Allothermally Heated Reactors for Solar-Powered Implementation of Sulphur-Based Thermochemical Cycles

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1. Introduction

Thermochemical cycles of the sulphur family recycle sulphur as the central element that appears in different compounds at changing oxidation state. Such cycles like the Hybrid Sulphur (HyS) and the Sulphur-Iodine (SI) cycle were originally conceived to produce hydrogen via water-splitting, but can be also modified to produce solid sulphur that can be combusted in air to produce high-temperature heat and hence can be used both as a renewable fuel as well as a seasonal solar energy storage medium [1]. These three cycles share the common step of the decomposition reaction of sulphuric acid (Table 1): first thermally to steam and SO_3 (1a) and subsequently the catalytic SO_3 dissociation (splitting) to SO_2 and oxygen (1b), their highest-temperature (700-950°C) step. These two endothermic steps are performed together in sequence and can be driven by heat supplied via concentrated solar irradiation, either directly on porous ceramic volumetric receivers/ reactors or allothermally via gaseous or solid particles heat transfer fluids (HTFs) heated in a solar receiver at sufficiently high temperature and transferring their enthalpy to a sulphuric acid decomposer downstream of the solar receiver [2]. In the latter case, structural materials and reactor design issues relevant to the corrosive characteristics of sulphuric acid chemistry at high temperatures can be much easier addressed.

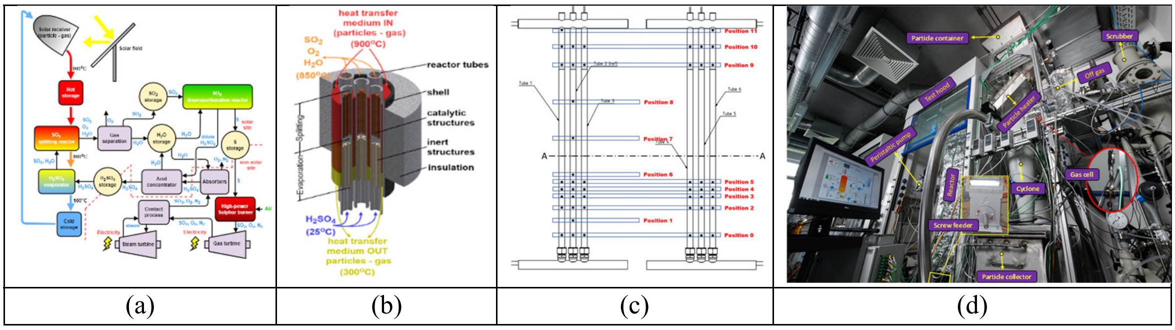
Reactions		Temperature (°C)	ΔH^0 (kJ/mol)
Sulphuric acid dissociation (1a)	$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$	450-500	+98
SO_3 splitting (1b)	$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2} O_2(g)$	700-950	+99

Table 1: High-temperatures steps common to the Hybrid Sulphur (HyS), Sulphur-Iodine (SI) and solid sulphur thermochemical cycles.

2. The novel particles-heated shell-and-tube sulphuric acid splitting reactor

In the perspective of scaling up the process and coupling it to a centrifugal particle solar receiver [3], as depicted in Fig. 1a, extensive analysis described in previous works [4, 5] concluded to the selection of a shell-and-tube type reactor/heat exchanger to perform the two reactions downstream of the receiver with solar-receiver-heated bauxite particles as HTF flowing downwards in the shell side and providing the necessary heat for the SO_3 splitting reaction at the upper part of the reactor and for the thermal dissociation of sulphuric acid at the lower. In the tube side, rising sulphuric acid vapours come into contact with a non-moving catalyst bed containing the catalyst in various structured forms like honeycombs or foams (Fig. 1b). A proof-of-concept, 2 kW reactor/heat exchanger comprised of six catalytic tubes (Fig. 1c), designed to be heated through bauxite particles flowing in the shell through an electrically- heated inclined belt feeder was constructed (Fig. 1d). Details on the catalytic systems selected and on the reactor's design and construction were provided in previous publications ([5], [6], respectively). Aspects addressed in the design and construction include 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 e.g. (stainless steel to SiC) and materials and reactor solutions to compensate for thermal expansion/contraction [7]. The unit was equipped with an in-house developed customized UV-Vis spectrometry system with a specifically designed corrosion and high-temperature resistant gas cell, for on-line analysis of produced SO_2.

The reactor successfully underwent multiple thermal and chemical test runs demonstrating the feasibility of both sulphuric acid decomposition as well as of SO_3 splitting. The temperatures reached in the lower sulphuric acid evaporation zone (~ 400ºC) 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 (~ 850ºC), resulting thus an overall effective average SO_3 conversion of 43.6%. Post-operation evaluation of the reactor parts and catalysts is currently ongoing together with re-design and development of an improved reactor version.



(a) (b) (c) (d)

Fig.1: (a) Schematic process diagram, combining a solar receiver with an allothermally-heated solid sulphur cycle for power production; (b) schematic of cascade reactor operation concept with particles or gas as HTF; (c) schematics of six reactor tubes included in the actual reactor within two 3-tube bundles indicating the thermocouple positions for temperature measurements along the tubes; (d) overall lab-scale particles-heated reactor/heat exchanger test setup unit with particles heater and necessary peripherals.

3. Conclusions and outlook

The development of high-temperature (> 850ºC) heat transfer fluids for CSP plants, provides for implementation of endothermic reactions via concentrated solar energy in suitably designed allothermally-heated reactors/heat exchangers placed away from the solar receiver. Such a 2-kW laboratory-scale reactor to perform 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. An improved version of the reactor is under construction incorporating design modifications based on lessons learned from the test campaigns, in the perspective of scaling up the process and coupling it to a centrifugal particle solar receiver operating on a solar tower.

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