Solar thermochemical hydrogen production: Experimental analysis and modelling of a solar reactor for decomposition of sulphuric acid

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Abstract

Solar thermal hydrogen production with sulphur based thermochemical cycles can reach significantly higher efficiency than conventional water electrolysis. For these cycles decomposition of sulphuric acid is a key step allowing to couple concentrated solar radiation into the process. DLR developed a two-chamber test reactor to technically realise and experimentally analyse this reaction in the solar furnace in Cologne. Moreover, a model of the second reaction chamber for decomposition of SO_3 was implemented and validated by experimental data.

1 Introduction

In the European research project **HycycleS** the Hybrid Sulphur Cycle (HyS) was analysed as a promising process to thermochemically produce hydrogen from water using concentrated solar radiation. Chemicals like sulphuric acid and sulphur dioxide work as energy carriers and are recycled within this two-step process (
Figure 1). In the first reaction the acid is decomposed by high temperature heat forming sulphur dioxide, which is subsequently electrolysed together with water in the second step. This electrolysis producing hydrogen and fresh sulphuric acid required only about a tenth of the energy needed for conventional electrolysis of water. Hence, overall efficiency of the water splitting can be significantly increased by the HyS.

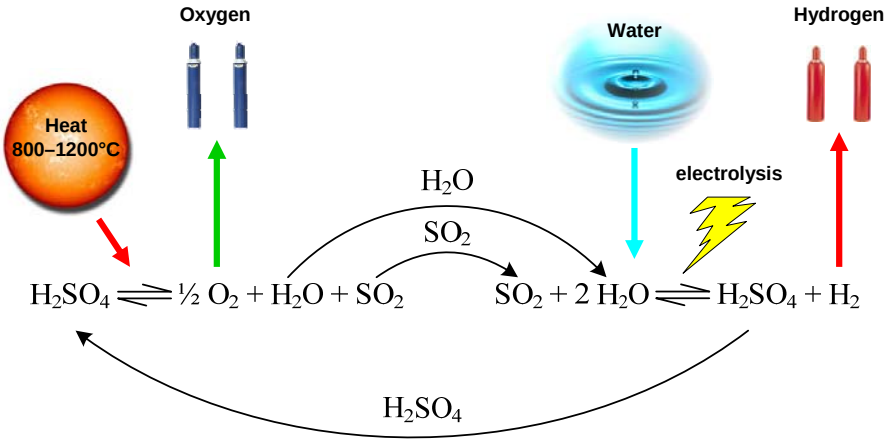

Figure 1: Hybrid-Sulphur-Cycle (HyS)

Decomposition of sulphuric acid is a highly endothermic reaction allowing to couple concentrated solar radiation into the HyS. DLR developed a receiver-reactor[1] to analyse this key step of the process in its solar furnace in Cologne. It consist of two separate chambers (Figure 2): in the evaporator liquid sulphuric acid is vaporised at a temperature of about 400°C forming SO_3, which is catalytically reduced to SO_2 in the decomposer at about 850°C. These reactions are carried out in absorbers of siliconized silicone carbide (SiSiC) heated by concentrated solar radiation. In the evaporator a foam structure is used, while the second chamber has an absorber in the shape of a honeycomb coated by a catalytic material to increase the reaction rate.

2 Results

In systematic testing series the performance of the reactor was analysed at various operating conditions examining different temperatures, volume flow rates and catalysts. These experiments are time consuming so that they are accompanied by modelling work to study operating points, which could not be realised in the solar furnace, and, by this, gain an in-depth understanding of the process. Modelling of the second reaction chamber for de-

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composition of SO_3 was performed with the software package Dymola® based on the Modelica® modelling language. In the preceding project HYTHEC a model of a similar reactor[2] had been developed, which was adapted to the conditions of the HycycleS reactor. The model consists of a set of interconnected sub-models of the absorber, the gas flow, the solar radiation and the isolating material. Central element is the sub-model of the honeycomb structure (Figure 3). Assuming a 2-dimensional rotation-symmetric characteristic of the system, the solar absorber is divided into cylindrical slices in axial direction, which are subdivided into rings along the radius with a cylinder in the middle. The model takes the solar power, the volume flow rate of sulphuric acid, the acid concentration, the volume flow rate of the carrier gas nitrogen and the temperature of the inlet gases as input parameters, and calculates the temperature distribution of the honeycomb, the conversion of SO_3, the temperature of the outlet gas and the thermal efficiency of the reaction chamber.

Figure 2: Solar reactor for decomposition of H_2SO_4

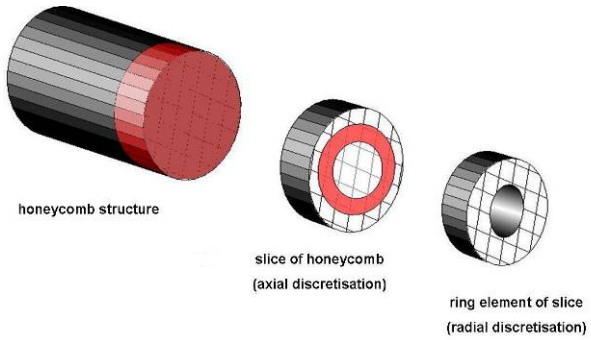

Figure 3: Discretisation of honeycomb absorber

3 Discussion

Validation of the model was carried out by comparing the simulated values with experimental data available from the solar furnace tests. These experiments were performed with a Fe_2O_3 catalyst and sulphuric acid of 50 w-% concentration. The average temperature of the absorber measured during these tests could be modelled with a relative deviation of less than 5% indicating that the thermal behaviour of the system is well simulated. The conversion of SO_3 calculated by the model corresponds to the experimental values within the accuracy of measurement at volume flow rates of more than 4 ml/min. At smaller acid flow rates, however, conversion is overestimated by the simulation. This is attributed to the kinetic parameters implemented in the model, which were derived for conditions far off equilibrium, while the presented experiments were carried out close to equilibrium. Of central interest is the efficiency of the reactor, which is only slightly effected by the chemical reaction as most of the energy is stored in form of sensible heat. As a result, the model accurately predicts the efficiency of the system.

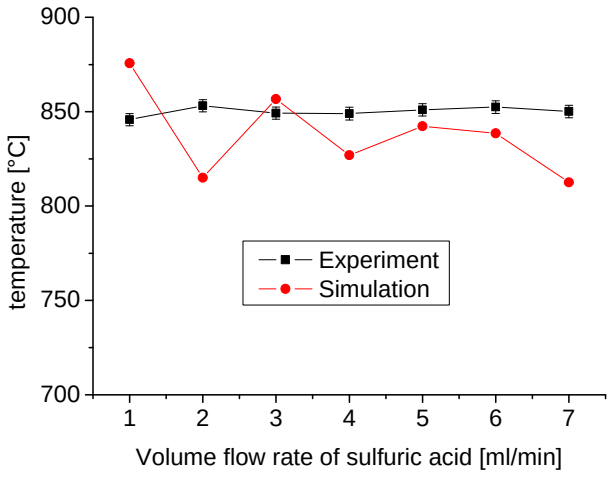

Figure 4: Mean honeycomb temperature

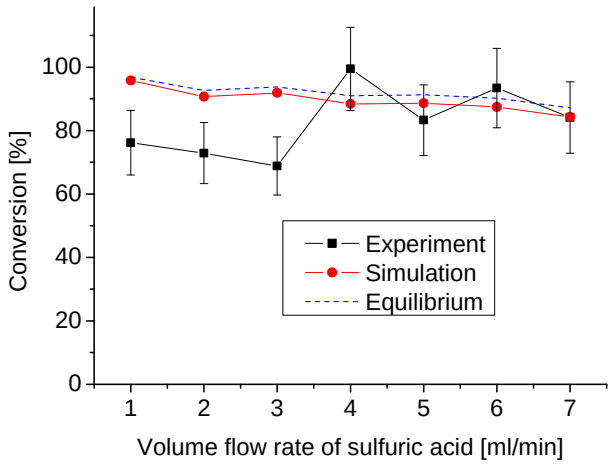

Figure 5: Conversion of SO_3

4 Conclusion and outlook

Decomposition of sulphuric acid with concentrated solar radiation was successfully carried out in a solar reactor developed in DLR's solar furnace in Cologne during the HycycleS project. Results of a systematic experimental analysis were used to validate a model of the second reaction chamber for reduction of SO_3. Modelling of the system's thermal behaviour is accurate while the chemical reaction can only be simulated at elevated flow rates. This, however, is sufficient as the model was especially developed to simulate the system's performance at high through-put, which could not be analysed experimentally. Moreover, simulation of transient behaviour during start-up and shut-down as well as during fluctuating of intermitting solar power can be carried out with the model to gain a better understanding of the process at realistic operating conditions. This information can then be used to conduct techno-economical studies and prepare the development of a pilot plant as the next step to realise the technology at industrial scale.

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