

**Scientific and Technological Alliance for
Guaranteeing the European Excellence in
Concentrating Solar Thermal Energy**



FP7 Grant Agreement number: 609837
 Start date of project: 01/02/2014
 Duration of project: 48 months

STAGE-STE D9.1

**Deliverable 9.1: Final report on vacuum
and pressurized solar reactor concepts**

WP9 – Tasks 9.1 and 9.2	Deliverable 9.1
Reached/Submitted:	January 30, 2017
Work Package Leader:	PSI
Task leaders:	CIEMAT, PSI
Author(s):	Gilles Flamant (CNRS), Alessandro Galia (UNIPA), José González (IMDEA), Anton Meier (PSI), Ronald Michalsky (ETHZ), Manuel Romero (IMDEA), Benedetto Schiavo (UNIPA), Luca Turchetti (ENEA), Christian Sattler (DLR), Aldo Steinfeld (ETHZ), Alfonso Vidal (CIEMAT), Christian Wieckert (PSI)
Revised by:	José González (IMDEA), Christian Wieckert (PSI)
Document version:	6
Reviewed/supervised by:	José González (IMDEA), Christian Wieckert (PSI)

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1. Introduction

In the frame of STAGE-STE, the partners of Tasks 9.1 and 9.2 are further developing the solar chemical reactor technology for high-temperature thermochemical processes that efficiently convert concentrated solar energy into storable and transportable fuels.

The design of the solar receiver and reactor is at the heart of developing a solar-driven fuel production system. Solar reactors can be classified as indirectly and directly heated reactors [1]. In directly heated reactors, the reactants are directly exposed to and heated by incoming solar radiation. In indirectly heated reactors, the incident solar energy is first absorbed by an opaque wall surface that transfers it to a heat transfer medium or reacting material on the other side of the wall.

The partners have designed, fabricated and experimentally tested many different solar reactor types. For each type, the reactor design is briefly described and applications are presented together with experimental and modelling results. The status of development is reported and major publications are listed.

In order to present a rather complete picture of the actual solar reactor technology for solar fuels processing, this report includes not only the most recent reactor concepts investigated by the partners within the integrated research programme STAGE-STE, but also ongoing and even terminated solar reactor development within national or other EC (FP5, FP6, FP7, and H2020) projects.

In this deliverable, nineteen different reactor types are described. Examples comprise solar reactor concepts for operation under non-atmospheric conditions (between 1 mbar and 5 bar) that are being developed for H₂O/CO₂-splitting thermochemical cycles based on metal oxides (mainly ZnO, SnO₂, ferrites and ceria) and tested at the 1-5 kW laboratory scale. The technical feasibility of chemical reactors concepts based on directly and indirectly heated fluidised bed reactors is studied at small scale of 1 kW. In a 10 kW two-cavity solar reactor, the effect of major reactor and process modifications is investigated including the introduction of continuous/semi-continuous feeding and the removal of the transparent quartz window. Novel concepts include the solar steam reforming of natural gas, biogas and bio-ethanol towards H₂ and mixtures of H₂ and CH₄ in a 5-10 kW membrane reactor as well as hydrothermal gasification/liquefaction of carbonaceous feedstocks in a continuous high-pressure reactor, both powered by solar-heated molten salts. Current state-of-the-art of solar reactors involves various devices at pilot scale (100 – 750 kW) dealing with hydrogen and synthesis gas production by carbothermal reduction and thermal dissociation of ZnO (100 kW and 300 kW), steam gasification of carbonaceous materials (150 kW and 500 kW) using packed-bed two cavities and gas-particle vortex reactors, water and water/CO₂ splitting by thermochemical cycles (50 and 750 kW) and methane dry reforming (400 kW) using directly irradiated porous reactors.

This report concludes providing a table that summarises all presented reactors, their main applications in solar thermochemistry, temperature and pressure ranges, as well as technology readiness level.

2. Indirectly heated solar reactor concepts

In indirectly irradiated solar reactors, the incident radiation is absorbed by a chemically inert solid and then transferred to the chemical reaction by conduction, convection, and radiation through an intermediate heat transfer medium (solid, gas, or multiphase fluid) [2]. Indirectly irradiated reactors have, in principle, the advantage of eliminating the need for a transparent window [3]. The disadvantages are linked to the limitations imposed by the materials of construction of the reactor walls: limitations in the maximum operating temperature, thermal conductivity, radiant absorptance, inertness, resistance to thermal shocks, and suitability for transient operation.

Indirectly irradiated reactors can be equipped with a transparent window as well. For example, in the two-cavity reactor the reaction chamber is separated from the window by an intermediate solid wall. This wall protects the window against particle contamination that may occur in directly irradiated reactors. The window on its part serves as sealing for the reactor against chemical reactions with atmospheric air. If gas-tight mounting of an air-resistant intermediate wall is possible, the transparent window can be removed, as recently demonstrated in STAGE-STE.

The various indirectly heated solar reactor configurations investigated by the STAGE-STE partners include a packed-bed two-cavity reactor (cf. Section 2.1), a packed bed cavity reactor (cf. Section 2.2), a multi-tube reactor (cf. Section 2.3), a gas-solid trickle-bed reactor (cf. Section 2.4), a falling particle vacuum reactor (cf. Section 2.5), a pressurised vortex flow solar reactor (cf. Section 2.6), a shell-and-tube membrane reactor heated with molten salts (cf. Section 2.5), and a high-pressure tubular reactor heated with molten salts (cf. Section 2.8).

References pertinent to specific solar reactors and their applications are provided at the end of each Section, while general references are given in Section 6.

2.1. Packed bed two-cavity reactor (beam-down)

Contact: Christian Wieckert (PSI)

Solar reactor design

A schematic of the two-cavity solar reactor is shown in Figure 1 (laboratory version as example). It features two cavities in series, with the upper cavity functioning as the solar absorber, and the lower cavity as the reaction chamber. With this arrangement, the “partition wall” between the two cavities protects the window against particles and condensable gases. The water-cooled mounting of the window in the aperture provides the gas-tight sealing of the reactor towards the ambient air (aperture diameter 65 mm, window diameter 140 mm in the laboratory version). The upper cavity also serves as a thermal shock absorber. Prior to experimental operation, the feedstock to be processed is placed in the lower cavity in form of a packed bed. Hence, the reactor is operated in batch mode, with the concept of using one batch per day in larger realisations (cooling and recharging of a new batch to be accomplished overnight). Both upper and lower cavities have a steel outer shell, protected by a thick insulation. The inner walls of the reaction chamber are made of 8 mm thick SiC-plates, on which the partition wall from graphite coated with SiC is loosely placed. To prevent product gases from flowing towards the window, a small inert gas stream is injected into the upper cavity and entering the lower cavity through small gaps around the partition wall. It then leaves the reaction chamber through the product gas exit along a SiC pipe towards the off-gas system, which is adapted to the process occurring in the solar reactor. The reactor is equipped with further gas inlets into the reaction chamber, one above the packed bed and another one at the bottom that allows flushing the packed bed with this gas. The latter is specifically of interest for the application of the reactor concept for steam gasification (see application 2 below), where steam is provided from below. The reactor is operated at temperatures up to 1400 °C (typically at 1100-1200 °C) and close to ambient pressure, with an adjustable pressure safety valve ensuring that the difference between reactor and ambient pressures does not exceed about 15 kPa, the maximum allowed for the flat quartz window.

The reactor is specifically designed for beam-down incident radiation, as can be obtained for larger plants through a Cassegrain optical configuration that makes use of a hyperbolic reflector at the top of the tower to re-direct sunlight to a receiver placed on the ground level.

Generic guidelines for the design of two-cavity reactors are provided in [1] and [2]. Further selected references introducing the reactor for specific processes are listed in the following section about the applications.

Recently, various options were investigated to avoid the use of a quartz window. This reactor modification requires a gas tight high-temperature sealing of the partition wall as well as the identification of partition wall materials that are stable in air at the high operational temperature (publication under preparation). Furthermore, concepts are investigated that are aiming to transport new batches of feedstock material into the hot furnace during solar operation. This would further increase the field of applications for this reactor type by allowing to process materials with significant non-volatile fractions, which in the one batch per day operation lead to reduced production rate due to the layer of solid products developing above the reacting materials underneath [3].

The two-cavity reactor is well suited for very different processes involving solids that are transformed to gases [4]. Table 1 provides an overview of some major applications investigated so far.

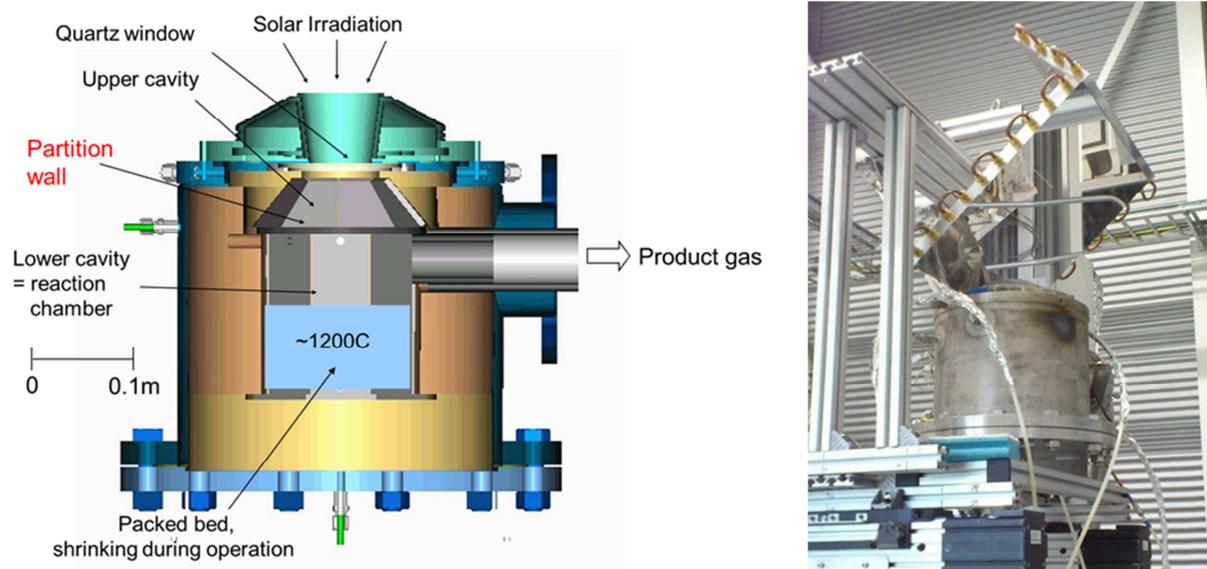


Figure 1 Left: Schematic of lab-scale two-cavity reactor developed at PSI. Right: Photo of solar reactor including a “45°-mirror” for providing beam down radiation during operation in the High-Flux Solar Simulator (HFSS) at PSI .

Table 1 Applications of packed bed two-cavity reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
ZnO + C (SOLZINC)	5-10 kW _{th} @ PSI	300 kW _{th} @ WIS	PSI, CNRS, WIS, ETHZ, Scanarc, Zoxy	EC (SERI, formerly BBW)
Waelz Oxide (Zn, Pb, O, Cl, etc.)	5-10 kW _{th} @ PSI	---	PSI, Montan University Leoben	BEFESA (Abengoa)
Gasification of C-Materials (SOLSYN)	5-10 kW _{th} @ PSI	150 kW _{th} @ PSA	PSI, Holcim, ETHZ	Holcim, CTI EU-FP7 STAGE-STE

Application 1: Solar carbothermal reduction of ZnO

Project name: SOLZINC (EU-FP5 project)

Partners: CNRS (administrative coordination), PSI (scientific coordination), WIS, ETHZ, Scanarc Plasma Technologies AB, Zoxy Energy Systems GmbH

Process: The solar-driven carbothermal reduction of ZnO is given by
 $ZnO + C \rightarrow Zn + CO$
 Solar-produced metallic Zn can be used either
 (1) as commodity or
 (2) in mechanically rechargeable Zn-air batteries/fuel cells, or
 (3) serve as part of the ZnO-Zn thermochemical cycle for the production of H₂ or syngas on demand.

Results/development status

The project included two stages:

- (1) Laboratory tests were performed using the two-cavity lab-scale reactor shown in Figure 1. A packed bed of ZnO and charcoal gravel (or other cokes/coals) was processed to Zn(g) and CO at temperatures of about 1200 °C [5]. Extensive process rate and material selection studies were performed [6].
- (2) Based on the results of (1), a 300 kW pilot solar reactor including an off-gas system for the production of Zn dust for use in Zn-air batteries was designed, built and operated (Figure 2) [7]. Up to 50 kg/h of Zn dust were produced. Based on the promising results, conceptual designs of a 2 MW demo plant and a 30 MW commercial plant have been worked out [8].

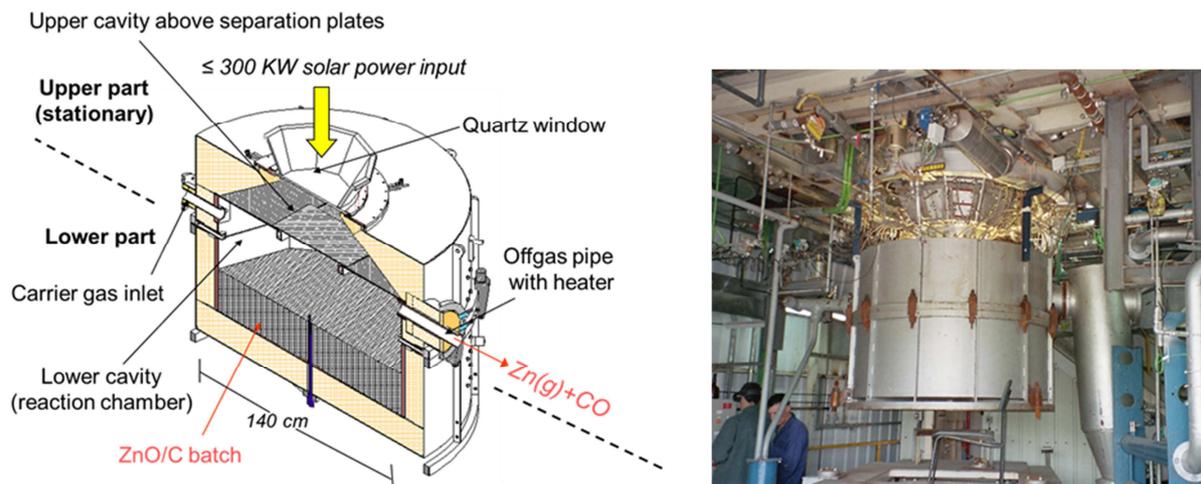


Figure 2 Left: Schematic of the 300 kW reactor. Right: Photo of the solar pilot plant in operation at the beam-down solar facility at the Weizmann Institute of Science in Rehovot/Israel [6].

Application 2: Solar purification of and carbothermal Zn production from Waelz Oxide

Project name: ---

Partners: PSI, Montan University Leoben/Austria; BEFESA (belonging to Abengoa until early 2013)

Process: Waelz Oxide is the major secondary Zn material generated from electric arc furnace dust (EAFD) from scrap recycling and consists of ZnO together with Pb, Cl and other compounds.

Two types of process tests were performed using the laboratory scale two-cavity reactor shown in Figure 1 [9]:

- (1) Thermal treatment of Waelz Oxide for depletion from Pb and Cl (“solar clinkering”).
- (2) Carbothermal reduction of (solar clinkered) Waelz Oxide

Results/development status

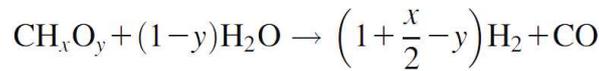
Successful tests were performed on laboratory scale (about 5 kW) for both processes: Solar clinkering at above 1265 °C resulted in a reduced amount of unwanted elements below 0.1 %, as targeted. Solar carbothermal reduction yielded condensed products containing 90 wt% Zn [9]. These experiments open new options for process routes in secondary Zn metallurgy.

Application 3: Steam gasification of carbonaceous materials

Project name: SOLSYN (Swiss project)

Partners: PSI, Holcim Group Support Ltd., ETHZ

Process: The key reaction of the solar-driven steam gasification of carbonaceous materials is given by



Carbonaceous materials incl. wastes are converted to solar upgraded syngas.

Results/development status

The project included two stages:

- (1) The process was investigated for many different carbonaceous materials using the laboratory scale two-cavity reactor shown in Figure 1 [10]. Reaction rate and material suitability tests were performed [10].
- (2) Design, fabrication, construction and operation of a 150 kW pilot two-cavity reactor for tests at the Plataforma Solar de Almería (Figure 3). A total of nine very different feedstocks, comprising wet, high volatile coals, charcoal, different industrial sludge and fluff, dried sewage sludge, tire chips and bagasse from sugarcane production, were successfully transformed into a solar upgraded syngas [11].

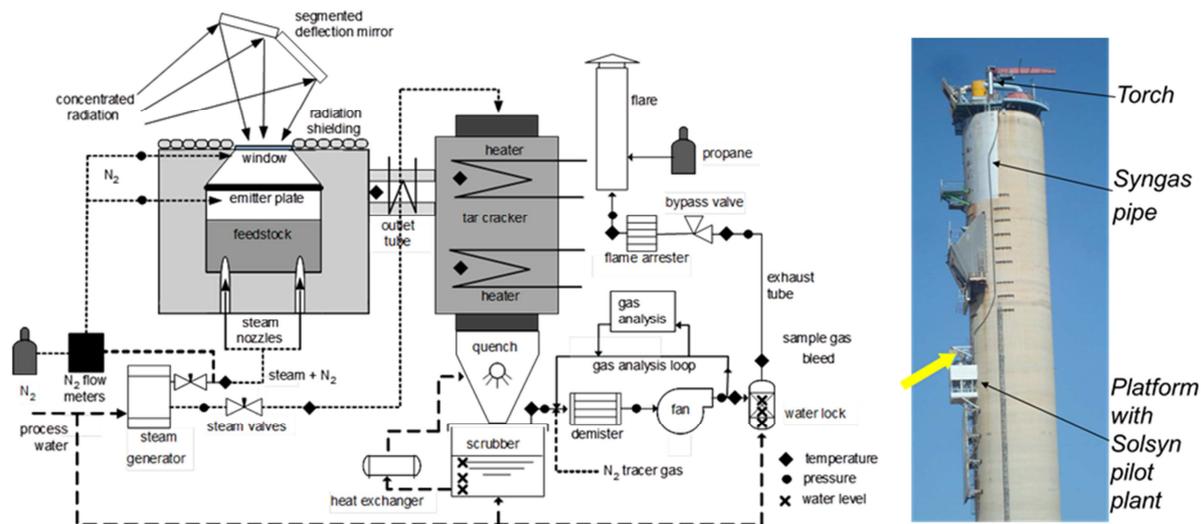


Figure 3 Left: Schematic of the SOLSYN pilot plant. Right: 150 kW SOLSYN pilot plant on the large solar tower at the Plataforma Solar de Almería (PSA).

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2.2. Packed-bed cavity reactor (horizontal)

Contact: Francesca Varsano (ENEA), Michela Lanchi (ENEA)

Solar reactor design

The solar reactor is a horizontally oriented cylindrical open cavity receiver made of Inconel 625, which traps the focused incident radiation. The thermal energy is delivered to the reaction chamber by conduction through the metal cavity walls. The cylindrical receiving cavity (diameter 64 mm, height 83 mm) is surrounded by an annular space (internal diameter 72 mm, external diameter 102 mm) in which two flow distributors are inserted. Different views of the reactor sections are shown in Figure 4 (a-c). Gases enter the reactor from a pipe positioned at the backside of the reactor (labelled IN in Figure 4 (a)) and are conveyed in the annular cavity. The gas flow then splits and flows into the packed bed formed by pellets of the active material, where heat exchange and chemical reactions take place. The flow recombines at the outlet, where effluent gases are collected through a second flow distributor to an outlet pipe (OUT) and sent to gas analysis. The cylindrical space between the cap and the cavity constitutes the vaporization chamber. In Fig. 4d the reactor dimensions are shown. Heat losses from the reactor are reduced through a 40 mm thick alumina-insulating jacket; no other materials were used to insulate the reactor.

The packed-bed cavity reactor has been tested in a small solar concentrating facility (about 1 kW) located on the roof of the Department of Chemistry of the University “La Sapienza” of Rome (see Figure 5). This facility is a solar furnace, composed of one heliostat (2.2 m by 2.0 m), with an azimuthal and vertical sun tracking system driven by photocells, and a parabolic reflector (diameter 1.5 m, horizontal axis), which has a focal distance of 0.64 m and a concentration factor of about 600. The concentrated solar radiation is directed towards the reactor-receiver cavity, placed in the focus of the concentrating dish.

Table 2 Application of horizontal packed bed two-cavity reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Na-Mn ferrite cycle	1 kW _{th} (on-sun) @ University “La Sapienza” of Rome	-	ENEA, La Sapienza	Italian Ministry of Education, University and Research

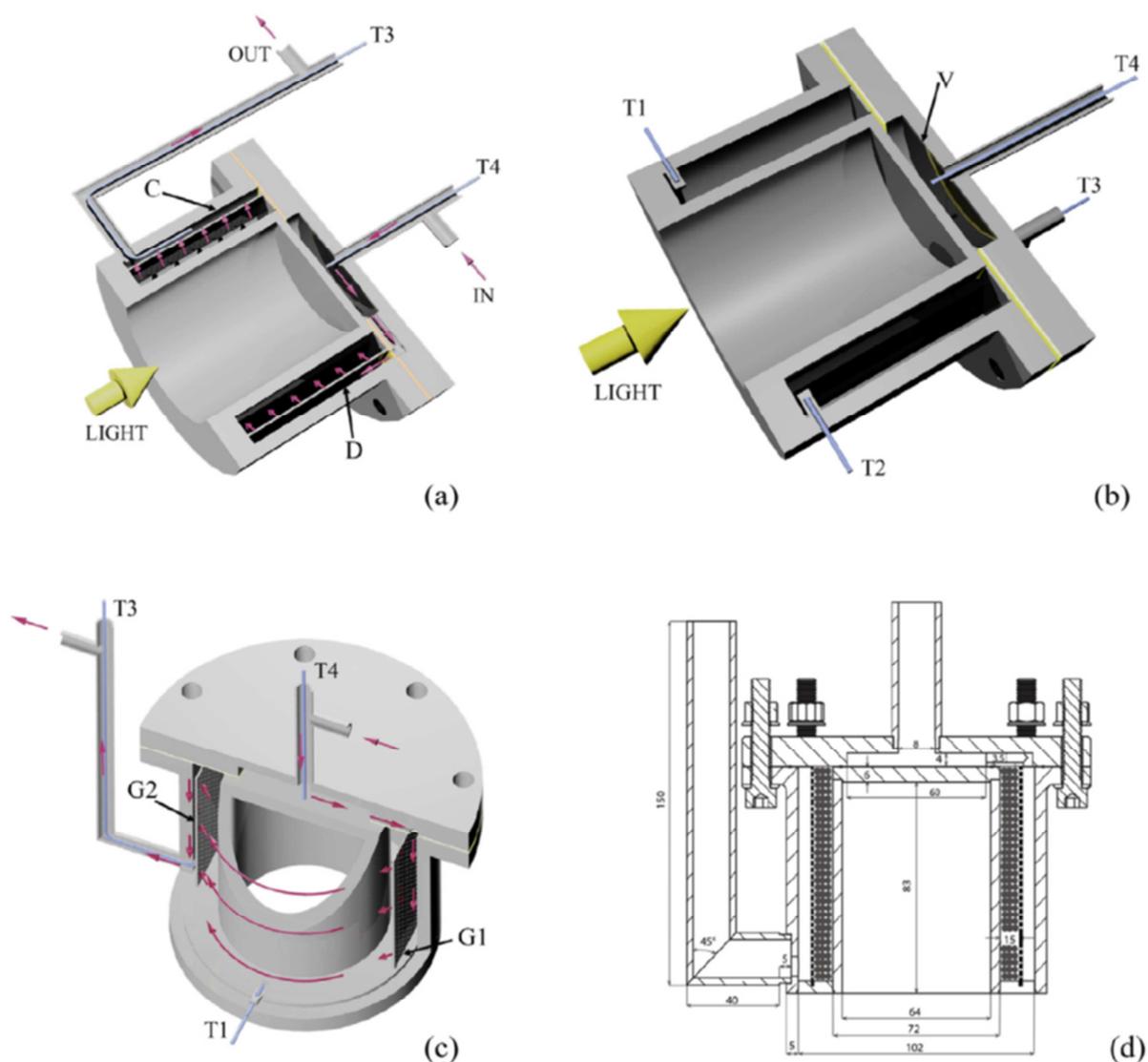


Figure 4 Scheme of the packed-bed cavity reactor. In (a) and (b), two orthogonal cross-sections of the reactor along the horizontal axis are reported. Tags T1 to T4 identify the position of thermocouples. G1 and G2 represent two planar grids that act as gas flow distributor and collector. Reactant fluids enter the reactor from the point IN in the pipe positioned at the backside of the reactor and flow through the chamber V where liquid water vaporizes. Gases enter in the distribution zone D and reach the packed bed flowing through the distributor grid G1. Here, gases split and flow inside the two halves of the packed-bed. Gases exiting the packed bed are collected, pass through the grid G2, and leave the reactor from the outlet pipe (OUT). In (c), the reactor is tilted to better evidence the gases' path (sketched by pink arrows). The active material is placed inside the annular space between cylindrical walls and fill the entire cavity as shown in (d) (2D view). Dimensions are reported in mm.

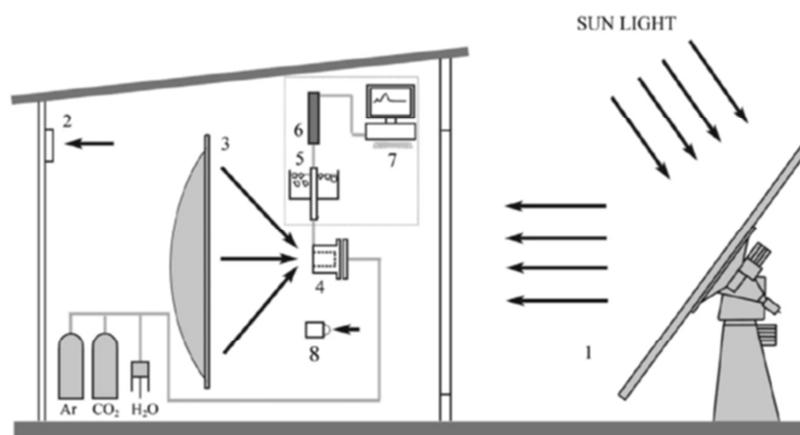


Figure 5 Scheme of the solar concentration facility, where the cavity packed-bed reactor has been tested for the mixed-ferrites cycle: a heliostat (1) is driven by a photocell (2) to reflect the incoming radiation on a concentrating parabolic mirror (3). The receiver cavity of the reactor (4) is placed in the focus of the parabolic mirror. The analytical system consists of a water-ice trap (5) and a silica gel trap (6) utilized to capture unreacted water, a gas chromatograph (7) to detect hydrogen and carbon dioxide output fluxes. A pyranometer (8) is placed on the incoming light path to measure the radiation intensity.

Application

Project name: TEPSI

Partners: ENEA, University “La Sapienza” of Rome (partners involved in the development and testing of the reactor)

Process: Sodium-manganese ferrite thermochemical cycle

Results/development status

After studying the reaction properties of a novel formulation of Na-Mn mixed ferrites in a laboratory reactor [1], a first design of the cavity reactor was thermally characterized in a series of on-sun heating tests carried out in the solar concentration facility [2]. Such tests showed that temperature distributions (up to 800 °C) suitable for the use of the novel active material developed could be achieved in the packed bed of the reactor. Subsequently, a second design of the reactor with minor changes in the material and gas flow pattern was developed; the new reactor was tested on-sun for both steps of the Na-Mn ferrite cycle at atmospheric pressure in the range 750 - 800 °C [3]. Hydrogen production rates in excess of 4.5 $\mu\text{mol g}^{-1} \text{min}^{-1}$ (referred to the mass of active material) were observed.

References

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2.3. Graphite tubes pilot scale solar reactor

Contact: Gilles Flamant (CNRS)

Solar reactor design

The multi-tube reactor, depicted in Figure 6, was designed for 50 kW of incident solar power [1]. The reactor body is made of an aluminium shell (800 mm × 780 mm × 505 mm) and contains a water-cooled front face with a 13cm-diameter aperture to let concentrated solar radiation entering within the reactor cavity. The radiation is absorbed by the graphite cavity (360 mm × 400 mm × 300 mm) that approaches blackbody behaviour. To avoid contact of graphite with the oxidizing atmosphere, the aperture is protected by a domed quartz window (360 mm o.d.) swept by a nitrogen gas flow. The space between the graphite cavity and the aluminium shell is filled with three different insulating layers to limit conduction losses. It is composed of a 85mm-thick graphite felt in contact with the cavity ($\lambda = 0.53 \text{ W m}^{-1} \text{ K}^{-1}$ at 1873 K), a 50mm-thick intermediate refractory ceramic fibre operating up to 1873 K (62% Al_2O_3 , 30% SiO_2 , $\lambda = 0.35 \text{ W m}^{-1} \text{ K}^{-1}$ at 1673 K), and a 50mm-thick outer microporous insulator operating up to 1273 K (20% ZrO_2 , 77.5% SiO_2 , 2.5% CaO , $\lambda = 0.044 \text{ W m}^{-1} \text{ K}^{-1}$ at 1073 K). Seven graphite tubes (800 mm length, 26 mm o.d., 18 mm i.d.) cross the graphite cavity horizontally and are heated both by direct solar radiation and by IR-radiation from the hot graphite cavity walls. In order to keep the position of the graphite cavity and to avoid mechanical stress on the tubes, four vertical alumina tubes mounted at the bottom support and hold the graphite cavity.

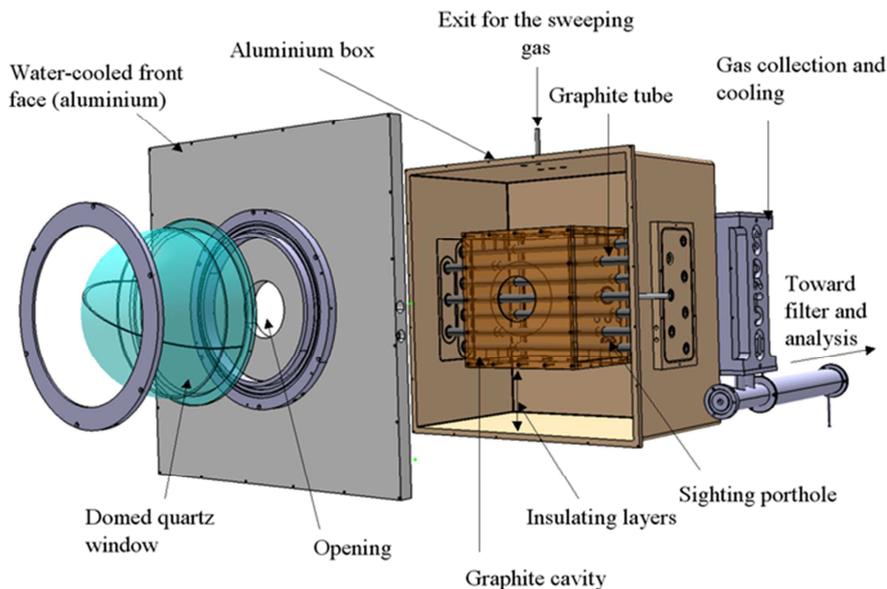


Figure 6 Graphite tubes pilot scale solar reactor (about 50 kW) designed, fabricated, and tested at CNRS.

The gas analysis system is composed of an online analyser for measuring hydrogen and methane concentrations (NGA 2000 MLT3, resolution of 1% of the full scale, range: 0-70% for H_2 , 0-10% for CH_4) as well as a gas chromatograph (micro GC Varian CP 4900) for identifying and quantifying the gas species in the course of the experiment. The micro GC is equipped with two channels: Channel 1 (MolSieve 5A PLOT 10M Backflush) for H_2 , N_2 , O_2 ,

CO, and CH₄; Channel 2 (PoraPLOT U 10M Backflush) for light hydrocarbons such as CH₄, C₂H₆, C₂H₄, C₂H₂, and H₂. The reactor was operated in the temperature range between 1608 and 1928 K for a gas residence time ranging from 37 ms to 71 ms.

Table 3 Application of the graphite tubes pilot scale solar reactor studied so far.

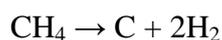
Application	Lab scale	Pilot scale	Project partners	Funding
Methane and natural gas cracking	---	50 kW _{th} @ CNRS	CNRS, DLR, PSI, WIS, CERTH, ABENGOA Solar, CREED, N-GHY, TIMCAL	EU-FP6 project SOLHYCARB

Application: Methane and natural gas cracking

Project name: EU-FP6 project SOLHYCARB

Partner: CNRS, DLR, PSI, WIS, CERTH, ABENGOA Solar, CREED, N-GHY, TIMCAL

Process: Solar thermolysis of methane and natural gas:



Results/development status

A pilot-scale solar reactor was designed and operated at the 1 MW solar furnace of CNRS for H₂ and carbon black (CB) production from methane splitting [1]. The reaction of CH₄ dissociation produces H₂ and carbon nanoparticles without CO₂ emissions and with a solar upgrade of 8% of the high heating value of the products. The reactor was composed of tubular reaction zones and of a graphite cavity-type solar receiver behaving as a blackbody cavity. Temperature measurements around the cavity showed a homogeneous temperature distribution. The influence of temperature (1608–1928 K) and residence time (37–71 ms) on methane conversion, hydrogen yield, and carbon yield was especially stressed. For 900 g/h of CH₄ injected (50% molar, the rest being argon) at 1800 K, this reactor produced 200 g/h H₂ (88% H₂ yield), 330 g/h CB (49% C yield) and 340 g/h C₂H₂ with a thermal efficiency of 15%. C₂H₂ was the most important by-product and its amount decreased by increasing the residence time. A 2D thermal model of the reactor was developed. It showed that the design of the reactor front face could be drastically improved to lower thermal losses. The optimised design could reach 77% of the ideal blackbody absorption efficiency (86% at 1800 K), i.e. 66%.

Reference

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2.4. Gas-solid trickle-bed reactor

Contact: Ronald Michalsky (ETHZ), Aldo Seinfeld (ETHZ)

Reactor design

Efficient high-temperature solar heat transfer is crucial for applications such as high-yield and high-selectivity solar-driven gasification of biomass. The ambient-pressure gas-solid trickle-bed reactor intends to achieve this. The left panel of Figure 7 gives a schematic of the reactor. A 1.2 m long alumina reactor tube having an inner diameter of 0.06 m and a wall thickness of 5 mm was situated inside an electrical tube furnace to simulate the conditions of absorbing cavity-receivers that are heated by concentrated solar radiation. Two 0.1-m-tall reticulate porous ceramic (RPC) pieces (Figure 7, right panel), were stacked and inserted into the alumina tube with the stack's top at the middle of the hot zone and held in place by another smaller diameter supporting alumina tube. The RPC was made of silicon infiltrated silicon carbide with a high thermal conductivity, i.e., $36 \text{ W m}^{-1} \text{ K}^{-1}$ at 1273 K, and an overall porosity of 89% with a nominal pore diameter of 2.54 mm, corresponding to 10 ppi (pores per inch) [1]. Details of the experimental setup are given elsewhere [1].

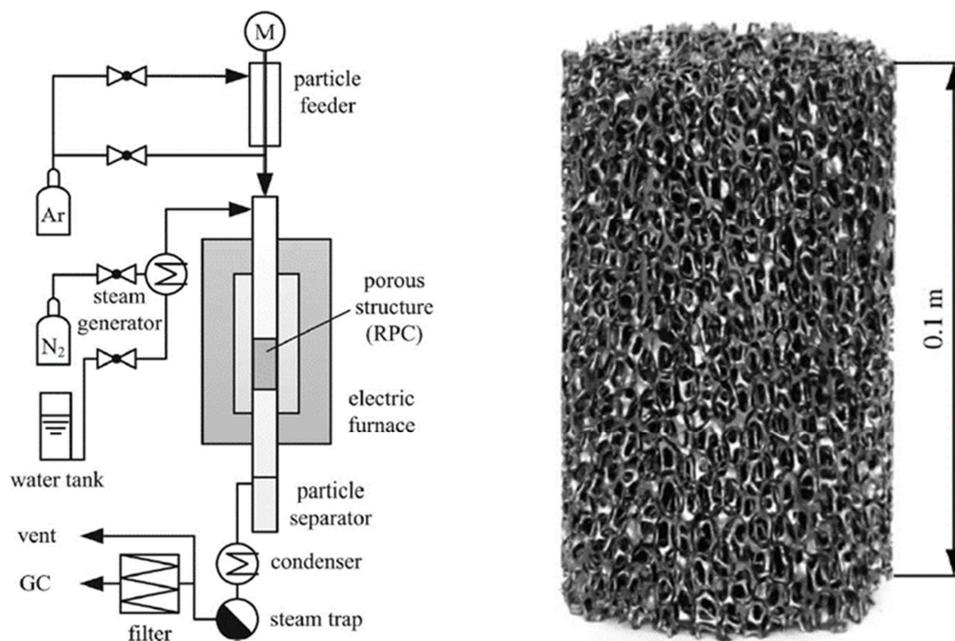
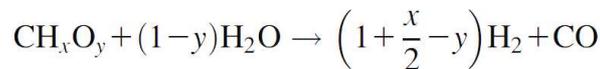


Figure 7 Left: Schematic of the gas-solid trickle-bed. Right: photograph of the of silicon infiltrated silicon carbide RPC (right). both images are adapted from [1].

Table 4 Application of gas-solid trickle-bed reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Biomass gasification	1-3 kW _{th} @ ETHZ	---	ETHZ, PSI	Brazilian-Swiss Joint Research Programme (BSJRP), STAGE-STE (EU-FP7 project)

Application: Biomass gasification*Project name:* -*Partners:* ETHZ, PSI*Process:* Key reaction:*Results/development status*

The reactor has been constructed and characterized successfully. The results are published in [1]. In summary, ETHZ investigated the performance of a gas-solid trickle-bed reactor constructed from a high thermal conductivity porous ceramic packing. Beech char particles were used as the model feedstock. A two-dimensional finite-volume model coupling chemical reaction with conduction, convection, and radiation of heat within the packing was developed and tested against measured temperatures and gasification rates. The sensitivity of the gasification rate and reactor temperatures to variations of the packing's pore diameter, porosity, thermal conductivity, and particle loading was numerically studied. A numerical comparison with a moving bed projected a more uniform temperature distribution and higher gasification rates due to the increased heat transfer via combined radiation and conduction through the trickle bed [1].

Reference

- [1] M. Kruesi, Z.R. Jovanovic, A. Haselbacher, A. Steinfeld, Analysis of solar-driven gasification of biochar trickling through an interconnected porous structure. *AIChE Journal*, 2015, 61, 867 – 879. doi:10.1002/aic.14672

2.5. Falling particle vacuum reactor

Contact: Christian Wieckert (PSI)

Solar reactor design

A novel solar-driven vacuum aerosol reactor concept for the carbothermal reduction of ZnO and other metal oxides has been designed, constructed and tested. The lab-scale reactor, proposed by ETHZ, is based on a dual-zone concept featuring a graphite absorber tube within a quartz tube enclosure, which forms the boundary of the vacuum zone as reported by Takacs [1] and Steinfeld et al. [2]. ZnO and carbon particles are dispersed and aerosolized above the reaction tube and travel downward inside an inert gas flow and under the influence of gravity. This reactor concept offers fourfold advantage: (1) The reaction zone is separated from the transparent quartz tube in two discrete regions; (2) it is suitable for continuous operation at various pressures below 1000 mbar; (3) it offers low thermal inertia and robustness against thermal shock; and (4) it is modular and thus easily scalable. A schematic description of the vacuum aerosol reactor is shown in Figure 8 [3].

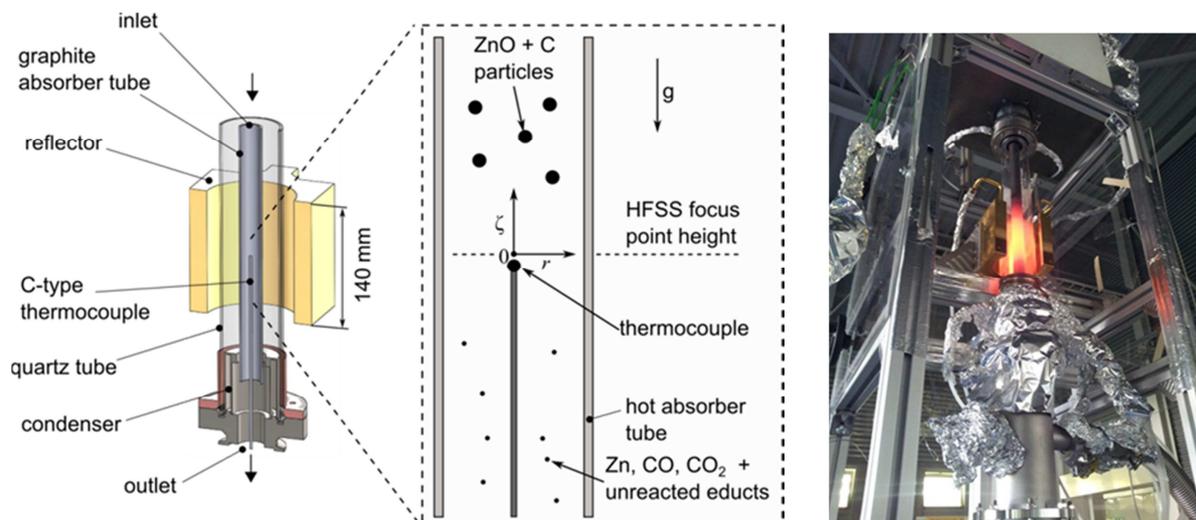


Figure 8 Left: Schematic of the vacuum aerosol reactor as a cross-sectional view, and an enlarged view of the graphite absorber tube showing the hot reaction zone and particle flow. Right: Vacuum reactor prototype after experimentation at PSI High-Flux Solar Simulator, showing after-glowing absorber tube (right). From [3].

The reactor developed at PSI incorporates a free hanging graphite drop tube (outer diameter 26 mm, thickness 1.5 mm, and length 550 mm) within a quartz tube enclosure (outer diameter 70 mm, thickness 2.5 mm, and length 500 mm). The quartz tube is sealed by Viton O-rings and water-cooled metal flanges to the stainless steel reactor housing. High-flux radiation from the High-Flux Solar Simulator (HFSS) is transmitted through the quartz tube and impinges on the outside surface of the graphite absorber tube. A gold plated, cylinder-shaped reflector with a rectangular opening (width 70 mm and height 140 mm) is used to minimize reradiation losses from the graphite absorber tube in the IR range. The tube section covered by the reflector constitutes the hot reaction zone. Aerosolized ZnO and carbon particles are introduced at the top inlet of the graphite tube in a downward flow by a custom-designed

particle feeder newly developed at PSI for feeding fine reactant powders controlled with a rotary valve [4]. The particles are rapidly heated through radiative heat transfer with the hot wall of the graphite tube while entering the reaction zone where the carbothermal reduction of ZnO begins. The produced zinc vapour is precipitated by a condenser made of a stainless steel cooling jacket (outer diameter 63 mm, wall thickness 9 mm, and length 70 mm) located at the lower end of the graphite tube. The non-condensable product gases, CO, CO₂, and unreacted feed material leave the system through a circular opening at the reactor outlet. The temperature is measured with a C-type thermocouple probe, enclosed in a Mo sheet, which is inserted inside the graphite tube. The tip of the thermocouple is located at the focal height of the HFSS. The graphite tube forms an approximate blackbody cavity around the thermocouple, thus shielding it from incoming radiation of the HFSS. The temperature measured is considered equivalent to the circumferential average temperature of the graphite tube wall assuming thermal equilibrium.

The application of vacuum has been proposed in order to reduce reaction temperatures for the carbothermal reduction of metal oxides.

Table 9 5 provides information on the application of the falling particle vacuum reactor for solar carbothermal ZnO reduction.

Table 5 Application of falling particle reactor under vacuum studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Solar carbothermal reduction of ZnO	1-3 kW _{th} @ PSI	---	PSI	Swiss Competence Centre Energy and Mobility (CCEM); <i>swisselectric</i> research

Application: Solar carbothermal reduction of ZnO

Project name: HyTech (Swiss project)

Partner: PSI

Process: The solar-driven carbothermal reduction of ZnO is given by:
 (1) $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}_2$ ($\Delta H = 352.5 \text{ kJ/mol}$; $T > 1400 \text{ K}$);
 The primary reaction route for the carbothermal reduction of zinc oxide (Eq. 1) is based on the solid gas reactions of ZnO with CO (Eq. 2) followed by the Boudouard reaction (Eq. 3):
 (2) $\text{ZnO(s)} + \text{CO(g)} \rightarrow \text{Zn(g)} + \text{CO}_2\text{(g)}$
 (3) $\text{CO}_2\text{(g)} + \text{C(s)} \rightarrow 2 \text{CO(g)}$

Results/development status

Proof-of-concept experiments were conducted with the High Flux Solar Simulator at PSI [5] as the source of process heat, resulting in successful testing of the reactor concept in conditions similar to those expected in typical solar concentrating systems for scaled-up reactor designs (Figure 8). The particles are rapidly heated to reaction temperature and reduced within residence times of less than 1 s. In initial continuous feeding experiments, maximum sustained temperatures close to 2000 K and heating rates as fast as 1400 K/min could be achieved for pressures between 1 and 1000 mbar. Reactant conversions of up to 44% were obtained at 1000 mbar [3]. It was

found that a reduction in system pressure leads to a decreased particle residence time (as low as 0.09 s), and therefore low conversion (as low as 1%), thus partially diminishing the positive thermodynamic effects of vacuum operation. Experiments with the solar drop-tube reactor were conducted to ascertain the reaction capacity of the system at pressures between 1 and 960 mbar by varying the reactant feed rate between 4 and 56 $\text{g}\cdot\text{min}^{-1}$ [6]. Experiments show that the zinc production rate is maximal at around 100 mbar and significantly diminishes under higher vacuum. Model and experimental results indicate that the reaction at 1 mbar is inhibited due to insufficient residence time and heat up of the particles in the reaction zone. Maximum experimental zinc production rate was $51.4 \text{ mmol}\cdot\text{min}^{-1}$, while feeding $56 \text{ g}\cdot\text{min}^{-1}$ of solid reactants and operating the reactor at 100 mbar with 9.8 kW of radiative input power. Extrapolation to higher feed rates with the reactor model predicts a peak zinc production capacity of $52.1 \text{ mmol}\cdot\text{min}^{-1}$ at a feed rate of $68 \text{ g}\cdot\text{min}^{-1}$, achieving a net thermal efficiency of 3.2%. Experimental results validate the robust and versatile reactor concept, and simultaneously highlight the necessity of balancing the system design in order to optimize the conflicting influence of vacuum operation and reacting particle residence time, e.g. by realising a suitably increased reaction zone.

References

- [1] M. Takacs, 2013. Development and Testing of a Scalable Solar Reactor for Vacuum Carbothermal Production of Aluminum. Master Thesis, ETH Zurich, Zurich, Switzerland.
- [2] A. Steinfeld, Z. R. Jovanovic, 2014. Methods and Systems for Reducing Metal Oxides. Patent Application No. WO2014067664 A2.
- [3] M. Brkic, E. Koepf, A. Meier, Continuous Solar Carbothermal Reduction of Aerosolized ZnO Particles under Vacuum in a Directly Irradiated Vertical-Tube Reactor. *J. Solar Energy Eng.*, 2016, 138(2), 021010/1-14. doi:10.1115/1.4032685
- [4] M. Brkic, E. Koepf, I. Alxneit, A. Meier, Vacuum Powder Feeding and Dispersion Analysis for a Solar Thermochemical Drop-Tube Reactor. *Chemical Engineering Science*, 2016, 152, 280-292. doi:10.1016/j.ces.2016.06.024
- [5] J. Petrasch, P. Coray, A. Meier, M. Brack, P. Häberling, D. Wüllemmin, A. Steinfeld, A Novel 50 kW 11,000 Suns High-Flux Solar Simulator Based on an Array of Xenon Arc Lamps. *J. Solar Energy Eng.*, 2007, 129(4), 405-411. doi:10.1115/1.2769701
- [6] M. Brkic, E. Koepf, A. Meier, Solar carbothermal reduction of aerosolized ZnO particles under vacuum: Modeling, experimentation, and characterization of a drop-tube reactor. *Chemical Engineering Journal* (2016). doi: 10.1016/j.cej.2016.12.057

2.6. Pressurized vortex flow solar reactor

Contact: Ronald Michalsky (ETHZ), Aldo Steinfeld (ETHZ)

Reactor description

Two solar reactor configurations, shown schematically in Figure 9, were investigated: 1) the indirectly irradiated (windowless) reactor denoted I-I (Figure 9a); and 2) the directly irradiated (windowed) reactor denoted D-I (Figure 9b). Both the I-I and D-I solar reactors feature a gas-particle vortex flow following a helical path. The I-I solar reactor consists of a flanged cylindrical SiC cavity, 30 mm-aperture, 95 mm-inner length, 40 mm-inner diameter, 5 mm-thick, with a hemispherical dome. This cavity serves as the solar absorber with an apparent absorptivity of 98.8% determined by Monte Carlo ray tracing. Graphite gaskets seal the flanges. A coaxial steel/Inconel 601 shell, lined with a SiO₂-Al₂O₃, creates an annular gap for the vortex flow. Concentrated solar radiation is absorbed by the SiC cavity, conducted through its walls, and transferred to the gas-particle vortex flow by combined conduction, convection, and radiation. To generate the vortex flow, Ar or CO₂ at a flow rate of up to 15 L_N/min was injected tangentially and directed toward the slurry feeding nozzle, as depicted in Figure 9a.

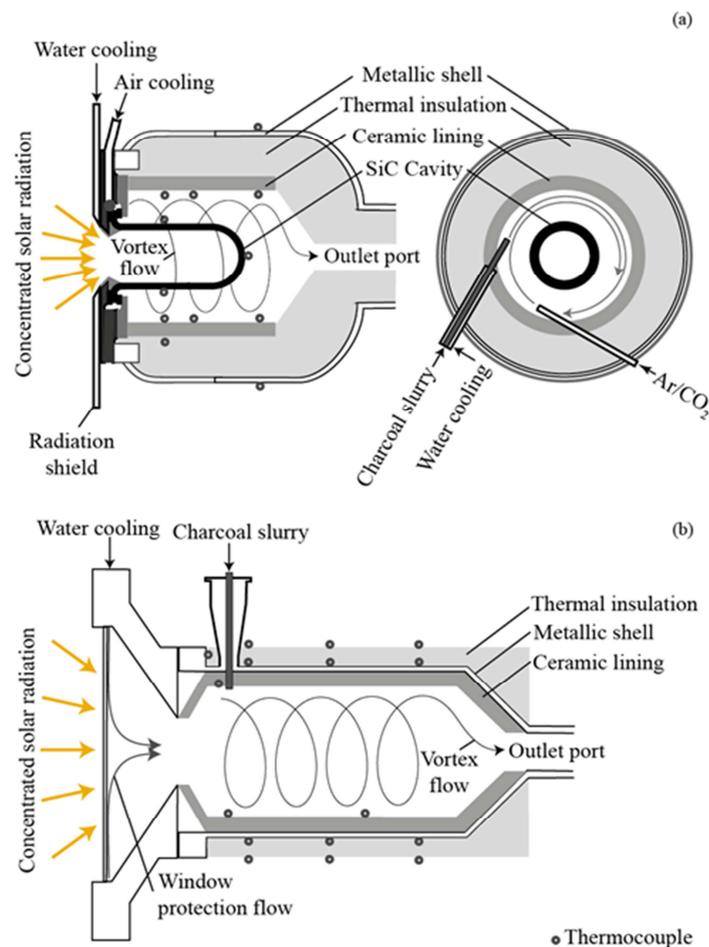


Figure 9 Schematic of: (a) the indirectly irradiated (I-I) solar reactor; and (b) the directly irradiated (D-I) solar reactor.

The design of the D-I solar reactor features a gas-particle vortex flow confined to a 200 mm-length and 100 mm-diameter cylindrical cavity-receiver, made of Inconel 601, and directly exposed to high-flux irradiation entering through a 50 mm-diameter aperture sealed with a 3mm-thick transparent quartz disk. Two Ar flows were injected: one via a tangential nozzle directly behind the window at a rate of 2 L_N/min to cool the window and protect it from particle deposition, and a second via four tangential nozzles behind the aperture at a rate of 3 L_N/min to support the vortex flow.

Table 6 Application of pressured vortex flow solar reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Steam gasification	3 kW @ ETHZ	---	ETHZ (PSI)	EU FP7 STAGE-STE, ETHZ

Application: Steam gasification of charcoal powder

Partner: ETHZ (PSI)

Process: Steam gasification of charcoal powder is mainly described by:
 $C + H_2O \rightarrow CO + H_2$

Results/development status

Experiments were carried out in a high-flux solar simulator under a solar concentration ratio equivalent to 3718 suns. For slurry feeding rates in the range 0.42 – 1.26 g/min, H₂O:C molar ratios in the range 1.48 to 1.98, and absolute reactor pressures in the range from 1 to 6 bar, the nominal reactor temperature was between 1009 and 1273 °C yielding high-quality syngas with a carbon conversion up to 94% within residence times of less than 5 seconds. The peak solar-to-fuel energy conversion efficiency, defined as the ratio of the heating value of the syngas produced to the solar radiative energy input plus the heating value of the slurry converted, reached 20%. The calorific value of the feedstock was solar upgraded by 35%, thus outperforming autothermal gasification in addition to delivering higher syngas output per unit of feedstock and eliminating the need for upstream air separation. High-quality pressurized syngas with no tars was produced, facilitating its integration to gas-to-liquid processing. Ar was substituted by CO₂, increasing the partial pressure of the gasifying agent and eliminating the consumption of expensive inert gas. The performance of this robust windowless design also was compared with that of an equivalent windowed configuration in which the gas-particle vortex flow was directly exposed to high-flux solar irradiation. Higher reaction extents as well as comparable solar-to-fuel energy conversion efficiencies and calorific upgrade factors were obtained on average with the indirectly irradiated solar reactor than with the directly irradiated solar reactor.

Reference

- [1] F. Müller, P. Poživil, P.J. van Eyk, A. Villarazo, P. Haueter, C. Wieckert, G. J. Nathan, A. Steinfeld, A pressurized high-flux solar reactor for the efficient thermochemical gasification of carbonaceous feedstock, *Fuel*, 2017, 193, 432-443. doi:10.2016/j.fuel.2016.12.036

2.7. Membrane reactor heated with molten salts

Contact: Luca Turchetti (ENEA)

Solar reactor design

The membrane reactor has a shell-and-tube configuration as depicted in Figure 10. A molten salt stream flows in the shell-side of the reactor and provides the required process heat. Reaction tubes are immersed in the molten salt flow and are composed by two coaxial elements: an external steel tube, which is in direct contact with molten salts, and an internal cylindrical hydrogen-permeable membrane (see details in Figure 11). The gaseous reactants are fed in the annular space between the two coaxial tubes (*retentate* space), where the catalyst is placed. A sweep gas such as steam or nitrogen can be fed inside the membrane (*permeate* space) in counter-current flow to enhance hydrogen permeation. Ten reaction tubes are present in the pilot reactor considered here; however, the reactor design can be easily scaled up to include more reaction tubes and increase the capacity.

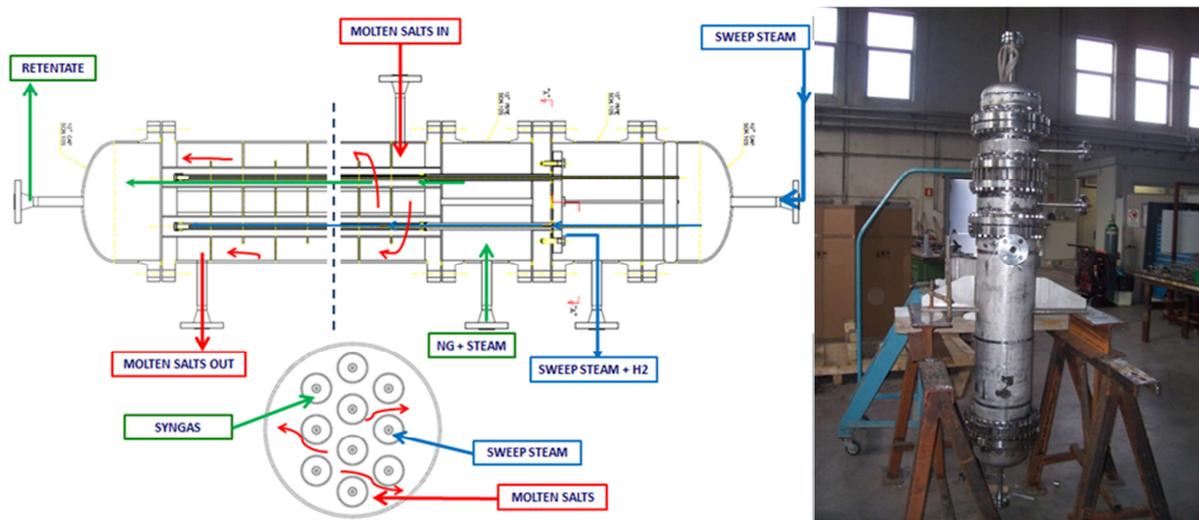


Figure 10 Integrated membrane reactor. Left: Reactor scheme. Right: lab-scale reactor.

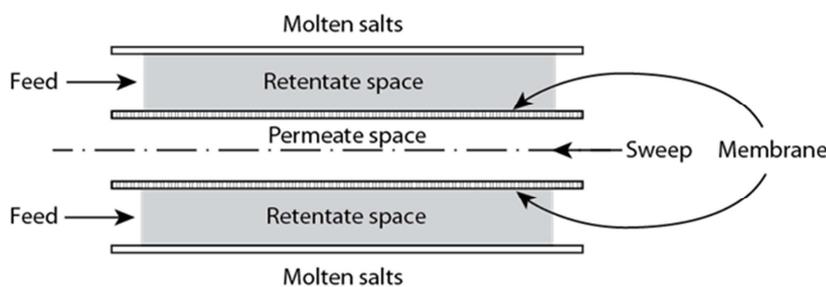


Figure 11 Details of the reaction tube as part of the membrane reactor.

Table 7 Application of integrated membrane reactor heated with molten salts.

Application	Lab scale	Pilot scale	Project partners	Funding
Compact Multifuel-Energy to Hydrogen Converter	yes	---	ENEA, Processi Innovativi Srl., Acktar Ltd., Technion, Fraunhofer Institute, University of Salerno, CERTH, Aristotle University of Thessaloniki, University “La Sapienza”, ECN, GKN Sinter Metals Engineering GmbH, and University “Campus Bio Medico” (Italy).	EU

Application: Compact Multifuel to Hydrogen Converter

Project name: CoMETHy (Compact Multifuel to Hydrogen Converter).

Partner: The consortium, coordinated by ENEA, was composed of 12 partners from the Academic, Research and Industrial fields: ENEA (Italy), Processi Innovativi Srl. (Italy), Acktar Ltd. (Israel), Technion (Israel), Fraunhofer Institute (Germany), University of Salerno (Italy), CERTH (Greece), Aristotle University of Thessaloniki (Greece), University “La Sapienza” (Italy), ECN (the Netherlands), GKN Sinter Metals Engineering GmbH (Germany), and University “Campus Bio Medico” (Italy).

Process: The reactor was designed for the low-temperature (450-550 °C) steam reforming of several carbonaceous feedstocks like methane, biogas and (bio)ethanol. By continuously removing hydrogen from the reaction space, the integrated membranes allow to push the conversion of the feedstock beyond the low values that could be obtained with conventional reformers at such low temperatures. The use of molten salts as heat transfer fluid in the reactor allows easy coupling with concentrating solar thermal technologies such as solar troughs and solar towers; furthermore, the of availability of consolidated molten salt heat storage solutions allows for a smoother and extended operation of the reactor.

Results/development status

The pilot reactor was commissioned and tested at the ENEA Casaccia Research centre in 2015. The pilot plant was coupled with ENEA’s existing molten salt loop (MoSE) and operated for about 700 h under molten salt flow, including several start-up and shutdown procedures as well as stand-by phases. A total of 150 h of continuous on-stream operation was attained with methane/steam feed.

Several operating conditions were tested in the experimental campaign including different molten salts inlet temperatures, sweep steam flow rate and steam-to-carbon ratio in the feed. Up to 3.5 Nm³/h of pure (>99.8% vol/vol) hydrogen were obtained under design conditions, exceeding the pilot target of 2.0 Nm³/h. Furthermore, no decay in the reactor performance was observed during the time on stream.

Although the pilot reactor was tested using only methane as feedstock, within the CoMETHy project the same reactor concept was successfully tested at the laboratory scale for biogas and bioethanol reforming as well.

References

- [1] A. Giaconia, G. Monteleone, B. Morico, A. Salladini, K. Shabtai, M. Sheintuch, D. Boettge, J. Adler, V. Palma, S. Voutetakis, A. Lemonidou, M.C. Annesini, M. den Exter, H. Balzer, L. Turchetti. Multi-fuelled Solar Steam Reforming for Pure Hydrogen Production Using Solar Salts as Heat Transfer Fluid. *Energy Procedia*, 2015, 69, 1750-1758. doi:10.1016/j.egypro.2015.03.144
- [2] A. Giaconia, L. Turchetti, G. Monteleone, et al. Development of a Solar-powered, Fuel-flexible Compact Steam Reformer: the Comethy Project. *Chemical Engineering Transactions*, 2013, 35, 433-438. doi:10.3303/CET1335072

2.8. High-pressure tubular reactor heated with molten salts

Contact: *Alessandro Galia (UNIPA), Benedetto Schiavo (UNIPA)*

Solar-driven continuous chemical process layout

The use of the molten salts as heat transfer fluid to drive chemical processes is a general strategy that allows separating the issue related to solar energy capture and storage from those typical of the chemical processes, such as feeding of the reagents, separation of the products, use of catalysts, optimization of chemical kinetics and transport phenomena, etc. In addition, the use of double tube or shell and tube exchanger-reactor is suitable for the production of commodities such as biofuels, and it appears as versatile for the adoption of specific reactor design to optimize the process figures of merit (cf. the membrane reactor from ENEA in Section 2.7).

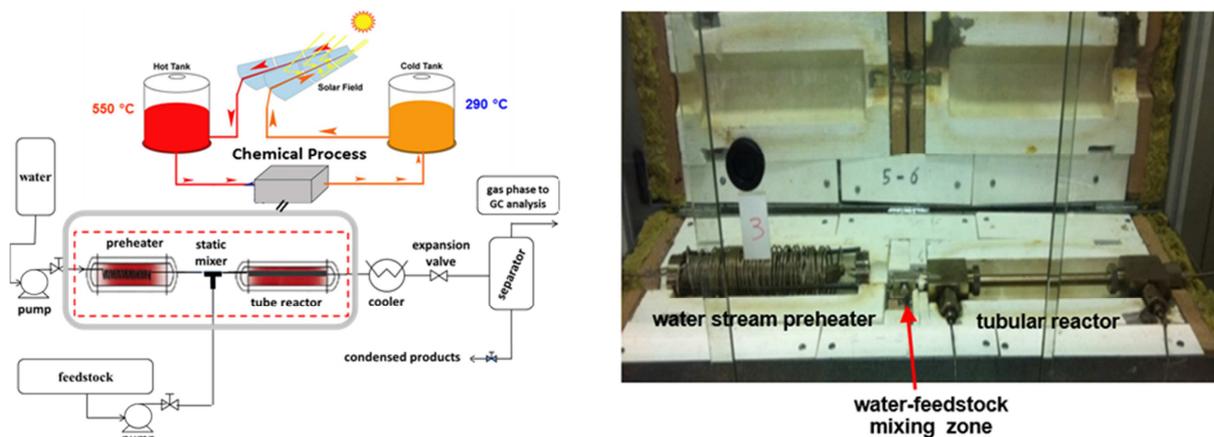


Figure 12 Continuous lab-scale high-pressure apparatus for solar hydrothermal processes. Left: Chemical process layout and conceptual scheme of the coupling with a molten salt CSP loop; right: lab-scale tubular reactor and water preheating section.

Here, a process layout with a lab-scale (10 mL) pressurized tubular reactor is considered for hydrothermal conversion of biomass into bio-crude or syngas (Figure 12). A pressurized water stream is warmed up inside the preheating section; in the mixing zone, the hot pressurized water is mixed with the feedstock stream, just before entering inside the high-pressure reactor. The product stream leaving the reactor is first depressurized, then gas, liquid and solid products are separated.

Beside experimental investigation of the process, also a conceptual analysis of the coupling of an industrial hydrothermal liquefaction (HTL) reactor with a concentrating solar power (CSP) plant has been performed in collaboration with ENEA. The integrated plant was designed to process 10,000 t/y of microalgae and the solar heat stored in the molten salts provides the energy that cannot be recovered by heat integration between the hot product stream and the pure water fed to the reactor. A minimum fuel-selling price of 2.19 USD/kg was estimated for the produced bio-oil, that is quite close to that reported in the literature for plant for HTL of microalgae with production capacity similar to that considered in our study.

Table 8 Application of continuous high-pressure reactor for hydrothermal processes.

Application	Lab scale	Pilot scale	Project partners	Funding
Hydrothermal liquefaction and gasification of biomass and model compounds	yes	---	University of Calabria, National Research Council, University of Salerno, University of Pisa, University of Messina, Politecnico di Torino, University of Naples Federico II, Politecnico di Milano	Italian Ministry of Scientific Research and Education – MIUR (PRIN2010-2011 grant)

Application: Hydrothermal liquefaction and gasification of biomass and model compounds

Project name: Innovative downstream processing of conversion of algal biomass for the production of jet fuel and green diesel

Partner: University of Calabria (UNICAL), National Research Council (CNR), University of Salerno (UNISA), University of Pisa (UNIPI), University of Messina (UNIME), Politecnico di Torino (POLITO), University of Naples Federico II (UNINA), Politecnico di Milano (POLIMI). ENEA was also involved as subcontractor of UNIPA.

Process: The process layout and the reactor were designed to work at temperatures up to 550 °C. The range 250 – 400 °C is generally adopted for hydrothermal liquefaction (HTL) of biomass or model compounds to obtain bio-oil as main product. Higher temperatures are used to move toward gasification. Binary (NaNO₃ and KNO₃) or ternary [Ca(NO₃)₂, NaNO₃, KNO₃] mixtures can be adopted as heat transfer fluid in the range 290-550 °C, which is adequate for the heat supply to HTL processes.

Results/development status

The continuous high-pressure reactor and layout were assembled and tested in the frame of the above-mentioned PRIN project.

Continuous gasification of glucose, glycine and glycerol was performed in the temperature range 450-550 °C. Gasification efficiency (GE)⁽¹⁾ of 40.7% and carbon gasification efficiency (CE)⁽²⁾ of 31.2% were obtained by feeding glucose at 0.8 wt% concentration and with a residence time of 16 s at 500 °C and 26 MPa; the concentration of H₂ in the produced gas was 53 mol%, the remaining gas fraction was mainly constituted by CH₄ (3 mol%), CO (13 mol%) and CO₂ (30 mol%). A higher hydrogen concentration (86 mol%) in the gas was obtained with glycine at 450 °C but with low gasification efficiency (<5%).

Hydrothermal conversion of rapeseed oil was also successfully performed at 490 °C with 9 s residence time and 8 wt% feedstock concentration, resulting in a bio-oil yield of 54 wt% and gasification efficiency of 20% with the following concentration (mol%) of hydrogen and hydrocarbons in the gas: 3.9, H₂; 15.9, CH₄; 25.7, C₂H₄; 13.6, C₂H₆; 17.4, C₂H₆.

Possibility of pumping concentrated (15 wt%) biomass (microalgae) slurries at the desired process pressure (260 MPa) was recently achieved.

The upgrade of the system by coupling with the molten salt circulation system will be developed in the frame of the new national project “*Smart Small Scale Solar Systems*” (S5) that should start at the beginning of 2017.

⁽¹⁾ Gasification efficiency (GE) = total weight of produced gas / initial feedstock

⁽²⁾ Carbon gasification efficiency (CE) = total carbon in the produced gas / initial carbon in the feedstock

References

- [1] A. Giaconia, L. Turchetti, A. Ienna, D. Mazzei, B. Schiavo, O. Scialdone, G. Caputo, A. Galia, Conceptual study of the coupling of a biorefinery process for hydrothermal liquefaction of microalgae with a concentrating solar power plant, accepted (minor revisions) for publication in SolarPACES 2016 AIP Conference Proceedings.
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- [4] B. Schiavo, D. Immordino, G. D’Aleo, L. Interrante, O. Scialdone, A. Galia, A continuous reaction system for hydrothermal liquefaction of microalgae. 2nd International Conference on Bioinspired and Biobased Chemistry & Materials - NICE 2014, Nice (F), 15-17 Oct 2014.

3. Directly heated solar reactor concepts

Directly illuminated reactors have the advantage of providing efficient radiation heat transfer directly to the reaction site [3]. The major drawback, when working with reducing or inert atmospheres, is the requirement of a transparent window, which is a critical and troublesome component, more so under high-pressure and severe gas environment. Directly heated reactors are classified as particle reactors or volumetric reactors [1]. For the volumetric reactors, the incident solar energy is directly absorbed by a catalytic absorber that transfers it to the feed gas. Based on the structure of the absorber used, volumetric reactors can be further classified as honeycomb, foam and structured fin based solar reactors. The honeycomb solar reactors have a wire mesh of ceramic material that is placed in the focal zone to absorb directly the incident solar energy [4]. When compared to honeycomb reactors, foam-based absorbers have the advantage of higher porosity that allows solar energy to penetrate deeper inside the material, and better radial heat transfer mechanism prevents any flow instability problems encountered during operation at higher temperature [5]. A comprehensive overview on directly heated solar particle reactor is given in a review article by Alonso and Romero [6].

The various directly heated solar reactor configurations investigated by the STAGE-STE partners include rotary reactors (Sections 3.1-3.3), a vortex flow reactor (Section 3.4), a fluidised bed reactor (Section 3.5), packed bed reactors (Sections 3.6-3.8) and cavity reactors with porous structures such as reticulated porous ceramics (RPCs) and monoliths for both steps of solar thermochemical cycles (Sections 3.9-3.11).

References pertinent to specific solar reactors and their applications are provided at the end of each Section, while general references are given in Section 6.

3.1. Directly heated rotary reactor

Contact: Christian Wieckert (PSI)

Solar reactor design

The 100 kW solar reactor, depicted in Figure 13, is designed to accept highly concentrated solar radiation into a reaction cavity capable of sustaining extremely high reaction temperatures (well above 2000 K) [1]. Additional details on a previous but similar configuration of the solar reactor can be found in literature [2], where results from initial experimentation with the pilot plant are reported. The solar reactor is closed from atmosphere by use of a flat disk quartz window (diameter, 600 mm; thickness, 12 mm) through which concentrated solar radiation passes (effective window diameter exposed to incoming solar radiation, 520 mm) and then converges onto a narrow aperture (diameter, 190 mm) which connects to the reaction cavity (central diameter, 580 mm; length, 830 mm). At the back of the reactor, a centrally located product outlet connects immediately into the quench device, where large volumes of inert gas can be injected to join the exiting reaction products.

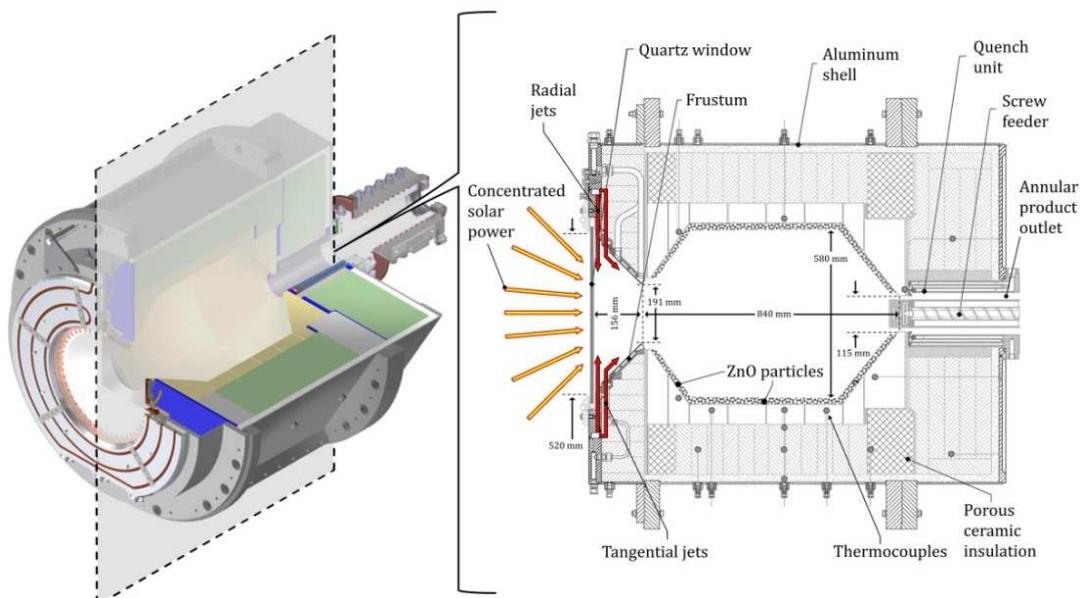


Figure 13 Cross-section schematic of the solar thermochemical reactor with key details and dimensions indicated. The outer diameter of the aluminium reactor shell is 1090 mm and the length is 1330 mm. From [3].

A retractable feeding mantle housing a powder screw feeder can enter into the reaction cavity through the product outlet path during a reactant feeding cycle. At the back of the reactor, a rotary joint interfaces with the end of the quench device and allows for the transfer of gas, water, power, and data communication to the rotating part of the reactor assembly. The reaction cavity is lined with interlocking Al_2O_3 bricks (flat section consists of elongated trapezoidal bricks with centre-line thickness 64 mm and length 128 mm) and typically contains a 10–20 mm thick layer of sintered ZnO. The bricks are backed and supported by various layers of alumina/silica porous ceramic insulation materials, all contained by a two-part hexagonal aluminium shell (5 mm thick welded aluminium plates). In the front of the reactor, both the mounting plate that holds the quartz window, and the cone-shaped frustum

(45° rim angle, copper substrate plasma coated with zirconia-supported alumina) between the window and the cavity aperture, are water-cooled. At the back of the reactor, the quench device is water-cooled as well. Access ports along the reactor's shell allow for data acquisition and sensing control.

Immediately inside the plane of the quartz window, a series of radially and tangentially oriented gas jets (24 radial jets with inner diameter 8 mm, 24 tangential jets with inner diameter 7 mm and injection angle of 64° from radial, with a 10 degrees axial inclination) are installed circumferentially [4]. These jets create a stabilized vortex flow that allows for the control and suppression of particle movement toward the quartz window inside the reactor, as well as to help sweep off products from the reaction surface. This reactor design is based on previous laboratory scale rotating reactors developed at PSI and ETH Zurich [5][6][7]. It is capable of achieving high thermal efficiency by (i) creating a uniform and high temperature reaction environment; (ii) delivering reactant ZnO powder directly and evenly dispersed into the reaction cavity for quasi-continuous operation; and (iii) allowing the reactant to be directly irradiated by incoming concentrated radiation whereby it serves the roles of radiant absorber, chemical reactant, and thermal insulator.

During reactor operation, 100 kW of nominal concentrated solar power as process heat is delivered to the reaction cavity to drive the thermal dissociation of ZnO powder. With powder dispersed evenly inside the reaction cavity due to rotation, the dissociation reaction becomes appreciable as the cavity temperature approaches 2000 K after 3–4 h of heating. The products Zn vapour and O₂ exit the reactor along with some auxiliary argon from the vortex flow, and pass through the quench device (where Zn vapour is condensed into particulates) before continuing to large filters where product particles are collected.

The solar rotary cavity reactor is suited for volatile thermochemical processes involving solids, which are transformed to gaseous products [8]. Table 9 provides information on the application of the rotary cavity reactor for solar thermal ZnO dissociation.

Table 9 Application of solar rotary cavity reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Solar thermal dissociation of ZnO (Swiss project Solar2Zinc)	5-10 kW _{th} @ PSI	140 kW _{th} @ CNRS	PSI, ETHZ	Swiss Federal Office of Energy (SFOE) EU-FP7 SFERA II EU-FP7 STAGE-STE

Application: Solar thermal dissociation of ZnO

Project name: Solar2Zinc

Partners: PSI, ETHZ

Process: The solar-driven endothermic reduction of ZnO is given by

$$\text{ZnO} \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 \quad (\Delta H = 456 \text{ kJ/mol}; T > 2000 \text{ K}).$$

Results/development status

Progress in experimental techniques and solar reactor design, as well as in modelling efforts [9]-[10], has been substantial. PSI, in collaboration with ETHZ, brought design, development and demonstration to the pilot scale

with a 100 kW_{th} solar reactor for ZnO dissociation. Two extended experimental campaigns were conducted in the MWSF in Odeillo, France [12]. The pilot plant experimental setup, depicted in Figure 14, consists of the solar reactor along with peripheral components including the powder reactant delivery system, product collect system, and reactor rotation mechanism.

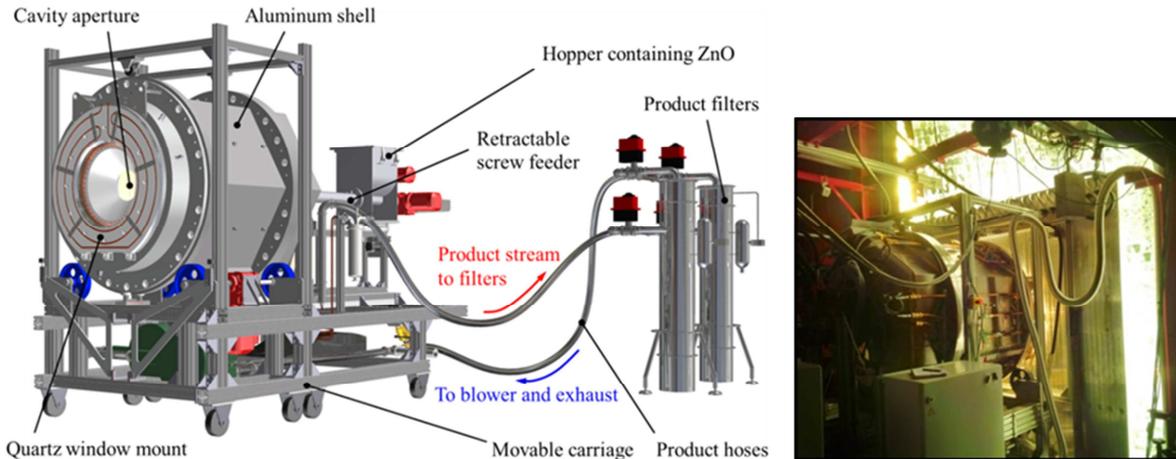


Figure 14 ZnO pilot plant layout utilized in experiments conducted at PSI and Odeillo in 2014, with critical components and peripherals labelled [3] (left). Image of the reactor during operation viewed from behind inside the experimental tower (right).

In the first campaign, experimentation was primarily hindered by insufficient power delivery through the quartz window, leading to limited dissociation rates [2]. During the second campaign, the improved solar reactor pilot plant was operated for over 97 h and achieved sustained reaction temperatures well above 2000 K, while demonstrating ZnO dissociation rates as high as 28 g/min totalling over 28 kg of processed reactant during 13 full days of experimentation [1]. In-situ, high temperature, flow visualization of the quartz window enabled the unimpeded operation of the solar reactor. As many as three consecutive full day experiments were conducted without complication. Solar power delivered to the reaction cavity ranged between 90 and 128 kW_{th}, at peak solar concentrations as high as 4671 kW/m². The products Zn and O₂ were quenched with Ar(g) and recovered in a filter battery, where collected particles contained molar Zn-content as high as 44%. During experimentation, switching between product-collection filter cartridges resulted in 54 unique experiments, where a maximum solar-to-chemical efficiency of 3% was recorded for the solar reactor. Robust characterization of the product-quenching device revealed inherent limitations in its effectiveness, and thus solar-to-fuel energy conversion efficiency was limited to 0.24% if it would have been possible to supply 4640 LN/min of Ar(g). Further, only a limitation on available experimental time prohibited the demonstration of significantly higher dissociation rates, achievable with higher ZnO reactant feed rates. While the use of large volumes of quenching Ar(g) to separate the reaction products remains a significant obstacle to achieving higher solar-to-fuel efficiencies, demonstration of solar reactor

technology at the pilot-scale represents significant progress toward the realization of industrial-scale solar fuels production.

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3.2. Solarized rotary kiln

Contact: José González-Aguilar (IMDEA), Manuel Romero (IMDEA)

Solar reactor design

The solar rotary kiln, shown in Figure 15, is composed of a reaction cavity, which consists of a fixed conical aperture with a large enough opening for the incoming radiation (an upper diameter of 110 mm, a lower diameter of 38 mm, and a height of 80 mm), and a rotary tube of alumina (with an outer diameter of 45 mm, an inner diameter of 35 mm, and a length of 500 mm). To avoid particles reaching the conical part, the reactor is tilted by 4 degrees with respect to the horizontal, and a ceramic ring is placed in the tube inlet. As particles can also move towards the outlet, another ceramic ring is placed at the end of the reaction zone.

Ceramic bricks are used as insulation in order to minimize heat losses. To achieve air tightness, the reactor has an external housing of stainless steel ($40 \times 35 \times 35 \text{ cm}^3$), where measuring instrumentation is also located, and a quartz window of high transmittance that allows particles to be directly irradiated and seals the cavity. This window should be clean during experiments, thus the inert gas feeding is performed by four gas inlets located at the lateral wall of the reactor. Twenty-eight K-type thermocouples are installed at different axial and radial distances, and two inside the tube. A window has been included in one of the lateral walls of the facility in order to measure temperatures with a pyrometer.

An electric motor rotating at 1390 rpm is employed to move the tube at approximately 92 rpm (9.63 rad/s) through a 1/15 reducer. The axial rotation of the tube produces homogeneous temperature, and high mass and heat transfer in the reaction zone. Samples are directly irradiated by concentrated radiation provided by a 7-kW_e high-flux solar simulator. Optical simulations and CFD analysis show that 1 kW of incident power and 1700 K can be achieved at the reaction zone, which is located at the secondary focus of the simulator.

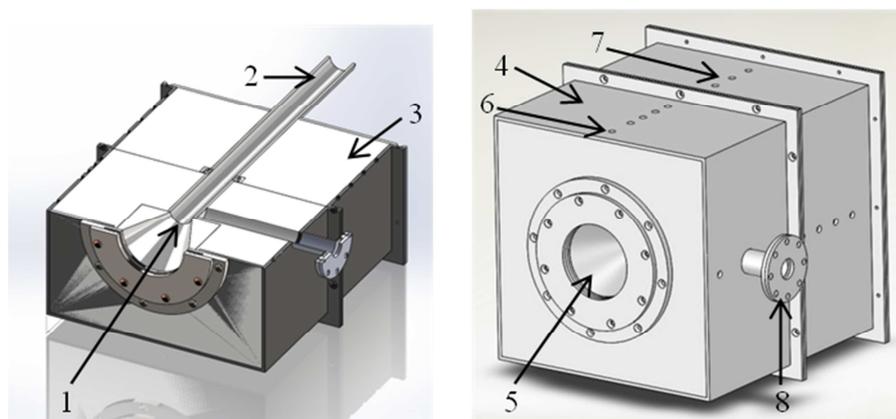


Figure 15 Scheme of rotary kiln: (1) cavity; (2) rotary tube of alumina; (3) ceramics bricks; (4) stainless steel housing; (5) quartz glass window; (6) gas inlet; (7) thermocouples places; (8) window for pyrometer.

The reactor could be used for multiple applications such as chemical reactions (solar chemistry), thermochemical processing or studies about mechanical strength and attrition of

different materials.

Table 10 Application of IMDEA's solarized rotary kiln studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Reduction of non-volatile metal oxides	1 kW _{th} @ IMDEA	---	IMDEA	SolarO2 (National project) ALCCONES (Regional project)

Application: Reduction of non-volatile metal oxides

Project name: SOLARO2 (National project), ALCCONES (Regional project)

Partner: IMDEA

Process: The solar-driven reduction of metal oxides M_xO_y (CeO₂ and manganese oxides) is given by:



Results/development status

The rotary kiln has been specially designed to operate with the 7-kW_e High-Flux Solar Simulator (HFSS) installed at IMDEA Energy. Thus, optical analysis by Monte Carlo ray tracing was conducted to select the optimal position of the reactor relative to the HFSS in order to achieve a total power at the reaction zone of around 1 kW.

Numerical simulations indicated that the maximum temperature was achieved at the reaction zone (1700 K). Commissioning experiments in the 7-kW_e HFSS demonstrated that it is possible to reach temperatures as high as 1500 K in the reaction zone. Thermochemical reaction experiments with manganese oxide cylindrical pellets (85% Mn₃O₄, 15% Mn₂O₃, mean particle size, 3.5 mm) were performed, with air being fed during the heating of the kiln, and nitrogen when temperatures reached 700 °C. The production of oxygen was measured at high temperatures from the reduction step of the thermochemical cycle [1].

Reference

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3.3. Reduced pressure rotary solar reactor

Contact: Gilles Flamant (CNRS)

Solar reactor design

The rotary cavity reactor design, depicted in Figure 16, was previously described for a flat window [1] and has been modified to feature a domed window [2]. The reactor axis was slightly bent downwards (5–10 degrees) to ease the feeding of oxide powder (ZnO above 99 wt%; Normapur Prolabo™, USA). Powder blocking was also avoided by steadily hitting the bottom of the stock of oxide powder to generate vibrations (2–5 Hz). A sieve was placed between the bottom of the oxide stock and the vertical feeding tube to prevent massive falls of oxide powder. Cavity and Archimedes screw (for oxide feeding) rotational speeds were controlled by setting the voltage of the motors. Neutral gas for dilution/quenching (nitrogen, 0.5-10 NL/min) was regulated with a mass-flow controller. About 30 mm was left between the Archimedes screw and the tip of the alumina tube designed to feed the cavity with oxide in order to avoid overheating of the steel screw. Oxide powder heaps in front of the screw simply fall by gravity, thanks to the vibrations. Reduced pressure was generated by a standard rotary vane pump and manually controlled through a vacuum valve with a ±10 mbar uncertainty. The maximal operating pressure was 850 mbar (atmospheric pressure at PROMES-CNRS laboratory). The minimal operating pressure was 180 mbar. A lower pressure could trouble the rotation of the gears.

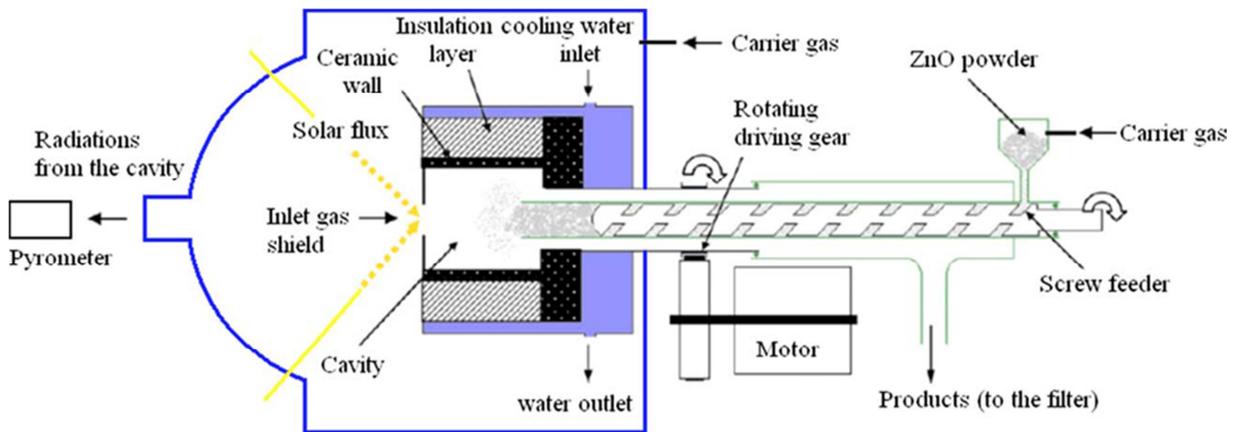


Figure 16 Reduced pressure rotary kiln solar reactor (about 1 kW) designed and tested at CNRS. From [1].

Table 11 Application of the CNRS reduced pressure rotary solar reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Reduction of ZnO and SnO ₂ powders	1 kW _{th} @ CNRS	---	CNRS	CNRS

Application: Reduction of ZnO and SnO₂ powders

Project name: ---

Partner: CNRS

Process: Reduction of ZnO and SnO₂ powders is given by, respectively:

*Results/development status*

A high-temperature lab-scale solar reactor prototype was designed, constructed and operated, allowing continuous ZnO thermal dissociation under controlled atmosphere at reduced pressure [2]. It is based on a cavity-type rotating receiver absorbing solar radiation and composed of standard refractory materials. The reactant oxide powder is injected continuously inside the cavity and the produced particles (Zn) are recovered in a downstream ceramic filter. Dilution/quenching of the product gases with a neutral gas yields Zn nanoparticles by condensation. The solar thermal dissociation of ZnO was experimentally achieved, the reaction yields were quantified, and a first concept of solar reactor was qualified. The maximum yield of particles recovery in the filter was 21% and the dissociation yield was up to 87% (Zn weight content in the final powder) for a 5 L_N/min neutral gas flow-rate (typical dilution ratio of 300).

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3.4. Gas-particle vortex flow reactor

Contact: Alfonso Vidal (CIEMAT)

Solar reactor design

The lab-scale gas-particle vortex flow solar reactor is schematically shown in Figure 17 [1]. It consists of a 210 mm-length 120 mm-i.d. cylindrical cavity-receiver, made out of Inconel 601, lined with Al_2O_3 , and insulated with $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ceramic foam. Concentrated solar radiation enters the cavity through a 50 mm-diam. aperture that was closed by a 3 mm-thick clear fused quartz window. The aperture is equipped with a diverging frustum for mounting the window where the radiation intensity is about 10 times smaller and dust deposition is unlikely to occur. Since radiation spillage can reach flux concentrations ratio greater than 1000 suns, this component is actively oil-cooled and kept in the range 393-453 K to prevent steam condensation. Further, the window is actively cooled (and kept clear from particles) by means of an aerodynamic protection curtain created by combined tangential and radial flow nozzles. The reactor was used for the steam-gasification of petroleum coke (petcoke). The petcoke-water slurry was kept stirred in a mixer located above the reactor and injected through an inlet port on the cavity top at a controlled mass flow rate by a feeding pump. Inside the cavity, the slurry forms a vortex flow that progresses towards the rear along a helical path. With this arrangement, the petcoke particles were directly exposed to the high-flux solar irradiation, providing efficient heat transfer directly to the reaction site. Energy absorbed by the reactants is used to boil and superheat the water, raise the reactants' temperature to above 1300 K, and to drive the gasification reaction. Reaction products exit through a 24 mm-diameter outlet tube at the rear side of the cavity. The feasibility of the petcoke-water slurry concept was demonstrated at the 5 kW power level at PSI's high-flux solar furnace.

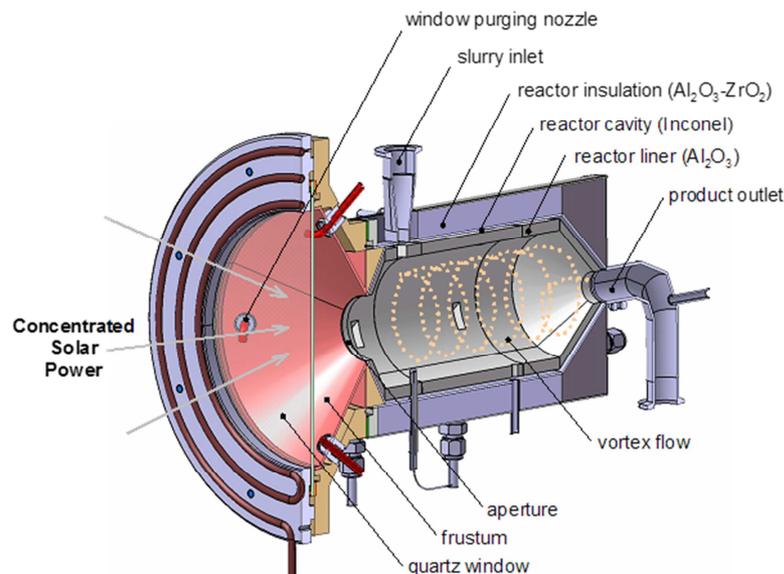


Figure 17 Scheme of lab-scale solar chemical reactor configuration for the steam-gasification of petcoke [1]. The reactants are injected as liquid slurry of petcoke particles and water.

A heat and mass transfer model was applied for the simulation of the vortex-flow particle reactor for the steam-gasification of carbonaceous materials [2]. Two solar reactors were

examined: the laboratory-scale 5 kW prototype, and the up-scaled version of 300 kW. The feedstock's particle size, the feeding flow rates, the solar power input, and the geometry of the reactors were varied to identify the optimal operational conditions for maximum solar-to-chemical energy conversion efficiency.

The scaled-up 500 kW pilot solar reactor consists of a well-insulated cylindrical cavity-receiver made of heat resistant steel and lined with Al₂O₃, able to withstand up to 1700 K and additionally insulated at the outside of the reactor. The cavity-type geometry is designed to effectively capturing the incident solar irradiation. The cavity has a length of 1.7 m and an inner diameter of 1.1 m. It contains a 0.5 m opening – the aperture – to let in the concentrated solar irradiation. The volume of the reactor is approximately 1.3 m³, with a length of 1.1 m. In front of the aperture, the cavity is equipped with a diverging conical funnel for mounting a segmented quartz reactor window with a diameter of 1.4 m, situated 0.5 m in front of the focal plane where temperatures are significantly lower. Experiments were performed at the Plataforma Solar de Almería (PSA).

Table 12 Application of gas-particle vortex flow reactor studied so far.

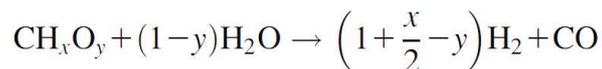
Application	Lab scale	Pilot scale	Project partners	Funding
Production of syngas from heavy crude oil	5 kW _{th} @ PSI	500 kW _{th} @ PSA- CIEMAT	PDVSA, ETHZ, CIEMAT	PDVSA

Application: Production of syngas from heavy crude oil

Project name: SYNPET

Partner: PDVSA (Venezuela), ETHZ (Switzerland) and CIEMAT (Spain).

Process: For the solar-driven gasification of petcoke, the overall chemical conversion can be represented by the simplified net reaction:



where x and y are the elemental molar ratios of H/C and O/C of the feedstock. The chemical product is synthetic gas (“syngas”).

Results/development status

All runs were performed with Petrozuata Delayed (PD) coke, and lower heating value (LHV) of 35,876 kJ/kg. Three different particles sizes were used: 1) ball milled, with an average particle diameter of 8.5 μm; 2) sewed, with particle diameter < 80 μm; and 3) sewed, with particle diameter < 200 μm. The slurry was prepared by stirring petcoke into demineralized water for a desired stoichiometric molar ratio (H₂O:C)_{slurry} in the range 1-3 (Figure 18). The total water-to-coke ratio (H₂O:C)_{total}, which includes the steam used to purge the window, varied in the range 1.5-10. The petcoke mass flow rate was between 0.6 and 3.61 g/min. The resulting average residence time for the coke particles was in the range 0.98 - 2.53 seconds [1].

The average and maximum degree of petcoke chemical conversion was 48% and 87%, respectively, using particles with diameters smaller than 80 micrometres. Lower water/petcoke stoichiometry lead to lower mass flow rates and higher residence times, thus resulting in higher petcoke conversions. Energy conversion efficiencies – defined as the portion of solar energy input stored as chemical energy – up to 5% (peak) and 2.5% (average) are reached. If sensible heat is included (which potentially can be recovered), energy conversion efficiencies of 17% (peak) and 11% were achieved [1].

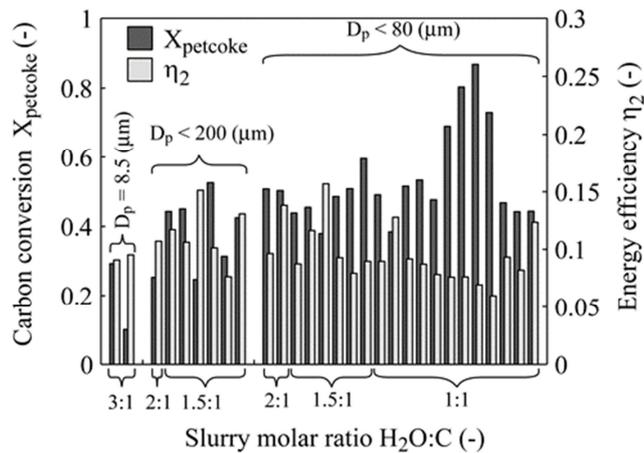


Figure 18 Petcoke chemical conversion and energy conversion efficiency obtained in the solar experimental runs, ordered according to particle size and slurry stoichiometry [1].

Experimental evaluation of the performance of the 500 kW solar gasification plant was carried out at the SSPS/CRS tower at PSA [3]. Thermal tests confirmed a good behaviour of the ceramic front cone and the window of the reactor, introducing air at flux density near 1.5 MW/m², which amounts to total absorbed power of 300 kW at the aperture. Start-up of the reactor lasts 2 or 3 hours due to the thick insulation of the system. A storage system could help shortening the start-up time (Figure 19).

A set of ten solar gasification experiments was performed with petcoke-water slurry feeding using 200 μm particles and water/petcoke stoichiometry of about 3. The solar power input was in the range 270-300 kW, resulting in a nominal reactor temperature in the range 1100-1350 K [3]. Reactants were continuously introduced at a mass flow rate of 15 kg/h of slurry with H₂O:C ratio equal 3, and additional 9 kg/h of steam to protect the window, corresponding to a total H₂O:C ratio of 4. Average values under approximate steady-state conditions are indicated by coloured curves in Figure 19: Reactor cavity temperature T_{reactor} = 1370 K, product gas composition H₂ = 48%, CO = 13%, CO₂ = 25%, and CH₄ = 5%.

Chemical conversion for steam and petcoke after a single pass reached up to 35%, lower than expected from previous tests with the 5 kW reactor. Energy conversion efficiencies reached peak values up to 21% for chemical energy only and 43% for chemical energy and sensible heat.

During the chemical test campaign, the transparency of the segmented quartz window was reduced in time by deposition of coke particles on the inside. In the course of the tenth chemical test, the window was broken. Currently, the project is stopped in order to solve the problem with the new window configuration.

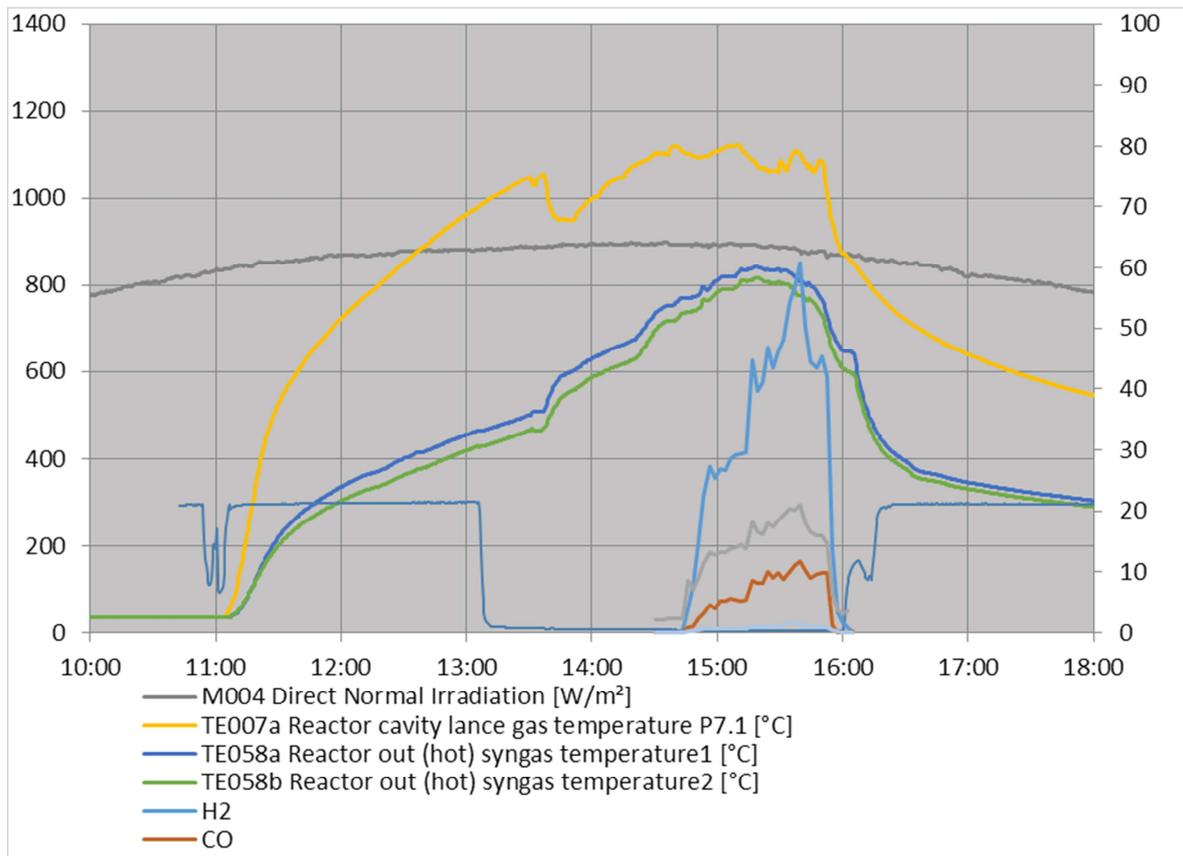


Figure 19 Results from a typical chemical test of the 500 kW SYNPET solar pilot plant at PSA.

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3.5. Directly irradiated fluidized bed reactor

Contact: Alfonso Vidal (CIEMAT), José González-Aguilar (IMDEA)

Solar reactor design

The fluidized bed solar reactor, shown in Figure 20, is composed of a cylindrical tube (78 mm of diameter) made of ceramic brick ending in a conical aperture (148 mm of total length) with a quartz window (diameter 216 mm), which let the samples to be directly irradiated by a 7-kW_e high-flux solar simulator. At the bottom of the cylinder, a porous ceramic piece acts as a sample holder and gas diffusor. The external housing is made of stainless steel.

The instrumental facility has comprises measuring devices and instrumentation together with mounts to hold the reactor and other devices. Four K-type thermocouples are installed at different positions: inside the reactor, within the sample, at the gas outlet and on the window surface. Furthermore, temperature is measured with a pyrometer and an infrared camera. For measuring pressure in the reactor, a relative pressure meter (0-2.5 bar) is located in the inner area, next to the window. Pressure drop is an important parameter in fluidized beds; consequently, a differential pressure meter (0-100 mbar) is also needed. The high-pressure measurement is made in the air entrance, at the bottom part, and the low one is in the reactor, after the bed. A gas analyser and a micro GC measure outlet gases composition.

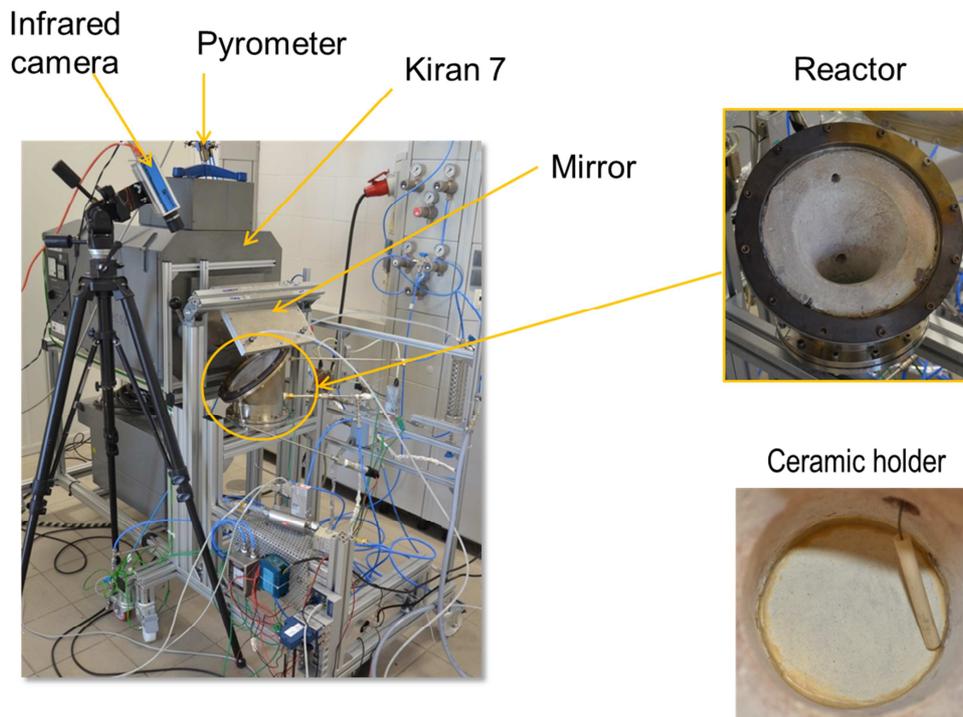


Figure 20 Photographs of the fluidized bed reactor and its experimental setup at IMDEA.

Table 13 Application of IMDEA directly irradiated fluidized bed reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Hydrogen production by thermochemical cycles	1kW _{th} @ IMDEA	---	IMDEA	ALCCONES (regional) EU-FP7 project STAGE-STE

Application: Hydrogen production by thermochemical cycles

Project name: ALCCONES (regional project), EU-FP7 project STAGE-STE

Partner: IMDEA, CIEMAT

Process: Hydrogen production by thermochemical cycles based on commercial nickel ferrites

Results/development status

Analysis of particle regimes (from packed bed to fluidised bed) has been accomplished, using various materials B, C, and D according to Geldart's classification at room temperature and under high-radiation fluxes.

Numerical models for radiation heat transfer and particle dynamics have been developed.

Hydrogen production tests using nickel ferrites have been performed.

3.6. Directly irradiated packed bed reactor

Contact: José González-Aguilar (IMDEA), Manuel Romero (IMDEA)

Solar reactor design

A lab-scale solar thermochemical reactor was designed and fabricated to study the thermal reduction of non-volatile metal oxides. The directly irradiated packed bed reactor operates simultaneously as solar collector and as chemical reactor. The vertical reactor, shown in Figure 21, is made of a stainless steel housing with ceramic bricks as insulation. The total height of the reactor is 225 mm, with two different diameters: 210 mm at the top and 172 mm at the bottom. The horizontal light beam from the 7-kW_e high flux solar simulator is reflected with an angle of 90° using a flat mirror and is then introduced vertically into the reactor through a quartz window and the conical aperture. The sample is placed in a crucible and directly irradiated in the reactor cavity. The mirror and the window are water-cooled (1 l/min) in order to avoid overheating. The cooling pipe at the window zone is made of copper due to its high thermal conductivity. The temperatures of the water at the inlet and outlet are measured by K-type thermocouples.

Inert gas (Ar) is injected into the conical aperture through four gas inlets located around the lateral wall on top of the cylinder. The gas outlet is located at the bottom of the reactor. The flowmeter is a MPC20-BBNSP1 Porter with a range of 0.4 to 20 SLPM. Seven K-type thermocouples are installed at different heights of the reactor and two K-type thermocouples are inserted through the bottom to measure sample and sample-holder temperatures. Besides, the sample temperature can be measured by a pyrometer. Relative pressure is measured at half height of the reactor by S-10 Wika device with a range of 0-10 bar.

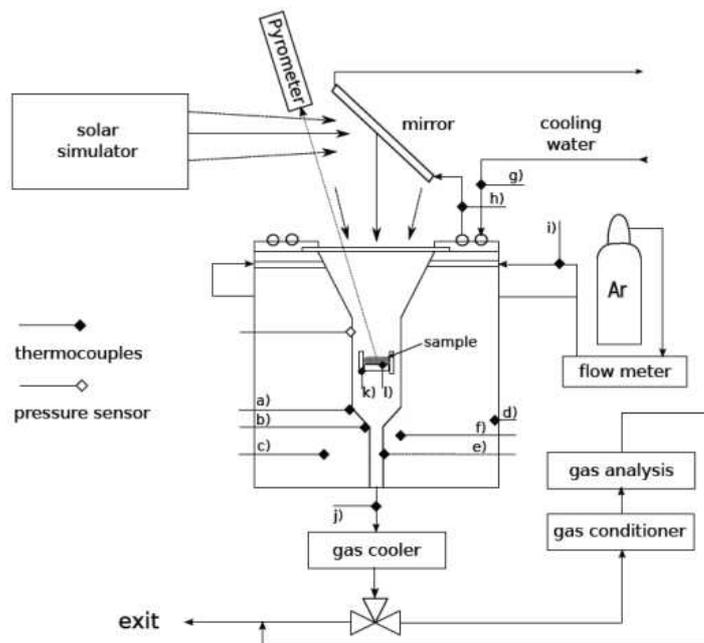


Figure 21 Schematic representation of test bed including the directly irradiated packed bed reactor.

The product gas is analysed by a system composed by two devices to measure in continuous way: Ultramat 23 for CO, CO₂, CH₄ and O₂ and Calomat 6 for H₂; and a micro GC to measure in semi-continuous way. The micro GC is equipped with three channels: Channel 1 and 2 (MolSieve 5Å PLOT 20M Unheated) are used to measure H₂, N₂, O₂, CO, and CH₄; the difference between channels 1 and 2 is the carrier gas, argon and helium, respectively; channel 3 (PoraPLOT Q 10M Heated) is used for light hydrocarbons such as CH₄, C₂H₆, C₂H₄, and C₂H₂.

The directly irradiated packed bed solar reactor is a versatile tool for investigating gas-solid reactions. It can be operated in horizontal [1] and vertical [2] configuration. Applications are summarized in Table 14.

Table 14 Applications of IMDEA's directly irradiated packed bed reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Kinetics determination of gas-solid reactions under high-radiation fluxes	1kW _{th} @ IMDEA	---	IMDEA, CIEMAT, URJC, INTA	SOLGEMAC
			IMDEA, CIEMAT, URJC, CSIC	ALCCONES
Solar gasification and solar pyrolysis of carbonaceous materials	1kW _{th} @ IMDEA	---	IMDEA IMDEA, CIEMAT, URJC, CSIC	STAGE-STE ALCCONES

Application 1: Kinetics determination of gas-solid reactions under high-radiation fluxes

Project name: SOLGEMAC (Regional project), ALCCONES (Regional project)

Partner: IMDEA, URJC, CSIC

Process: The solar-driven reduction of metal oxides M_xO_y (ceria and manganese oxides) is given by:



Results/development status

A methodology for determining kinetics (i.e. to identify kinetic mechanism and obtain kinetic parameters) in gas-solid reactions systems has been developed and successfully tested with pellets made of manganese oxides and ceria. The directly irradiated packed bed reactor results in a complementary characterization tool to the solar-driven thermogravimeter [1].

Unsteady 1D and 2D-axisymmetric numerical models of heat and mass transfer in the reactor have been developed. The models allow identifying heat transfer modes in the reactant and verifying that the reactor behaves as a plug flow reactor [2].

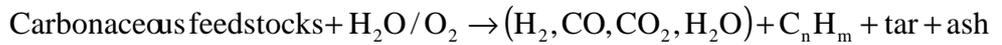
Internal lining and sample holder have been recently modified in order to extend the reactor applicability to other material forms and shapes such as foams.

Application 2: Solar gasification and pyrolysis of carbonaceous materials

Project name: ALCCONES (Regional project), FP7 IRP STAGE-STE

Partner: IMDEA

Process: Pyrolysis and gasification of carbonaceous materials according to the chemical reaction:



Results/development status

Solar-driven pyrolysis and gasification of carbonaceous materials has been demonstrated in repeatable experiments [3]. Tested materials comprise low-grade carbonaceous materials such as Mexican petcoke or sewage sludge and biomass such as micro-algae and straw (see Figure 22).

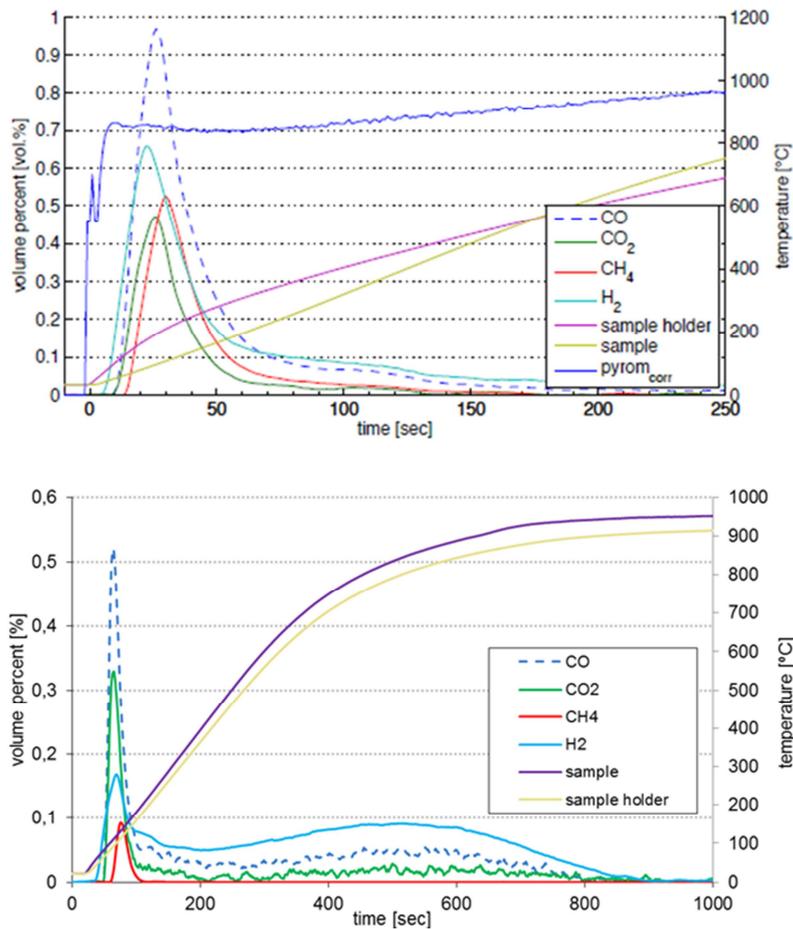


Figure 22 CO, CO₂, CH₄, H₂ composition and temperature as a function of time during the solar-driven pyrolysis (top) and gasification (bottom) of straw.

References

- [1] E. Alonso, M. Romero. A directly irradiated solar reactor for kinetic analysis of non-volatile metal oxides reductions. *Int. J. Energy Research* 2015, 39 (9), 1217-1228. doi:10.1002/er.3320
- [2] S. Bellan, C.C. Suarez, J. Gonzalez-Aguilar, M. Romero. Numerical study of a beam-down solar thermochemical reactor for chemical kinetics analysis. ASME 2014 8th International Conference on Energy Sustainability, ES 2014 Collocated with the ASME 2014 12th International Conference on Fuel Cell Science, Engineering and Technology, Boston, Massachusetts, USA, June 30–July 2, 2014. doi:10.1115/ES2014-6573
- [3] L. Arribas, N. Arconada, N., D. González-Fernández, C. Löhrl, J. Gonzalez-Aguilar, M. Kaltschmitt, M. Romero. Solar-driven pyrolysis and gasification of low-grade carbonaceous materials. World Hydrogen Energy Conference (WHEC 2016), Zaragoza, Spain, June 13-16, 2016; *Int. J. Hydrogen Energy*, in press.

3.7. Upward moving bed solar reactor

Contact: Gilles Flamant (CNRS)

Solar reactor design

The upward moving bed solar reactor, depicted in Figure 23, is composed of a Pyrex™ window and a cylindrical, water-cooled reactor shell (depth: 76 mm, diameter: 88 mm) made of stainless steel [1]. The cavity materials consist of pure sintered alumina (Degussit™ AL23, $T_{max} = 2223$ K) for the tubes and plates, zirconia felt for the aperture plate (yttria-stabilized zirconia fibres, Zircar™ ZYF-50, thickness: 1.3 ± 0.4 mm, $T_{max} = 3223$ K) and alumino-silicate for the insulation (Promat™ Promaform 1600, $T_{max} = 1873$ K). They were qualified in a previous study [2] with respect to chemical and thermal stability. The refractory cavity is composed of a 30 mm-long alumina tube (30 mm i.d., 4 mm thick) with gas input/output bored via a diamond saw. It is closed at the bottom by a 7 mm-thick and 37 mm-diameter cylindrical plate (with a centred 15.5 mm i.d. hole) and at the top by a 3 mm-thick aperture plate (88 mm o.d., 12 mm-diameter aperture) made of 2 layers of zirconia felt. This set of refractory parts is inserted into a modular insulation filling the inside of the reactor body.

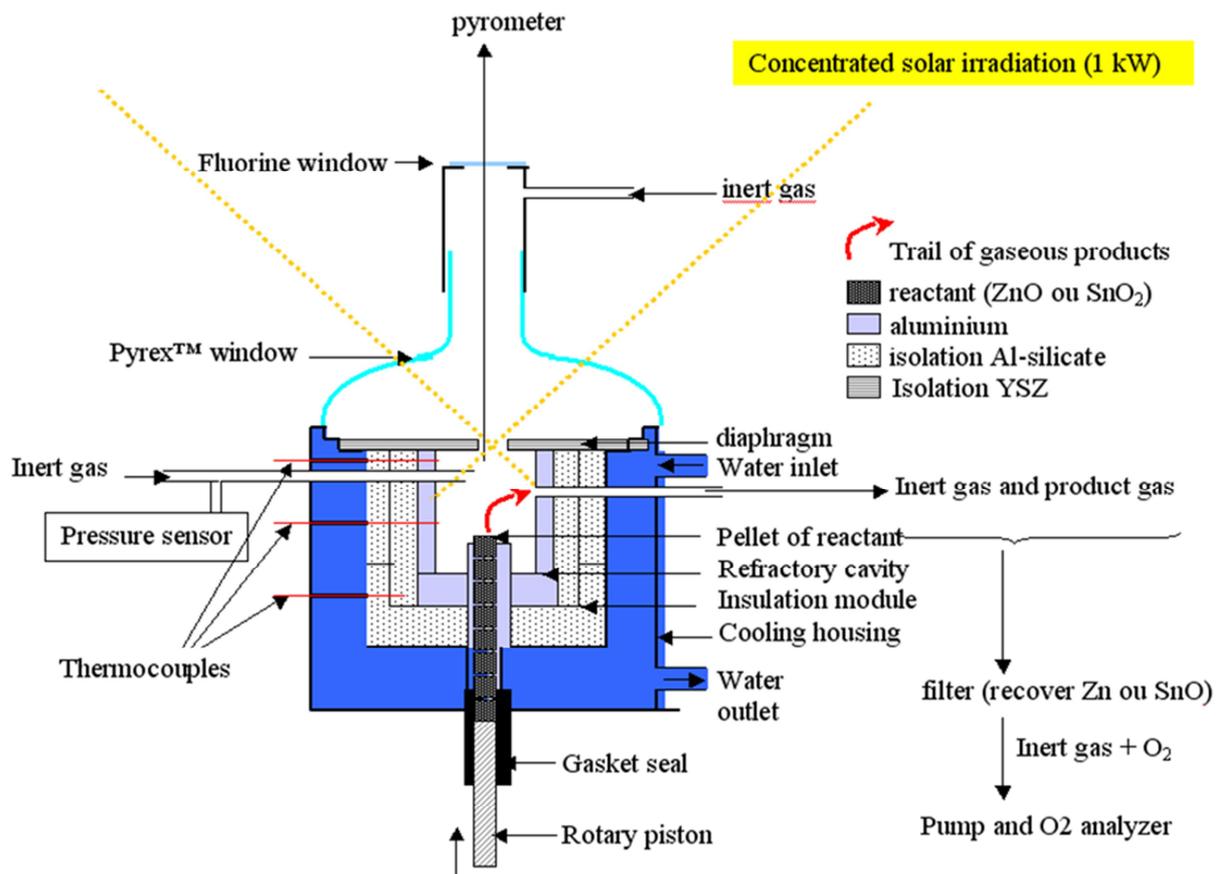


Figure 23 Schematic of upward moving bed solar reactor (about 1 kW) developed and tested at CNRS.

The reactant consists of 3-8 mm-thick pellets (8 mm-diameter) brought forth by compressing up to 2 g of commercial oxide powder (SnO_2 or ZnO , ProlaboTM, mean diameter of about one micron, purity above 99%). They are stacked in a 60 mm-long alumina feeding tube (10 mm i.d., 15 mm o.d.) exceeding of 7 mm the bottom of the refractory cavity. This pile of pellets forms an oxide “rod” that is pushed upward via a screw piston manually rotated for achieving a continuous reactant injection during an experimental run. Both the powders and the insulation are preliminarily calcined during 5 h at 1073 K to eliminate impurities and organic traces (organic binders) that could hinder O_2 measurements.

Neutral gas (N_2 or Ar) is introduced via the aperture to protect the glass window from the convective flow of product gases (Figure 23). Additional inert carrier gas is optionally injected from an inlet port located at the upper side of the cavity (3 mm i.d. tube), also connected to a pressure sensor (Pfeiffer VacuumTM PCR260 capacitance gauge) in order to measure the operating pressure inside the cavity. Gas flow rates are regulated with mass-flow controllers (BrooksTM calibrated with N_2 , precision: $0.7\% \pm 0.2\%$ of the full scale, scale: 0-5 $\text{L}_\text{N}/\text{min}$). Although a gas pre-heater is not directly implemented in this reactor, the hot aperture plate (heated by the solar irradiation fraction that does not enter the cavity and by inside IR radiation from the cavity) acts as a gas pre-heater. The inert carrier gas and gas products (O_2 and reduced species) exit the cavity via an outlet tube at the opposite side of the cavity. This outlet tube is a 15-cm long alumina tube (5 mm i.d. and 6 mm o.d.) that is used in order to avoid direct contact between the hot gases and the cold walls. Indeed, condensation of $\text{Zn}_{(\text{g})}$ or $\text{SnO}_{(\text{g})}$ vapours on water-cooled walls can be responsible for significant deposits. At larger scale, this can be limited via an annular flow of neutral gas at the reactor output, also used for quenching. Then, the condensed species are carried up to a specific nanoparticle filter located 20 cm downstream.

Table 15 Application of the CNRS upward moving bed solar reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Reduction of ZnO and SnO_2 powders	1 kW_th @ CNRS	---	CNRS	CNRS

Application: Reduction of ZnO and SnO_2 powders

Project name: ---

Partner: CNRS

Process: Reduction of ZnO and SnO_2 powders is given by, respectively:



Results/development status

The high-temperature thermal dissociation reaction of ZnO and SnO_2 was investigated, as part of two-step thermochemical water-splitting cycles for H_2 production [1]. A lab-scale solar reactor (1 kW) was designed, built, and operated for continuous dissociation of volatile oxides under reduced pressure. In this reactor, compressed oxide powders placed in a vertical ceramic cavity are irradiated by highly concentrated solar energy. The

reactor design allows moving the reaction front for achieving continuous reactant feeding. ZnO and SnO₂ thermal dissociations were successfully performed at about 1900 K, with the recovery of up to 50% of products as nanopowders with high specific surface area (in the range 20–60 m²/g) and with mass fractions of reduced species up to 48 wt% for Zn and 72 wt% for SnO. The performed O₂ measurements confirmed the kinetics of ZnO dissociation and gave an activation energy of 380 ± 16 kJ/mol, based on an ablation regime of the ZnO surface.

References

- [1] M. Chambon, S. Abanades, G. Flamant. Thermal dissociation of compressed ZnO and SnO₂ powders in a moving-front solar thermochemical reactor. *AICHE Journal* 2011, 57 (8), 2264-2273. doi:10.1002/aic.12432
- [2] M. Chambon, S. Abanades, G. Flamant. Design of a lab-scale rotary cavity-type solar reactor for continuous thermal dissociation of volatile oxides under reduced pressure. *ASME J Solar Energy Eng.* 2010, 132, 021006. doi:10.1115/1.4001147

3.8. Controlled atmosphere crucible solar reactor

Contact: Gilles Flamant (CNRS)

Solar reactor design

A solar pyrolysis system was designed and constructed by setting a biomass pyrolysis reactor at the focal point of a vertical solar furnace (Figure 24). In such a solar furnace, a sensor detects the sun location and sends an order to a tracking system. The heliostat is continuously adjusted to face the sun correctly such that its reflected beam is vertical to illuminate a down-facing parabolic mirror (2 m diameter and 0.85 m focal length). The maximum power and maximum flux density are approximately 1.5 kW and 12,000 kW/m², respectively. A shutter with moving parallel carbon composite blades modulates the reflected solar beam and thus the incident radiation, and therefore the concentrated flux impinging on the sample and its temperature. A transparent Pyrex balloon reactor with 185 mm diameter (6 L volume), set at the focus, is swept with an argon flow controlled by a mass flowmeter (Bronkhorst, EL-FLOW®). A portable infrared gas analyser (3100 SYNGAS) is used to monitor the oxygen concentration during the sweeping process. The sweep gas is used to keep the reactor wall and fluorine window clean. A needle valve adjusts the gas flow through the outlet of the reactor, which eventually controls the reactor pressure. The sample surface temperature is measured by a “solar-blind” optical pyrometer (KLEIBER monochromatic operating at 5.2 μm, in a H₂O absorption band) through a fluorine window (transparent at this wavelength).

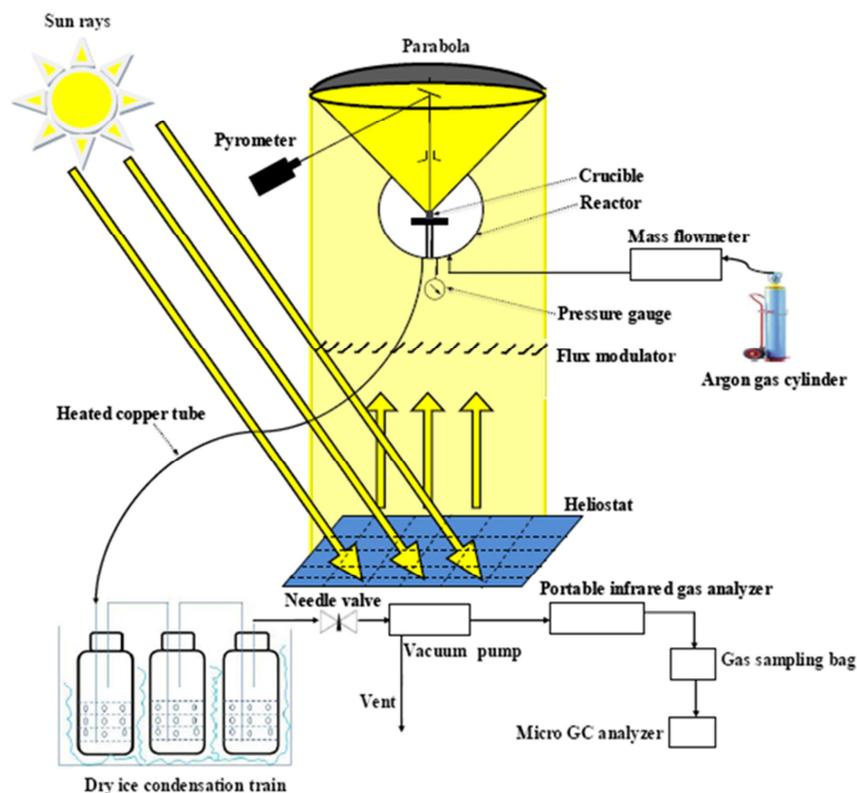


Figure 24 Controlled atmosphere crucible solar reactor (about 1 kW) designed and tested at CNRS.

The targeted heating rate and final temperature are set by a PID controller, which controls the shutter opening based on the measured sample temperature.

The pyrolysis products (condensable vapours and incondensable gases) first pass through a liquid collection system, which consists of a heated copper tube and one dry ice condensation train. The dry ice condensation train consists of three impinger bottles containing approximately 100 ml isopropanol solvent (2-propanol) for each one. The copper tube is maintained at about 250 °C. All the impinger bottles are immersed in dry ice (temperature between around -25 °C and -15 °C). A needle valve and a vacuum pump are placed downstream the condensation train. Then, the incondensable gases are aspirated by the vacuum pump and collected in a sampling bag. Finally, the composition of the gaseous products is analysed by gas chromatography (SRA Instruments MicroGC 3000).

Table 16 Application of the CNRS controlled atmosphere crucible solar reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Solar pyrolysis of biomass under heating rate (5-450°C/s) and plateau temperature control (600-2000°C).	1.5 kW _{th} @ CNRS	---	CNRS	CNRS

Application: Solar pyrolysis of biomass

Project name: ---

Partner: CNRS

Process: Solar pyrolysis of biomass under heating rate (5-450 °C/s) and plateau temperature control (600-2,000 °C).

Results/development status

The solar pyrolysis of beech wood was investigated with the objective of determining the optimal pyrolysis parameters for maximizing the LHVs (lower heating values) of the gas products because they can be further utilized as fuel gas for power generation, heat and production of transportable fuels [1]. The investigated variables were the pyrolysis temperature (600–2,000 °C), heating rate (5–450 °C/s), argon flow rate (6–12 L_N/min) and pressure (0.44–1.14 bar). The results indicate that the product yields (liquid, char and gas), gas composition (H₂, CH₄, CO, CO₂ and C₂H₆) and LHV are strongly influenced by the pyrolysis parameters. The total gas LHV greatly increases with increasing temperature (from 600 to 1,200 °C) and increasing heating rate (from 5 to 50 °C/s), which is mainly due to increases in the CO and H₂ yields. The variation in the gas LHV with pressure and argon flow rate is slight. A maximum gas production of 62% with a LHV of 10,376 ± 218 (kJ/kg of wood) is obtained under solar pyrolysis conditions of 1,200 °C, 50 °C/s, 0.85 bar and 12 L_N/min. This heating value is almost identical to that of the initial beech wood, thus confirming that valuable combustible gases can be produced via the solar pyrolysis of beech wood.

Reference

- [1] K. Zeng, D. Gauthier, R. Li, G. Flamant. Solar pyrolysis of beech wood: Effect of pyrolysis parameters on products distribution and gas products composition. *Energy*, 2015, 93, 1648-1657. doi:10.1016/j.energy.2015.10.008

3.9. Cavity reactor for ceria

Contact: Ronald Michalsky (ETHZ), Aldo Seinfeld (ETHZ)

Reactor design

The schematic of the experimental setup is shown in Figure 25(a); it features the main system components of the production chain to solar kerosene from H_2O and CO_2 via the ceria-based thermochemical redox cycle. The key component is the solar reactor, shown schematically in Figure 25(b). Its main features are briefly summarized here. It consisted of an insulated cavity-receiver with a 4 cm-diameter aperture to let in concentrated solar radiation. The reactor front was sealed by a 24 cm-diameter, 3 mm-thick clear fused quartz disk window. A compound parabolic concentrator (CPC) was incorporated onto the aperture to boost the solar concentration ratio to mean values of up to 3000 suns. A reticulated porous ceramic (RPC) foam-type structure, made of ceria, was contained within the cavity as a cylinder composed of four 20 mm-thick, 60 mm-i.d., 100 mm-o.d. rings, and a single 20 mm-thick, 100 mm-o.d. disk. The total mass of the CeO_2 cylinder was 948 g. Temperatures were measured at the outer surface of the RPC with B-type thermocouples. Reacting gases were injected through radial inlet ports and product gases exited through an outlet port at the rear plate. Details of the experimental setup are given elsewhere [1].

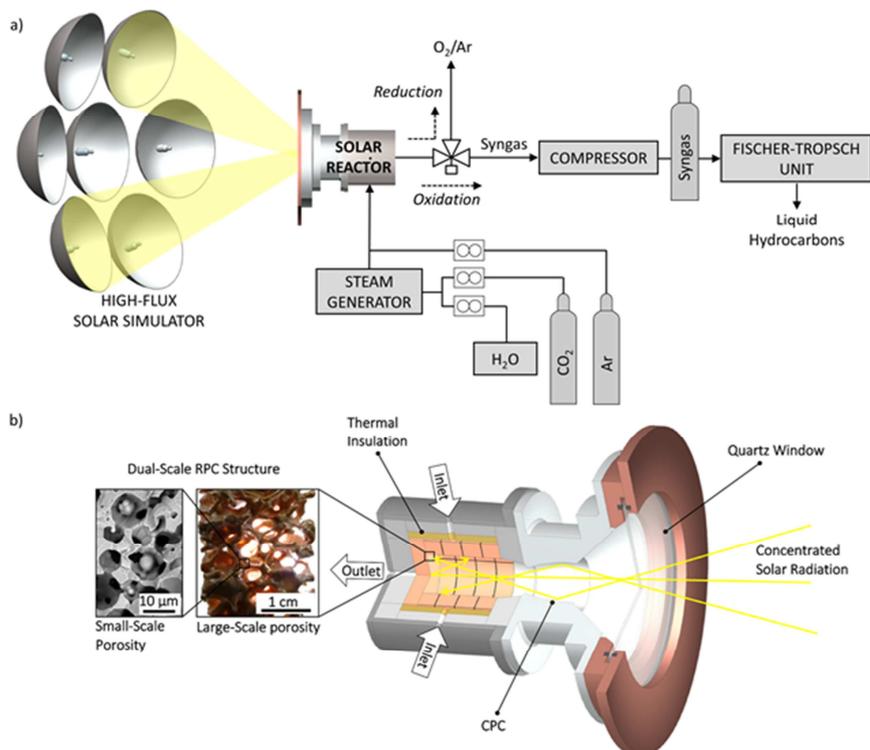


Figure 25 a) Schematic of the experimental setup, featuring the main system components of the production chain to solar kerosene from H_2O and CO_2 via the ceria-based thermochemical redox cycle; b) Schematic of the solar reactor configuration. The cavity-receiver contains a reticulated porous ceramic (RPC) structure, made from ceria, with dual-scale porosity in the mm- and μm -scale. Images are adapted from [1].

Table 17 Application of cavity reactor for ceria studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Splitting of CO ₂ and H ₂ O	2.8-3.8 kW _{th}	50 kW _{th} (2017)	ETHZ	European Commission under Contract No. 285098, Project SOLAR-JET; Swiss Competence Center Energy & Mobility

Application: Splitting of CO₂ and H₂O

Project name: -

Partners: ETHZ

Process: Key reactions: The ceria-based thermochemical cycle is represented by:
High-temperature reduction:



Low-temperature oxidation with H₂O:



Low-temperature oxidation with CO₂:



where the non-stoichiometry δ denotes the reduction extent. In the first, high-temperature solar endothermic reduction step, ceria is partially reduced to a non-stoichiometric state. In the subsequent low-temperature exothermic oxidation step, the reduced ceria is reacted with H₂O and/or CO₂ to generate H₂ and/or CO.

Results/development status

Experimentation was performed at the High-Flux Solar Simulator (HFSS) of ETH Zurich. The results are published in reference [1]. Briefly, during the first endothermic reduction step at 1450-1600 °C, the RPC was directly exposed to concentrated thermal radiation with power inputs ranging from 2.8-3.8 kW and mean solar flux concentration ratios of up to 3000 suns. In the subsequent exothermic oxidation step at 700-1200 °C, the reduced ceria was stoichiometrically reoxidized with CO₂ and/or H₂O to generate CO and/or H₂. The RPC featured dual-scale porosity: mm-size pores for volumetric radiation absorption during reduction and μm -size pores within its struts for enhanced oxidation rates. For cycle duration of 25 min, mean reduction rates were 0.17 mL_{O₂} min⁻¹ g⁻¹_{CeO₂} and mean oxidation rates were 0.60 mL_{CO} min⁻¹ g⁻¹_{CeO₂}. The solar-to-fuel energy conversion efficiency was 1.72 %, without sensible heat recovery. No attempt was undertaken to recover the sensible heat of exiting hot gases or of the RPC during the temperature swing between the reduction and oxidation steps. In total, 291 stable redox cycles were performed, yielding 700 standard litres of syngas, which was compressed to 150 bars and further processed via Fischer-Tropsch synthesis to a mixture of naphtha, gasoil, and kerosene. To the best

of our knowledge, this was the first experimental coupling of solar syngas production from H₂O and CO₂ with the storage, compression, and FT-processing to liquid hydrocarbons.

The development of this reactor type is continued within the H2020 project SUN-to-LIQUID, aiming at a demonstration on a scale of 50 kW concentrated solar power input.

Reference

- [1] D. Marxer, P. Furler, J. Scheffe., H. Geerlings, C. Falter, V. Batteiger, A. Sizmann, A. Steinfeld, Demonstration of the entire production chain to renewable kerosene via solar thermochemical splitting of H₂O and CO₂, *Energy & Fuels*, 2015, 29, 3241-3250. doi: 10.1021/acs.energyfuels.5b00351

3.10. Pressurized volumetric receiver

Contact: Christian Sattler (DLR)

Reactor design

The idea was to use solar heated pressurized volumetric air receivers for the steam reforming of carbonaceous feedstocks like natural gas or liquefied petroleum gas (LPG). Improving the technology of the previously successfully tested SOLASYS receiver [1].



Figure 26 SOLASYS Installation on the solar tower of the Weizmann Institute of Science, Rehovot, Israel (2001).

With the latest reactor SOLREF, a cost reduction of 5% [2] could be achieved with an advanced volumetric receiver (Figure 27). It was able to be operated at high pressure of up to 15 bar and temperatures of up to 950 °C to reach higher conversion rates of methane to hydrogen and higher efficiency [3]. The receiver was more compact than the SOLASYS and the redesign prevented the deposition of carbon in the reactor. The reactor was purged with either CO₂ or hydrogen to avoid steam condensation in the cold parts of the reformer.

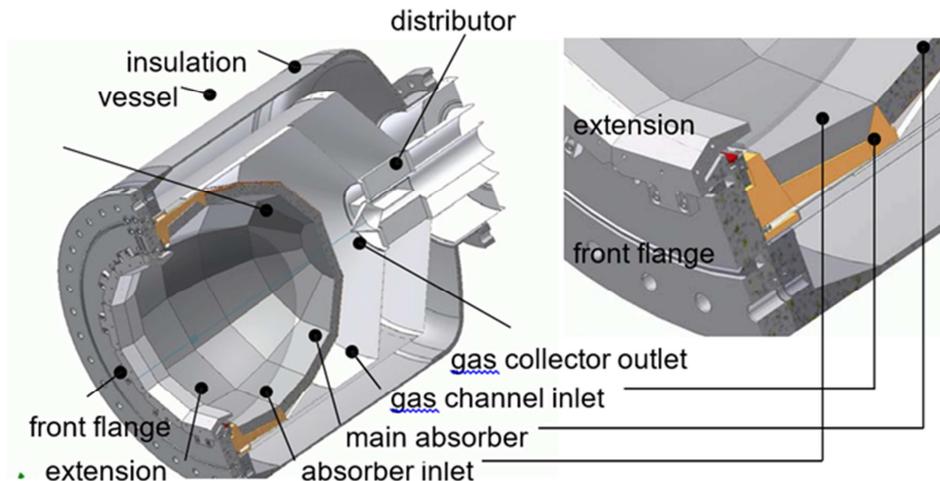


Figure 27 The SOLREF reactor.

In the beginning of 2009, the SOLREF reactor was mounted on top of the solar tower at the Weizmann Institute of Science (WIS) in Rehovot, Israel (Figure 28). In a pre-test phase, leak tightness, temperature durability and, in general, proper functioning of all parts were tested. In

the beginning of 2010, thermal tests were carried out successfully and afterwards the system produced hydrogen in the second quarter of 2010 (Figure 29).



Figure 28 SOLREF Installation on the solar tower of the Weizmann Institute of Science, Rehovot, Israel (2010).

Liquified petroleum gas (LPG) was reacted with water to produce syngas. The formed CO was shifted with additional water to maximize the hydrogen yield:

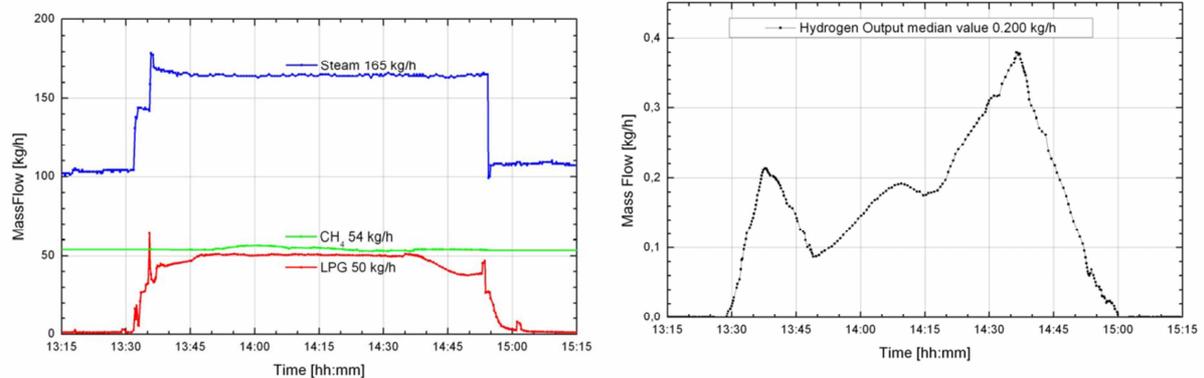
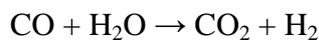
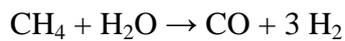


Figure 29 Left: Input of reactant gases in absolute measures into the SolRef reactor during solar testing. The numbers indicating the level taken into account for the stoichiometric equation. Right: Output of hydrogen gas in absolute measures in the same time frame. The mean value is 0.200 kg/h.

Table 18 Application of pressurized volumetric receiver reactor studied so far.

Application	Lab scale	Pilot scale	Project partners	Funding
Solar reforming	---	400 kW _{th} @ WIS	CERTH, WIS, DLR, Johnson Matthey, ETHZ, Hexion, SHAP, Region Basilicata	EU-FP6 project SOLREF

Application: Hydrogen production by solar reforming of methane

Project name: EU-FP6 project SOLREF

Partners: CERTH, WIS, DLR, Johnson Matthey, ETHZ, Hexion, SHAP, Region Basilicata

Process: Key reactions: Solar reforming of LPG:



Results/development status

A 400 kW solar reactor was designed and tested up to 950°C and 15 bar on the solar tower of the Weizmann Institute of Science, Rehovot (WIS), Israel, until 2010. Under these conditions methane could be converted close to the theoretical balance of 78%.

Reference

- [1] S. Möller, R. Buck, R. Tamme, M. Epstein, D. Liebermann, M. Meri, U. Fisher, A. Rotstein, C. Sugarmen, Solar Production of Syngas for Electricity Generation: SOLASYS Project Test-Phase, In: Proceedings of the 11th SolarPACES Int. Symposium on Concentrated Solar Power and Chemical Energy Technologies, Zürich, 04.-06.11.2002.
- [2] S. Möller, D. Kaucic, C. Sattler, Hydrogen Production by Solar Reforming of Natural Gas: A Comparison Study of Two Possible Process Configurations, J. Sol. Energy Eng, 2005, 128(1), 16-23. doi:10.1115/1.2164447
- [3] S. Möller, S. Friedmann, M. Walter, J. ten Dam, SOLREF – Development of an Advanced Solar High-Temperature Reformer. In: Proceedings of ISEC2006: ASME International Solar Energy Conference. ISEC2006, 2006-07-08 - 2006-07-13, Denver, CO (USA).

3.11. Monolithic honeycomb reactors

Contact: Christian Sattler (DLR)

Reactor design

The first examples of honeycomb reactors for solar-aided chemistry applications can be traced back to 1989 when researchers at WIS deposited Rh first on alumina and then on cordierite honeycombs and irradiated it in their solar furnace to catalyse the reaction of CO₂ methane reforming. However, such honeycomb reactors have first been used for thermochemical water splitting when the HYDROSOL research group introduced the concept of monolithic honeycomb solar reactors for performing redox pair cycles [1]. The reactor is inspired, on the one hand, from solar-radiation-absorbing honeycomb volumetric receivers made of silicon carbide (SiC) employed in solar tower power plants using air as heat transfer medium [2, 3] and, on the other hand, from the well-known automobile catalytic converters [4]. It has no moving parts and is based on the incorporation of active redox pair powders as coatings on multi-channeled monolithic honeycomb structures capable of achieving and sustaining high temperatures when irradiated with concentrated solar radiation.

The operating concept is shown in

Figure 30(a). When steam passes through the solar reactor, the coating material splits water vapour by “trapping” its oxygen and leaving pure hydrogen in the effluent gas stream. In a subsequent step, the oxygen-“trapping” coating is thermally reduced by increasing the amount of solar heat absorbed by the reactor. Such redox-material-coated honeycombs (

Figure 30(b)) have achieved continuous solar-operated water splitting- thermal reduction (WS-TR) cycles. The issue of continuous production has been resolved with a modular dual-chamber fixed honeycomb absorber design and implementation shown in

Figure 30(c) [5]. One part of the modules splits water while the other is being regenerated. After completion of the reactions, the regenerated modules are switched to the splitting process and vice versa by switching the feed gas [6]. Due to its modularity and the lack of movable parts, this design is amenable to straightforward scale-up and can be effectively coupled with a solar platform facility placed on a solar tower for continuous mass production of hydrogen. Indeed, such a modular, dual-chamber, ferrite-coated honeycomb HYDROSOL reactor has been scaled up to the 100 kW level, mounted on a solar tower facility (Plataforma Solar de Almería, Spain) and achieved continuous solar-operated WS-TR cycles demonstrating the “proof-of-concept” of the proposed design (

Figure 30(d) and (e)) [7]. In such a facility, the different heat demands for the two process stages were realized not by moving the reactors, but by adjusting the flux density on each module when the status of the cycle is switched from regeneration to splitting and vice versa, via partitioning the heliostat field and providing two “switchable” focal spots with independent power modulation [8].

An optimization of the reactor shape has been carried out to reduce the quite high re-radiation losses due to the high temperatures and the large exposed absorber surface area revealed by experiments and simulations [9]. For the 750 kW plant, a new reactor design has been proposed [10] where the overall shape of the absorber is close to a hemisphere and a suitable secondary reflector is included as well (Figure 31). The reactor-receiver consists of two parts:

a receiver “flat” part made of non-redox, square-shaped honeycombs at the front plate of the reactor (just behind the quartz window) and a “domed” part at the rear which is the reactor part consisting of the redox-coated modules. The introduction of a spherical shape of the absorber and a suitable secondary reflector ensures a more homogeneously distributed solar flux and therefore a more homogeneous temperature distribution than that of the previous, “flat design” version. The cavity design ensures also that the thermal radiation is more efficiently absorbed inside the reactor since different parts of the absorber face each other instead of facing the environment like in the previous flat design. Furthermore, the whole reactor set-up and all components were designed in a way allowing easy maintenance and replacement of parts, in particular of the individual absorber monoliths.

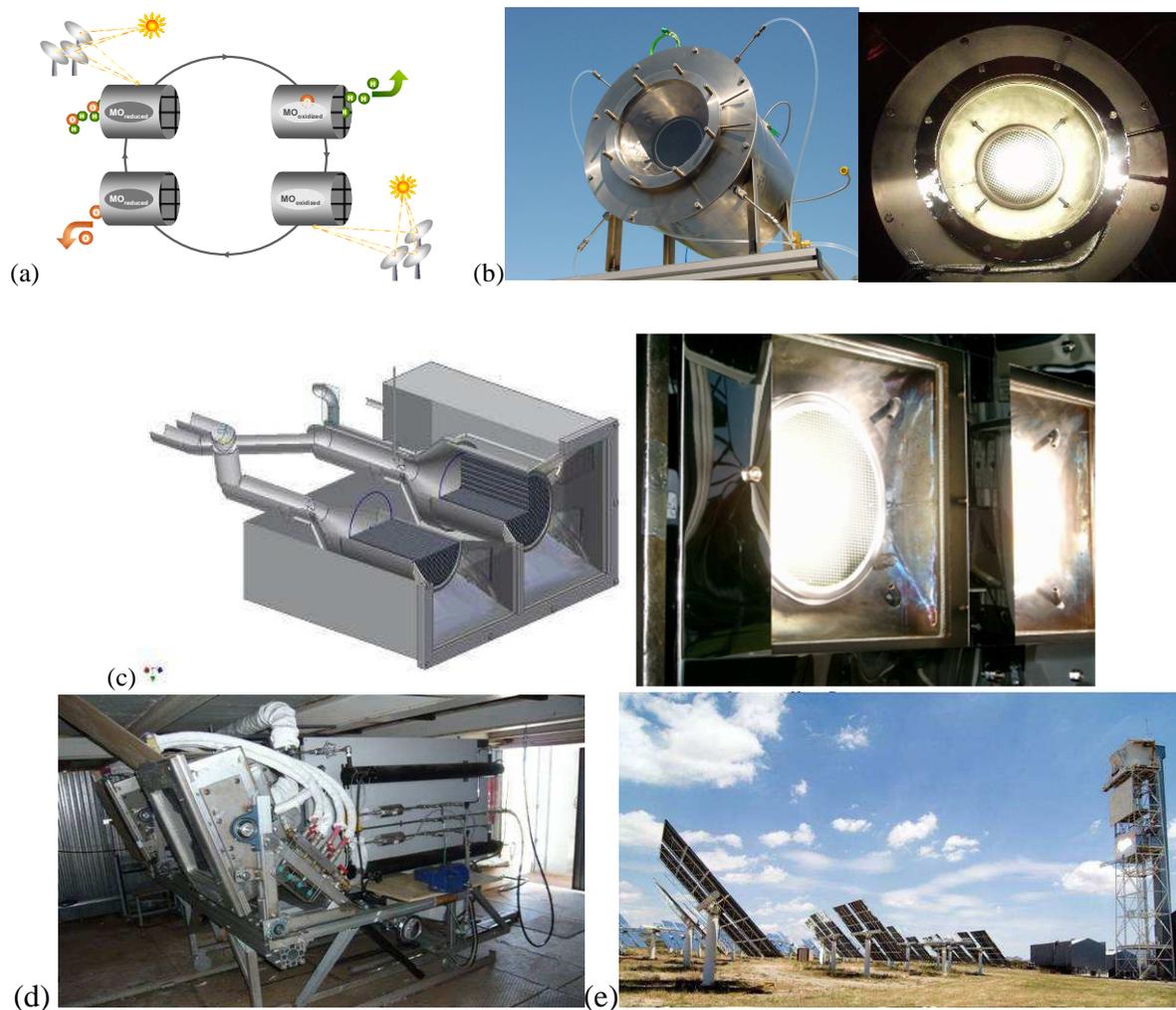


Figure 30 Solar reactors employing honeycombs; the HYDROSOL reactor technology evolution: (a) operating concept; (b) first single-chamber reactor assembled and in operation; (c) the continuous solar hydrogen production operation concept and the first dual-chamber reactor in operation; (d) the 100 kW-scale dual-chamber reactor on the top of the PSA solar tower; (e) operation of the reactor coupled with the solar field.

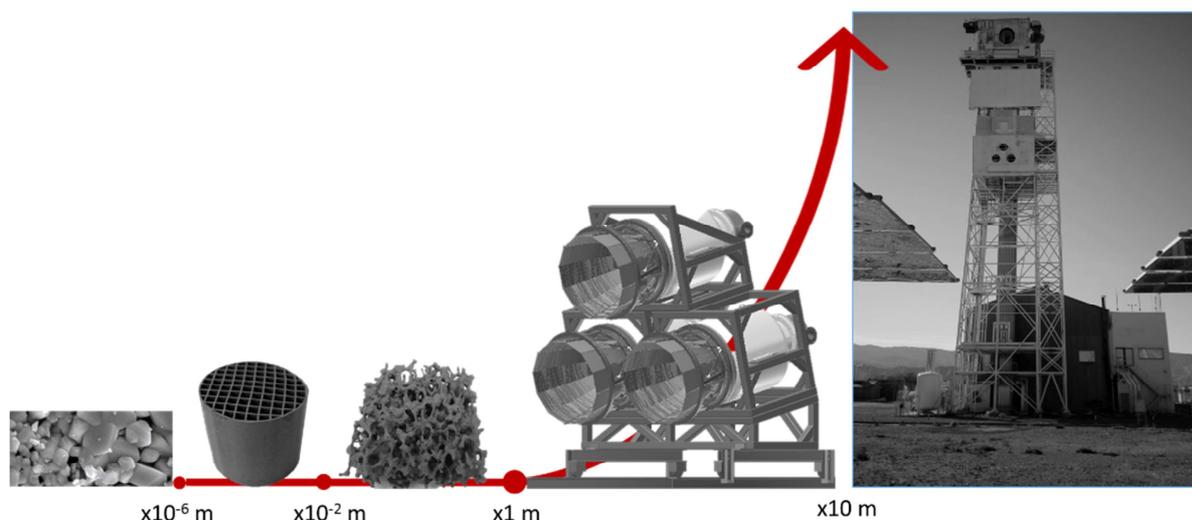


Figure 31 Development from the materials to the 750 kW HYDROSOL Plant reactor.

Table 19 Application of ceramic monolith volumetric reactor studied so far.

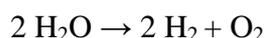
Application	Lab scale	Pilot scale	Project partners	Funding
Thermochemical water splitting	< 10 kW _{th} @ DLR	---	CERTH, DLR, Johnson Matthey, Stobbe Tech Ceramics	EU-FP5 project HYDROSOL
Thermochemical water splitting	---	100 kW _{th} @ CIEMAT-PSA	CERTH, DLR, Johnson Matthey, Stobbe Tech Ceramics, CIEMAT,	EU-FP6 project HYDROSOL 2
Thermochemical water splitting	---	750 kW _{th} @ CIEMAT-PSA	CERTH, DLR, CIEMAT, HyGear, HELPE	EU FCH JU project HYDROSOL Plant

Application: Hydrogen production by thermochemical water splitting

Project name: EU-FP5 project HYDROSOL, EU-FP6 project, HYDROSOL 2, EU FCH-JU project HYDROSOL 3D, EU FCH JU project HYDROSOL Plant

Partner: CERTH/CPERI APTL, DLR, CIEMAT, Johnson Matthey, Stobbe Tech Ceramics, HyGear, HELPE

Process: Solar thermochemical splitting of water:



Results/development status

A 750 kW solar reactor was designed and is presently set up on the SSPS tower of the Plataforma Solar de Almería, Spain. It will start operation in spring 2017. H₂ will be produced by thermochemical water splitting. The reactor is composed of three reaction chambers with windows and secondary concentrators. The goal is to produce 3 kg H₂ in one week of

operation.

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4. Summary and Outlook

This deliverable report provides an overview of the solar reactor concepts and related thermochemical processes for the production of solar fuels, which the partners in STAGE-STE are experienced with. It covers a large spectrum of reactor concepts in terms of operating pressures and temperatures, direct or indirect heating by concentrated radiation, feeding of reactants, etc. Related to the solar reactor development, numerous different thermochemical processes have been investigated. So far, solar reactors have been realized in the power range from 1 kW laboratory scale for fundamental studies up to 750 kW pilot scale for pre-commercial investigations.

Table 20 summarises all reactors described in this report. The table includes main applications in the field of solar thermochemistry, tested working conditions in terms of temperature, pressure and solar thermal power ranges, technology readiness level and main remarks, e.g. focused on current performance in terms of solar-to-fuel conversion efficiency, which are closely related to STAGE-STE WP9 KPIs.

This compilation of experience and know-how with solar thermochemical reactors and processes within the STAGE-STE consortium also provides valuable input for the recommendations for further European R&D activities in the field (Deliverable D9.4: “Technology Roadmap for Solar Fuels”).

Table 20 Summary of reactor types described in D9.1.

Section	Reactor type	Main application(s) so far	Temperature range (°C)	Pressure range	Reactor size(s), concentrated radiation power input	TRL	Remarks
2.1	Packed bed two-cavity reactor (PSI)	(i) Carbothermal reduction of ZnO (Solizinc); (ii) Thermal treatment of waelz oxide; (iii) Steam gasification of carbonaceous materials (Solizyn)	1,000 - 1,400	Ambient	5 kW (lab); 150kW (pilot Solizyn at CIEMAT-PSA), 300 kW (pilot Solizinc)	5	Thermal efficiency up to about 30% Up to 50kg/h Zn-dust production Solar upgrade up to 30% (LHV of produced syngas versus LHV of converted feedstock)
2.2	Packed bed cavity reactor (ENEA)	Hydrogen production using thermochemical cycle based on Na-Mn mixed ferrites	750 - 800	1 bar	1 kW (solar power concentrated in the cavity)	3 - 4	
2.3	Graphite tubes pilot scale solar reactor (CNRS)	Thermal decomposition of methane and natural gas	1,335 - 1,655	1 bar	50 kW	4 - 5	Solar upgrade of 8% of the high heating value of the products
2.4	Gas-solid trickle-bed reactor (ETHZ)	Biomass gasification	900 - 1,000	Ambient	1-3 kW (lab)	3 - 4	Carbon conversion up to 52%
2.5	Falling particle vacuum reactor (PSI)	Carbothermal reduction of ZnO	1,300 - 1,700	1 - 1,000 mbar	5 kW	3 - 4	
2.6	Pressurized vortex flow solar reactor (ETHZ)	Steam gasification of charcoal powder	1,000 - 1,300	1 - 6 bar	3 kW, 3,700 suns (lab)	4	Carbon conversion up to 94%, Solar-to-fuel energy conversion efficiency up to 20%
2.7	Shell-and-tube membrane reactor heated with molten salts (ENEA)	Steam methane reforming	450 - 550	9.5 bar	2 Nm ³ /h H ₂ - 10 kW _{th}	5	
2.8	Molten salts heated reactor for hydro-thermal liquefaction (UNIPA/ENEA)	Hydrothermal liquefaction and gasification of biomass and model compounds	200 - 550	Ambient - 300 bar	tubular reactor volume: 10 mL, Heating: 3.5 kW (lab)	2 - 3	Continuous high pressure (260 bar) process carried out. Upgrade to TRL 4 expected in next 1-2 years
3.1	Directly heated rotary reactor (PSI)	Thermal dissociation of ZnO	1,600 - 2,000	Ambient	10 kW (lab), 100 kW (pilot)	4 - 5	ZnO dissociation rates up to 28 g/min totalling over 28 kg during 13 full days of pilot experimentation
3.2	Solarized rotary kiln (IMDEA)	Reduction of non-volatile metal oxides	700 - 1,300	Ambient	1 kW	3	Only for lab-scale experiments for determination of materials abrasion and mechanical strength
3.3	Reduced pressure rotary solar reactor (CNRS)	Reduction of ZnO and SnO ₂ powders	up to 1,600	180 - 850 mbar	1 kW	3	Max. dissociation yield: 87% (Zn weight content in the final powder) with a typical dilution ratio of 300.
3.4	Gas-particle vortex flow reactor (CIEMAT, ETHZ)	Production of syngas from heavy crude oil	825 - 1,075	2 bar	5 kW (ETHZ/PSI), 500 kW (CIEMAT-PSA)	4	Chemical conversion for steam and petcoke after a single pass reached up to 35% (500 kW reactor)
3.5	Directly irradiated fluidized bed reactor (CIEMAT/IMDEA)	Hydrogen production by thermochemical cycles	800 - 1,000	Ambient	1 kW	3	Only for lab-scale experiments
3.6	Directly irradiated packed bed reactor (IMDEA)	(i) Kinetics determination of gas-solid reactions under high-radiation fluxes; (ii) Solar gasification and solar pyrolysis of carbonaceous materials	Ambient - 1,800	Ambient + 300 mbar	1 kW	3	Only for lab-scale experiments on determination of chemical kinetics
3.7	Upward moving bed solar reactor (CNRS)	Reduction of ZnO and SnO ₂ powders	up to 1,600	180 mbar	1 kW	3	Only for lab-scale experiments
3.8	Controlled atmosphere crucible solar reactor (CNRS)	Solar pyrolysis of biomass	600 - 2,000	0.44 - 1.14 bar	1.5 kW	3	A maximum gas production of 62% with a LHV of 10,376 ± 218 (kJ/kg of wood) (4,200 °C, 50 °C/s, 0.85 bar and 12 NL/min)
3.9	Cavity reactor for Ceria (ETHZ)	Splitting of CO ₂ and H ₂ O	700 - 1,600	ambient	2.8-3.8 kW, 3000 suns (lab)	4	Solar-to-fuel energy conversion efficiency up to 1.72 % (without sensible heat recovery). Scale-up under realization expected to bring the TRL to 5.
3.10	Pressurized volumetric receiver (DLR)	Solar Steam Reforming of Methane Rich Gas	up to 900	15 bars	400 kW	5	CH ₄ conversion 94.6%
3.11	Monolithic honeycomb reactor (Hydrosol) (DLR)	Splitting of H ₂ O	800 - 1,300	ambient	< 10 kW Solar Furnace, 100 kW Tower, 750 kW under constr. Tower	5	Upgrade to TRL 6 expected in 2017 in 750 kW plant under construction

5. List of abbreviations

ALCCONES	Spanish regional project “Storage and Conversion of Concentrating solar energy”
APTL	Aerosol and Particle Technology Laboratory (part of CERTH, Greece)
BSJRP	Brazilian-Swiss Joint Research Programme
CCEM	Swiss Competence Center Energy and Mobility
CE	Carbon gasification efficiency
CERTH	Centre for Research and Technology Hellas, Greece
CFD	Computational Fluid Dynamics
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain
CNR	Italian National Research Council
CNRS	Centre National de la Recherche Scientifique, France
CoMETHy	Eu-FP7-JTI project “Compact Multifuel Energy to Hydrogen Converter”
CPC	Compound Parabolic Concentrator
CREED	Centre de Recherches pour l’Environnement, l’Énergie et le Déchet, France
CSP	Concentrating Solar Power
CTI	Swiss Commission for Technology and Innovation
D-I	Directly irradiated
DLR	Deutsches Zentrum für Luft- und Raumfahrt (German Aerospace Centre), Cologne, Germany
EC	European Commission
ENEA	Italian National Agency for New Technologies, Energy and the Sustainable Economic Development
EAFD	Electric Arc Furnace Dust
ETHZ	Eidgenössische Technische Hochschule Zürich, Switzerland
EU	European Union
FP5,6,7	Fifth, Sixth, Seventh Framework Programme (EU)
GE	Gasification efficiency
HELPE	Hellenic Petroleum (Greek company)
HFSS	High-Flux Solar Simulator
HTL	Hydrothermal Liquefaction

HyTech	Swiss Project “Hydrogen production and storage”
HYDROSOL-PLANT	Eu-FP7-JTI project “Thermochemical HYDROgen production in a SOLar monolithic reactor: construction and operation of a 750 kWth PLANT”
I-I	Indirectly irradiated
IMDEA	Instituto Madrileño de Estudios Avanzados, Spain
IR	Infrared
KPI	Key performance Indicator
LHV	Lower Heating Value
L _N	Normal Liter
LPG	Liquefied Petroleum Gas
MoSE	Molten Salt Loop
MWSF	MegaWatt Solar Furnace, Odeillo, France
PD	Petrozuata Delayed coke
PDVSA	Petróleos de Venezuela SA, Venezuela
POLIMI	Politecnico di Milano, Italy
POLITO	Politecnico di Torino, Italy
PRIN	Research Project of National Interest (Italy)
PROMES	Laboratoire PROcédés, Matériaux et Energie Solaire (CNRS)
PSA	Plataforma Solar de Almería, Spain
PSI	Paul Scherrer Institute, Switzerland
RPC	Reticulate Porous Ceramic
SERI	Swiss State Secretariat for Education, Research and Innovation
SFOE	Swiss Federal Office of Energy
SHAP	Solar Heat And Power (Italian company)
SLPM	Standard Liter per Minute
SOLAR-JET	EU-FP7 project “Solar chemical reactor demonstration and Optimization for Long-term Availability of Renewable JET fuel”
SOLARO2	Spanish project “Oxygen generation and transport by means of solar thermochemical processes based on manganese oxides”
SOLASYS	EU-Joule3 project “Novel solar assisted fuel driven power system”
SOLGEMAC	Spanish regional project “Modular, Efficient and Dispatchable High Flux Solar Thermal Power Systems”
SOLHYCARB	EU-FP6 project “Hydrogen from Solar Thermal Energy: High Temperature Solar Chemical Reactor for Co-production of hydrogen and carbon black from natural gas cracking”

SOLSYN	Swiss project “Solar Fuels for Cement Manufacturing”
SOLZINC	EU-FP5 project “Solar carbothermic production of Zn from ZnO”
SSPS/CRS	Small Solar Power System / Central receiver System
SUN-to-LIQUID	EU-H2020 project “Integrated solar-thermochemical synthesis of liquid hydrocarbon fuels”
TEPSI	Italian project “High temperature thermochemical cycles for hydrogen production”
UNICAL	University of Calabria
UNIME	University of Messina, Italy
UNINA	University of Naples Federico II, Italy
UNIPA	University of Palermo, Italy
UNIFI	University of Pisa, Italy
UNISA	University of Salerno, Italy
WIS	Weizmann Institute of Science, Rehovot, Israel
WS-TR	Water splitting-thermal reduction
XRD	X-Ray Diffraction

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