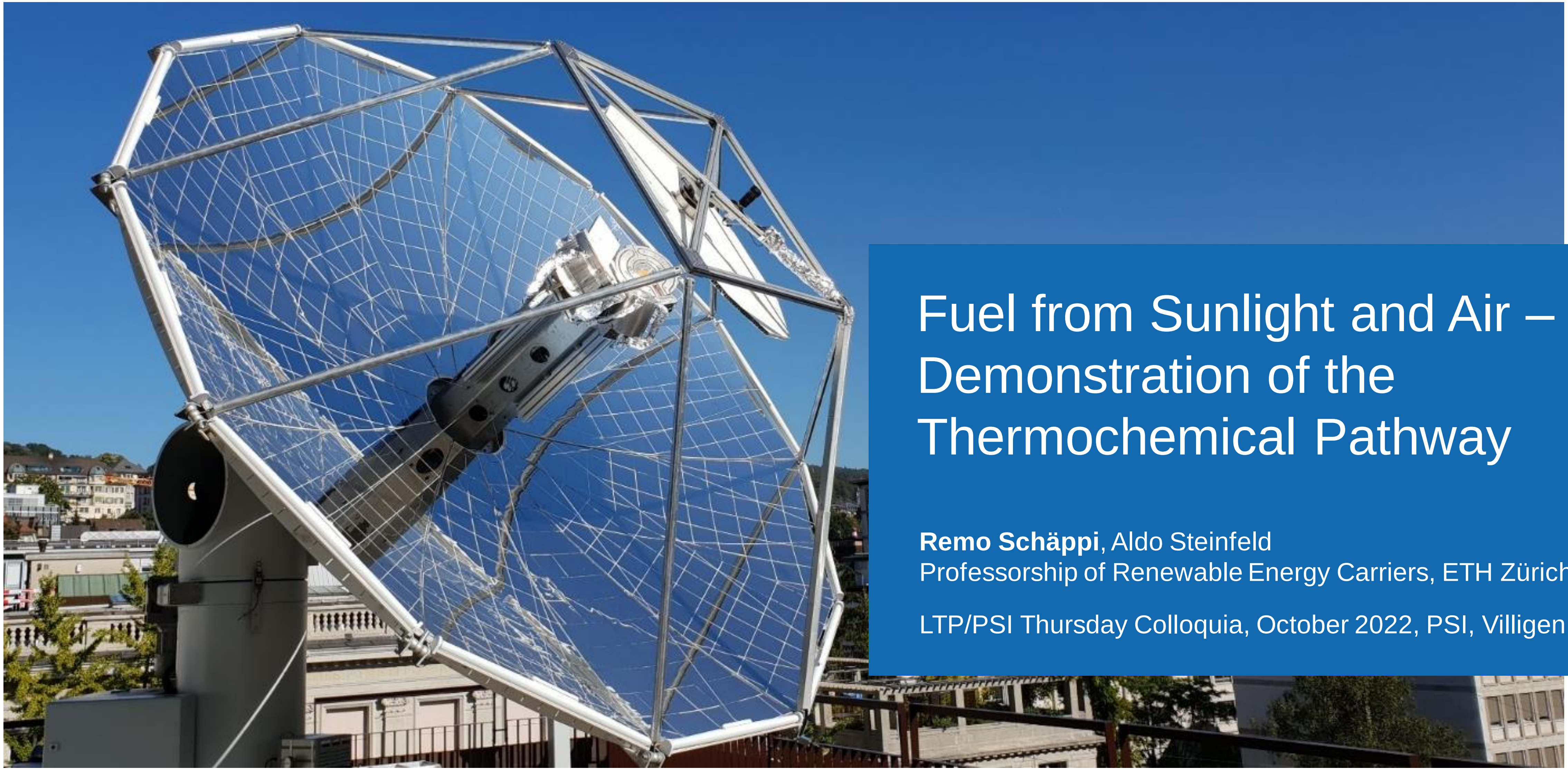
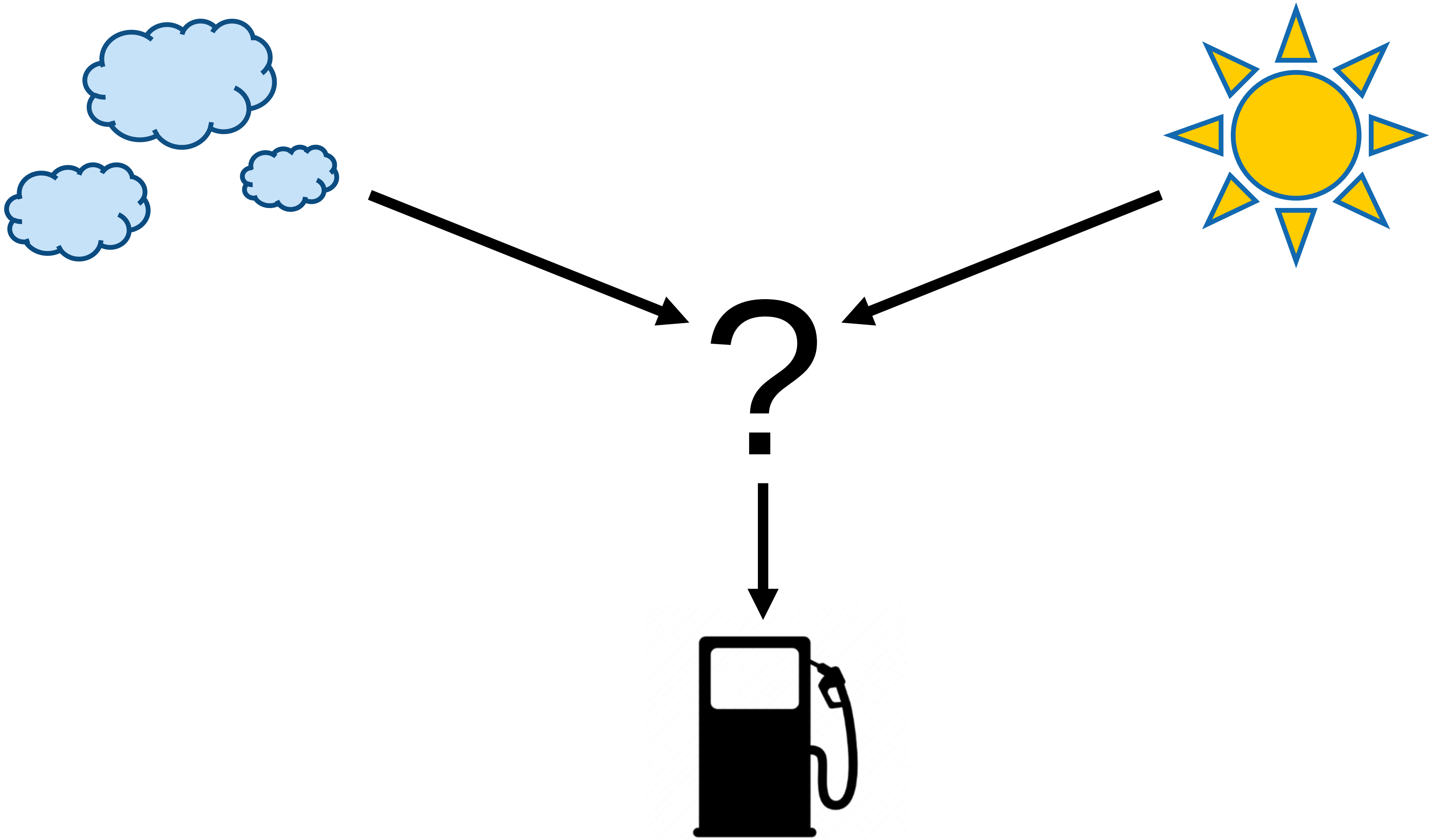


Fuel from Sunlight and Air – Demonstration of the Thermochemical Pathway

Remo Schäppi, Aldo Steinfeld
Professorship of Renewable Energy Carriers, ETH Zürich

LTP/PSI Thursday Colloquia, October 2022, PSI, Villigen

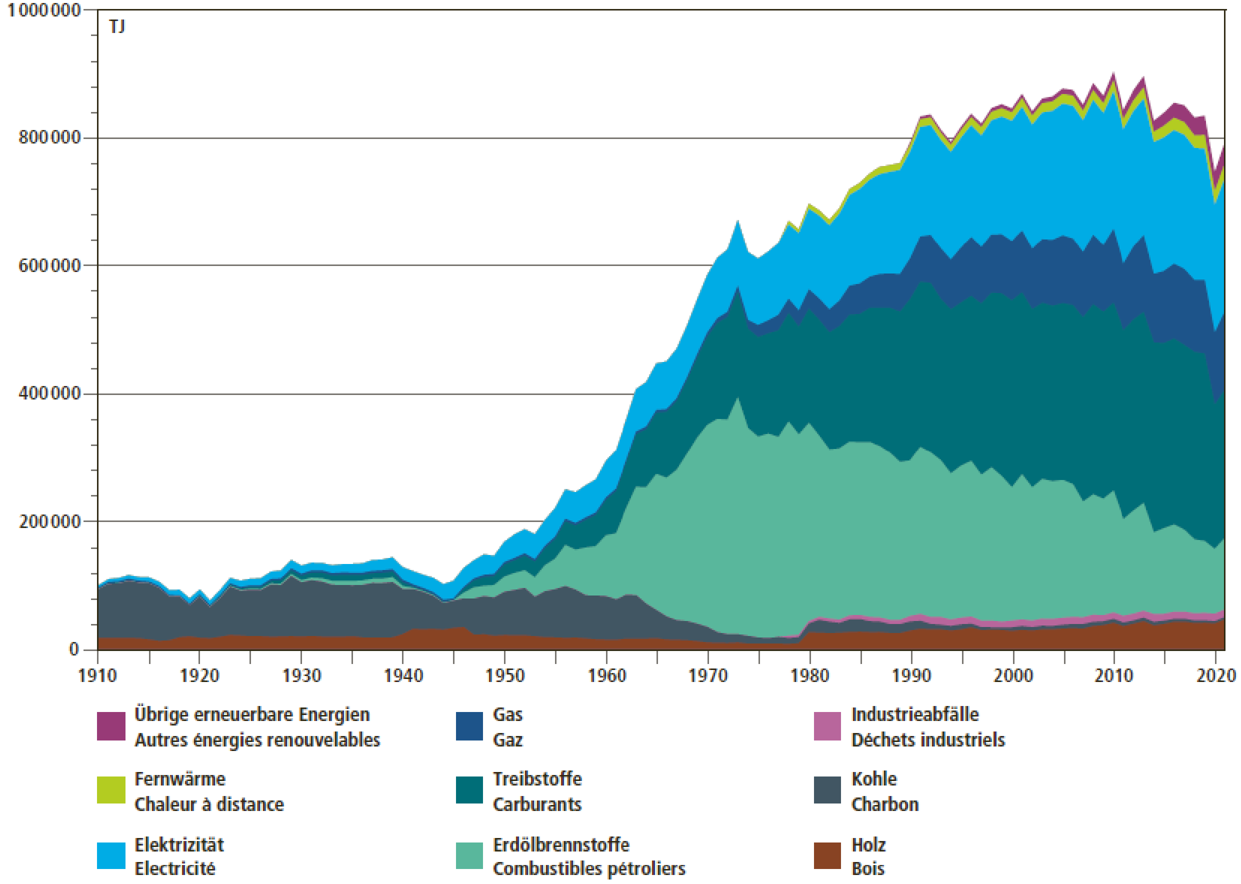
Fuel production from sunlight and air



Energy consumption in Switzerland

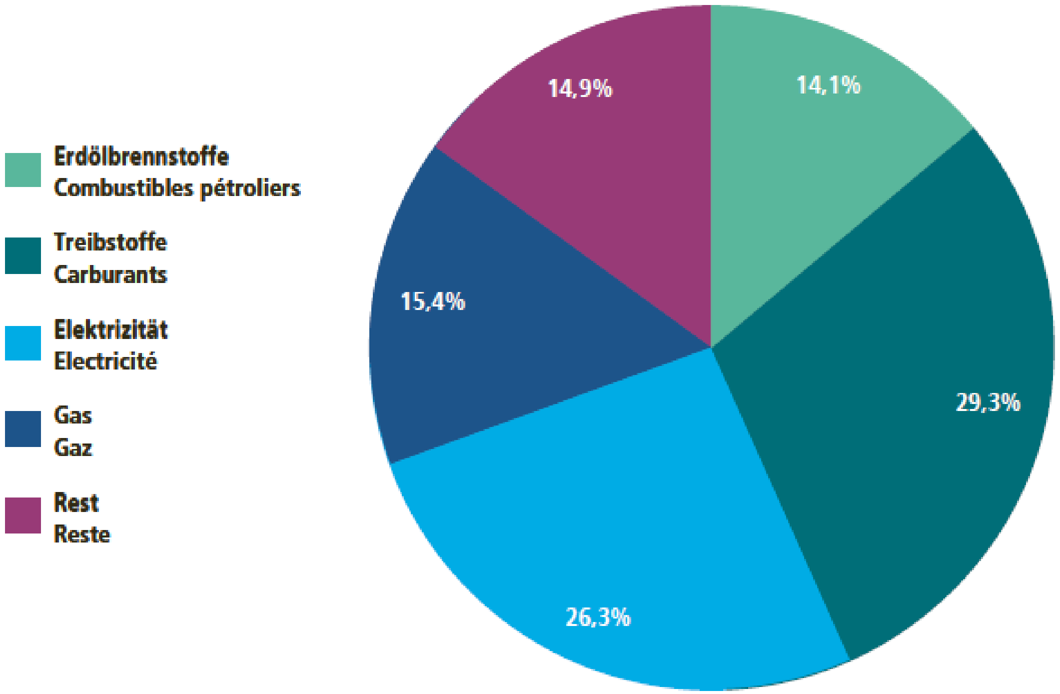
Total final consumption by source

Fig. 1 Endenergieverbrauch 1910–2021 nach Energieträgern
Consommation finale 1910–2021 selon les agents énergétiques



BFE, Schweizerische Gesamtenergiestatistik 2021 (Fig. 1)
OFEN, Statistique globale suisse de l'énergie 2021 (fig. 1)

Fig. 2 Aufteilung des Endverbrauchs nach Energieträgern (2021)
Répartition de la consommation finale selon les agents énergétiques (2021)

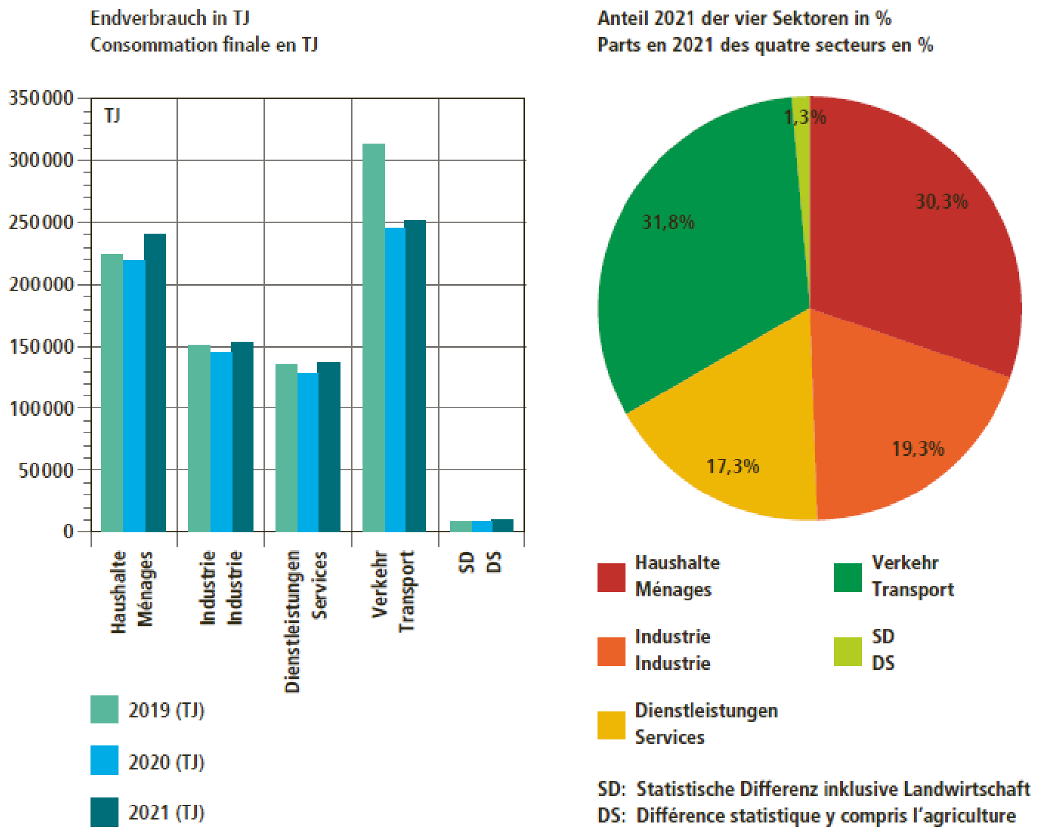


BFE, Schweizerische Gesamtenergiestatistik 2021 (Fig. 2)
OFEN, Statistique globale suisse de l'énergie 2021 (fig. 2)

Energy consumption in Switzerland

Total final consumption by sector

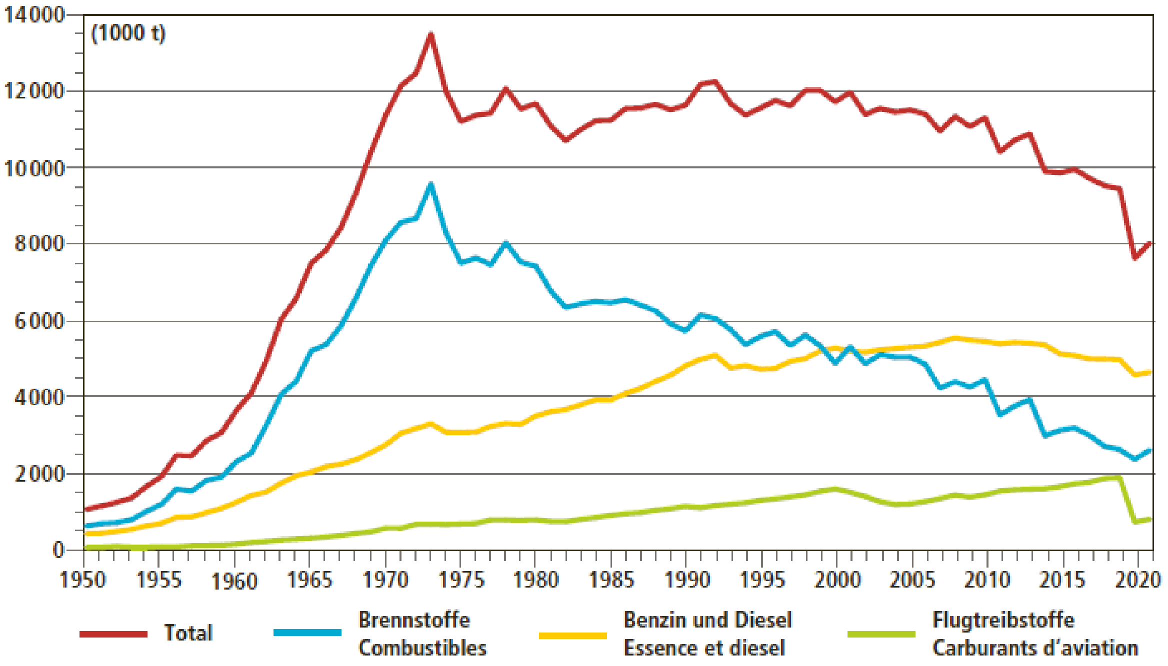
Fig. 3 Aufteilung des Energie-Endverbrauchs nach Verbrauchergruppen
Répartition de la consommation finale d'énergie selon les groupes de consommateurs



BFE, Schweizerische Gesamtenergiestatistik 2021 (Fig. 3)
OFEN, Statistique globale suisse de l'énergie 2021 (fig. 3)

Final consumption of oil products

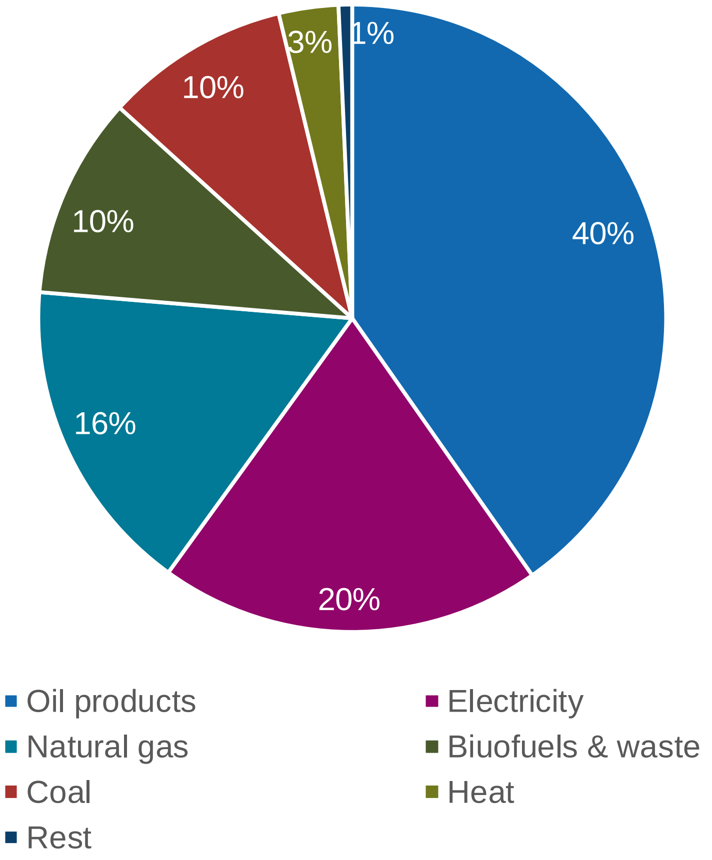
Fig. 10 Entwicklung des Endverbrauchs der Erdölprodukte
Evolution de la consommation finale des produits pétroliers



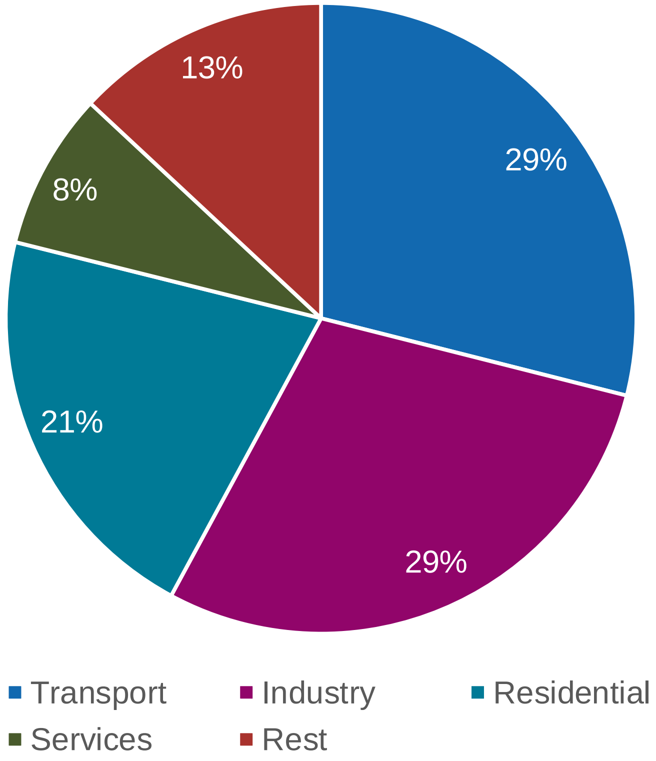
BFE, Schweizerische Gesamtenergiestatistik 2021 (Fig. 10)
OFEN, Statistique globale suisse de l'énergie 2021 (fig. 10)

World energy consumption and supply (418 EJ)

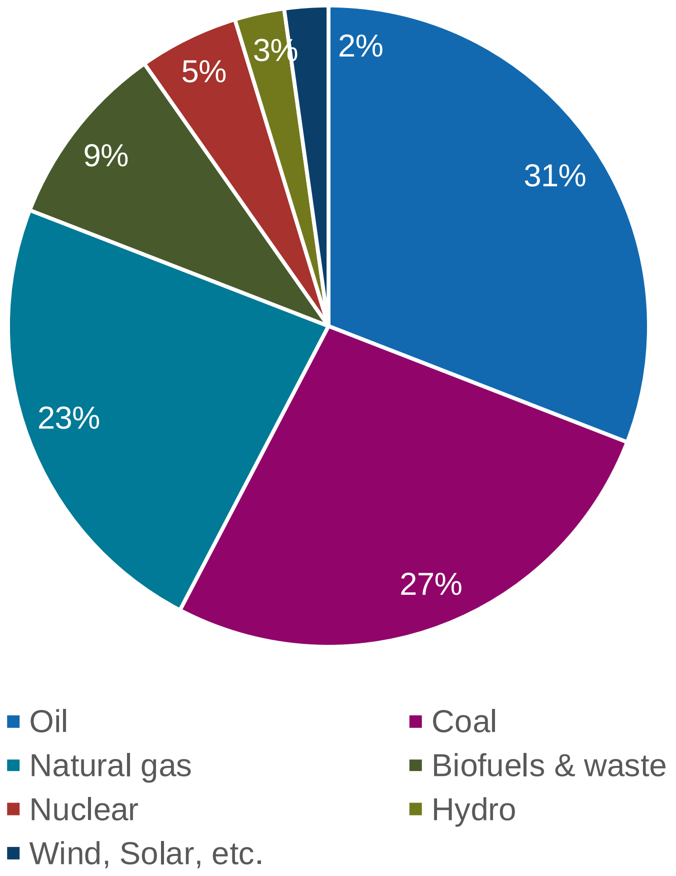
Total final consumption by source



Total final consumption by sector



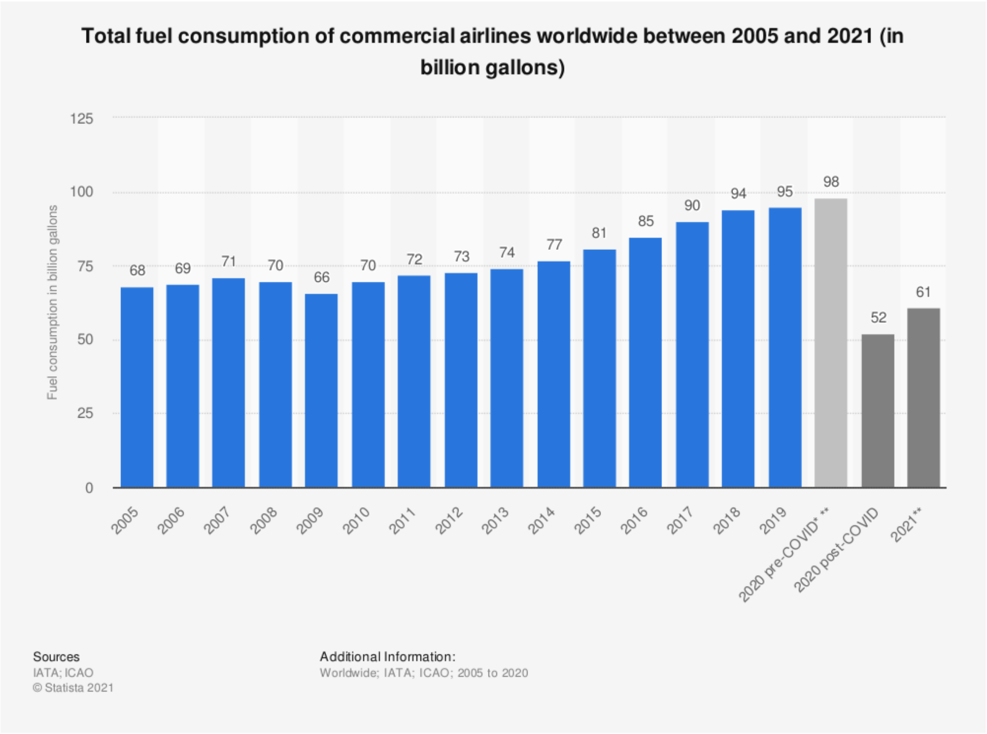
Total energy supply by source

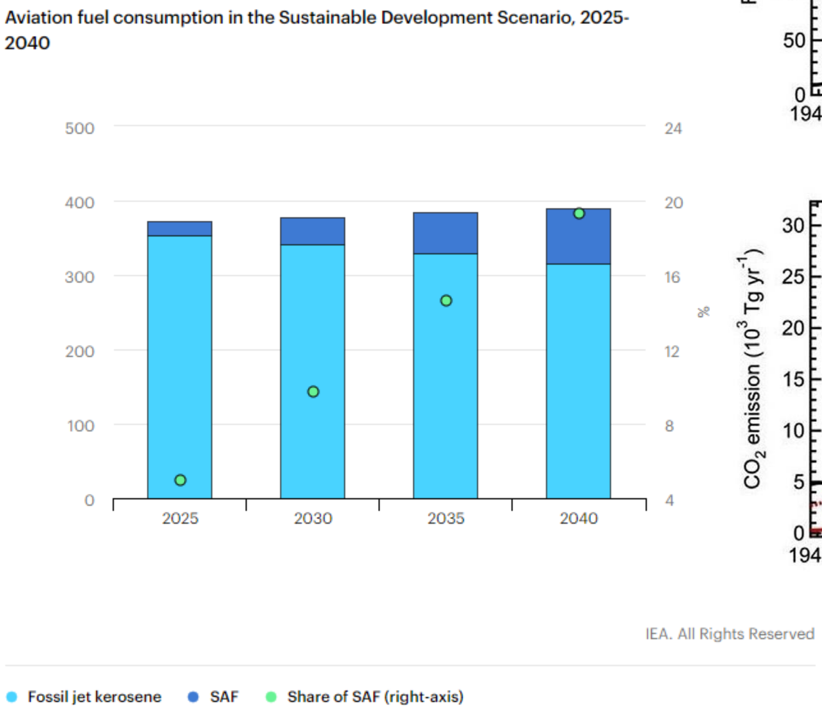


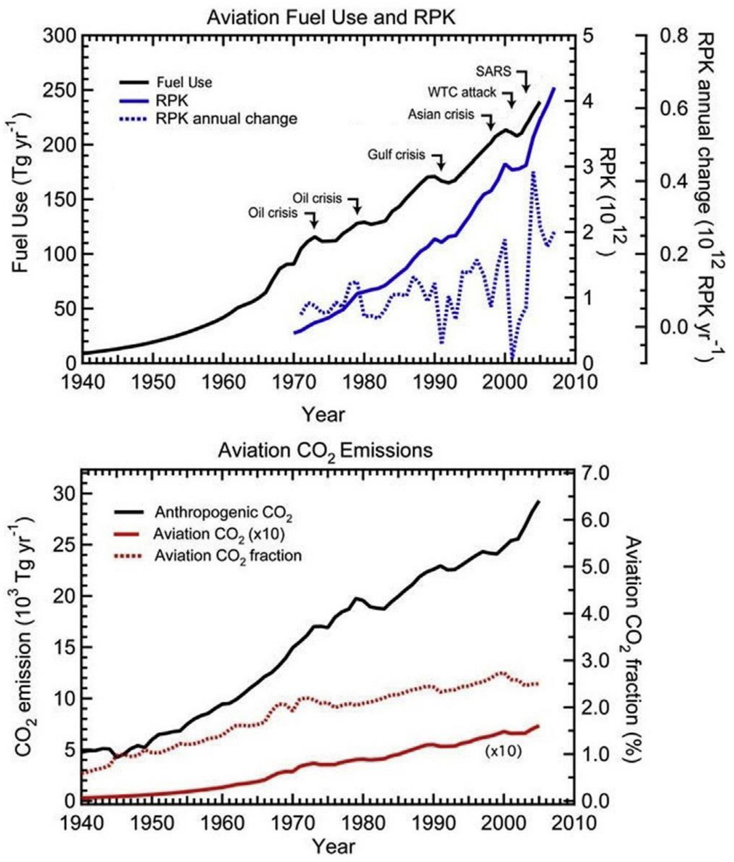
Quelle: IEA, 2019

Aviation fuel use and CO_2 emissions

- ~2-2.5% of total anthropogenic CO_2 emissions
- ~12% of CO_2 emissions from transport sources

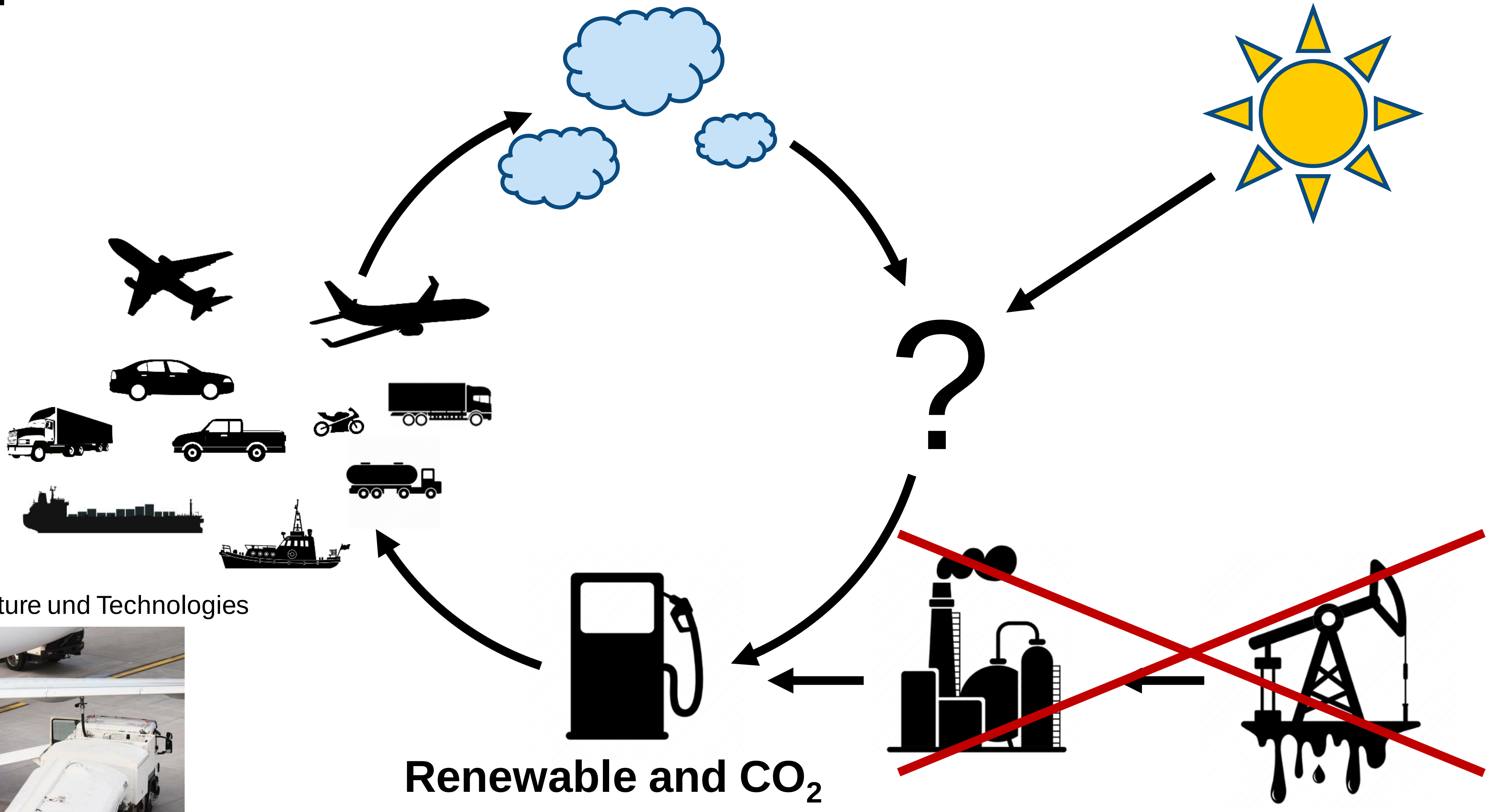






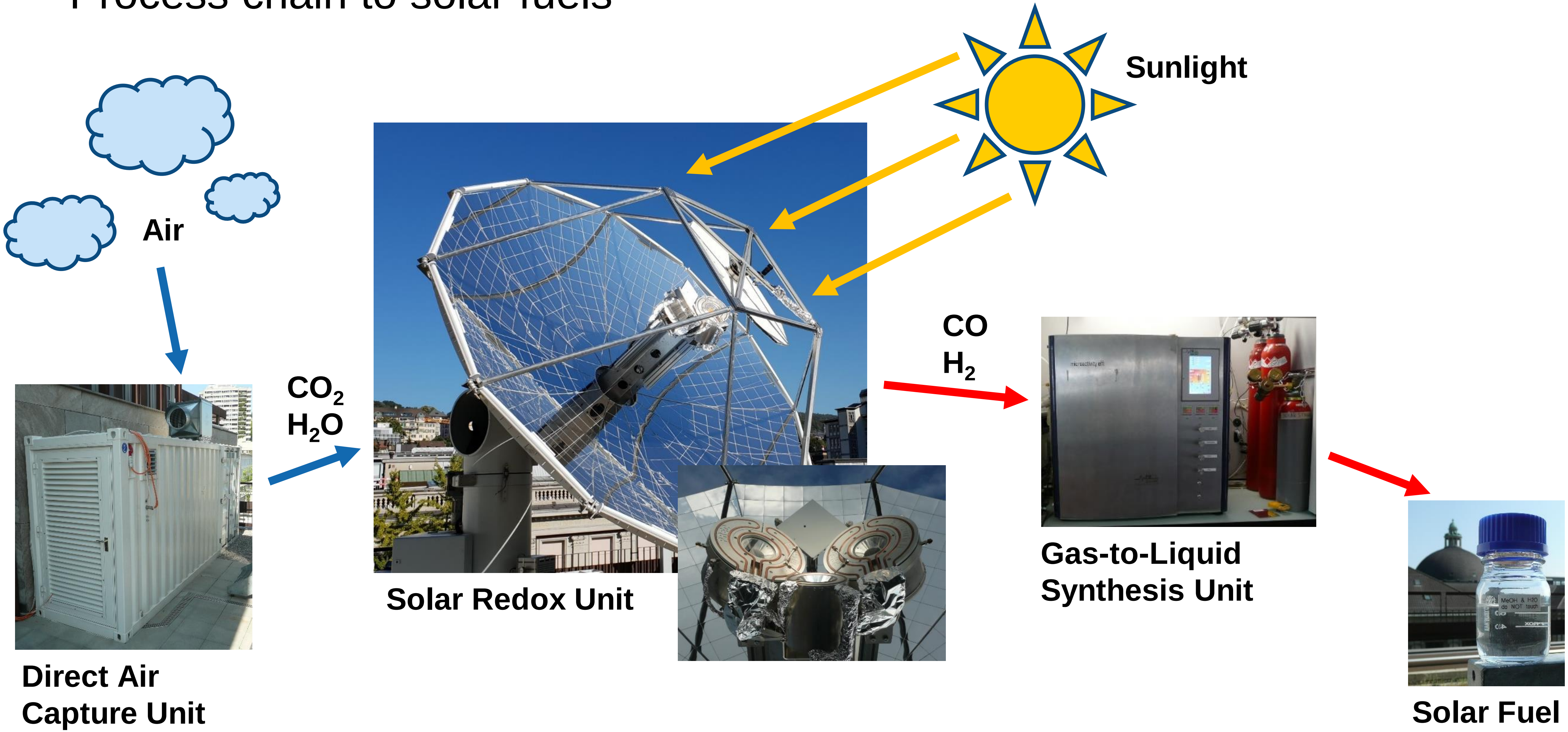
Sources:
IATA; ICAO
ATAG
IEA, *Aviation fuel consumption in the Sustainable Development Scenario, 2025-2040*, IEA, Paris
M. Grote et al. / Atmospheric Environment 95 (2014) 214-224

Fuel production

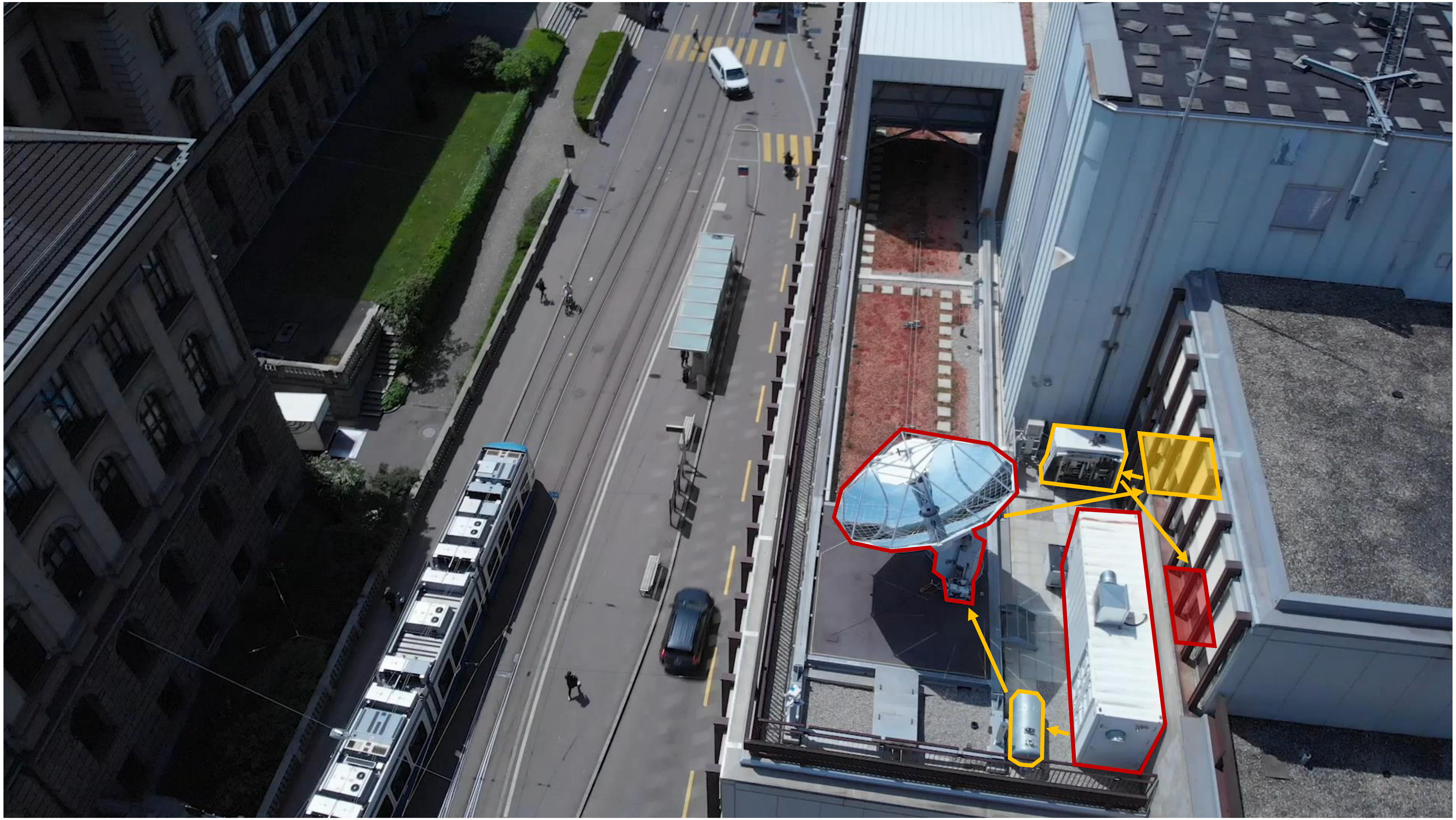


Existing Infrastructure und Technologies

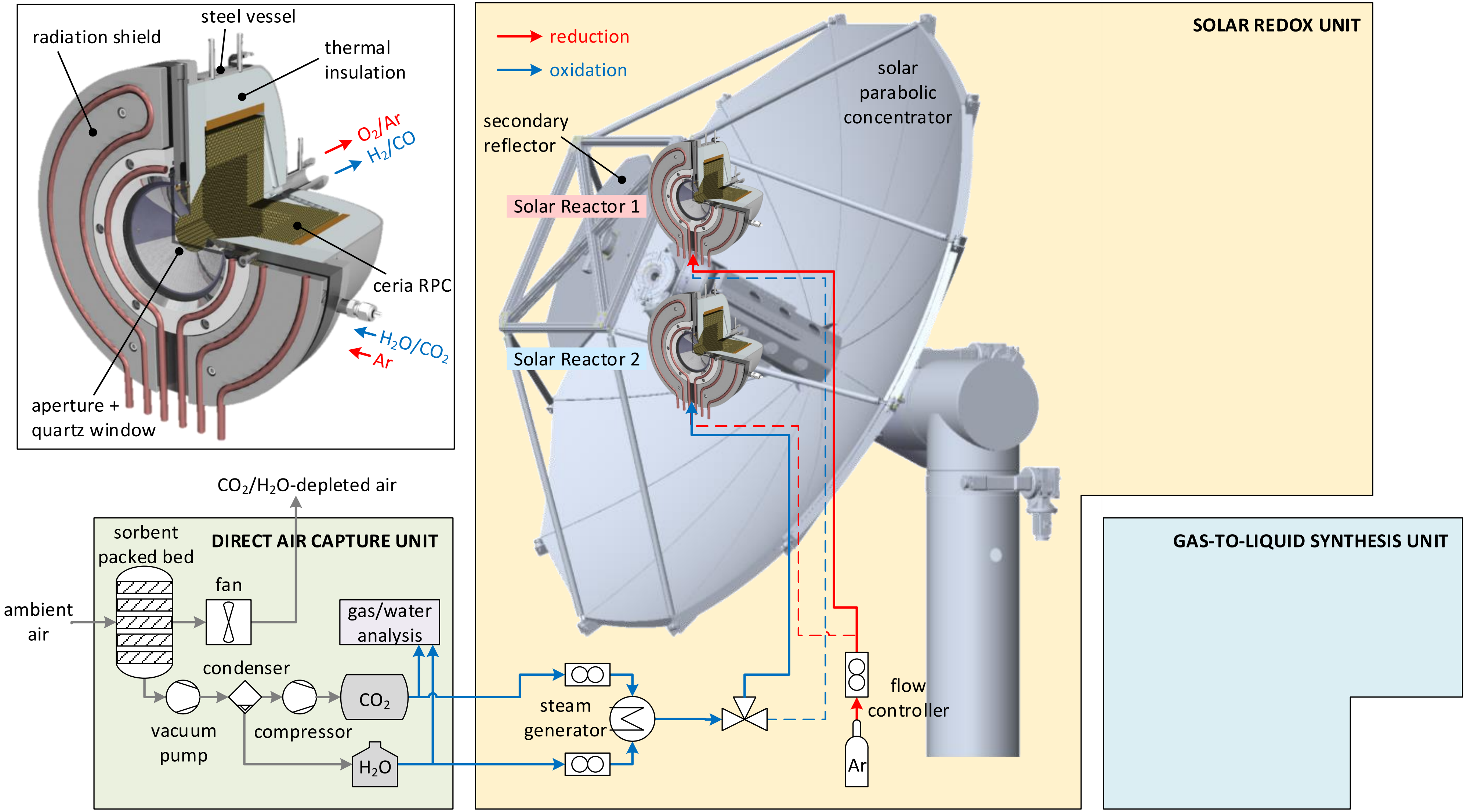
Process chain to solar fuels



Setup on the roof of ETH machine laboratory in Zürich

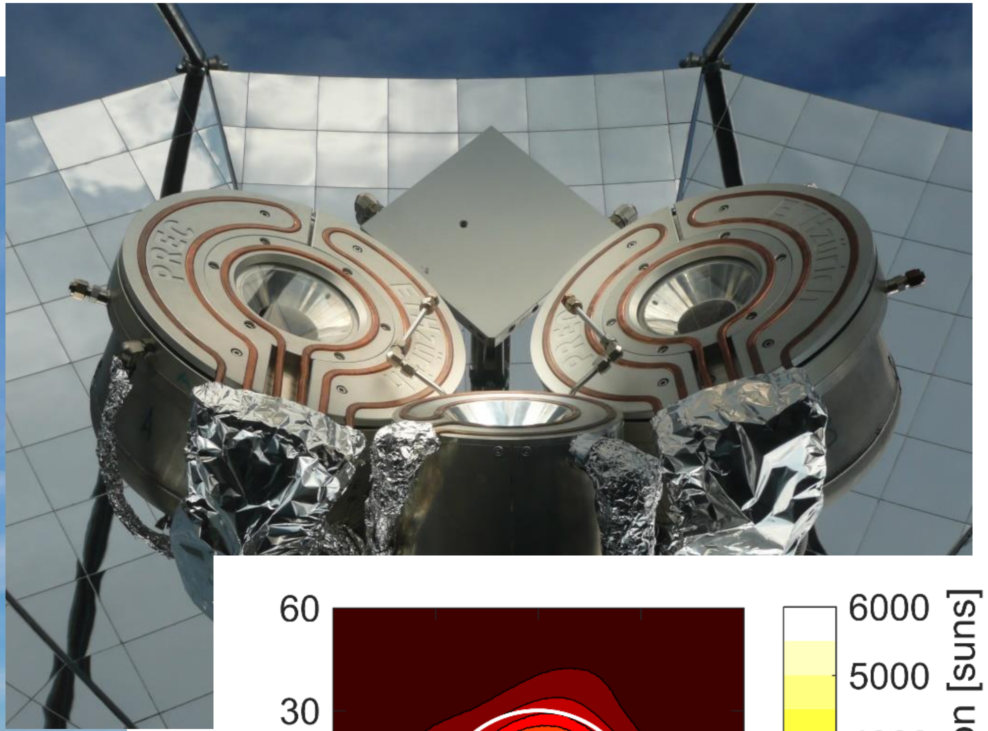


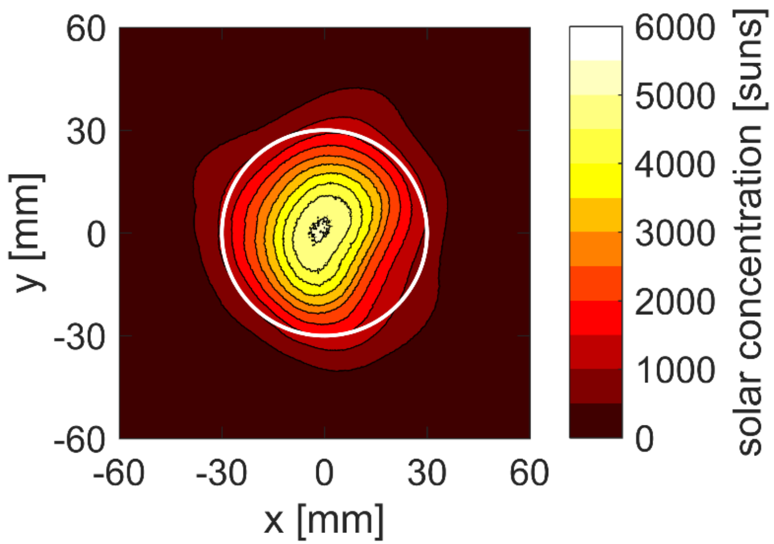
Schematic of the implemented process chain



Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

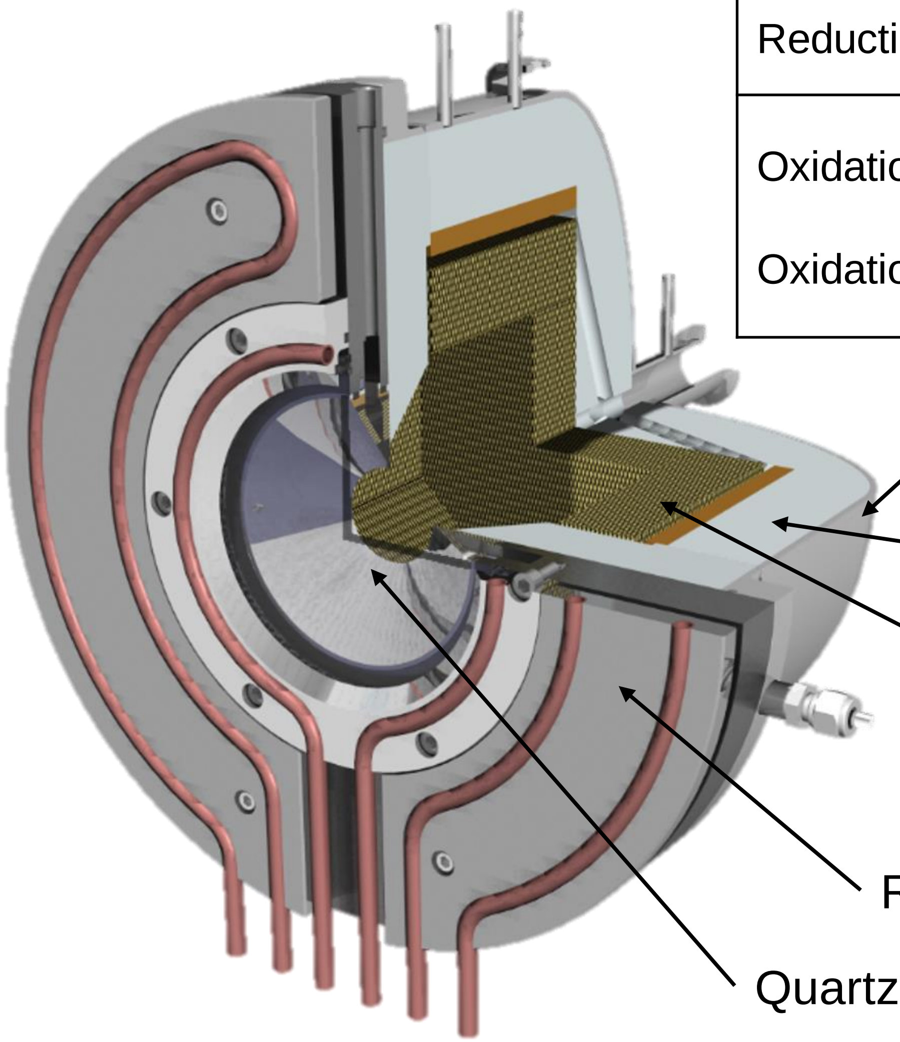
Solar Redox Unit

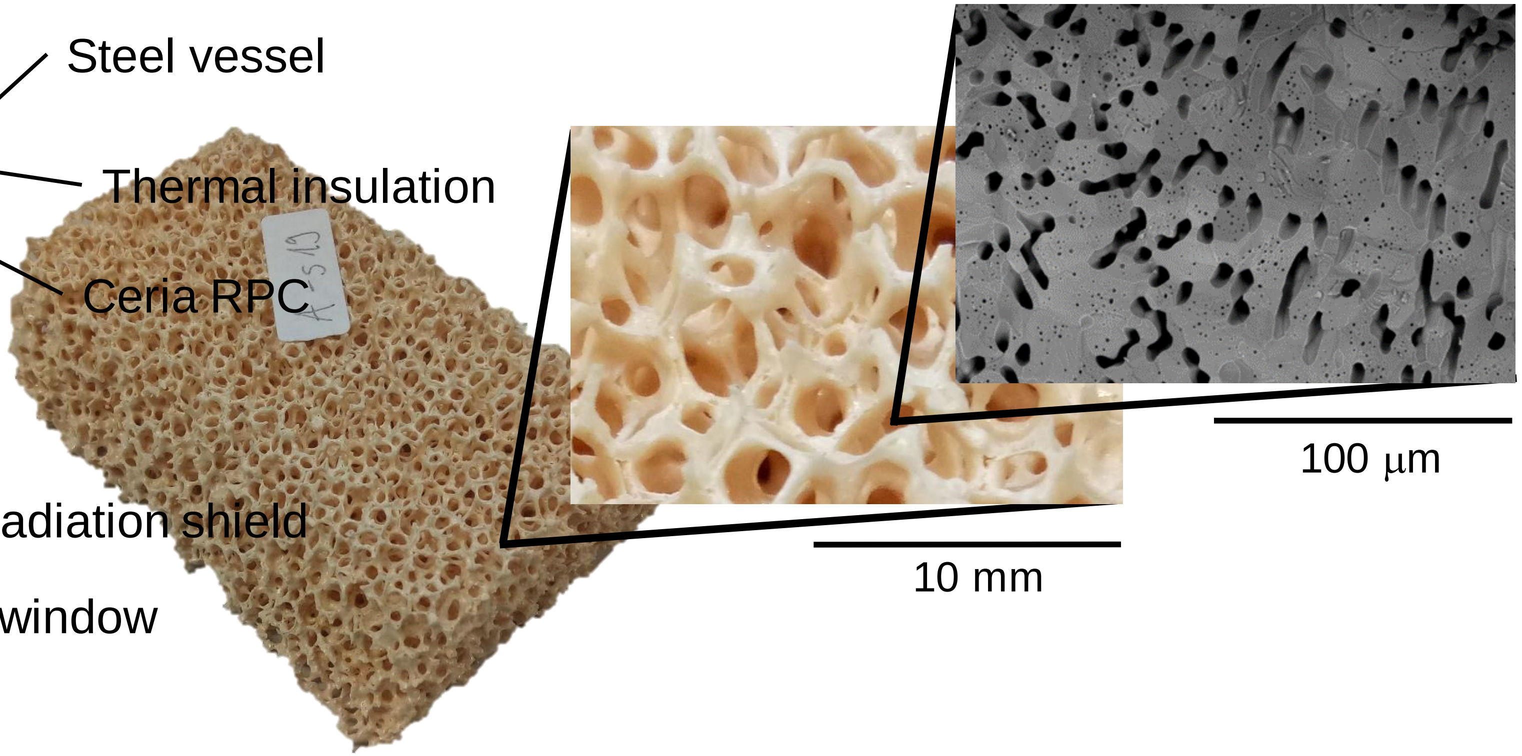




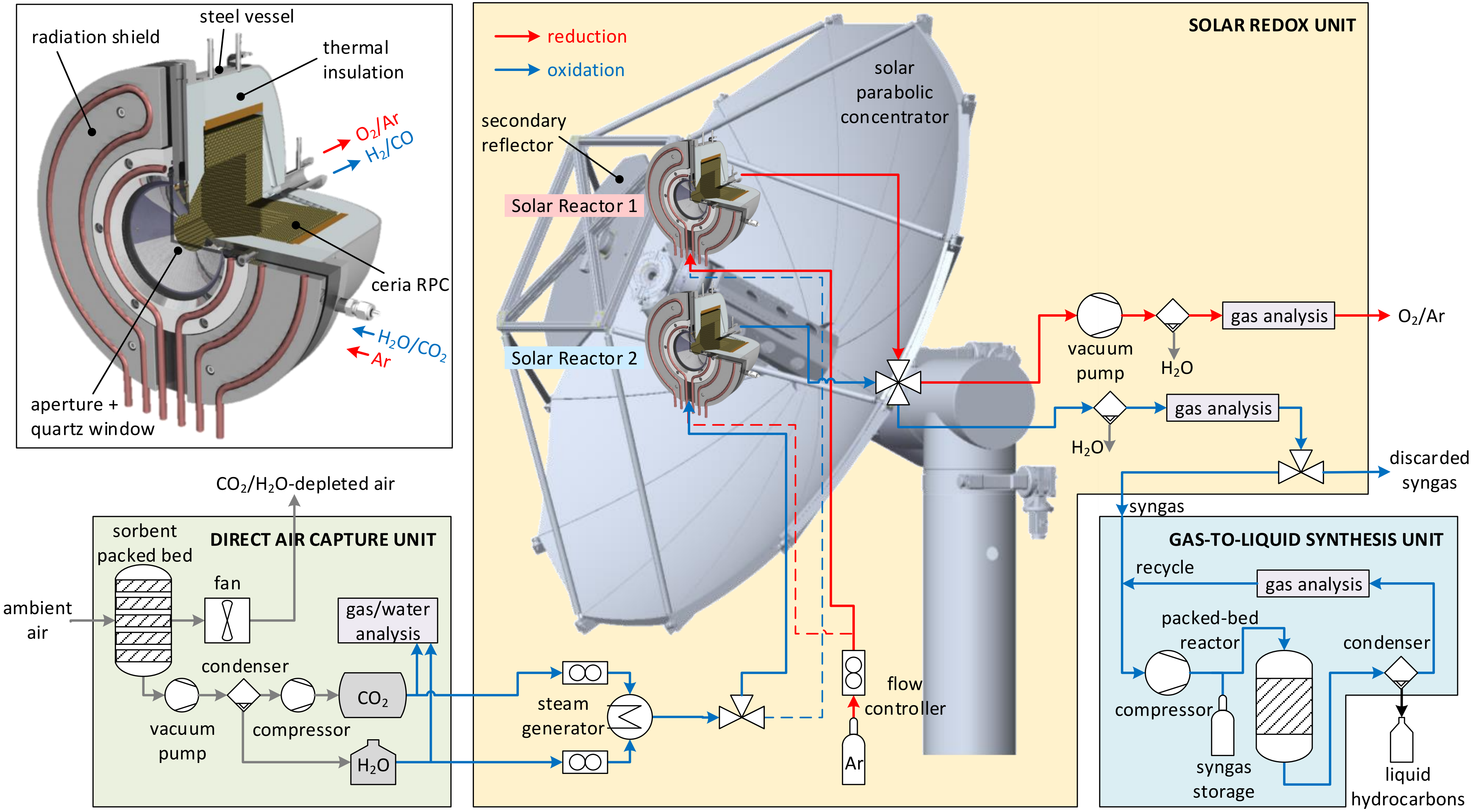
Solar Reactors

Reduction: $\Delta H \approx$ 475 kJ per ½ mole O_2	$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{ox}}} \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{red}}} + \frac{1}{2}\mathrm{O}_2$
Oxidation with CO_2: $\Delta H \approx$ -192 kJ/mol CO_2	$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{red}}} + \mathrm{CO}_2 \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{ox}}} + \mathrm{CO}$
Oxidation with H_2O: $\Delta H \approx$ - 234 kJ/mol H_2	$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{red}}} + \mathrm{H_2O} \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{ox}}} + \mathrm{H}_2$





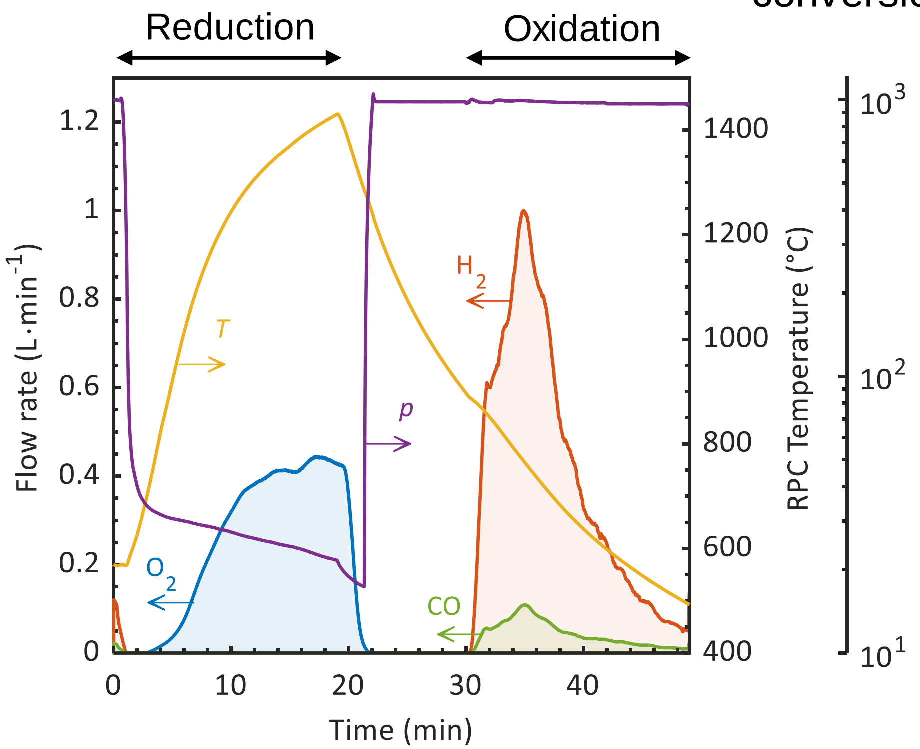
Schematic of the implemented process chain

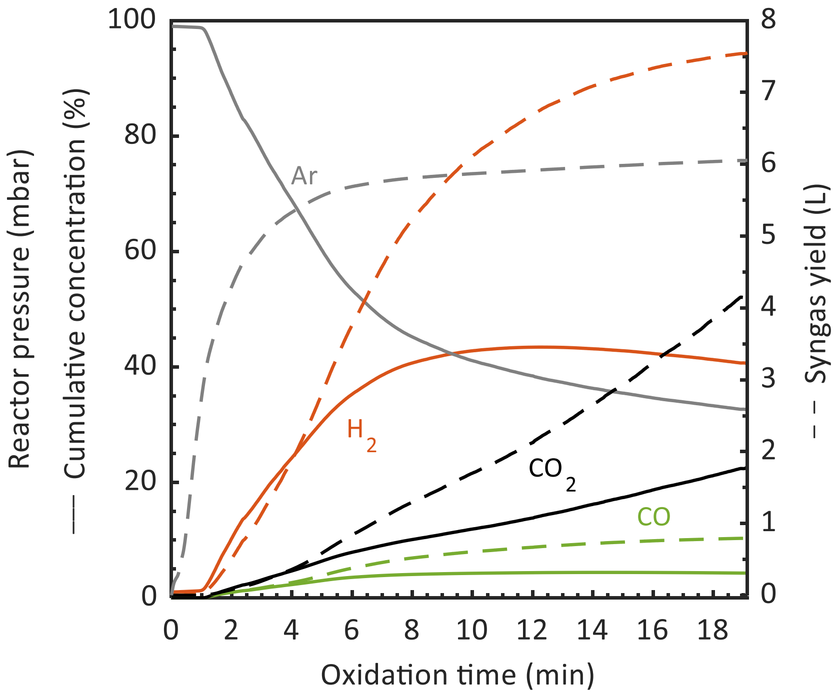


Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Exemplary Cycle Targeting Syngas for Methanol Synthesis

<u>Target:</u>
H_2/CO_x ratio: 2 – 3
Depending on catalyst and CO_2 conversion





- Full oxidation:
  - 18.5 L of syngas
  - 40.7% H_2, 4.3% CO, 22.4% CO_2, 32.6% Ar
  - H_2/CO_x ratio: 1.52
  - CO_2 conversion: 16.1%

Conditions	**Reduction**	**Oxidation**
Power input	5.1 kW	Off-sun (0 kW)
Gas flow	0.5 l/min Ar	0.4 l/min CO_2 9.8 g/min H_2O
Pressure	25 mbar	1 bar

Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Exemplary Cycle Targeting Syngas for Methanol Synthesis

<u>Target:</u>
H_2/CO_x ratio: 2 – 3
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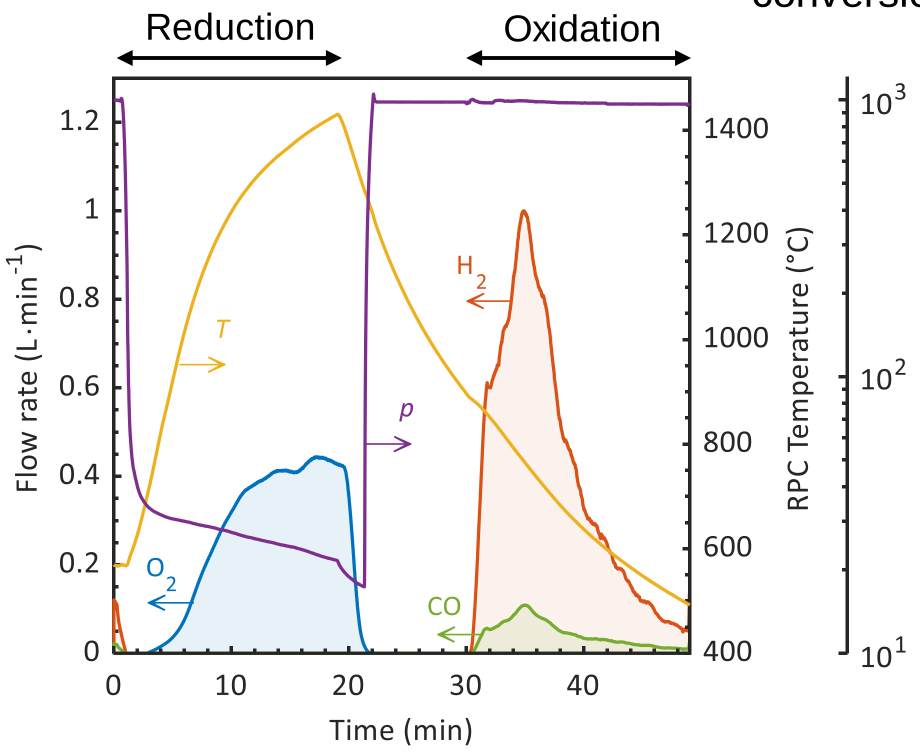
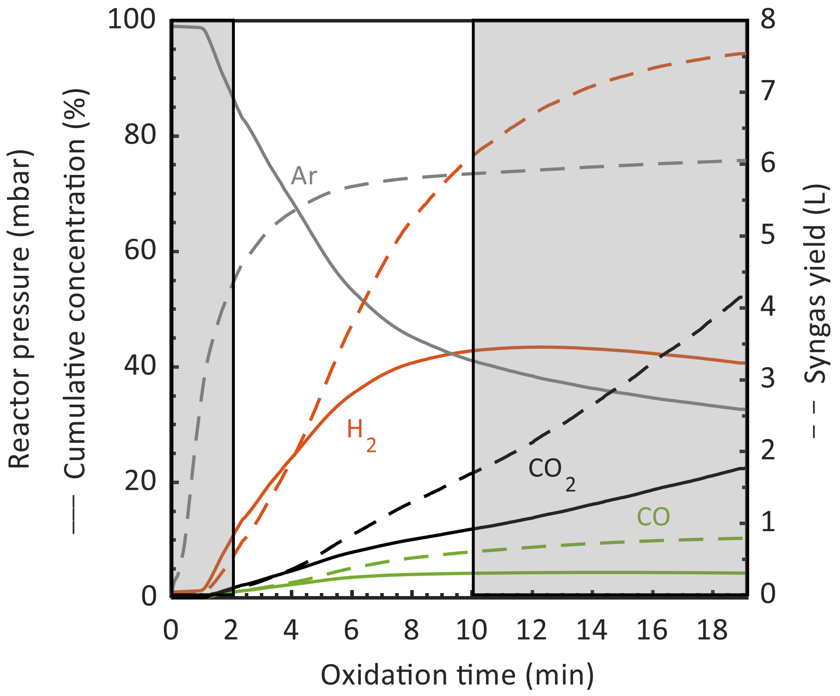




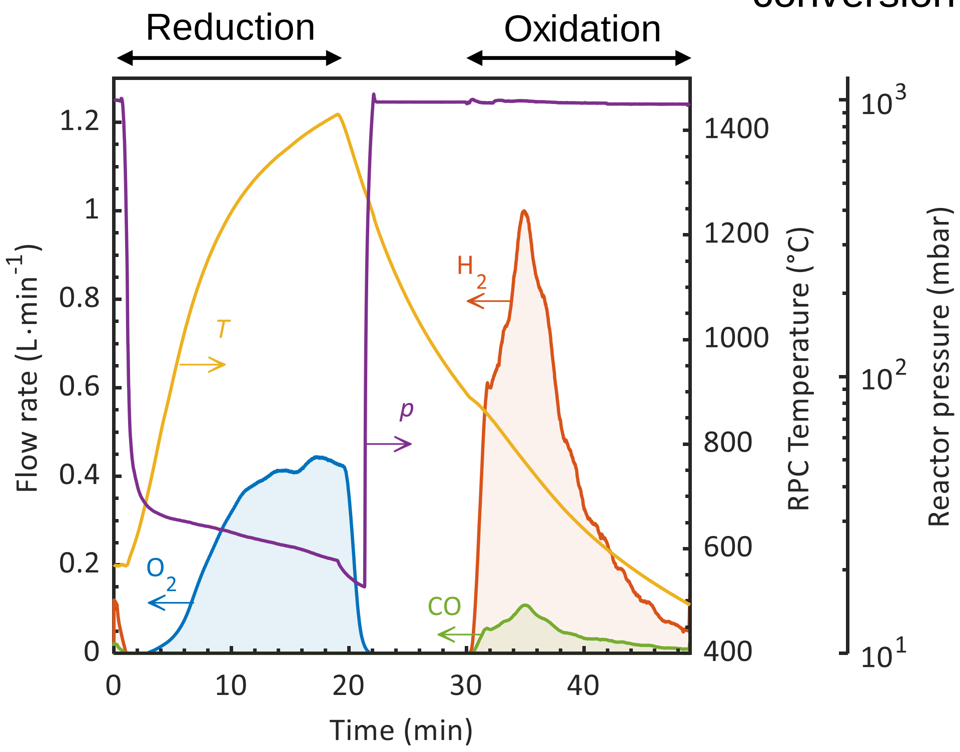
Conditions	Reduction	Oxidation
Power input	5.1 kW	Off-sun (0 kW)
Gas flow	0.5 l/min Ar	0.4 l/min CO_2 9.8 g/min H_2O
Pressure	25 mbar	1 bar

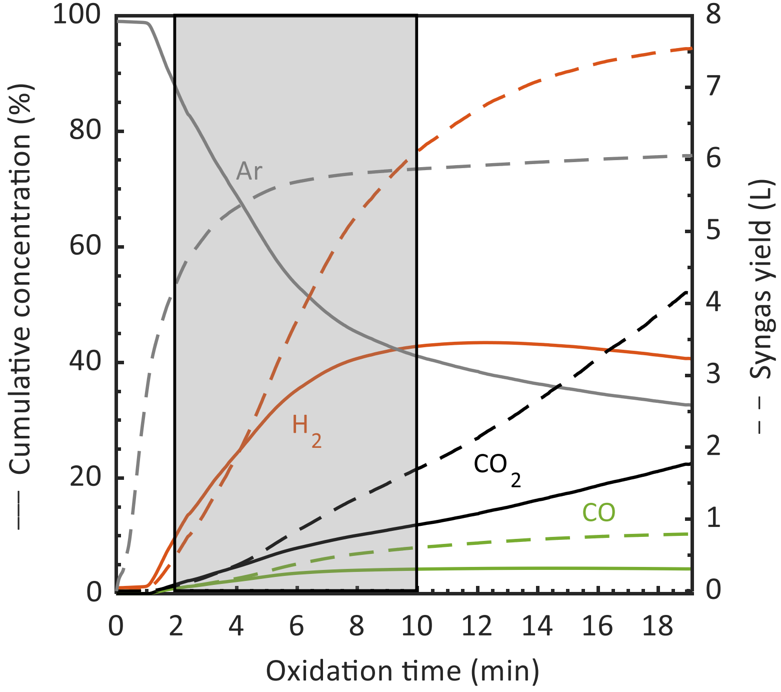
- 0 - 2 min:
  - 4.9 L of syngas
  - 10.2% H_2, 0.9% CO, 1.6% CO_2, 87.3% Ar
  - H_2/CO_x ratio: 4
  - CO_2 conversion: 36%
- 10 min - full oxidation:
  - 4.2 L of syngas
  - 33.6% H_2, 4.5% CO, 57.7% CO_2, 4.2% Ar
  - H_2/CO_x ratio: 0.54
  - CO_2 conversion: 7.2%

Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Exemplary Cycle Targeting Syngas for Methanol Synthesis

<u>Target:</u>
H_2/CO_x ratio: 2 – 3
Depending on catalyst and CO_2 conversion



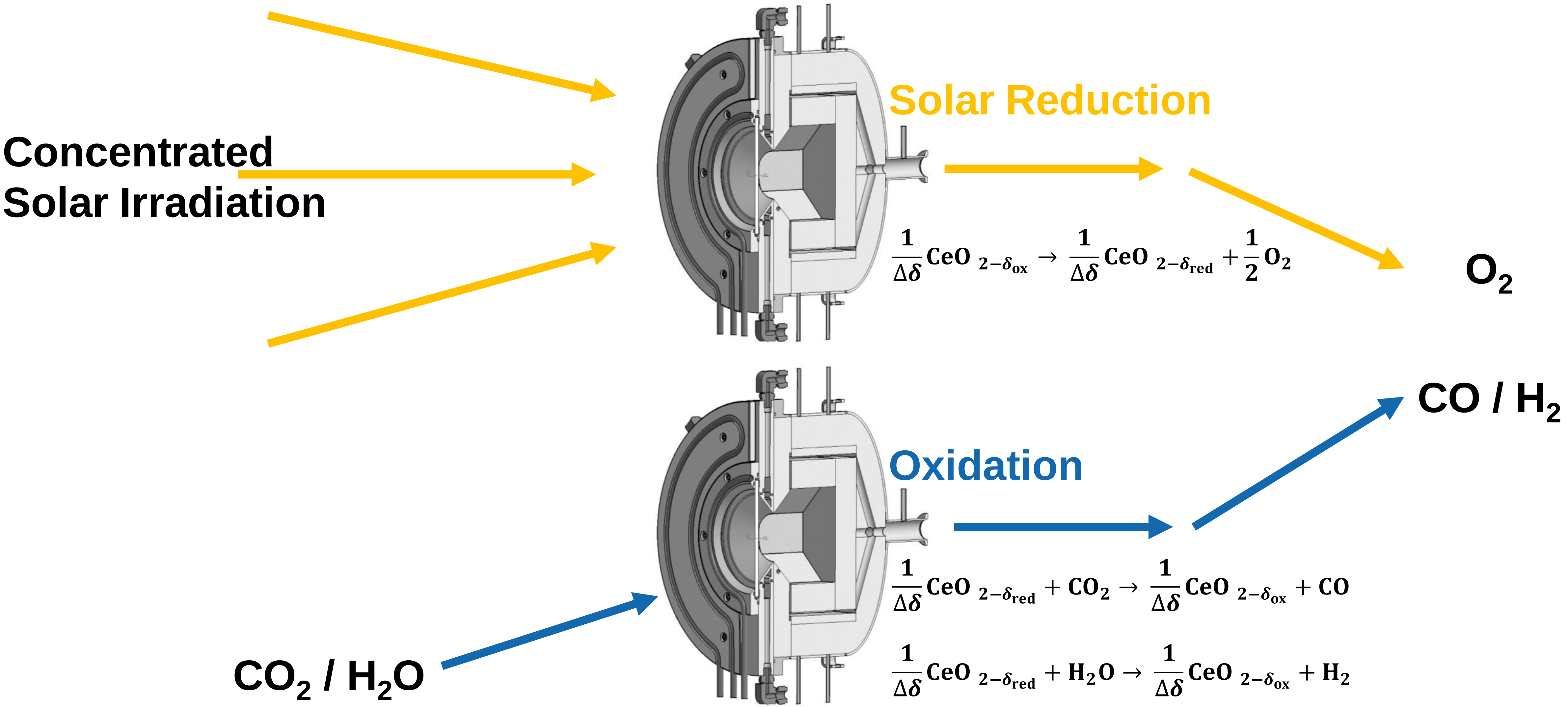


Conditions	Reduction	Oxidation
Power input	5.1 kW	Off-sun (0 kW)
Gas flow	0.5 l/min Ar	0.4 l/min CO_2 9.8 g/min H_2O
Pressure	25 mbar	1 bar

- Full oxidation:
  - 18.5 L of syngas
  - 40.7% H_2, 4.3% CO, 22.4% CO_2, 32.6% Ar
  - H_2/CO_x ratio: 1.52
  - CO_2 conversion: 16.1%
- Collection 2-10 min:
  - 9.4 L of syngas
  - 59.9% H_2, 6% CO, 17.2% CO_2, 16.9% Ar
  - H_2/CO_x ratio: 2.58
  - CO_2 conversion: 25.7%

Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Parallel Operation of two Reactors



$$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{ox}} \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{red}} + \frac{1}{2}\mathrm{O}_2$$

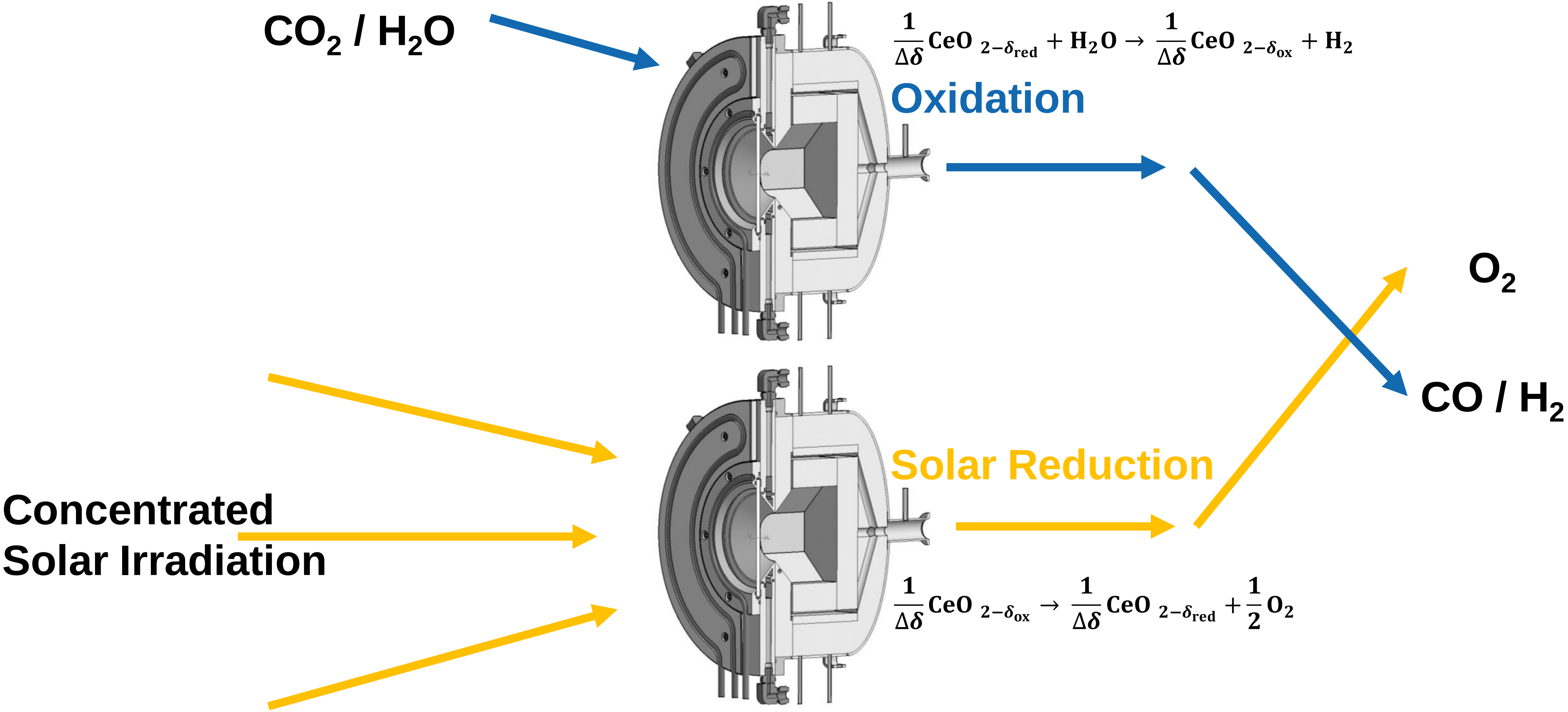
$$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{red}} + \mathrm{CO}_2 \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{ox}} + \mathrm{CO}$$

$$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{red}} + \mathrm{H}_2\mathrm{O} \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{ox}} + \mathrm{H}_2$$

Parallel Operation of two Reactors

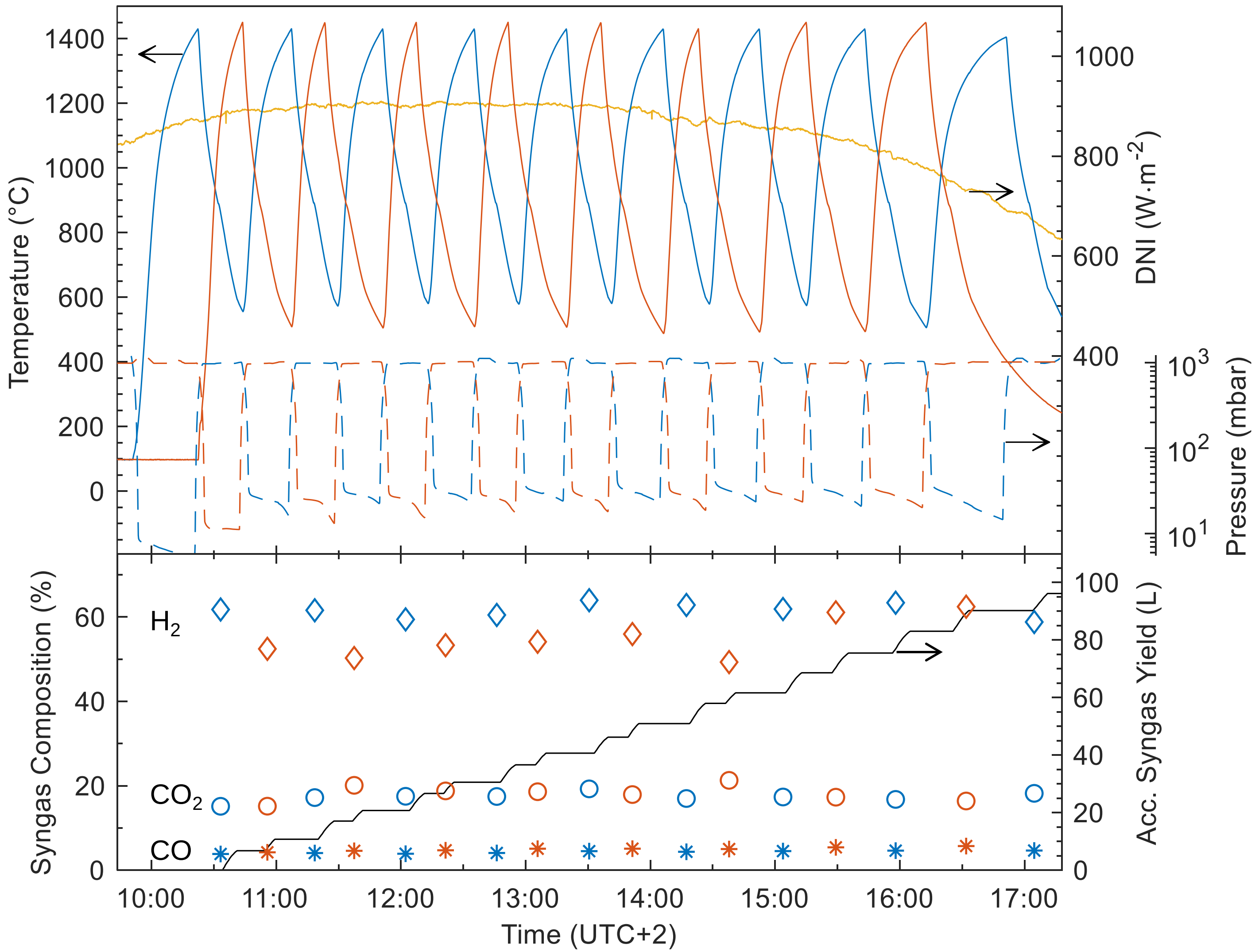
$$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{red}}} + \mathrm{CO}_2 \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{ox}}} + \mathrm{CO}$$

$$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{red}}} + \mathrm{H_2O} \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{ox}}} + \mathrm{H}_2$$



$$\frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{ox}}} \rightarrow \frac{1}{\Delta\delta}\mathrm{CeO}_{2-\delta_{\mathrm{red}}} + \frac{1}{2}\mathrm{O}_2$$

Exemplary Day Targeting Syngas for Methanol Synthesis



- 17 cycles:
  - 96.2 L of syngas
  - 57.2% H_2, 4.4% CO, 16.8% CO_2, 17.7% Ar
  - H_2/CO_x ratio: 2.7
  - CO_2 conversion: 21%

- **Increase $\eta_{solar-to-fuel}$:**
- $\eta_{solar-to-fuel} = \frac{Q_{fuel}}{Q_{solar}+Q_{inert}+Q_{pump}} =$ 1.9 – 3.8% (5.6% on solar tower)
- Optimize operation parameters/setup
- Optimise porous ceramic structure (all participating)
- Heat recovery (T-swing)

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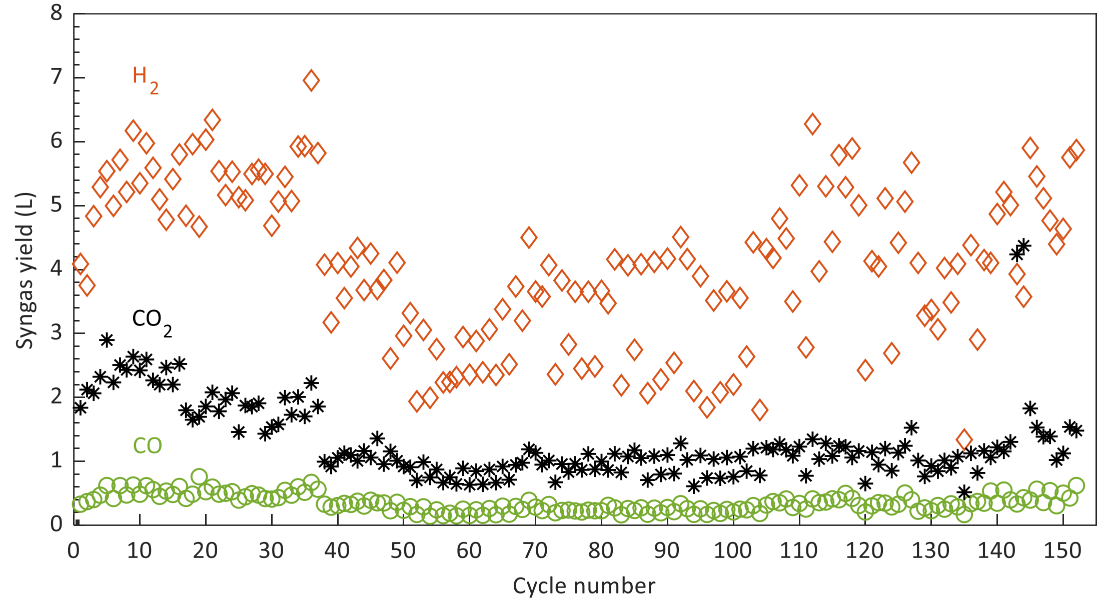
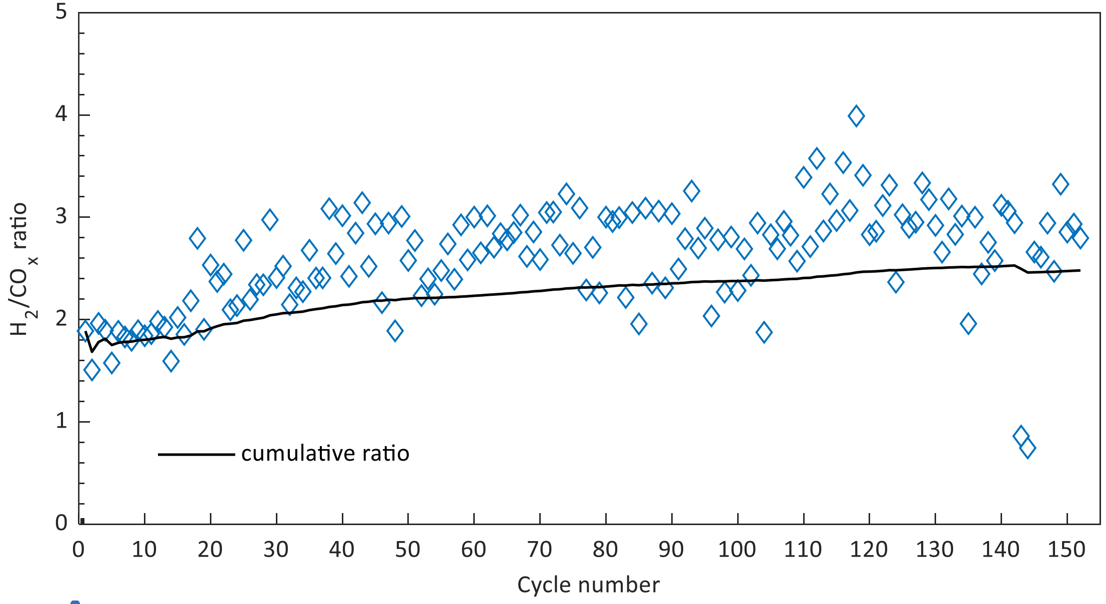
Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Production Campaign Targeting Syngas for Methanol Synthesis





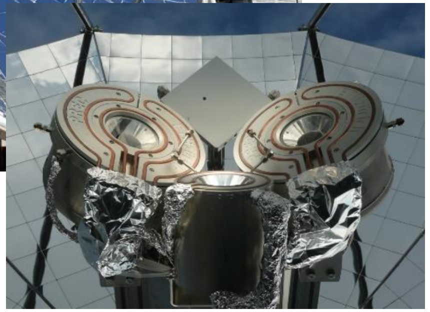
- 152 cycles:
  - 1069.7 L of syngas
  - 58.4% H_2, 5% CO, 18.6% CO_2, 18% Ar
  - H_2/CO_x ratio: 2.48
  - CO_2 conversion: 21%

Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Efficiency of the implemented process chain

Direct Air Capture Unit

CO_2
H_2O



Solar Redox Unit

CO
H_2

Gas-to-Liquid Synthesis Unit

$\eta_{\text{DAC}} \approx 90\%$

$\eta_{\text{optical}} = 59.6\%$ $\eta_{\text{solar-to-syngas}} = 1.9 - 3.8\%\ (5.6\%)$ $\eta_{\text{GTL}} = 75\%$

$$\eta_{\text{solar redox unit}} = \eta_{\text{optical}} \cdot \eta_{\text{solar-to-syngas}} = 1.1 - 2.3\%$$

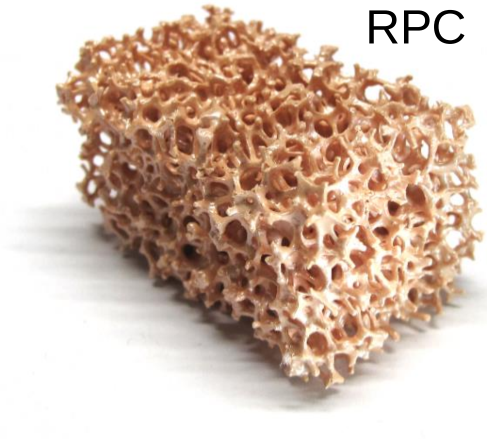
$$\boldsymbol{\eta_{\text{system}}} = \eta_{\text{DAC}} \cdot \eta_{\text{solar redox unit}} \cdot \eta_{\text{GTL}} = \mathbf{0.8\%}$$

$$\text{potential of exceeding } \eta_{\text{system}} = 13\%$$

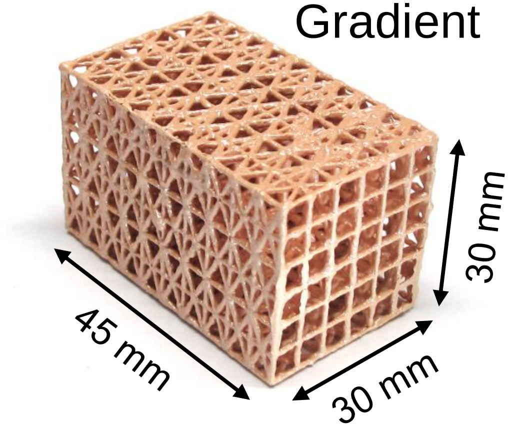
Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Research Projects to Optimise Ceramic Structures

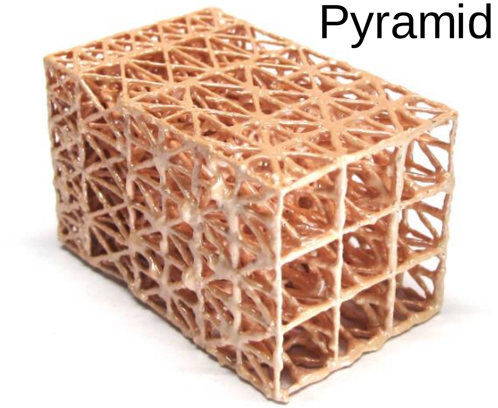
RPC

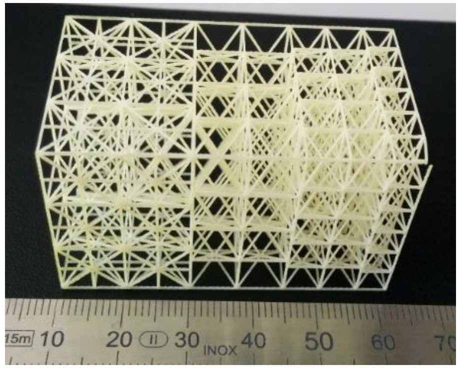


Gradient

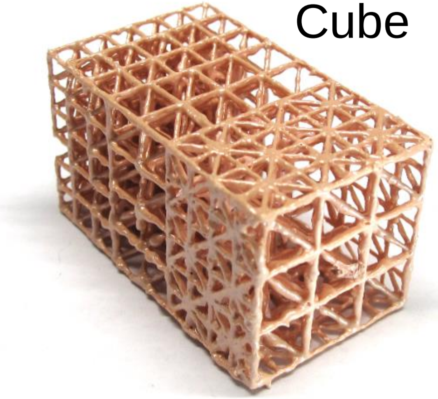


Pyramid

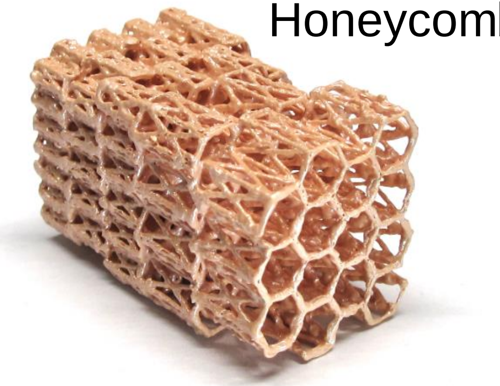


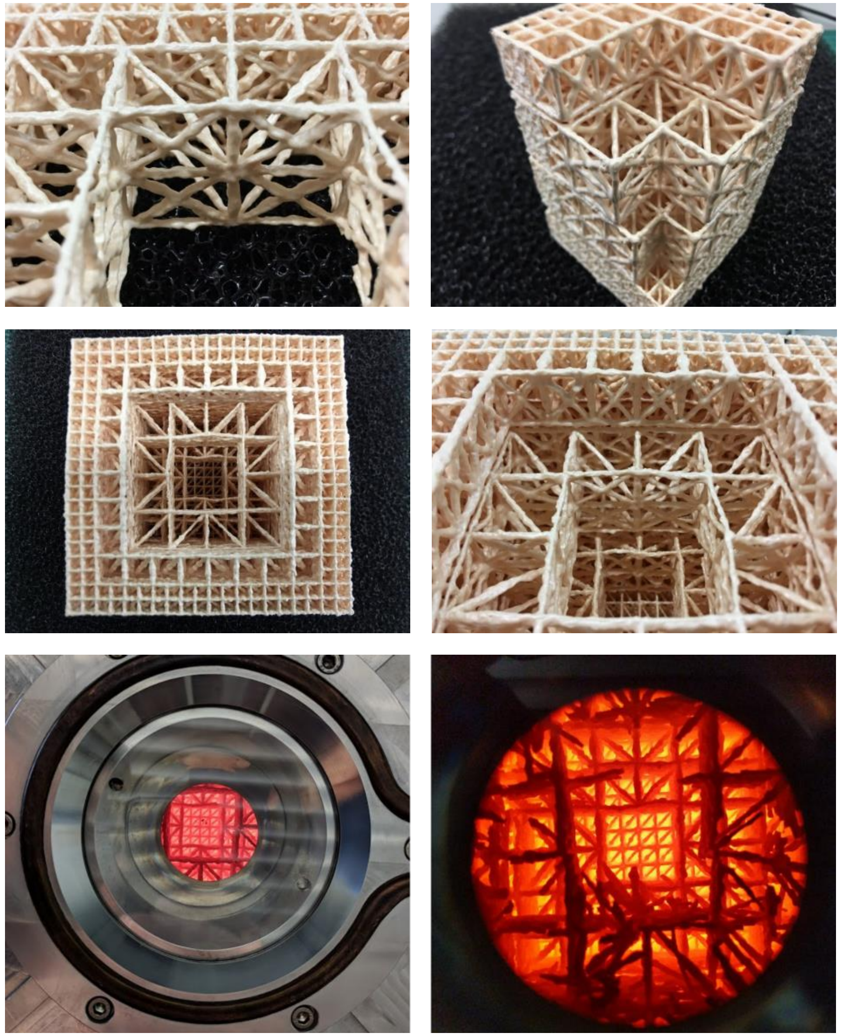


Cube



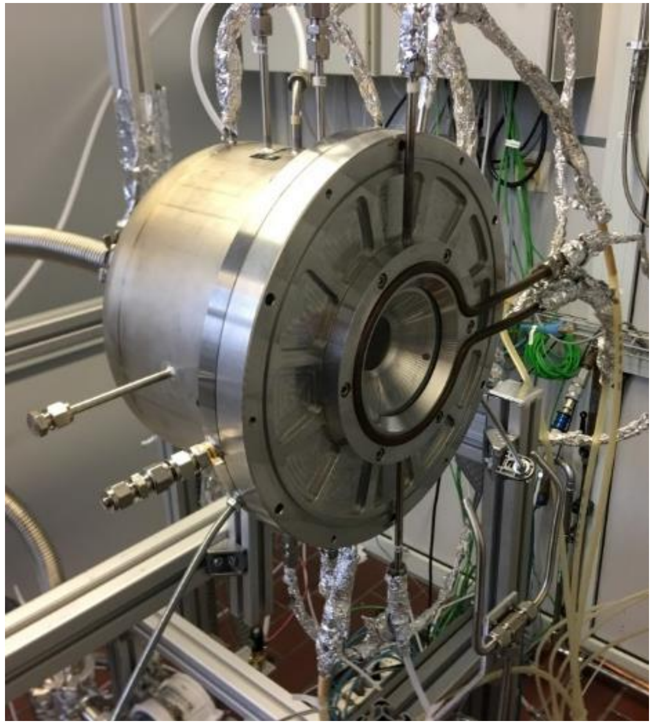
Honeycomb

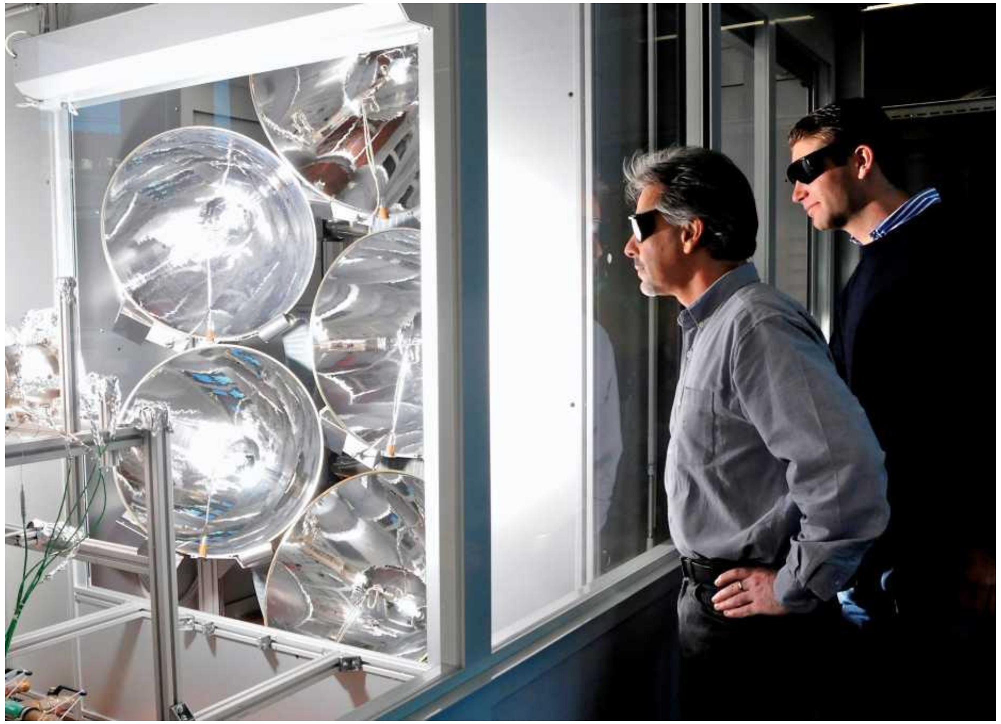




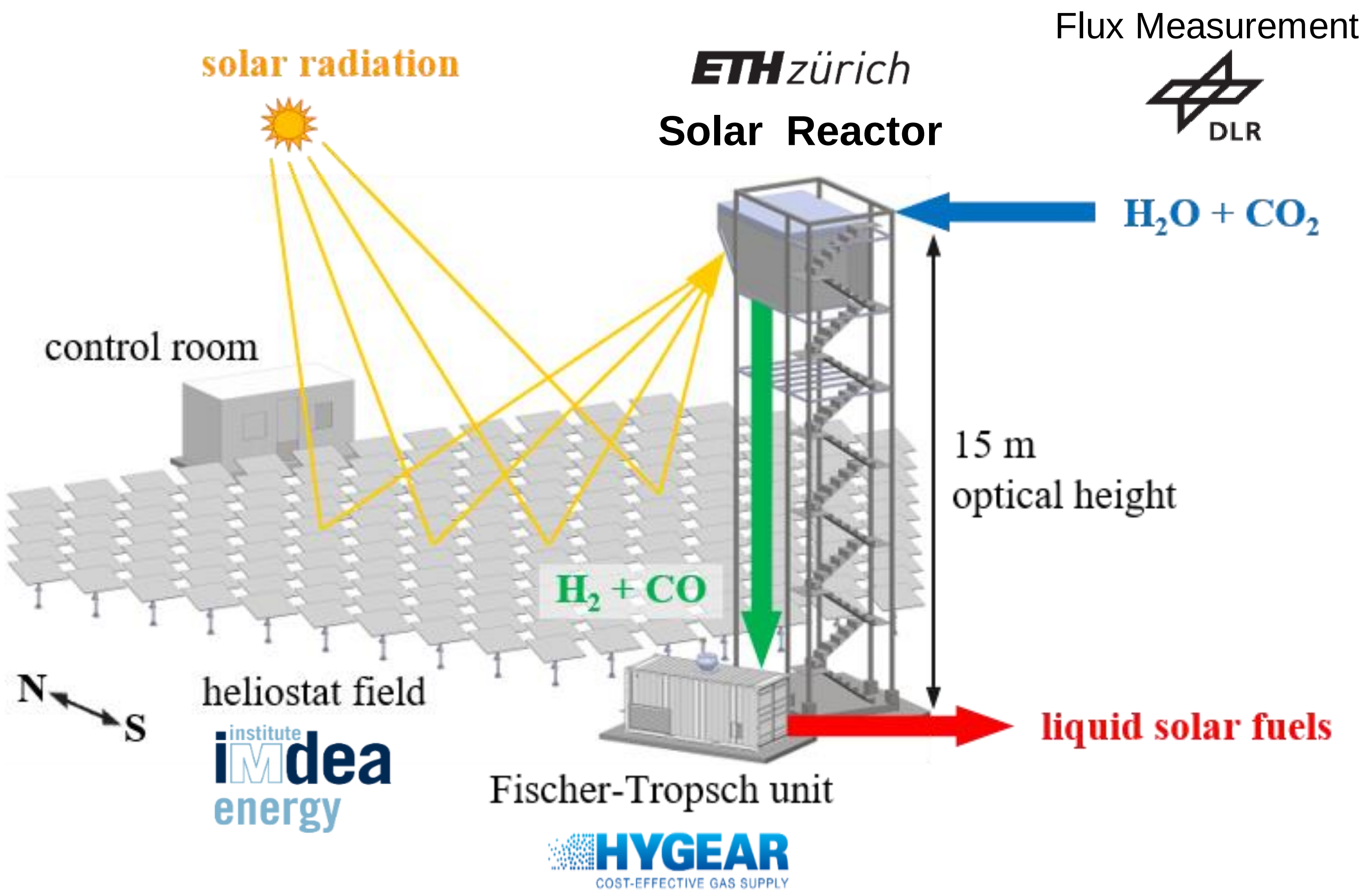
High-flux solar simulator

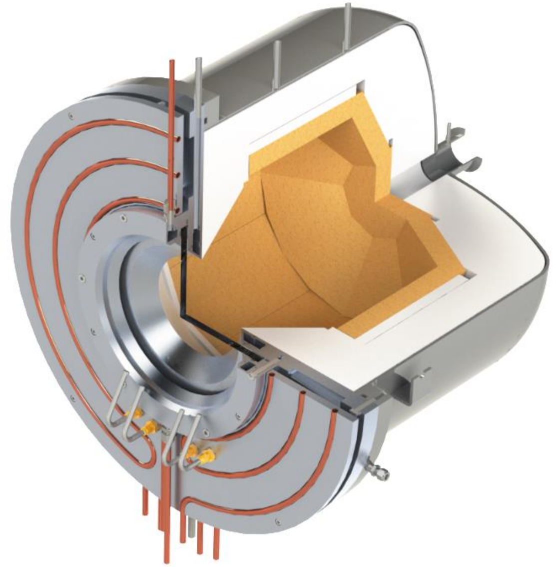
- Indoor test stand for solar reactors and installations





Sun-to-liquid Project (Móstoles, Spain)

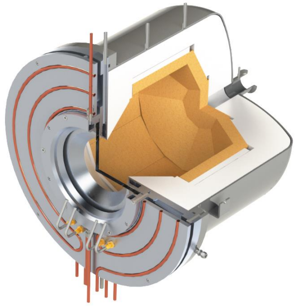


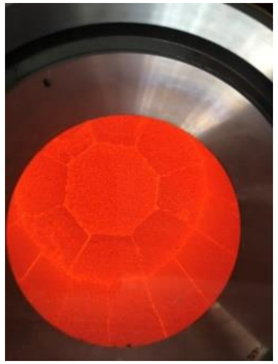


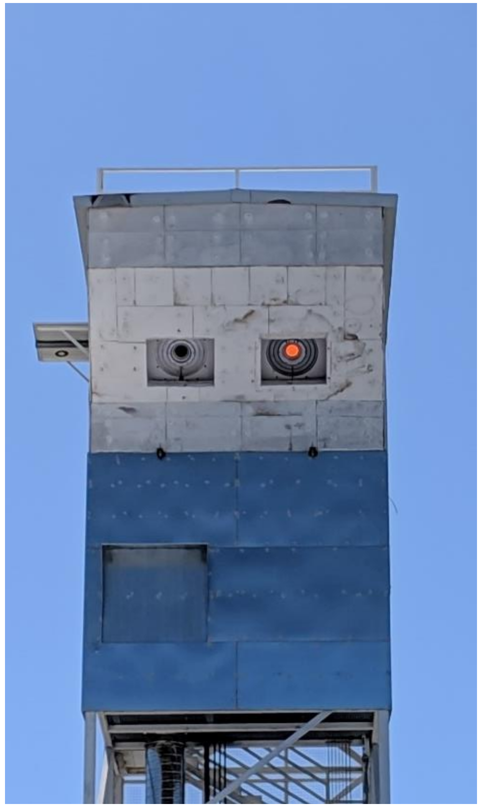
Generation 2
50 kW Pilot-scale
RPC

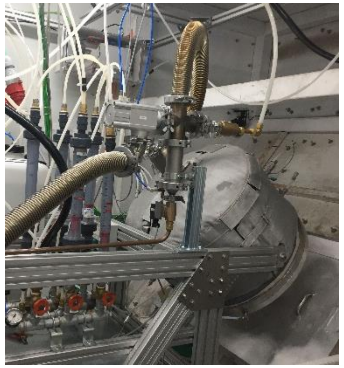
Sun-to-liquid Project (Móstoles, Spain)

- Upscaling: 50 kW reactor
- Tower with169 heliostats

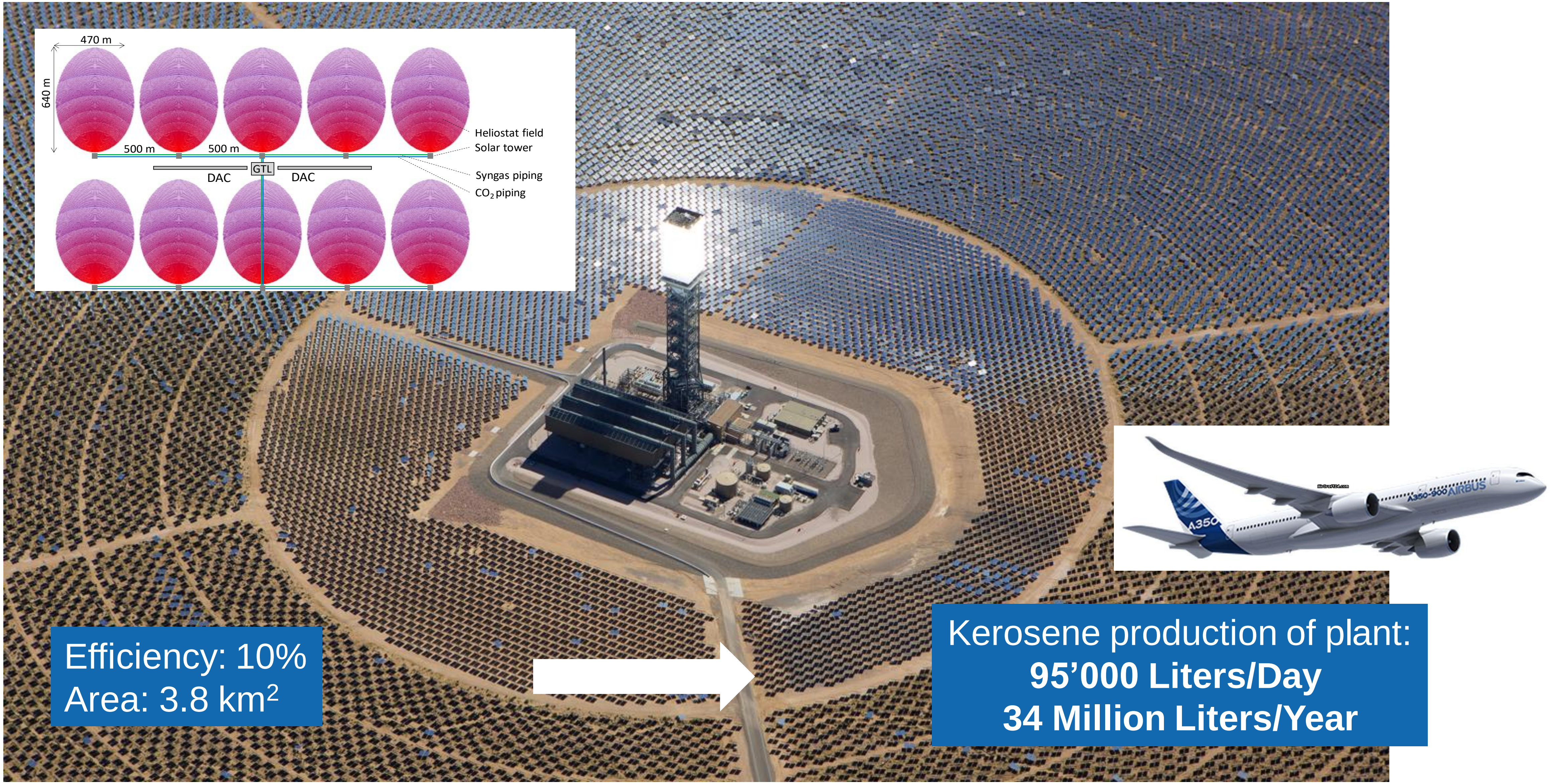








Industrial Production Example: 10 x 100MW

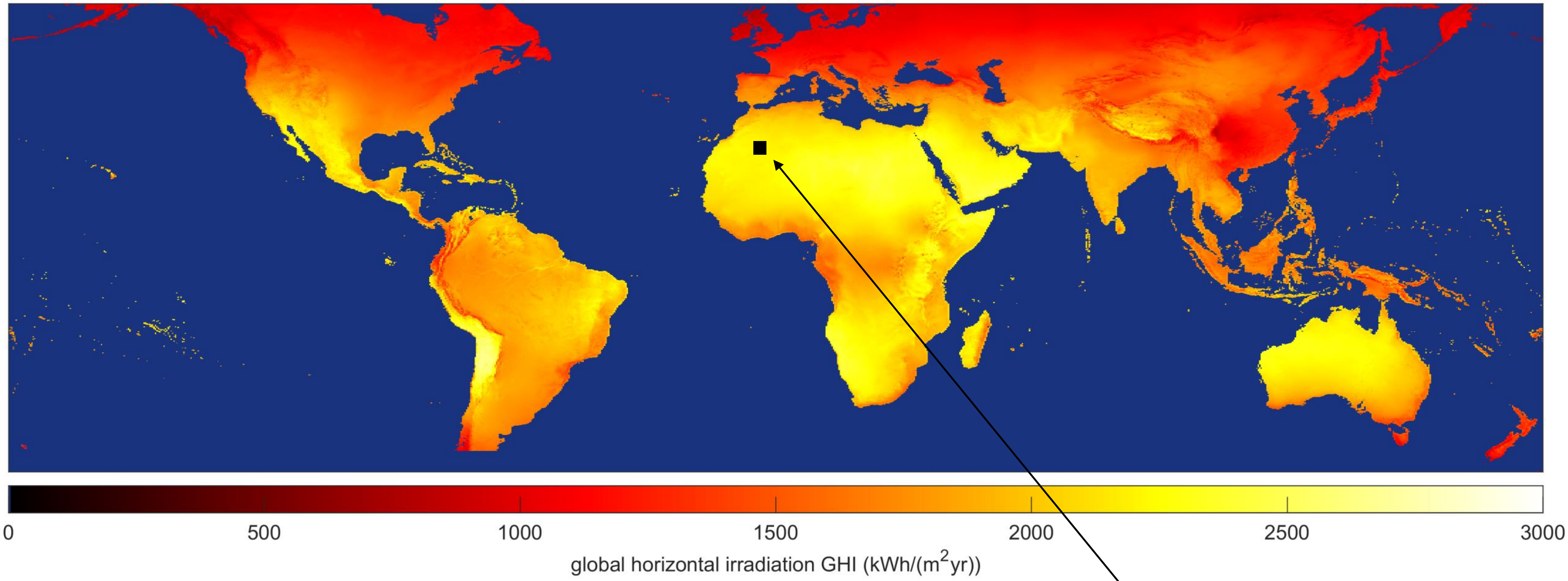


Efficiency: 10%
Area: 3.8 km^2

Kerosene production of plant:
95'000 Liters/Day
34 Million Liters/Year

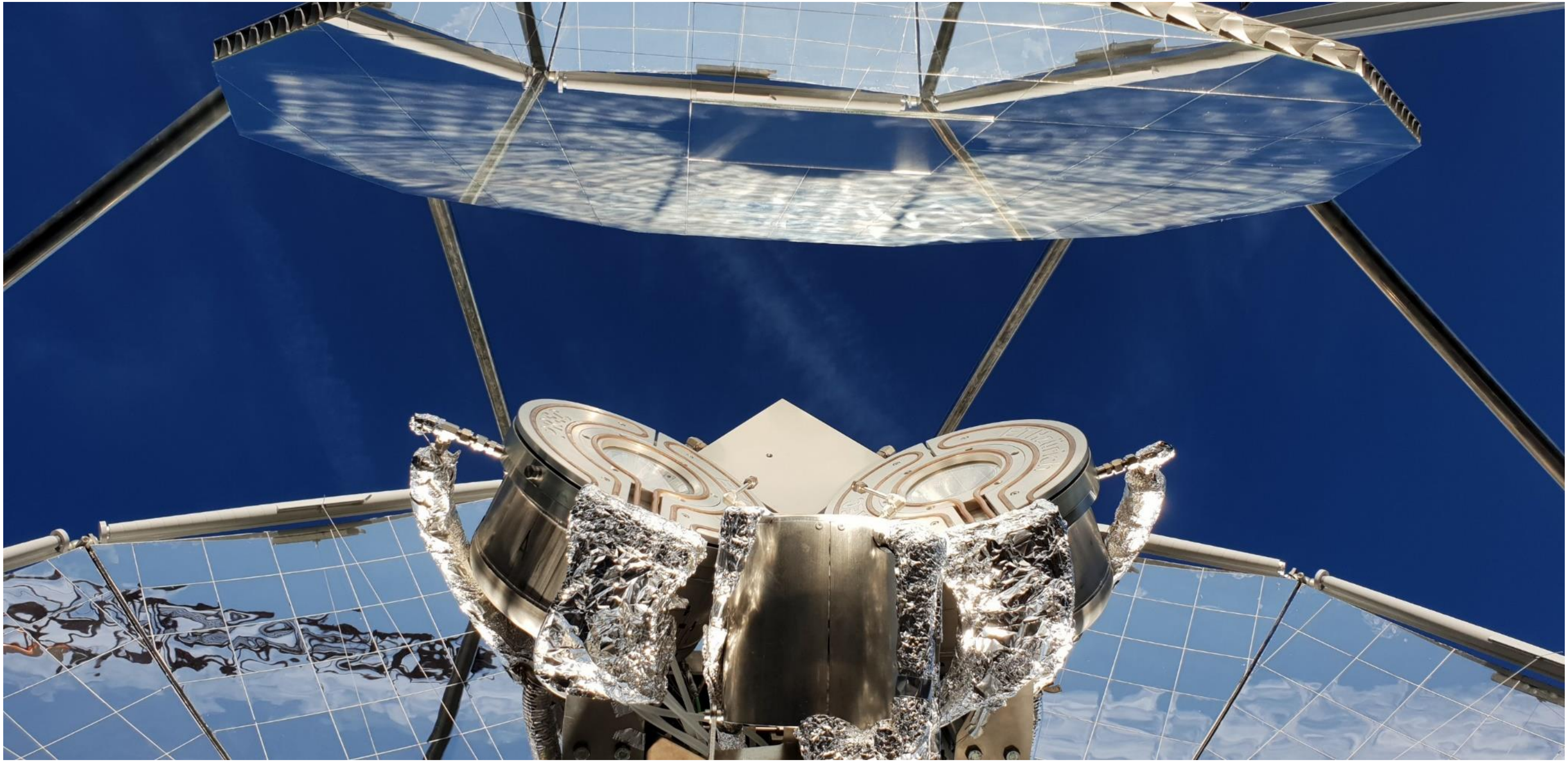
Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Where to build solar fuel plants?

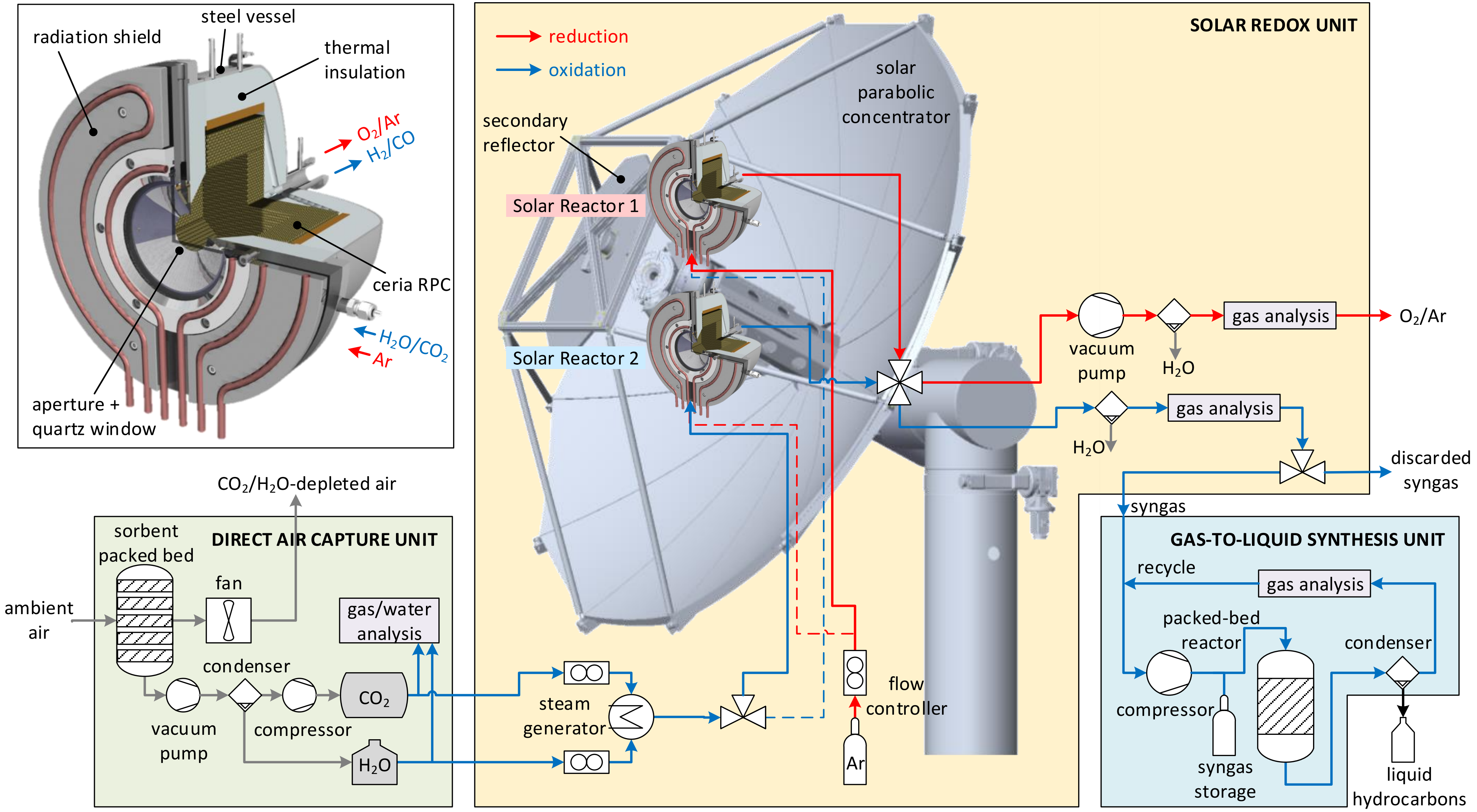


Global energy consumption traffic (2018): 2.890 Gtoe = $3.3611 \cdot 10^{13}$ kWh
Yearly solar irradition: 2000 kWh/m^2
Efficiency: 15%

Land requirements: 109’000 km^2
335 x 335 km



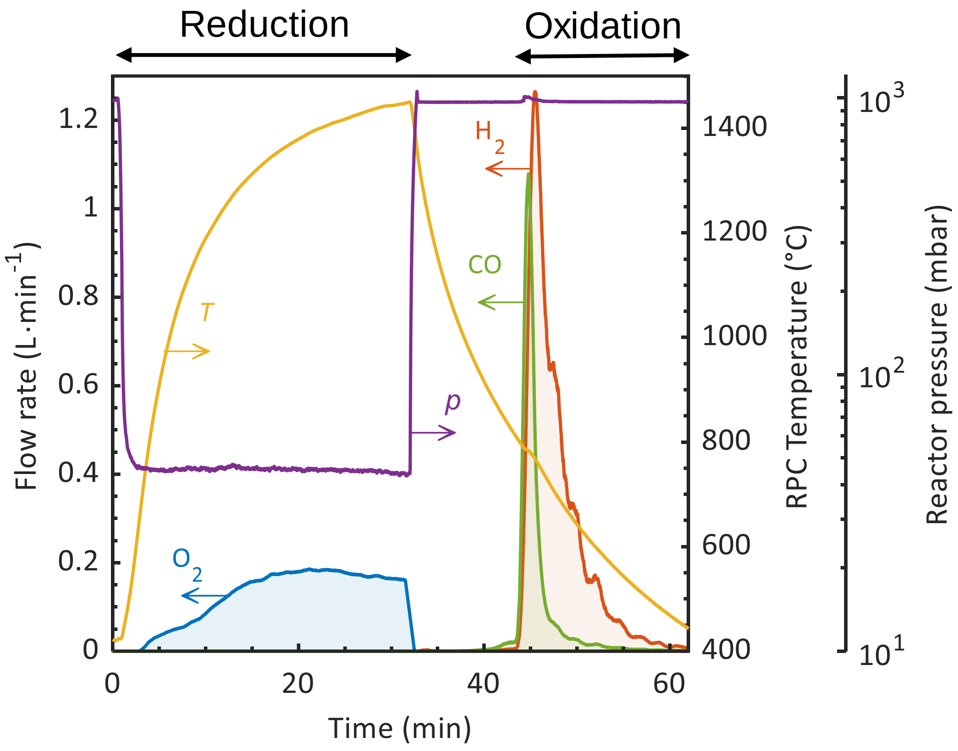
Schematic of the implemented process chain

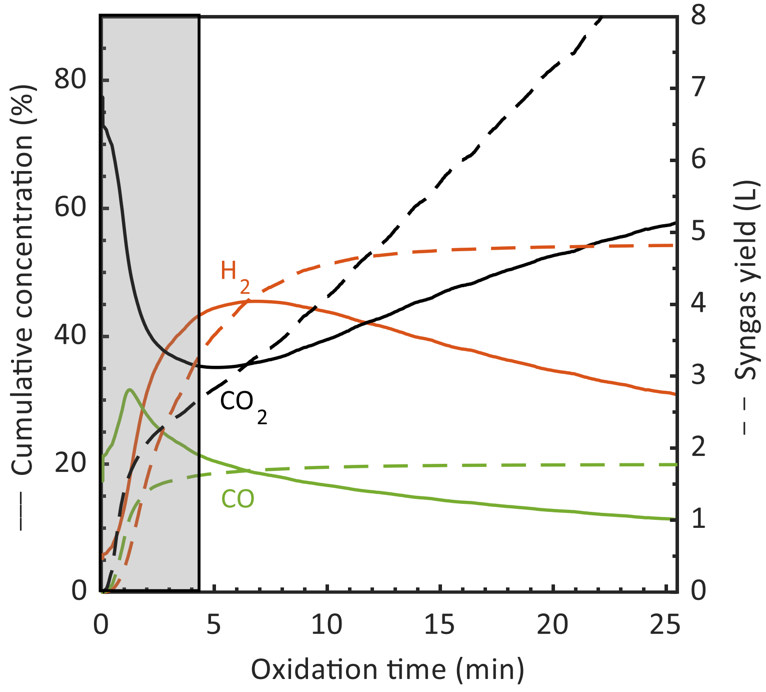


Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

Exemplary Cycle Targeting Syngas for Fischer-Tropsch Synthesis

<u>Target:</u>
H_2/CO ratio: 2



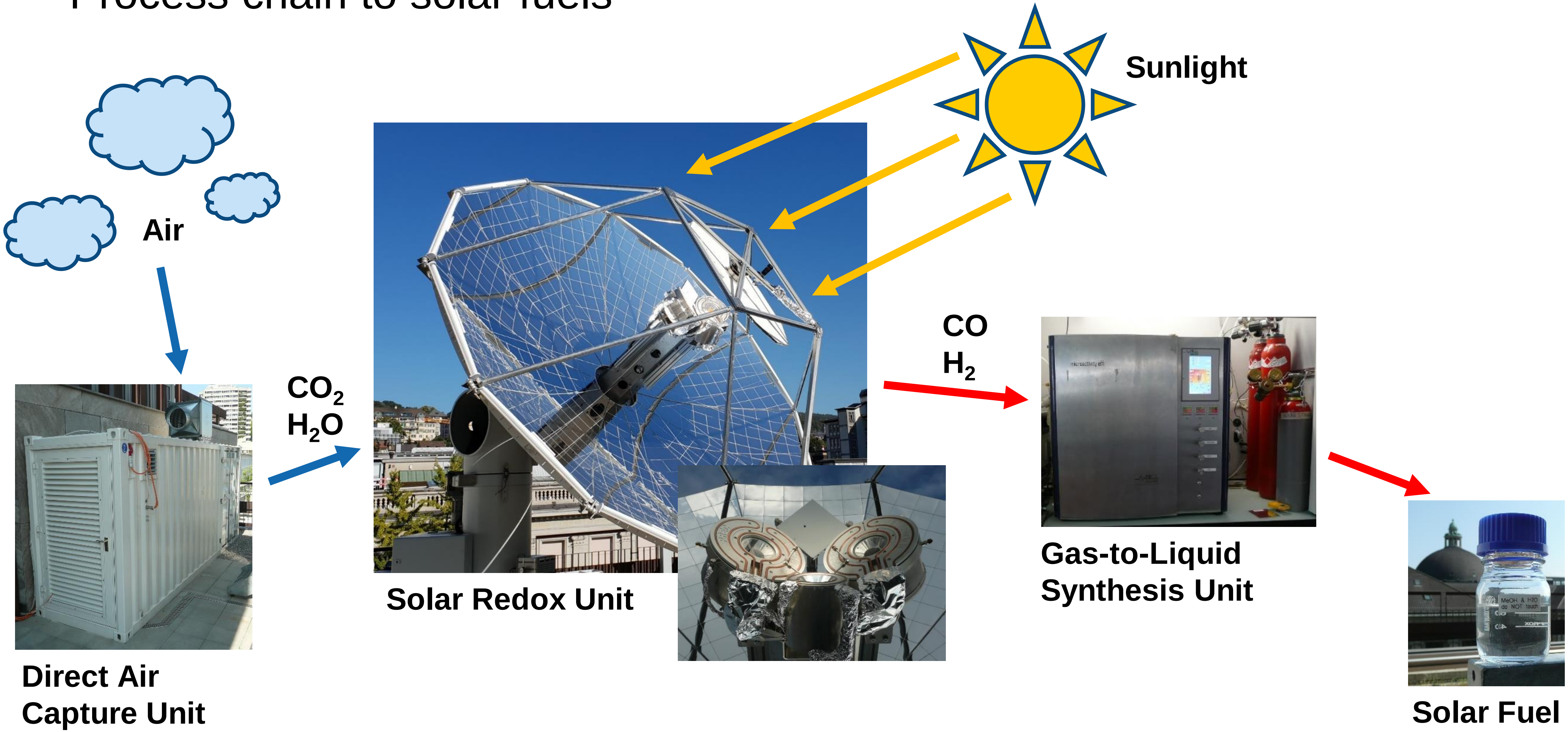


Conditions	Reduction	Oxidation
Power input	4.1 kW	Off-sun (0 kW)
Gas flow	0.5 l/min Ar	0.2 l/min CO_2 9.8 g/min H_2O
Pressure	50 mbar	1 bar

- Full oxidation:
  - 15.6 L of syngas
  - 31.0% H_2, 11.4% CO, 57.6% CO_2
  - H_2/CO ratio: 2.72
  - CO_2 conversion: 16.5%
- Collection 0-4.25 min:
  - 7.52 L of syngas
  - 43.1% H_2, 21.5% CO, 35.4% CO_2
  - H_2/CO ratio: 2
  - CO_2 conversion: 37.9%

Source: Schäppi, R. *et al.* Drop-in Fuels from Sunlight and Air. *Nature* (2021).

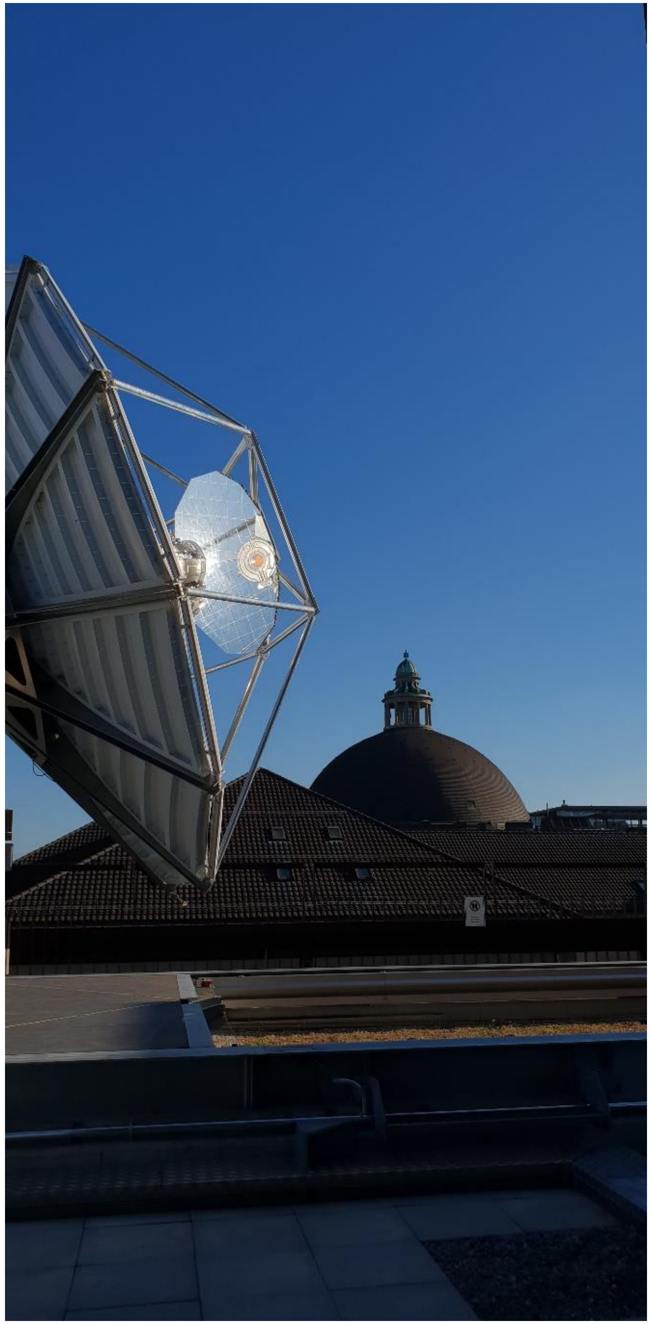
Process chain to solar fuels



Conclusions

- Successful demonstration of the entire process chain from ambient air and sunlight to liquid solar fuels
- Syngas produced suitable for downstream methanol or Fischer-Tropsch synthesis
- Stable fully automated full day consecutive cycling
- Produced methanol and kerosene from sunlight and air

- Schäppi, R., Rutz, D., Dähler, F., Muroyama A., Haueter P., Lilliestam J., Patt A., Furler P., Steinfeld A., **Drop-in Fuels from Sunlight and Air**. *Nature* (2021).



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