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Economic comparison of solar hydrogen generation by means of thermochemical cycles and electrolysis

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ABSTRACT

Hydrogen is acclaimed to be an energy carrier of the future. Currently, it is mainly produced by fossil fuels, which release climate-changing emissions. Thermochemical cycles, represented here by the hybrid-sulfur cycle and a metal oxide based cycle, along with electrolysis of water are the most promising processes for 'clean' hydrogen mass production for the future. For this comparison study, both thermochemical cycles are operated by concentrated solar thermal power for multistage water splitting. The electricity required for the electrolysis is produced by a parabolic trough power plant. For each process investment, operating and hydrogen production costs were calculated on a 50 MW_{th} scale. The goal is to point out the potential of sustainable hydrogen production using solar energy and thermochemical cycles compared to commercial electrolysis. A sensitivity analysis was carried out for three different cost scenarios. As a result, hydrogen production costs ranging from 3.9–5.6 €/kg for the hybrid-sulfur cycle, 3.5–12.8 €/kg for the metal oxide based cycle and 2.1–6.8 €/kg for electrolysis were obtained.

1. Introduction

As one of the most promising future energy carriers, hydrogen is currently produced from fossil resources using reforming or gasification processes. This leads to carbon dioxide (CO_2) emissions of 0.3–0.4 m^3CO_2/m^3H_2 [1] and thus augments the greenhouse effect. In fact, hydrogen can only be considered as an environmentally friendly and sustainable alternative to fossil energy carriers, if it is produced from renewable energy and without harmful emissions. Thermochemical cycles (TCC) and electrolysis of water are environmentally friendly and most promising alternatives for the long-term CO_2-free hydrogen production, if operated by concentrated solar power. Both will be explained in detail and compared concerning their economic efficiency (investment, H_2 output, H_2 production costs) subsequently. The calculations of heat balances, solar field size and shape were made for plants with an annual average thermal power of 50 MW at a suitable site. The measure for the scale of the plant is the amount of heat coupled into the process. Costs for hydrogen compression, storage and distribution are not considered in this study.

2. Process description and plant layout

TCCs are processes which decompose water into hydrogen and oxygen via chemical reactions using intermediate reactions and substances. All of these intermediate substances are recycled within the process. Thus, the sum of all the reactions is equivalent to the dissociation of the water molecule. Theoretically, only heat is necessary to process these chemical steps [2]. This can be provided by concentrated solar energy using a central receiver system (CRS). The CRS consists of mirrors, so-called heliostats, which concentrate the sunlight

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Nomenclature

AF	annuity factor
CO_2	carbon dioxide
CRS	central receiver system
CSP	concentration solar power
DLR	German Aerospace Center
DNI	direct normal irradiation
e^-	electron
H_2SO_4	sulfuric acid
HPC	hydrogen production costs
i_r	interest rate
LEC	levelized electricity costs
MO	metal oxide
n	lifetime
O&M	operation and maintenance
OH^-	hydroxyl group
P_H	produced amount of hydrogen
PV	present value
R_{O_2}	revenue of oxygen
SO_2	sulfur dioxide
SO_3	sulfur trioxide
TCC	thermochemical cycles
TCI	total capital investment
TDI	total direct investment
TiO_2	titanium dioxide

onto the receiver. The receiver located on the top of the tower is made up of honeycomb-structured ceramics acting as an absorber for the solar radiation and as a chemical reactor.

Solar thermochemical hydrogen generation based on metal oxides and the hybrid-sulfur cycle are among those few candidates having the highest potential in terms of the feasibility of scale-up [3]. On the contrary, electrolysis, which is the electrochemical decomposition of water into hydrogen and oxygen [4], is an already mature technology which is seen as a benchmark for future hydrogen production.

Altogether, thermochemical cycles have the potential of a higher efficiency than alkaline electrolysis [3] and hence have the potential to reduce the production costs of hydrogen from water significantly.

2.1. *Thermochemical hydrogen production based on metal oxides*

The first considered process is a two-step thermochemical cycle based on metal oxides (MO) serving as the catalyst. The reaction scheme is as follows:

$$MO_{reduced} + H_2O \rightarrow MO_{oxidized} + H_2 (\text{splitting } 800\,^\circ C)$$

$$MO_{oxidized} \rightarrow MO_{reduced} + O_2 (\text{regeneration } 1200\,^\circ C)$$

The metal oxide acts as redox system which is fixed on the surface of a porous absorber. One promising redox system is the class of mixed iron oxides, as investigated, e.g. within the EU-Project HYDROSOL I + II, [5,6]. At the beginning, the metal oxide is present in a reduced form. By adding water vapor at 800 °C, oxygen is abstracted from the water molecules and hydrogen is produced. When the metal oxide system is saturated – meaning fully oxidized – it is heated for regeneration at 1100 °C to 1200 °C in an oxygen-lean atmosphere. Oxygen is exhausted from the redox system using nitrogen as a flushing gas [5]. The product gas passes through heat exchangers and is cooled down before residual water is separated. The receiver surface is divided into several square apertures; two apertures make up one receiver pair (Fig. 1). One aperture is applied for the dissociation of the water vapor, while the other one is used for the regeneration of the redox system. Thus, hydrogen can be produced continuously by alternating the reaction steps.

2.2. *Hybrid-sulfur cycle*

The hybrid-sulfur cycle, occasionally called "Westinghouse Cycle" [7], was investigated within the EU-project HYTHEC [8]. It is based on the decomposition of sulfuric acid (H_2SO_4) as a high temperature thermochemical step and the low temperature electrolytic reaction of water and sulfur dioxide (SO_2) [9]. The high temperature step consists of two sections: initially H_2SO_4 is thermally decomposed into water vapor and sulfur trioxide (SO_3) and the latter is reduced at temperatures up to 1200 °C to SO_2 and oxygen. Oxygen is separated and might be used as a byproduct.

In the low temperature step, SO_2 is oxidized to H_2SO_4 at the anode of an electrolyzer, while hydrogen is formed at the cathode according to the reaction scheme [10]:

$$H_2SO_4 \rightarrow H_2O + SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2 + H_2O$$

(thermal decomposition 1200 °C)

$$2H_2O + SO_2 \rightarrow H_2SO_4 + H_2 (\text{electrolysis } 85\,^\circ C)$$

For this process, a solar tower could consist of two cylindrical apertures; one for the electrical power generation and the other one for the chemical receiver reactor (Fig. 4). A helium-based Brayton cycle[1] could also be used for power generation. After the decomposition of the sulfuric acid, the hot gases flow through heat exchangers to transfer the excess heat to incoming streams. Oxygen is separated from the product gas flow by absorber units. Water is added to the cycle in the electrolyzer to oxidize the purified SO_2 to H_2SO_4 and hydrogen.

2.3. *Electrolysis*

Water electrolysis means the electrochemical splitting of water into oxygen and hydrogen using a conductive electrolyte (salts, acids, bases). In this case, an alkaline electrolyte is considered. Hydrogen is generated at the cathode while oxygen is produced at the anode of the electrolyzer. The charge equalization proceeds by ionic conduction. A porous membrane is located between the two electrodes to prevent the mixture of the product gases. To be a CO_2-free

[1] The Brayton cycle is a cyclic process generally associated with the gas turbine.