

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SciVerse ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Exergetic life cycle assessment of a hydrogen production process

Ahmet Ozbilen\*, Ibrahim Dincer, Marc A. Rosen

Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario L1H 7K4, Canada

## ARTICLE INFO

### Article history:

Received 29 September 2011

Received in revised form

27 December 2011

Accepted 1 January 2012

Available online 3 February 2012

### Keywords:

Exergetic life cycle assessment

Exergy

Sustainability

Environment

Hydrogen production

## ABSTRACT

Exergetic life cycle assessment (ExLCA) is applied with life cycle assessment (LCA) to a hydrogen production process. This comparative environmental study examines a nuclear-based hydrogen production via thermochemical water splitting using a copper–chlorine cycle. LCA, which is an analytical tool to identify, quantify and decrease the overall environmental impact of a system or a product, is extended to ExLCA. Exergy efficiencies and air pollution emissions are evaluated for all process steps, including the uranium processing, nuclear and hydrogen production plants. LCA results are presented in four categories: acidification potential, eutrophication potential, global warming potential and ozone depletion potential. A parametric study is performed for various plant lifetimes. The ExLCA results indicate that the greatest irreversibility is caused by uranium processing. The primary contributor of the life cycle irreversibility of the nuclear-based hydrogen production process is fuel (uranium) processing, for which the exergy efficiency is 26.7% and the exergy destruction is 2916.3 MJ. The lowest global warming potential per megajoule exergy of hydrogen is 5.65 g CO<sub>2</sub>-eq achieved a plant capacity of 125,000 kg H<sub>2</sub>/day. The corresponding value for a plant capacity of 62,500 kg H<sub>2</sub>/day is 5.75 g CO<sub>2</sub>-eq.

Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

The energy carrier hydrogen is expected by many to become an important fuel. Since its oxidation does not emit greenhouse gases (GHGs), its use does not contribute climate change, provided it is derived from clean energy sources. Numerous researchers anticipate that hydrogen will replace petroleum products for fuelling of transportation vehicles, decreasing dependence on petroleum. Hydrogen is abundant in nature in the form of water. Hydrogen gas needs to be produced and there are several ways this can be accomplished including steam reforming of natural gas, coal gasification, water electrolysis and thermochemical water splitting.

Hydrogen production using thermochemical water splitting cycles has significant potential advantages, in terms of economics and environmental impact. Water can be directly split in one step, but the required temperature is too high to be practical. However, a series of selected chemical reactions can be utilized to achieve the same result at lower temperatures [1]. A variety of thermochemical water decomposition cycles have been identified [2], but few have progressed beyond theoretical calculations to working experimental demonstrations. Most of these cycles require process heat at temperatures exceeding 800 °C. Due to its lower temperature requirements (around 530 °C), the copper–chlorine cycle for thermochemical water decomposition has advantages over

\* Corresponding author.

E-mail addresses: [Ahmet.Ozbilen@uoit.ca](mailto:Ahmet.Ozbilen@uoit.ca) (A. Ozbilen), [Ibrahim.Dincer@uoit.ca](mailto:Ibrahim.Dincer@uoit.ca) (I. Dincer), [Marc.Rosen@uoit.ca](mailto:Marc.Rosen@uoit.ca) (M.A. Rosen).  
0360-3199/\$ – see front matter Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.  
doi:10.1016/j.ijhydene.2012.01.003

other cycles [3], including reduced material and maintenance costs. Moreover, the Cu–Cl cycle has some advantages over other existing hydrogen production methods, and it can utilize low-grade/waste heat to improve its efficiency [4].

Fossil fuels, nuclear energy and renewable energy resources can be used for hydrogen production. Although renewable energy resources are usually considered the most environmentally benign alternative, an important challenge is to obtain sustainable large-scale hydrogen production. Fossil fuels lead to significant environmental impacts. Using nuclear energy for hydrogen production is consequently advantageous for two main reasons: nuclear plants do not emit GHGs during operation, and nuclear energy can support large-scale hydrogen production [5]. For these reasons, thermochemical water decomposition linked with nuclear plants is a promising process for hydrogen production. The Generation IV SCWR (super-critical water cooled reactor) is viewed as a particularly suitable nuclear option for pairing with the Cu–Cl thermochemical cycle.

Although hydrogen is a clean energy carrier since its oxidation mainly emits water, environmental impacts can arise during its production. Hence, the environmental impact of hydrogen production methods should be investigated. Hydrogen production using thermochemical water splitting driven by clean energy sources has lower environmental impacts than conventional methods for hydrogen production. The environmental impacts of the Cu–Cl cycle have not been comprehensively studied, although related research is available for the other hydrogen production methods.

Relations between exergy and environmental impact have been applied by many researchers. Some of the more significant applications related to the present article are described here.

- Ayres et al. [6] discuss exergy, waste accounting, and life-cycle analysis and argue that thermodynamics offers a means of accounting for resource inputs and waste outputs in a systematic and uniform way. They further state that exergy is appropriate as a measure of resource stocks and flows as well as waste emissions and their potential for environmental harm.
- Daniel and Rosen [7] examine material emissions produced for 13 fuel cycles for automobiles, on mass and exergy bases. Chemical exergies of fuel life cycle emissions are compared with the masses of fuel cycle emissions. For the emissions data used, the chemical exergy results suggest that compressed natural gas use in motor vehicles produces emissions that are the furthest from equilibrium with the natural environment, relative to all other fuel life cycle paths considered. It is also shown that diesel use in grid-independent hybrid electric vehicles has the lowest chemical exergies of emissions for all 13 fuel–vehicle combinations considered, suggesting a lower potential for environmental impact. It is concluded that the exergy methodology presented for assessing the potential for environmental impact may aid the development and design of environmentally benign transportation technologies.
- Neelis et al. [8] analyze a several hydrogen production and storage systems for automotive applications using exergetic life cycle assessment. Eight fuel supply and use chains are

analyzed. Exergy analysis is shown to provide additional useful information compared to conventional energy analysis based on the heating values of fuels, since exergy can be used for both fuel and non-fuel resources and can play an important role in the quantification of resource depletion in fuel chains. Vehicles with compressed hydrogen storage are shown to be the most exergy efficient on a normalized (MJ/km) basis.

- Boyano et al. [9] apply exergoenvironmental analysis to a steam methane reforming process for hydrogen production. Exergoenvironmental analysis is a combination of exergy analysis and environmental assessment, in which the environmental impacts obtained by LCA or other environmental assessment tools are apportioned to the exergy streams. The results identify the components with the highest environmental impacts and possible improvements, and provide useful information for designing systems with lower overall environmental impacts. Components in which chemical reactions occur are observed to have higher exergy destructions than other components. The overall environmental impact can be reduced by decreasing the exergy destructions within components, which usually requires the use of efficient modern equipment, expensive materials and efficient designs.
- Granovskii et al. [10] use exergetic life cycle assessment to evaluate the exergy efficiency, economic effectiveness and environmental impact of producing hydrogen using wind and solar energy in place of fossil fuels. In that work, exergy efficiencies and greenhouse gas and air pollution emissions are evaluated for all process steps, including crude oil and natural gas pipeline transportation, crude oil distillation and natural gas reforming, wind and solar electricity generation, hydrogen production through water electrolysis, and gasoline and hydrogen distribution and utilization. The use of wind power to produce hydrogen via electrolysis, and its application in a fuel cell vehicle, is seen to exhibit the lowest rates of fossil fuel and mineral resource consumption. The authors suggest that “renewable” hydrogen can help address long-term environmental problems.

Life cycle assessment (LCA) is essentially a cradle to grave analysis to investigate environmental impacts of a system or process or product. A life cycle assessment is useful for the Cu–Cl thermochemical hydrogen production. However, the concept of exergy has only begun to be introduced into the LCA approach [11]. The depletion of exergy reservoirs and emissions of exergy to the environment need to be reduced to move towards sustainable development, and the extension of LCA to exergetic life-cycle analysis (ExLCA) supports such efforts. ExLCA is a useful tool to investigate all irreversibilities throughout the life of the system by performing exergy analysis for all stages in its life cycle. The main objective of the research reported here is to perform exergy based LCA for nuclear-based hydrogen production. This objective includes the evaluation of 1) exergy efficiencies and destructions for the life time of the nuclear-based hydrogen production system, 2) environmental impacts per megajoule exergy content of hydrogen for various lifetimes, in four impact categories (acidification potential, eutrophication potential, global warming potential and ozone depletion potential), and

3) the variation of acidification and global warming potentials with various exergy efficiencies of the hydrogen plant.

## 2. Exergetic life cycle assessment (ExLCA)

Exergy is defined as the maximum amount of work which can be produced by a system or a flow of matter or energy as it comes to equilibrium with a reference environment. Exergy measure the potential of the system or flow to cause change as a consequence of not being in stable equilibrium relative to the reference environment [12]. Unlike energy, exergy is not subject to a conservation law (except for ideal, or reversible, processes). Rather exergy is consumed or destroyed, due to irreversibilities in any real process. The exergy consumption is proportional to the entropy created due to irreversibilities associated with the process. For exergy analysis, the reference state must be specified, in terms of its temperature, pressure and chemical composition.

Exergy losses occur during the lifetime of a product or a process. Reducing these losses, particularly those due to the use of non-renewable energy forms, helps improve sustainability. Exergy, sustainability and environmental impact are related [12]:

- As exergy efficiency approaches 100%, environmental impacts approaches zero, because exergy is converted from one source to another without any consumptions and emissions.
- Sustainability approaches zero as exergy efficiency approaches zero, because nothing is accomplished although exergy-containing resources are consumed.

Since exergetic life cycle assessment method is not very common compared to conventional life cycle assessment, a comprehensive explanation of it is provided in the following sections.

### 2.1. General framework for ExLCA

The frameworks or flow diagrams of ExLCA (see Fig. 1) and LCA are similar. The main steps of ExLCA, and their similarities and differences from the main steps of LCA, are as follows:

#### 2.1.1. Goal and scope definition

The first step for ExLCA is identical with that for LCA, and involves clarifying the system and the audience considered. The targets and insights of interest from ExLCA are identified. In defining the scope of the ExLCA, the system boundary, which indicates the region to be analyzed, is specified. The scope of the system also has to define the function of the system. A functional unit (e.g. one kg of hydrogen produced), which is a measure of the performance, must be determined. The primary aim of the functional unit is to provide a reference for relating the inputs and outputs. Further details on goal and scope definition are presented elsewhere [13].

#### 2.1.2. Inventory analysis

The inventory analysis of ExLCA is more detailed than that for LCA. A complete flow diagram for the mass and energy flows

involved in each of the life cycle stages is required in ExLCA. Therefore, all inputs and outputs must be identified and quantified. Data collection often involves a combination of measuring process-specific data and acquiring data from literature or calculating data by process modelling. Due to logistical as well as other barriers (such as a reluctance by industry to share data considered confidential), obtaining data to be used in life cycle inventory is often difficult [14]. The material and energy balances have to be closed, which is not always the case in LCA [11]. Sometimes, a more simplified black-box approach is preferred for ExLCA, in which only the inputs and outputs of the life cycle steps are taken into account.

#### 2.1.3. Impact assessment

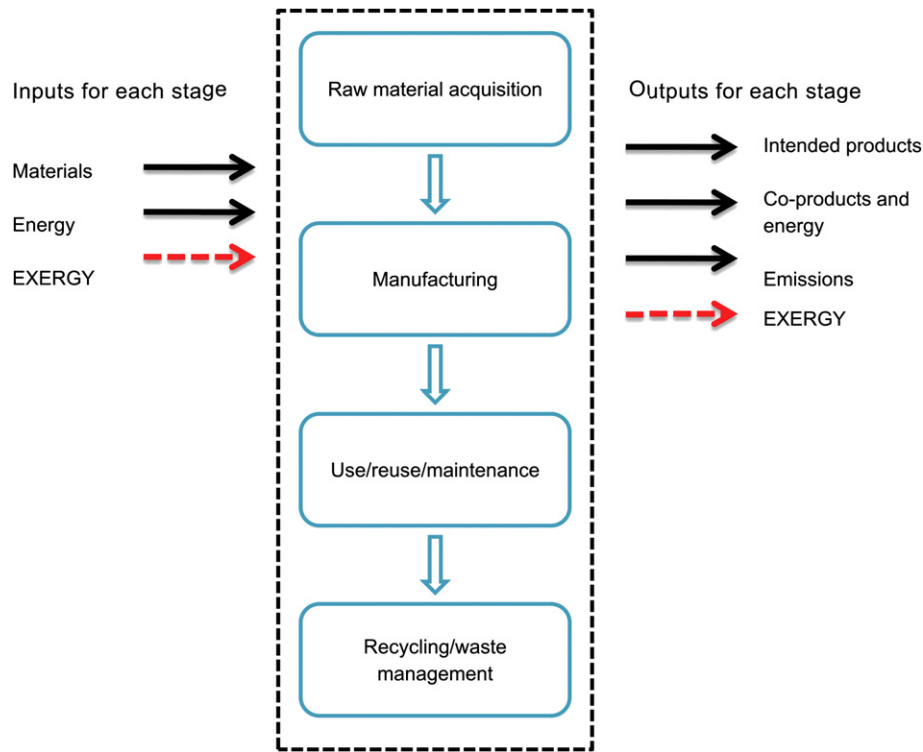
ExLCA impact analysis focuses on the determination of the exergies of flows, and the exergy destructions and exergy efficiencies of the overall process and its subprocesses. Determination of exergy contents of flows is often a combination of utilizing data reported in the literature or by relevant organizations and calculating data with exergy analysis (as noted in Section 2.2). A limited impact classification phase is included in ExLCA.

#### 2.1.4. Improvement analysis

The improvement analysis in ExLCA is intended to reduce its life cycle irreversibilities [11]. The summation of all exergy destructions in the life cycle, which are calculated using exergy analysis, identifies the life cycle irreversibility of the product or the process. The results of ExLCA are interpreted to develop conclusions and recommendations that relate to the goal and scope of the study, that can help decision makers identify and choose an appropriately environmentally benign alternative, bearing in mind that the decision process is also affected by technical, economic, social and other factors.

The Center of Environmental Science of Leiden University (CML) published an “operational guide to the ISO standards” in 2001 [15], which has a set of impact categories and characterization methods and factors for a list of substances (accounting for resources from and emissions to nature) to use in the impact assessment phase of LCA. Guinee et al. [15] explain each environmental impact category. The impact categories used in this study are as follows:

- Acidification Potential (AP): AP is the deposition of acidifying pollutants on soil, groundwater, surface waters, biological organisms, ecosystems and materials, and is measured in units of kg SO<sub>2</sub>-eq. Major contributors to this category are SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>x</sub>. The natural environment, the anthropogenic environment, human health and natural resources are protection areas where AP has notable effects.
- Eutrophication Potential (EP): Eutrophication comprises all potential impacts of excessive levels of macronutrients, mainly nitrogen and phosphorus. Nutrient enrichment may cause an undesirable shift in species composition and elevated biomass production in both aquatic and terrestrial ecosystems. Nitrogen and phosphorus, as well as other emissions causing similar effects, are grouped in the eutrophication impact category. The unit of EP is kg PO<sub>4</sub>-eq.
- Global Warming Potential (GWP): GWP is the impact of human emissions on the radiative forcing (i.e. thermal



**Fig. 1 – General framework for ExLCA, in the form of a flow diagram showing how the inputs and outputs of matter, energy and exergy are considered for all steps in the life cycle of a product or process.**

radiation absorption) of the atmosphere, and is measured in units of kg CO<sub>2</sub>-eq. Global warming, which leads to climate change, may affect ecosystem and human health. Most GHG emissions enhance radiative forcing, which increases the earth's surface temperature (the "greenhouse effect").

- **Ozone Depletion Potential (ODP):** Ozone depletion is the thinning of the stratospheric ozone layer due to ozone-depleting emissions. A greater fraction of solar UV-B radiation reaches the earth's surface as a result of this thinning, which has potentially harmful impacts on human and animal health, terrestrial and aquatic ecosystems, biochemical cycles and materials. Hence, ODP, which is measured in units of kg R11-eq, affects four protection areas: human health, the natural environment, the anthropogenic environment and natural resources.

Throughout ExLCA, the calculation of exergy values requires that the conditions and composition of the reference environment be specified.

## 2.2. Exergy analysis

Exergy analysis is an assessment tool based on exergy, in which exergy flows, balances, destructions and efficiencies are determined for an overall process or system and its subparts. Exergy analysis permits many of the shortcomings of energy analysis to be overcome. Exergy analysis is based on the second law of thermodynamics, and is useful in identifying the causes, locations and magnitudes of process inefficiencies. Exergy analysis acknowledges that, although energy

cannot be created or destroyed, it can be degraded in quality, eventually reaching a state in which it is in complete equilibrium with the surroundings and hence of no further use for performing tasks [16].

An exergy balance for a process or system can be written as follows:

$$\text{Input exergy} - \text{Output exergy} - \text{Destroyed exergy} = \text{Accumulated exergy} \quad (1)$$

The exergy quantities in an exergy balance are described below, following the presentations by Moran [17], Kotas [18] and Dincer and Rosen [16]:

**Exergy of a matter flow ( $Ex_{\text{flow}}$ ):**  $Ex_{\text{flow}}$  can be expressed in terms of physical, chemical, kinetic and potential components. That is

$$Ex_{\text{flow}} = Ex_{\text{ph}} + Ex_{\text{o}} + Ex_{\text{kin}} + Ex_{\text{pot}} \quad (2)$$

**Exergy of thermal energy ( $Ex_Q$ ):** The exergy associated with a thermal energy transfer  $Q$  can be expressed as

$$Ex_Q = \sum_{i=1}^5 \left[ Q_i \left( 1 - \frac{T_0}{T_i} \right) \right] \quad (3)$$

where  $T_i$  and  $T_0$  are system and reference environment temperatures, respectively.

**Exergy of electricity:** The exergy associated with electricity is equal to the energy.

After calculating all exergy contents in a system, exergy efficiencies and exergy destructions can be calculated as follows:

$$\psi = \frac{Ex_{out}}{Ex_{in}} \quad (4)$$

$$Ex_{dest} = Ex_{out} - Ex_{in} \quad (5)$$

where  $Ex_{out}$  is the total exergy content of the outputs and  $Ex_{in}$  is the total exergy content of the inputs.

### 3. Assessment

#### 3.1. System description

Nuclear-based hydrogen production via thermochemical water splitting system and its component subsystems are described. Data used in this research are obtained from literature and normalization procedures are applied. The hydrogen production system has three main subsystems:

- Fuel (uranium) processing
- Nuclear Plant
- Hydrogen Plant

Fig. 2 shows an overview of the system. The first stage of the system is fuel (uranium) processing, which involves mining, milling, conversion, enrichment and fuel fabrication.

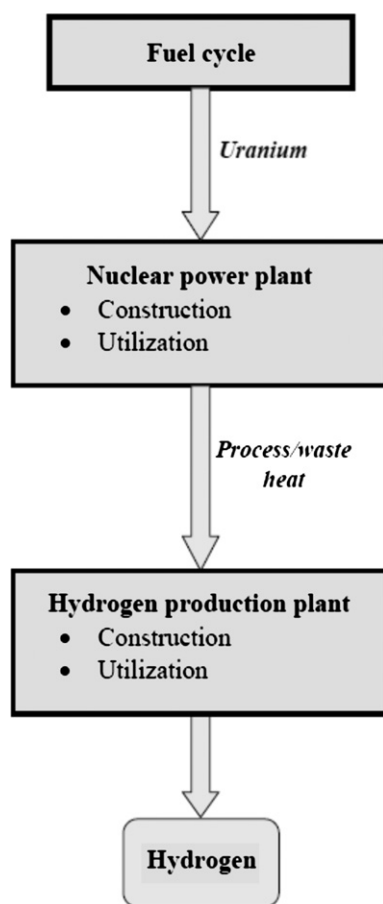


Fig. 2 – Overview of a nuclear-based hydrogen production system.

Fabricated uranium ( $UO_2$ ) is then transferred to the nuclear plant. The output thermal and electrical energy from the nuclear plant is input to the hydrogen plant, and the product of the hydrogen plant is hydrogen.

Various Cu–Cl cycles for thermochemical water decomposition are defined in the literature, and characterized by the number of major chemical steps they incorporate. Although all of the Cu–Cl thermochemical cycles consist of a series of chemical reactions, the net reaction for each is



Hence water, thermal energy and electricity are the external inputs to the Cu–Cl thermochemical cycle, and oxygen and hydrogen are outputs.

##### 3.1.1. Hydrogen production plant based on a Cu–Cl cycle

The Cu–Cl thermochemical cycle uses a series of intermediate copper and chlorine compounds. The chemical reactions form a closed internal loop, which recycles all chemicals on a continuous basis without emitting greenhouse gases or other substances [3]. Fig. 3 shows a conceptual schematic of the five-step Cu–Cl cycle.

The cycle considered here involves five main steps: (1) HCl (g) production using such equipment as a fluidized bed, (2) oxygen production, (3) copper (Cu) production, (4) drying and (5) hydrogen production. In the first step (HCl production),  $CuCl_2$  reacts with water to produce HCl and  $Cu_2OCl_2$  at a temperature of around 450 °C in a fluidized bed. In the  $O_2$  production step, oxygen and CuCl are produced by splitting  $Cu_2OCl_2$ . Cu–Cl which is the output of the second step moves to the third step (copper production) in which copper is produced from molten CuCl. The reaction temperature for this step is as low as 25 °C. Moreover, this reaction requires electricity. In the drying step, the aqueous  $CuCl_2$  is dried to solid  $CuCl_2$  which is used in HCl production. In the final step, hydrogen production, solid copper particles from step 2 (Cu production) react with HCl from HCl production. The hydrogen

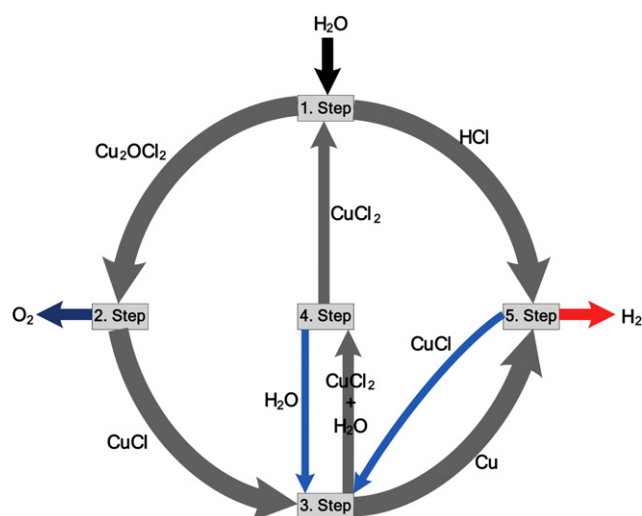


Fig. 3 – The five-step Cu–Cl thermochemical cycle for  $H_2$  production [5].



**Table 1 – Overall inputs and outputs (per kg hydrogen produced) for hydrogen and nuclear plants using the five-step Cu–Cl cycle.**

Hydrogen Plant					Nuclear Plant (SCWR)				
Input			Output		Input	Output			
Heat (MJ)	Electrical energy (MJ)	Water (kg)	Oxygen (kg)	Hydrogen (kg)	Uranium (g)	Electrical energy (MJ)	Reactor Thermal Energy (MJ)	Waste Energy (MJ)	
195.7	50.3	9	8	1	0.404	313.1	195.7	195.7	

production step is exothermic and occurs at a temperature of 450 °C. The outputs are hydrogen gas and CuCl.

The four-step copper–chlorine cycle combines step 3 and step 4 in the five-step cycle to reduce the complexity and equipment requirements. In the three-step Cu–Cl cycle, the hydrogen production step and the combined step in the four-step cycle are united.

The heat requirements for each step of the five-step Cu–Cl thermochemical cycle, as evaluated by Wang et al. [19], are used to calculate total thermal energy requirement of the cycle. It is noted in that study that the required heat input to the system is 554.7 kJ/mol H<sub>2</sub> and the total heat output of the system is 232 kJ/mol H<sub>2</sub>. Assuming only low grade heat, i.e., 163.3 kJ/mol H<sub>2</sub> is recovered (equivalent to 70% heat recovery), the external thermal energy requirement of the system is 391.4 kJ/mol H<sub>2</sub>. The electrical energy requirement of the copper production step is 62.6 kJ/mol H<sub>2</sub>. Also, it has been estimated that 38 kJ/mol H<sub>2</sub> of work is required for auxiliary equipment [20]. Hence, the net energy requirement of the system can be estimated as 492 kJ/mol H<sub>2</sub>.

To calculate the thermal and total energy requirements of the five-step Cu–Cl thermochemical cycle per kg hydrogen produced, the evaluated and estimated values are modified using the molar mass of H<sub>2</sub> (2 g/mol) as follows:

Total thermal energy requirement of five-step Cu–Cl cycle

$$= [391.4 \text{ kJ}/(1 \text{ mol H}_2)] \times [(1 \text{ mol H}_2)/(2 \text{ g H}_2)] \times [(1000 \text{ g})/(1 \text{ kg})] \\ = 195.7 \text{ MJ/kgH}_2 \quad (7)$$

and

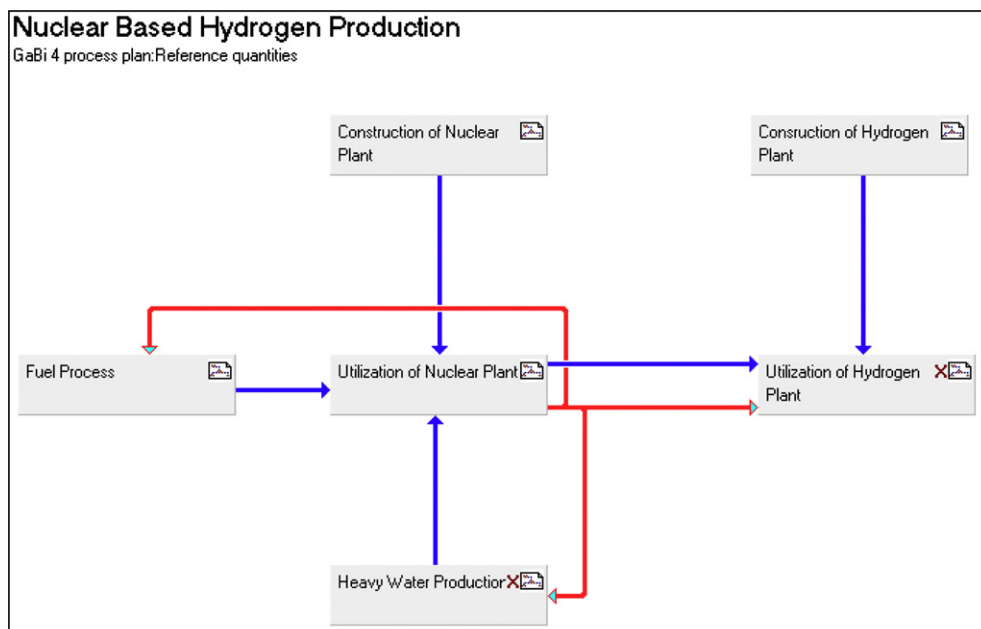
Total electrical energy requirement of five-step Cu–Cl cycle

$$= [(62.6 + 38) \text{ kJ}/(1 \text{ mol H}_2)] \times [(1 \text{ mol H}_2)/(2 \text{ g H}_2)] \\ \times [(1000 \text{ g})/(1 \text{ kg})] = 50.3 \text{ MJ/kgH}_2 \quad (8)$$

Using stoichiometry and molar masses, the water input to the system and output oxygen (O<sub>2</sub>) are calculated. In order to obtain 1 kg of H<sub>2</sub>, i.e. 500 mol of H<sub>2</sub>, 500 mol of H<sub>2</sub>O (9 kg) must be input and 250 mol of O<sub>2</sub> (8 kg) must be output from the system. Table 1 shows the material and energy inputs and outputs per kg H<sub>2</sub> production for the five-step Cu–Cl cycle.

### 3.1.2. Nuclear plant

Atomic Energy of Canada (AECL) proposes linking a Generation IV SCWR (super-critical water cooled reactor) with a hydrogen plant using a Cu–Cl thermochemical cycle. SCWR is planned to operate at sufficiently high temperatures and pressures to facilitate cogeneration of electricity and hydrogen [21].



**Fig. 4 – GaBi 4 model of overall system.**

The analysis in this study is based on the thermal energy requirement for the Cu–Cl cycles. The electrical energy output of the nuclear plant is used to meet the electrical energy requirements of the hydrogen production plant and other processes, i.e., uranium mining, heavy water production, etc.

The mass of uranium fuel  $m_u$  needed to obtain the required thermal energy is evaluated as follows (Solli, 2004):

$$m_u = \frac{Q}{B_d} \quad (9)$$

where  $Q$  is heat produced and  $B_d$  is the discharge burn-up. Here  $Q$  must be the total heat produced by the nuclear plant, which is thermal energy  $Q_{th}$  plus electrical work  $W_{el}$ . The discharge burn-up for  $UO_2$  is 20,000 MWd/te U (484.375 MWh/kg) [22], which is equal to 1743.75 GJ/kg U. Applying Eq. (9), the uranium requirements of the SCWR are calculated. In addition, the study of Piro and Duffey [22] is used to find ratios of electrical energy produced to thermal energy (process heat and waste heat). The resulting overall inputs and outputs of the nuclear plant combined with the five-step Cu–Cl cycle are also shown in Table 1.

### 3.1.3. Fuel (uranium) processing

Mining, milling, conversion, enrichment and fuel fabrication are the five main steps of fuel processing. Uranium ore is first extracted from the environment via mining, and is then concentrated in the form of  $U_3O_8$  in the milling stage. The  $U_3O_8$  is then converted to  $UF_6$ . Enrichment is the next stage and increases the concentration of the fissile isotope U-235 to a desired level (4% for a SCWR). In the final stage (fuel production), the chemical composition is altered to  $UO_2$  for use in SCWR.

The uranium requirements for nuclear plant linked with the five-step Cu–Cl thermochemical cycle are evaluated using Eq. (4). Solli [23] points out that the input uranium should be taken as double in mass of the output uranium for the milling stage of analysis, which is applied in the analysis.

The amount of uranium required to achieve the desired fuel enrichment is determined as follows:

$$\text{Natural uranium required} = \frac{x_p - x_t}{x_n - x_t} \quad (10)$$

Here,  $x_n$  is the natural enrichment level (i.e. 0.71% U-235),  $x_p$  is the enrichment level to produce 1 kg enriched uranium and  $x_t$  is the tailings enrichment, which is assumed to be 0.3% U-235. Hence, for 1 kg of 4% enriched uranium, 9.02 kg natural uranium is needed. Considering the issues mentioned above, in order to obtain 0.404 g enriched uranium 3.64 g natural uranium is input to enrichment stage and 7.29 g uranium ore is required.

### 3.2. LCA of overall system

LCA is applied to the overall systems for nuclear-based hydrogen production using five-step Cu–Cl thermochemical cycles. The analyze are all based on one kg of hydrogen production and utilize data (inputs/outputs for the subsystems) from previous sections of this article as well as data from reports in the literature [23,24] for some of the inputs and outputs associated with relevant processes. We also provide

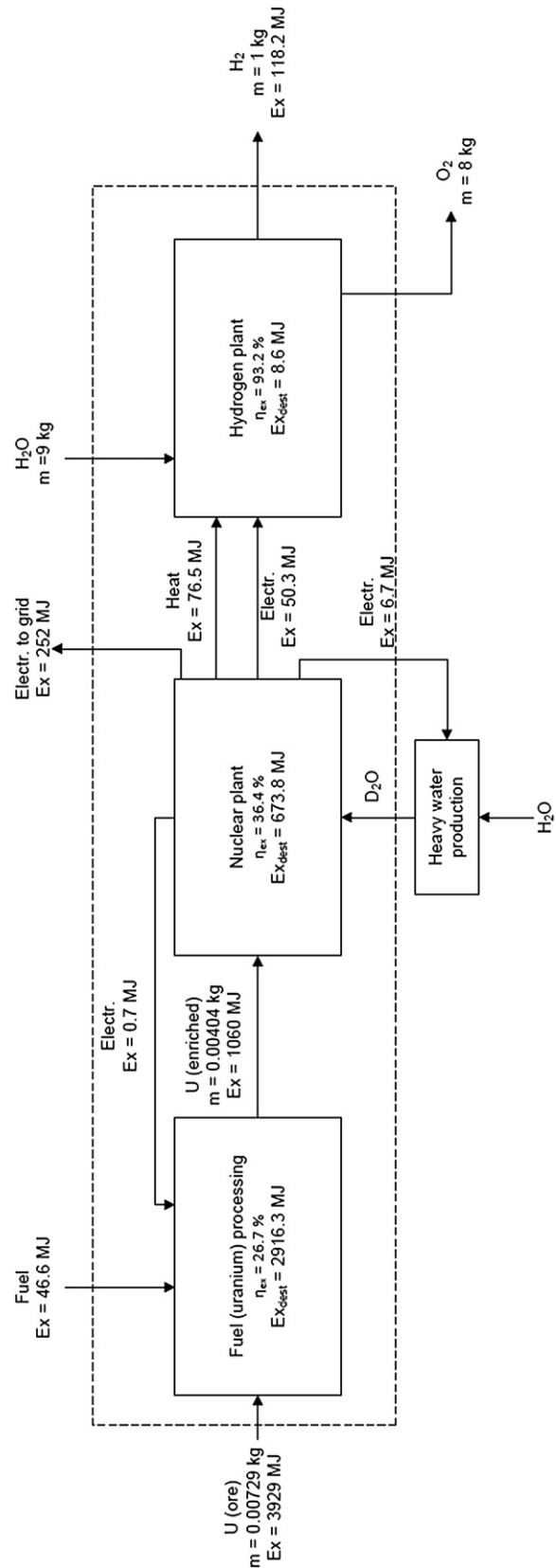


Fig. 5 – Exergy diagram of the life cycle of nuclear-based hydrogen production.

inventory data, i.e., overall inputs and outputs for all steps. The GaBi 4 LCA software is used to conduct the LCIA. This involves modelling with GaBi 4 the overall system and its stages.

After the subsystems (fuel processing, nuclear plant, hydrogen plant) and subprocesses (mining, milling, etc.), have been modelled, they are linked to determine the overall environmental impacts of the systems. Electrical requirements of each of the processes are assumed to be supplied by the electrical output of the nuclear power plant. Fig. 4 shows the plan of the overall system. The red line in the system denotes electrical energy transfer. It exists because not all the generated electricity is used by the hydrogen plant; excess electricity is sent to the grid. The icon in the top right corner of each process indicates that the processes have sub-plans. For example, fuel processing has sub-plans including mining, milling, etc. Further information about modelling and analysis is presented elsewhere [25]. Environmental impacts are then evaluated.

### 3.3. ExLCA of overall system

The black-box approach has been used for the ExLCA. A simplified mass balance is used. All input and output exergy values have been calculated and/or found in the literature. The exergy of 1 kg H<sub>2</sub> is 118.2 MJ. The work exergy is the electrical energy requirement of the hydrogen plant which is 50.3 MJ as stated earlier. To calculate the exergy content of heat, Eq. (3) has been used, and the reference environment temperature is taken as 25 °C in this study in order to be consistent with other studies in the literature. The exergy of the heat input to hydrogen plant is 76.46 MJ per kg hydrogen production.

To find the exergy content of enriched uranium, i.e. the uranium input to nuclear plant, Eq. (6) has been used. 0.00404 kg of 4% enriched uranium has a fission reaction heat output of 1329 MJ. Assuming an average reaction temperature of 1200 °C and ambient temperature of 25 °C, Eq. (7) gives 1060 MJ exergy content for 4% enriched uranium.

Hermann [26] states that U-235 has a specific exergy of 77 TJ/kg. Applying this to our case, where the mass of uranium

ore used is 0.00729 kg having 0.7% U-235, the exergy input with uranium ore for fuel processing is 3929 MJ.

The sum of the chemical exergy contents of fuels (coal, natural gas and diesel fuel), which are used in fuel processing stages (mining, milling, conversion, enrichment and fuel fabrication), is calculated as 46.61 MJ. In the analysis, the exergies of emissions are neglected, since it is assumed that these emission diffuse into the environment and dissipate.

## 4. Results and discussion

ExLCA results are presented in Fig. 5, which lists exergy efficiencies and destructions. The primary contributor to the life cycle irreversibility of nuclear-based hydrogen production is fuel (uranium) processing, which has an exergy efficiency of 26.7% and exergy destruction of 2916.3 MJ. Nuclear plant operation has less exergy destruction (673.8 MJ) and a higher exergy efficiency (36.4%) than fuel processing. The hydrogen plant has the highest exergy efficiency (93.2%) and lowest destruction (8.6 MJ). The exergy efficiency of the overall nuclear-based hydrogen production system is as follows:

$$\psi_{\text{system}} = \frac{Ex_{\text{out}}}{Ex_{\text{in}}} = \frac{Ex_{\text{H}_2} + Ex_{\text{grid electricity}}}{Ex_{\text{U ore}}} = \frac{(118.2 + 252) \text{ MJ}}{3927 \text{ MJ}} = 0.094 (\text{or } 9.4\%) \quad (11)$$

Environmental impacts are also presented for the Cu–Cl thermochemical hydrogen production process, based on one MJ exergy of hydrogen production. The results of Ozbilen et al. [27] are used and normalized to one MJ exergy of hydrogen for the following CML 2001 impact categories: acidification potential (AP), eutrophication potential (EP), global warming potential (GWP), ozone depletion potential (ODP). Environmental effects of nuclear-based hydrogen production using the five-step Cu–Cl thermochemical cycle in terms of the considered impact categories are calculated by altering the lifetime of the overall system from 10 years to 100 years for two plant capacities (125,000 and 62,500 kg H<sub>2</sub> production per day).

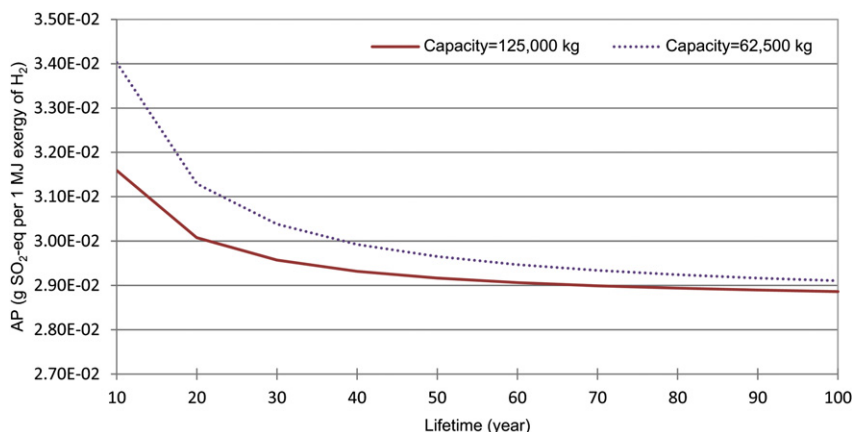


Fig. 6 – Variation of AP (per 1 MJ exergy of H<sub>2</sub>) with lifetime of the system.



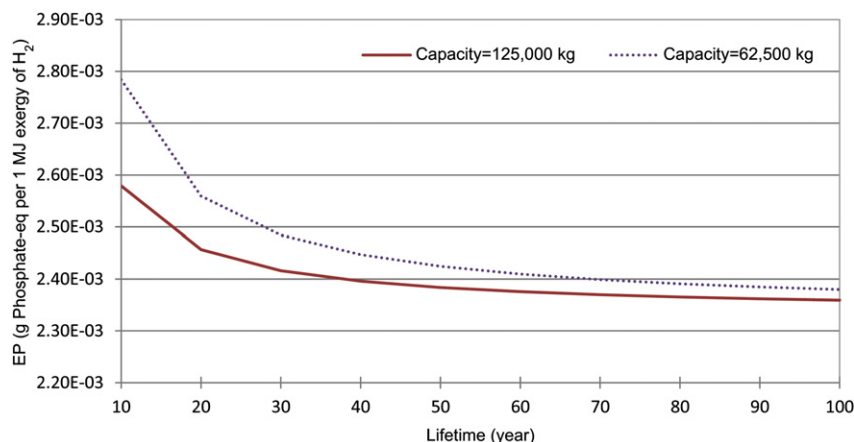


Fig. 7 – Variation of EP (per 1 MJ exergy of H<sub>2</sub>) with lifetime of the system.

Fig. 6 shows change in AP for various plant lifetimes. While the lowest AP (0.029 g SO<sub>2</sub>-eq) is observed for the five-step Cu–Cl cycle over a 100 year plant lifetime, the highest AP per 1 MJ exergy of hydrogen is approximately 0.034 g SO<sub>2</sub>-eq. The effect of capacity is significant for shorter lifetimes, however the gap between the AP curves decreases for longer lifetimes.

Fig. 7 shows the variation of EP values with system lifetime. The lowest EP ( $2.35 \times 10^{-3}$  kg Phosphate-eq) is observed for the five-step Cu–Cl cycle with a 100 year plant lifetime and a plant production capacity of 125,000 kg hydrogen per day. The EP is also low ( $2.38 \times 10^{-3}$  kg Phosphate-eq) for the reference plant lifetime (60 years). If the production capacity reduces to half (62,500 kg), the EP becomes  $2.41 \times 10^{-3}$  kg Phosphate-eq/MJ exergy of H<sub>2</sub>, for a 60 year plant lifetime.

GWP values for several plant lifetimes are given in Fig. 8 for the nuclear-based hydrogen production system. The lowest GWP is 5.65 g CO<sub>2</sub>-eq/MJ exergy of hydrogen for a plant capacity of 125,000 kg H<sub>2</sub>/day. Also, the GWP with a plant capacity of 62,500 kg H<sub>2</sub>/day is 5.75 g CO<sub>2</sub>-eq, which demonstrates that the effect of plant capacity is negligible for longer lifetimes.

ODP values, which are mainly caused by utilization of the nuclear plant and mining, are presented in Fig. 9. The difference in ODP values between the reference lifetime (60 years) and a lifetime of 100 years is seen to be relatively small (as low as  $1.0 \times 10^{-9}$  g R11-eq) which indicates that lifetime is not a significant factor for the five-step cycle and for the selected plant capacity of 125,000 kg H<sub>2</sub>/day. The lowest ODP ( $1.21 \times 10^{-7}$  g R11-eq) is observed with a plant capacity of 125,000 kg/day hydrogen production and a 100 year lifetime. Also, the highest ODP ( $1.37 \times 10^{-7}$  g R11-eq) is observed with a plant capacity of 62,500 kg/day and a 10 year plant lifetime.

The significance of heat recovery in the cycle, which increases the exergy efficiency of the hydrogen plant, can be seen in terms of AP and GWP in Fig. 10. GWP can be reduced to as low as 5.4 g CO<sub>2</sub>-eq per MJ exergy of hydrogen if a 98% exergy efficiency is obtained. AP can also be reduced from an initial value of 0.041 to 0.027 g SO<sub>2</sub>-eq per 1 MJ exergy of hydrogen if the exergy efficiency increases from 67% to 98%.

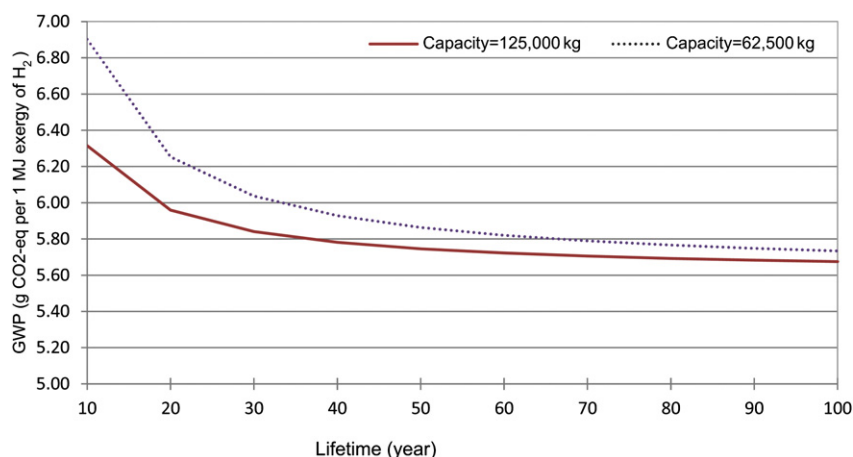


Fig. 8 – Variation of GWP (per 1 MJ exergy of H<sub>2</sub>) with lifetime of the system.

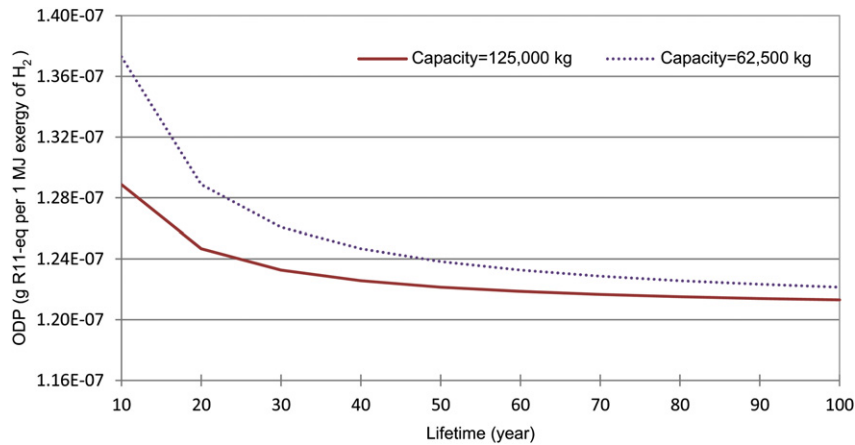


Fig. 9 – Variation of ODP (per 1 MJ exergy of  $H_2$ ) with lifetime of the system.

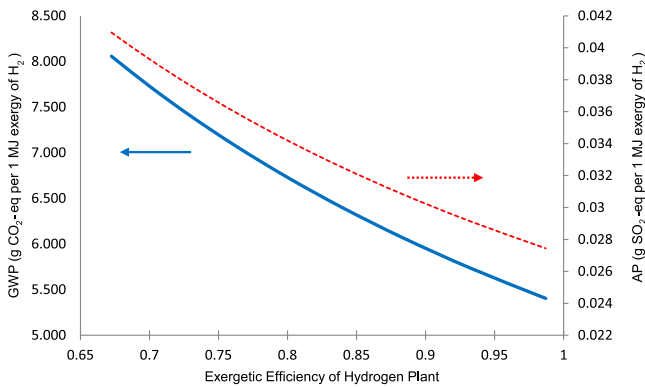


Fig. 10 – Variation of GWP and AP with exergy efficiency of hydrogen plant.

## 5. Conclusions

The environmental impacts of nuclear-based hydrogen production via thermochemical water decomposition using the Cu–Cl cycle are quantified and presented using exergetic life cycle assessment. ExLCA is a beneficial addition to LCA for introducing thermodynamic analysis throughout the life cycle analysis of the system. The parametric studies performed for a range of plant lifetimes demonstrate that the effect of plant lifetime on environmental impact per kg hydrogen production diminishes at large-scale production capacities. This result is attributable to the fact that the fixed impacts, e.g. impacts due to construction of the hydrogen plant, are relatively small for large production rates and plant lifetimes.

ExLCA results show that the greatest irreversibility is caused by uranium processing, hence the fuel processing stage of hydrogen production has significant potential for increased exergy and energy efficiencies and reduced environmental impacts. The following conclusions are also drawn from the study:

- The main contributor of life cycle irreversibility of nuclear-based hydrogen production is fuel (uranium) processing, for which the exergy efficiency is 26.7% and the exergy destruction is 2916.3 MJ.

- The lowest GWP per megajoule exergy of hydrogen is 5.65 g  $CO_2$ -eq, for a plant capacity of 125,000 kg  $H_2$ /day. The corresponding GWP for a plant capacity of 62,500 kg  $H_2$ /day is 5.75 g  $CO_2$ -eq.
- GWP can be reduced to as low as 5.4 g  $CO_2$ -eq per megajoule exergy of hydrogen if a 98% exergy efficiency is obtained. AP can also be reduced from an initial value of 0.041 to 0.027 g  $SO_2$ -eq per megajoule exergy of hydrogen, if the exergy efficiency is increased from 67% to 98%.

Future studies should be more focussed on the exergy destructions within fuel processing and techniques to improve the exergy efficiency of this stage. The analysis identified a larger potential margin for improvement in uranium processing than in the thermochemical hydrogen production cycle, so decision makers and engineers should focus improvement efforts more on the fuel processing stage.

## Acknowledgement

The authors acknowledge gratefully the financial support provided by the Ontario Research Excellence Fund.

## Nomenclature

$B_d$	Discharge burn-up, GJ/kg U
$Ex_{dest}$	Exergy destruction, MJ
$Ex_{in}$	Exergy input, MJ
$Ex_{flow}$	Exergy of a matter flow, MJ
$Ex_{kin}$	Kinetic exergy, MJ
$Ex_o$	Chemical exergy, MJ
$Ex_{out}$	Exergy output, MJ
$Ex_{ph}$	Physical exergy, MJ
$Ex_{pot}$	Potential exergy, MJ
$Ex_Q$	Exergy of thermal energy, MJ
$m_u$	Mass of uranium fuel, kg
$Q$	Heat, MJ
$T_i$	System temperature, K
$T_o$	Reference environment temperature, K

$x_n$	Natural uranium U-235 concentration
$x_p$	Enriched uranium U-235 concentration
$x_t$	Uranium tailings U-235 concentration
$\psi$	Exergy efficiency

## Acronyms

AP	Acidification potential
CML	Center of Environmental Science of Leiden University
EEA	Extended exergy analysis
EP	Eutrophication potential
ExLCA	Exergetic life cycle assessment
GHG	Greenhouse gas
GWP	Global warming potential
ISO	International Standards of Organization
LCA	Life cycle assessment
LCIA	Life cycle impact assessment
ODP	Ozone depletion potential

## REFERENCES

- [1] Serban M, Lewis MA, Basco JK. Kinetics study of the hydrogen and oxygen production reactions in the copper-chloride thermochemical cycle. New Orleans: AIChE Spring National Meeting, Conference Proceedings. 2690–2698. Website, <http://hydrogen.uoit.ca/assets/Default/documents/Public/Lewis-AIChE04.pdf>; 2004. 2004 [accessed 17.04.10].
- [2] Funk JE. Thermochemical hydrogen production: past and present. *International Journal of Hydrogen Energy* 2001;26: 185–90.
- [3] Naterer GF, Gabriel K, Wang ZL, Daggupati VN, Gravelsins R. Thermochemical hydrogen production with a copper-chlorine cycle. I: oxygen release from copper oxychloride decomposition. *International Journal of Hydrogen Energy* 2008;33:5439–50.
- [4] Naterer GF, Suppiah S, Lewis M, Gabriel K, Dincer I, Rosen MA, et al. Recent Canadian advances in nuclear-based hydrogen production and the thermochemical Cu–Cl cycle. *International Journal of Hydrogen Energy* 2009;34:2901–17.
- [5] Orhan MF, Dincer I, Rosen MA. An exergy–cost-mass analysis of a hybrid copper-chlorine thermochemical cycle for hydrogen production. *International Journal of Hydrogen Energy* 2010;35:4831–8.
- [6] Ayres RU, Ayres LW, Martinas K. Exergy, waste accounting and life-cycle analysis. *Energy* 1998;23:355–63.
- [7] Daniel JJ, Rosen MA. Exergetic environmental assessment of life cycle emissions for various automobiles and fuels. *Exergy, an International Journal* 2002;2:283–94.
- [8] Neelis ML, van der Kooi HJ, Geerlings JJC. Exergetic life cycle analysis of hydrogen production and storage systems for automotive applications. *International Journal of Hydrogen Energy* 2004;29:537–45.
- [9] Boyano A, Blanco-Marigorta AM, Morosuk T, Tsatsaronis G. Exergoenvironmental analysis of a steam methane reforming process for hydrogen production. *Energy* 2011;36: 2202–14.
- [10] Granovskii M, Dincer I, Rosen MA. Exergetic life cycle assessment of hydrogen production from renewables. *Journal of Power Sources* 2007;167:461–71.
- [11] Cornelissen RL. Thermodynamics and sustainable development: the use of exergy analysis and the reduction of irreversibility. University of Twente; 1997.
- [12] Rosen MA, Dincer I. Exergy as the confluence of energy, environment and sustainable development. *Exergy, an International Journal* 2001;1:3–13.
- [13] International Organization for Standardization (ISO). ISO 14041, environmental management – life cycle assessment – goal and scope definition and inventory analysis; 1998.
- [14] Curran MA. Life cycle assessment: an international experience. *Environmental Progress* 2000;19:65–71.
- [15] Guinée JB, Gorée M, Heijungs R, Huppes G, Kleijn R, ADe Koning, et al. Handbook on life cycle assessment. Operational guide to the ISO standards. I: LCA in perspective. IIa: guide. IIb: operational annex. III: scientific background. Dordrecht: Kluwer Academic Publishers; 2002.
- [16] Dincer I, Rosen MA. *Exergy: energy, environment and sustainable development*. UK: Elsevier; 2007.
- [17] Moran MJ. *Availability analysis: a guide to efficient energy use*. New York: American Society of Mechanical Engineers; 1989.
- [18] Kotas TJ. *The exergy method of thermal plant analysis*. Malabar, Florida: Krieger; 1995.
- [19] Wang ZL, Naterer GF, Gabriel KS, Gravelsins R, Daggupati VN. Comparison of sulphur-iodine and copper-chlorine thermochemical hydrogen production cycles. *International Journal of Hydrogen Energy* 2010;35:4820–30.
- [20] Rosen MA, Naterer GF, Chukwu CC, Sadhankar R, Suppiah S. Nuclear-based hydrogen production with a thermochemical copper-chlorine cycle and supercritical water reactor: equipment scale-up and process simulation. *International Journal of Hydrogen Energy*; 2010. doi:10.1002/er.1702.
- [21] Naterer GF, Suppiah S, Stolberg L, Lewis M, Wang Z, Daggupati V, et al. Canada's program on nuclear hydrogen production and the thermochemical Cu–Cl cycle. *International Journal of Hydrogen Energy* 2010;35:10905–26.
- [22] Pioro IL, Duffey RB. *Heat transfer and hydraulic resistance at supercritical pressures in power engineering applications*. New York: ASME Press; 2007.
- [23] Solli C. Fission or fossil: a comparative life cycle assessment of two different hydrogen production methods. Master's thesis, Norwegian University of Science and Technology; 2004.
- [24] Lubis LL, Dincer I, Rosen MA. Life cycle assessment of hydrogen production using nuclear energy: an application based on thermochemical water splitting. *Journal of Energy Resources Technology*; 2010. doi:10.1115/1.4001603.
- [25] Ozbilen AZ. Life cycle assessment of nuclear-based hydrogen production via thermochemical water splitting using a copper-chlorine (Cu–Cl) cycle. Master's thesis, University of Ontario Institute of Technology; 2010.
- [26] Hermann WA. Quantifying global exergy resources. *Energy* 2006;31:1349–66.
- [27] Ozbilen A, Dincer I, Rosen MA. Environmental evaluation of hydrogen production via thermochemical water splitting using the Cu–Cl cycle: a parametric study. *Internal Journal of Hydrogen Energy* 2011;36:9514–28.