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Process modelling and heat management of the solar hybrid sulfur cycle

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ARTICLE INFO

Article history:
Received 23 September 2014
Received in revised form
26 January 2015
Accepted 29 January 2015
Available online 26 February 2015

Keywords:
Thermochemical cycle
Hybrid sulfur
Flow sheet
Solar tower
Volumetric receiver
Sulfuric acid

ABSTRACT

Thermochemical cycles for water splitting are considered as a promising example of emission-free routes for large-scale hydrogen production – with potentially higher efficiencies and lower costs compared to low temperature electrolysis of water. The hybrid –sulfur cycle was chosen as one of the most promising cycles from the 'sulfur family' of processes. A process model has been established to study the main parameters influencing efficiency with specific attention paid to dynamic effects when coupled to solar heat. The process is separated into two sections – one at steady-state, and the other one fictively imposed by transients. This allows a first analysis with respect to reasonable energy and mass flow management, while considering concepts of coupling such a process to a concentrating solar system in a later step. Process efficiencies are calculated based on conservative assumptions, revealing the most important development tasks for the future. The extensive usage of recoverable high temperature heat – including the heat from the highly corrosive condensing phases – is a key factor to attain reasonable efficiencies for industrial application. With idealised heat recovery rates – limited by thermodynamic considerations, but excluding heat exchange between stationary and dynamic sections – and for decomposer temperatures appropriate for volumetric solar receiver operation, a thermal process efficiency close to 30% is predicted for stationary operation based on the lower heating value of hydrogen. Subsequent investigations will derive annual yields, taking into account the effect of coupling to solar energy.

Introduction

Only water and biomass are viable long term candidate raw materials for regenerative hydrogen production. Thermochemical cycles and electrolysis have the greatest likelihood of successful large-scale hydrogen production from water. The former have the potential of better efficiencies than the electrolysis route because the heat can be used directly. Hence, they have the potential to reduce the production costs of hydrogen from water significantly. The required energy can be either provided by a high temperature nuclear reactor (HTR) or by concentrated solar radiation. Many thermochemical cycles have been studied in the 1970–1980s for

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http://dx.doi.org/10.1016/j.ijhydene.2015.01.168

massive hydrogen production. Besides the so-called redox-cycles which have drawn a lot of attention in recent years [1,2], two cycles from the so-called sulfur-family emerged as being competitive in the available comparative studies [3,4]: the iodine–sulfur cycle [5] and the hybrid–sulfur cycle (HyS), also known as the Westinghouse cycle [6]. Rosen [7] presents the current status of research on thermochemical cycles and indicates that innovations to reduce peak process temperatures are necessary to increase process efficiency. The focus of the present contribution will be the integration of the HyS with a concentrating solar plant.

The hybrid sulfur cycle was originally conceived by Westinghouse Electric. Subsequently, the *ISPRA* project addressed the reaction closure step of the Westinghouse cycle, the thermal decomposition of sulfuric acid, and incorporated it as the *Mark 11* process which led to the development of the Cristina process [8].

Broggi et al. [9], Bilgen and Bilgen [10], Bilgen [11] proposed a modified version of the Cristina process which used oxygen instead of air as the energy vector and developed a process model for the modified Cristina process resulting in smaller components at comparable efficiencies. The flowsheet, although comprehensive for its time, presents overly simplified unit operation steps in the concentration of spent acid and separation of light constituents rendering it infeasible by today's standards of process technology. Hammache and Bilgen [12] adopted the flowsheet from Bilgen [11] and depicted day and night operation for a solar driven process. More recently, Hinkley et al. [13,14] designed a process model for the hybrid sulfur cycle in *Aspen HYSYS* and investigated different techniques of separating gas mixtures of SO_2 and O_2. The group of Gorensek and Summers conducted a highly comprehensive design and study of HyS driven by nuclear energy [15,16] as well as of HyS driven by concentrated solar energy [17]. The presented analysis provides a base line process concept to investigate coupling to solar heat at differentiated temperature levels, e.g. by means of directly irradiated reactor receivers as currently developed at DLR [18,19]. Depending on the concept for coupling to concentrated solar power (CSP), strong dynamics and day–night cycles might be imposed on the process. Thus, it has been divided into a high and a low temperature section, enabling to decouple the solar dependent units from stationary operated units. The impact of unit arrangement and heat management on overall efficiency is studied.

Currently, the authors are involved in integrating a dynamic model of a proposed reactor-receiver concept into the presented process model – covering considerations on solar field design and receiver performance. This will allow a transient simulation of the process to be presented in a follow-up paper.

Model of the HyS process

The hybrid sulfur process for hydrogen generation is depicted in Fig. 1, showing the superior process and auxiliary steps:

- SO_2 depolarized electrolyser (SDE)
- concentration of sulfuric acid
- cracking of sulfuric acid to produce SO_2
- gas separation to segregate O_2

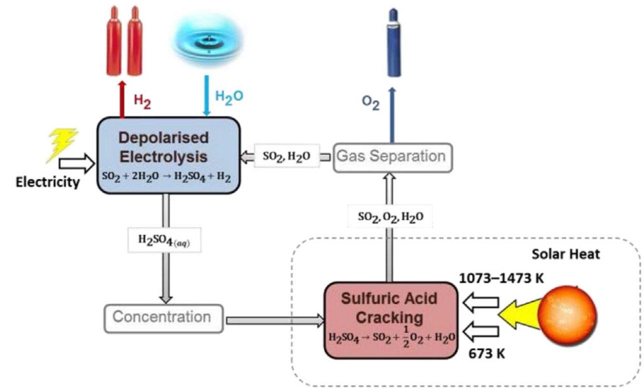

Fig. 1 – Scheme of HyS-Process.

In an SO_2 depolarized electrolyser (SDE), sulfurous acid is electrochemically converted to sulfuric acid and hydrogen.

The exiting stream of sulfuric acid – significantly diluted depending on the water content of the system – is then optionally concentrated to fulfil the optimum inlet parameters for the subsequent steps and the energetic optimum of the process.

The concentrated sulfuric acid is then evaporated and subsequently decomposed into steam, sulfur dioxide and oxygen in a process requiring heat at a high temperature levels and a suitable catalyst.

The oxygen must subsequently be separated from the product stream and can be used as by-product of the process.

Closing the cycle, sulfur dioxide highly diluted in water is fed back to the electrolyser.

Modelling the process

A flow sheet has been established in Aspen Plus™ to analyze energy and material streams of the HyS process, and to identify the aspects most critically impacting the process efficiency and thus, most important for necessary future research and development.

The flow sheet (Fig. 3) is designed to investigate the coupling of CSP to provide the required process heat. In order to minimize the impact of solar energy availability and fluctuations, a stationary and a dynamically operated section are introduced with buffer tanks as an interface between the two sections. There is no direct exchange of material and energy streams from one section to the other.

Dynamic section

The dynamic section of the process consists of concentration and decomposition of sulfuric acid including the auxiliary operations to get the products to the desired state for buffering.

The main purpose of the **concentration** step is to optimize the energy demand of the whole process by utilising the amount of sensible heat in the decomposer carried by the