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Chemical Plant Analysis of Hydrogen Production Based on the Hybrid Sulfur-Ammonia Water Splitting Cycle

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Solar-powered thermochemical water splitting cycles (TWSC) can potentially reach overall efficiencies of 35-40%, far exceeding that of other solar-to-H_2 conversion systems (e.g. PV-electrolysis, photo-electrochemical, photocatalytic, photo-biological). However, existing solar TWSC face number of challenges that have slowed their practical application: (i) the utilization of only the thermal (IR) component of the solar irradiation, neglecting a photonic (UV-Vis) component, (ii) the intermittent nature of the solar resource, and (iii) the reliance on technically-challenging reagents transport and separation stages. This work presents the process simulation and preliminary sensitivity analysis of the hybrid photo-thermal sulfur-ammonia water splitting cycle; a novel photo-thermochemical process that takes advantage of a wider spectrum of the solar radiation. The developed process consists of mainly five-unit operations (a photochemical, three thermochemical & an absorber). It incorporates also two thermal energy storage systems based on process fluids (molten salts and gases) rather than external heat transfer fluids. An optimum solar-to-H_2 efficiency of 25.5 % was predicted, on the basis of 7,000 kmol.h^{-1} produced H_2, higher than previous attempts. At the same time, to achieve this higher efficiency, higher reactor temperatures than those predicted by previous thermodynamic calculations are needed. Finally, the preliminary sensitivity analysis shows that mainly the mid-temperature thermochemical reactor and the composition of the feed affect the overall performance of the cycle.

1. Introduction

Use of fossil fuel has become a greater concern in recent times mainly because of environmental issues. Thus, the search for an environmentally friendly source of energy has become urgent. Sustainable production of energy i.e hydroelectric, wind, geothermal, biomass, solar photovoltaic, solar-thermal, and solar-photo-thermal (Rosen, 2010), etc. each possesses its own pros and cons. The solar Thermochemical Water Splitting Cycles (TWSC) belong to a family of processes based on the production of hydrogen from water using mainly solar energy input. TWSC range from two to multi-step cycles and utilize a variety of materials such as metal oxides (Xiao et al., 2012), mixed metal oxides (Lorentzou et al., 2013), metal halides and metal sulfides (Zamfirescu et al., 2010), sulfur compounds (Wang et al., 2010), etc. All these processes have their own advantages and disadvantages over one another. For example, the processes with metal/metal oxides demonstrate very high theoretical hydrogen yield, but very high temperatures (~2,000 °C) needed for reducing the metal oxides. The metal halide processes operate at low temperatures (~530 °C) but at such temperatures effective catalysis is a challenge (Naterer et al., 2008). The sulfur-iodine cycles seemed very promising, but the separation of gaseous iodine from hydrogen proved to be difficult (Kasahara et al., 2007). All these solar TWSC share one common disadvantage; they all use only the thermal part of the solar radiation neglecting the substantial photonic segment. Therefore, hybrid photo-thermal water splitting cycles have been proposed. For example, Zhang et al. (2016) investigated the metal/metal oxide cycle using TiO_2 photocatalyst and Muradov et al. (2015) the hybrid

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sulfur-ammonia cycle using a CdS based photocatalyst. In most such cycles, hydrogen production occurs at low temperatures, but there is still a need for high temperature steps for the oxygen sub-cycle. Moreover, a full solar cycle poses even more operating challenges due to the intermittent nature of the solar energy. A resolution to this issue is the incorporation of a (thermal) energy storage system able to level out solar insolation variations due to weather conditions or even extend the operation of the solar plant beyond day light hours. Such systems have been studied extensively for TWSC (Kasahara et al., 2007), solar-PV and wind electricity production (Petrakopoulou et al., 2016), and in general hydrogen production from renewable systems (Sharifian and Harasek, 2015). Most thermal energy storage systems indirectly store thermal energy by means of a thermo-fluid e.g. in a thermocline of solids, oil, molten salts. Usually, such systems operate at average temperatures (e.g. around 600 °C for a molten salt system) and also at low energy efficiencies, because of the need to transfer heat to the process fluids, e.g. reactants (Pardo et al., 2014). Especially the latter increases the complexity of integrating a thermal energy storage system into a TWSC. There is a need to develop a solar thermochemical water splitting cycle that can utilize both photonic and thermal part of solar energy with an integrated thermal energy storage system for longer and more resilient operation.

This analysis focuses on the hybrid photo-thermochemical sulfur-ammonia water splitting cycle as proposed by T-Raissi et al. (2006) owing to its advantages over plain solar thermal cycles and high theoretical efficiency of around 60 % (Kalyva et al., 2016). A variation of this cycle has been studied by Littlefield et al. (2012) where an electro-catalytic step was proposed, instead of the photocatalytic one. A detailed process analysis and optimization resulted in an overall cycle efficiency of 23% (Littlefield et al. 2012). Aim is to assess the efficiency of the hybrid photo-thermal sulfur-ammonia cycle integrating a thermal energy storage system that is based on the process fluids rather than using an external heat transfer fluid. Solar energy is collected with a new type of collectors proposed by Huang (2014). The utilization of the solar energy and the collected data are not described in this paper, as they will be published in a future work.

2. Materials and methods

A process flow diagram was developed using a widely used process simulator (AspenPlus©) to solve the material and energy balances. There are many studies that employed the same platform for hydrogen production process' simulation (Drljo et al., 2014) and optimization (Hunpinyo and Narataruksa, 2016). Nevertheless, as described earlier (Kalyva et al., 2017), this process simulator cannot handle solid species efficiently, especially when they undergo phase transformations. Therefore, two different methods have been combined here to properly handle thermodynamic (equilibrium) calculations for the studied process and obtain valid convergence as detailed below.

2.1 The hybrid photo-thermal sulfur-ammonia water splitting cycle

The concept of hybrid photo-thermal sulfur-ammonia cycle has been described extensively in literature. The cycle employs two main sub-cycles for the photocatalytic hydrogen production and the thermochemical, molten salt, oxygen production. Table 1 presents the reactions that highlight the essence of this process.

Table 1: Reactions of the hybrid photo-thermal sulfur-ammonia cycle

SO_2	+	H_2O	+ $2NH_3$	↔	$(NH_4)_2SO_3$			(Chem. Absorption, 25 °C)	(1)
$(NH_4)_2SO_3$	+	H_2O		↔	$(NH_4)_2SO_4$	+	H_2	(Photochemical, 80 °C)	(2)
$(NH_4)_2SO_4$	+	K_2SO_4		↔	$2NH_3$	+	$K_2S_2O_7$+ H_2O	(Thermochemical, 400 °C)	(3)
			$K_2S_2O_7$	↔	SO_3	+	K_2SO_4	(Thermochemical, 550 °C)	(4)
			SO_3	↔	SO_2	+	$1/2O_2$	(Thermochemical, 850 °C)	(5)

The net result of the above set of reactions Eqs(1)-(5) is the splitting of water into hydrogen and oxygen, while every other component is recycled. Hydrogen production Eq(2) takes place at ambient temperature in the presence of a photo-active catalyst and solar light. The liquid products, mainly ammonium sulfate, react at high temperature, with potassium sulfate and release ammonia (in two steps via the interim formation of ammonium bisulfate; not included in the reaction scheme above) and water forming pyrosulfate Eq(3). Following, potassium pyrosulfate decomposes successively back to potassium sulfate salt and sulfur trioxide and then to sulfur dioxide and oxygen Eq(4)-(5). The gaseous products are combined with ammonia and water to close the overall cycle while the salt is recycled to Eq(3). Each of the reactions in Eq(3), Eq(4) and Eq(5) takes place in a separate thermochemical reactor labelled low, medium and high-temperature reactors, respectively. The required energy for both sub-cycles is covered by solar photo and thermal energy following an overall allocation of 19% and 81%, respectively (Muradov et al., 2015).

2.2 Thermodynamic models

Considering many ionic species of pure fused salt, Littlefield et al. (2012) used Electrolytic Non-Random Two-Liquid method with a symmetric reference state (ENRTL-SR) in his study. However, this is not necessary because in current study all thermodynamic properties for all salts (e.g. enthalpy and Gibbs free energy of formation, heat capacity) have been configured and adopted manually from our previous work (Kalyva et al., 2015) for the all possible phases (both solid and liquid). Therefore, in this study we used Non-Random Two-Liquid method (NRTL) as thermodynamic model instead of ENRTL-SR method. This NRTL model is recommended for non-ideal solution and takes into account all available forces involved in a solution. The phase diagram of K_2SO_4-$K_2S_2O_7$ salt (Lindberg et al., 2006) to account the effect of binary interactions on the equilibrium calculations.

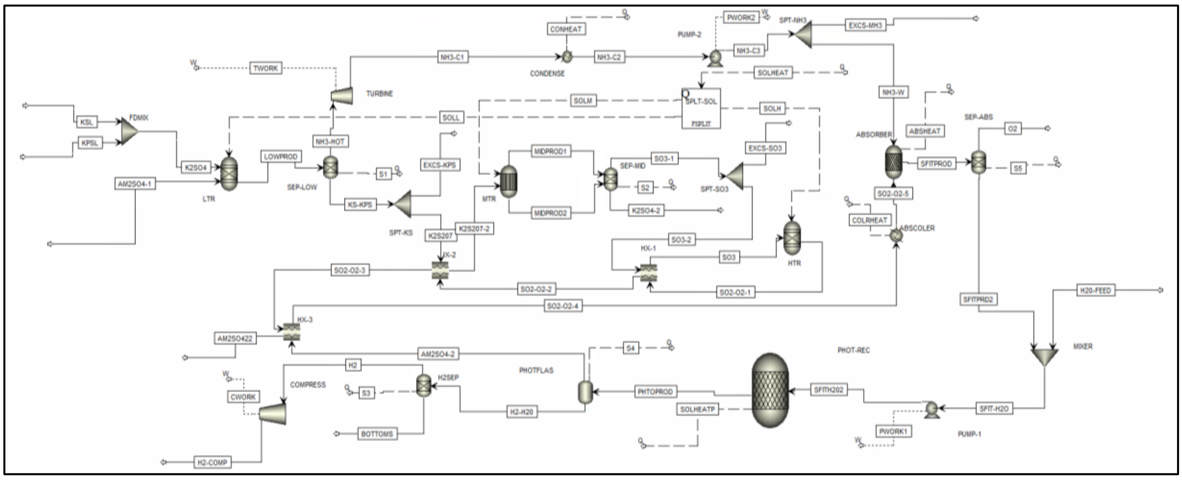


Figure 1 : Developed Process Flow Diagram (PFD) of the hybrid photo-thermal sulfur-ammonia water splitting cycle (only for indicative use)

2.3 Process and reactor specifications

The developed process flow diagram is illustrated in Figure 1. There are in total five reactor units: low-temperature reactor, mid-temperature reactor, high-temperature reactor, chemical absorber and photocatalytic reactor. The reactants conversion is either “known”, or fixed, or are estimated via thermodynamic equilibrium calculations. For the absorber, since ammonia is very soluble in water, a 100% conversion of ammonia was assumed. Similarly, 95% conversion of ammonium sulfite was assumed for the photocatalytic reactor. For both the low- and high-temperature reactors, a Gibbs free energy minimization approach was used to determine the equilibrium condition. On the other hand, the conversion at the mid-temperature reactor was specified indirectly by forcing the simulator to follow the gas-liquid equilibrium line of the phase diagram in determining the final product composition. This is because the equilibrium constant was extracted from the phase diagram of the binary solution of potassium sulfate and pyrosulfate (Lindberg et al., 2006). Then, it was employed in a design specification block as a function of temperature and the ratio of the two salts mole fraction (potassium sulfate and pyrosulfate). In addition to the reactors, the process includes a number of heat exchangers and turbines to recover heat energy along with a limited number of compressors and separators for a more accurate representation of the process and estimation of the overall energy requirements Moreover, based on previous thermodynamic analysis, the boundary conditions of each reactor were set to 410 ˚C to 500 ˚C, 800 ˚C to 890 ˚C and 800 ˚C to 950 ˚C for the Low-, Mid-, and High-temperature reactors, respectively. These constraints are to impose the condition of an all-liquid process, i.e. no-solidification of the salts involved.

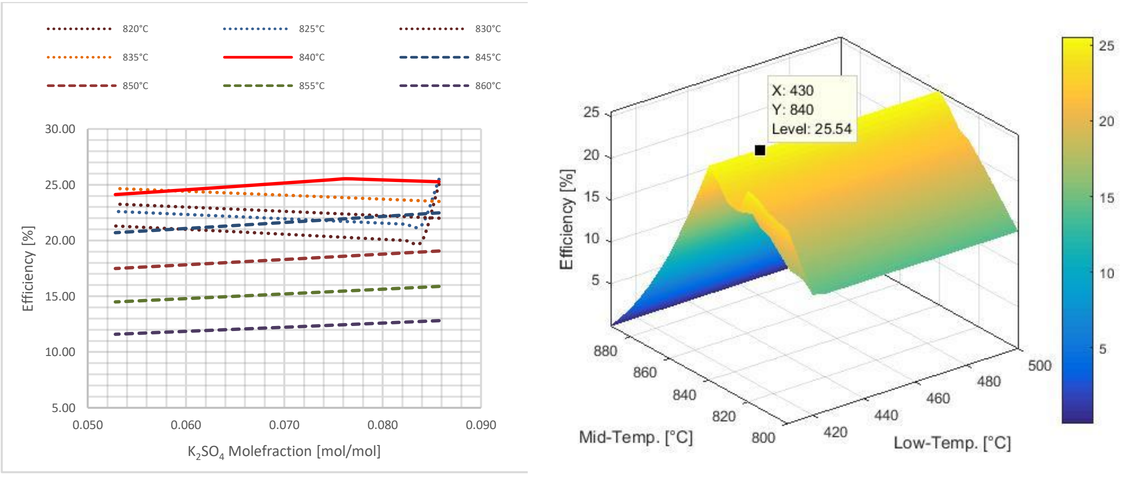
3. Results and discussion

3.1 Process efficiency

The process simulation was executed at steady state conditions, i.e. constant input of solar energy and feed material, while all calculations assumed the same feed of K_2SO_4-$K_2S_2O_7$ salt at around 4,757 kg/kg hydrogen product. The overall efficiency was calculated based on Eq(6).

$$Efficiency=\frac{Lower\ haeatin\ value\ of\ hydrogen\ produced}{Net\ consumption\ of\ energy} \qquad (6)$$

Multiple simulations were executed varying multiple process parameters such as the temperatures of the reactors, feed composition, along with different process configuration (e.g. heat exchangers and turbines). Figure 1 illustrates the final version of the process flow diagram. In this context, it was estimated that to accommodate the constraint of an all-liquid process, the salt temperature must be above 406˚C to ensure liquid operation. And considering operational flexibility the we specified the Low-temperature reactor's temperature as 430 ˚C. At this temperature, the composition of K_2SO_4 in the salt has to be 7.6 % or less to make sure complete liquid operation. This is contrary to the thermodynamic calculations presented earlier. Further tests need to be conducted but an initial indication is that the equilibrium constraint introduced following the method of Littlefield et al. (2012) might need further refinements. Nevertheless, Figure 2 presents results for the effect of feed composition and the temperature of the low- and mid-temperature reactors on the overall cycle efficiency. More specifically, the process efficiency demonstrates a monotonic and quasi-linear behaviour with varying feed composition at all temperatures (Figure 2a) reaching maximum efficiency at $[K_2SO_4] = 0.076$ molar fraction at 840°C. An examination of the results revealed that the performance is reduced mainly because of the reduction of the produced hydrogen rather than the requirements for more input energy. This means that the performance of the process is driven by equilibrium constants at each reactor. Among which, the mid-temperature reactor estimated to have the biggest contribution. Examining multiple combinations of the temperatures of the low- and mid-temperature reactors, a similar behaviour was observed. Figure 2b shows the optimum operating temperature of the Mid-temperature reactor is 830 ˚C. at this temperature the developed process demonstrated maximum efficiency. From Figure 2b it can also be concluded that overall efficiency varies very little with variation in temperature of Low-temperature reactor. The process demonstrates the maximum performance, ~60.3 % (25.54 % if we consider only the useable energy in efficiency calculation), at 430 ˚C and 840 ˚C for the Low-, and mid-temperature reactor temperature respectively. These simulations refer to 850 °C temperature at the high-temperature reactor. Contrary to the low- and mid-temperature reactors, efficiency increases with the temperature increase of the high-temperature reactor, reaching 31 % (taking into account useable energy only) at 950 ˚C at 950 °C. Nevertheless, it was considered material wise to remain below 900°C (Pardo et al., 2014). This reported solar energy needs to be corrected by the efficiency of the solar contractor.



(a) (b)

Figure 2: Sensitivity analysis of overall efficiency on a) feed molten salt composition and b) temperatures of low- and mid-temperature reactors

Efficiency calculation, using Eq(6), represents the solar-H_2 energy efficiency assuming that the whole spectrum of solar energy is exploited. Previous calculations (Muradov et al., 2015) estimated that 8 1% is needed for the thermal portion of the cycle and 19% for the photoreactor, setting indirectly the wavelength cut-off to around 520 nm. Here a similar calculation, Eq(7) shows that only ~16 % of the total solar energy is required for the photoreactor. In other words, the cut-off wavelength could be less, which indirectly reduces the need for a photocatalyst that absorbs a significant part of the visible spectrum.

$$\frac{\textit{Photon Energy}}{\textit{Thermal energy for } (\textit{LowT}+\textit{MidT}+\textit{HighT}) \textit{ reactors}} *100 \qquad (7)$$

3.2 Thermal energy storage

Following the selection of the reactor temperatures, the incorporation of a dual thermal energy storage system into the process of the hybrid photo-thermal sulfur-ammonia cycle was examined. This is one of the innovative aspects of this work and the conceptual diagram is shown in Figure 3. The first system is based on the molten salts (potassium sulfate and pyrosulfate), that are also two of the main reactants of the process, and covers the energy "gap" between the low- and mid-temperature reactor. The second system is based on the hot gases released from the mid- and high-temperature reactor and covers mainly the energy "gap" of the mid-reactor. In principle, there could be two additional systems based on the interim product (ammonium bisulfate) of Eq(3) and the synthesis of ammonium sulfite Eq(1) in the absorber. Preliminary calculations were not proved successful owe to convergence issues during the process simulation, therefore neither was included in this study. Nevertheless, the dynamic simulation of the whole process is in progress in order to identify the conditions under which the proposed system can operate for an extended period beyond the daylight and be resilient to solar insolation fluctuations. The variation of the solar radiation for the region of Doha in Qatar was investigated by Perez-Astudilloa and Bachour (2014) and their data were used to analyse the dynamic performance of the process.

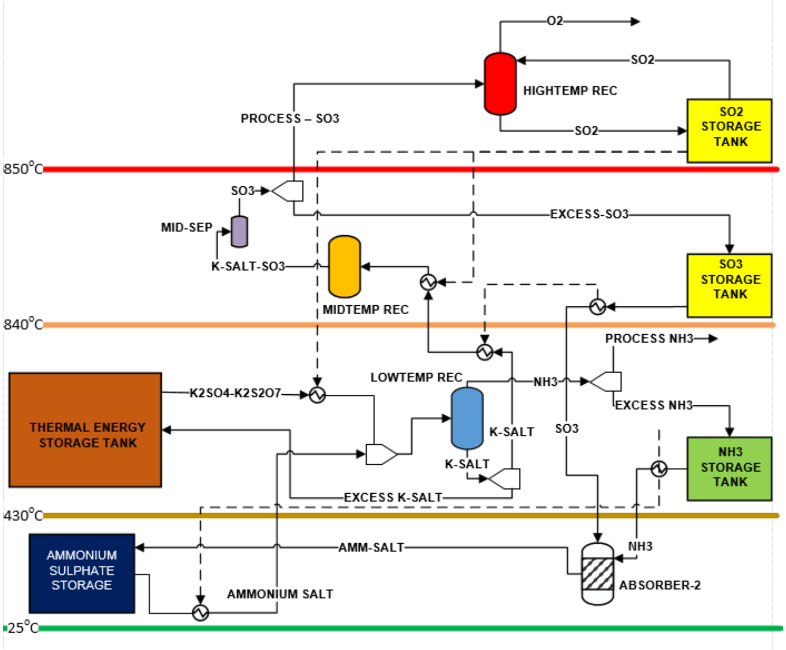


Figure 3: Schematic diagram of a conceptual thermal energy storage system.

4. Conclusions

Hydrogen production from renewable energy resources such as solar, is the main focus of current research. In this study, the plant configuration for the hybrid photo-thermal sulfur-ammonia water splitting cycle was investigated using modern process design tools. A rigorous sensitivity analysis showed that the mid-temperature reactor and feed composition are the two most influential process parameters governing the solar-H_2 energy conversion efficiency of the process. The predicted cycle efficiency reported in this study was calculated to be around 60.3 % (25.54 %) based on 7,000 kmol $H_2.h^{-1}$ production capacity. This is a significant improvement compared to earlier estimations of around 23 % using an electro-catalytic hydrogen sub-cycle (Littlefield et al., 2012) than the photocatalytic step proposed here. In addition, the same analysis resulted to different "optimum" reactor temperatures than the ones estimated by earlier thermodynamic analysis i.e. of 840 ^oC and 850 ^oC for the mid- and high-temperature reactor, respectively, while the Low-temperature reactor temperature has increased to 430 ^oC.to ensure complete liquid operation and operational flexibility. Finally, a conceptual flow diagram was presented that integrates two different thermal energy systems within the studied cycle, using process fluids (molten salts and hot gases) rather an external heat transfer fluid. Thus, the number of heat transfer operations was reduced. In the future, a dynamic simulation of the overall process will indicate the possibility of extended operation beyond the daylight hours and to increase its resilience to solar insolation fluctuations.

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