DEVELOPMENT AND TEST OF A SOLAR DECOMPOSER OF SULPHURIC ACID FOR THERMOCHEMICAL HYDROGEN PRODUCTION

D. Thomey, F. Lennartz, D. Schöllgen, L. de Oliveira, J.-P. Säck, M. Roeb, C. Sattler
German Aerospace Center (DLR), Solar Research
Linder Hoehe, 51147 Koeln, Germany
E-mail: dennis.thomey@dlr.de

ABSTRACT

Decomposition of sulphuric acid is a key step of sulphur based thermochemical cycles for hydrogen production by thermal splitting of water. The Hybrid Sulphur Cycle (HyS) consisting of two reaction steps [1] is considered as one of the most promising cycles: Firstly, sulphuric acid is decomposed by high temperature heat of 800-1200°C forming sulphur dioxide (SO_2), which in a second step is used to electrochemically split water. Compared to conventional water electrolysis only about a tenth of the theoretical voltage is required making the HyS one of the most efficient processes to produce hydrogen by concentrated solar radiation [2]. As a result, this thermochemical cycle has the potential to significantly reduce the amount of energy required for water splitting and to efficiently generate hydrogen free of carbon dioxide emissions.

The European research project HycycleS (Materials and components for Hydrogen production by sulphur based thermochemical cycles) [4] aims at a technical realisation of the Hybrid Sulphur Cycle. One objective of the project is to develop and qualify a solar interface, meaning a device to couple concentrated solar radiation into the endothermal steps of the chemical process. Therefore a test reactor for decomposition of sulphuric acid by concentrated solar radiation was developed and tested in the solar furnace of DLR in Cologne. Based on the preceding project HYTHEC (HYdrogen THErmochemical Cycles) [3] an optimised reactor concept with two chambers was constructed [5]: In the evaporator liquid sulphuric acid is vaporised on a solar absorber made of a foam structure of siliconized silicon carbide (SiSiC) at a temperature of about 400°C. The product gas mainly consisting of sulphur trioxide (SO_3) and water vapour is subsequently conveyed to a second chamber, the decomposer, in which SO_3 is reduced on a catalytically activated SiSiC honeycomb structure at a design temperature of 850°C. A UV/Vis spectrometer in the exhaust section of the reactor analyses the amount of SO_2 produced during decomposition. Tests in concentrated solar radiation were carried out for temperatures of the honeycomb of up to 950°C decomposing sulphuric acid of 50 and 96 weight-percent. Mass and energy flow of the process were calculated in able to determine energy efficiency and chemical conversion. The influence of process parameters like temperature, flow rates and space velocity on chemical conversion and reactor efficiency was analysed in detail. If catalysts like iron oxide (Fe_2O_3) and mixed oxides (i.e. $CuFe_2O_4$) were used a conversion of SO_3 to SO_2 of more than 80% at a thermal efficiency of over 25% could be reached.

INTRODUCTION

By generating hydrogen from water solar energy can be chemically stored to compensate for daily and seasonal fluctuations of the insolation as well as regional differences of sun light available. Benchmark system for this process is the alkaline electrolysis, which requires the production of electrical energy and, hence, is limited in its efficiency by the efficiency of the power generation. Direct splitting of water applying thermal energy, however, would require temperatures in excess of 2000°C in order to gain sufficient amounts of hydrogen. Therefore, thermochemical cycles are introduced dividing the water splitting reaction into several sub-steps, which proceed at technically manageable temperatures. The Hybrid Sulphur Cycle (HyS) depicted in Figure 1 is considered as one of the most promising cycles [1].

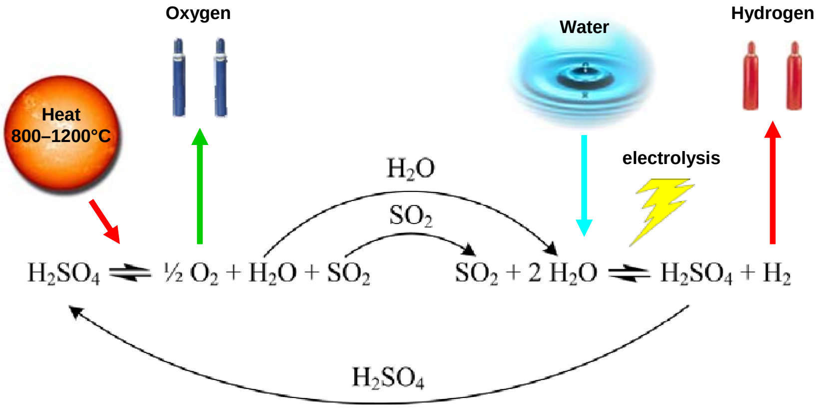


Fig.1. Hybrid Sulphur Cycle (HyS).

It consists of an endothermal high-temperature step of 800-1200°C and a slightly exothermal electrochemical reaction proceeding at about 80°C. High temperature heat required to decompose sulphuric acid in the first reaction can be provided by concentrated solar radiation. The emerging sulphur dioxide is, subsequently, electrolysed together with additional water forming hydrogen and fresh sulphuric acid, which is recycled to the first reaction step. The theoretical voltage required is nearly an order of magnitude smaller than for the conventional water electrolysis. As a result, the overall efficiency of the HyS is about 50% higher than for the benchmark system [2].

In the European research project HycycleS (Materials and components for Hydrogen production by sulphur based thermochemical cycles) [4] materials and technical applications for realisation of the Hybrid Sulphur Cycle were developed and analysed. Major task is the construction of a test reactor for decomposition of sulphuric acid and its operation in the solar furnace of DLR in Cologne. During the preceding project HYTHEC (HYdrogen THErmochemical Cycles) [3] solar thermal dissociation of H_2SO_4 was successfully demonstrated in a single chamber receiver-reactor. This application was the starting point for the development of an optimised reactor concept with two separate reaction chambers [5].

DEVELOPMENT OF SOLAR REACTOR

Decomposition of sulphuric acid can be divided into to reaction steps:

1. Vaporisation of liquid sulphuric acid (400°C): $H_2SO_{4\,(l)} \rightarrow SO_{3\,(g)} + H_2O_{\,(g)}$

2. Catalytic dissociation of sulphur trioxide (850°C): $SO_{3\,(g)} \rightarrow SO_{2\,(g)} + \frac{1}{2}\, O_{2\,(g)}$

The design temperatures of the two reactions given in brackets differ significantly. As a result, a multi-chamber design was developed to separate the steps and thermodynamically optimise the process (Figure 2).

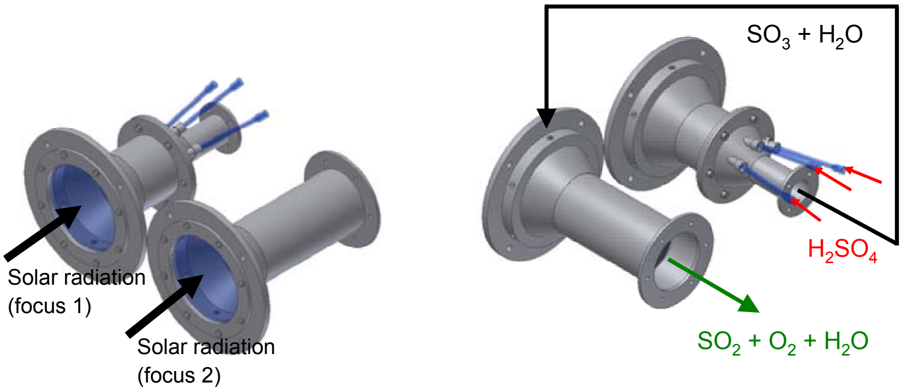


Fig.2. Design of solar reactor for decomposition of sulphuric acid.

Both compartments are made of high-alloyed steel and closed by a quartz glass window at the front side to avoid discharge of acidic gases and at the same time allow solar radiation to enter the system. Siliconized silicone carbide (SiSiC) structures (Figure 3 a) are used to absorb the radiation and transfer the produced heat to the reaction gases. Liquid sulphuric acid is fed to the first chamber, the evaporator, from behind via three quartz glass tubes. Vaporisation is carried out inside a SiSiC foam structure irradiated at the front side. The produced vapour is conveyed to the second chamber by a joule heated steel piping. In the decomposer a SiSiC honeycomb structure is used to dissociate the sulphur trioxide forming sulphur dioxide and oxygen. A catalyst coating is applied to this absorber to increase the reaction rate and reach high reaction rates at temperatures below 1000°C. The two reaction steps proceeds inside the solar absorbers so that this type of solar systems is named receiver-reactor. The power directed to the reactor is regulated separately for both chambers using a segment shutter (Figure 3 b) located in front of the system. The product gas at the outlet is analysed by spectrometry to determine the amount of SO_2 and evaluate the chemical performance of the reactor. Moreover, temperatures of gases and solid material are measured at different positions in the reactor by a set of thermocouples. In addition, the solar flux distribution in the front plain of both absorbers is measured before the beginning of the experimental campaign in order to evaluate the thermal efficiency of the system. In a modified version of the reactor an electrical evaporator was installed to separately operate the decomposer. With this application vaporisation was more stable and less effected by fluctuations of solar irradiation.


(a) (b)

Fig.3.Solar reactor (a) with foam absorber in evaporator (left) and honeycomb in decomposer and (b) during operation in DLR's solar furnace.

Gas analysis system for measurement of sulphur dioxide concentration

The concentration of SO_2 is measured behind the decomposer by UV/Vis spectrometry applying Beer-Lambert's law:

$$E = -\lg\left(\frac{I}{I_0}\right) = \varepsilon \cdot c_{SO2} \cdot d \tag{1}$$

In order to achieve the highest accuracy, the absorption band of SO_2 is evaluated at its absorption peak, which was determined during the experiments to be at a wavelength of about $\lambda = 286$ nm (Figure 4).

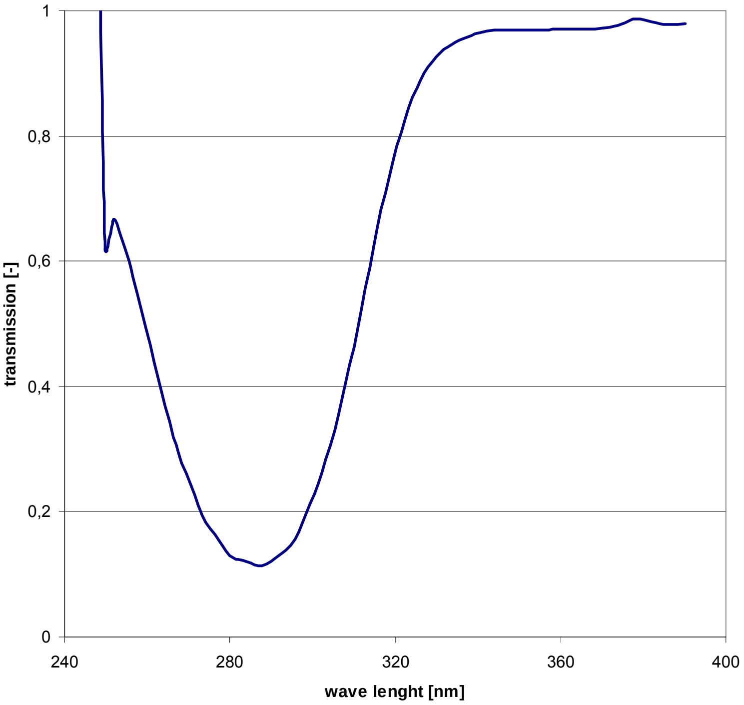


Fig.4. Transmission of product gas measured by UV/Vis spectrometry.

For measurement of the absorbance, the exhaust pipe is equipped with two parallel sight glasses to send a light beam of a xenon arc lamp through the gas stream. The transmitted fraction of the light with a spectrum in the range of ultraviolet to visible is analysed with a UV/Vis-spectrometer (EPP 2000, StellaNet Inc.). Up-stream of the spectrometric measurement compressed air is injected strongly diluting the gases as the spectrometer can only be operated at a SO_2 mole fraction well below 5%. The molar absorptivity is determined by a calibration, during which a defined amount of sulphur dioxide gas is injected into the system. This calibration needs to be carried out at the same temperature as during the experiments with sulphuric acid as ε is strongly dependent on the gas temperature.

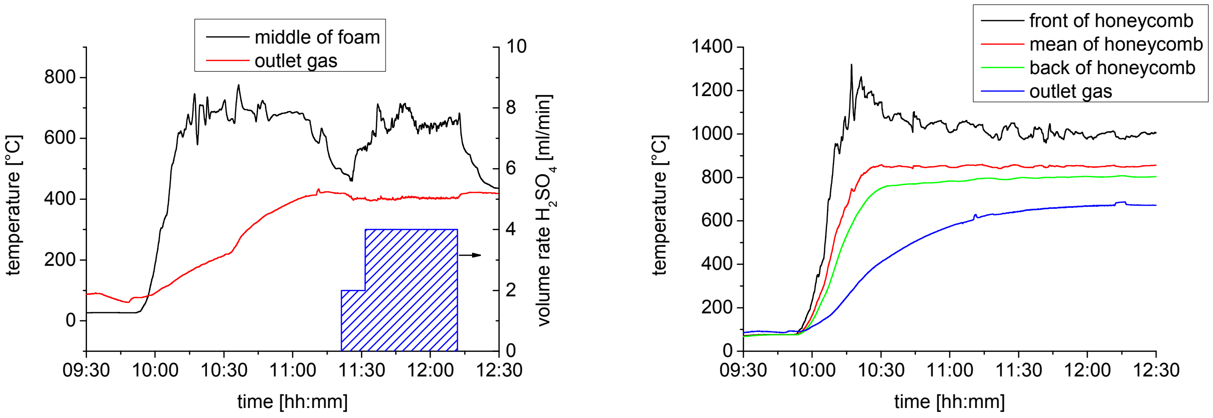
EXPERIMENTAL RESULTS

During an extended experimental analysis between 2009 and 2010 more than 70 operation points at steady state have been studied (Table 1). Two different catalysts were tested in the decomposer as well as one blank honeycomb. Has mentioned before, an electrical evaporator was used for some of the experiments.

Table 1. Overview of experiments.

Catalyst		**blank**	**Fe_2O_3**		**$CuFe_2O_4$**	
Evaporator		solar	solar		solar	electrical
Number of experiment		17	17	11	7	20
Sulphuric acid concentration	w%	50	50	96	96	96
Sulphuric acid flow rate	ml/min	1…7	1…7	2…6	2…4	2…6
Mean honeycomb temperature	°C	850	850	650…950	650…950	750…900
Residence time	s	0.3	0.3…1	0.2…0.5	0.5	0.5…0.7
Weight hourly space velocity	1/h	n/a	0.6…4.0	1.4…4.4	1.4…2.9	1.4…4.4

As an example, temperatures of the evaporator and decomposer chamber during one of the experiments are depicted in Figure 5. This test was started by heating up the reactor for about 1.5 hours to reach an outlet temperature of the carrier gas nitrogen coming from the evaporator of about 400°C and a mean temperature of 850°C for the honeycomb. At that moment, the highest temperature in the foam was about 600°C, which immediately dropped when H_2SO_4 of 50 w% at a volume flow rate of 4 ml/min was injected. In order to maintain an outlet temperature of 400°C, the solar power for this chamber had to be increased. During the whole time the power for the decomposer was adjusted in a way to keep the mean temperature of the honeycomb at a constant level. The temperature distribution in the honeycomb was quite uniform with a temperature difference between front (1000°C) and back (800°C) of only about 200°C. As a result, the temperature of the gases at the outlet of the decomposer reached a value of about 700°C.



(a) (b)

Fig.5. Temperature distribution in (a) the evaporator during injection of sulphuric acid and (b) the corresponding temperatures in the decomposer.

Conversion of sulphur trioxide in decomposer

The performance of the solar reactor is evaluated by a set of parameters derived from the experimental data. The conversion of sulphur trioxide is important to determine the chemical performance of the reactor. It is defines as the amount of sulphur dioxide at the outlet of the decomposer related to the amount of sulphur trioxide in the reaction gas before entering the honeycomb:

$$X_{SO3} = \frac{\dot{n}_{SO2,out}}{\dot{n}_{SO3,in}} \qquad (2)$$

The molar flux of SO_2 is determined by applying Beer-Lambert's law to the spectrometric measurement (Eqn. 1) while the molar flux of SO_3 at the inlet is derived from the volume flow rate of the acid pump assuming complete dissociation of sulphuric acid to SO_3 and H_2O at the inlet of the decomposer:

$$\dot{n}_{SO3,in} = \frac{\dot{V}_{acid} \cdot \rho_{acid} \cdot w_{acid}}{M_{H2SO4}} \tag{3}$$

In Figure 6 the conversion of SO_3 in the decomposer chamber is given for a blank honeycomb and a Fe_2O_3 coating. The amount of sulphuric acid has nearly no effect on the catalytic conversion with an average value of 76% because the thermodynamic maximum of about 90% has almost been reached. By contrast, a mean value of about 40% was measured for the uncoated absorber, which drops to 20% at 7 ml/min of acid. Accordingly, equilibrium was not reached for this homogenous reduction with a blank honeycomb.

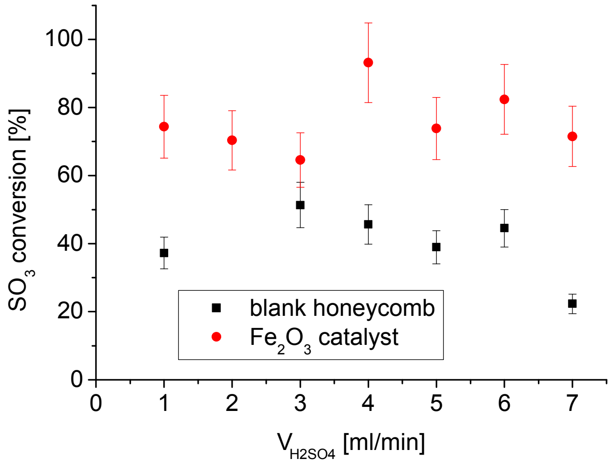
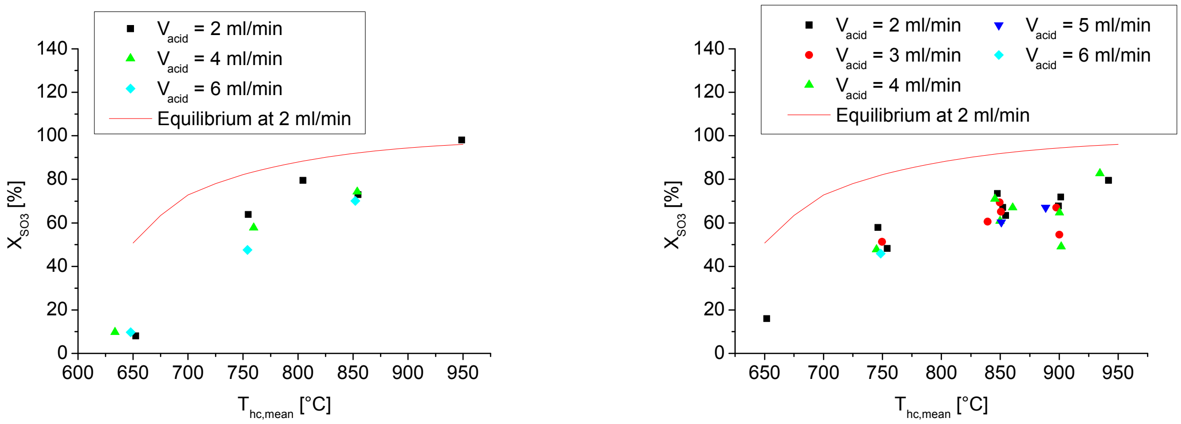


Fig.6. Conversion of SO_3 at 850°C and different flow rates of sulphuric acid with 50 w% for a blank honeycomb and a Fe_2O_3 catalyst.

Variation of the temperature strongly affects conversion as indicated by Figure 7. For the two catalysts tested similar conversions were reached whereas Fe_2O_3 seems to be slightly more active. In order to decompose more than 60% of the SO_3, a mean honeycomb temperature in excess of 800°C is required. Variation of acid flow rate in the range of 2 to 6 ml/min has little effect on the conversion. A significant increase of the volume flow would be required in order to analyse its influence on the chemical reaction.



(a) (b)

Fig.7. Conversion of SO_3 at different temperatures and flow rates of sulphuric acid with about 94 w% for (a) a Fe_2O_3 and (b) $CuFe_2O_4$ catalyst.

Residence time and weight hourly space velocity in honeycomb

The residence time determines the time reaction gases need to pass through the absorber of the decomposer. It is defined as the ratio of the open volume of the honeycomb structure (total volume of all channels) and the volume flow rate of all gases:

$$\tau_{res} = \frac{V_{hc,open}}{\dot{V}_{hc,gas}} \tag{4}$$

Due to decomposition of SO_3 into SO_2 and O_2 the gas volume increases over the length of the absorber. For simplification, we assume that the volume flow rate is constant and equals the flow rate at the outlet of the honeycomb structure. Moreover, the gas temperature is assumed to be equal to the mean temperature of the absorber. In general, conversion of SO_3 decreases if the residence time is increased. For the experiments presented here, however, only little impact was found.

By contrast, the weight hourly space velocity (WHSV) only considers the effective mass of H_2SO_4 injected into the system and relates this to the mass of catalyst applied to the absorber:

$$\mathrm{WHSV} = \frac{\dot{m}_{\mathrm{acid}} \cdot w_{\mathrm{acid}}}{m_{\mathrm{cat}}} = \frac{\dot{m}_{\mathrm{H2SO4}}}{m_{\mathrm{cat}}} \tag{5}$$

In this equation inert gases are not considered and have, hence, no effect on the space velocity. WHSV is proportional to the volume flow rate of sulphuric acid.

Thermal efficiency of reactor

To evaluate the performance of the solar reactor as a whole and to separately qualify the two reaction chambers, four different thermal efficiencies are defined. All of them relate the enthalpy difference of the fluids in the reactor to the solar power directed to the system. The net efficiency of the evaporator is defined as:

$$\eta_{\mathrm{net,evap}} = \frac{\dot{Q}_{\mathrm{net,evap}}}{P_{\mathrm{solar,evap}}} \tag{6}$$

relating the net energy needed to vaporise the liquid acid to the solar power directed to the evaporator. Moreover, the net efficiency of the decomposer is introduced as the ratio of net energy consumed during dissociation of SO_3 and solar power directed to the decomposer:

$$\eta_{\mathrm{net,decomp}} = \frac{\dot{Q}_{\mathrm{net,decomp}}}{P_{\mathrm{solar,decomp}}} \tag{7}$$

Both net efficiencies also include the amount of sensible heat consumed by the produced gases. In order to qualify the complete system, we define an overall net efficiency

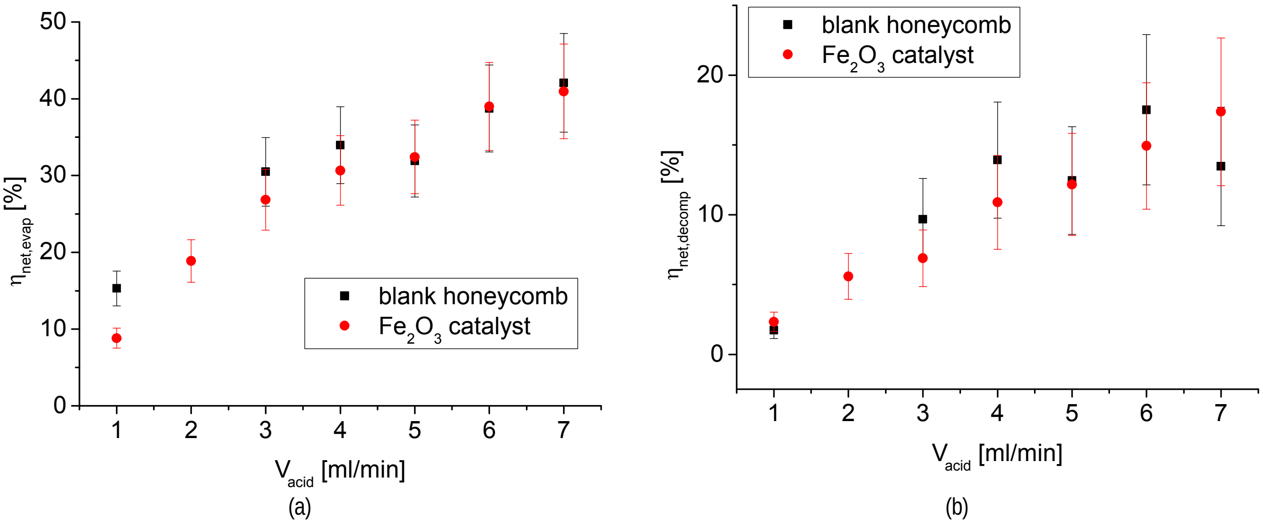
$$\eta_{\mathrm{net}} = \frac{\dot{Q}_{\mathrm{net,evap}} + \dot{Q}_{\mathrm{net,decomp}}}{P_{\mathrm{solar,evap}} + P_{\mathrm{solar,decomp}}} = \frac{\dot{Q}_{\mathrm{net}}}{P_{\mathrm{solar}}} \tag{8}$$

relating the sum of solar power and energy consumption of evaporator and decomposer. Furthermore, an overall reactor efficiency is introduced, which additionally considers sensible heat consumed by the inert carrier gas nitrogen:

$$\eta_{\mathrm{reactor}} = \frac{\dot{Q}_{\mathrm{net}} + \dot{Q}_{\mathrm{inert}}}{P_{\mathrm{solar}}} = \frac{\dot{Q}_{\mathrm{reactor}}}{P_{\mathrm{solar}}} \tag{9}$$

For the blank and Fe_2O_3 coated samples, of which conversions are presented in Figure 6, the thermal efficiencies of the two chambers and the reactor as a whole are given in Figures 8 and 9, respectively. During the experiments, the operating conditions of the first chamber were kept constant. Moreover, they are, as expected, not affected by the reaction in the second chamber. Accordingly, nearly the same net efficiency was found for the evaporator during homogenous and catalytic reduction of SO_3 in the decomposer (Figure 8 a). With increasing volume flow rate of acid, this efficiency considerably increases reaching a maximum value of about 40% at 7 ml/min requiring a solar power of 900 W.

The net efficiency of the decomposer is less than half of that of the evaporator (Figure 8 b). Throughout the examined range of flow rates the efficiencies of homogenous and catalytic decomposition correlate within their error ranges because the reaction enthalpy of the process is much smaller than the amount of sensible heat required. Again the efficiency is higher at greater volume flow rates with a maximum value of about 17%. The solar power consumed by the decomposer with a Fe_2O_3-coated honeycomb stays nearly constant for the given operating points with a mean value of about 1100 W.



(a) (b)

Fig.8. Net efficiency for different temperatures volume flow rates of (a) evaporator and (b) decomposer.

In Figure 9 the overall efficiencies of the solar reactor are given for the experiments with the Fe_2O_3 catalyst. Both values increase with increasing volume flow rate of acid indicating that a further increase of the flow rate would lead to even higher efficiencies. At 7 ml/min a net efficiency of 28% was found at a solar power of about 2000 W. During these experiments the amount of carrier gas in the system was decreased at increasing acid flow rate to keep the residence time of gases in the honeycomb at a constant value of 0.5 seconds. Consequently, the efficiencies depicted approach one another at high flow rates.

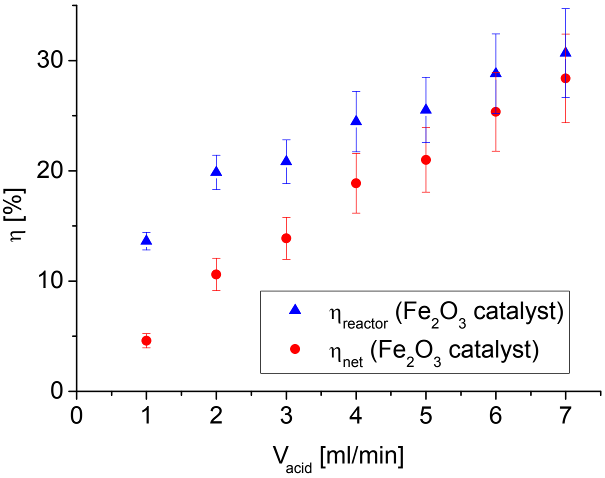
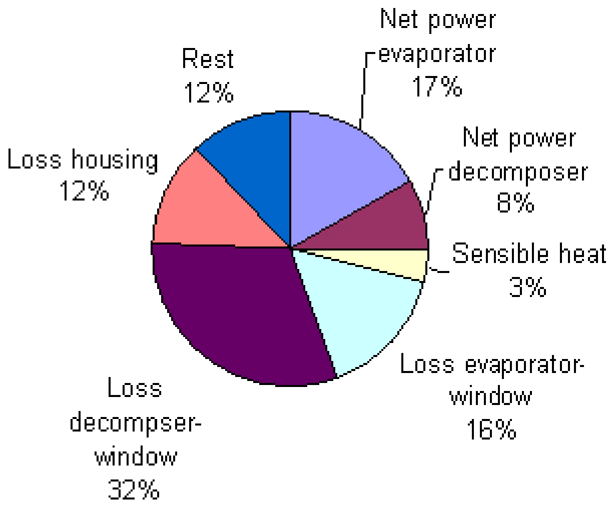


Fig.9. Overall efficiencies of the solar reactor (Fe_2O_3 catalyst).

Energy balance of reactor

In Figure 10 a pie chart is given for one exemplary operating point illustrating the different proportions of power consumed by the reactor. The net efficiency of 25% can easily be identified. Moreover, the heat loss at the windows is given with a total proportion of 48% including re-radiation of the absorbers and the windows as well as convection at the windows. Only a small proportion is lost via the housing while an unspecified residual of 12% remains in this analysis. Obviously, re-radiation losses are predominant for this system.



$P_{S,evap}$	870 W
$P_{S,decomp}$	1141 W
Catalyst	Fe_2O_3
V_{H2SO4}	6 ml/min
$T_{hc,mean}$	852 °C
Conversion	82 %
$\eta_{net,evap}$	39 %
$\eta_{net,decomp}$	15 %

Fig.10. Energy balance of the solar reactor.

CONCLUSIONS

For the technical realisation of solar decomposition of sulphuric acid a receiver-reactor has been developed and constructed. It consists of two chambers for vaporisation of liquid acid and subsequent reduction of sulphur trioxide.

In systematic testing series at DLR's solar furnace homogenous and catalytic decomposition of SO_3 have been analysed using Fe_2O_3 and $CuFe_2O_4$ as catalysts. Various volume flow rates between 1 and 7 ml/min of sulphuric acid at concentrations of 50 and 94 w% have been examined at temperatures of the second chamber of 650 to 950°C. In an energy balance of the system, a thermal efficiency of up to 28% was found while re-radiation of the solar absorbers was identified as the main heat loss. The multi-chamber concept of the reactor is scalable and mainly uses commercial materials like steel and silicon carbide while only few components are made of quartz. Hence, this development is an important step in the direction of an industrial realisation of solar hydrogen production by sulphur based thermochemical cycles.

Acknowledgement

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NOMENCLATURE

c	molar concentration, mol/m^3
d	optical path length, m
E	absorbance, -
I	intensity, W/m^2
m	mass, kg
M	molar mass, kg/mol
$\dot{m}$	mass flow, kg/s
$\dot{n}$	molar flux, mol/s
P	power, W
$\dot{Q}$	heat flow, W
T	temperature, °C
V	volume, m^3
$\dot{V}$	volume flow rate, m^3/s
w	mass concentration, kg/kg
w%	weight percent
X	conversion, -

Greek Letters

ε	molar absorptivity, m^2/mol
η	thermal efficiency, -

λ	wave length, m
ρ	density, kg/m^3
τ	time, s

Subscripts

0	reference (intensity)
hc	honeycomb
res	residence
S	solar

REFERENCES

[1] Brecher, L. E., S. Spewock, et al. 1977. The Westinghouse Sulfur Cycle for the thermochemical decomposition of water. *International Journal of Hydrogen Energy* 2(1): 7-15.

[2] Kolb, G. J. and R. B. Diver. 2008. Screening Analysis of Solar Thermochemical Hydrogen Concepts. Sandia National Laboratories.

[3] Le Duigou, A., J.-M. Borgard, et al. 2007. HYTHEC:An EC funded search for a long term massive hydrogen production route using solar and nuclear technologies. *International Journal of Hydrogen Energy* 32: 1516-1529.

[4] Roeb, M., D. Thomey, et al. 2011. HycycleS: a project on nuclear and solar hydrogen production by sulphur-based thermochemical cycles. *International Journal of Nuclear Hydrogen Production and Applications* 2(3): 202-226.

[5] Thomey, D., S. Hüttner, et al. 2010. Entwicklung eines Reaktors für die Schwefelsäurespaltung mit konzentrierter Solarstrahlung als Teil eines thermochemischen Kreisprozesses zur Wasserstofferzeugung. ProcessNet Jahrestreffen Reaktionstechnik, Würzburg, Germany.