Analysis of the Selected Processes for Hydrogen Production

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Abstract: Hydrogen is industrially produced mainly from fossil fuels by the natural gas steam reforming, the coal gasification and as a by-product of the naphtha reforming. In the future, 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. In the study, two most promising water splitting thermo-chemical cycles (Westinghouse cycle and Sulphur-Iodine cycle) were compared with two different processes for hydrogen production (coal gasification and coal pyrolysis). Results obtained from LCA of these processes are reported in the paper.

Key-Words: hydrogen production, life cycle analysis, water splitting thermochemical cycles, Westinghouse cycle, Sulphur-Iodine cycle, solar energy, gasification, pyrolisis

1 Introduction

Hydrogen is the most plentiful chemical element in the universe, but elemental hydrogen is relatively rare on Earth. Hydrogen is found f.e. in great abundance in stars and gas giant planets and plays a vital role in powering stars through nuclear fusion. Hydrogen can be produced from a variety of sources. Nowadays, hydrogen is industrially produced from fossil fuels (mainly from natural gas) [15, 23].

Hydorgen is considered to be an ideal energy carrier in the foreseeable future. It can be produced from water using a variety of sources such as solar energy, nuclear energy or fossil fuels. Hydrogen economy will need significant new primary sources of hydrogen.

Production of hydrogen without generation of CO_2 needs renewable sources such as solar, wind or water energy and its accumulation in form of hydrogen. Hydrogen production through water splitting thermochemical cycles (WSTC) that is processes accomplishing the decomposition of water into hydrogen and oxygen is an environmentally attractive way to produce hydrogen without using fossil fuels [13].

The concept of the WSTC was proposed in the 1960's and since then over one-hundred thermo-chemicals cycles were described. Two of the simplest and most promising water splitting thermo-chemical cycles were chosen for our study: the Westinghouse cycle and the Sulphur-Iodine cycle. Their life cycle analysis was performed using SimaPro code and results were compared with LCA of two other processes for hydrogen production (coal gasification and coal pyrolisis).

The outline of this paper is as follows: In the first section WSTC processes for hydrogen production are briefly characterized. The main sub-systems of both selected WSTC (the Westinghouse cycle and the Sulphur-Iodine cycle) are described. Life cycle analysis is shortly revealed in the next section and then input conditions for the simulation in SimaPro are published. The main results and conclusions are reported.

2 Hydrogen Production

Combustion of fossil fuels currently provides about 86 % of the world's energy needs. Hydrogen is an environmentally attractive alternative to displace fossil fuels, but current hydrogen production uses fossil fuels as a raw material. Use of hydrogen reduces greenhouse gases only if the hydrogen is produced with non-fossil energy sources [2, 13].

Hydrogen can be produced and converted into useful energy using variety of energy sources such as renewables (e.g. biomass, wind energy, solar energy), nuclear and fossils, and using variety of technologies. Direct water dissociation is a non-practical way to produce hydrogen, due to relatively high temperatures (and coupled material problems) and the small fraction of hydrogen at the thermodynamic equilibrium.

It is possible to overcome aforementioned problems by water splitting thermo-chemical cycles (WSTC), which are the processes for decomposition of water into hydrogen and oxygen though chemical reactions using intermediate substances which are recycled [1]–[4].

The WSTC were extensively studied in the late 1970s and '80s, but they have had only a little interest in the past 10 years. While there is no question about the technical feasibility and the potential for high efficiency, cycles with proven low cost and high efficiency have to be developed commercially yet [1]. Several of them have been successfully tested and evaluated including their chemistry, bench scale studies and process engineering studies.

Some of the WSTC are purely chemical processes and others contain also electrochemical steps and consist of both endothermic and exothermic reactions. The main endothermic reactions take place at temperature running in the range 700 – 1200 °C. Therefore, only the high temperature sources should be chosen for this process e.g. solar or nuclear energy.

The basic idea of the water splitting thermo-chemical cycles which use solar energy (Fig. 1) is to concentrate the sunlight with the help of solar systems and to obtain the heat at high temperature for driving a chemical transformation and production of storable and transportable fuel [3]. The products at high temperature exiting solar reactor are separated and quenched. Finally an ideal fuel cell is used to produce the work and the reactants are sent back to the solar reactor. Two most promising WSTC are the Westinghouse cycle (WH cycle) and the Sulphur-Iodine cycle (SI cycle) and they were chosen for the study.

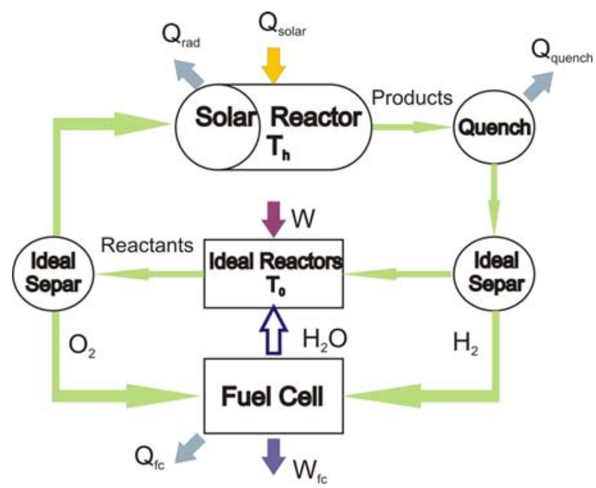

Fig. 1 Schematic model of solar energy conversion

2.1 Westinghouse cycle

The Westinghouse cycle (WH cycle) is a two-step thermo-chemical cycle for decomposition water into hydrogen H_2 and oxygen O_2.

Hydrogen is produced by electrolysis. Sulphur dioxide SO_2 and water H_2O are reacted electrolyticaly 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 [6]. The reactions in the WH cycle are as follows:

$$SO_2 + 2H_2O = H_2 + H_2SO_4 \quad electrolysis, 25 - 100°C \tag{1}$$

$$H_2SO_4 = H_2O + SO_2 + \frac{1}{2}O_2 \quad thermo-chemical, 800 - 850°C \tag{2}$$

There are four major sub–systems in the cycle: *concentrator, decomposer, separator and electrolyser*. The sub-systems are schematically shown in Fig. 2 and briefly described below.

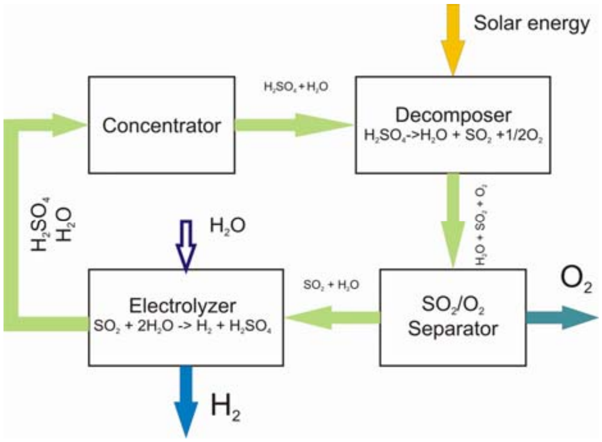

Fig. 2 Simplified schematic model of the WH cycle

Concentrator: The role of the concentrator is to remove water from sulphuric acid by heating and flashing [1, 6]. They can be separated due to different boiling points. The efficient liquid mixture of sulphuric acid and water is sent to the decomposer and vaporized water to the electrolyser.

Decomposer: According to the obtained results from [1] and [6], operation conditions for solar reactor corresponding to pressure of 1 bar and temperature of 830 °C were set. The reaction is endothermic and the high temperature is required for the sulphuric acid decomposition. Therefore, only the high temperature heat sources are usable for this process (solar or nuclear energy). In decomposer sulphuric acid H_2SO_4 is decomposed into sulphur trioxide SO_3, which is latter being decomposed at high temperature into sulphur dioxide SO2 and oxygen O_2. The hot decomposed gas is sent to the cooler and then to the separator tank where vapour mixture of SO_3, SO_2 and O_2 is separated. Vapour mixture of SO_2 and O_2 is transmitted to the separator sub-system and liquefied SO_3 to the electrolyser.

Separator: Vapour mixture of SO_2 and O_2 is compressed by a compressor (to achieve high pressure for efficient separation) and then is sent to the separation tank. A large fraction of liquid SO_2 is transferred to the heater and then to the electrolyser. Gas O_2 and portion part of SO_2 is transferred to chiller for future separation which nearly completes separation of SO_2 from O_2 at a very low temperature. The separated portion part of SO_2 is sent to the electrolyser and O_2 as a by-product can be stored for future utilization. This two steps separation permits to obtain a very pure oxygen at the inlet as the by-product. 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 impact to the hydrogen production.

Electrolyser: The role of the electrolyser is to produce hydrogen at the cathode and sulphuric acid at the anode. Sulphuric acid is then circulated through a closed loop. [6]

The improvement of the Westinghouse cycle was focusing on optimization of SO_2/O_2 separation sub-system because maximization of SO_2 entering to electrolyzer has the big impact to the hydrogen production and therefore also for efficiency of the cycle.

Industrial scale-up studies have a great importance, for the assessment of safety aspects of the process, the feasibility of the main components at industrial scale, and H_2 production costs [21].

2.2 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.

In the SI cycle, similar as in the WH cycle, H_2SO_4 is decomposed into SO_3 and water and later into SO_2 and oxygen. Oxygen is also available as a process by-product. Iodine is added to run Bunsen reaction and to produce two immiscible aqueous acid phases: mixture of water and sulphuric acid, which is send in a close loop, and mixture of hydrogen iodide, iodine and water (called HIx phase). Iodine and hydrogen are separated from HI and I_2 is recycled in the cycle. The SI cycle consists of three pure thermo-chemical steps that sum to the dissociation of the water. [14, 16] The SI cycle generates hydrogen in the following three steps chemical reactions:

$$H_2SO_4 = H_2O + SO_2 + \frac{1}{2}O_2 \quad \textit{Endothermic reaction}, 830 - 900°C \tag{3}$$

$$H_2O + SO_2 + I_2 = H_2SO_4 + 2HI \quad \textit{Exothermic Bunsenr reaction}, 120°C \tag{4}$$

$$2HI = H_2 + I_2 \quad \text{(5)}$$
$$\textit{Endothermic reaction},\ 300 - 450°C$$

The SI cycle can be divided into thee major sub–systems, based on three main reactions of the cycle: *Gibbs reactor*, *Bunsen reactor* and *Equilibrium reactor*. The sub-systems are schematically shown in Fig. 3 and briefly described below.

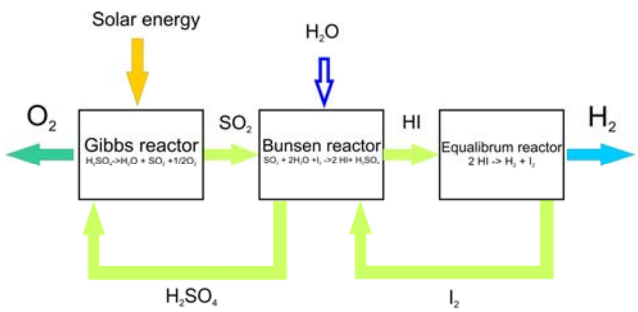

Fig. 3 Simplified schematic model of the SI cycle

Gibbs reactor: The role of the Gibbs rector section is sulphuric acid concentration and decomposition. Sulphuric acid is decomposed into sulphur trioxide and later into sulphur dioxide, oxygen and water. The small amount of SO_3 is founded in the outlet of the Gibbs reaction. Later SO_3 reacts with water and produce diluted H_2SO_4 which is recycled in Bunsen reactor. [17]

Bunsen reactor: In Bunsen reactor are produced and separated two immiscible aqueous acids. The separation is made with a large excess of iodine, by formation of two immiscible liquids: *a light liquid (H_2SO_4/H_2O)* which is lower density phase contains aqueous sulphuric acid and *a heavy liquid (HI/I_2/H_2O)* which is mixture of hydrogen iodine, iodine and water called HI_x. Hydrogen is lately generated from the heavy phase, which is higher density phase. Reaction proceeds exothermically and iodine and water are later recycled in the cycle. [2, 3]

Equilibrium reactor: In equilibrium reactor, hydrogen iodine HI is concentrated and thermal decomposed at moderate temperature 450°C. The result from equilibrium reactor is split in a liquid-gas separator. The hydrogen product and some HI are separated from most of the I_2 which is returned to the main solution reaction in Bunsen reactor. The gaseous H_2 product is then separated from HI, which is send back to equilibrium reactor, using membrane and pure hydrogen is the final product.
For the SI cycle an optimization study for HI separation was carried out in order to maximize hydrogen production. H_3PO_4 was used for this separation to break up an azeotrope and maximize amount of recycled I_2.

3 Life Cycle Analysis

Life cycle analysis (LCA) is the assessment of environmental impact of a given product or service throughout its lifespan. It can be consider as a tool for analyzing the environmental burden of products at all stages of their life cycle [9, 10, 11].

The LCA is an objective evaluation method for establishing energy and environmental loads of a process, a product or an activity. All energy, material, and waste flows released to the environment are evaluated and accounted [9, 10].

The evaluation process of life cycle analysis covers the whole life cycle (considering three main phases *construction*, *operation* and *dismantling*), including extraction of raw materials, fabrication processes, transport, distribution, utilization/ production, re-use, internal recycle and final disposal.

On the present, the LCA is an environmental quality standard, part of the ISO 14000 family (International Organization for Standardization). The methodological framework accepted worldwide for the LCA currently recognizes four phases (see, Fig. 4).

1. Goal and scope definition (ISO 14041)**:** means definition of the case study and the reasons behind it.

2. Inventory Analysis: during this phase the flows of energy and materials throughout the production process are assessed, reconstructing thus the transformation from raw materials to final product. The issue is an ordered list of all inputs and outputs, which is actually a model of the real system. [9]

3.Life Cycle Impact Assessment (LCIA, ISO 14042)*:* this phase allows passing from data collected during the inventory analysis to the assessment of the environmental impact. The purpose is environmental determination of all effluents and raw material consumptions documented in the inventory analysis. It is necessary in this part to select the *impact categories, category indicators* and *characterization models*. It is common practice to refer directly to an assessment method, e.g.: Eco-Indicator 95/99. The next step is the classification, that is, assignment of the results of the inventory analysis to the different impact categories identified. This is automatically done following the rules defined in the selected method of assessment. Final step is characterisation, that is, calculation of the category indicator. This implies multiplying the result of the inventory analysis with the characterization factors for each category. At the end of these steps the indicator for each category of impact is built. [9, 10, 11]

4. Interpretation (ISO 14043)***:*** is the last phase of the LCA study, which aim is to suggest the changes necessary to reduce the environmental impact of the processes or activity considered, evaluate them in order to improve the process itself. Its purpose is checking and evaluating the results, comparing them with the goal and scope, and establishing the limits and completeness of the analysis. [10, 11]

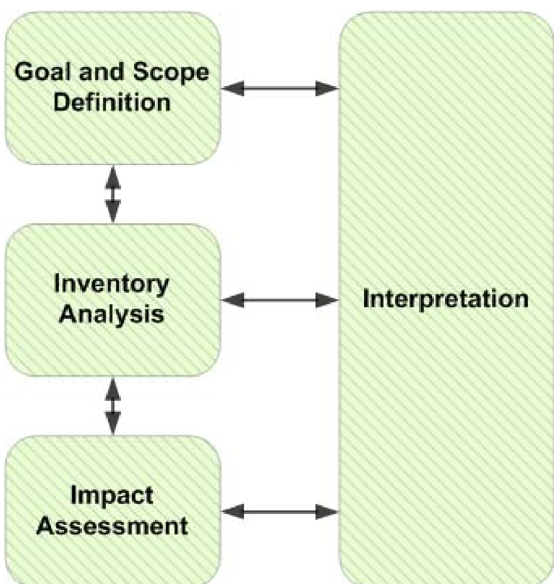

Fig. 4 Illustration of the LCA phases

The aim of the performed LCA analyses was to assess the relative impact of the following four different hydrogen production processes – *the coal gasification, the coal pyrolysis, the Westinghouse cycle and the Sulphur-Iodine cycle.*

Table 1 Hydrogen production and the input of fuel for compared processes

	Coal / Coal Equivalent*	**Hydrogen production**	**Specific production**
	kg/hr	**kg/hr**	**H_2/kg of coal**
Pyrolysis	112 400	4 190	0,04
Gasification	112 400	14 660	0,13
WH cycle*	1 624	379	0,23
SI cycle*	1 682	373	0,22

3.1 Simulation in SimaPro 7.0

Simulations were performed in SimaPro 7.0, which is basically a database able to reconstruct the "history" of several processes and materials and to aggregate the elemental pollutants inventory in order to obtain values for the selected environmental effect indicators [9, 10].

A critical issue is the definition of functional unit because all measurement will be referred to it during LCA. The functional unit is a reference unit to which all inlet and outlet flows will be referred. For the study, as a functional unit was chosen *1 kg of produced hydrogen*.

One of the inputs in operation phase of the cycles is electric power which is needed for supply of pumps, compressor, cooler and electrolyser. In gasification and purification system coal is used as the input (a row material). For comparison of all mentioned processes, the recalculation to coal equivalent (Table 1) of needed electric power (in the WH cycle and the SI cycle) was performed (CO_2 emissions were also considered).

Very simplified models of selected processes for hydrogen production were chosen because all other flows in the system are internal and have no impacts on the environment. Oxygen was considered as an avoided product in the WH cycle and the SI cycle because of reusing it e.g. in fuel cells and sulphur was considered as an avoided product in gasification and pyrolysis process.

For later comparison of the hydrogen production processes some input parameters of plants construction phase (the WH cycle and the SI cycle) were set as follows:

- Nominal power of plants – 26 MW
- Plant life – 20 years
- Working hours – 2600 hours/year
- Effective surface of plants – 26000 m^2
- Number of mirrors – 376

For coal gasification and coal pyrolysis were some input parameters of construction phase set as follows:

- Nominal power of plants – 421 MW_e
- Plant life – 20 years
- Working hours – 8000 hours/year

Table 2 Operation phase inputs – the WH cycle

	Input	Input scaled to the functional unit	Unit
H_2O	3473,47	9,17	kg
SO_2	70,35	0,19	kg
Electric power	4873,11	12,86	kW
Coal Equivalent	-	4,29	kg

The plants are not really exist, but grown out from the real power plants modification. Data for operation phase of the WH cycle and the SI cycle were obtained from Aspen Plus simulation and are summarized in Table 2 – Table 5. They were scaled to the functional unit and output steams were allocated according to six principal categories (Raw materials, Primary fuel, Feedstock, Stream of waste, Emission in the air, Emission in water.).

Table 3 Operation phase outputs – the WH cycle

	Output	Output scaled to the functional unit	Unit
H_2	378,81	1	kg
O_2	2884,13	7,61	kg
SO_2	70,35	0,19	kg
CO_2	-	11,32	kg

Data used for the operation phase of coal gasification were obtained from literate (Integrated Gasification Combined-Cycle (IGCC) plant designs based on the Shell entrained-flow gasifier, [12]) and are shown in Table 6. The operation phase's data of coal pyrolisis were gain from process simulation in Aspen Plus, alike for the WH cycle and the SI cycle, and are summarized in Table 6. Data used for the construction phase of both cycles were taken from literature and were adopted and modified to our conditions from the existed power plants.

Table 4 Operation phase inputs – the SI cycle

	Input	Input scaled to the functional unit	Unit
H_2O	4313,28	11,71	kg
I_2	25,46	0,000001	kg
Electric power	4769,55	100,39	kW
HI	1442,70	14,26	kg
H_3PO_4	1763,91	4,73	kg
CO_2	-	11,26	kg

Table 5 Operation phase outputs – the SI cycle

	Output	Output scaled to the functional unit	Unit
H_2	372,73	1,00	kg
O_2	2898,12	9,69	kg
HI	1442,70	14,26	kg
I_2	25,46	0,001	kg
CO_2	-	11,26	kg
H_2O	42,61	0,11	kg

Table 6 Parameters of the coal pyrolysis and coal gasification

	Gasification	Pyrolysis
	scaled to the functional unit	
Power (MWe)	412,8	412,8
Coal input (kg)	7,67	26,83
Air input (kg)	161,45	369,45
Water input (kg)	3,28	8,19
MEA input (kg)	8,12E-04	1,39E-04
H_2 (kg)	1,00	1,00
Electricity out (MWh)	22,28	14,36

	Gasification	Pyrolysis
Water output (kg)	2,0	1,82
S recovered (kg)	2,76E-02	2,26E-02
Waste to landfill (kg)	1,83	11,9
Heat lost (kWh)	175,69	0,1
Stack gases (kg)	149,43	395,1

In the simulations was chosen ***Eco-Indicator 99*** which is a "Damage-oriented" method of LCA. The weighting has been developed by an expert panel group. All types of impact are reduce to three damage macro-categories, which are originated by the original impact categories. Eco-Indicator 99 refers to three impact categories: ***human health, ecosystem quality, resources.*** [9, 10, 11]

3.2 Results of the Simulation

Results from the construction phase, the operation phase and the life cycle analysis of the compared processes for hydrogen production are shown in Fig. 5 – Fig. 7.

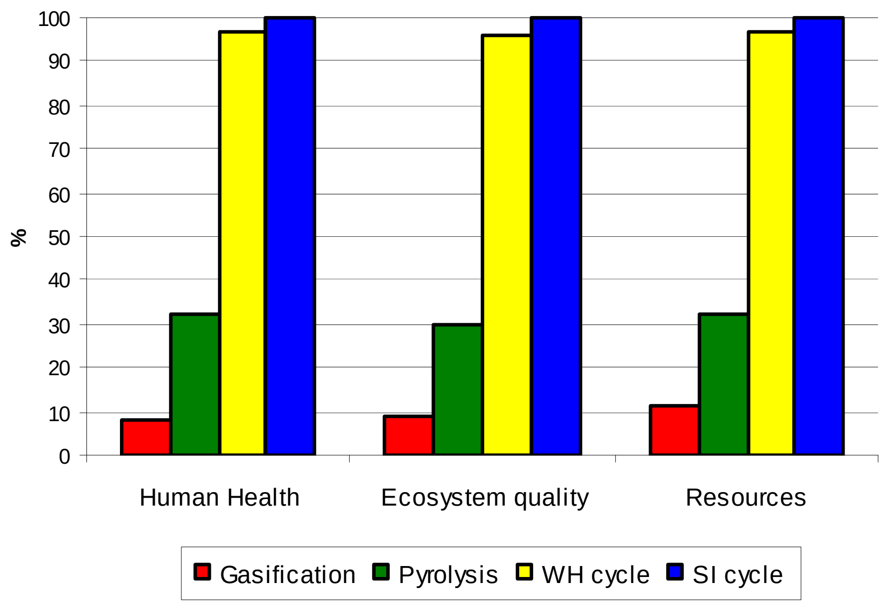

Fig. 5 Comparison of construction phase of WH cycle, SI cycle, gasification and pyrolysis

Pyrolysis is most impacting in all categories of the LCA (Fig. 7). The impact of used coal is much higher during the pyrolysis process in comparison with gasification. It is due to the amount of produced hydrogen during gasification is nearly 3,5 times higher then during pyrolysis. The WH cycle is more impacting in comparison with the coal gasification in terms of the human health indicators during the operation phase but with respect to ecosystem quality and resources it is less impacting. It is due to relatively high amount of SO_2 which has negative impact to human health. For coal gasification and coal pyrolysis the main impact to ecosystem quality is due to climate changes which are related to the emission of CO_2 and other substances that influence the climate change.

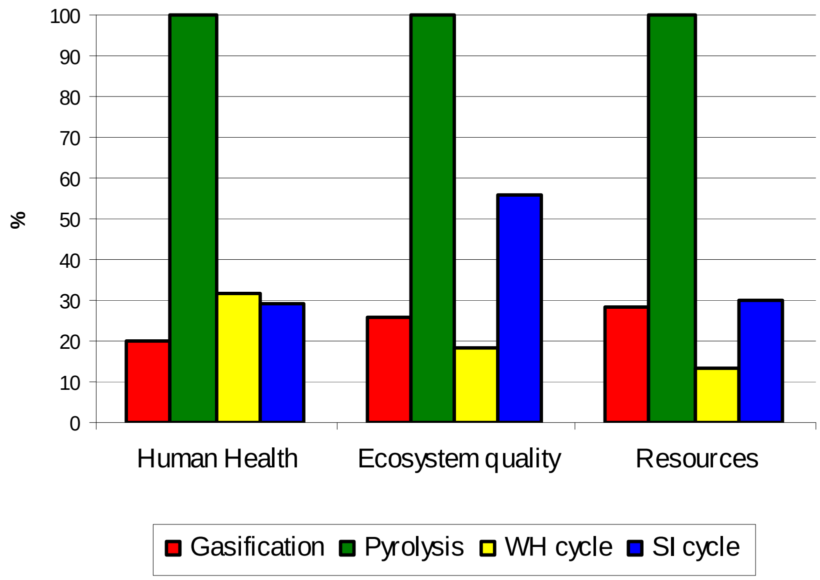

Fig. 6 Comparison of operation phase of the WH cycle, the SI cycle, gasification and pyrolysis

From the result of the construction phase (Fig. 5) follows that the biggest impact on the Eco-Indicator 99 categories have the WH cycle and the SI cycle. During their construction phase, in comparison with gasification and pyrolysis, materials for solar field mirror construction were used, which have the biggest influence on the results. On the other hand, during operation phase (Fig. 6) the worst results are obtained from pyrolysis. The higher impact of SI cycle is because of problems with recycled iodine used during the simulation of the SI cycle in Aspen Plus. The future improvement of the SI cycle simulation is necessary and the subsequent LCA.

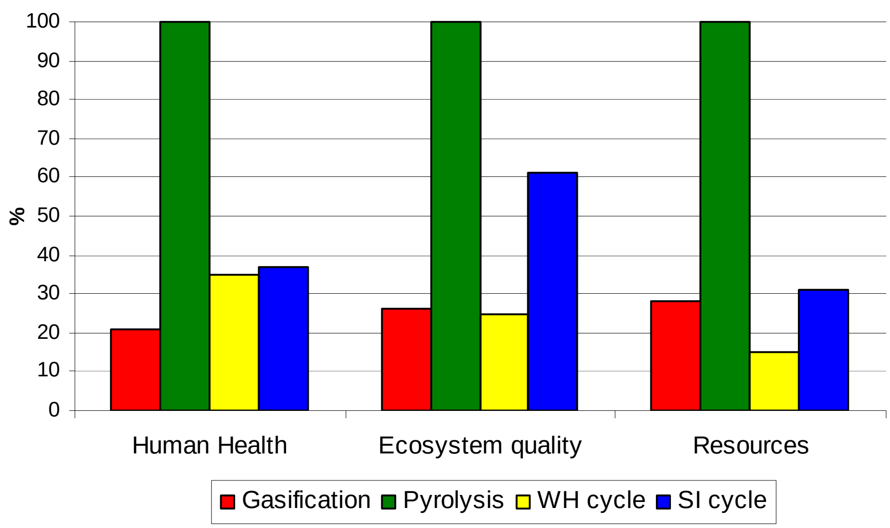

Fig. 7 Comparison of LCA (construction and operation phase of WH cycle, SI cycle, gasification and pyrolysis

The WH cycle and the SI cycle use renewable source (solar energy) during operation phase. Use of solar energy as a heat source is very promising due to utilization of renewable sources for hydrogen production. On the other hand solar energy apparatus use materials which have big impact to environment and also to the human health.

When the whole LCA of four processes is considerate, disadvantages of construction phase are negligible in comparison with operation phase. Therefore attention is focused mainly on operation phase because other phases are almost negligible.

4 Conclusion

Based on Aspen Plus simulation results life cycle analyses of the WH cycle and the SI cycle were made and their LCA were compared with two other processes for hydrogen production (coal gasification and coal pyrolysis). The LCA results confirm that the water splitting thermochemical cycle are attractive methods for hydrogen production due to low environmental impact. Furthermore, the utilization of solar energy as a heat source decreases a detrimental environmental impact of hydrogen production.

The SI cycle is similarly to the WH cycle water splitting thermochemical cycle and use similarly solar energy as a heat source. The similar results were expected. Problems with HI separation process and imperfection in oxygen separation have a big influence to LCA results and a negative impact has also usage of H_3PO_4. Let us assume that after improvement of the SI cycle simulation in Aspen Plus the LCA results will be more similar to the WH cycle results. All results are recalculated to the functional unit (1 kg of produced hydrogen), so the impact of each process depends also on overall hydrogen production

There is still space for improvement of both water splitting thermochemical cycle simulation by optimization of particular parts (e.g. separation of H_2SO_4/HI mixture which is the most critical part in the SI cycle), in order to improve the cycle's efficiency and maximize the hydrogen production, which have influence to the life cycle analysis results.

New results from simulation in AspenPlus code could be applied for the life cycle analysis and also a dismantling phase could be considered in the future in order to realize a complete LCA study.

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