



# Analysis of a Solar Hybrid Sulfur Ammonia Copper Oxide Thermochemical Cycle for Hydrogen Production

Moustafa Soliman<sup>1</sup>, Abdel Moniem Abomosalam<sup>2</sup>, Noran Shedid<sup>2</sup>, Mohamed Othman<sup>2</sup>, Toka Hatem<sup>2</sup>, Marc Samer<sup>2</sup>

<sup>1</sup>Professor, Chemical Engineering Department, The British University in Egypt

<sup>2</sup>Student, Chemical Engineering Department, The British University in Egypt

Corresponding Author: Moustafa Aly Soliman

Date of Submission: 18-03-2021

Date of Acceptance: 01-04-2021

**ABSTRACT:** Solar energy conversion to hydrogen by water splitting is a promising technique because it is sustainable and environmentally friendly. One option for water splitting is through thermochemical cycles in which one of the steps is electrolytic or photocatalytic.

In this paper, the economics of a thermochemical process that combines photocatalysis, photovoltaics, high temperature thermal energy and energy storage to harvest solar energy is assessed.

This paper focuses on the standard hybrid sulfur ammonia thermochemical cycle (SA) in which the electrolytic step of the hydrogen production from ammonium sulfite solution is augmented by a photocatalytic step. Trying to make use of most of solar radiation we use beam splitter to separate solar radiation to wave length less than 520 nm, between 520 to 800 nm and to more than 800 nm. The spectrum less than 520 nm is used to run a photocatalytic hydrogen production unit. The spectrum between 520 to 800 nm is used to generate electricity through photovoltaic cells which is used to run electrolytic hydrogen production unit. The spectrum greater than 800 nm is used to satisfy the heat requirements of the thermochemical plant. We investigate the economic advantage of replacing the sulfate or sulfuric acid decomposition step by reaction with cuprous oxide to produce cupric oxide which is then decomposed to cuprous oxide and oxygen at high temperature.

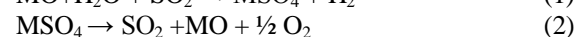
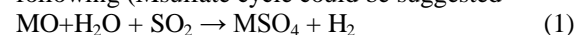
**KEYWORDS:** Sulfur ammonia, Thermochemical cycle, Copper oxides, Solar energy

## I. INTRODUCTION

Water splitting to hydrogen using solar energy is one of the scientific challenges in this century. Solar energy can be used to provide heat for thermal and thermochemical decomposition of water. It can be used to provide light for

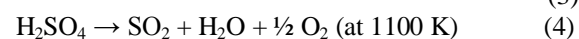
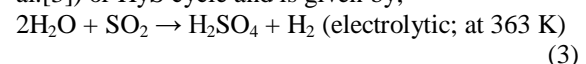
photocatalytic or photoelectrocatalytic decomposition of water. It can also be transformed to electricity using photo-voltaic cells (PV) which can be used for water electrolysis. PV-electrolysis is a mature technology, and is usually used for evaluating other solar hydrogen production systems. PV cells efficiency varies from 6 to 18% for amorphous and polycrystalline silica. Water electrolysis efficiency of 70-80% is achievable. This gives an overall solar-to- H<sub>2</sub> energy conversion efficiency of PV-electrolysis systems of 15-20%. On the other hand, thermochemical water splitting cycles efficiencies of 35-40% can be realised. Closed thermochemical cycles are a set of reactions which splits water into hydrogen and oxygen with some chemicals which are recycled. In a future hydrogen economy, heat from solar collectors or from cooling nuclear reactor may be used to produce hydrogen from water through thermochemical water splitting cycles.

Soliman et al.[1],[2] appear to be first to propose cycles based on sulfur chemistry. The following (MSulfate cycle) could be suggested



Where M is a metal or hydrogen

Metal Sulfate Cycles were investigated but hydrogen production could not be demonstrated. Other products could be obtained. For example, if the metal oxide is CuO, we might obtain Chevruel's salt  $\text{Cu}_3(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$  and no hydrogen. If M is H<sub>2</sub>, the thermodynamics of the first step is not favourable and this step should be electrolytic. This is known as Westinghouse hybrid cycle (Brecker et al.[3]) or HyS cycle and is given by;

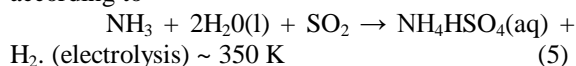




Such a cycle is called hybrid thermochemical cycle because it contains an electrolytic step. The reversible potential for the sulfur dioxide depolarized electrolysis (SDE) is only 0.17 V, while that of water electrolysis minimum of 1.23V at 298K and 1 bar. Sulfuric acid should be produced at high concentration to reduce the amount of water that goes to the decomposition reactor. This causes corrosion problems in the electrolysis step and the decomposition step, the cycle efficiency is calculated from the formula

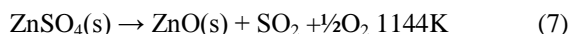
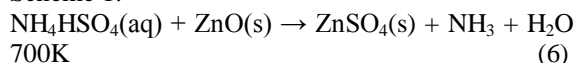
Cycle efficiency =  $100 \times (\text{LHV enthalpy of formation for } H_2O) / (\text{Net heat into flowsheet} + (\text{Work Terms}) \times 0.5)$

Carty et al. [4] studied the optimum conditions to run a proposed flowsheet for the HyS cycle and concluded that a maximum process temperature should be as high as possible, the optimum acid concentration is between 65 and 85 wt.% and the optimum pressure in the decomposition loop is between 5.15–10.3 bar. To avoid dealing with concentrated sulfuric acid in the electrolytic step and its subsequent evaporation which is highly corrosive and endothermic, Soliman [5] proposed to use ammonia in the electrolytic step according to

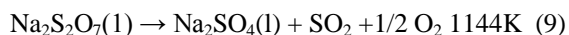
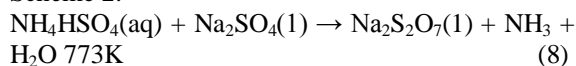


In this cycle, the ammonium hydrogen sulfate obtained can be decomposed using either of the following two schemes:

Scheme 1:



Scheme 2:



This scheme avoids the use of solids handling

It is possible to replace the electrolytic step in the direct electrolysis of water or in hybrid thermochemical cycle by photocatalytic or photoelectrocatalytic reaction, (Raissi et al [6]). They arrived to almost the same cycles as above. The ammonia reaction goes to the ammonium sulfate instead of ammonium hydrogen sulfate, and potassium sulfate is used instead of sodium sulfate. This sulfur ammonia cycle is called SA cycle.

Littlewood [7] simulated a plant for the SA cycle and his work was followed by Luc [8] who created a process flowsheet and carried out its simulation using Aspen plus. Solar thermal energy is used to provide the thermal energy for the process and electricity needed is generated internally from waste heat.

To make the process continuous a phase-change thermal-storage system with NaCl is used. Plant cost estimation was performed for a plant producing 0.029 kmol/s hydrogen giving hydrogen cost of 11.89 \$/kg.

The solar plant capital cost is 55 m\$ and the chemical plant capital cost is 17m\$.

More research works were carried out by Kalyva et al [9], Shazeda et al [10], and Vagia et al [11].

We could use copper oxides instead of ammonia as a modification for the HyS cycle (Foh et al [12]). The cycle was called H-5. Schreiber et al. [13] added to the cycle the decomposition of cupric oxide to cuprous oxide and oxygen to make it possible to produce oxygen and sulfur dioxide in separate steps and avoid their separation step. The cycle was called H-7.

Gonzales et al. [14] simulated the copper sulfate cycle using Aspen Plus and studied its economics for a plant producing 3.47 kmol/s of hydrogen. The capital cost for the plant is \$360 m excluding the heat source.

Graf et al. [15] used concentrated solar thermal systems at the 50MWt power level to run HyS process. Capital costs estimates for 0.06 kmol/s H<sub>2</sub> production are \$66.4 m for the solar plant and \$41.0 m for the chemical plant. This gives a hydrogen production cost of \$7.6/kg and \$8.1/kg from water electrolysis plant.

Liberatore et al [16] carried out an optimization study with different scenarios for 0.03kmol/s H<sub>2</sub> production rate including different solar energy utilization, and sulfuric acid co-production. This study indicated that the optimum sulfuric acid concentration in the electrolyser is about 20%. Most of the previous studies claim that acid concentration should be more than 60%.

Hinkley et al. [17] studied the economics of using photovoltaics to run an electrolyser plant which could be direct alkaline electrolysis or SDE. For 0.58 kmol /s H<sub>2</sub> production, they estimated the capital cost for SDE \$96 million and for the sulfuric acid decomposition plant \$690 millions.

Corgnale, and Summers [18] studied the economics of a solar HyS plant for 0.77 kmol/s H<sub>2</sub> production. A solar tower provides 333.6 MW for heat requirements. Based on 2005 costs, the solar



plant costs \$312.6 millions and the HyS plant 138.3 m\$ of which 52.5\$ for the electrolyser. To these costs it was added 34% indirect costs. This gives a hydrogen production cost of \$ 4.8/kg.

In this work, we study a cycle which is a combination of SA and H-7 cycles. It has the advantages that oxygen and sulfur dioxide are produced in separate steps. The cycle features the use of molten cuprous oxide as a thermal storage material and a reactant. Aspen plus is used to simulate the plant and provide mass and energy balances for a hybrid CuO plant with 150 MW (720 kg/h H<sub>2</sub> production capacity). The predicted plant efficiency is about 41.5%, and the estimated hydrogen production cost is about \$6.3/kg. The proposed plant generates oxygen gas as a by-product.

## II. MATERIALS AND METHODS

### Process Description:

Solar energy is collected by a heliostat field and directed to a solar tower where a spectral splitter diverts radiation toward a solar receiver. In the receiver, cuprous oxide is heated, melted and is used to drive a thermochemical plant. In the thermochemical plant, molten cuprous oxide is used to supply the heat required for the high temperature reduction reactor where CuO particles are reduced and melted into molten CuO/Cu<sub>2</sub>O equation (15). The cuprous oxide is also used to reduce sulfur trioxide to sulfur dioxide, equation (14). Equations (10-13) describe standard steps in the SA cycle which consists of absorbing recycled sulfur dioxide

into aqueous ammonia to form ammonium sulfite (equation (10) which is photocatalytically or electrochemically oxidized to ammonium sulfate and hydrogen (equation (11)). Ammonium sulfate solution is heated to give ammonia and sulfuric acid (equation (12), Hansen [19]). Sulfuric acid is decomposed to sulfur trioxide (equation (13)) Molten cuprous oxide is reacted with sulfur trioxide according to equation (14) to give solid copper oxide and sulfur dioxide which is directed to the absorber. Cupric oxide is sent to the high temperature reactor.

The process flow diagram using Aspen plus is shown in Figure 1. Additional amounts of NH<sub>3</sub>, SO<sub>2</sub> and O<sub>2</sub>(g) must be fed to the system in order to make up for losses.

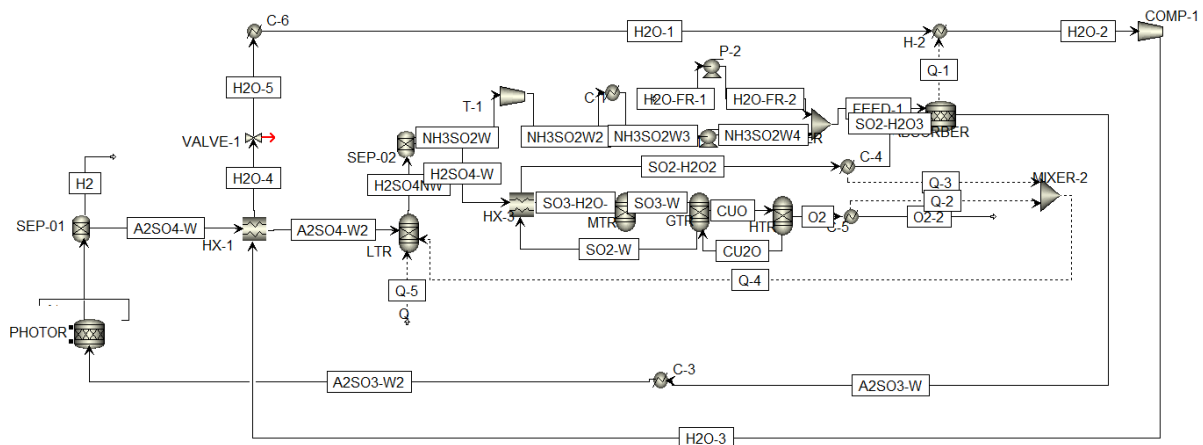
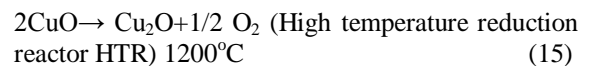
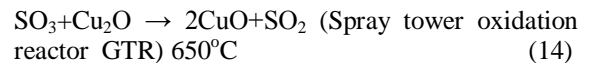
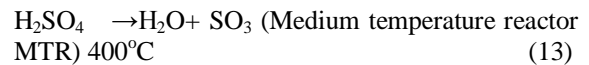
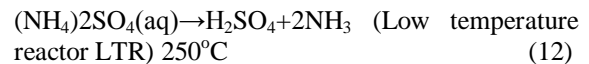
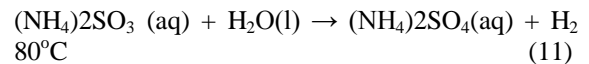
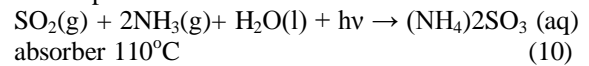


Fig 1. Process Flow Diagram

We envisage a solar field of 150 MW thermal. It consists of a heliostat field with a solar tower. The heliostat field contains thousands of heliostats

which concentrate the sunlight onto a receiver situated on the top of the tower. The receiver can achieve temperatures of about 1250°C. This



requires a land area of  $4 \times 10^6 \text{ m}^2$ , reflective area  $6 \times 10^5 \text{ m}^2$ , with 200 m tower height and installed cost of 158 m\$ (based on  $\$130/\text{m}^2$  of heliostats area) including thermal storage system, receiver (Luc [8]).

Trying to make use of most of solar radiation, the solar light is split into three spectra using optical surfaces (Zamfirescu and Dincer [20], Kaleibari et al [21]). These three spectra are of wave length less than 520 nm, between 520 to 800 nm and to more than 800 nm. The spectrum less than 520 nm is used to run a photocatalytic hydrogen production unit. The spectrum between 520 to 800 nm is used to generate electricity through photovoltaic cells which is used to run electrolytic hydrogen production unit. To estimate how much of the radiation lies between two wavelengths, one can use an equation or tables given by (Howell et al. [22]). We estimated that for wavelengths less than 520 nm, 27 % of the solar energy is contained. 31% is contained between 520 nm and 800 nm and 42% is contained in wavelength more than 800 nm.

Assuming photocatalytic hydrogen production efficiency of 30 %, 17 % for PV, 156% for electricity to hydrogen and operating hours of ten hours, we obtain 3.2 MW, (out of 40.0 MW solar, reactors area  $185000 \text{ m}^2$ . Cost 5 m\$) for photocatalytic hydrogen, 3.8 MW (out of 46.5 MW solar, area of PV modules  $267580 \text{ m}^2$ , cost, 50 m\$) for electrolytic hydrogen and 63.5 MW thermal with 14 h storage (95% capacity factor) for chemical plant thermal requirements. The chemical plant will include a Rankine cycle to generate electricity (20.8 MW) from the heat of reaction and the heat from electrolytic hydrogen production. This is used in the electrolyser with an efficiency of 156% to give 17.5 MW  $\text{H}_2$ . which requires 11.2 MW electric power) To the rest of 9.4 MW, we add 4.73 MW of electric power coming from a condensing turbine for the hot ammonia stream coming from the LTR. This makes 14.13 MW electric power. We still need 16.12 MW for electric power of a heat pump that makes use of the heat from the absorber. 2 MW difference can be obtained from the electric power generated from absorber cooler and oxygen at 255 C. 21.3 MW  $\text{H}_2$  comes from 13.65 MW electricity, for current density  $100 \text{ mA}/\text{cm}^2$  and 0.8 V, electrode area  $=17000 \text{ m}^2$ . For a cost of  $723 \text{ \$/m}^2$ , electrolyser cost =12.4 m\$

Heat duty for HTR=31.1 MW, heat duty for GTR=14.0 MW heat duty for MTR=10.57MW and heat duty for LTR=3.37 MW, total =59.04 MW. Plant efficiency  $=24.5 \times 100/59.04=41.5\%$ . This value is much higher than that obtained by Littlefield [7] of

22% and Luc [8] of 13%. This high value is because of the proper use of solar energy and the exploitation of waste heat. Wu et al [23] indicated that CuO/Cu<sub>2</sub>O pair can be used as thermal storage system. Latent heat of fusion for cuprous oxide=70 kJ/mol, mol mass=143, melting point =1235°C, density of solid =6000 kg/m<sup>3</sup>. To ensure continuous operation, material and energy storage are required. We assume 10 hours of sunshine:14 hours of storage, storage, temperature 1250 °C

Thermal storage capacity of cuprous oxide= $(60 \times 24)/14=103.0 \text{ MW}$

Mass of cuprous oxide= $(103 \times 143)/70=210 \text{ kg/s} \times 14 \times 3600=10584000 \text{ kg}$

Vol= $10584000/(6000 \times 0.95)=1857 \text{ m}^3$   
(24 m\$)

We need also 5 M ammonium sulfate solution storage of  $0.1 \text{ kmol./s} \times 14 \times 3600$  This gives  $1008 \text{ m}^3$ .(6 m\$)

Cost Analysis:

The Plant Parameters for Base Case are as follows; Pressure 9 bar, concentration of  $(\text{NH}_4)_2\text{SO}_4$  in electrolyser product stream 5 M, reaction temperatures are as given in equations (10-15), electrolytic reactor current density  $100 \text{ mA}/\text{cm}^2$ , voltage 0.8 V, operating hours 10 hours. Cost parameters will be taken from Hinkley et al 2011. such as amortized capital cost 11.5% of fixed capital cost. Electrolyser and solar fields costs vary significantly in the literature. The region of Aswan in Egypt has an annual insolation of around  $2.3 \text{ MWh}/\text{year.m}^2$ . For this reason, it was selected for the present feasibility study.

### III. RESULTS AND DISCUSSION

Photocatalytic Reactor Cost:

With reference to the paper by James et al 2009; the photoreactors are baggies fitted with windows of high density polyethylene, cost of photocatalyst=300\$/kg. One baggie produces  $61.7 \text{ kg H}_2/\text{day}$ , area  $3941 \text{ m}^2$ .

For  $0.0131 \text{ kmol/s H}_2$ , we need 36 baggie, area  $144000 \text{ m}^2$ , 1 baggie cost 78000\$ (2005)= $78000 \times 607.5/468.2=101200$ \$ (2019); 36 baggies cost=3.6 m\$. It is mentioned that they use  $74.6 \text{ kg}/18$  baggie of catalyst. For 36 baggies, it would be 149.2, cost= $149.2 \times 300=44760$  \$.

Electrolytic Reactor Cost:

For  $0.0869 \text{ kmol/s}$  electrolyser, current density  $100 \text{ mA}/\text{cm}^2$ , voltage=0.8 V, electrode area =  $17200 \text{ m}^2$  at a cost of  $723 \text{ \$/m}^2$  (Luc [8]), electrolyser cost is 12.4 m\$.



Table 1 gives the equipment installed cost and table 2 gives a breakdown for hydrogen production cost.

Our objective is to bring down hydrogen production cost to \$3/kg. The most expensive component of the entire hydrogen production plant is the solar field, representing 58% of the total plant cost. The reduction of solar field cost is very important for this process to be viable. To reduce heat requirements, we may use ammonium bisulfite/ammonium bisulfate pair instead of ammonium sulfite/ammonium sulfate pair. We could also use concentrating parabolic trough to provide the heat for the MTR.

The following modifications could be suggested to the present cycle; Ammonium sulfate solution is heated to give ammonia and ammonium hydrogen sulfate (equation (12)') which is reacted with cuprous oxide to give copper sulfate. It reacts with cuprous oxide to give cupric oxide and sulfur dioxide to be sent to the absorber.

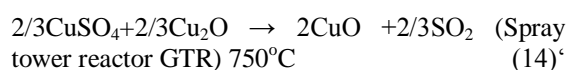
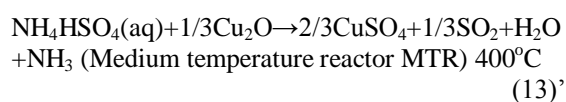
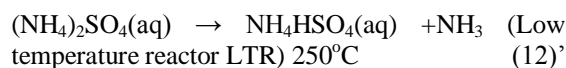
Table 1: Cost Results Based on 150 MW Modular Plant Design

Equipment	Costs (m \$)
<b>Installed Investment Breakdown</b>	
<b>Solar Plant Module</b>	
Heliostats	78
Receiver	40
Thermal Storage	24
Tower Cost	3
Balance of Plant	13
<b>Total</b>	<b>158</b>
<b>PV Plant</b>	<b>50</b>
<b>Chemical Plant</b>	
Photocatalytic Reactor	3.6
Electrolytic Reactor	12.4
Absorber	2.9
LTR	2.05
MTR	0.66
GTR	0.25
HTR	1.66
Heat Exchanger	4
Pumps	2
Rankine cycle equipment	15

Compressor	8
Turbine	2
Storage tanks	6
Misc	2
<b>Total</b>	<b>62.52</b>
<b>Overall Total</b>	<b>270.52</b>

Table 2: Hydrogen Production Cost Breakdown

Operating Costs (\$m/yr)		
Amortised Capital Related	11.5 of fixed capital	31.2
Fixed O & M	5% of fixed capital	13.5
By-product		-5
<b>Total</b>		<b>39.7</b>
Average Hydrogen Production 17280 kg/day		
Hydrogen Production Cost \$/kg		6.3



#### IV. CONCLUSIONS

Both thermal and photonic components of sunlight are made use of to operate a high temperature solar thermochemical plant. Cost reduction can be achieved for the solar tower system and the electrolyser. and overall efficiency can be increased. Overall, CuO/Cu<sub>2</sub>O has advantage in being able to obtain oxygen and sulfur dioxide separately. Drawbacks include incomplete reduction of cupric oxide and its handling.

This paper provides alternatives for cycles based on sulfur chemistry which has the potential of being industrially adopted.



## REFERENCES

- [1]. Soliman M.A., Carty R.H., Conger W.L., Funk J.E., 1975, New thermochemical cycles for hydrogen production. *Canadian Journal of Chemical Engineering*, 53, 164–169.
- [2]. Soliman M.A., Conger W.L., Carty R.H., Funk J.E., Cox K.E., 1976, Hydrogen production via thermochemical cycles based on sulfur chemistry. *International Journal of Hydrogen Energy*, 1: 265–270.
- [3]. Brecher L.E., Spewock S., Warde C.J., 1977, The Westinghouse sulfur cycle for the thermochemical decomposition of water. *International Journal of Hydrogen Energy*, 2:7–15.
- [4]. Carty R., Cox K., Funk J., Soliman M., Conger W., 1977, Process sensitivity studies of the Westinghouse sulfur cycle for hydrogen generation. *International Journal of Hydrogen Energy* 2:17–22.
- [5]. Soliman M.A., 1978, A highly efficient thermochemical cycle for hydrogen production, *Alternative Energy Sources*, Vol. 8, Hemisphere, Washington, 3541-3550.
- [6]. Raissi, A., Muradove, N., Huang, C., Adebisi, O., 2007, "Hydrogen from Solar via Light-Assisted High-Temperature Water Splitting Cycles", *Journal of Solar Energy Engineering*, v.129, 184–189.
- [7]. Littlefield, J., 2012, "Solar Thermochemical Hydrogen Production Plant Design," M.S. Thesis, University of California, San Diego, CA.
- [8]. Luc W. W., 2013 "A Continuous Solar Thermochemical Hydrogen Production Plant Design", M.S. Thesis University of California San Diego, CA
- [9]. Kalyva A.E., Vagia E.C., Konstandopoulos A.G., Srinivasa A.R., T-Raissi A., Muradov N., Kakosimos K.E., 2015, Investigation of the solar hybrid photo-thermochemical sulfur-ammonia water splitting cycle for hydrogen production. *Chemical Engineering Transactions*, 45, 361–366.
- [10]. Shazeda A. R., Kalyva E. A., Vagia E. C., Srinivasac A. R., Raissi A. T., Muradov N., Kakosimos K. E., 2017, Chemical Plant Analysis of Hydrogen Production Based on the Hybrid Sulfur-Ammonia Water Splitting Cycle. *Chemical Engineering Transactions*, 61, 433–438.
- [11]. Vagia E.C., Muradov N., Kalyva A., T-Raissi A., Qin N., Srinivasa A.R., Kakosimos K.E., 2017, Solar hybrid photo-thermochemical sulfur ammonia water-splitting cycle: Photocatalytic hydrogen production stage. *International Journal of Hydrogen Energy*, 34, 20608–20624
- [12]. Foh S.E., Schreiber J.D., Dafler J.R., 1978, A copper-oxide, copper-sulfate water splitting cycle. In: Thirteenth Intersociety Energy Conversion Engineering Conference, San Diego, CA, August 20–25, 1158–1163.
- [13]. Schreiber J.D., Remick R.J., Foh S.E., Mazumder M.M., 1980, A hybrid water-splitting cycle using copper sulfate and mixed copper oxides. In: Fifteenth Intersociety Energy Conversion Engineering Conference, Seattle.
- [14]. Gonzales R.B., Law V.J., Prindle J.C., 2009, Analysis of the hybrid copper oxide-copper sulfate cycle for the thermochemical splitting of water for hydrogen production. *International Journal of Hydrogen Energy*, 34, 4179–4188.
- [15]. Graf D., Monnerie, N., Roeb M., Schmitz M., Sattler C., 2008, Economic comparison of solar hydrogen generation by means of thermochemical cycles and electrolysis. *International Journal of Hydrogen Energy* 33, 4511–4519.
- [16]. Liberatore R., Bassi A., Turchetti L., Venturin M., 2018, Multi-objective optimization of a hydrogen production through the HyS process powered by solar energy in different scenarios, *International Journal of Hydrogen Energy* 43, 8683–8697
- [17]. Hinkley J. T., O'Brien J. A., Fell C. J., Lindquist S. E., 2011, Prospects for solar only operation of the hybrid sulphur cycle for hydrogen production. *International Journal of Hydrogen Energy* 36, 11596–11603.
- [18]. Corgnale C., Summers W.A., 2011, Solar hydrogen production by the Hybrid Sulfur process. *International Journal of Hydrogen Energy* 36, 11604–11619.
- [19]. Hansen T., US Publication Application number, 20040234441 Chemical and thermal decomposition of ammonium sulphate into ammonia and sulphuric acid.
- [20]. Zamfirescu C., Dincer I., 2014, Assessment of a new integrated solar energy system for hydrogen production. *Solar Energy*, 107, 700–713
- [21]. Kaleibari S.S., Yanping, Z., Abanades, S., 2019, Solar-driven high temperature hydrogen production via integrated spectrally split concentrated photovoltaics (SSCPV) and solar power tower, *International Journal of Hydrogen Energy* 44, 2519–2532.



- 
- [22]. Howell J.R., Siegel R., Menguc M.P., 2016 Thermal Radiation Heat Transfer, CRC Press, 6th ed.
- [23]. James B.D, Baum G. N., Perez J., Baum K. N., 2009, Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production, Directed Technologies Inc., (US DOE Contract no. GS-10F-009J), Arlington, VA.
- [24]. Wu S., Zhou C., Doroodchi E., Moghtaderi B., 2019, A unique phase change redox cycle using CuO/Cu<sub>2</sub>O for utility-scale energy storage. Energy Conversion and Management, 188, 366–380.