ENERGY AND EXERGY ANALYSES OF A COPPER-CHLORINE THERMOCHEMICAL WATER DECOMPOSITION PILOT PLANT FOR HYDROGEN PRODUCTION

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Abstract

Nuclear-based hydrogen production via thermochemical water decomposition using a copper-chlorine (Cu-Cl) cycle consists of a series of chemical reactions in which water is split into hydrogen and oxygen as the net result. This is accomplished through reactions involving intermediate copper and chlorine compounds, which are recycled. Energy and exergy analyses are reported here of a Cu-Cl pilot plant, including the relevant chemical reactions. The reference environment is taken to be at a temperature of 298.15 K and atmospheric pressure (1 atm). The chemical exergy of a substance, which is the maximum work that can be obtained from it by taking it to chemical equilibrium with the reference environment at constant temperature and pressure, is calculated with property data for the substance and the reference environment, with enthalpy and entropy values calculated using Shomate equations. The reaction heat, exergy destruction and efficiencies in each chemical reaction vary with the reaction temperature and reference-environment temperature. A parametric study with variable reaction and reference-environment temperatures is also presented.

Keywords: Hydrogen, thermochemical water decomposition, energy, exergy, nuclear.

1. Introduction

Hydrogen is widely believed to be world's next-generation fuel, because of its lower environmental impact and greenhouse gas emissions, in comparison to fossil fuels. Hydrogen demand is expected to increase very rapidly over the next decade.

A U.S. Department of Energy goal is to identify new technologies for producing hydrogen that are more cost effective, without greenhouse gas emissions. Thermochemical cycles are one of the most promising options in these regards. In thermochemical cycles, a series of reactions occur in which water is thermally decomposed into hydrogen and oxygen and all other chemicals are recycled. Only heat and water are consumed.

Others have examined processes for hydrogen production using nuclear energy. A fission reactor as a primary energy source with hydrogen as an energy carrier was suggested by Torjman et al. [1], and an assessment of hydrogen production from nuclear energy presented. A complete nuclear-electro-hydrogen energy system was proposed for a medium size city (population of 500,000), and the entire energy requirement was assessed including residential, industrial and transportation needs. A preliminary economic and environmental impact study was performed on the proposed system [1]. Yildiz et al. [2] examined several alternatives for coupling nuclear and hydrogen production technologies, accounting for their thermal-to-hydrogen energy efficiency. Most studies of hydrogen production have focused on energy and neglected exergy considerations, which can reveal useful insights.

The objectives of this study are to perform energy and exergy analyses of a Cu-Cl pilot plant for hydrogen production, including the relevant chemical reactions, and also to evaluate system efficiencies. Nuclear-based hydrogen production via a copper-chlorine thermochemical cycle consists of a series of chemical reactions in which water is split into hydrogen and oxygen. This is accomplished through reactions involving intermediate copper and chlorine compounds, which are recycled. In the present study, the reference environment is taken to be at a temperature of 298.15 K and atmospheric pressure (1 atm). The chemical exergy of a substance is calculated with property data for the substance and the reference environment, with enthalpy and entropy values calculated using Shomate equations. A parametric study with variable reaction and reference-environment temperatures is also performed.

2. Thermodynamic background

When a chemical reaction occurs, the bonds within molecules of the reactants are broken, and atoms and electrons rearrange to form products. During chemical reactions mass is conserved, so the mass of the products equals the mass of the reactants, even though the elements exist in different chemical compounds in the reactants and products. However, the number of moles of products may differ from the number of moles of reactants.

The conservation of energy principle applies whether or not a chemical reaction occurs within the system. However, the methods used for evaluating the properties differ somewhat for reacting and nonreacting systems. In thermodynamic property tables for nonreacting system, values for specific internal energy u, enthalpy h, and entropy s are given relative to some arbitrary datum state where the enthalpy (or alternatively the internal energy) and entropy are set to zero. This approach is satisfactory for evaluations involving differences in property values between states of the same composition, for then the arbitrary datum cancel. However, when a chemical reaction occurs, reactants change and products are formed, so differences cannot be calculated for all substances involved. For reacting systems, it is necessary to evaluate quantities like h, u, and s so there are no inconsistencies in properties.

An enthalpy datum for the study of reacting systems can be established by assigning arbitrarily a value of zero to the enthalpy of the stable elements at a state called the standard reference state and defined by $T_{ref} = 298.15$ K and $P_{ref} = 1$ atm. Note that only stable elements are assigned a value of zero enthalpy at the standard state. The term stable simply means that the particular element is in a chemically stable form.

Using such a datum, enthalpy values can be assigned to compounds for use in the study of reacting systems. The enthalpy of a compound at the standard state equals its enthalpy of formation, symbolized $\overline{h}_f^\circ$. The enthalpy of formation is the energy released or absorbed when the compound is formed from its elements, the compound and elements all being at T_{ref} and P_{ref}. The specific enthalpy of a compound at a state other then the standard state is found by adding the specific enthalpy change between the standard state and the state of interest to the enthalpy of formation.

Several considerations enter when writing energy balances for systems involving chemical reaction. Some of these apply generally, without regard for whether reaction takes place. For example, it is necessary to determine work and heat transfers, as well as the importance of kinetic and potential energy. Other considerations relate to the occurrence of combustion or other reactions. For example, it is important to know the states and conditions of the reactants before reaction occurs, and if they are premixed. The state of the products also must be assessed, e.g., if water formed on reaction has condensed.

The model proposed by Szargut for the calculation of the standard chemical exergy of elements and organic and inorganic substances has been revised by Rivero et al. [3]. These revised values of standard chemical exergy are compared with those of Szargut [3]. Using Szargut's model, the variations of chemical exergy with reference-environment temperature from -30˚C to 45˚C, pressure from 0.6 to 1.1 bar and relative humidity from 10% to 100% were investigated, for gaseous fuels and atmospheric gases, by Ertesvåg [4]. A new quantitative structure–property relationship three-parameter correlation ($R^2 = 0.9977$) of standard chemical exergy for a diverse set of 134 organic substances was developed by Gharagheizi et al. [5] by application of a genetic algorithm search.

3. Other exergy applications

Many applications of exergy to energy systems have been reported, illustrating the insights obtainable. Gao et al. [6] performed an exergy analysis of a coal-based polygeneration system for power and chemical production. The exergy regeneration performances of chemical recuperation with CO_2-natural gas reforming were presented by Cao et al. [7].

Energy and exergy analyses of energy consumptions in the industrial sector in South Africa have been analysed (Oladiran et al. [8]). An energy and exergy analysis of a raw mill and raw materials preparation unit was performed of a cement plant in Turkey by Utlu et al. [9] using the operating data. Energy and exergy balances of blast furnace iron making and DIOS-type direct iron-smelting processes, and exergy losses in these processes, are discussed by Ostrovski et al. [10]. Energy and exergy analyses are applied by Camdali et al. [11] to a dry system rotary burner with pre-calcinations in a cement plant of an important cement producer in Turkey using actual data. The rotary burner includes thermal and chemical processes. First and second law efficiencies were determined [11].

The effects on the results of energy and exergy analyses of variations in dead-state properties were studied by Rosen et al. [12]. That work involved (i) examination of the sensitivities of energy and exergy values to the choice of the dead-state properties and (ii) analysis of the sensitivities of the results of energy and exergy analyses of complex systems to the choice of dead-state properties. A case study of a coal-fired electrical generating station was considered [12]. Exergy losses in gasification and combustion of solid carbon were compared by Prins et al. [13] by conceptually dividing the processes into several subprocesses: instantaneous chemical reaction, heat transfer from reaction products to reactants (internal thermal energy exchange) and product mixing. The thermodynamic performance of a water electrolysis process for producing hydrogen was investigated by Rosen [14], using both energy and exergy analyses. Three cases were considered in which the principal driving energy inputs are (i) electricity, (ii) the high-temperature heat used to generate the electricity, and (iii) the heat source used to produce the high-temperature heat [14].

Bonnet et al. [15] studied the coupling of an Ericsson engine, with a system involving natural gas combustion. In designing this plant, they utilized energy, exergy and exergo-economic analyses. This study focused on the design and the performance of a real engine rather than a purely theoretical thermodynamic cycle, and allowed a balancing of energy performance with heat exchanger sizes, the plotting of exergy Grassmann diagrams, and evaluation of the cost of thermal and electric energy production [15].

4. System studied

Thermochemical cycles consist of a series of reactions in which water is thermally decomposed and all other chemicals are recycled. Only heat and water are consumed. Unfortunately, most thermochemical cycles require process heat at high temperatures, exceeding 850-900°C. Recently, Atomic Energy of Canada Limited and the Argonne National Laboratory in the U.S. have been developing low-temperature cycles, designed to accommodate heat sources around 500-550°C. 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 cycles. 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.

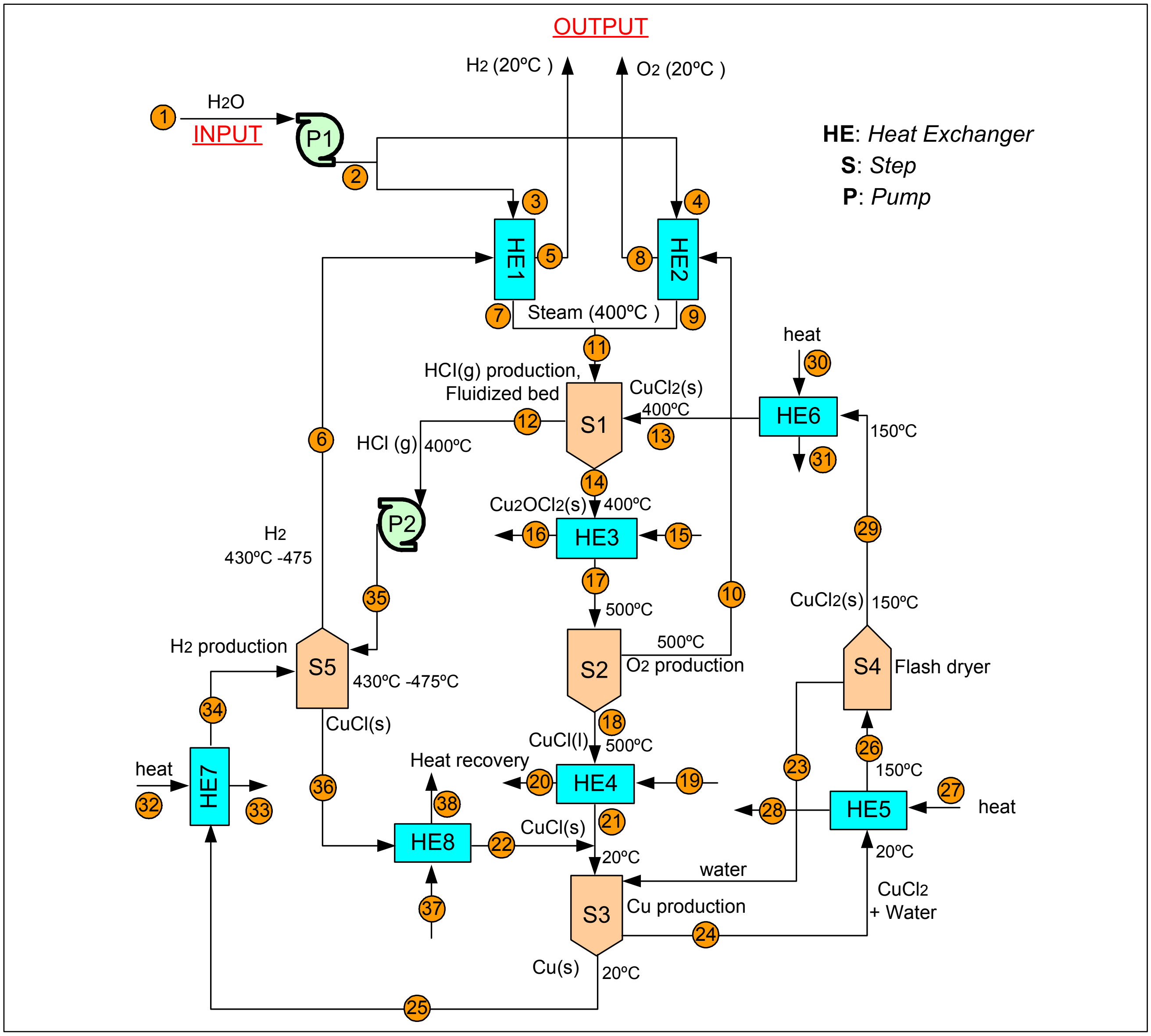

Figure 1. Conceptual layout of a thermochemical Cu-Cl hydrogen production cycle.

Table 1. Steps of Cu-Cl cycle with their corresponding reaction.

Step	**Reaction**	**Temp. Range (˚C)**	**Pres. (kPa)**	**Feed/Output** (note: Q-*thermal energy,* V-*electrical energy*)	
1	$2CuCl_2(s)+H_2O(g)\rightarrow$ $CuO+CuCl_2(s)+2HCl(g)$	400	101.325	Feed: Output:	Powder/granular $CuCl_2(s)+H_2O+$ Q Powder/granular $CuO*CuCl_2(s)+2HCl(g)$
2	$CuO+CuCl_2(s)\rightarrow$ $2CuCl(l)+1/2O_2(g)$	500	101.325	Feed: Output:	Powder/granular $CuO*CuCl_2(s)+$Q Molten CuCl salt + O_2
3	$4CuCl(s)+H_2O\rightarrow$ $2CuCl_2(aq)+2Cu(s)$	Reference-environment (electrolysis)	101.325	Feed: Output:	Powder/granular CuCl and H_2O + V Electrolytic Cu and slurry containing $H_2O+CuCl_2$
4	$CuCl_2(aq)\rightarrow CuCl_2(s)$	>100	101.325	Feed: Output:	Slurry containing $CuCl_2(aq)+$Q Powder/granular $CuCl_2+H_2O$ vapors
5	$2Cu(s)+2HCl(g)\rightarrow$ $2CuCl(l)+H_2(g)$	430-475	101.325	Feed: Output:	Electrolytic Cu + dry HCl + Q H_2 + CuCl(l) salt

A conceptual layout of a Cu-Cl pilot plant is illustrated in Figure 1. Thermochemical water decomposition, potentially driven by nuclear heat with a copper-chlorine cycle, would split water into hydrogen and oxygen through intermediate copper and chlorine compounds. This cycle consists of three thermal reactions and one electrochemical reaction. The cycle involves five steps: (1) the HCl(g) production step using such equipment as a fluidized bed, (2) the oxygen production step, (3) the copper (Cu) production step, (4) the drying step, and (5) the hydrogen production step. A chemical reaction takes place in each step, except the drying step. 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 externally to the atmosphere. The five steps the copper-chlorine cycle are described in Table 1. The Cu-Cl cycle is one of the most promising ways to produce hydrogen efficiently, without emitting any greenhouse gases to the atmosphere.

5. Analysis

In this analysis, we assume that reactants and products are at the reaction temperature and a pressure of 1 atm, and that all chemical reactions occur in steady state, adiabatic processes and proceed to completion. The analysis considers one mol of hydrogen produced per cycle, so all quantities are provided in terms of per mol of hydrogen produced. The thermodynamic data for $CuO*CuCl_2$ were not available, so enthalpies and entropies are calculated for an equimolar mixture of $CuCl_2$ and CuO.

Since mass is conserved in chemical reactions, the mass of products and reactants are equal and the mass balance can be expressed as follows:

$$\dot{m}_{in} = \dot{m}_{out} \quad \text{or} \quad \dot{m}_{reactants} = \dot{m}_{products} \tag{1}$$

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 the system with $W = 0$. For a steady state reaction process, the energy balance reduces to

$$Q = H_p - H_R = \sum n_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum n_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R \tag{2}$$

Also, the exergy balance for a process involving chemical reactions can be written as

$$\sum Ex_{in} - \sum Ex_{out} - Ex_{destruction} = \Delta Ex_{system} \tag{3}$$

For a steady-state system, ΔEx_{system} is zero. The exergy associated with a system at a specified state is the sum of two contributions: thermomechanical and chemical [16]. The total exergy is

$$\overline{ex} = \underline{(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \frac{V^2}{2} + gz} + \overline{ex}^{ch} \tag{4}$$

Here, the underlined term is the thermomechanical contribution and $\overline{ex}^{ch}$ is the chemical contribution. Combining Eqs. (3) and (4) yields

$$\begin{aligned} \overline{ex}_{destruction} &= \sum[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \frac{V^2}{2} + gz + \overline{ex}^{ch}]_{in} \\ &\quad - \sum[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \frac{V^2}{2} + gz + \overline{ex}^{ch}]_{out} + (1 - \frac{T_0}{T_{reaction}})Q \end{aligned} \tag{5}$$

where Q is the heat that interacts with the system (negative for exothermic reactions). For the chemical reactions in the Cu-Cl cycle, it is reasonable to assume the kinetic exergy ($V^2/2$) and potential exergy (gz) of substances are equal to zero. Then,

$$\begin{aligned} \overline{ex}_{destruction} &= \sum[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{in} - \sum[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{out} \\ &\quad + (1 - \frac{T_0}{T_{reaction}})Q \end{aligned} \tag{6}$$

After writing mass, energy and exergy balances for the chemical reaction in each step, enthalpy and entropy values of each compound are evaluated with Shomate equations [17] as follows:

$$\overline{h} - \overline{h}_0 = A * T + B * \frac{T^2}{2} + C * \frac{T^3}{3} + D * \frac{T^4}{4} - E * \frac{1}{T} + F - H \tag{7}$$

and

$$\overline{s} = A * \ln(T) + B * T + C * \frac{T^2}{2} + D * \frac{T^3}{3} - E * \frac{1}{2T^2} + G \tag{8}$$

where T is 1/1000 of the specified temperature (in K) of compound and A, B, C, D, E, F, G and H are constants, given in Table 2 for each compound.

Table 2. Enthalpy of formation, reference entropy and Shomate constants for chemical compounds.

Compound	$\overline{h}_f^\circ$ (kJ/kmol)	$\overline{s}_0$ (kJ/kmol*K)	A	B	C	D	E	F	G	H
$H_2O(g)$	-241,830	188.84	30.09200	6.832514	6.793435	-2.534480	0.082139	-250.8810	223.3967	-241.8264
$CuCl_2(s)$	-205,850	108.06	70.21882	23.36132	-14.86876	4.053899	-0.366203	-228.9405	184.6378	-205.8532
HCl(g)	-92,310	186.90	32.12392	-13.4580	19.86852	-6.853936	-0.049672	-101.6206	228.6866	-92.31201
CuO(s)	-156,060	42.59	48.56494	7.498607	-0.055980	0.013851	-0.760082	-173.4272	94.85128	-156.0632
$O_2(g)$	0	205.07	29.65900	6.137261	-1.186521	0.095780	-0.219663	-9.861391	237.9480	0
CuCl(l)	-131,180	93.75	66.94400	-3.69e-10	2.16e-10	-3.900e-11	-9.813e-12	-151.1374	174.7653	-131.1780
CuCl(s)	-138,070	87.04	75.27100	-26.8321	25.69156	-7.357982	-1.847747	-165.7299	174.6644	-138.0720
$H_2O(l)$	-285,830	69.95	-203.606	1523.290	-3196.413	2474.455	3.855326	-256.5478	-488.716	-285.8304
Cu(s)	0	33.17	17.72891	28.09870	-31.25289	13.97243	0.068611	-6.056591	47.89592	0
$H_2(g)$	0	130.68	33.0661	-11.3634	11.432816	-2.772874	-0.158558	-9.980797	172.7079	0

With the specific enthalpy and entropy values, we can calculate the specific chemical exergy $\overline{ex}^{ch}$ value of each compound. Evaluating the thermomechanical contributions can be thought of as bringing the system without change in composition from the specified state to T_0 and P_0, the condition where the system is in thermal and mechanical equilibrium with the environment. Depending on the nature of the system, this may be a real or hypothetical condition.

The chemical exergy based on a typical exergy reference environment exhibiting standard values of the environmental temperature T_0 and pressure P_0 such as 298.15 K and 1 atm is called standard chemical exergy. To determine the standard chemical exergy of any substance not present in the environment, we consider the reaction of the substance with other substances for which the standard chemical exergies are known, and write

$$\overline{ex}^{ch} = -\Delta G + \sum_{P} n\overline{ex}^{ch} - \sum_{R} n\overline{ex}^{ch} \tag{9}$$

where ΔG is the change in Gibbs function for the reaction, regarding each substance as separate at temperature T_0 and pressure P_0. The other two terms on the right side of Eq. (9) are evaluated using the known standard chemical exergies, together with n values, which express the moles of these reactants and products per mole of the substance whose chemical exergy is being evaluated.

For example, the chemical exergy of copper chloride ($CuCl_2$) is obtained from its constituent elements, for which standard chemical are known. The formation reaction for copper chloride is

$$\mathrm{Cu} + \mathrm{Cl_2} \rightarrow \mathrm{CuCl_2}$$

Applying Eq. (9) to this reaction we obtain

$$\overline{ex}^{ch}_{CuCl_2} = \left[\bar{g}_{CuCl_2} - \bar{g}_{Cu} - \bar{g}_{Cl_2}\right](T_0, P_0) + \overline{ex}^{ch}_{Cu} + \overline{ex}^{ch}_{Cl_2} \tag{10}$$

The change in the Gibbs function for this reaction is

$$\begin{aligned} \bar{g}_P - \bar{g}_R &= (\bar{h} - T\bar{s})_{CuCl_2} - (\bar{h} - T\bar{s})_{Cu} - (\bar{h} - T\bar{s})_{Cl_2} \\ &= (\bar{h}_{CuCl_2} - \bar{h}_{Cu} - \bar{h}_{Cl_2}) - T(\bar{s}_{CuCl_2} - \bar{s}_{Cu} - \bar{s}_{Cl_2}) \end{aligned} \tag{11}$$

where $\bar{g}_P$ and $\bar{g}_R$ denote, respectively, the Gibbs function of the reactants and products, per kmol of copper chloride. In the present case, all substances are at the same temperature and pressure, 25˚C and 1 atm, which correspond to the standard reference state values. At the standard reference state, the enthalpies and Gibbs functions for copper (Cu) and chlorine (Cl_2) are zero by definition. Thus, in Eq. (11),

$$\bar{g}_R = \bar{h}_{Cu} = \bar{h}_{Cl_2} = 0 \text{ and } \bar{g}_P = (\bar{g}^{o}_{f})_{CuCl_2}$$

and

$$\bar{g}_P = (\bar{g}^{o}_{f})_{CuCl_2} = (\bar{h}^{o}_{f})_{CuCl_2} - T_0(\bar{s}^{o}_{CuCl_2} - \bar{s}^{o}_{Cu} - \bar{s}^{o}_{Cl_2}) \tag{12}$$

where the superscript ^{o} denotes properties at T_0 and P_0. Combining Eqs. (10) and (12) yields

$$\overline{ex}^{ch}_{CuCl_2} = (\bar{h}^{o}_{f})_{CuCl_2} - T_0(\bar{s}^{o}_{CuCl_2} - \bar{s}^{o}_{Cu} - \bar{s}^{o}_{Cl_2}) + \overline{ex}^{ch}_{Cu} + \overline{ex}^{ch}_{Cl_2} \tag{13}$$

With this procedure, we obtain the standard chemical exergy of other compounds that participate in the Cu-Cl cycle. The formation reactions for these compounds are given in Table 3, and the specific enthalpy, entropy and Gibbs function of formation of the elements composing these compounds are given in Table 4 along with their standard chemical exergies. Standard chemical exergies of all compounds involved in the Cu-Cl cycle, obtained using these data, are illustrated in Table 5.

Table 3. Formation reactions for several compounds in the Cu-Cl cycle.

Compound	Reaction of formation
H_2O	$H_2 + 1/2O_2 \rightarrow H_2O$

$CuCl_2$	$Cu + Cl_2 \rightarrow CuCl_2$
HCl	$1/2H_2 + 1/2Cl_2 \rightarrow HCl$
CuO	$Cu + 1/2O_2 \rightarrow CuO$
CuCl	$Cu + 1/2Cl_2 \rightarrow CuCl$

Table 4. Enthalpy, entropy and Gibbs free energy of formation, and standard chemical exergy of elements.

Elements	$\overline{h}_f^o$ (kJ/kmol)	$\overline{s}^o$ (kJ/kmol K)	$\overline{g}_f^o$ (kJ/kmol)	$\overline{ex}^{ch}$ (kJ/kmol)
H_2	0	130.57	0	236,090
O_2	0	205.03	0	3970
Cu	0	33.17	0	132,600
Cl_2	0	223.08	0	123,600

Table 5. Gibbs free energy of formation and standard chemical exergy for compounds involved in the Cu-Cl cycle.

Compound	Specific Gibbs free energy of formation, $\overline{g}_f^o$ (kJ/kmol)	Specific standard chemical exergy, $\overline{ex}^{ch}$ (kJ/kmol)
H_2O(g)	-228,638	9437
$CuCl_2$(s)	-161,667	94,533
HCl(g)	-95,314	84,531
CuO(s)	-128,304	6281
O_2(g)	0	3970
CuCl(l)	-115,994	78,414
CuCl(s)	-120,876	73,524
H_2O(l)	-237,180	900
Cu(s)	0	132,600
H_2(g)	0	236,090

3.1 Fluidized bed (HCl production)

The fluidized bed step in the Cu-Cl chemical cycle is also called HCl production step because HCl gas is produced by the chemical reaction. As illustrated in Figure 1, steam and $CuCl_2$(s) enter the fluidized bed as reactants, and HCl(g) and $CuO*CuCl_2$(s) are produced by the reaction:

$$2\,CuCl_2\,(s) + H_2O\,(g) \xrightarrow{Q} CuO * CuCl_2\,(s) + 2\,HCl(g)$$

Reactants enter and products exit the fluidized bed at the reaction temperature of 400˚C, and the reaction is adiabatic and occurs at steady state. Data for $CuO*CuCl_2$ as a compound could not be found. For this reason, Lewis et al. [18] represent $CuO*CuCl_2$ as a simple mixture of CuO and $CuCl_2$. We deal with $CuO*CuCl_2$ similarly, treating it as a mixture and calculating its thermodynamic properties with the properties of CuO and $CuCl_2$ based on their mass fractions.

The step in this reaction involves the endothermic hydrolysis of $CuCl_2$, and gives a reasonable result above 300˚C. The free energy for this reaction is positive over the reaction temperature range of 300 to 400˚C.

The mass balance equation of the reaction is

$$n_{11}\overline{m}_{11} + n_{13}\overline{m}_{13} = n_{12}\overline{m}_{12} + n_{14}\overline{m}_{14} \tag{14}$$

where $\overline{m}$ and n are molar mass and mole number of the compound respectively.

The heat transfer for this chemical process can be determined with an energy balance as

$$Q = \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{14} + \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{12} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{13} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{11} \tag{15}$$

and the exergy balance equation can be written as

$$\begin{aligned}\overline{ex}_{destruction} &= n_{11}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{11} + n_{13}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{13} \\ &\quad - n_{12}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{12} - n_{14}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{14} \\ &\quad + \left(1 - \frac{T_0}{T_{reaction}}\right)Q\end{aligned} \tag{16}$$

3.2 Oxygen production

In the oxygen production step of the Cu-Cl cycle (see Figure 1), $CuO*CuCl_2(s)$ is heated and reacts to form $O_2(g)$ and CuCl(l). The reaction is adiabatic and takes place at 500°C at steady state. That is, a mixture of CuO and $CuCl_2$ generates O_2 according to the following chemical reaction:

$$\mathrm{CuO * CuCl_2\,(s)} + Q \rightarrow \mathrm{2CuCl\,(l)} + \frac{1}{2}\mathrm{O_2}$$

The step also involves the endothermic thermal decomposition of an oxychloride (Cu_2Cl_2O). As we explained earlier, oxychloride is produced by heating an equimolar mixture of $CuCl_2$ and CuO. The temperature range for this reaction is 450 to 530°C, which is the highest temperature requirement in the cycle. In the reaction, as explained in [19], $CuCl_2$ in the oxychloride (Cu_2Cl_2O) decomposes to CuCl and Cl_2. The chlorine then reacts with CuO to release oxygen and forms additional CuCl.

From Figure 1, the mass balance for this reaction is

$$n_{17}\overline{m}_{17} = n_{18}\overline{m}_{18} + n_{10}\overline{m}_{10} \tag{17}$$

The heat transfer for this chemical process can be determined with an energy balance as

$$Q = \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{18} + \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{10} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{17} \tag{18}$$

The exergy destruction can be found with an exergy balance:

$$\begin{aligned}\overline{ex}_{destruction} &= n_{17}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{17} - n_{18}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{18} \\ &\quad - n_{10}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{10} + \left(1 - \frac{T_0}{T_{reaction}}\right)Q\end{aligned} \tag{19}$$

3.3 Copper production

In the copper (Cu) production step of Cu-Cl cycle, as illustrated in Figure 1, solid cuprous monochloride (CuCl) and water react with at 20°C, and solid copper (Cu) and copper chloride in aqueous form are produced.

The chemical formula for this reaction is

$$4\mathrm{CuCl}\,(\mathrm{s}) + \mathrm{H_2O}\,(\mathrm{l}) \xrightarrow{Q} 2\mathrm{CuCl_2}\,(\mathrm{s}) + 2\mathrm{Cu}\,(\mathrm{s}) + \mathrm{H_2O}\,(\mathrm{l})$$

Based on Figure 1, a mass balance can be written as

$$n_{21}\overline{m}_{21} + n_{22}\overline{m}_{22} + n_{23}\overline{m}_{23} = n_{24}\overline{m}_{24} + n_{25}\overline{m}_{25} \tag{20}$$

The heat transfer for this chemical process can be found with an energy balance:

$$Q = \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{24} + \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{25} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{21} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{22} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{22} \tag{21}$$

The corresponding exergy balance is

$$\begin{aligned}\overline{ex}_{destruction} &= n_{21}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{21} + n_{22}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{22} \\ &+ n_{23}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{23} - n_{24}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{24} \\ &- n_{25}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{25} + (1 - \frac{T_0}{T_{reaction}})Q\end{aligned} \tag{22}$$

3.4 Evaporator (flash dryer)

In the flash dryer, the only physical step in the Cu-Cl cycle, copper chloride ($CuCl_2$) is dried by evaporating water in a steady state process. As illustrated in Figure 1, a mixture of copper chloride and water enter the evaporator at 20˚C, and water vapor and copper chloride exit separately at 150˚C:

$$2\mathrm{CuCl_2}\,(\mathrm{aq}) \rightarrow 2\mathrm{CuCl_2}\,(\mathrm{s})$$

With Figure 1, a mass balance for this process can be expressed as

$$(n_{H_2O})_{in} = (n_{H_2O})_{out} \text{ and } (n_{CuCl_2})_{in} = (n_{CuCl_2})_{out} \tag{23}$$

An energy balance can be written as follows:

$$n_{26}\overline{h}_{26} + Q_{in} = n_{23}\overline{h}_{23} + n_{29}\overline{h}_{29} \tag{24}$$

Combining the Eq. (24) with the mass balance,

$$Q_{in} = n_{CuCl_2}(\overline{h}_{CuCl_2@150°C} - \overline{h}_{CuCl_2@80°C}) + n_{H_2O}(\overline{h}_{H_2O@150°C} - \overline{h}_{H_2O@80°C}) \tag{25}$$

An exergy balance can be written as

$$\overline{ex}_{destruction} = [n_{26}\overline{ex}_{26} + (1 - \frac{T_0}{T_{evaporator}})Q_{in}] - [n_{23}\overline{ex}_{23} + n_{29}\overline{ex}_{29}] \tag{26}$$

3.5 H_2 production

In the hydrogen production step, hydrogen chloride gas (HCl) and copper (Cu) enter and are converted to hydrogen gas (H_2) and solid cuprous monochloride (CuCl), as seen in Figure 1. The reaction takes place at 450˚C at steady state.

The hydrogen generation reaction, $2\mathrm{HCl}\,(\mathrm{g}) + 2\mathrm{Cu}\,(\mathrm{s}) \rightarrow 2\mathrm{CuCl}\,(\mathrm{l}) + \mathrm{H_2}\,(\mathrm{g})$, is heterogeneous, exothermic and reversible (in the sense that the reaction can for forwards and backwards). The preferred operation temperature is 425˚C to 450˚C so that the formation of solid cuprous monochloride (CuCl) does not passivate the copper metal surface. Passivation is prevented by running the reaction above the melting point of the CuCl, at about 425˚C.

For this process, a mass balance can be expressed as

$$n_{33}\overline{m}_{35} + n_{34}\overline{m}_{34} = n_{36}\overline{m}_{36} + n_{6}\overline{m}_{6} \tag{27}$$

The heat transfer for this chemical process can be found with an energy balance:

$$Q = \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{24} + \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{25} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{21} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{22} - \left[n\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)\right]_{22} \tag{28}$$

The exergy destruction can be found with an exergy balance:

$$\begin{aligned}\overline{ex}_{destruction} = {} & n_{21}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{21} + n_{22}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{22} \\ & + n_{23}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{23} - n_{24}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{24} \\ & - n_{25}[(\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{ex}^{ch}]_{25} + (1 - \frac{T_0}{T_{reaction}})Q\end{aligned} \tag{29}$$

6. Results and Discussion

The first results obtained are property data needed in the analysis. The Gibbs free energy and the standard chemical exergy of compounds, which are calculated by Eq. (12), (13) respectively, are given in Table 5. These values are based on reference temperature and pressure of 25˚C and 1 atm, respectively. As illustrated in the table the Gibbs free energy of elements that are stable at this temperature and pressure is zero.

The variations of the reaction heats for steps 1, 2, 3 and 5 with reactions temperature are illustrated in Figure 2. As explained earlier, all the steps are endothermic except the fifth. The reaction in fifth step, in which hydrogen production occurs, is exothermic and the heat produced is seen in Figure 1 to be rejected from the system. As reaction temperature increases, the reaction heat for steps 1, 3 and 5 decreases while that for step 2 increases. In all cases, the relations are nearly linear.

Figure 3 illustrates the variation of specific exergy destruction with reaction temperature for the first step in the Cu-Cl cycle, for several reference-environment temperatures. Exergy destruction is seen in the figure to increase nonlinearly with reaction temperature for all cases. The rate is change of specific exergy destruction with reaction temperature is greatest at lower reaction temperatures. The effect of reference-environment temperature on specific exergy destruction is minor.

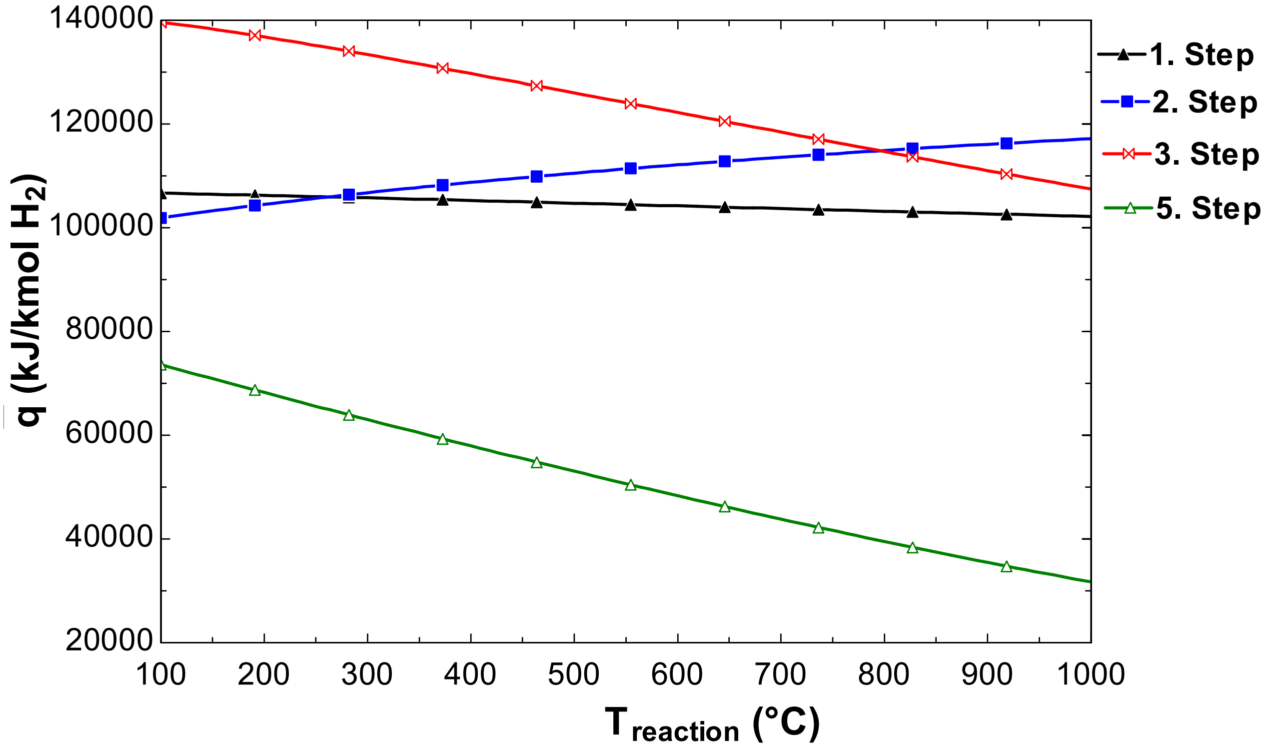

Figure 2. Variation of reaction heat with reaction temperature for several steps in the Cu-Cl cycle.

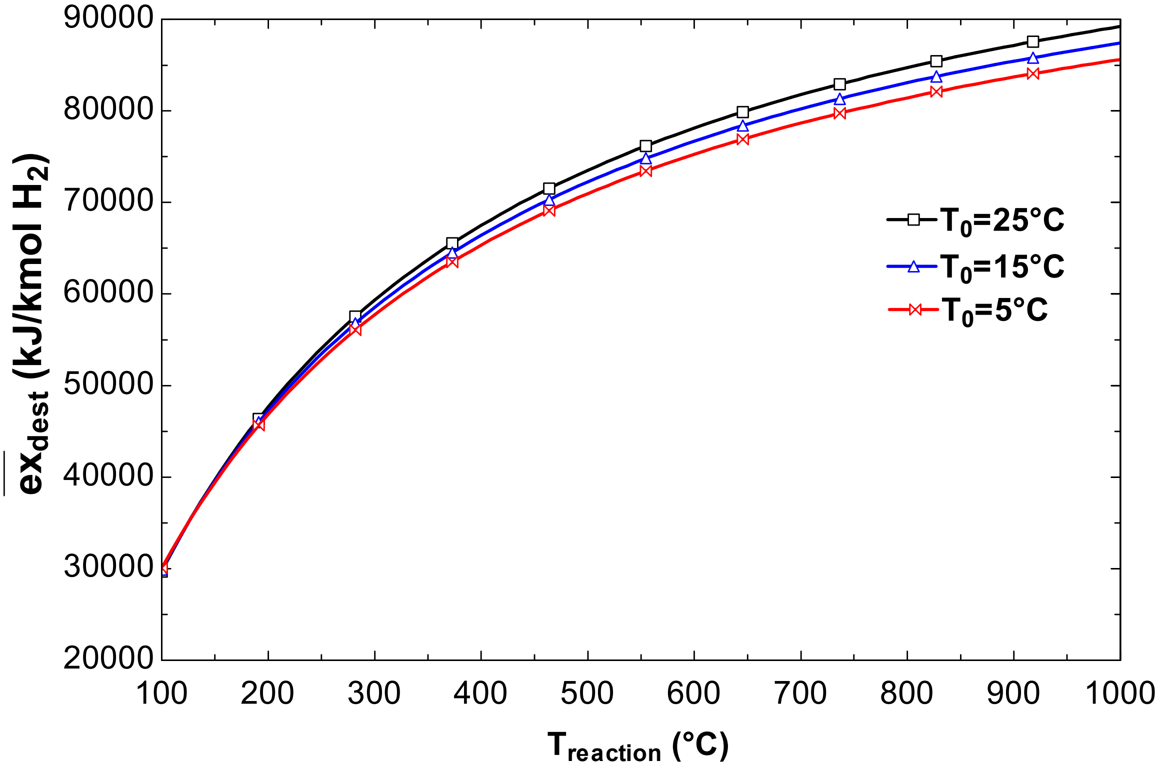

Figure 3. Variation of the specific exergy destruction for the first step in the Cu-Cl cycle with reaction temperature, for several reference-environment temperatures.

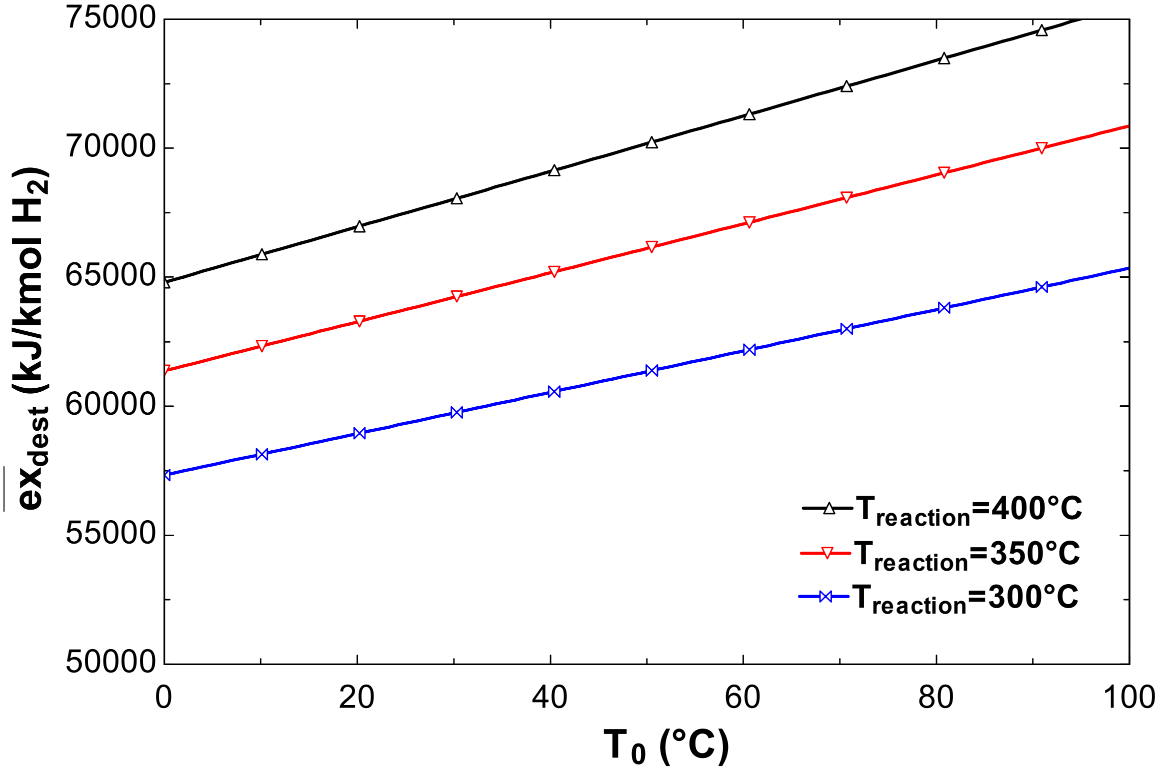

Figure 4. Variation of the specific exergy destruction for the first step in the Cu-Cl cycle with reference-environment temperature, for several reaction temperatures.

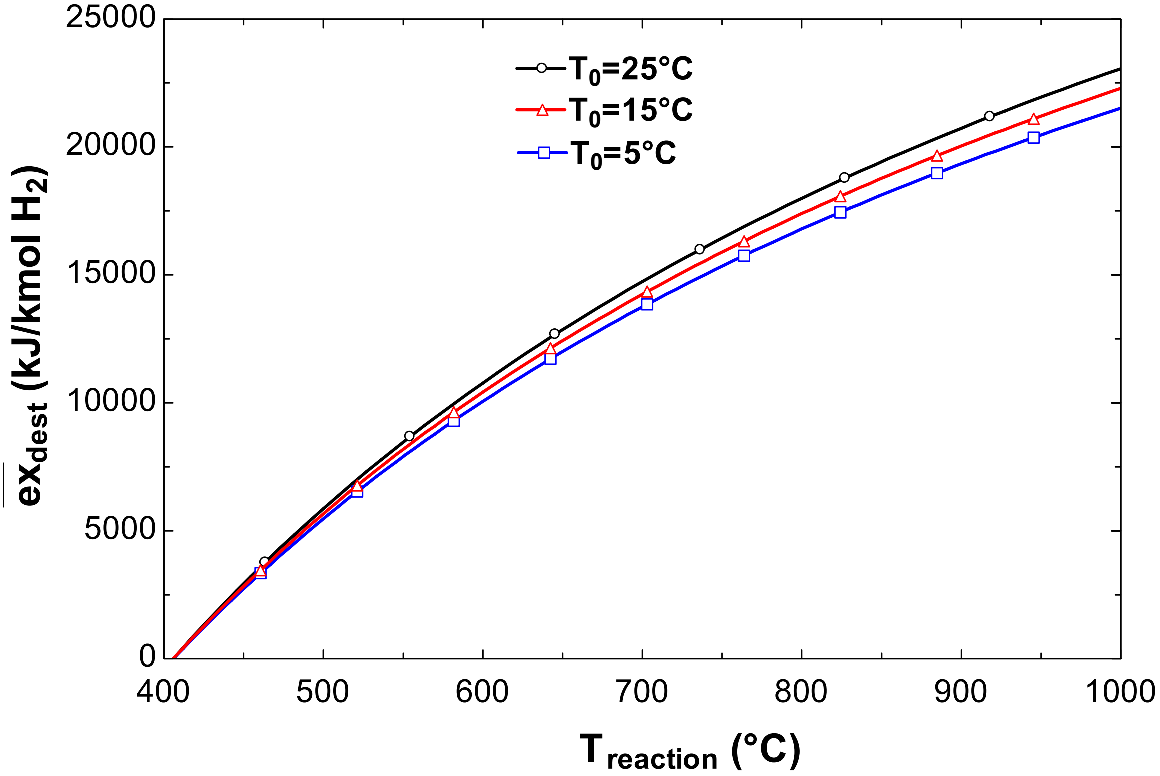

Figure 5. Variation of the specific exergy destruction for the second step in the Cu-Cl cycle with reaction temperature, for several reference-environment temperatures.

In Figure 4, the variation of specific exergy destruction in the first step with reference-environment temperature is illustrated. Several reaction temperatures (300, 350 and 400˚C) are considered in the temperature range of 300-400˚C at which the reaction occurs. The specific exergy destruction increases approximately linearly with reference-environment temperature. Also, the specific exergy destruction decreases with decreasing reaction temperature.

Figure 5 shows the variation of specific exergy destruction of the second step (oxygen production), with reaction temperature for three reference-environment temperatures (5, 15 and 25˚C). The specific exergy destruction of the reaction increases nonlinearly with increasing reference-environment temperature. The rate is change of specific exergy destruction with reaction temperature is greatest at lower reaction temperatures. This effect of reference-environment temperature on specific exergy destruction is minor, and can be seen more clearly in Figure 6, where the variation of specific exergy destruction with reference-environment temperature is illustrated for several reaction temperatures (450, 500 and 530˚C). In this figure the specific exergy destruction is observed to increase approximately linearly with reference-environment temperature.

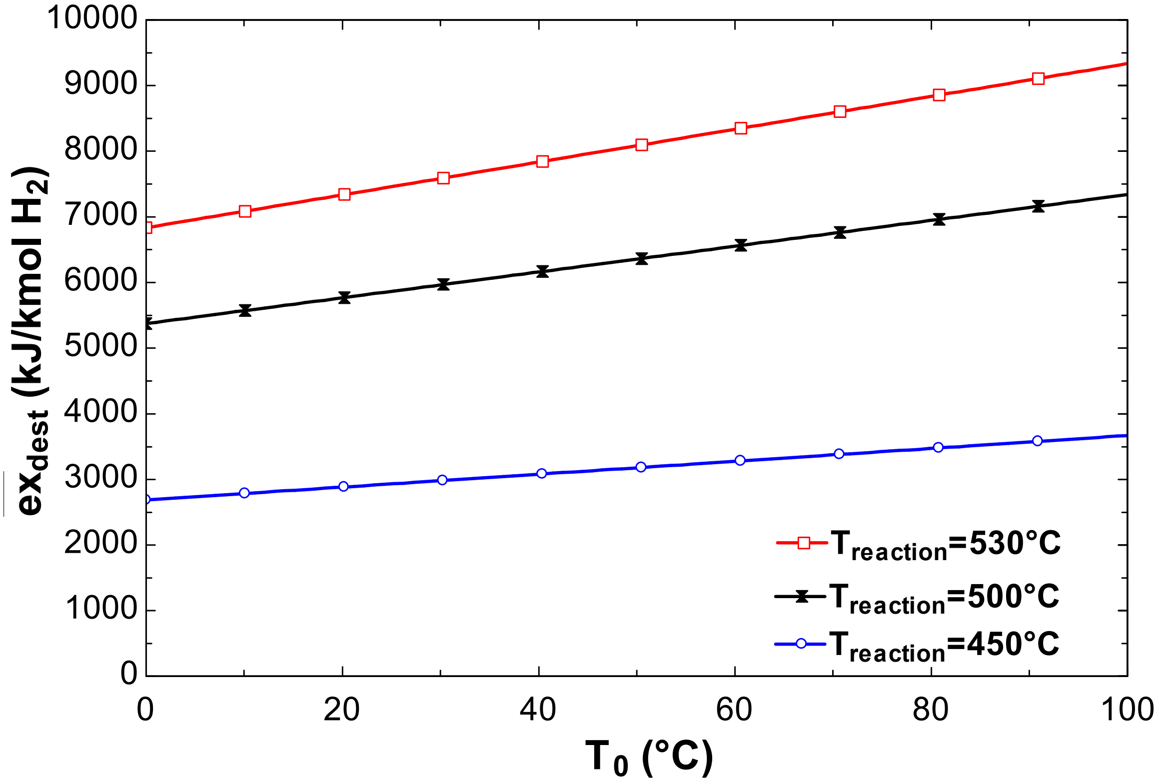

Figure 6. Variation of the specific exergy destruction for the second step in the Cu-Cl cycle with reference-environment temperature, for several reaction temperatures.

The variations of specific exergy destruction for the copper production step with reaction and reference-environment temperature are shown in Figures 7 and 8. In these figures, the specific exergy destruction is seen to decrease sharply as reaction temperature decreases and to increase as reference-environment temperature decreases. The relations are approximately linear. Reference-environment temperatures of 5, 15 and 25˚C and reaction temperatures of 45, 80 and 100˚C are considered.

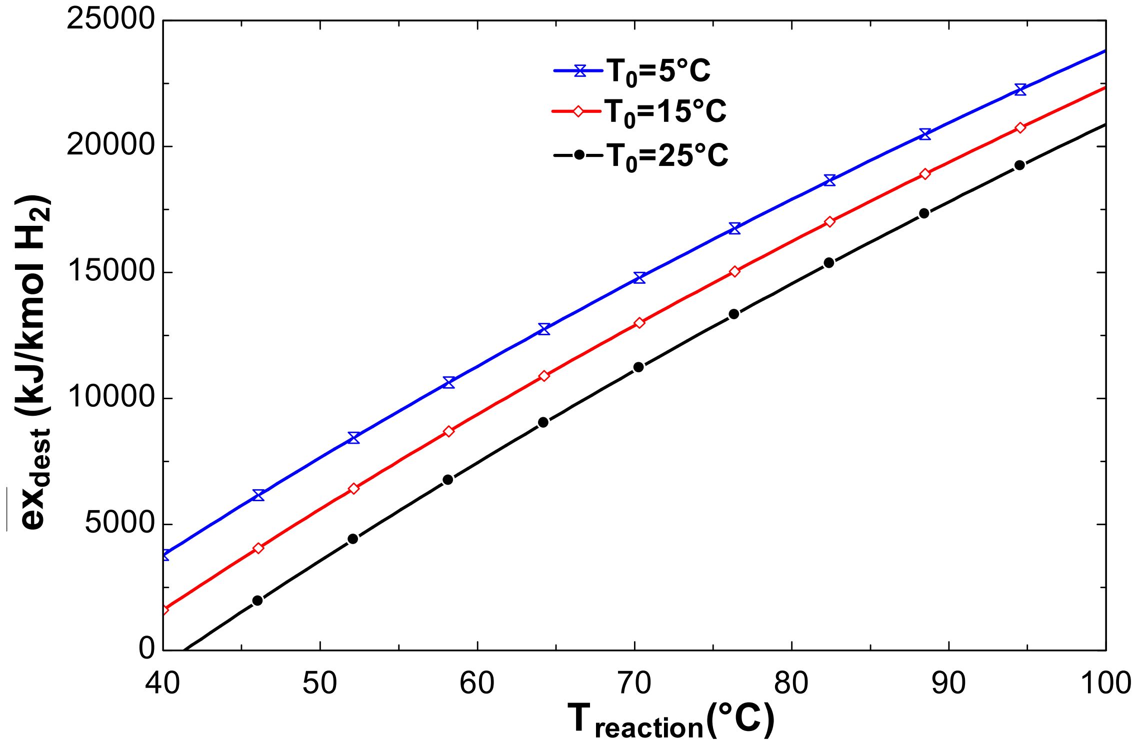

Figure 7. Variation of the specific exergy destruction for the third step in the Cu-Cl cycle with reaction temperature, for several reference-environment temperatures.

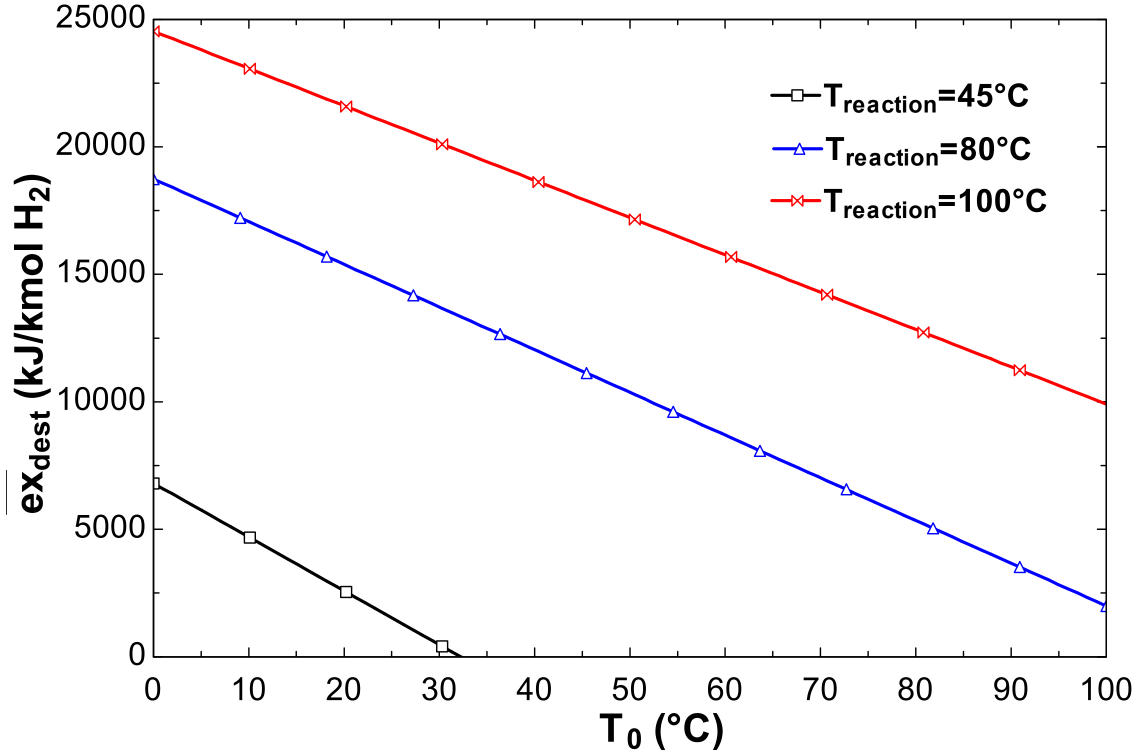

Figure 8. Variation of the specific exergy destruction for the third step in the Cu-Cl cycle with reference-environment temperature, for several reaction temperatures.

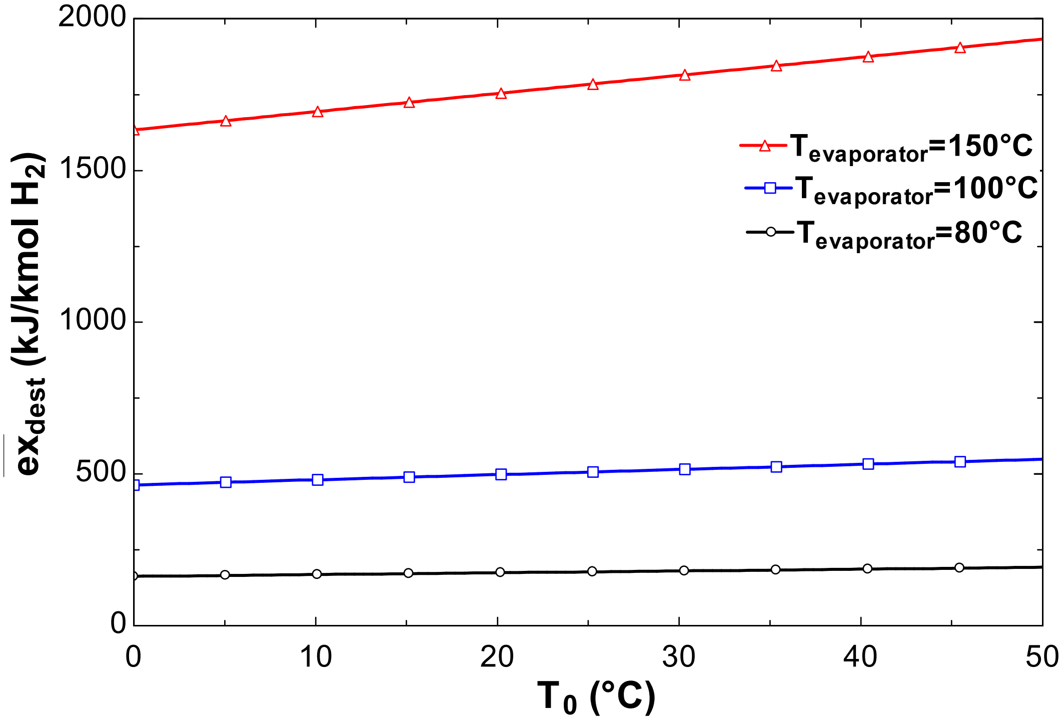

Figure 9. Variation of the specific exergy destruction for the fourth step in the Cu-Cl cycle with reference-environment temperature, for several evaporator temperatures.

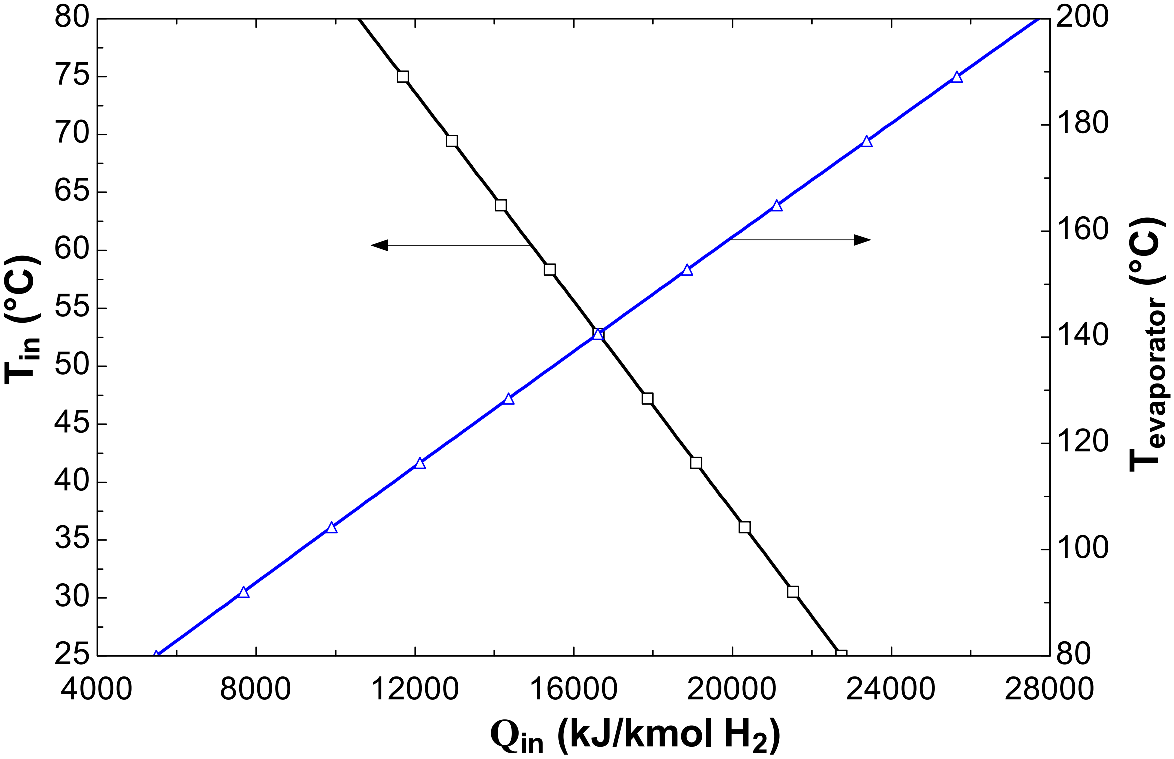

Figure 10. Variation with evaporator inlet heat of evaporator temperature and inlet temperature of copper chloride solution.

In Figure 9, the variation of the specific exergy destruction in the evaporator with reference-environment temperature is illustrated, for evaporator temperatures of 80, 100 and 150˚C. In this figure the specific exergy destruction is observed to increase approximately linearly with reference-environment temperature. Also, the specific exergy destruction increases markedly as evaporator temperature rises.

The effect of varying the inlet heat Q_{in} on the evaporator inlet temperature T_{in} and the evaporator temperature $T_{evaporator}$ is illustrated in Figure 10. The heat needed to evaporate water is seen to be approximately directly proportional to the evaporator temperature, but to decrease approximately linearly as inlet temperature increases. The evaporator inlet temperature is determined in previous step (copper production), where the reaction temperature varies between 25 and 80˚C.

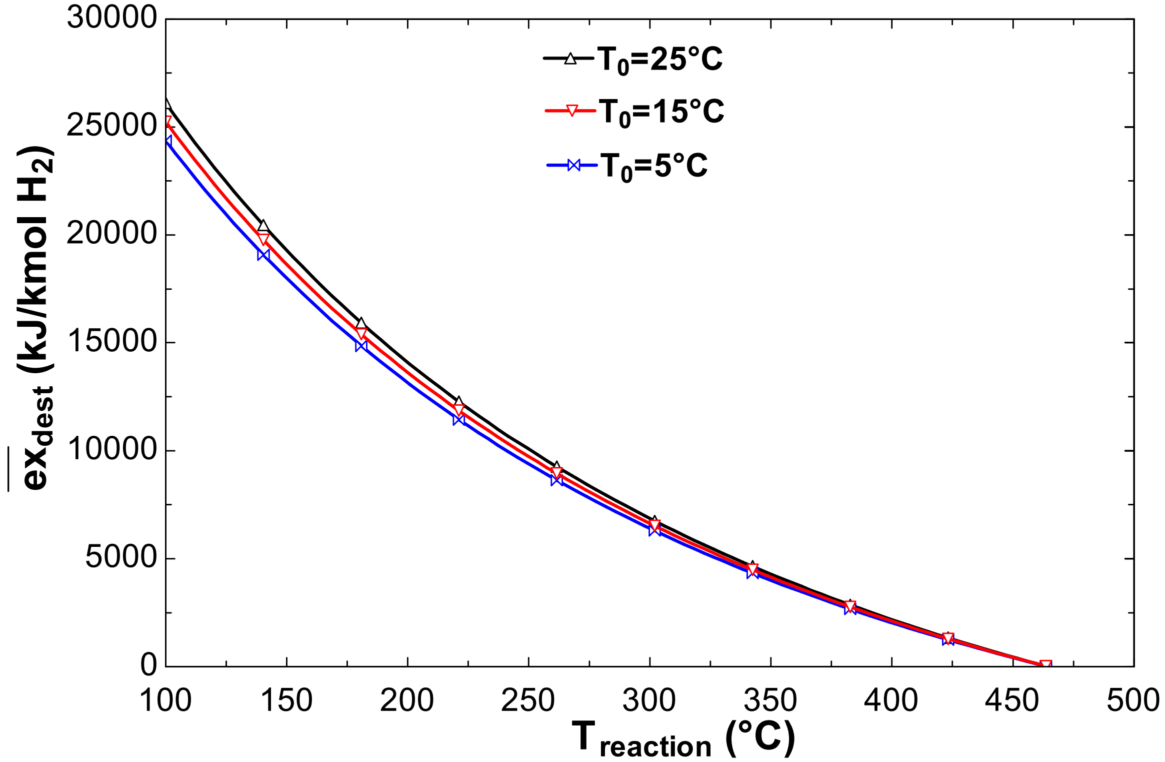

Figure 11. Variation of the specific exergy destruction for the fifth step in the Cu-Cl cycle with reaction temperature, for several reference-environment temperatures.

The variation with reaction temperature of the specific exergy destruction in the hydrogen production step, which is the only exothermic step of Cu-Cl cycle, is illustrated in Figure 11. In contrast to other reactions, the specific exergy destruction for this step decreases nonlinearly as reaction temperature increases. The rate is decrease of specific exergy destruction with reaction temperature is greatest at lower reaction temperatures. The effect of reference-environment temperature on specific exergy destruction is minor in Figure 11, and is illustrated alternatively in Figure 12. It is observed in Figure 11 that the specific exergy destruction is zero at a reaction temperature of 470˚C and becomes negative for higher reaction temperatures, which is thermodynamically impossible. Thus, the hydrogen production reaction must occur at temperatures below 470˚C.

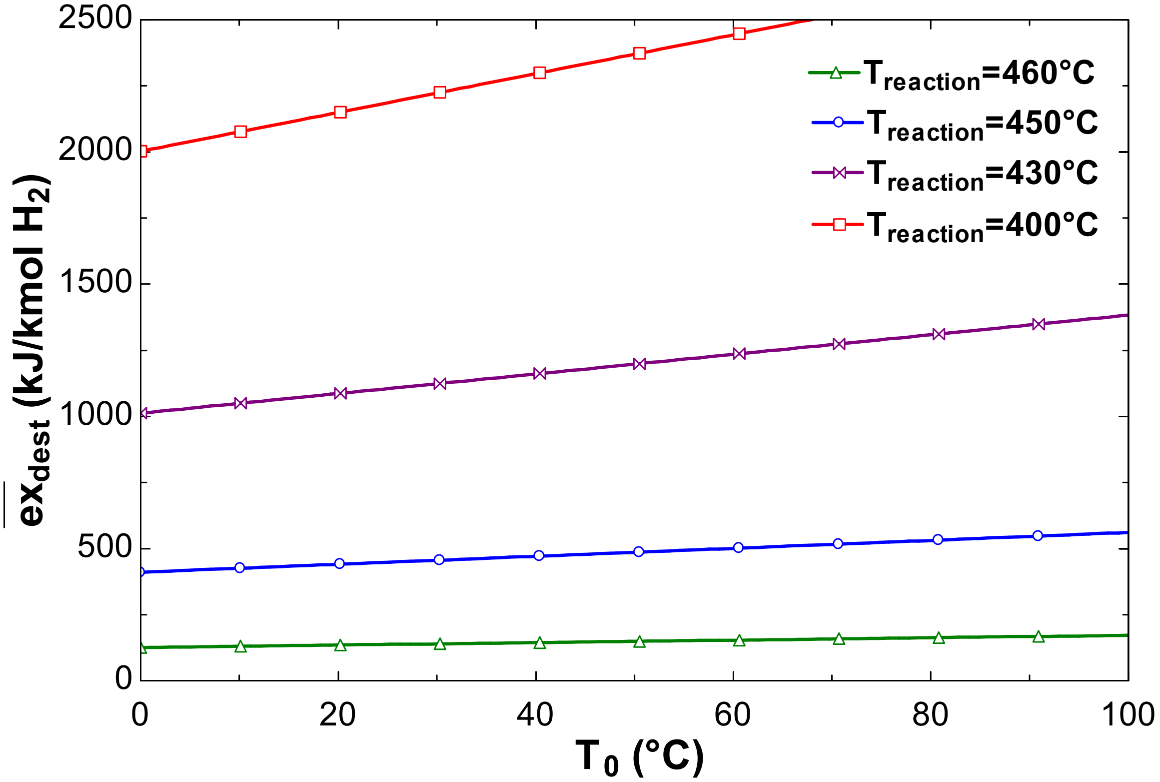

Figure 12. Variation of the specific exergy destruction for the fifth step in the Cu-Cl cycle with reference-environment temperature, for several reaction temperatures.

7. Conclusions

The energy and exergy analyses reported in this paper of a pilot plant for a Cu-Cl thermochemical water decomposition cycle for hydrogen production has allowed several conclusions to be drawn. For each of the steps in the cycle, the variations of exergy destruction due to irreversibilities with parameters like process and reference-environment temperature have been quantified and characterized. In particular, a parametric study is reported of how the reaction heat, inlet and outlet exergies, and exergy destruction in each chemical reaction vary with the reaction temperature and reference-environment temperature. This information should assist efforts to understand the thermodynamic losses in the cycle, and to improve efficiency. Future work is expected to focus on assessing efficiencies based on energy and exergy for the overall each of the Cu-Cl thermochemical water decomposition cycle and each of the steps comprising it.

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Nomenclature

E	Energy
Ex	Exergy
$\overline{ex}^{ch}$	Specific chemical exergy
G	Gibbs function

$\bar{g}$	Specific Gibbs free energy
$\bar{g}_f^0$	Specific Gibbs free energy of formation
H	Enthalpy
$\bar{h}$	Specific enthalpy
$\bar{h}^0$	Specific enthalpy at reference state
$\bar{h}_f^0$	Specific enthalpy of formation
$\dot{m}$	Mass flow rate
n	Mole number
Q	Reaction heat
$\bar{q}$	Molar reaction heat
R	Correlation coefficient
$\bar{s}$	Specific entropy
$\bar{s}^0$	Specific entropy at reference state
$\bar{s}_f^0$	Specific entropy of formation
$T_{reaction}$	Reaction temperature
$T_{evaporator}$	Evaporator temperature
T_0	Reference temperature
V	Velocity
z	Elevation
ΔG	Change in Gibbs function for the reaction

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