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Guaranteeing the European Excellence in
Concentrating Solar Thermal Energy**



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pressurized solar reactor concepts assessed**

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Table of contents

1. INTRODUCTION.....	3
2. INDIRECTLY HEATED SOLAR REACTOR CONCEPTS.....	4
2.1. PACKED BED TWO-CAVITY REACTOR	5
2.2. GRAPHITE TUBES PILOT SCALE SOLAR REACTOR	10
2.3. GAS-SOLID TRICKLE-BED REACTOR	12
2.4. FALLING PARTICLE VACUUM REACTOR	14
2.5. MEMBRANE REACTOR HEATED WITH MOLTEN SALTS	17
3. DIRECTLY HEATED SOLAR REACTOR CONCEPTS	20
3.1. DIRECTLY HEATED ROTARY REACTOR.....	21
3.2. SOLARIZED ROTARY KILN	25
3.3. REDUCED PRESSURE ROTARY SOLAR REACTOR.....	27
3.4. GAS-PARTICLE VORTEX FLOW REACTOR.....	29
3.5. DIRECTLY IRRADIATED FLUIDIZED BED REACTOR	34
3.6. DIRECTLY IRRADIATED PACKED BED REACTOR	36
3.7. UPWARD MOVING BED SOLAR REACTOR.....	40
3.8. CONTROLLED ATMOSPHERE CRUCIBLE SOLAR REACTOR.....	43
4. SUMMARY AND OUTLOOK	46
5. LIST OF ABBREVIATIONS.....	47
6. GENERAL REFERENCES	48

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 and heated by incoming solar radiation. In indirectly heated reactors, the incident solar energy is first absorbed by an opaque surface that transfers it to a heat transfer medium or reacting gas on the other side.

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 current 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 projects.

In this milestone report, thirteen different reactor types and sixteen applications are described. More reactor types and applications will be included in Deliverable D9.1.

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, 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 powered by solar-heated molten salt.

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, fluid, or multiphase) [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 can 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 (Section 2.1), a multi-tube reactor (Section 2.2), a gas-solid trickle-bed reactor (Section 2.3), a falling particle vacuum reactor (Section 2.4), and a membrane reactor heated with molten salts (Section 2.5).

2.1. Packed bed two-cavity reactor

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. A small inert gas stream entering the upper cavity leaves through small gaps around the partition wall between upper and lower cavities to the lower cavity and then through the product gas exit through an SiC pipe towards the off-gas system. This 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 one at the bottom allowing flushing the packed bed with this gas. This is specifically of interest for the application of the reactor concept for gasification (see application 2 below), in which e.g. 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 hyperbolical 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 these applications.

Recently we study options to avoid the window, which 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, we are conceptually investigating options to bring new batches into the hot furnace, which would further increase the field of applications for this reactor type (publication under preparation).

The two-cavity reactor is well suited for very different processes involving solids, which are transformed to gas. Table 1 provides an overview of some major applications investigated so far.

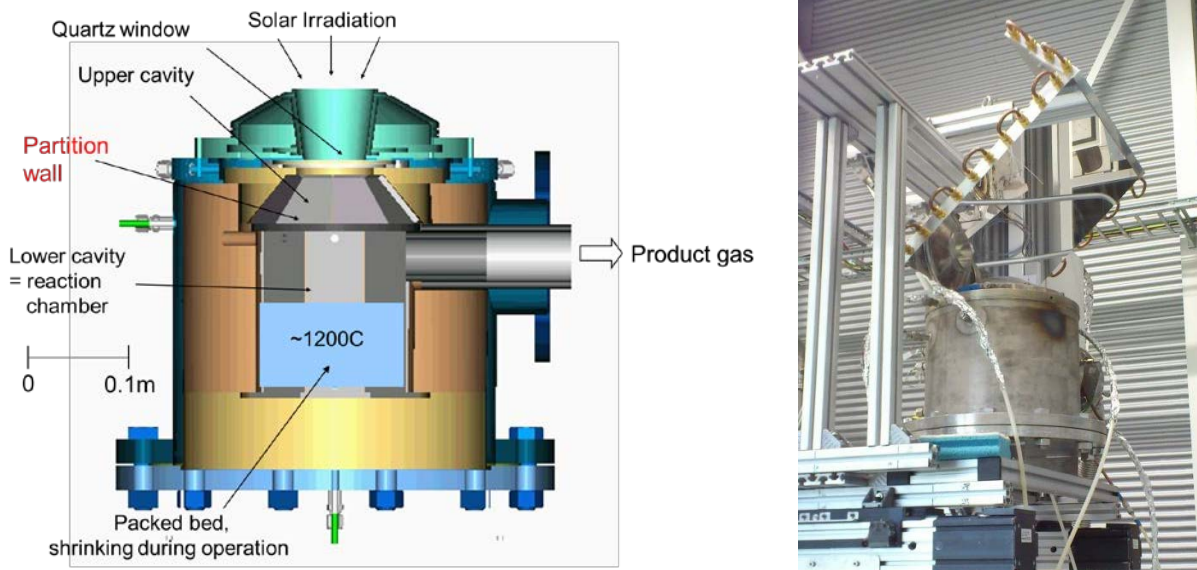


Figure 1 Schematic of lab-scale two-cavity reactor developed at PSI (left). Photo of reactor including a 45°-mirror for providing beam down radiation (right).

Table 1 Applications of packed bed two-cavity reactor.

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,..)	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 using the two-cavity lab-scale reactor shown in Figure 1. A packed bed of ZnO and charcoal gravel was processed to Zn(g) and CO at temperatures of about 1200°C [3]. Extensive process rate and material selection studies were performed [4].
- (2) Based on the results of (1), a 300 kW pilot solar reactor including an off-gas system for production of Zn dust for use in Zn-air batteries was designed, built and operated at WIS (Figure 2) [5]. 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 [6].

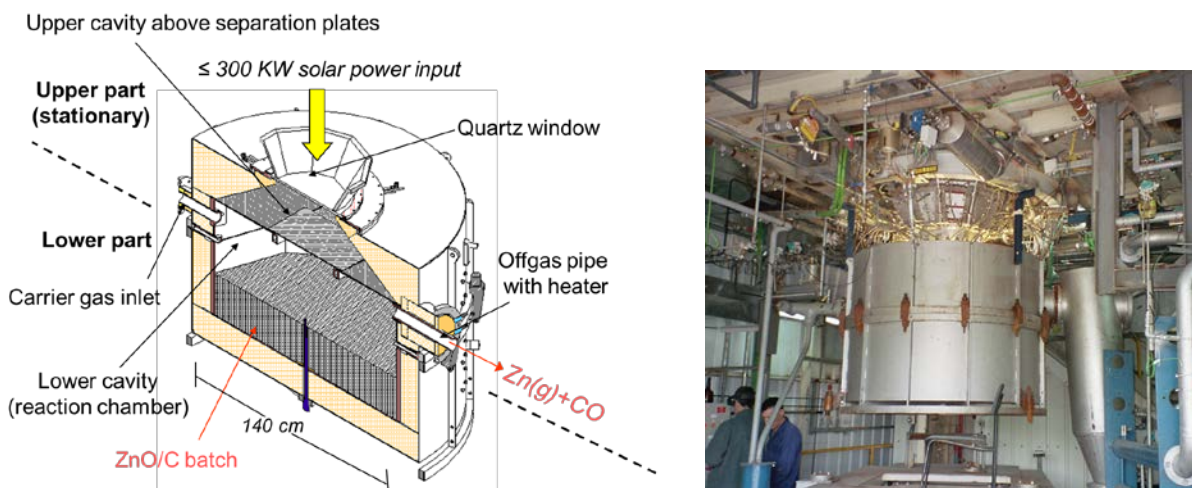


Figure 2 Schematic of the 300 kW reactor (left). Photo of the solar pilot plant in operation at the WIS beam-down solar facility (right).

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 (EAF) dust from scrap recycling.

Results/development status

Two types of process tests were performed using the laboratory scale two-cavity reactor shown in Figure 1 [7]:

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

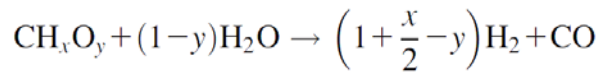
These successful experiments open new options for process routes in secondary Zn metallurgy [7].

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, mostly wastes, are converted into solar upgraded syngas.

Results/development status

The project included two stages:

- Investigation of the process for many different carbonaceous materials using the laboratory scale two-cavity reactor shown in Figure 1 [8]. Reaction rate and material suitability tests were performed [8].
- Based on the promising results design, building and operation of a 150 kW pilot two-cavity reactor at 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 [9].

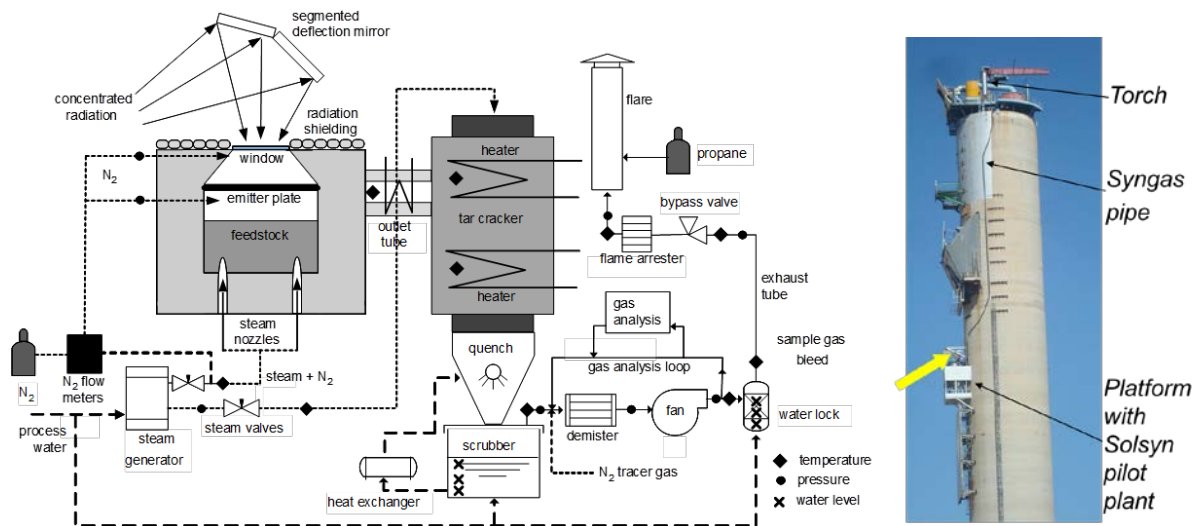


Figure 3 Schematic of the SOLSYN pilot plant (left). 150 kW SOLSYN pilot plant on the large solar tower at the Plataforma Solar de Almería (right).

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- [7] N. Tzouganatos, R. Matter, C. Wieckert, J. Antrekowitsch, M. Gamroth, A. Steinfeld, Thermal Recycling of Waelz Oxide using Concentrated Solar Energy. *Journal of Metals*, 2013, 65, 1733-1743. doi:[10.1007/s11837-013-0778-x](https://doi.org/10.1007/s11837-013-0778-x)
- [8] N. Piatkowski, C. Wieckert, A. Steinfeld, Experimental investigation of a packed-bed solar reactor for the steam-gasification of carbonaceous feedstocks. *Fuel Processing Technology*, 2009, 90, 360-366. doi:[10.1016/j.fuproc.2008.10.007](https://doi.org/10.1016/j.fuproc.2008.10.007)
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2.2. Graphite tubes pilot scale solar reactor

Contact: Gilles Flamant (CNRS)

Solar reactor design

The multi-tube reactor, depicted in Figure 4, was designed for 50 kW of incident solar power [1]. The reactor body is made of an aluminium shell (800x780x505 mm) and contains a water-cooled front face with a 13 cm-diameter aperture to let concentrated solar radiation entering within the reactor cavity. The radiation is absorbed by the graphite cavity (360x400x300 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 85 mm-thick graphite felt in contact with the cavity ($\lambda=0.53 \text{ W m}^{-1} \text{ K}^{-1}$ at 1873 K), a 50 mm-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 50 mm-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.

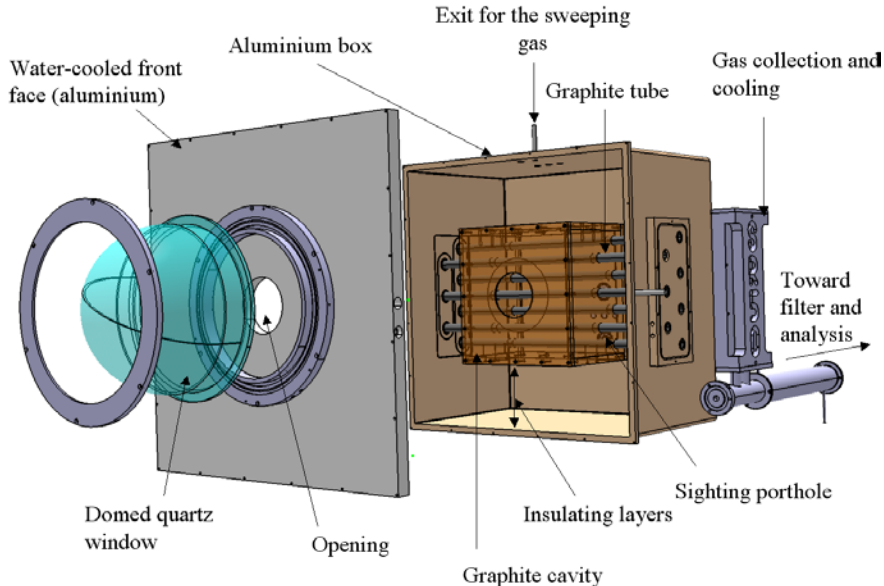


Figure 4 Graphite tubes pilot scale solar reactor (about 50 kW) designed, fabricated, and tested at CNRS.

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 2 channels: Channel 1 (MolSieve 5A PLOT 10M Backflush) for H₂, N₂, O₂, CO, 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 1608 K–1928 K for a gas residence time ranging from 37 ms to 71 ms.

Table 2 Application of the graphite tubes pilot scale solar reactor.

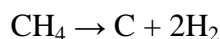
Application	Lab scale	Pilot scale	Project partners	Funding
Methane and natural gas cracking	---	50 kW _{th} @ CNRS	CNRS, DLR, PSI, WIS, CERTH, ABENGOA Solar, CREED, N-GHY, TIMCAL	EU-FP6 project SOLHYCARB

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 7 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

- [1] S. Rodat, S. Abanades, J.-L. Sans, G. Flamant. A pilot-scale solar reactor for the production of hydrogen and carbon black from methane splitting. *International Journal of Hydrogen Energy*, 2010, 35 (15), 7748-7758. doi:[10.1016/j.ijhydene.2010.05.057](https://doi.org/10.1016/j.ijhydene.2010.05.057)

2.3. Gas-solid trickle-bed reactor

Contact: Ronny 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 5 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 5, 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].

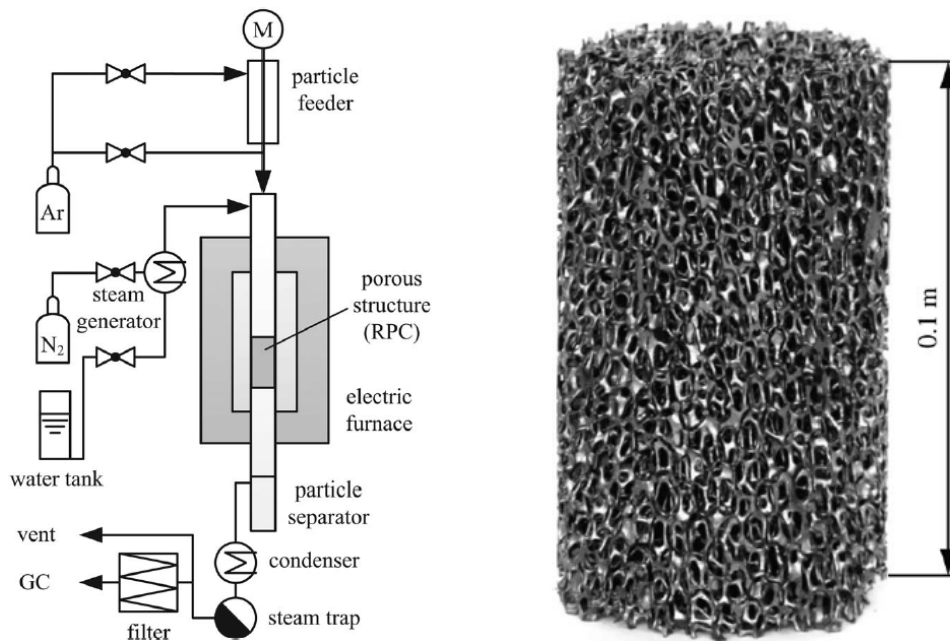
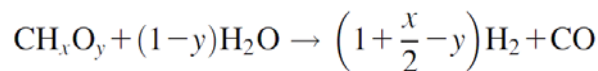


Figure 5 Schematic of the gas-solid trickle-bed (left) and photograph of the of silicon infiltrated silicon carbide RPC (right), both adapted from [1].

Table 3 Application of gas-solid trickle-bed reactor.

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

2.4. Falling particle vacuum reactor

Contact: Anton Meier (PSI), 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, developed at 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 6 [3].

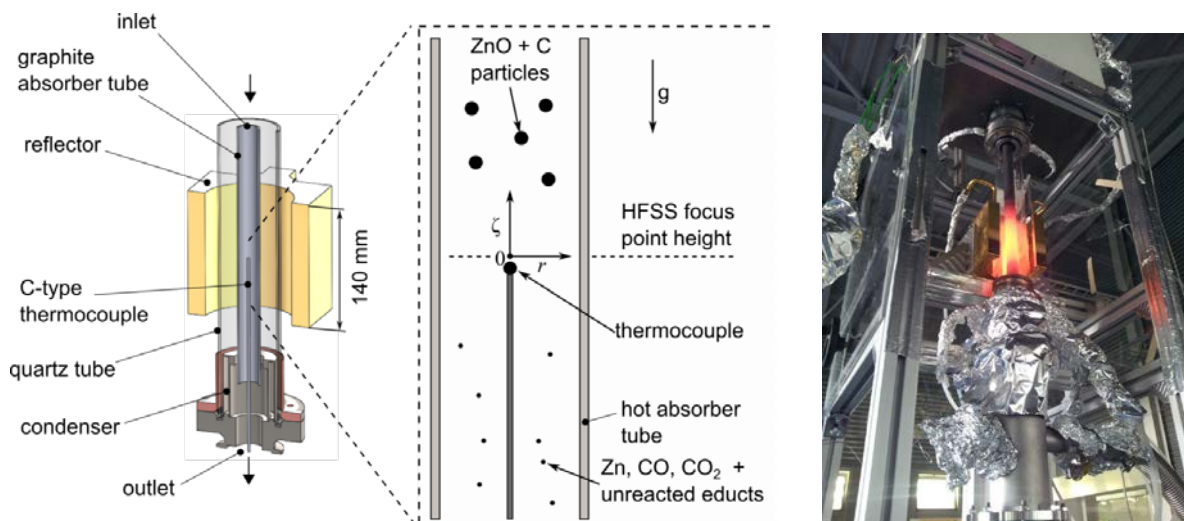


Figure 6 Schematic of the vacuum aerosol reactor as a cross-sectional view, and an enlarged view of the graphite absorber tube showing the hot reaction zone and particle flow (left). Vacuum reactor prototype after experimentation at PSI's High-Flux Solar Simulator, showing after-glowing absorber tube (right). From [3].

The reactor 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 6 provides information on the application of the falling particle vacuum reactor for solar carbothermal ZnO reduction.

Table 4 Application of falling particle reactor under vacuum.

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

Application: Falling particle reactor under vacuum

Project name: HyTech (Swiss project)

Partner: PSI

Process: The solar-driven carbothermal reduction of ZnO is given by:
 (1) $ZnO + C \rightarrow Zn + CO_2$ ($\Delta H = 352.5$ kJ/mol; $T > 1400$ 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) $ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2(g)$
 (3) $CO_2(g) + C(s) \rightarrow 2 CO(g)$

Results/development status

Proof-of-concept experiments were conducted with PSI’s High Flux Solar Simulator [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 6). The particles

are rapidly heated to reaction temperature and reduced within residence times of less than 1 s. In the 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. 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. 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.

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2.5. 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 7. A molten salt stream flows in the shell-side of the reactor and provides for 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 8). 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.

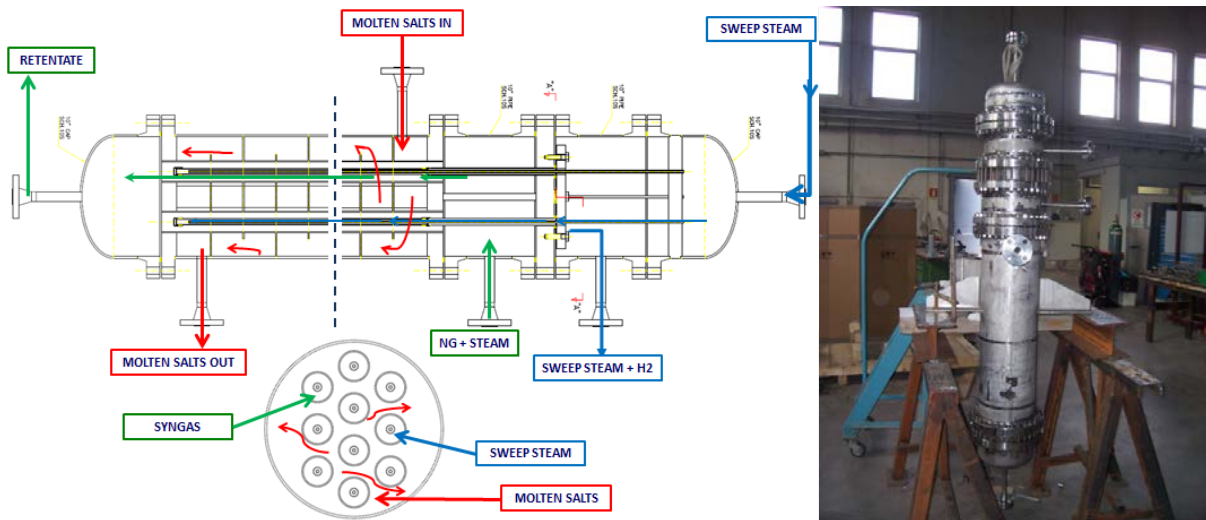


Figure 7 Integrated membrane reactor. Reactor scheme (left); lab-scale reactor (right).

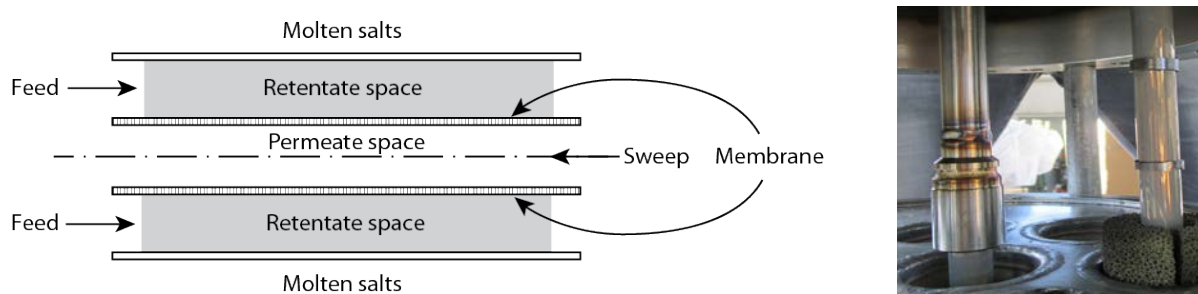


Figure 8 Details of the reaction tube as part of the membrane reactor.

Table 5 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 CSP 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 only using 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.

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3. Directly heated solar reactor concepts

Directly illuminated reactors have the advantage of providing efficient radiation heat transfer directly to the reaction [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 under high-pressure and severe gas environment. Directly heated reactors are classified as volumetric and particle 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]. As compared to honeycomb reactors, foam based absorbers have the advantage of higher porosity that allows for 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), and packed bed reactors (Sections 3.6-3.8).

3.1. Directly heated rotary reactor

Contact: Anton Meier (PSI), Christian Wieckert (PSI)

Solar reactor design

The 100 kW solar reactor, depicted in Figure 9, 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.

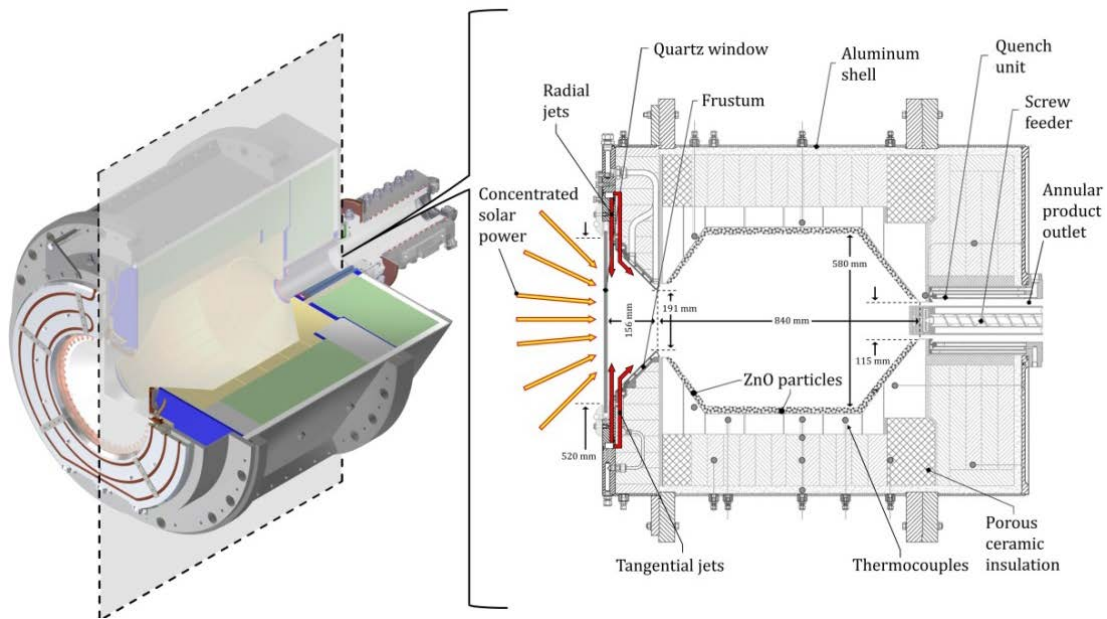


Figure 9 Cross-section schematic of the solar thermochemical reactor with key details and dimensions indicated. The outer diameter of the aluminium reactor shell is 1090 mm, and the length is 1330 mm. From [3].

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. 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° 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, based on previous laboratory scale rotating reactors developed at PSI and ETH Zurich [5][6][7], 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. Table 6 provides information on the application of the rotary cavity reactor for solar thermal ZnO dissociation.

Table 6 Application of solar rotary cavity reactor.

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 [8]-[9], 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 [10]. The pilot plant experimental setup, depicted in Figure 10, consists of the solar reactor along with peripheral components including the powder reactant delivery system, product collect system, and reactor rotation mechanism.

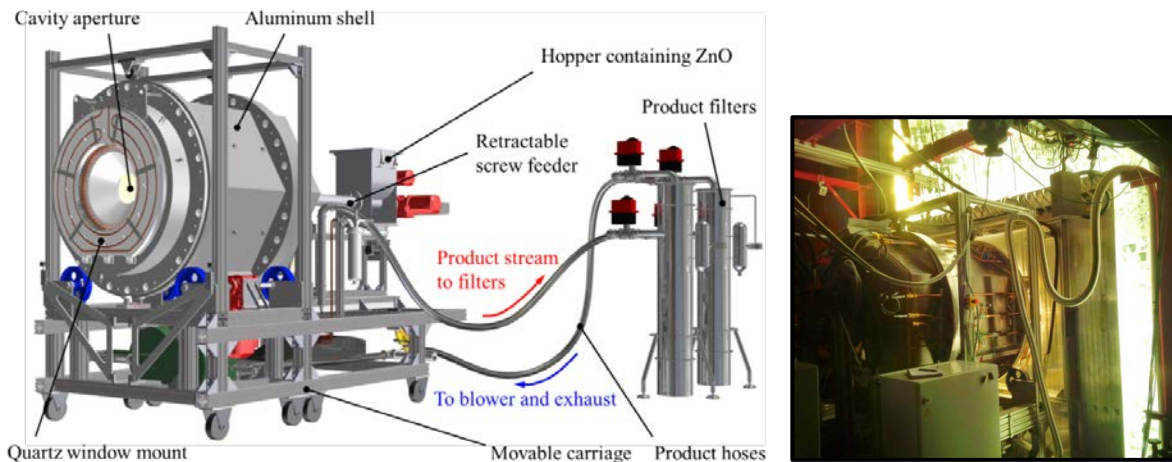


Figure 10 ZnO pilot plant layout utilized in experiments conducted at PSI and Odeillo in 2014, with critical components and peripherals labelled [3] (left). Image of the reactor during operation viewed from behind inside the experimental tower (right).

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 11, 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 11 cm, 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 4° 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. 28 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-kWe 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.

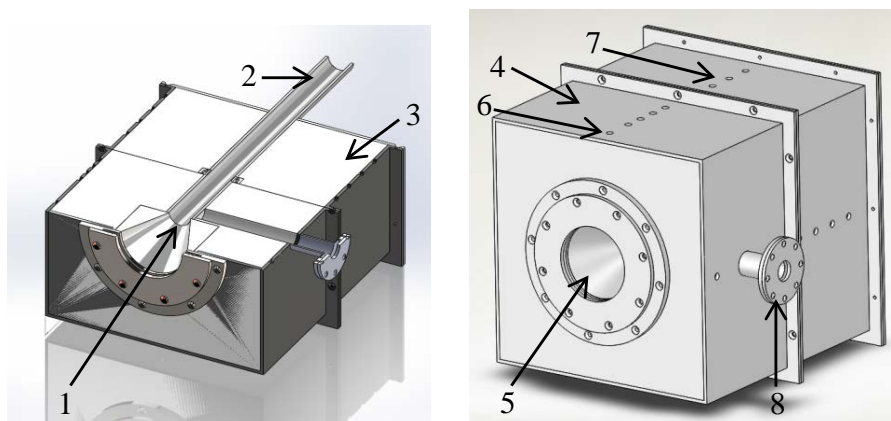


Figure 11 Scheme of rotary kiln: (1) cavity; (2) rotary tube of alumina; (3) ceramics bricks; (4) stainless steel housing; (5) quartz glass window; (6) gas inlet; (7) thermocouples places; (8) window for pyrometer.

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 7 Application of IMDEA's solarized rotary kiln.

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 12, 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.

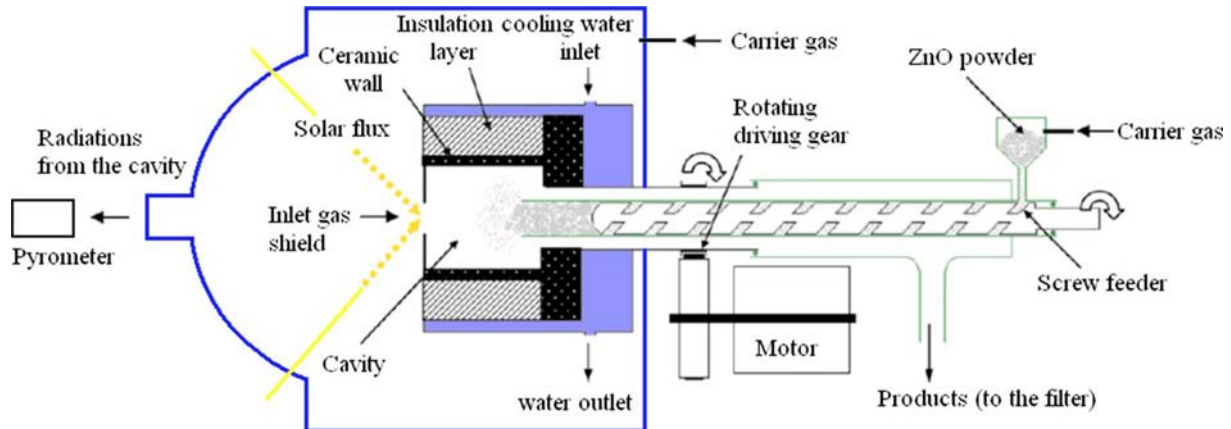


Figure 12 Reduced pressure rotary kiln solar reactor (about 1 kW) designed and tested at CNRS. From [1].

Table 8 Application of the CNRS reduced pressure rotary solar reactor.

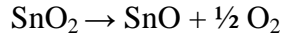
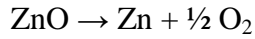
Application	Lab scale	Pilot scale	Project partners	Funding
Reduction of ZnO and SnO ₂ powders	1 kW _{th} @ CNRS	---	CNRS	CNRS

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 NL/min neutral gas flow-rate (typical dilution ratio of 300).

Reference

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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 13 [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 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.

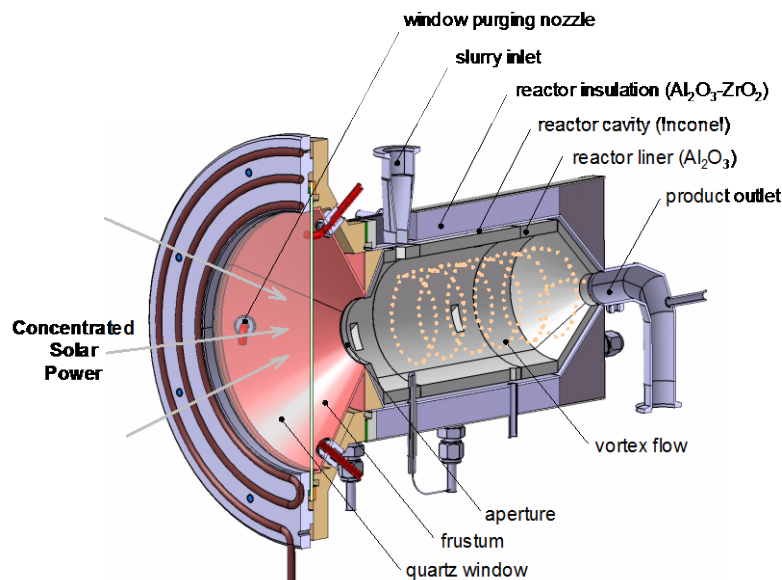


Figure 13 Scheme of lab-scale solar chemical reactor configuration for the steam-gasification of petcoke [1]. The reactants are injected as liquid slurry of petcoke particles and water.

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 an 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 9 Application of gas-particle vortex flow reactor.

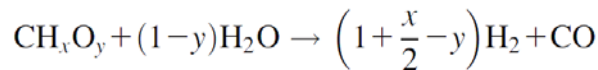
Application	Lab scale	Pilot scale	Project partners	Funding
Production of syngas from heavy crude oil	5 kW _{th} @ PSI	500 kW _{th} @ PSA- CIEMAT	PDVSA, ETHZ, CIEMAT	PDVSA

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 14). 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].

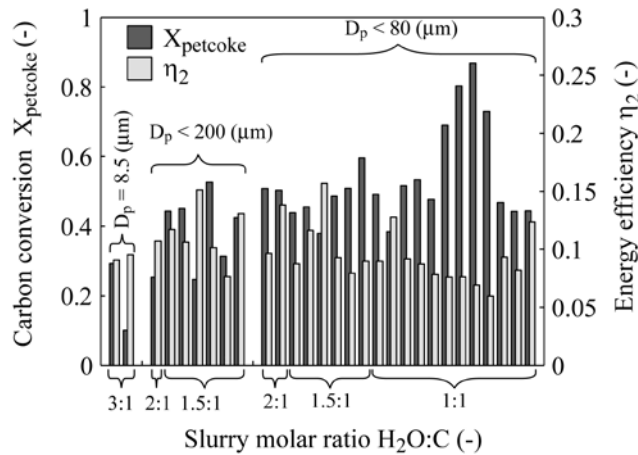


Figure 14 Petcoke chemical conversion and energy conversion efficiency obtained in the solar experimental runs, ordered according to particle size and slurry stoichiometry [1].

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 15).

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 to 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 15: 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.

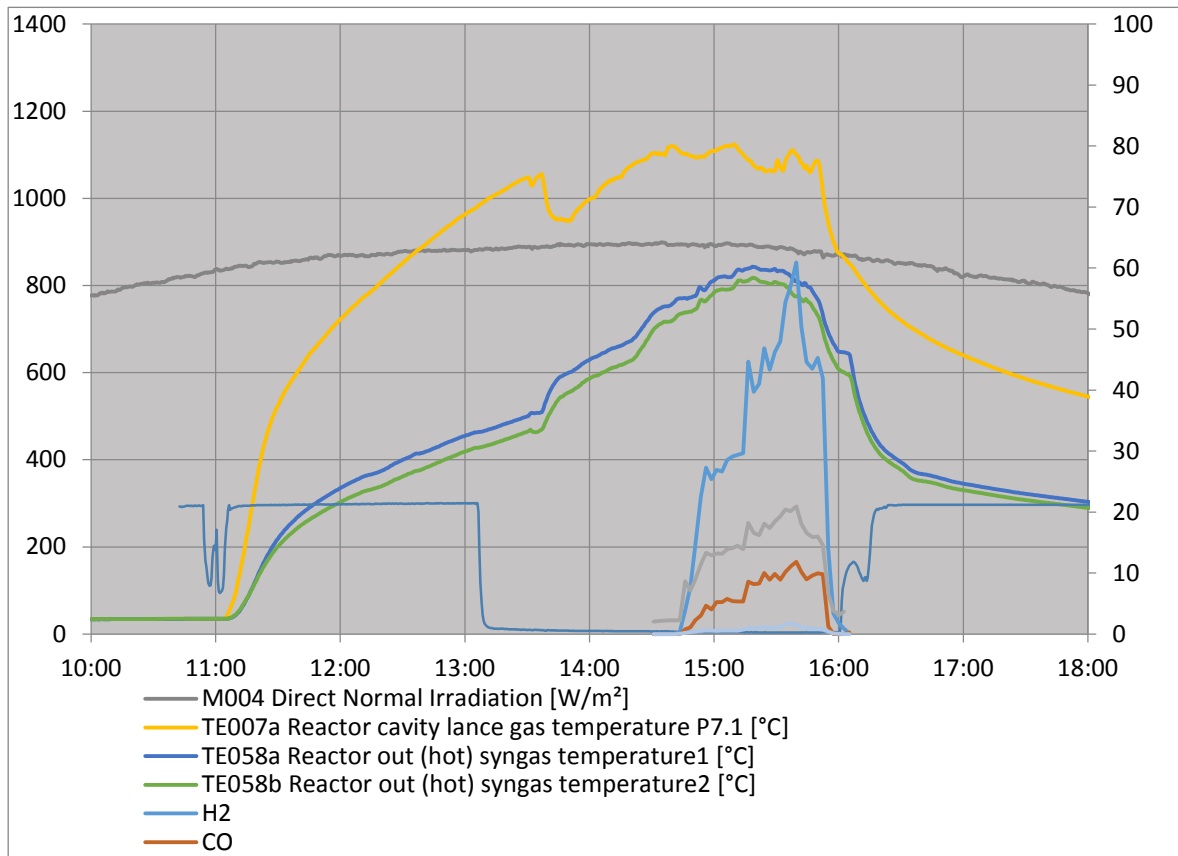


Figure 15 Results from a typical chemical test of the 500 kW SYNPEP solar pilot plant at PSA.

References

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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 16, 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 the 7-kW_e high-flux solar simulator (Kiran 7). At the bottom of the cylinder, a porous ceramic piece acts as a sample holder and gas diffuser. The external housing is made of stainless steel.

The instrumental facility has measuring 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.

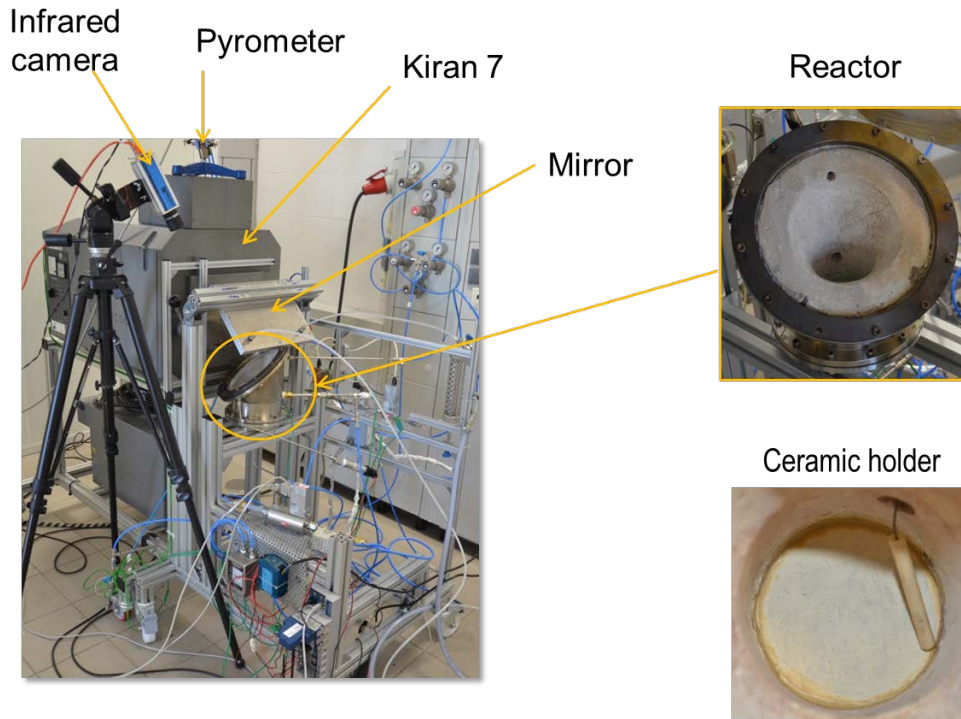


Figure 16 Photographs of the fluidized bed reactor and its experimental setup at IMDEA.

Table 10 Application of IMDEA's directly irradiated fluidized bed reactor.

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 IMDEA's solar simulator setup (Figure 17), 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 at the bottom. The horizontal light beam from the 7-kWe high flux solar simulator is reflected with an angle of 90° using a flat mirror and then is 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 its 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. 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. 7 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.

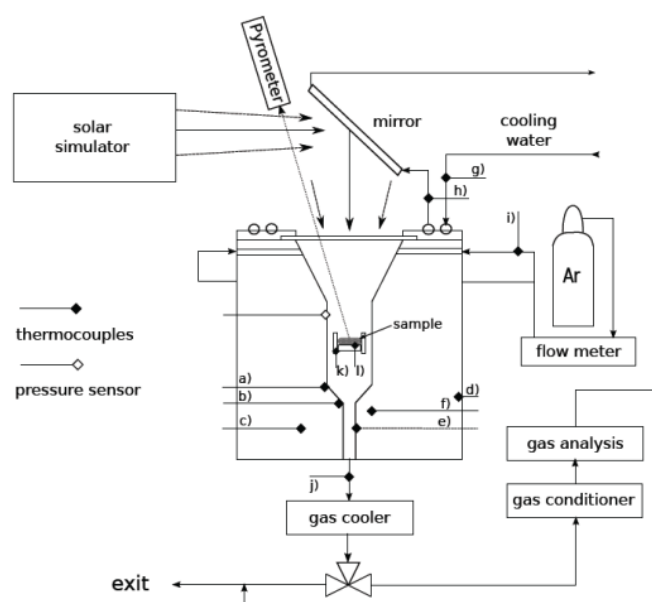


Figure 17 Schematic representation of test bed including the directly irradiated packed bed reactor.

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 3 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 11.

Table 11 Application of IMDEA's directly irradiated packed bed reactor.

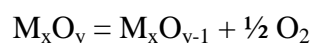
Application	Lab scale	Pilot scale	Project partners	Funding
Kinetics determination of gas-solid reactions under high-radiation fluxes	1kW _{th} @ IMDEA	---	IMDEA, CIEMAT, URJC, INTA	SOLGEMAC
			IMDEA, CIEMAT, URJC, CSIC	ALCCONES
Solar gasification and solar pyrolysis of carbonaceous materials	1kW _{th}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

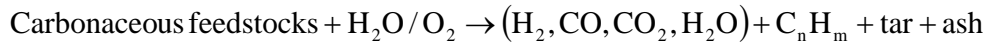
Internal lining and sample holder have been recently modified in order to extend the reactor applicability to other material forms and shapes such as foams.

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 18).

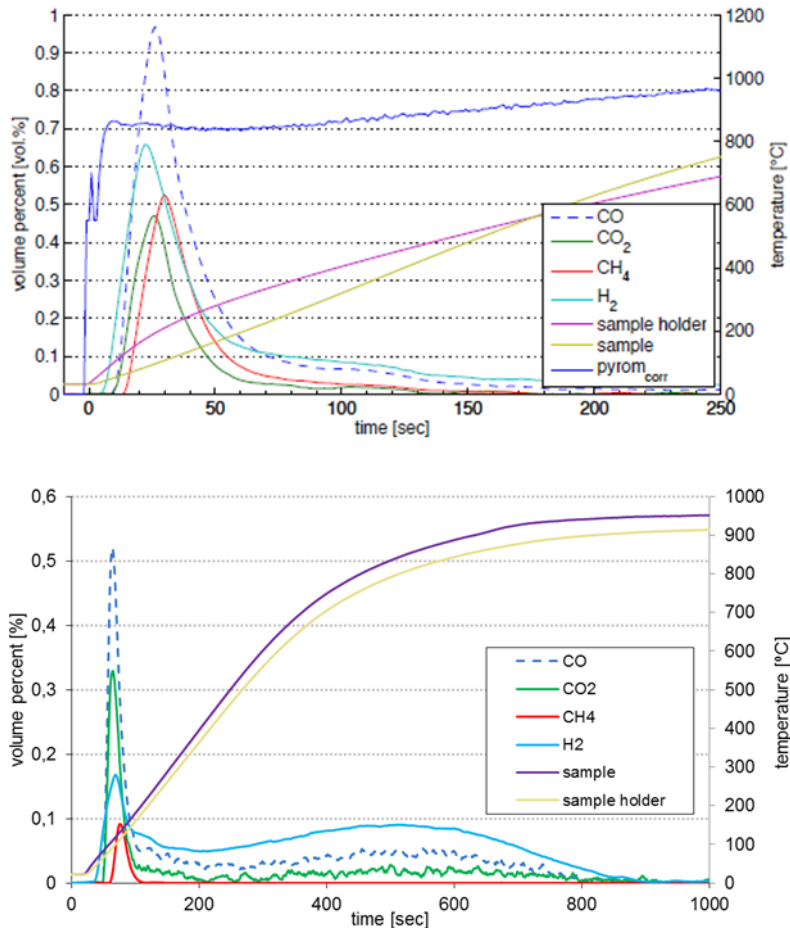


Figure 18 CO, CO₂, CH₄, H₂ composition and temperature as a function of time during the solar-driven pyrolysis (top) and gasification (bottom) of straw.

References

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3.7. Upward moving bed solar reactor

Contact: Gilles Flamant (CNRS)

Solar reactor design

The upward moving bed solar reactor, depicted in Figure 19, 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. 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 , Prolabo™, 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 19). 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 Vacuum™ PCR260 capacitance gauge) in order to measure the operating pressure inside the cavity. Gas flow-rates are regulated with mass-flow controllers (Brooks™ calibrated with N_2 , precision: $0.7\% \pm 0.2\%$ of the full scale, scale: 0-5 NL/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 $\text{Zn}_{(g)}$ or $\text{SnO}_{(g)}$ 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.

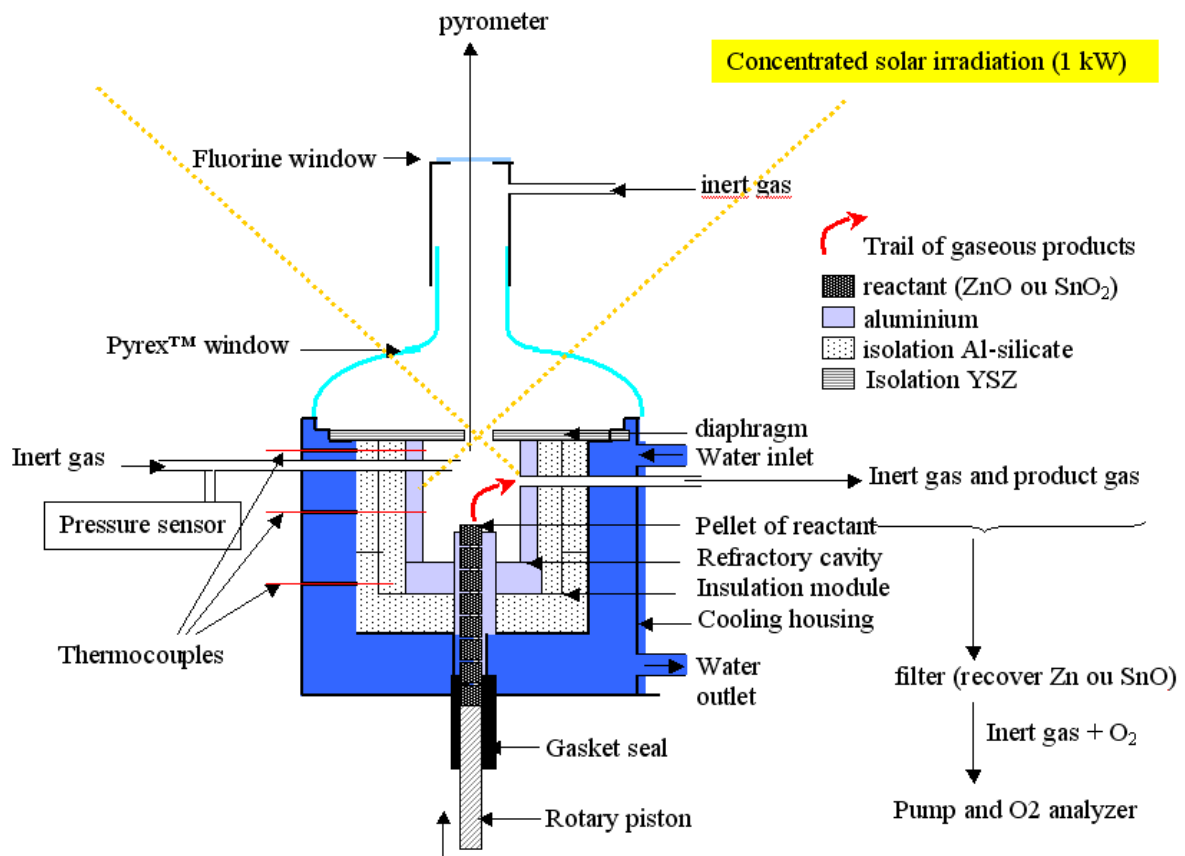


Figure 19 Schematic of upward moving bed solar reactor (about 1 kW) developed and tested at CNRS.

Table 12 Application of the CNRS Upward moving bed solar reactor.

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:
 $ZnO \rightarrow Zn + \frac{1}{2} O_2$
 $SnO_2 \rightarrow SnO + \frac{1}{2} O_2$

Results/development status

The high-temperature thermal dissociation reaction of ZnO and SnO₂ was investigated, as part of a two-step thermochemical water-splitting cycle for H₂ 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

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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 20). 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). 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).

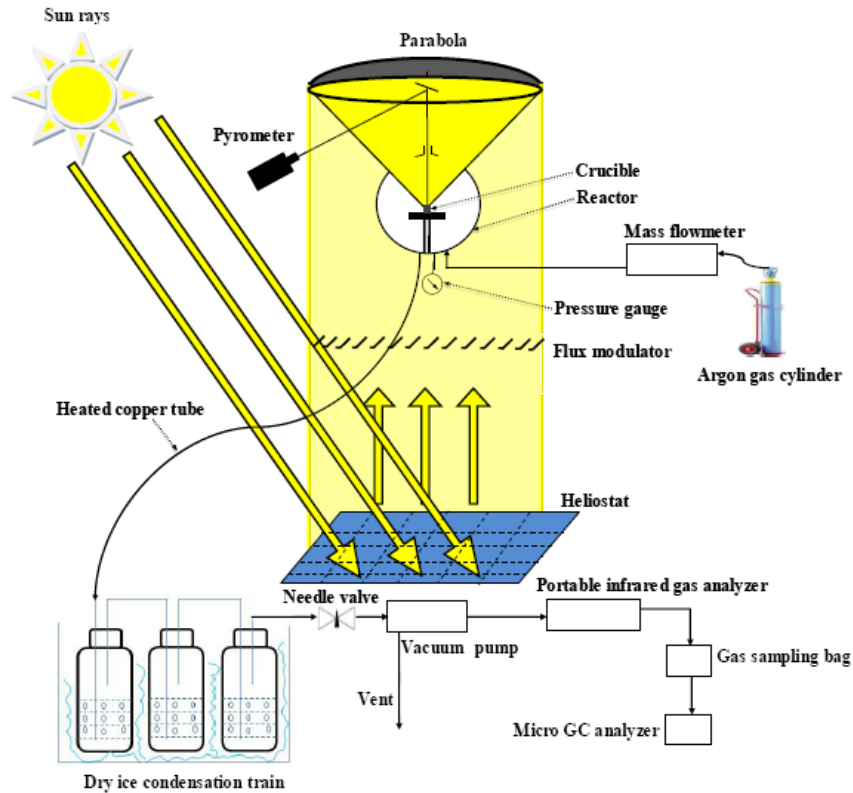


Figure 20 Controlled atmosphere crucible solar reactor (about 1 kW) designed and tested at CNRS.

Table 13 Application of the CNRS controlled atmosphere crucible solar reactor.

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 (600-2000°C).

Results/development status

The solar pyrolysis of beech wood was investigated with the objective of determining the optimal pyrolysis parameters for maximizing the LHV_s (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 (600–2000°C), heating rate (5–450°C/s), argon flow rate (6–12 NL/min) and pressure (0.44–1.14 bar). The results indicate that the

product yields (liquid, char and gas), gas composition (H_2 , CH_4 , CO , CO_2 and C_2H_6) and LHV are strongly influenced by the pyrolysis parameters. The total gas LHV greatly increases with increasing temperature (from 600 to 1200°C) and increasing heating rate (from 5 to 50°C/s), which is mainly due to increases in the CO and H_2 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 $10,376 \pm 218$ (kJ/kg of wood) is obtained under solar pyrolysis conditions of 1200°C, 50°C/s, 0.85 bar and 12 NL/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

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4. Summary and Outlook

This milestone 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 WP9 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 500 kW pilot scale for pre-commercial investigations.

This is an intermediate status report. For the related project Deliverable D9.1 (“Final report on vacuum and pressurised solar reactor concepts”) – due in January 2017 – the descriptions of the solar reactors and their development status will be updated. Additional reactor types and applications are supposed to be included, such as the indirectly heated pressurized vortex flow reactor, the monolithic honeycomb reactor used in the HYDROSOL project, and the cavity reactor used for the ceria cycle within the SOLAR-JET project.

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

5. List of abbreviations

CERTH	Centre for Research and Technology Hellas, Greece
CFD	Computational Fluid Dynamics
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain
CNRS	Centre National de la Recherche Scientifique, France
CoMETHy	Compact Multifuel Energy to Hydrogen Converter
CSP	Concentrating Solar Power
CTI	Swiss Commission for Technology and Innovation
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
ETHZ	Eidgenössische Technische Hochschule Zürich
FP5,6,7	Fifth, Sixth, Seventh Framework Programme
IMDEA	Instituto Madrileño de Estudios Avanzados, Móstoles, Spain
IR	Infrared
HFSS	High-Flux Solar Simulator
LHV	Lower Heating Value
MWSF	MegaWatt Solar Furnace, Odeillo, France
NL	Normal Liter
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
SLPM	Standard Liter per Minute
WIS	Weizmann Institute of Science, Rehovot, Israel
XRD	X-Ray Diffraction

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