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Efficiency analysis of a hybrid copper–chlorine (Cu–Cl) cycle for nuclear-based hydrogen production

Mehmet F. Orhan, 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

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ABSTRACT

The role of the Cu–Cl cycle for thermochemical water decomposition, potentially driven by heat from a nuclear power generation station, in producing hydrogen in a sustainable way is investigated by examining efficiencies. The energy efficiency of the cycle is found to be 45% and the exergy efficiency 10%. The energy and exergy efficiencies of the cycle are observed to vary with temperatures of the reactions and reference-environment, and cycle heat losses. A parametric study is carried out considering several heat losses, reaction and reference-environment temperatures, and component-efficiency scenarios.

1. Introduction

Energy is a key requirement of an industrial society. It is, therefore, not surprising that many organizations analyze future needs for energy and the availability of various energy sources. Energy consumption growth is closely linked to population growth, although changes in lifestyles and efficiency improvements also have a substantial influence on per capita annual energy consumption. The split of population among urban and rural portions also affects energy demand [1], as does rising living standards, particularly in less industrialized countries.

Increasing global energy consumption has led to global problems like a depletion of many energy resources and impact on the global climate as well other facets of the environment [2]. At present, 90% of the total primary energy demands are satisfied by fossil fuels [3], the combustion of which is linked to the emission of significant amounts of CO_2, the primary greenhouse gas.

Research is ongoing into clean, economic, stable, safe and abundant energy resources and technologies that provide the potential to mitigate global warming and to become large and stable energy supplies. Various alternative energy options to fossil fuels exist, including solar, geothermal, hydraulic and nuclear energy. While reserves of natural energy are limited, many indicate that nuclear energy may be able to contribute a significant share of energy supply and utilization well into the future. Nuclear energy has been almost exclusively utilized in the past for electric power generation, but the direct utilization of nuclear thermal energy provides the potential to increase energy efficiency and thereby facilitate energy savings in the near future. Hydrogen production has been cited as a highly beneficial use for nuclear thermal energy [4].

Most of the hydrogen produced worldwide today is from fossil fuels, primarily through steam reforming of natural gas. Fossil fuels can also be utilized to obtain hydrogen via other reactions (gasification, catalytic decomposition, partial oxidation, etc., of coal and other heavy hydrocarbons). Unfortunately, such fossil-fuel-based hydrogen is not environmentally benign and does not contribute toward reducing greenhouse gas emissions. Hydrogen has to be extracted from water, using non-fossil fuels, in order to avoid environmental problems and resource limitations of fossil-fuel-based production technologies.

The nuclear energy-driven thermochemical cycle is one of several water-splitting processes for producing hydrogen that has good potential for the future. Another is water electrolysis, which is commercial but also potentially subject to lower overall efficiencies due the inefficiency of the conversion of thermal energy to electrical energy in thermal power stations. This inefficiency can be avoided through thermochemical cycles that consist of a sequence of chemical reactions yielding a net reaction of decomposition of water [5].

Thermochemical water-splitting with a copper–chlorine (Cu–Cl) cycle is an alternative that could be linked with nuclear reactors

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* Corresponding author.
E-mail addresses: Mehmet.Orhan@uoit.ca (M.F. Orhan), Ibrahim.Dincer@uoit.ca (I. Dincer), Marc.Rosen@uoit.ca (M.A. Rosen).

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Nomenclature

E	energy (kJ)
Ex	exergy (kJ)
$\overline{ex}$	specific molar exergy (kJ/kmol)
H	enthalpy (kJ)
h	specific enthalpy (kJ/kg)
$\bar{h}$	specific molar enthalpy (kJ/kmol)
$\bar{h}^\circ$	specific molar enthalpy at reference state (kJ/kmol)
$\bar{h}_f^\circ$	specific molar enthalpy of formation (kJ/kmol)
n	number of moles per cycle (kmol/kmol H_2)
Q	heat (kJ)
$\bar{q}$	specific molar reaction heat (kJ/kmol)
$T_{reaction}$	reaction temperature (°C)
T_0	reference-environment temperature (°C)

Greek letters

η_e	energy efficiency
η_{ex}	exergy efficiency

to thermally decompose water into oxygen and hydrogen, through intermediate copper and chlorine compounds. Several studies of the Cu–Cl cycle have been carried out that aim to improve its overall efficiency. For example, the main steps of the Cu–Cl cycle have been assessed thermodynamically by Orhan et al. [6–10], using energy and exergy methods and considering relevant chemical reactions. Energy and exergy efficiencies of the steps in the cycle have been evaluated and parametric studies have been carried out on energetic and exergetic aspects considering variable reaction and reference-environment temperatures [6–10].

Heat is transferred between various endothermic and exothermic reactors in the Cu–Cl cycle, through heat exchangers that supply or recover heat from individual processes. Naterer et al. [11] have examined the heat requirements of these steps, in efforts to recover heat and minimize the net heat supply to the cycle, thereby improving its overall efficiency [11].

Naterer et al. [12] have examined the evaporative drying of aqueous cupric chloride ($CuCl_2$) droplets in the copper–chlorine (Cu–Cl) thermochemical cycle of hydrogen production. Analytical solutions have been developed for the cupric chloride spraying and drying processes, including empirical correlations for heat and mass transfer, based on a single droplet of aqueous $CuCl_2$ solution [12].

Selected design issues associated with reactor scale-up in the thermochemical copper–chlorine (Cu–Cl) cycle for hydrogen production have been studied by Wang et al. [13], focusing on the hydrogen, oxygen and hydrolysis reactors [13].

Orhan et al. [14] have performed an economic analysis of a Cu–Cl pilot plant with an associated parametric study. The analysis takes into account the different types of costs such as energy, operation and maintenance costs, fixed charges on capital investment, etc. The costs with their percentage ranges and factors that affect accuracy and scaling have been examined. Through this scaling method, the total capital investment and total cost of a Cu–Cl pilot plant have been estimated by scaling against the corresponding costs of a sulphur–iodine (S–I) thermochemical water decomposition plant for hydrogen production. The sensitivity studies show that costs vary significantly with the pilot plant capacity, the components cost breakdown and the capacity factor. Parametric studies with variable plant capacities, approximations and capacity factors have been performed [14].

The objectives of this study are to describe and quantify the variation of reaction heat for each of the steps in the Cu–Cl thermochemical water decomposition cycle with parameters like process temperature, and to determine overall energy and exergy efficiencies of the cycle for several scenarios. A parametric study is reported of how the reaction heat in each chemical reaction and overall energy and exergy efficiencies of the Cu–Cl cycle vary with reaction and reference-environment temperatures.

2. Description of the copper–chlorine cycle

Most thermochemical cycles require process heat at high temperatures, exceeding 850–900 °C. However, existing nuclear power plants are typically water-cooled plants operating at 250–500 °C. Recently, Atomic Energy of Canada Limited and Argonne National Laboratory in the U.S. have been developing low-temperature cycles, designed to accommodate heat sources around 500–550 °C [15]. Such cycles can be more readily integrated with nuclear reactors. For this temperature range, the copper–chlorine (Cu–Cl) cycle is one of the most promising. Several Cu–Cl cycles have been examined in the laboratory and various alternative configurations identified. Proof-of-principle experiments that demonstrate the feasibility of the processes have been undertaken and a preliminary assessment of the cycle efficiency has demonstrated its potential.

A conceptual layout of the Cu–Cl process proposed by the authors is illustrated in Fig. 1. Thermochemical water decomposition, potentially driven by nuclear heat, occurs via intermediate copper and chlorine compounds (Fig. 2). This cycle consists of three thermal reactions and one electrochemical reaction. The cycle involves five 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. A chemical reaction takes place in each step, except drying. The chemical reactions form a closed internal loop that re-cycles all of the copper–chlorine compounds on a continuous basis, without emitting any greenhouse gases to the atmosphere. The five steps in the copper–chlorine cycle are described in Table 1.

3. Analysis

The heat transfer for a chemical process involving no work interaction W is determined from the energy balance $\dot{E}_{in} - \dot{E}_{out} = \Delta\dot{E}_{system}$ applied to a system with $W=0$ [16]. For a steady state reaction process, the energy balance reduces to

$$\bar{Q} = \bar{H}_P - \bar{H}_R = \sum n_P(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_P - \sum n_R(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_R \qquad (1)$$

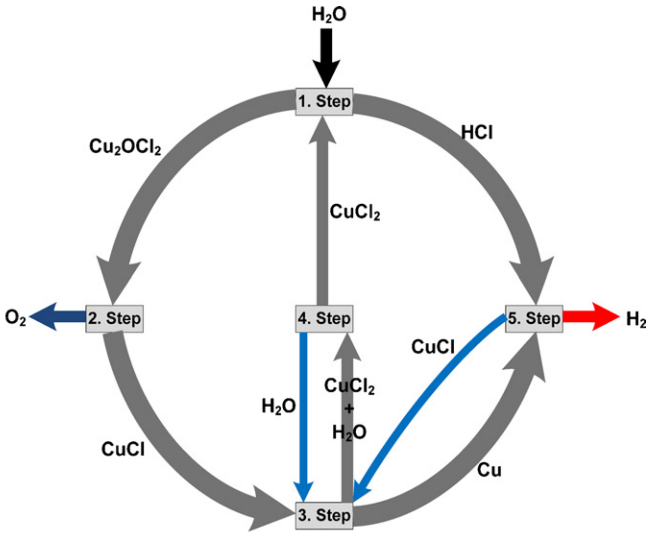

Fig. 1. The Cu–Cl thermochemical cycle for hydrogen production.

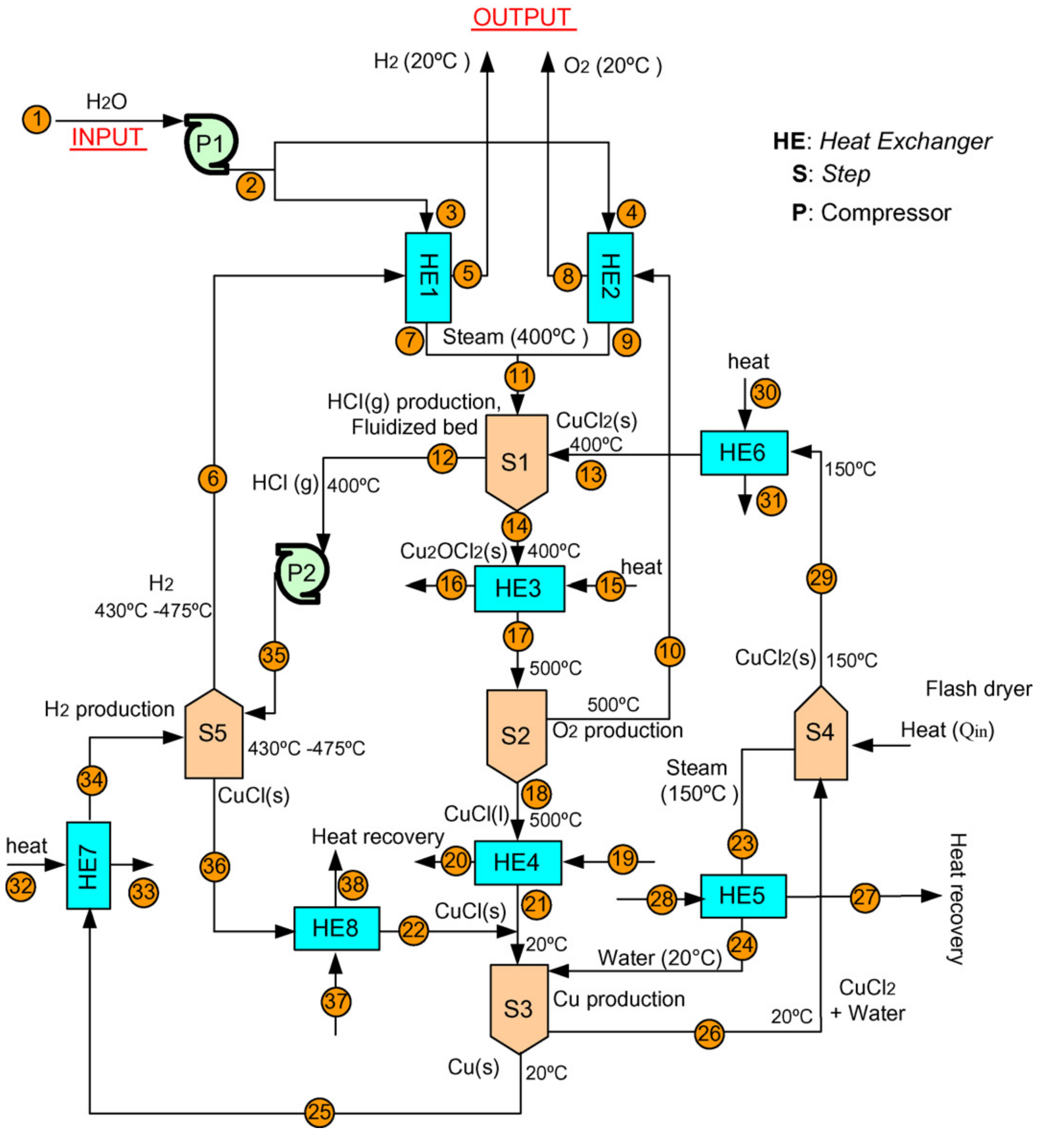

Fig. 2. Conceptual layout of a thermochemical Cu–Cl hydrogen production cycle.

The overall energy efficiency of the Cu–Cl cycle, η_e, can be described as the fraction of energy supplied that is converted to the energy content of H_2 based on its lower heating value:

$$\eta_e = \frac{\overline{LHV}_{H_2}}{\overline{Q}_{in} + \overline{Q}_{loss}} \tag{2}$$

where $\overline{LHV}_{H_2}$ is the lower heating value per kmol of hydrogen, $\overline{Q}_{loss}$ is the total heat loss from the Cu–Cl cycle and $\overline{Q}_{in}$ is the total energy used by the process to produce a unit amount of product hydrogen. The total energy demand of the Cu–Cl cycle is the sum of the reaction heats of the five main steps described above. Note that in this summation, the exothermic reaction heat (i.e., the fifth step) is taken as negative, assuming this heat can be used for other endothermic reactions. The lower heating value of hydrogen is 240,000 kJ/kmol H_2.

As pointed out earlier, this analysis considers a hypothetical Cu–Cl plant for hydrogen production that has not been designed or constructed. Thus, many parameters needed for the analyses are unknown, including quantity, capacity and material of equipment (pumps, heat exchangers, compressors, fluidized bed, evaporator, etc.). Therefore, in overall efficiency calculations we consider for simplicity only the five main steps of the Cu–Cl cycle and assume

Table 1
Primary steps in the Cu–Cl cycle with the corresponding reactions at 101 kPa pressure.

Step	Reaction	Reaction type	Temperature range (°C)
1	$2CuCl_2\,(s) + H_2O\,(g) \rightarrow Cu_2OCl_2\,(s) + 2HCl\,(g)$	Endothermic	400
2	$Cu_2OCl_2\,(s) \rightarrow 2CuCl\,(l) + 1/2O_2\,(g)$	Endothermic	500
3	$4CuCl\,(s) + H_2O \rightarrow 2CuCl_2\,(aq) + 2Cu\,(s)$	Electrolysis	Ambient
4	$2CuCl_2\,(aq) \rightarrow 2CuCl_2\,(s)$	Physical drying	>100
5	$2Cu\,(s) + 2HCl\,(g) \rightarrow 2CuCl\,(l) + H_2\,(g)$	Exothermic	430–475

Table 2
Reaction energy of the Cu–Cl cycle steps and their associated specific exergies at specified temperature and pressure of 101 kPa.

Step	Name	Reaction heat (kJ/kmol H_2)	Electricity (kJ/kmol H_2)	Specific exergy (kJ/kmol H_2)	Temperature (°C)
1	Fluidized bed	105,266	–	58,654	400
2	O_2 production step	110,523	–	67,915	500
3	Cu production step	–	140,557	140,557	25
4	Dryer	18,346	–	5421	150
5	H_2 production step	−55,493	–	-32,620	450

no heat losses occur in these steps, individually. However, overall we assume a total heat loss Q_{loss} from the Cu–Cl cycle as a percentage of total heat input Q_{in} to the cycle.

The overall exergy efficiency of the Cu–Cl cycle expressed as

$$\eta_{ex} = \frac{\overline{ex}_{out}}{\overline{ex}_{in}} \quad (3)$$

Using the exergy balance for the system, the exergy efficiency can be written alternatively as

$$\eta_{ex} = 1 - \frac{\overline{ex}_{destroyed}}{\overline{ex}_{in}} \quad (4)$$

where $\overline{ex}_{destroyed}$ is the specific exergy destruction and $\overline{ex}_{in}$ and $\overline{ex}_{out}$ are the input and output exergy. Detailed analyses of the determination of inputs, outputs and the destroyed exergy of each step have been given elsewhere [6–10]. For the overall cycle, we obtain the total input and destroyed exergy as the sum of the inputs and destroyed exergy of the individual steps. In the summation of input exergy, the exothermic reaction (i.e., the fifth step) is taken as negative, which assumes this energy can be used for other endothermic reactions.

4. Results and discussion

In Table 2, the reaction energy changes of the steps in the Cu–Cl cycle at specified temperature and pressure are given. Also, variations of the reaction heats for steps involving a reaction are illustrated in Fig. 3 for various temperatures of the reactions. All steps are endothermic except the fifth (hydrogen production), in which heat produced and rejected from the system (Fig. 3). As reaction temperature increases, the reaction heat for steps 1, 3 and 5 (absolute value for the fifth step) decreases while that for steps 2 and 4 increases. In all cases, the relations are nearly linear. As can be seen from Fig. 3, even though the curve for the fifth step rises, its absolute value decreases since it is in the negative range (because the reaction is exothermic). The curve shows that the amount of energy released from the fifth reaction decreases with increasing reaction temperature.

Figs. 4–6 show the variations of energy (η_e) and exergy (η_{ex}) efficiencies of the Cu–Cl cycle with the temperatures of the steps.

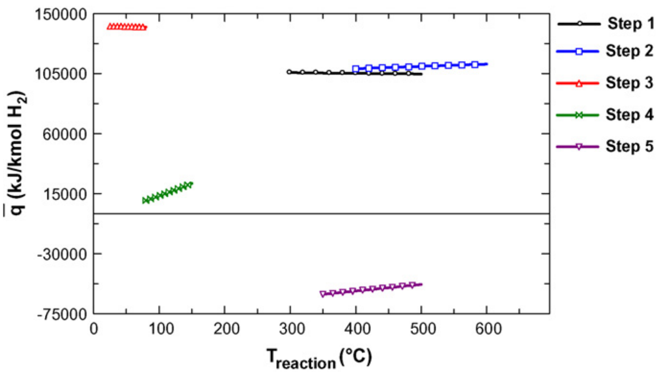

Fig. 3. Variation of reaction heat with reaction temperature for several steps in the Cu–Cl cycle.

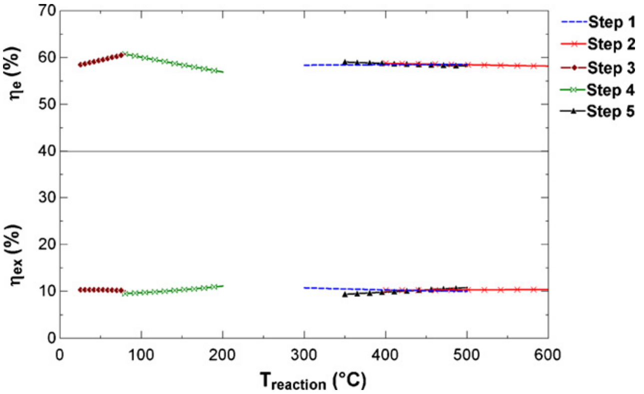

Fig. 4. Variation of efficiencies of the Cu–Cl cycle with the temperatures of the steps assuming an overall heat loss of 20% of the total input energy to the cycle.

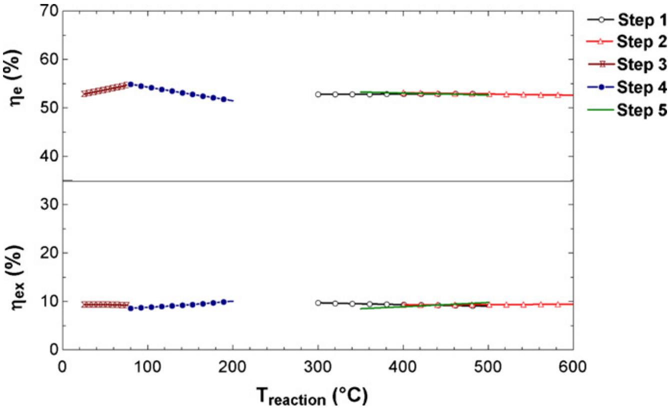

Fig. 5. Variation of efficiencies of the Cu–Cl cycle with the temperatures of the steps assuming an overall heat loss of 30% of the total input energy to the cycle.

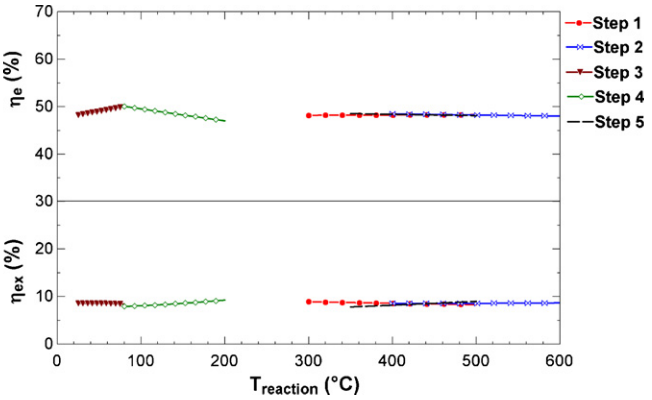

Fig. 6. Variation of efficiencies of the Cu–Cl cycle with the temperatures of the steps assuming an overall heat loss of 40% of the total input energy to the cycle.

These results are obtained assuming 20, 30 and 40% of the total energy entering the Cu–Cl cycle is lost. The percentages (20%, 30% and 40%) are assumptions used to examine the effect of losses on the overall cycle efficiency. Based on previous studies [6–9], we expect that the losses from the cycle are in these ranges. As the Cu–Cl plant is only being developed, many parameters needed for analyses are unknown, such as capacity and equipment material for pumps, heat exchangers, compressors, fluidized bed, evaporator, etc. For simplicity, therefore, we consider in overall efficiency calculations only the five main steps of the Cu–Cl cycle and assume no heat losses in these steps, individually. However, overall we assume a total heat loss (Q_{loss}) from the Cu–Cl cycle as a percentage of total heat (Q_{in}) entering the cycle.

The expected values of step temperatures of the cycle are given in Table 2. When we vary a step temperature in the analysis, the other step temperatures remain constant, at the values in Table 2. For example, to investigate the relation between T_1 and efficiencies, T_2, T_3, T_4 and T_5 are fixed at the values in Table 2. The results in Figs. 4–6 assume reactions proceed to completion in each step of the cycle. Fig. 7 shows the variations of efficiencies of Cu–Cl cycle with step temperatures, assuming 30% of the total input energy is lost as waste heat and assuming an 80% reaction efficiency for each step. These assumptions help provide more realistic results.

In Fig. 4, assuming an overall heat loss of 20% of the total input energy to the cycle, the overall energy efficiency of the cycle is observed to vary between 55% and 62%, and the overall exergy efficiency between 8% and 13%. When we increase the heat loss from the cycle to 30% of total energy input (as shown in Fig. 5), the range for energy efficiency decreases to between 50% and 55%, and for exergy efficiency to between 7% and 12%. The effect of heat loss from the cycle on its overall energy and exergy efficiencies is depicted more clearly in Fig. 6, for the case in which an overall heat loss of 40% of the total input energy is assumed. In that figure, the energy efficiency varies from 45% to 50% and exergy efficiency from 6% to 11%. It can be inferred from the results presented in Figs. 4–6 that the effect of heat losses from the cycle is greater for energy efficiencies than for exergy efficiencies. Increasing the thermal energy losses from the cycle by 10% of the energy input to the cycle results in a 5% decrease in the energy efficiency but only a 1% decrease in the exergy efficiency.

The results presented in Figs. 4–6 also appear to be higher than expected, based on values obtained in other studies [6–13]. This difference is likely attributable to the fact that we assumed a complete reaction for each step in the present calculations. To obtain more realistic values, we carry out an assessment in which we assume a reaction efficiency of 80% for the steps in the Cu–Cl cycle involving a chemical reaction and that 30% of the total input energy to the cycle becomes heat loss. An 80% reaction efficiency for each step is an assumption based on expected values that are usual for these kinds of chemical reactions and it is used to assess the effect of reaction efficiency on the overall cycle efficiency. For example, we consider by how much the overall cycle efficiency drops if the reaction efficiency is changed to 80% from 100%. Based on these two assumptions, the overall energy efficiency of the cycle varies from 42% to 44% and exergy efficiency from 6% to 8% (see Fig. 7).

In all cases presented in Figs. 4–7, the energy efficiency of the cycle increases with increasing reaction temperature for steps 1 and 3, and decreasing reaction temperature for steps 2, 4 and 5. Also, the overall exergy efficiency of the cycle increases with increasing reaction temperature for steps 2, 4 and 5, and decreasing reaction temperature for steps 1 and 3. The effect of reaction temperature of steps 3 and 4 on the energy and exergy efficiencies is significant while the effect of reaction temperature of other steps is minor.

The variation of energy and exergy efficiencies of the cycle with reference-environment temperature (T_0) is illustrated in Fig. 8. The exergy efficiency decreases with increasing T_0, while the energy efficiency remains constant.

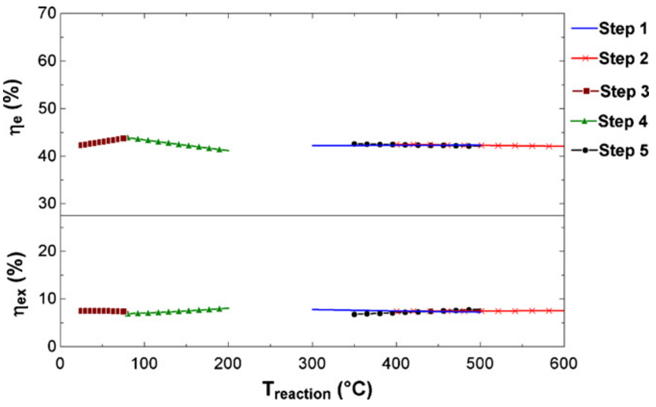

Fig. 7. Variation of efficiencies of Cu–Cl cycle with the temperatures of the steps assuming an overall heat loss of 30% of the total input energy to the cycle and an 80% reaction efficiency for each step.

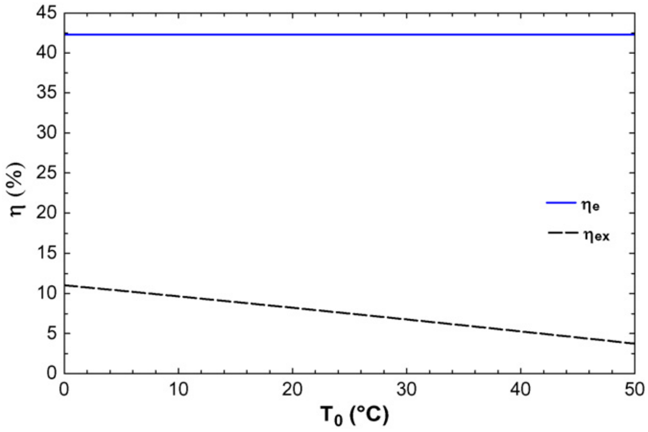

Fig. 8. Variation of efficiencies of the Cu–Cl cycle with reference-environment temperature assuming an overall heat loss of 30% of the total input energy to the cycle and an 80% reaction efficiency for each step.

5. Conclusions

For each of the steps in the Cu–Cl thermochemical water decomposition cycle, the variations of reaction heat with parameters like process temperature have been quantified and characterized. Also overall energy and exergy efficiencies of the cycle have been obtained for several scenarios. A parametric study is reported of how the reaction heat in each chemical reaction and overall energy and exergy efficiencies of the Cu–Cl cycle vary with reaction and reference-environment temperatures. It can be concluded that:

- As reaction temperature increases, the input energy needed (the output energy released, in the case of exothermic reaction) to drive the chemical reactions for steps 1, 3 and 5 decreases while that for steps 2 and 4 increases.
- The overall energy efficiency of the cycle varies from 42% to 44% and exergy efficiency from 6% to 8%, assuming a reaction efficiency of 80% for the steps in the Cu–Cl cycle involving chemical reaction and that heat loss is equivalent to 30% of the total input energy to the cycle.
- The exergy efficiency decreases with increasing reference-environment temperature, while the energy efficiency remains constant.

- The energy and exergy efficiencies of the cycle are observed to vary with temperatures of the reactions and reference-environment, and cycle heat losses. The overall efficiencies (energy and exergy) of the process can be increased by optimizing these design parameters. Thus, a sensitivity analysis is carried out considering several heat losses, reaction and reference-environment temperatures, and component-efficiency scenarios to use these results in future design and optimization activities for the cycle.

This information should assist efforts to understand the thermodynamic losses in the cycle and to improve efficiency. It is concluded that the Cu–Cl thermochemical water decomposition cycle exhibits good potential for future applications in hydrogen production.

Acknowledgement

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