

# Comparison of thermo-chemical water splitting cycles

Miroslava, Smitková, František, Janíček

## Abstract

Nowadays hydrogen is industrially produced mainly from fossil fuels (mostly from natural gas). In the long term, with respect of a lack of fossil fuels, hydrogen produced from water can play a very important role in the energy system. One of the way how to produce hydrogen from water are water splitting thermo-chemical cycles which replace thermal decomposition of water with several partial reactions.

**Keyword:** hydrogen, water splitting thermo-chemicals cycles, Westinghouse cycle, Sulphur-Iodine cycle

## Introduction

Hydrogen is considered to be an ideal energy carrier in the foreseeable future and it can be produced from water by using a variety of sources – solar energy, nuclear energy or fossil fuels. A hydrogen economy will need significant new sources of hydrogen.

Hydrogen production via water splitting thermochemical cycle (WSTC), a process that accomplishes the decomposition of water into hydrogen and oxygen, is an environmentally attractive way to produce hydrogen without using fossil fuels. [8]

The concept of water splitting thermo-chemical cycles was first proposed in the 1960's with a thermodynamic study and since then, over one-hundred chemical cycles have been proposed. Some of them are purely chemical processes and others contain also electrochemical steps. WSTC consist of both endothermic and exothermic reactions. For our study were chosen: Westinghouse cycle (thermo-chemical and electrolytic steps) and Sulphur-Iodine cycle (pure thermo-chemical cycle).

The outline of this paper is following: In the first and second section basics approach of both cycles (the WH cycle and the SI cycle) are described. In next section the efficiencies of both cycles are calculated and reported.

## 1. Basics of the Westinghouse cycle

Westinghouse cycle (WH cycle) is a two-step thermo-chemical cycle for decomposition of water into hydrogen  $H_2$  and oxygen  $O_2$ . Hydrogen is produced by electrolysis of sulphur dioxide and water mixture at low temperature, which also results in the formation of oxygen and sulphuric acid. Sulphur dioxide  $SO_2$  and water  $H_2O$  are reacted electrolytically to produce hydrogen  $H_2$  and sulphuric acid  $H_2SO_4$ . The resultant sulphuric acid  $H_2SO_4$  is vaporised to produce steam and sulphur trioxide  $SO_3$ , with the latter being subsequently decomposed at high temperature into sulphur dioxide  $SO_2$  and oxygen  $O_2$ . The oxygen is available as a process by-product. The required thermal and electrical energy can be provided by concentrated sunlight to reach higher temperature. [7]

The reactions in the WH cycle are following:



First reaction is electrolysis and runs at temperature between 25 – 100 °C. Second thermo-chemical reaction runs at high temperature at about 850 °C.

Schematically is Westinghouse cycle illustrated in figure 1. There are four major sub-systems in the cycle: **concentrator, decomposer, separator and electrolyser**.

### 1.1 Description of the sub-systems

The role of concentrator is removing water from sulphuric acid by heating and flashing [4]. They could be separate due to different boiling points.

Due to results proposed by [4] was chosen operation conditions for solar reactor at pressure 1 bar (100 kPa) and temperature 830 °C. The reaction is endothermic and the high temperature is needed for sulphuric acid decomposition. Therefore, only the high temperature heat sources could be chosen for this process (solar or nuclear energy).

In decomposer sulphuric acid  $H_2SO_4$  is decomposed into sulphur trioxide  $SO_3$ , which is later being decomposed at high temperature into sulphur dioxide  $SO_2$  and oxygen  $O_2$ .

The hot decomposed gas is send to cooler and then to separator tank where vapour mixture of  $SO_3$ ,  $SO_2$  and  $O_2$  is separated. Vapour mixture of  $SO_2$  and  $O_2$  is send to separator sub-system and liquefied  $SO_3$  is send to the electrolyser.

Vapour mixture of  $SO_2$  and  $O_2$  is compressed by compressor (to achieve high pressure for efficient separation and then is send to separation tank. A large fraction of liquid  $SO_2$  is send to heater and then to electrolyser. Gas  $O_2$  and portion part of  $SO_2$  is send to chiller for future separation which nearly completes separation of  $SO_2$  from  $O_2$  in very low temperature. The separated portion part of  $SO_2$  is send to electrolyser and by-product  $O_2$  could be for example stored for future utilization. These two step separations permit to obtain very pure oxygen at the inlet as a by-product.

The role of electrolyser is generated hydrogen. Hydrogen is generated at the cathode and sulphuric acid at the anode and then is circulated through a closed loop. [7]

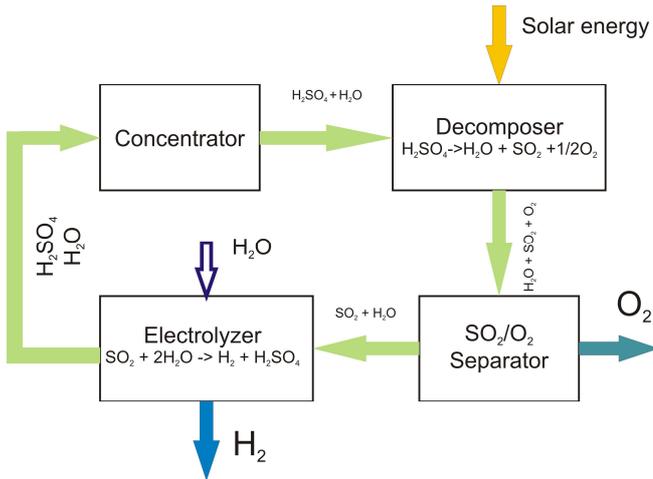
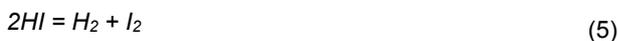


Fig.1 Westinghouse cycle – simplified scheme

## 2. Basics of the Sulphur Iodine cycle

The Sulphur-Iodine cycle (SI cycle) is, as well as the WH cycle, one of the most promising candidates for thermo-chemical hydrogen production. It consists of three pure thermo-chemical steps that sum to the dissociation of water. The SI cycle generates hydrogen in following three steps chemical reactions:



The first exothermic reaction called Bunsen reaction runs at temperature about 120 °C. Second endothermic reaction, similar to WH cycle, needs temperature about 850 °C. The last reaction where hydrogen is produced is endothermic and runs at temperature between 300 – 450 °C.

Schematically is simplified model of Sulphur-Iodine cycle illustrated in figure 2. The SI cycle can be divided to three major sub-systems, based on three main reactions of the cycle: **Gibbs reactor, Bunsen reactor and Equilibrium reactor.**

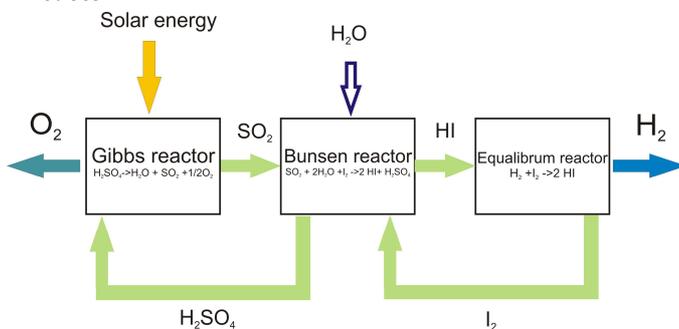


Fig.2 Sulphur Iodine cycle – simplified scheme

### 2.1 Description of the sub-systems

Reaction in Gibbs reactor of the SI cycle is the same as in a solar reactor of the WH cycle. This reaction is the major endothermic reaction and the temperature has a big influence to the efficiency, so only the high temperature heat

sources could be chosen for this process (solar or nuclear energy).

In Bunsen reaction (exothermic reaction) SO<sub>2</sub> and I<sub>2</sub> are added to water to produce sulphuric acid H<sub>2</sub>SO<sub>4</sub> and hydrogen iodide HI. The large amount of water and iodine are necessary for separation of the H<sub>2</sub>SO<sub>4</sub> and HI. The separation is made with a large excess of iodine, by formation of two immiscible liquids: a *light liquid* (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O) and a *heavy liquid* (HI/I<sub>2</sub>/H<sub>2</sub>O) which is mixture of hydrogen iodine, iodine and water called HI<sub>x</sub>. Hydrogen is lately generated from the heavy phase, which is higher density phase. The HI decomposition process uses extractive distillation of the HI, I<sub>2</sub>, H<sub>2</sub>O mixture to recover I<sub>2</sub> and H<sub>2</sub> produce, with a large recirculation I<sub>2</sub> flow back to the Bunsen reaction section.

In equilibrium reactor, hydrogen iodine HI is concentrated and decomposed at moderate temperature 450°C. The result from equilibrium reactor is split in a liquid-gas separator. The hydrogen product and un-reacted HI are separated from I<sub>2</sub>, which is returned to the main solution reaction in Bunsen reactor. The gaseous H<sub>2</sub> product is then separates from HI by using membrane, which is send back to equilibrium reactor, and pure hydrogen is the final product. [5, 7]

## 3. Efficiency calculation

Aspen Plus code was chosen as the process simulator for this work. Aspen Plus® is employed for chemical process simulation and for developing process flow sheet, process analyses and optimization and includes the capability of simultaneously regressing model parameters of many different types in order to generate a thermodynamic model for a specific chemical system. Values obtained from simulation were used for evaluation of both cycles.

Efficiencies of both cycles were calculated as ratio between net useful work with respect to solar energy in solar reactor to decomposed H<sub>2</sub>SO<sub>4</sub>. Results were compared with theoretical values.

The WH cycle total work calculation consider following:

- mass flow rate of hydrogen M<sub>H2</sub> and the low caloric value of hydrogen LCV<sub>H2</sub>,
- amount of work produce in turbine W<sub>Turb</sub> during the cycle,
- work needs in electrolyser W<sub>EL</sub>, compressor W<sub>Com</sub>, cooler W<sub>Cool</sub> and pumps W<sub>P</sub>.

Products leaving reactor at very high temperature (1103 K) are cooling down. Water used for their cooling in heat recover steam generator is lately used in turbine to produce work and part of this water is use as auxiliary steam in others parts of the cycle.

Therefore the WH cycle efficiency can be calculated following:

$$\eta_{eff} = \frac{(M_{H_2} LCV_{H_2} + W_{Turb}) - (W_P + W_{EL} + W_{Com} + W_{Cool})}{Q_{Solar}} \tag{6}$$

In similar way the SI cycle efficiency was calculated. There were take into account following:

- mass flow rate of hydrogen (the amount of hydrogen produced in SI cycle is comparable with amount of hydrogen produced in WH cycle, see Table 1)
- work needs in pumps W<sub>P</sub> and compressor W<sub>Comp</sub>.

The SI cycle efficiency was calculated following:

$$\eta_{eff} = \frac{(M_{H_2} LCV_{H_2}) - (W_P + W_{Comp})}{Q_{Solar}} \quad (7)$$

Efficiencies of both cycles are shown in Tab. 1 and are compared with theoretical efficiencies which were calculated following:

$$\eta_{theor} = \frac{W_{net}}{Q_{solar}} \quad (8)$$

Where  $W_{net}$  [kJ/mole] is the maximum amount of net useful work that the products leaving the reactor could produce if they combined at temperature  $T$  (the temperature of reactants entered to solar reactor) and  $Q_{solar}$  [kJ/mole] is the total solar heat input. [6]

	Unit	WH cycle	SI cycle
$M_{H_2 produced}$	kg/hr	378	373
$W_{net}$	kJ/mole	158	158
$Q_{solar}$	kJ/mole	479	482
$\eta_t$	%	33	32
$\eta_{eff}$	%	30	26
$\eta_{eff} / \eta_{theor}$	%	91	81

**Tab.1 Properties of the WH cycle and the SI cycle**

## Conclusion

Detailed simulation models of two 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 plant energetic efficiencies, with respect to their thermodynamic theoretical values.

There is still space for improvement of both WSTC cycles simulation by optimization of particular parts (f.e. separation of  $H_2SO_4/HI$  mixture which is the most critical part in the SI cycle).

In spite of these problems both WSTC are very promising due to utilization of renewable sources for hydrogen production.

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## Abstrakt

Vodík je v súčasnosti vyrábaný hlavne z fosílnych palív (najmä zo zemného plynu). V dlhodobom horizonte, kedy sa očakáva postupný nedostatok fosílnych palív, sa stane výroba vodíka z vody veľmi zaujímavou možnosťou, najmä ak sa potvrdia domnienky niektorých odborníkov ohľadne smerovania energetiky k vodíkovému hospodárstvu. Sľubnou metódou výroby vodíka sú aj termochemické cykly dekompozície vody, pri ktorých sú vodík a kyslík získavané chemickými reakciami s využitím medziproduktov.

**Mgr. Miroslava Smitkova**  
**prof. Ing. František Janiček, PhD.**

Slovenská Technická Univerzita  
Fakulta elektrotechniky a informatiky  
Katedra elektroenergetiky  
Ilkovicova 3, 812 19 Bratislava  
Tel.: +421 2 602 91 783  
miroslava.smitkova@stuba.sk  
frantisek.janicek@stuba.sk