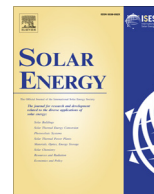




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Solar hydrogen production via sulphur based thermochemical water-splitting

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ABSTRACT

The first technical developments on thermochemical cycles for hydrogen production are based on the use of sulphur as a redox material. After the oil crises of the 1970s, high temperature (over 1200 K) heat from nuclear very high temperature reactors (VHTRs) was considered as a promising energy vector to produce fuels for the transport sector. The chemical reactions to convert water into hydrogen must fit to this heat source. As metal-oxide based cycles need higher temperature levels they were not taken into account at that time. The development of the sulphur cycles lost momentum during the 1980s because of cheap fossil fuels. But in the beginning of the 2000s they came back into the focus with the intention to reduce CO₂ emissions. At that time their coupling to heat from concentrated solar radiation in large scale was developed. The interest from the nuclear energy side faded again when the interest in VHTRs lost momentum. In parallel concentrated solar technologies were not implemented fast enough. The developments were mainly achieved by research institutions that concentrated more on the metal-oxide technologies. However, sulphur based cycles remain very promising because the necessary temperature is low compared to metal-oxide cycles and sulphur and sulphuric acid are amongst the most important chemical products offering a high potential of synergies with other processes. The present analysis gives an overview on recent developments and the state-of-the-art of this type of cycles, has a look on the most important performance parameters involved, and gives an outlook on further potential and necessary developments.

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1. Introduction

On the way to “hydrogen economy” (Winter and Nitsch, 1988), obviously the ideal raw material for hydrogen production is water, due to its abundance, its low price and the absence of CO₂ emissions during its dissociation (water splitting) to hydrogen and oxygen. However, due to its unfavourable thermodynamics, the single-step thermal dissociation of water to hydrogen and oxygen is one of the most challenging processes to produce hydrogen in practice. Although water thermolysis is conceptually simple, the need for a high-temperature heat source above 2500 K to achieve a reasonable degree of dissociation is a major barrier to technical success. So is the requirement for an effective technique to separate H₂ and O₂ at high temperatures to avoid an explosive mixture of the two gases.

Thermochemical cycles are a repeating set of two or more consecutive chemical reactions that divide the single water decomposition reaction in various steps, their “net” sum being the splitting

of H₂O to H₂ and O₂. They all include a maximum-temperature, endothermic step needed for the release of O₂, which however takes place at a temperature lower than that of the single-step water thermolysis. Furthermore, in such cycles hydrogen and oxygen are produced in different steps. The temperatures required for the endothermic step of these cycles to reach full conversion are still moderately high ranging between 1100 and 2300 K. Involving a highly endothermic step, thermochemical cycles need the input of external energy which can be provided by a source of high-temperature process heat. To meet the requirement of “clean” hydrogen production, the necessary heat needs to be supplied entirely from renewable or carbon-neutral energy, i.e. sunlight via concentrated solar power (CSP) or nuclear energy (Fletcher and Moen, 1977; Graves et al., 2011; Radosevich et al., 1986).

The screening and search of appropriate thermochemical cycles started in the 1960s. The number of theoretical possibilities was immense (Funk and Reinstrom, 1966). In the 1970s and early 1980s, many studies and assessments were carried out to identify the most promising cycles based on different criteria such as thermodynamics, theoretical efficiencies and projected cost (Beghi, 1981; Beghi, 1986; Funk, 1976; Pretzel and Funk, 1987). In general,

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Nomenclature

H ₂	hydrogen	YSZ	yttria-stabilized-zirconia
O ₂	oxygen	DLR	Deutsches Zentrum für Luft- und Raumfahrt e.V. (German Aerospace Center)
H ₂ O	water	CSIRO	Commonwealth Scientific and Industrial Research Organisation
Al ₂ O ₃	aluminum oxide	ETH	Eidgenössische Technische Hochschule Zürich
H ₂ SO ₄	sulphuric acid	PSI	Paul-Scherer-Institute
SO ₃	sulphur trioxide	MWSF	Megawatt Solar Furnace
SO ₂	sulphur dioxide	PROMES	Laboratoire PROCédés, Matériaux et Energie Solaire
Br ₂	bromine	MIECM	mixed oxygen-ion and electron-conducting membrane
HBr	hydrobromic acid	TGA	thermogravimetric analysis
SiSiC	siliconized silicon carbide	JRC	Joint Research Center
V ₂ O ₅	vanadium pentoxide	JAEA	Japanese Atomic Energy Agency
e ⁻	electron	KAERI	Korean Atomic Energy Research Institute
(g)	gaseous	KIER	Korean Institute of Energy Research
ΔG	Free enthalpy	SNL	Sandia National Laboratories
TR	thermal reduction	SRNL	Savannah River National Laboratory
WS	water splitting	VHTR	Very High Temperature (Nuclear) Reactor
CSP	concentrated solar power		
CDS	carbon dioxide splitting		
FT	Fischer-Tropsch process		

most of the development effort applied during those years was promoted by research institutions and industries from the nuclear energy sector, with the intention to diversify the use of thermal energy supplied by nuclear reactors (Quade and Meyer, 1979). To this end, the programs developed by the Joint Research Centre (JRC) of the European Union in Ispra, Italy (Beghi, 1986), by General Atomics (Norman et al., 1982a) and Westinghouse in USA (Farbman, 1979), and by the Japanese Atomic Energy Research Institute (Shimizu et al., 1991) are particularly worth mentioning. In the late 1980s, the interest in thermochemical cycles decreased drastically. Since then until the late 1990s only marginal progress was reported mainly on the UT-3 cycle developed by and named after the University of Tokyo (Sakurai et al., 1996) and on the Sulphur–Iodine (SI) cycle originally proposed and named after the company General Atomics (Brown et al., 2003).

Since the turn of the millennium research and development of thermochemical cycles has taken up momentum again. The driving force was the production of hydrogen as a greenhouse-gas-free energy vector to fulfil the requirements of the Kyoto Protocol (de Chazournes, 1998) of lowering overall emissions of six greenhouse gases – carbon dioxide, methane, nitrous oxide, sulphur hexafluoride, hydrofluorocarbons, and perfluorocarbons – over the period of 2008–2012. In parallel, in contrast to the work conducted 30–40 years ago, concentrated solar radiation moved stronger into the focus of interest than nuclear heat as a heat source.

To recover the 1970s knowledge, theoretical studies and thermodynamic analysis of cycles have been frequent since then. In addition new hardware especially for the use of concentrated solar radiation has been developed and tested for cycles originally developed for coupling to nuclear reactors (Le Duigou et al., 2007). The main focus was on developing technologies for massive hydrogen production. Since line focusing solar concentrating systems like parabolic troughs and linear Fresnel collectors are not able to achieve the necessary temperature efficiently, point focusing systems like mainly heliostat field and tower and parabolic mirrors or at a minor extent solar dishes were used for heat provision (International Energy Agency OECD/IEA, 2014). High temperature hydrogen production processes are best suited for professionally operated centralized production plants, especially because of the higher efficiency of large plants, the difficult reaction conditions and the safety requirements of the installations. Therefore the majority of the research and development work was concentrated

on implementing thermochemical cycles with solar towers. However, also dishes remain an option especially for very high temperatures (Siegel et al., 2013). Concentrating the solar radiation efficiently is one of the crucial requirements of solar thermochemical water splitting. Another one is to identify suitable materials for substrates and containments being stable against the reaction system and environmental influences. In particular the extreme thermal and chemical conditions require advanced solutions. Solar absorbance and resistance against thermal shocks and fatigue must be considered. A number of relevant receiver, reactor and receiver-reactor technologies were developed for solving this issue and will be discussed.

The present work is a review on the activities on sulphur-based thermochemical cycles with emphasis on CSP-driven implemented concepts. The thermodynamics of the common step of the sulphuric acid decomposition reactions is discussed in the beginning, followed by a presentation of the sulphur cycles proposed so far and their respective reaction schemes. The next section presents the catalytic systems employed for the SO₃ dissociation step and relevant reaction mechanisms. The following two sections concern the chemical reactors designed and implemented so far to perform these reactions, starting from non-solar reactors. Subsequently, the possibility for coupling this reaction with CSP technologies and the relevant solar reactors are presented, before closing with the discussion on current technology developmental level and particular issues for future work.

2. Sulphur and sulphuric acid-based cycles

Among the many thermochemical cycles schemes (Roeb et al., 2013a), those of the Sulphur Family recycle sulphur as the central element that appears in different compounds at changing oxidation state. In general they involve more than two steps, and in this respect their chemistry is more complicated than other two-step cycles based on e.g. redox pair oxides (Agrafiotis et al., 2015). They all have in common the decomposition reaction of sulphuric acid; this is actually their high-temperature, endothermic reaction step that can be solar-heated. The temperatures required for this step though, are in the 1000–1200 K range, much lower thus than the respective temperatures needed for the high-temperature step of the redox-pair based oxide cycles. On the other hand, the major

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