

SOLAR HYDROGEN PRODUCTION FROM WATER SPLITTING: MASS/ENERGY BALANCES AND POSSIBLE IMPROVEMENTS

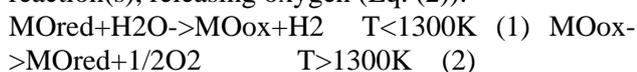
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Introduction

Water splitting thermo chemical cycles driven by solar energy could potentially lead to a sustainable mass production of hydrogen [1]. Thermo chemical cycles consist of the multi-step thermal dissociation of water into hydrogen and oxygen. Chemical intermediates are involved in exothermic reaction(s), generating hydrogen by water splitting (Eq. (1)), and in endothermic reaction(s), releasing oxygen (Eq. (2)).



A database including over 280 cycles was developed and screened to select the most suitable for coupling with concentrated solar thermal energy [2]. Chiefly, metal oxide cycles are the most attractive for high efficiency hydrogen production. High temperatures, which can be provided by concentrated solar energy, are generally required for the endothermic reaction. Laboratory scale experimental devices have been developed to test the chemical reactions and to determine their conversion and kinetics [3]. However, process analysis and scale up of these cycles have not yet been considered in detail.

The objectives of this paper are a process analysis for hydrogen production from thermo chemical cycles driven by concentrated solar energy. The ZnO/Zn, Fe₃O₄/FeO and Fe₂O₃/Fe₃O₄ cycles were selected for a case study regarding their high potential, the amount of available data on the reactions involved and their level of development.

Results and discussion

First, the process analysis was focused on mass and energy balances for a hydrogen production of 1 mole/s taking into account the energy efficiencies at different levels. Second, improvements were assumed for the most energy consuming steps, and energy recoveries were considered. Then, a simple flow sheet was realised, including the heat exchangers necessary for the heat recoveries. In these conditions, the theoretical cycle efficiency was a maximum, depending only on the thermodynamic properties of the chemicals.

Mass/energy balances

Zinc oxide cycle: Zinc oxide reduction at high temperature produces two gases that exit the

reactor. Unfortunately, a reverse reaction (recombination of solid Zn and O₂) occurs during cooling, which gives back ZnO. A quenching device must be connected to the reactor outlet in order to reduce the recombination (negligible below 600 K) and to limit the formation of ZnO. A conversion rate of the recombination reaction is applied to the quenching step. The average recombination rate was about 39%. Thus, the global reaction yield of ZnO to Zn was 61% in that case. Hydrolysis of zinc is not complete due to the formation of a layer of ZnO at the surface of the particles, which blocks the diffusion of steam into the core of the particles and stops the reaction. The highest conversion rate was obtained when zinc was vaporized at 1023 K, condensed as nanoparticles and then hydrolyzed. With such a process, a complete hydrolysis can be assumed. A mass balance was performed taking into account experimental chemical conversions. The real streams containing unproductive compounds require higher amounts of energy for their heating than in the theoretical case assuming complete reactions. In the solar reactor, 1.64 mole/s of ZnO are heated at 2000 K to be reduced into Zn, and a fraction of the Zn is reoxidized in the quenching step. The real energy efficiency of the thermo chemical cycle can be determined from the new energy inputs calculated by accounting for partial chemical conversions.

Iron oxide cycles: Unlike the ZnO/Zn cycle, iron oxide cycles are “non volatile” cycles because the reduced oxide remains in a condensed state. A continuous flow of inert gas is injected through the reactor to sweep the oxygen evolved by the reaction. Thus, the chemical equilibrium is displaced toward FeO formation until complete reduction. Complete hematite (Fe₂O₃) reduction into magnetite (Fe₃O₄) was demonstrated for the same reason. Thus, the recombination reaction is the main difference with the ZnO/Zn cycle, and it is not favored in the case of iron oxide systems because O₂ is swept out of the reactor. For instance, separation of products can be achieved efficiently in the solar reactor if a counter current flow is chosen with a gas outlet located opposite of the solid outlet. Similarly to Zn, a passivation phenomenon is also encountered during FeO hydrolysis due to the formation of an oxide layer. Thus, the chemical conversion of direct

hydrolysis is limited to 75%. Concerning the Fe₂O₃/Fe₃O₄ three step cycle, Fe₃O₄ hydrolysis is possible when using a better oxidizing compound than water. The reaction between Fe₃O₄ and melted sodium or potassium hydroxide generates hydrogen and a mixed oxide. This mixed oxide is reactive with water in a third reaction. These two reactions are assumed complete up to 100%.

Possible improvements

In the case of solar concentrated systems, energy is supplied in the high temperature solar reactor settled at the focal point of the concentrating system. Besides, the heat required in the H₂ generation step must be recovered from the high temperature step of the process. This recovered energy corresponds to the heat released during cooling of the stream exiting the solar reactor. Then, the heating of streams can be obtained by recovering the heat released at the exit of the solar reactor. The second possible improvement for the ZnO/Zn cycle deals with reduction of the heat released during quenching, which can be obtained by improving the quenching efficiency. For the same quenching rate, the main factor governing recombination is the partial pressures of zinc and oxygen, which can be reduced by a total pressure decrease and/or an inert gas flow rate increase. Both of these modifications require a work input for pumping or compressing in order to purify and reuse the inert gas. A recombination rate limited to 20% instead of 39% leads to an energy saving of 212.9 kJ per mole of hydrogen produced. These improvements for the ZnO/Zn cycle result in a cycle energy efficiency increase from 25.2% to 42.9%. For iron oxide cycles, the optimised cycle energy efficiency, accounting for heat recoveries, is about 35%. The ZnO/Zn cycle efficiency is more dependent on partial chemical conversions than that of the

Fe₃O₄/FeO cycle. For the ZnO/Zn cycle, a part of the ZnO injected in the solar reactor is heated and converted into Zn but recombines into ZnO during quenching. Thus, the enthalpies of the heating and of the endothermic reaction are lost. For the Fe₃O₄/FeO cycle, partial conversion in the hydrolyser leads to a mixture of FeO and Fe₃O₄. Then, the remaining FeO, after hydrolysis, must be heated in the solar reactor, which induces an additional energy input. However, this additional required energy due to partial chemical conversions only corresponds to 14% of the total energy required by the Fe₃O₄/FeO cycle, while it is about 39% of the total energy in the case of the ZnO/Zn cycle.

Conclusions

Hydrogen could be produced at large scale from solar thermo chemical cycles. The main source of improvement lies in recombination during quenching of gas products after reduction. Further process improvement is heat recoveries during products cooling to perform the exothermic hydrolysis reaction. The optimised global process efficiency (from solar energy to hydrogen) is estimated to reach 17.4%, 18.6% and 20.8% for Fe₃O₄/FeO, Fe₂O₃/Fe₃O₄ and ZnO/Zn cycles, respectively.

References

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