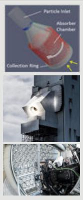
# Allothermally heated reactors for solar-powered implementation of sulphur-based thermochemical cycles

Vamshi Krishna Thanda, Dennis Thomey, Michael Wullenkord, Kai-Peter Eßer, Christos Agrafiotis*, Dimitrios Dimitrakis, Martin Roeb, Christian Sattler

German Aerospace Center (DLR), Institute of Future Fuels, Cologne/Juelich Germany, *christos.agrafiotis@dlr.de

## Motivation

- Recent developments of solar receivers capable of delivering **solid or gaseous heat transfer fluids at temperatures ≥ 900°C.**
- **Several industrially important endothermic reactions,** considered to be implemented via Concentrated Solar Thermal technologies including the Sulphur-based thermochemical cycles, **take place at temperatures lower than this level.**
- **Commonality of the highest-temperature sulphur trioxide splitting step among three Sulphur-based cycles**: the Hybrid Sulphur (HyS) and the Sulphur Iodine (SI) for production of Hydrogen and the Solid Sulphur cycle for storage of solar energy in solid Sulphur.
- **Implementation of high-temperature step of thermochemical cycles on solar reactors/receivers difficult and with several drawbacks** (high re-radiation losses, capability to maintain the high temperatures achieved only within a limited length, complex heat recovery architectures).



(a) the Hybrid Sulphur cycle

| | Reaction | Temperature |
|---|---|---|
| Sulphuric acid decomposition | $H_2SO_4(aq) \rightarrow H_2O(g) + SO_3(g)$ | 450-500°C |
| | $SO_3(g) \rightarrow SO_2(g) + ½ O_2(g)$ | 700-950°C |
| Electrolysis | $2 H_2O + SO_2 \rightarrow H_2SO_4 + H_2(g)$ | |
| Anode: | $SO_2 + 2 H_2O \rightarrow H_2SO_4 + 2 H^+ + 2 e^-$ | 80°C |
| Cathode: | $2 H^+ + 2 e^- \rightarrow H_2$ | |

(b) the Sulphur-Iodine cycle

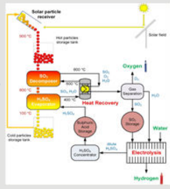
| | Reaction | Temperature |
|---|---|---|
| Sulphuric acid decomposition | $H_2SO_4(aq) \rightarrow H_2O(g) + SO_3(g)$ | 450-500°C |
| | $SO_3(g) \rightarrow SO_2(g) + ½ O_2(g)$ | 700-950°C |
| Bunsen reaction | $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$ | 25-125°C |
| HI decomposition | $2HI \rightarrow I_2(g) + H_2(g)$ | 127-727°C |

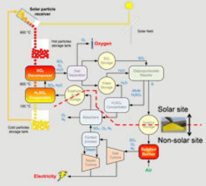
(c) the solid Sulphur cycle

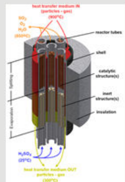
| | Reaction | Temperature |
|---|---|---|
| Sulphuric acid decomposition | $2H_2SO_4(aq) \rightarrow 2H_2O(g) + 2SO_3(g)$ | 450-500°C |
| | $2SO_3(g) \rightarrow O_2(g) + 2SO_2(g)$ | 700-950°C |
| Disproportionation | $2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(s)$ | 50-200°C |
| Sulphur Combustion | $S(l) + O_2(g) \rightarrow SO_2(g)$ | 500-1500°C |

## Concept set forth

- Perform the two sulphuric acid decomposition steps **"allothermally" via the enthalpy of solid particles heated in a centrifugal particle receiver developed by DLR,** in a shell-and-tube catalytic reactor/heat exchanger not collocated with the solar receiver.





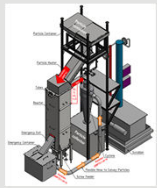


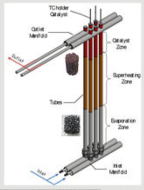
## Objectives

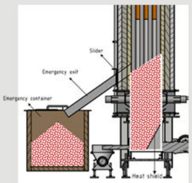
- Design a scalable reactor concept for the allothermal implementation of both steps of the sulphuric acid decomposition reaction.
- Develop and qualify a proof-of-concept, lab-scale reactor to demonstrate feasibility of allothermal sulphuric acid decomposition via electrically-heated particles before scale-up to solar platform testing.

## Experimental

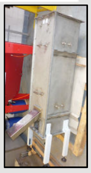
- A 2 kW shell-and-tube reactor/heat exchanger comprised of six catalytic tubes, heated via bauxite particles flowing in the shell through an electrically-heated inclined belt feeder was constructed.
- In the tube side, rising sulphuric acid vapours come into contact with a non-moving structured catalytic bed. Each tube consists of an outer stainless steel and an inner SiSiC tube, the latter coming into contact with the reactive gases.
- $Fe_2O_3$-coated SiC foams comprised the catalytic systems, having demonstrated reproducible near-equilibrium conversion at 850°C, under a broad range of sulphuric acid flow rates as well as minute pressure drop even under high catalyst loadings (35-45 wt. %).
- Similar, non-coated SiC foams of Ø24mm x 40mm were employed in the lower, sulphuric acid thermal dissociation zone as flow diffusers and heat transfer media upon which the $H_2SO_4$ vapors decompose Three non-coated and five coated foams were placed in each one of the six tubes.
- Aspects addressed in the design and construction included materials solutions for the manifolds for the injection of the sulphuric acid solution, evaporator tubes, sealants, special ceramic adhesives to join anti-corrosive metallic-to-ceramic tubing (stainless steel to SiC) and materials and reactor solutions to compensate for thermal expansion/contraction.
- During the shutdown or emergency, the hot particles inside the reactor are vented out via an emergency exit (on the reactor door) into a water-cooled emergency container.
- The particle heating system consists of a 100-liters-volume particle container and a 1-meter-long, 35°-inclined heater tube wrapped with resistively heated elements and encapsulated with insulation.
- Thermocouples were placed on the surface of every tube at different positions to measure temperature distribution along them.

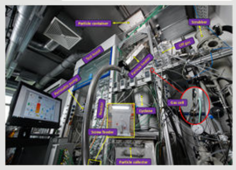






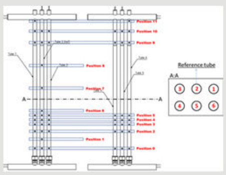






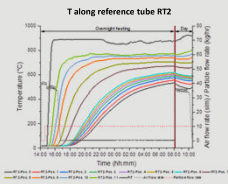
## Results

- The particle heater and the reactor performance were thermally tested prior to any chemical tests and the critical temperatures like particle inlet temperature (PIT), temperatures at position 1 (beginning of the tubes), position 6 (end of the evaporator zone) and position 11 (top of the catalytic zone) were reviewed during multiple thermal tests.
- During the start-up of every experiment, the reactor shell is filled completely with cold particles. Then when the particle heater is turned on, the screw feeder (at the bottom of the reactor) enables the hot particles into the reactor by replacing the cold particles. The speed of the screw feeder defines the temperature of the hot particles falling into the reactor.
- With a constant particle flow rate of approximately 10 kg/hr **the heater could deliver constant PIT of 890°C, higher than the targeted 850°C for the $SO_3$ splitting step** where the employed catalysts have demonstrated near-equilibrium conversion.
- By applying overnight heating (i.e. running the test setup overnight with the same, low flow rate of particles) the temperature distribution measurements on **reference tube RT2** showed that the temperature **of position 11 (top of catalyst zone) was close to 800°C and that at position 1 (beginning of the evaporator zone) above 400°C.**
- However, despite the fact that the reference reactor tube reached the targeted temperature, the temperatures of the six tubes at the same "vertical" position were not equal**.** This issue is attributed to uneven particle flow pattern around the tubes: injection of hot particles closer to reference tube, non-symmetric shell design (heat shield at the right-hand side).



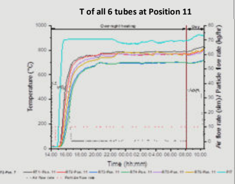


One of the six tubes (tube 2) served as a reference, equipped with more thermocouples (TCs); the remaining five tubes had the same number of thermocouples placed at the same position.

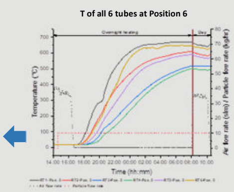




**RT2:** temperature of position 11 (top of catalytic zone**)** ~ **800°C,** very close to targeted, and at position 1 (beginning of evaporator zone) > **400°C.**









Different temperatures of 6 tubes at same "vertical" position. At top of catalytic zone (position 11), tube 1 has reached ~ 800°C, but temperatures of tubes 3 and 4 were ~ 100°C lower.

## Summary & Outlook

- A 2-kW lab-scale reactor for thermal sulphuric acid decomposition and catalytic sulphur trioxide splitting was in-house designed, built and tested with **electrically heated bauxite particles,** demonstrating the in-principle feasibility of the proposed concept.
- The reactor successfully underwent multiple thermal test runs demonstrating the in-principle feasibility of both sulphuric acid decomposition as well as of $SO_3$ splitting. The temperatures reached in the lower sulphuric acid evaporation zone (~ 400°C) were sufficient to ensure complete sulphuric acid evaporation. However, the ones reached in the upper $SO_3$ splitting zone were of the order of 750°C, high enough to demonstrate $SO_3$ splitting but not reaching the levels required for satisfactory conversion (~ 850°C).
- An improved reactor version incorporating design modifications based on lessons learned from the test campaigns, is under construction in the perspective of scaling up the process and coupling it to a centrifugal particle solar receiver on a solar tower.

## Acknowledgements

This work was performed within the projects "PEGASUS: Power generation by solar particle receiver driven sulphur storage cycle" having received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727540 and "HySelect: Efficient water splitting via a flexible solar-powered hybrid thermochemical-sulphur dioxide depolarized electrolysis cycle" supported by the Clean Hydrogen Partnership and its members Hydrogen Europe and Hydrogen Europe Research.

Clean Hydrogen Partnership

DLR