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Modelling of westinghouse and sulphur-iodine water splitting cycles for hydrogen production

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ABSTRACT

Hydrogen as an ideal energy carrier can play a very important role in future energy systems for hydrogen production can be used a variety of technologies and sources. One of the most promising methods for large-scale hydrogen production is thermo-chemical water decomposition using heat energy from nuclear, solar and other sources.

The water splitting thermo-chemicals cycles are processes where water is decomposed into hydrogen and oxygen via chemical reactions, using intermediate substances which are recycled. Two cycles were retained interesting and chosen for our study: WestingHouse cycle (WH cycle) and Sulphur-Iodine cycle (SI cycle). For both cycles solar energy has been considered as heat source during the endothermic step of the cycle. Detailed simulation models of both cycles were performed using Aspen Plus code and a thermodynamic analysis was conducted to evaluate the effective plant energetic efficiencies, with respect to their thermodynamic theoretical values. The advantages and disadvantages of both cycles were taken into account. For the WH cycle, an optimization study for SO_2/O_2 separation process, in order to maximize hydrogen production, was carried out. The obtained results are reported.

Keywords

Hydrogen production, water splitting thermo-chemical cycles, WestingHouse cycle, Sulphur-Iodine cycle

1. Introduction

At present energy demand is met by fossil fuels. Specialists in the field of energy are thinking that the transformation of the existing energy system is necessary and that the current global crisis represents an open door for this change. In 2009, for the first time since 1982 world energy consumption decreased.

Two contrasting trends are visible: energy consumption growth in several developing countries, specifically in Asia (+4%), while in OECD countries consumption was severely cut by 4.7% in 2009 [12]. In Europe consumptions shrank by 5% due to the slowdown in economic activities. China became the world's largest energy consumer (18% of the total) since its consumption surged by 8% during 2009 (from 4% in 2008) [12, 13]. In spite of the aforementioned evidence, predictions for world primary show that an energy demand will increase by 36% till 2035, or 1.2% per year on average [12]. Irrefutable transformation could bring usage of hydrogen, which is considered an ideal energy carrier in the foreseeable future.

Hydrogen can be produced from water using a variety of energy sources such as renewable energy sources, nuclear energy or fossil fuels and a

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transition toward hydrogen economy will need significant new primary sources of hydrogen.

Nowadays hydrogen is produced mainly from fossil fuel (especially by methane reforming). During the recent years researches have focused on the development of technologies and processes in order to produce hydrogen without usage of energy sources which has a negative impact on human health and environment [11].

Another more promising methods for hydrogen production is the water splitting thermo-chemical cycle (WSTC). Through this hydrogen can be produced in an environmentally attractive way, without using fossil fuels [11,14].

Water direct dissociation by thermolysis is a non-practical way for obtaining hydrogen, due to the high temperature required (over 2700°C) and for the small content of hydrogen at the thermodynamic equilibrium (5 – 6 % w/w).

It is possible to overcome the above-mentioned problems by using WSTC, where water is decomposed into hydrogen and oxygen via chemical reactions, using intermediate substances which are recycled at end of the cycle. Usually these cycles consist of both endothermic and exothermic reactions and the main endothermic process take place at a temperature varying in the range of 700–1200 °C. Over one-hundred water splitting thermo-chemicals cycles can be found in the literature [1,3,4]. Some of them are purely chemical processes, while others contain electro-chemical steps as well. A lot of them have been studied and evaluated, but most of these studies consider only particular experimental aspects of the entire processes, especially using small size laboratory reactors. In our work for the selected thermo-chemical processes detailed simulations models of the entire cycles have been performed.

In particular, two of the most promising cycles were chosen for our study: Westinghouse cycle (thermo-chemical and electrolytic steps) [2,3,9] and Sulphur-Iodine cycle (pure thermo-chemical cycle) [4,5,7,8,14].

Detailed simulations of both cycles were performed in Aspen Plus code and a thermodynamic analysis was conducted to evaluate the effective plant energetic efficiencies, with respect to their thermodynamic theoretical values. Results show that water splitting thermo-chemical cycles can be considered as a perspective technology for large scale hydrogen production plants. Based on the accomplished simulations in Aspen Plus, both WSTC cycles (WH cycle and SI cycle) have comparable amount of produced hydrogen and thermal efficiencies. The main differences are in the used technology: SI cycle is a pure thermo-chemical cycle, while WH cycle contains an electrolytic step as well, which decreases the number of steps in the process (number of steps influences the overall cycle efficiency). Moreover both cycles have problems with gas separation processes which should be improved.

The outline of this paper is as follows: in section 1 a very general method to perform a thermodynamic analysis of thermo-chemical cycles is explained; in section 2 simulation models of both cycles (WH cycle and SI cycle) are described; in section 3 main simulation results are discussed together with a SWOT analysis of both thermo-chemical processes. Finally, the main conclusions are reported.

2. Thermodynamics of thermochemical conversion

The study of solar thermo-chemical systems is based on first and second thermodynamic laws, which establish the minimum amount of solar energy required to produce particular fuel or chemical substances and whether or not the chosen path for producing the fuel is physically possible. Both types of information are required for a complete process design [2].

Thermodynamics is a powerful tool used in the field of solar thermochemistry. Other problems for evaluation of the water splitting thermo-chemical cycles concern the rates of the chemical reactions and safety aspects related to the materials used in the process. The complex interactions between solar flux, reactant feed conditions, and chemical kinetics are important for designing reactors that convert solar energy efficiently into chemical fuels. Low activation energy to favour kinetics, large enthalpy change to maximize energy conversion capacity, and small molar volume of products to minimize handling/storage volume are some of the general guidelines for the selection of the solar chemical processes.

Using the general method proposed by [2], the theoretical efficiencies, work outputs, irreversibility of the WH cycle and the SI cycle were calculated. According to this method, each WSTC can be summarized using the general scheme shown in Fig.1.

The basic idea is to concentrate the sunlight with the help of solar systems and obtain heat at high temperature for driving a chemical transformation of reactants into products inside a solar reactor [2]; this process is strongly endothermic and takes place at high temperature (700-1200°C).

The products at high temperature exiting from solar reactor are quenched and separated in order to get pure hydrogen. Finally an ideal fuel cell is used to produce useful work; also an ideal chemical reactor is used to regenerate fresh reactants which are send back to the solar reactor.

For the investigated cycles the efficiency based on the first thermodynamic law can be calculated as:

$$\eta_c = \frac{W_{net}}{Q_{solar}}, \qquad (1)$$

Where W_{net} [J/mol] is the net useful work obtained by the products leaving the reactor at the investigated operating condition of temperature and pressure.

With reference to the general scheme of Fig.1, the maximum available work W_{max} [J/mol] can be calculated as the sum of the net useful work plus the lost work due to irreversibilities in the solar reactor and during quenching:

$$W_{\max} = W_{net} + T_0 (Ir_{reactor} + Ir_{quench}) \qquad (2)$$

As it is well known, the theoretical maximum efficiency of any energy-conversion processes is limited by the Carnot efficiency of an equivalent heat engine that results in:

$$\eta_{car} = \frac{W_{\max}}{Q_{solar}} = 1 - \frac{T_0}{T_h} \qquad (3)$$

Irreversibilities in the solar reactor $Ir_{reactor}$ [J/mol.K] arise from the non-reversible chemical transformation and re-radiation losses to the surroundings at temperature T_0 [K]:

$$Ir_{reactor} = \left(\frac{-Q_{solar}}{T_h}\right) + \left(\frac{Q_{rerad}}{T_0}\right) + \dot{n}\Delta S_{R,T_0 \to P,T_h} \qquad (4)$$

Products exiting in the solar reactor at T_h [K] are cooled rapidly to T_0 [K]. The irreversibility associated with quenching is calculated according to the following equation:

$$Ir_{quench} = \left(\frac{Q_{quench}}{T_0}\right) + \dot{n}\Delta S_{P,T_h \to P,T_0} \qquad (5)$$

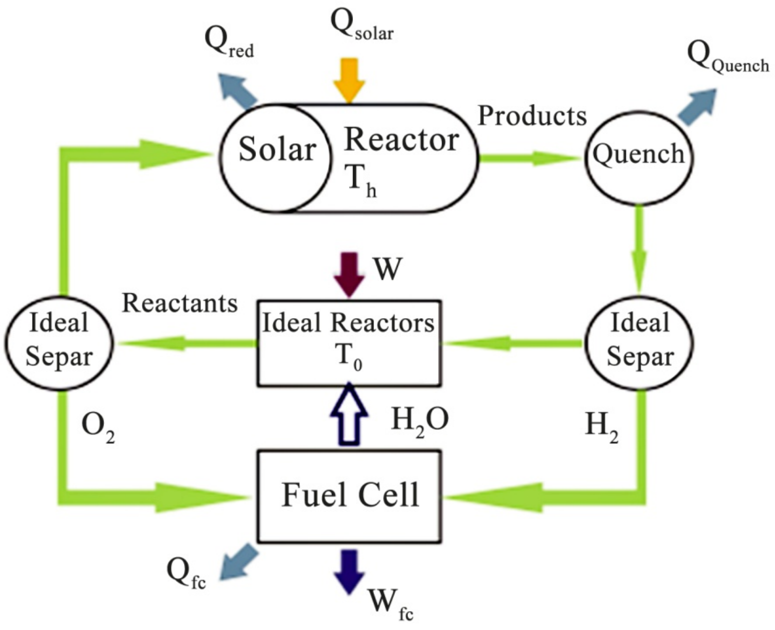

Fig. 1: Schematic of solar energy conversion

Therefore, the maximum theoretical efficiency η_{theor} which can be obtained using a solar energy source in a WSTC can be expressed as:

$$\eta_{theor} = \eta_{car}\eta_{rerad} , \tag{6}$$

Where η_{rerad} represents re-radiation efficiency, which takes into account the loss of energy in the solar reactor by re-radiation. It can be expressed as [2]:

$$\eta_{rerad} = 1 - \frac{c_b T_h{}^4}{c_s I_0} \tag{7}$$

Where I_0 [kW/m^2] is solar constant , c_b is Stefan-Boltzmann constant and c_s solar flux concentration ratio.

The general scheme of fig.1 doesn't take into account the work that could be produced during the quench phase, when the products at high temperature exchanged heat (Q_{quench}) with the surrounding. Therefore, with respect to the general analysis method proposed by Ref. [2], it was considered also the efficiency η_{pwq} , that takes into account the theoretical work and can be obtained during the quench phase for the product at the outlet of the solar reactor. Then the efficiencies η_1 and η_2 based on the second thermodynamic law have been defined as;

$$\eta_1 = \frac{\eta_c}{\eta_{theor}} \qquad \eta_2 = \frac{\eta_{pwq}}{\eta_{theor}} \tag{8}$$

The main results of thermodynamic analysis are summarized in Table 1. Efficiency η_{pwq} takes into account work as well which could by produced during the quenching phase, when products at high temperature T_h (outlet of solar reactor) exchange temperature with surroundings at temperature T_0.

Table 1. Main results of thermodynamic analysis for the investigated cycles

	WH cycle	SI cycle
W_{net} (kJ/mol)	158	158
Q_{solar} (kJ/mol)	479	482
Irr_{total} (kJ/mol/K)	0.37	0.43
η_{car} (%)	64	65
η_{theor} (%)	63	64
η_{pwg} (%)	44	40
η_c (%)	33	32
η_2 (%)	70	63

3. Modeling of westinghouse cycle and sulphuriodine cycle

The concept of water splitting thermo-chemical cycles was proposed in 1960s and since then over one-hundred thermo-chemical cycles have been described; several of them have been successfully tested and evaluated, including chemical processes and process engineering studies [1]. Some WSTC are purely chemical processes and others combine electrochemical steps as well and for this reason they are called hybrid cycles. As a general rule electrochemical step decreases the number of reactions required. For our purposes one pure thermo-chemical cycle with a relatively small number of reactions (Sulphur-Iodine cycle) and one hybrid cycle (Westinghouse cycle), both belonging to the most promising cycles, were selected.

3.1. WestingHouse Cycle

Westinghouse cycle (WH cycle) is a hybrid two-step thermo-chemical process for decomposition of water into H_2 and O_2. The reactions in the WH cycle are as follows:

$SO_2(g) + 2H_2O(l) = H_2(g) + H_2SO_4(l)$ (electrolysis, 25–100 °C)

$H_2SO_4(g) = H_2O(g) + SO_2(g) + ½O_2(g)$ (thermo-chemical, 800 – 850 °C)

Sulphur dioxide and water react electrolytically to produce hydrogen and H_2SO_4. The resultant H_2SO_4 is vaporised to produce steam and SO_3, with the latter being subsequently decomposed at high temperature into SO_2 and O_2. Energy for H_2SO_4 decomposition is obtained from the solar reactor. The oxygen is available as the process by-product [2].

Schematically the WH cycle is illustrated in Fig. 2. There are four major sub-systems in the WH cycle: concentrator, decomposer, separator and electrolyser. The role of concentrator is removing water from sulphuric acid by heating and flashing. They could be separate due to the high difference in the boiling points. The temperature at which a certain amount of water vapour is generated depends on the pressure. Higher pressure needs higher temperature, and lower pressure needs lower temperature for vaporizing the

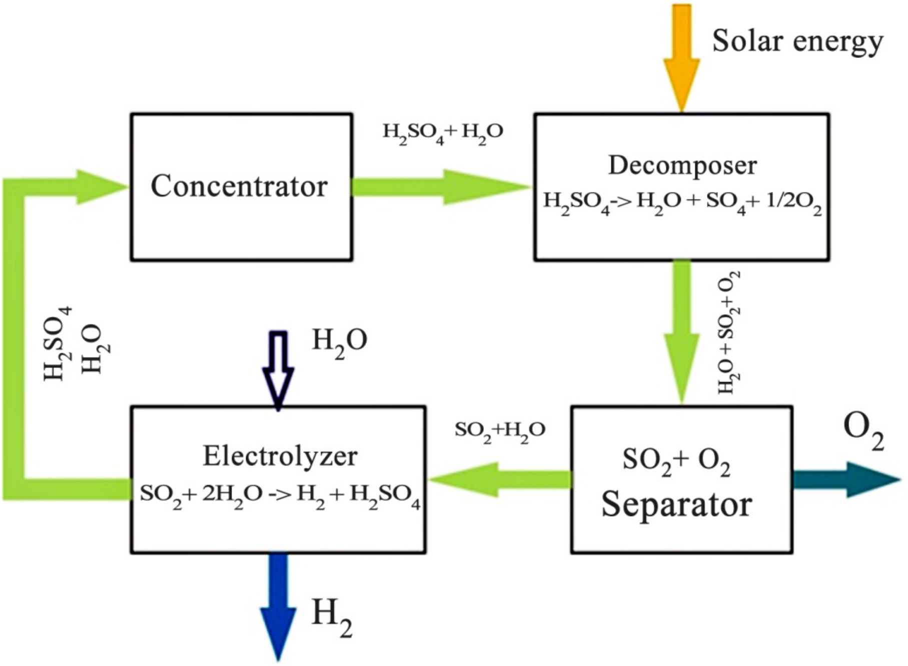

Fig.2: Westinghouse cycle – simplified scheme

same amount of water. It is possible to enhance separation of water and sulphuric acid by changing conditions in the flash, but higher energy is demanded which has an influence on the final cycle efficiency.

In decomposer H_2SO_4 is transformed into water and SO_3. The latter is decomposed at high temperature into SO_2 and O_2. The hot products at the reactor outlet are sent to the cooler and then to the separator tanks, where vapour mixture of SO_2 and O_2 is separated from liquid water. Then the vapour mixture of SO_2 and O_2 is sent to separator sub-system operating at high pressure (20 bar) and low temperature (- 45 °C). In these conditions SO_2 becomes liquid and can be separated from O_2 in the gas phase. The obtained SO_2 is sent to electrolyser. The work consumed during the O_2/SO_2 separation phase is one of the major factors that influence the overall cycle efficiency; the work of compressor and cooler have been included in efficiency calculation. Moreover, hydrogen production depends strongly of the amount of SO_2 send to electrolyser and for this reason SO_2/O_2 separation sub-system was optimized using sensitivity analysis in order to maximize oxygen production in gas phase and sulphur dioxide production in the liquid phase. Sensitivity analysis was made by using different operating conditions for cooler (four temperatures: -85 °C, - 65 °C, - 45 °C, - 30 °C) and compressor (three pressures: 10 bar, 20 bar, 30 bar). Obviously for obtaining a very pure oxygen stream at the outlet lower temperatures in the cooler should be used, with a significant increase in the work consumed in the processes. Therefore a good compromise was reached, according to the details available in section 3.1. The electrolyser produces generated hydrogen: hydrogen is generated at the cathode and sulphuric acid at the anode. Finally, a steam generator was used to recover energy during the quench phase, producing saturated steam at pressure 35 bar and temperature 242 °C. A portion of the produced steam was used in the auxiliaries of the plant, mainly in the concentrator, while the remaining was sent to a steam turbine producing electrical work (W_{turb}).

3.2. Sulphur-Iodine cycle

The Sulphur-Iodine cycle (SI cycle) generates hydrogen in three pure thermo-chemical steps. The reactions in the SI cycle are the as follows:

$2H_2O + SO_2 + I_2 = H_2SO_4 + 2HI$ (120°C, Exothermic, Bunsen reaction)

$H_2SO_4 = H_2O + SO_2 + ½O_2$

(830 – 900°C, Endothermic)

$2HI = H_2 + I_2$

(300 – 450°C, Endothermic)

A simplified scheme of Sulphur-Iodine cycle is illustrated in Fig. 3. The SI cycle can be divided into three major sub-systems, based on three main reactions of the cycle: Gibbs's reactor, Bunsen's reactor and equilibrium reactor.

In the Gibbs's reactor H_2SO_4 is decomposed into SO_3 and H_2O and later into SO_2 and oxygen (same reaction as WH cycle). H_2SO_4 decomposition is the major endothermic step of the process and the temperature has a big influence in the cycle efficiency.

In Bunsen reactor SO_2 and I_2 are added to an excess of water to produce H_2SO_4 and hydrogen iodide and un-reacted water (HI_x phase). In comparison to Gibbs reactor, Bunsen reaction is running at relatively mild temperature of 120°C. In Bunsen reactor large amount of water and iodine are necessary for separation of the H_2SO_4 and HI. H_2SO_4/HI separation is the most critical aspect of the cycle. According to experimental results, the separation is made by formation of two immiscible liquid phases: a light H_2SO_4/H_2O phase and a heavy $HI/I_2/H_2O$ phase (called HI_x). Moreover, from an experimental study, it is knwon that HI/H_2O solution forms an azeotrope, with a HI molar concentration varying in the molar range of 13-15% [5].

Due to the azeotrope, HI_x mixture cannot be separated by simple distillation. Considering the mentioned problems, the HI_x separation section uses H_3PO_4 to recover I_2, HI and H_2O [4, 8]. Indeed H_3PO_4 realizes to different purposes:

1. it helps I_2 separation from HI_x solution by a liquid to liquid extraction column.
2. it breaks the $HI-H_2O$ azeotrope.

More details about this section are explained in section 3.2. Then I_2 and H_2 are separated from HI and I_2 is recycled in the cycle.

The HI decomposition process to produce I_2 and H_2 takes place at temperature at about 450 °C and has been modelling using an equilibrium reactor [4, 5].

4. Simulation and improvement of the cycles

Aspen Plus code was chosen as the process simulator for this work. Aspen Plus® is used for process chemical simulation, process analyses and optimization; it includes vast chemical properties database and many different thermodynamic models to describe the investigated chemical system [6].

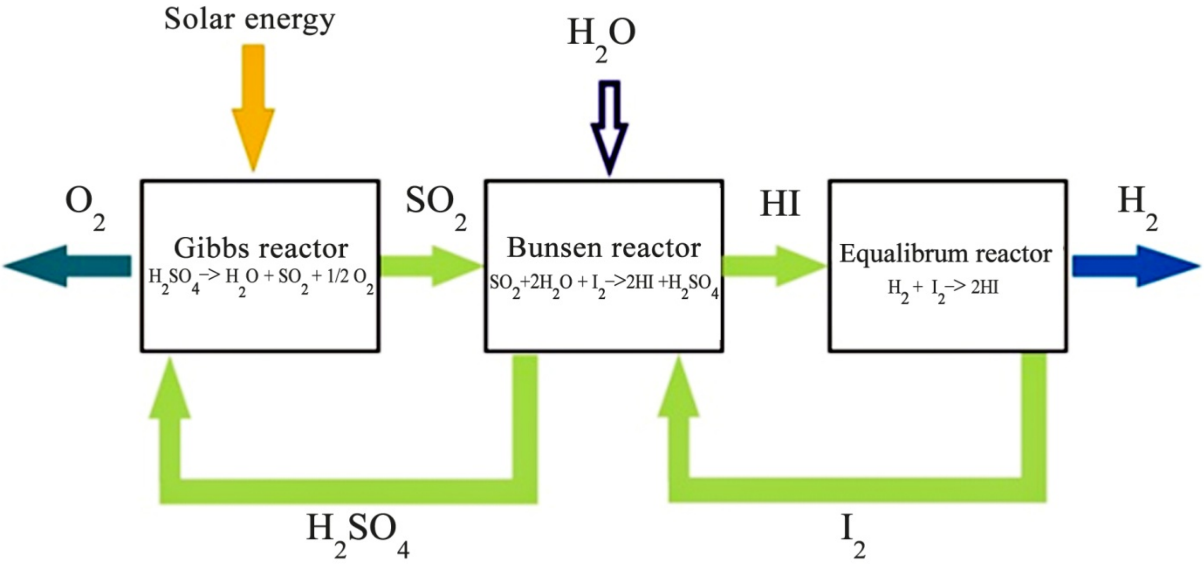

Fig.3: Sulphur-Iodine cycle - simplified scheme

4.1. Westinghouse cycle model

In WH cycle simulation the Peng-Robinson equation of state was chosen to simulate the behaviour of system.

As it was mentioned above, maximization of SO_2 yield has a great impact on the hydrogen production. The SO_2/O_2 separation section is shown in Fig. 4.

For an SO_2/O_2 efficient separation the vapour mixture is compressed up to a 20 bar and then is sent to a separation tank operating at low temperature (- 45°C). After, the high pressure SO_2 liquid phase undergoes a throttling process until a pressure of 1 bar and then it is totally converted in gas phase in a heat exchanger. Finally, the SO_2 gas is sent to electrolyser where is converted in H_2SO_4. The steps separation permits to obtain very pure oxygen as a by-product which could be, for example, stored for future utilization.

The mass fraction and the purity of SO_2 at the outlet of separation system were calculated in different conditions and the obtained results are summarized in Figures 5 and 6. These quantities have been defined as follows:

$$SO_{2\ mass\ fraction} = \frac{SO_{2\ to\ electrolyser}}{SO_{2\ total\ input}} \tag{9}$$

$$SO_{2\,purity} = \frac{SO_{2\ to\ electrolyser}}{\left(SO_2 + O_2\right)_{to\ electrolyser}} \tag{10}$$

Sensitivity analyses were selected as the best operating conditions of pressure and temperature to maximize the hydrogen production in the electrolyzer. In particular, the sensitivity analysis was made using four different temperatures for the cooler system (-85 °C, -65 °C, -45 °C, -30 °C) and three different pressures for the compressor (10 bar, 20 bar, 30 bar).

The best results were obtained at temperature - 85 °C and pressure 30 bar. Nevertheless the energy needed for achieving these conditions has a big impact on the overall efficiency of the thermo-chemical cycle and a good compromise in the operating conditions can be obtained setting T = -45 °C and p = 20 bar. In these conditions the SO_2 mass fraction at the outlet of the separation system is 98.8 % and the purity of recycled sulphur dioxide is 99.4 %.

Oxygen production was calculated as a ratio between total oxygen inlet to separation subsystem and oxygen output.

4.2. Sulphur-Iodine cycle model

Aspen Plus® simulation code incorporates also the capability to describe the behaviour of electrolytes via several different models, including an electrolytic version of the non-random two liquid techniques [3], which was used during the simulation of the SI cycle.

As it was explained above, the liquid at the outlet of Bunsen's reactor is composed of two immiscible liquid phases. As it was discussed by Ref [10], the light liquid phase is composed of a mixture of H_2O and H_2SO_4 , approximately in the molar ratio of 4:1 (H_2SO_4+4 H_2O). Instead, the heavy liquid phase, called HI_x phase, is composed of a mixture of HI, H_2O and I_2 , approximately in the molar ratio of 2:10:8 (2 H_2O+ 10 H_2O + 8 I_2). In the Aspen code the two immiscible liquid phases were defined as new components with molecular formula equal to $H_{10}SO_8$ and $H_{22}I_{18}O_{10}$, respectively. Chemical and physical properties for the new components, such as molecular structure, boiling temperature, molecular weight, vapour pressure and others, were obtained either from experimental values either established or via theoretical calculation [8].

As it was mentioned in section 2, the separation of HI from the HI_x phase is the most critical aspect of entire process, due to the formation of azeotropic solution between HI and H_2O.

Several alternative separations have been proposed in the literature to resolve this azeotrope. Finally, according to Ref. [7], the use of H_3PO_4 was chosen for our purpose. A scheme of the HI_x separation process is shown in Fig. 7. It is composed of two steps operating in series:

1. separating HI and H_2O from the I_2 in HI_x (red oval) using liquid to liquid extraction column.
2. breaking the HI-H_2O azeotrope (blue oval) using H_3PO_4.

In the first step HI_x solution is treated with a concentrated aqueous solution of phosphoric acid H_3PO_4 (88.56% w/w); I_2 is quantitatively recovered at the bottom of the column, while a

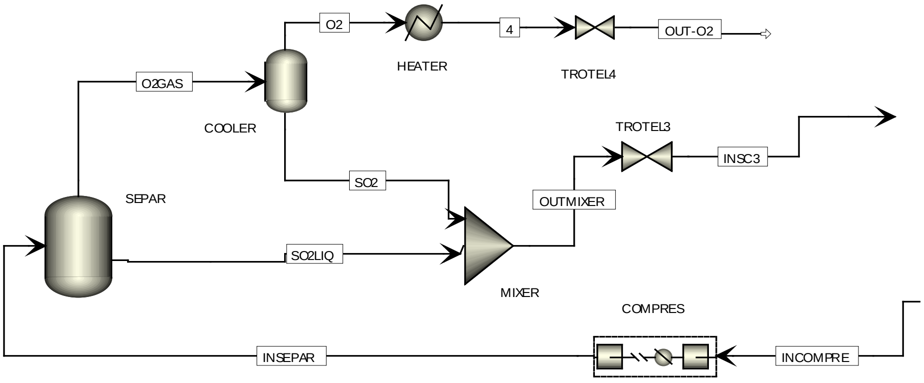

Fig. 4: SO_2/O_2 separation sub-system in the WH cycle

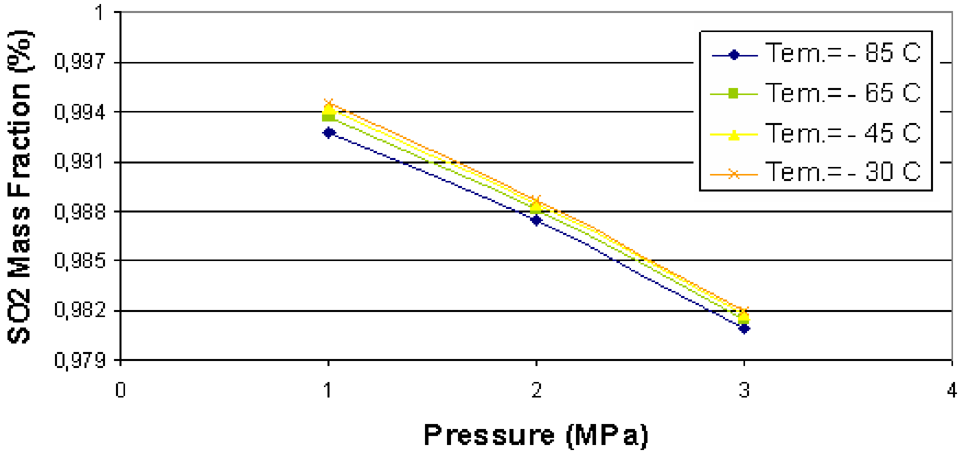

Fig. 5: Comparison of SO_2 mass fraction at different conditions at the outlet of SO_2/O_2 separation system

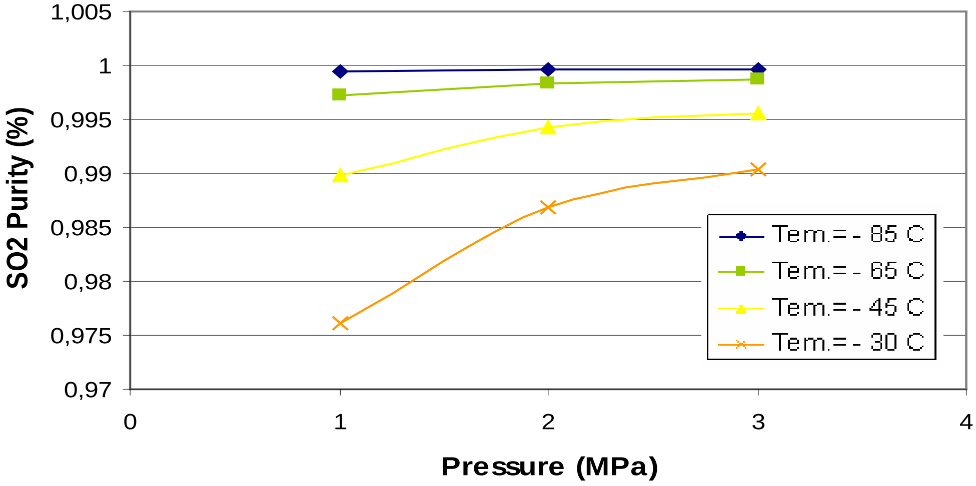

Fig. 6: Comparison of SO_2 purity at different conditions at the outlet of SO_2/O_2 separation system

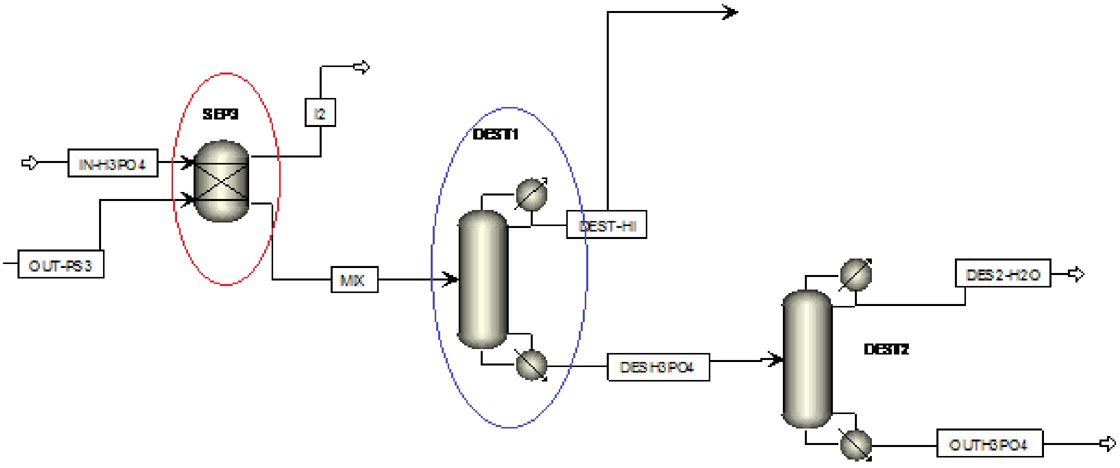

Fig. 7: HI separation process scheme of SI cycle

solu tion of $HI/H_2O/H_3PO_4$ is collected a the top of liquid extractor. The separated I_2 is recycled to Bunsen reactor.

In the second step, the $HI/H_2O/H_3PO_4$ solution is transferred to an extractive distillation column, where HI separation takes place; then HI is moved to equilibrium reactor and the mixture of phosphoric acid and water is sent to another distillation column where water is recycled in a close loop to Bunsen reactor and H_3PO_4 is also recycled in the extraction column.

4.3 Efficiencies of the cycles

On the basis of the Aspen Plus simulation results the efficiencies for the selected thermo-chemical cycles were calculated, together with other relevant process parameters.

Regardless of the fuel, high temperature for the reactions process involve a high energetic efficiency in the cycle and if we consider an ideal thermal cycle the maximum efficiency is associated with the Carnot efficiency.

On the other hand, high temperatures constitute also high losses by re-radiation from the solar receiver and the aperture size for the solar receiver is a compromise between maximizing radiation capture and minimizing radiation losses. For the aforementioned reasons it is not possible to operate thermo-chemical process at the highest upper temperature and each WSTC operates at an individual preferred operating temperature.

Overall cycle's efficiencies can be taken into account as one of the criteria for establishing industrial potential of the WSTC. Another criterion, for example, can be represented by the solar collection area needed to produce a given amount of fuel.

The investment costs related to the solar concentrating system represents usually half of the total investment costs for the entire solar chemical plant [8]. Thus, high efficiency indicates favourable competitiveness.

Effective efficiencies of both cycles were calculated as the ratio between net useful work with respect to the solar energy input in the solar reactor and the results were compared with the respective theoretical values.
In the WH cycle the net work was calculated taking into account the following contributions:

- mass flow rate of hydrogen (M_{H2}) and the low calorific value of hydrogen (LCV_{H2});
- amount of work produced in turbine (W_{Turb}) during the cycle;
- work needed in electrolyser (W_{EL}), compressor (W_{Com}),cooler (W_{Cool}) and pumps W_P.

Therefore the WH effective cycle efficiency can be calculated as follows:

$$\eta_{eff} = \frac{(M_{H2}LCV_{H2}+W_{Turb})-(W_P+W_{EL}+W_{Comp}+W_{Cool})}{Q_{Solar}} \qquad (11)$$

In a similar way the SI cycle efficiency was calculated taken into account the following contributions:

- mass flow rate of hydrogen (the amount of hydrogen produced in SI cycle is comparable with the amount of hydrogen produced in the WH cycle, see Table 2);
- work needed in pumps (W_P) and compressor (W_{Comp}).

The SI cycle effective efficiency was calculated as follows:

$$\eta_{eff} = \frac{(M_{H2} LCV_{H2}) - (W_P + W_{Comp})}{Q_{Solar}} \qquad (12)$$

The main results of the simulation for both cycles are summarised in Table 2. From the simulation in Aspen Plus code was calculated as effective efficiency of the cycles. Effective efficiency of the SI cycles is lower than that in the WH cycle. The main impact to lower effective efficiency of the SI cycles has HI decomposition process which has to be improved. Moreover, the work needed in distillation process was not taken into account in the SI cycle calculation. For this reason effective efficiency will be much lower when also this contribution is considered. After HI decomposition process optimization, which is the most problematic aspect of the SI cycle, effective efficiency should significantly increase. Hydrogen production and also the efficiencies of both cycles are comparable. The theoretical maximum efficiency is limited by the Carnot efficiency of an equivalent heat engine.

Table 2. Simplified results of cycles efficiencies

	unit	WH cycle	SI cycle
$M_{H2produced}$	kg/hr	378	373
W_{turb}	kW	809	-
$W_{P,EL,Comp,Cool}$	kW	5411	-
W_{P+Comp}	kW	-	4770
Useful work	kW	8024	7655
Solar power	kW	26957	29815
η_{eff}	%	30	26
η_{theor}	%	44	40
η_{eff}/η_{theor}	%	68.2	65

4. 4. SWOT analysis of the cycles

Each of water splitting thermo-chemical cycles has its own advantages and disadvantages. Hydrogen production from water is the main goal of several research projects, but there is no industrial practice usage of the WSTC. Evaluation of the Strengths, Weaknesses, Opportunities and Threats of the WestingHouse cycle and the Sulphur-Iodine cycle were performed and is summarized in SWOT analysis, see table 3 for the WH cycle and table 4 for the SI cycle.

5. Conclusion

The use of water splitting thermo-chemical cycles is a perspective technique for a large scale hydrogen production. In comparison with direct water decomposition by electrolysers, the WSTC replaces electricity with heat, using several partial reactions available at reasonable operating temperatures. Detailed simulation models of two of the most promising water splitting thermo-chemical cycles (WestingHouse cycle and Sulphur-Iodine cycle) were performed in Aspen Plus code and a thermodynamic analysis was conducted to evaluate the effective energetic efficiencies, with respect to their thermodynamic theoretical values. In both cycles solar energy is used as a heat source. For the WH cycle a optimization study for SO_2/O_2 separation process was performed to obtain pure O_2 at the output and maximize recycled SO_2 , which has a strong impact on the overall hydrogen production. For the SI cycle an optimization study for HI_x separation was carried out in order to maximize hydrogen production. H_3PO_4 was used for this separation to break up azeotrope and maximize the amount of recycled I_2. One of the main disadvantages of the WH cycle is electrolysis step and the high energy consumption needed for SO_2/O_2 separation process. In the SI cycle a very problematic is the separation system of HI_x liquid phase into I_2 and HI.

Based on the performed simulations, both cycles have comparable amount of produced hydrogen, and thermal efficiencies. The main cycle´s differences are in the used technology: the SI cycle is a pure thermo-chemical cycle while the WH cycle contains also electrolytic step, which decreases the number of steps in the

Table 3. SWOT analysis of the WH cycle

Strengths	**Weaknesses**
• Two step decomposition • Use available and non-toxic chemicals • High efficiency • Hydrogen is produced at lower temperature then by direct water decomposition • Overcome conventional condensation cycle in power plants to obtain electric energy because the main source is heat obtained from solar reactor	• Electrolytical step increase energy demands • In electrolyser are over–potentials need to overcome energy barriers due to mass transfer • Reactants looses, reduce backwards reactions
Opportunities	**Threats**
• Decrease of dependence on fossil fuels import • Decrease of emissions and negative impact on environment • Recycling of used chemicals • Hydrogen production in massive production rate	• Corrosion problems (use of aggressive materials, e.g. sulphur compound) • High hydrogen production costs • High investment costs • Construction materials have to be resistant to high temperature and should have good thermal conductivity

Table 4. SWOT analysis of the SI cycle

Strengths	**Weaknesses**
• Pure thermo-chemical cycle • Use available and non-toxic chemicals • High efficiency • Hydrogen is produced at lower temperature then by direct water decomposition • Overcome conventional condensation cycle in power plants to obtain electric energy because the main source is heat obtained from solar reactor	• Separation of heavy and light phase, increase energy demands, usage of other chemical (H_3PO_4) • Reactants looses, reduce backwards reactions
Opportunities	**Threats**
• Decrease of dependence on fossil fuels import • Decrease of emissions and negative impact on environment • Recycling of used chemicals • Hydrogen production in massive production rate	• Corrosion problems (use of aggressive materials, e.g. sulphur compound) • High hydrogen production costs • High investment costs • Construction materials have to be resistant to high temperature and should have good thermal conductivity

process (number of steps has an influence on the overall cycle efficiency). Material demands of both cycles are similar and corrosion has to be taken into account. Furthermore, it will be advisable the comparison of obtained results with experimental results in order to improve the simulation models, especially for what concerns the chemical and physical properties of HI_x phase. Finally, as next activities for the future is scheduled to perform a process optimization for the cycles, in order to improve the cycle efficiency and maximize the hydrogen production.

At present there are still many technical questions to answer in order to make the possibility of introducing hydrogen as energy carrier at global level, regarding both its production, with the development of large-scale low-cost sustainable processes, and its utilization, with the design of high efficiency and low-cost fuel cells and the set up of safe massive hydrogen storage devices. The present research in the field of WSTC is concentrated on technological problems of cycles, environmental and economical aspects. Based on the performed simulation of the WH and SI cycles were performed life cycle analysis (LCA) of these processes in order to compare their environmental impacts, also with reference to other hydrogen production technologies (coal gasification, coal pyrolysis). Till now only two phases of LCA (construction and operational phase) were carried out, while final dismantling phase has to be completed. In any case the results obtained from our preliminary LCA (not including dismantling phase) show that pyrolysis and gasification construction phase have a very small impact (lower than 2%) to overall LCA; on the contrary, plant operation has the major impact (up to 98%), due to a big amount of coal used in both processes.

Situation in LCA of both WSTC cycles is instead opposite. The construction phase's impact is at about 20% and the rest falls into operation phase. Hydrogen production via WSTC, can be reasonably considered as one of the more suggestive solutions for the energetic system in the future. Moreover, in comparison with conventional processes for hydrogen production, WSTC are more environmental friendly, especially when the solar heat is used.

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7. Numenclature

η_c	Carnot cycle efficiency [%]
η_{theor}	Theoretical cycle efficiency [%]
η_{pwg}	Theoretical cycle efficiency including work production in quench [%]
η_{eff}	Effective cycle efficiency [%]
η_{reread}	Re-radiation efficiency [%]
M_{H2}	Mass flow rate [kg/s]
T	Temperature [K]
W_{net}	Net useful specific work [kJ/mole]
W_{fc}	Ideal fuel cell specific work [kJ/mole]
LCV_{H2}	Low caloric value of hydrogen [120 MJ/kg]
$Ir_{reactor}$	Solar reactor irreversibility [kJ/mole/K]
Ir_{quench}	Quenching irreversibility [kJ/mole/K]
$\dot{n}$	Molar flow rate of reactant [mole/s]
Q_{solar}	Total solar heat input [kJ/mole]
Q_{quench}	Heat rejected to the surroundings by the quenching process [kJ/mole]
Q_{rerad}	Heat rejected by reradiation [kJ/mole]
I_0	Solar constant [kW/m^2]
c_b	Stefan-Boltzmann constant [5.67.10^{-8} W/m^2/K^4]
c_s	Solar flux concentration ratio
T_h	Solar reactor temperature [K]
T_o	Reference temperature [K]
ΔS	Entropy change [kJ/mole/K]

Acronyms

R	Reactants
P	Products
OECD	Organisation for Economic Co-operation and Development
SWOT	Strengths, Weaknesses, Opportunities and Threats

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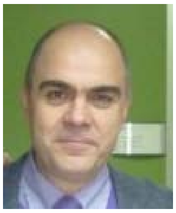
Biographies



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