Simulation and optimization of Westinghouse cycles

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Abstract: Nowadays, hydrogen is industrially produced mainly from fossil fuels by natural gas steam reforming, coal gasification and as by-product of naphtha reforming. Next step of research topic of hydrogen production from renewable sources is utilization of power from solar, wind or water energy and its accumulation in form of hydrogen. This paper deals with the one of most promising water splitting thermo-chemical cycle – Westinghouse cycle. Simulation and optimization of the WH cycle was performed and obtained results are reported.

Key-Words: hydrogen production, water splitting thermo-chemical cycles, Westinghouse cycle

1 Introduction

Hydrogen production from water is the main goal of several research programmes. Direct water dissociation is a non-practical way of obtaining hydrogen, due to relatively high temperatures (above 3 500 K) and the small content of hydrogen at the thermodynamic equilibrium. The goal is to make hydrogen production by water thermolysis occur at reasonable temperatures (below 2 500 K).

The thermo-chemical cycles are processes where water is decomposed into hydrogen and oxygen via chemical reactions using intermediate elements which are recycled. Over one-hundred water splitting thermochemical cycles can be found on literature. These methods of obtaining hydrogen from water consists of both endothermic and exothermic reactions, some of them are purely chemical processes and others that contain electrochemical steps.

One of the most promising cycles was chosen for our study: Westinghouse cycle (thermo-chemical and electrolytic steps) [1, 4]. Detailed simulation of the cycles was performed in Aspen Plus code and also its optimization and improvement of the cycle was performed.

The outline of this paper is following: In the first section basics approach of the WH cycle is published. Then, the description of WH cycle simulation is presented in following section. The improvement and optimization of the WH cycle was performed and is published in the last section. The main conclusions are reported.

2 Basics of Westinghouse cycle

Westinghouse cycle (WH cycle) is a two-step thermochemical cycle for decomposition of water into hydrogen H2 and oxygen O2. 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 SO2 and water H2O are reacted electrolytically to produce hydrogen H2 and sulphuric acid H2SO4. The resultant sulphuric acid H2SO4 is vapourised to produce steam and sulphur trioxide SO3, with the latter being subsequently decomposed at high temperature into sulphur dioxide SO2 and oxygen O2. 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. [4]. The reactions in the WH cycle are following:

\[
H_2SO_4 (g) = H_2O(g) + SO_2(g) + \frac{1}{2} O_2(g)
\text{ thermo-chemical, 800 - 850 °C (1)}
\]

\[
SO_2 (g) + 2 H_2O (l) = H_2(g) + H_2SO_4 (l)
\text{ electrolysis, 25 - 100 °C (2)}
\]

Schematically is Westinghouse cycle illustrated in figure 1. There are four major sub-systems in the cycle: concentrator, decomposer, separator and electrolyser.
Following short description of four aforementioned major sub–systems in the WH cycle:

- **Concentrator**: The role of concentrator is removing water from sulphuric acid by heating and flashing [1, 4]. They could be separate due to different boiling points. The efficient liquid mixture of sulphuric acid and water (in our case approx. 40 % H$_2$SO$_4$ and 60 % H$_2$O) are send to the decomposer and vaporized water is send to electrolyser.

- **Decomposer**: Due to results proposed by [1, 4], was chosen operation conditions for solar reactor at pressure 1 bar 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$_2$SO$_4$ is decomposed into sulphur trioxide SO$_3$, which is latter 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 complete 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. This two step separation permit to obtain very pure oxygen at the inlet as a by-product.

- **Separator**: SO$_2$/O$_2$ separation sub-system was optimized to maximize O$_2$ production in gas phase and SO$_2$ production in liquid phase. The maximization of SO$_2$ has the big impact to the hydrogen production.

- **Electrolyser**: The role of electrolyser is generated hydrogen. Hydrogen is generated at the cathode and sulphuric acid at the anode and then is circulated though a closed loop. [4]

### 3 Simulation and optimization of Westinghouse cycle

Aspen Plus (Aspen Plus®, Aspen Technology, Inc. (AspenTech.)) 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. There are many different modelling techniques. For WH cycle simulation, following the recommends in [3], was chosen Peng-Robinson method (PENG-ROB) which uses Peng-Robinson equation of state.

#### 3.1 Optimization of separation sub-system

SO$_2$/O$_2$ separation sub-system was optimized to maximize O$_2$ production in gas phase and SO$_2$ production in liquid phase. The maximization of SO$_2$ has the big impact to the hydrogen production. The SO$_2$/O$_2$ separation section is shown in Figure 2.
in gas phase is send to cooler for follow-up separation which nearly complete separation of SO₂ from O₂ at very low temperature (-45 °C). The separated portion part of SO₂ is also send to mixer and after heating send to electrolyser. This two steps separation permit to obtain very pure oxygen at the inlet as a by-product which could be, for example, stored for future utilization.

The mass fraction and the purity of SO₂ outlet send to electrolyzer were calculated in different conditions (Figure 3 and Figure 4). Using sensitivity analysis were chosen the best conditions to optimize hydrogen production. The sensitivity analysis was made by using different conditions for cooler: four different temperatures (- 85 °C, - 65 °C, - 45 °C, - 30 °C) and three different pressures (10 bar, 20 bar, 30 bar).

Mass fraction was calculated as:

$$MFrac_{SO_2} = \frac{MF_{SO_2}}{TMF} \quad (3)$$

Where

- $MFrac_{SO_2}$ – Mass Fraction of SO₂ (%)
- $MF_{SO_2}$ – Mass flow of SO₂ (inlet to electrolyser, kg.s⁻¹)
- $TMF$ – Total mass flow (inlet to electrolyser, kg.s⁻¹)

Purity was calculated as:

$$P_{SO_2} = \frac{MF_{SO_2}}{MF} \quad (4)$$

Where

- $P_{SO_2}$ – Purity of SO₂ (%)
- $MF$ – Mass flow of SO₂+O₂ (inlet to electrolyser, kg.s⁻¹)

The best results were obtained at temperature $T = -85$ °C and pressure $p = 30$ bar (3 MPa). Energy needed for achieve these conditions has impact to overall efficiency of the thermo-chemical cycle and a good compromise in the operating conditions is obtained for $T = -45$ °C and pressure $p = 20$ bar (2 MPa). Final mole fraction at the outlet from SO₂/O₂ separation system is 98,8 % and purity of recycled sulphur dioxide is 99,4 %.

3 Conclusion

Detailed simulation of Westinghouse cycle was performed in AspenPlus code. The goal of the optimization process of the WH cycle was to improve conditions in separation section. During the optimization process was increased purity of O₂ at the outlet and was maximized amount of recycled SO₂. The maximization of SO₂ has the big impact to the hydrogen production because SO₂ and water H₂O are reacted electrolytically in electrolyser to produce hydrogen H₂ and H₂SO₄ which is later recycled in the process.

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