

Exergy analysis of heat exchangers in the copper–chlorine thermochemical cycle to enhance thermal effectiveness and cycle efficiency

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Abstract

Most existing nuclear power plants in North America are typically water-cooled and operate at 250–500°C. For this temperature level, the copper–chlorine (Cu–Cl) cycle is one of the most promising cycles that can be integrated with nuclear reactors for hydrogen production by decomposing water into its constituents. In this study, we analyze the heat exchangers in the Cu–Cl thermochemical cycle so as to enhance heat transfer effectiveness and thereby improve the cycle efficiency. The thermal management options for internal and external heat transfer are studied and heat recovery opportunities are investigated and compared. Each heat exchanger in the cycle is examined individually based on the chemical/physical behavior of the process, and the most appropriate options are recommended. A thermodynamic analysis and associated parametric studies are performed for various configurations to contrast their efficiencies and effectivenesses.

Keywords: hydrogen production; thermochemical water decomposition; thermodynamic analysis; exergy analysis; heat transfer; copper–chlorine cycle; heat exchangers

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1 INTRODUCTION

Most thermochemical cycles require process heat at high temperatures, exceeding 850–900°C. However, existing nuclear power plants are typically water-cooled and operate at 250–500°C. Recently, Atomic Energy of Canada and Argonne National Laboratory in the USA have been developing low-temperature thermochemical cycles designed to accommodate heat sources around 500°C. Such cycles can be integrated with nuclear reactors. For this temperature level, the copper–chlorine (Cu–Cl) cycle is one of the most promising cycles.

The hybrid Cu–Cl thermo/electro-chemical cycle for decomposing water into its constituents has been proposed as a method for hydrogen production. The cycle is expected to be driven in an environmentally benign manner using nuclear energy. The process involves a series of closed-loop chemical reactions. The cycle involves five steps; of which, three are thermally driven chemical reactions and one is an electrochemical reaction. However, since each step is at different temperature, the product of a step needs to be cooled or heated to next step's temperature before entering it. Thus, there are many heat

recovery opportunities within the cycle. The recovered energy as well as the energy that is released from the exothermic reactions could be re-used in the cycle. Heat is transferred between various endothermic and exothermic reactions in the Cu–Cl cycle through heat exchangers that supply or recover heat from individual processes. Effective thermal management within the Cu–Cl cycle is crucial for achieving high efficiency. The cycle's efficiency is improved drastically when all heat released by the products of reactions is recycled internally. Therefore, the energy handling and hence heat exchangers within the cycle make a great deal in terms of overall effectiveness of the cycle.

Many have studied heat exchangers in the literature. For example, heat transfer and exergy loss in a concentric double-pipe exchanger equipped with swirl generators has been investigated by Akpınar and Bicer [1], and the same methodology has been applied to a concentric double-pipe exchanger equipped with helical wires [2]. Exergetic optimization of a heat exchanger has been studied by Cornelissen and Hirs [3]. Durmus *et al.* [4] have studied heat transfer and pressure drop in plate heat exchangers having different surface profiles. Franco and Giannini [5] have studied the optimum thermal design of

modular compact heat exchangers structure for heat recovery steam generators. They have analyzed a particular kind of compact heat exchanger, a plate-fin heat exchanger, conceptually based upon the cross-flow heat exchangers. The use of this compact heat exchanger has been proposed to obtain basic modular element for the construction of small size heat recovery steam generators [5]. The exergy transfer effectiveness of a heat exchanger has been examined by Wu *et al.* [6], where exergy transfer effectiveness is defined to describe the performance of heat exchangers operating above/below the surrounding temperature with/without finite pressure drops. Sahin *et al.* [7] have reported a thermoeconomic performance optimization for a single-pass counter-flow heat exchanger model. In the considered model, the irreversibilities due to heat transfer between the hot and cold streams are taken into account and other irreversibilities such as those due to pressure drops and flow imbalances have been ignored. Sarkar *et al.* [8] have reported irreversibility analyses of both the evaporator and the gas cooler of a CO₂-based transcritical heat pump for combined cooling and heating, employing water as the secondary fluid.

The second-law efficiency has been mainly used as performance evaluation criteria of heat exchangers [9–13]. For instance, a second-law analysis has been presented by Das and Roetzel [14] for thermally dispersive flow through a plate heat exchanger. Naphon [15] has presented theoretical and experimental results of a second-law analysis of the heat transfer and flow for a horizontal concentric tube heat exchanger, with hot and cold water as the working fluids. Similarly, a second-law analysis of cross-flow heat exchangers has been carried out by Gupta and Das [16] in the presence of non-uniform flow. The non-uniformity is modeled using an axial dispersion model and taking into account back mixing and flow maldistribution.

In many studies, heat exchangers have been analyzed for heat recovery. Matrix heat exchangers have been applied by Ahuja and Green [17] for thermomechanical exergy recovery from liquid hydrogen. Similarly, Jaber *et al.* [18] have studied heat recovery options from molten CuCl in the Cu–Cl thermochemical cycle for hydrogen production. They examine convective heat transfer between molten CuCl droplets and air in a counter-current spray flow heat exchanger. Esen *et al.* [19] have performed energy and exergy analyses of a ground-coupled heat pump system with two horizontal ground heat exchangers. Energy and exergy efficiencies are investigated as a function of the depth of trenches for the heating season. Kurtbas *et al.* [20] have investigated the effects of propeller-type turbulators on entropy generation and exergy loss rates in the inner pipe of a co-axial heat exchanger. In this study, we analyze the heat exchangers in the Cu–Cl thermochemical cycle so as to enhance heat transfer effectiveness and thereby improve the cycle efficiency. The thermal management options for internal and external heat transfer are studied and heat recovery opportunities are investigated and compared. Each heat exchanger in the cycle is examined individually based on the chemical/physical behavior of the process, and the most appropriate options are recommended. A thermodynamic analysis and associated parametric studies on heat transfer aspects of heat

exchangers are performed for various configurations to investigate the relationships between heat exchanger effectivenesses and overall system efficiencies.

2 SYSTEM DESCRIPTION

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. 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 equipment such 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 of 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.

3 ANALYSIS

A detailed Aspen Plus flowchart of the Cu–Cl cycle is shown in Figure 2, denoting heat exchangers as HE. As can be seen from this figure, HE6, 7, 8, 10 and 11 are the heat exchangers that heat recovery from the cycle taking place while heat input takes place through HE1, 2, 3, 4, 5 and 9. Heating in HE1, 2, 3, 4, 5 and 9 may easily be done in various ways. In fact, this study will focus on some heat recovery options to improve the cycle efficiency.

In the Cu–Cl cycle, heat recovery from molten CuCl is required at various points within the cycle. HE7 and 8 in Figure 2 are heat exchangers in which the convective heat transfer between molten CuCl droplets and air essentially occurs. Recovering heat from molten CuCl is very challenging due to the phase transformations of molten CuCl, as it cools from liquid to different solid states. This is a type of multiphase flow, similar to droplet/particle flows in spray columns, packed beds and other devices involving the interaction between particles or droplets with gas streams. Direct contact heat transfer between droplets and air involves physical interactions that accomplish very efficient heat transfer and also allows for mass transfer to occur, which in some cases may be desirable, for example, in cooling towers. Figure 3 shows a schematic of a counter-current spray flow heat exchanger. In the figure, a flow configuration where molten CuCl droplets are injected from the top of a heat exchanger, and counter

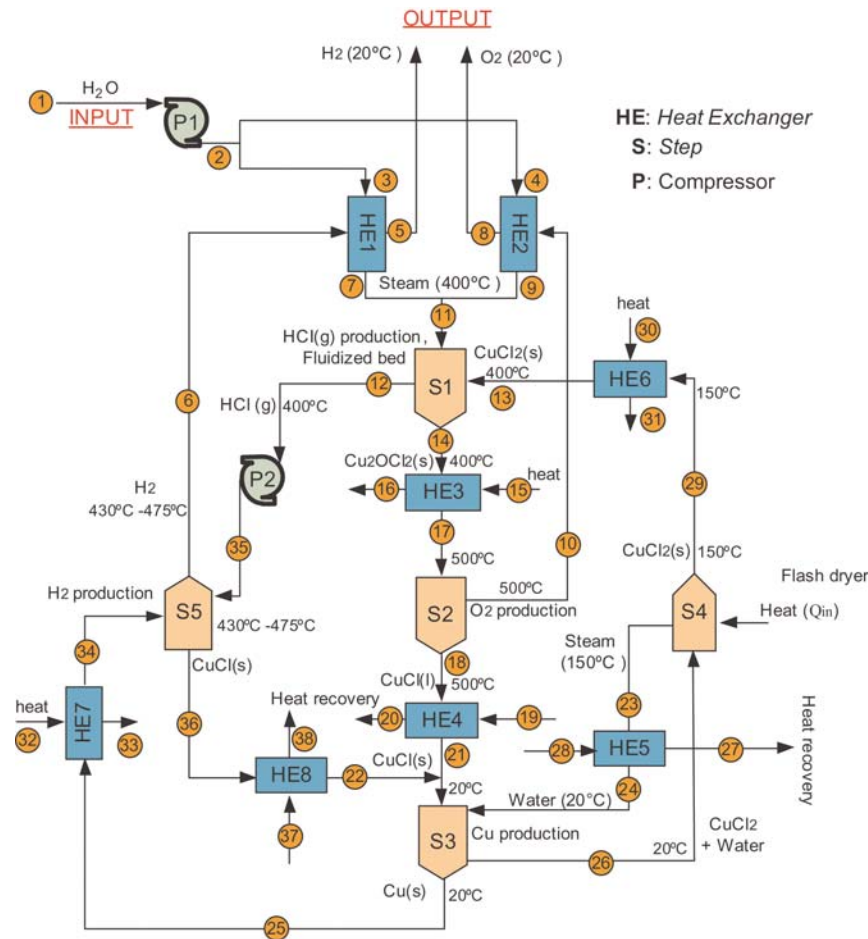


Figure 1. Conceptual layout of a thermochemical Cu-Cl hydrogen production cycle.

Table 1. The five steps in the Cu-Cl cycle with their corresponding reactions.

| Step | Reaction | Temperature range |
|------|--|-------------------|
| S1 | $2\text{CuCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CuO}\cdot\text{CuCl}_2(\text{s}) + 2\text{HCl}(\text{g})$ | 400°C |
| S2 | $\text{CuO}\cdot\text{CuCl}_2(\text{s}) \rightarrow 2\text{CuCl}(\text{l}) + 1/2\text{O}_2(\text{g})$ | 500°C |
| S3 | $4\text{CuCl}(\text{s}) + \text{H}_2\text{O} \rightarrow 2\text{CuCl}_2(\text{aq}) + 2\text{Cu}(\text{s})$ | 25–80°C |
| S4 | $\text{CuCl}_2(\text{aq}) \rightarrow \text{CuCl}_2(\text{s})$ | >100°C |
| S5 | $2\text{Cu}(\text{s}) + 2\text{HCl}(\text{g}) \rightarrow 2\text{CuCl}(\text{l}) + \text{H}_2(\text{g})$ | 430–475°C |

flowing air enters from the bottom, ascends and recovers heat from the falling droplets.

In HE6, 10 and 11 of Figure 2, heat transfer takes place between liquid and gas substances. In HE10 and 11, produced H₂ and O₂ cooled down before leaving the cycle while water condensates in HE6. Numerous heat exchanger options are available for these kinds of heat interactions. For example, cross-flow plate serpentine heat exchanger [9] that shown in Figure 4 could be a good option since it provides effective heat transfer between cold and hot streams. A counter-flow heat exchanger model [7] and the hot and cold fluid temperature distributions are shown in Figure 5. The hot fluid, with a mass flow

rate of \dot{m}_1 and a specific heat, $C_{p,1}$, enters the system at an inlet temperature, $T_{1,in}$, and exits at a temperature of $T_{1,out}$ (in k).

On the other hand, the cold fluid enters the system with a mass flow rate of \dot{m}_2 (in kg/s) and a specific heat at constant pressure (J/Kg K), $C_{p,2}$, at an inlet temperature, $T_{2,in}$, and exit at an exit temperature $T_{2,out}$. The heat transferred from the hot stream is equal to the heat received by the cold stream and heat loss to surroundings as

$$\dot{Q}_h = \dot{Q}_c + \dot{Q}_{loss} \quad (1)$$

where \dot{Q} is heat transfer rate in W.

Assuming that there is negligible heat transfer between the exchanger and its surroundings,

$$\dot{Q}_h = \dot{Q}_c \quad (2)$$

With negligible potential and kinetic energy changes and applying the steady-flow energy equation,

$$(\dot{m}C_p)_1(T_{1,in} - T_{1,out}) = (\dot{m}C_p)_2(T_{2,out} - T_{2,in}) \quad (3)$$

$$C_1(T_{1,in} - T_{1,out}) = C_2(T_{2,out} - T_{2,in}) \quad (4)$$

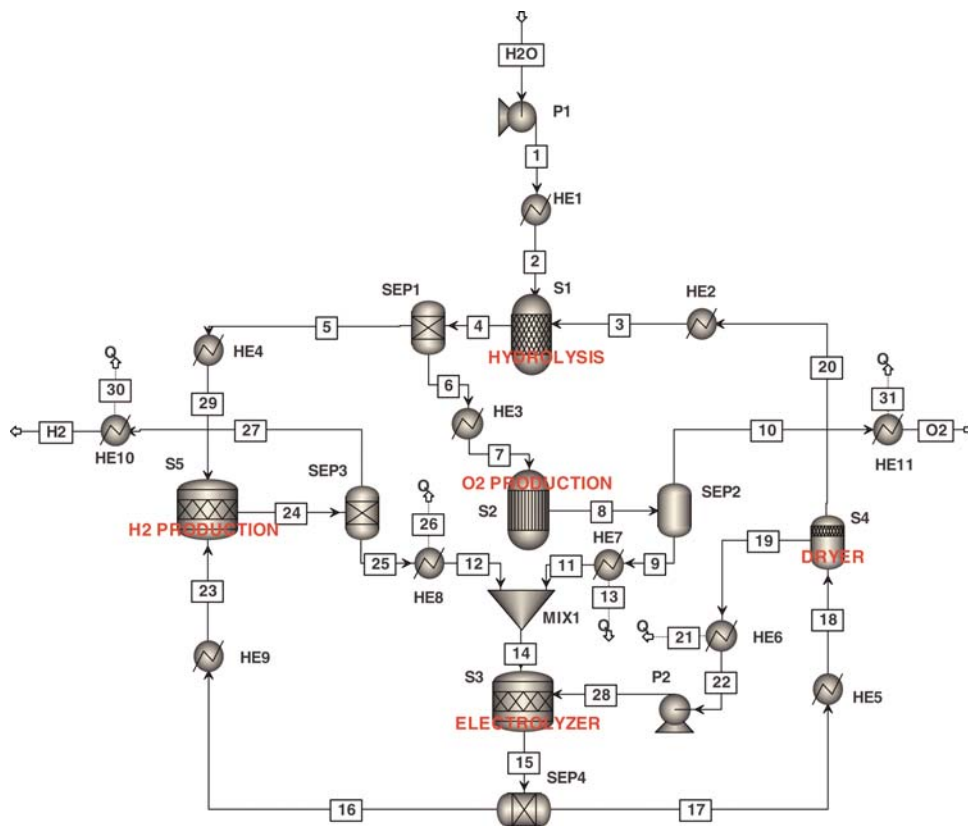


Figure 2. Simplified Aspen Plus process flowsheet of a five-step Cu-Cl cycle.

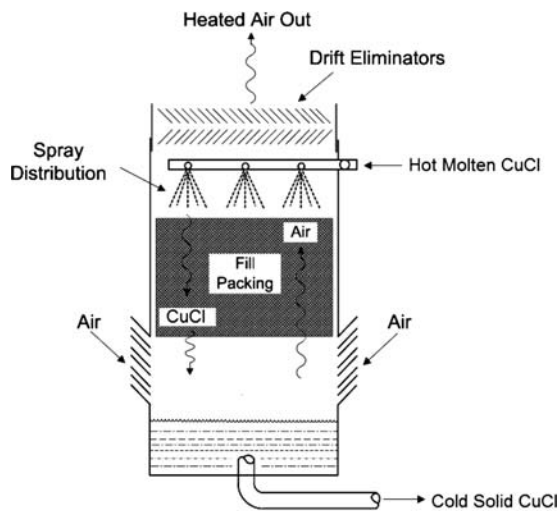


Figure 3. Schematic of the counter-flow spray heat exchanger.

where C_1 and C_2 are the hot and cold fluid heat capacity rates, respectively. The effectiveness of the heat exchanger (ϵ) can be defined as the ratio of the actual heat transfer rate for a heat exchanger to the maximum possible heat transfer rate:

$$\epsilon = \frac{\dot{Q}}{\dot{Q}_{\max}} = \frac{C_1(T_{1,\text{in}} - T_{1,\text{out}})}{C_{\min}(T_{1,\text{in}} - T_{2,\text{in}})} = \frac{C_2(T_{2,\text{out}} - T_{2,\text{in}})}{C_{\min}(T_{1,\text{in}} - T_{2,\text{in}})} \quad (5)$$

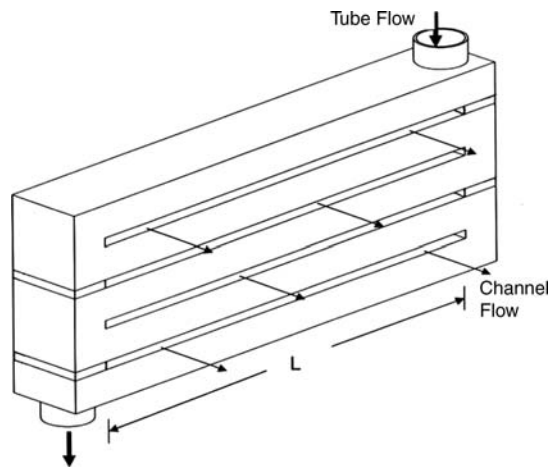


Figure 4. A cross-flow serpentine heat exchanger.

For counter-flow heat exchangers, the effectiveness is given [6, 7] as

$$\epsilon = \frac{1 - e^{-NTU(1-c)}}{1 - ce^{-NTU(1-c)}} \quad (6)$$

where $c = C_{\min}/C_{\max}$ is the ratio of the minimum side heat capacity rate to the maximum side heat capacity rate and $NTU = UA/(\dot{m}C_p)_{\min}$ represents the number of heat transfer

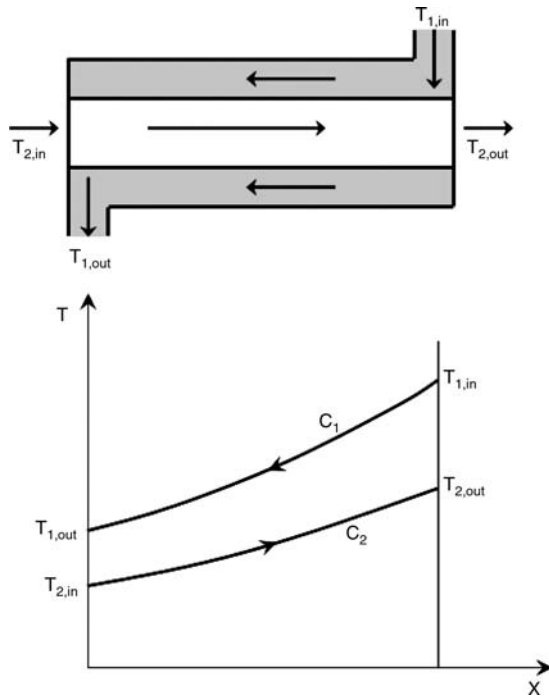


Figure 5. A counter-flow heat exchanger with the temperature profile.

units. For the counter-flow heat exchangers with the best effective condition ($c = 1$), the effectiveness is

$$\varepsilon = \frac{NTU}{1 + NTU} \quad (7)$$

Using Equation (5), the actual heat transfer rate is

$$\dot{Q} = \varepsilon C_{\min}(T_{1,\text{in}} - T_{2,\text{in}}) \quad (8)$$

Then, the outlet temperatures of the hot and cold streams can be derived from the above equations as

$$T_{1,\text{out}} = T_{1,\text{in}} - \varepsilon \frac{C_{\min}}{C_1} (T_{1,\text{in}} - T_{2,\text{in}}) \quad (9)$$

and

$$T_{2,\text{out}} = T_{2,\text{in}} + \varepsilon \frac{C_{\min}}{C_2} (T_{1,\text{in}} - T_{2,\text{in}}) \quad (10)$$

The logarithmic mean temperature difference of a counter-flow heat exchanger is given as,

$$\Delta T_{\text{lm}} = \frac{(T_{1,\text{out}} - T_{2,\text{in}}) - (T_{1,\text{in}} - T_{2,\text{out}})}{\ln((T_{1,\text{out}} - T_{2,\text{in}})/(T_{1,\text{in}} - T_{2,\text{out}}))} \quad (11)$$

Rearranging Equation (11) by using Equations (9) and (10),

$$\Delta T_{\text{lm}} = \frac{(T_{1,\text{in}} - T_{2,\text{in}})\varepsilon C_{\min}((1/C_2) - (1/C_1))}{\ln[(1 - \varepsilon(C_{\min}/C_1))/(1 - \varepsilon(C_{\min}/C_2))]} \quad (12)$$

Actual heat transfer rate can also be written in terms of the log mean temperature difference as

$$\dot{Q} = UA\Delta T_{\text{lm}} \quad (13)$$

Substituting Equation (12),

$$\dot{Q} = UA \frac{(T_{1,\text{in}} - T_{2,\text{in}})\varepsilon C_{\min}((1/C_2) - (1/C_1))}{\ln[(1 - \varepsilon(C_{\min}/C_1))/(1 - \varepsilon(C_{\min}/C_2))]} \quad (14)$$

The total exergy (Ex) of a system is the summation of physical exergy (Ex_{PH}), kinetic exergy (Ex_{KN}), potential exergy (Ex_{PT}) and chemical exergy (Ex_{CH}):

$$Ex = Ex_{\text{PH}} + Ex_{\text{KN}} + Ex_{\text{PT}} + Ex_{\text{CH}} \quad (15)$$

In this study; chemical, potential and kinetic exergies are neglected since physical exergy accounts for the majority of exergy of a heat exchanger. Therefore, the flow exergy (in W) of a control volume can be written as

$$\dot{Ex} = \dot{m}(h - h_0 - T_0(s - s_0)) \quad (16)$$

where s is specific entropy in J/kg K and h is specific enthalpy in J/kg.

Also, the exergy balance can be written as

$$\sum \dot{Ex}_{\text{in}} - \sum \dot{Ex}_{\text{out}} - \dot{Ex}_{\text{destruction}} = \Delta \dot{Ex}_{\text{system}} \quad (17)$$

For a steady-state process, $\Delta Ex_{\text{system}}$ is zero. Combining Equations (16) and (17) for a process involving no work interactions yields the exergy destruction (including exergy loss) as

$$\begin{aligned} \dot{Ex}_{\text{destruction}} = & \sum \dot{m}[(h - h_0) - T_0(s - s_0)]_{\text{in}} \\ & - \sum \dot{m}[(h - h_0) - T_0(s - s_0)]_{\text{out}} \\ & + \sum \left(1 - \frac{T_0}{T_k}\right) \dot{Q}_k \end{aligned} \quad (18)$$

where \dot{Q}_k represents the heat transfer rate occurring at the k th location on the boundary of the control volume where the instantaneous temperature is T_k . Then, the exergy destruction rate in an open-system heat exchanger is

$$\begin{aligned} \dot{Ex}_{\text{destruction}} = & \dot{m}_1(h_{1,\text{in}} - h_{1,\text{out}}) + \dot{m}_2(h_{2,\text{in}} - h_{2,\text{out}}) \\ & - T_0[\dot{m}_1(s_{1,\text{in}} - s_{1,\text{out}}) + \dot{m}_2(s_{2,\text{in}} - s_{2,\text{out}})] \end{aligned} \quad (19)$$

From Equation (4),

$$\dot{m}_1(h_{1,\text{in}} - h_{1,\text{out}}) = \dot{m}_2(h_{2,\text{out}} - h_{2,\text{in}}) \quad (20)$$

Then, Equation (19) can be reduced to

$$\dot{Ex}_{\text{destruction}} = T_0[\dot{m}_1(s_{1,\text{out}} - s_{1,\text{in}}) + \dot{m}_2(s_{2,\text{out}} - s_{2,\text{in}})] \quad (21)$$

If the entropy changes of the hot and cold streams are expressed in terms of constant pressure specific heats as

$$\begin{aligned} s_{1,\text{out}} - s_{1,\text{in}} = & C_{p,1} \ln(T_{1,\text{out}} - T_{1,\text{in}}) \quad \text{and} \\ s_{2,\text{out}} - s_{2,\text{in}} = & C_{p,2} \ln(T_{2,\text{out}} - T_{2,\text{in}}) \end{aligned} \quad (22)$$

Substituting Equation (22) into Equation (21),

$$\dot{Ex}_{\text{destruction}} = T_0 \left[\dot{m}_1 C_{p,1} \ln \left(\frac{T_{1,\text{out}}}{T_{1,\text{in}}} \right) + \dot{m}_2 C_{p,2} \ln \left(\frac{T_{2,\text{out}}}{T_{2,\text{in}}} \right) \right] \quad (23)$$

Considering the equations for C_1 , C_2 and c , Equation (23) can be rearranged as

$$\dot{Ex}_{\text{destruction}} = T_0 \left[C_{\min} \ln \left(\frac{T_{1,\text{out}}}{T_{1,\text{in}}} \right) + C_{\max} \ln \left(\frac{T_{2,\text{out}}}{T_{2,\text{in}}} \right) \right] \quad (24)$$

Substituting Equation (5) into Equation (24),

$$\begin{aligned} \dot{Ex}_{\text{destruction}} = T_0 & \left[C_{\min} \ln \left[1 - \varepsilon \left(1 - \frac{T_{2,\text{in}}}{T_{1,\text{in}}} \right) \right] \right. \\ & \left. + C_{\max} \ln \left[1 + \varepsilon c \left(\frac{T_{1,\text{in}}}{T_{2,\text{in}}} - 1 \right) \right] \right] \quad (25) \end{aligned}$$

Finally, exergy efficiency (η_{ex}) can be formulated as

$$\eta_{\text{ex}} = 1 - \frac{\dot{Ex}_{\text{destruction}}}{\sum \dot{Ex}_{\text{in}}} \quad (26)$$

Rearranging Equation (26),

$$\eta_{\text{ex}} = \frac{1 - \frac{T_0 [C_{\min} \ln [1 - \varepsilon (1 - (T_{2,\text{in}}/T_{1,\text{in}}))] + C_{\max} \ln [1 + \varepsilon c ((T_{1,\text{in}}/T_{2,\text{in}}) - 1)]}{\dot{m}_1 [(h_{1,\text{in}} - h_0) - T_0 (s_{1,\text{in}} - s_0)] + \dot{m}_2 [(h_{2,\text{in}} - h_0) - T_0 (s_{2,\text{in}} - s_0)]}}{1} \quad (27)$$

After formulating the energy and exergy balances for the heat exchangers in the Cu–Cl cycle, now we can evaluate the effect of the effectiveness of the heat exchangers (ε) on the overall efficiency of the cycle ($\eta_{\text{Cu–Cl cycle}}$). The overall efficiency of the Cu–Cl cycle is defined as energy out divided by energy in. Based on the low heating value for hydrogen, the efficiency of the process is,

$$\eta_{\text{Cu–Cl cycle}} = \frac{\text{LHV}_{\text{H}_2}}{Q_{\text{net}} + W} \quad (28)$$

where LHV_{H_2} is the lower heating value of hydrogen, W the electrical work required for an electrolyzer and shaft work for other processes and Q_{net} the net heat (after subtracting the recovered heat) used by the process to produce a unit amount of product hydrogen. Therefore, Equation (28) can be rewritten as,

$$\eta_{\text{Cu–Cl cycle}} = \frac{\text{LHV}_{\text{H}_2}}{((Q_{\text{required}}/\varepsilon) - \varepsilon Q_{\text{recovered}}) + W} \quad (29)$$

The lower heating value of hydrogen is 240 kJ/mol H_2 .

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

$$\eta_{\text{ex,Cu–Cl cycle}} = \frac{Ex_{\text{out}}}{Ex_{\text{in}}} \quad (30)$$

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

$$\eta_{\text{ex,Cu–Cl cycle}} = 1 - \frac{Ex_{\text{destroyed}}}{Ex_{\text{in}}} \quad (31)$$

where $Ex_{\text{destroyed}}$ is the exergy destruction in the process, and Ex_{in} and Ex_{out} are the input and output exergy. For overall cycle, we obtained the total input and destroyed exergy of the cycle by adding these input and destroyed exergy of the individual steps. Again, in the summation of input exergy, the exothermic reaction (i.e. the hydrogen production reaction) is taken as negative, assuming that this energy can be used for other endothermic reactions.

4 RESULTS AND DISCUSSION

Using the above derived equations, here we obtained some results to validate our equations and to give some general idea about heat exchangers that can be helpful while building the Cu–Cl cycle. Variation of exergetic efficiency is given in Figure 6. It shows that at $T_{1,\text{in}}/T_{2,\text{in}}=1.2$, the exergetic efficiency value significantly decreases with the effectiveness of the heat exchanger. This implies that, for acquiring high exergy efficiency, a heat exchanger with high effectiveness must be chosen. Figure 6 also shows that there is a maximum exergy efficiency value that can be achieved. This peak is taken place at a C_1/C_2 value of 1. Any value other than $C_1/C_2=1$, either increasing or decreasing, the exergy efficiency value would dramatically drop. For the C_1/C_2 values larger than 1.0, the heat capacity rate of the hot stream is larger than that of the cold stream. An increase in the C_1/C_2 value results in an increase in the amount of thermal energy in the hot stream emanating from the heat exchanger without being recovered by the cold stream. Hence, the exergy efficiency value decreases with an increase in the C_1/C_2 value. For the C_1/C_2 values smaller than 1.0, the heat capacity rate of the cold stream is larger than that of the hot stream. A decrease in the C_1/C_2 value causes a descent of the exit temperature of the cold stream. A descent of the exit temperature of the cold stream implies that the amount of recovered exergy is small. Hence, the exergy efficiency value decreases with the C_1/C_2 value.

Figure 7 shows the exergy efficiency values at $T_{1,\text{in}}/T_{2,\text{in}}=2.4$. A similar trend as those shown in Figure 6 was obtained. Comparing Figures 6 and 7, it shows that the effect of ε and total value on the exergy efficiency value increases with a decrease in the $T_{1,\text{in}}/T_{2,\text{in}}$ value. This implies that, for a heat exchanger using in a low temperature heat recovery process, the effectiveness could be an important factor affecting the exergy efficiency.

The dimensionless outlet temperatures of the hot and cold streams which depend on c are shown in Figure 8. The introduced optimization technique given above is an efficient method for defining the optimal performance and design parameters for given c values by considering the heat transfer rate

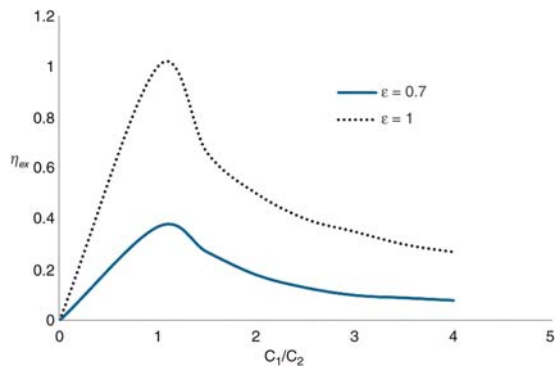


Figure 6. Variation of exergy efficiency at $T_{1,in}/T_{2,in} = 1.2$.

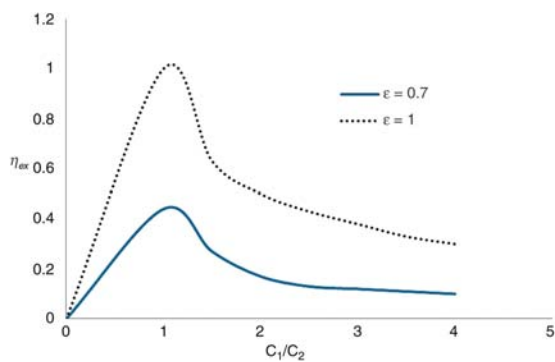


Figure 7. Variation of exergy efficiency at $T_{1,in}/T_{2,in} = 2.4$.

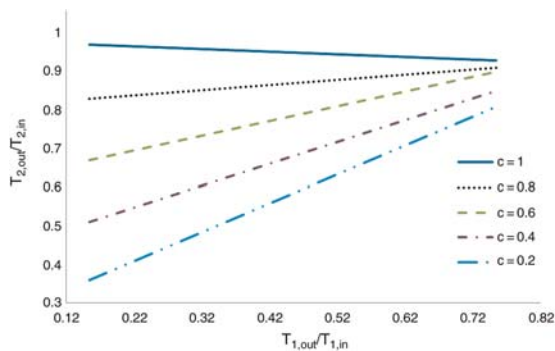


Figure 8. Variation of the dimensionless outlet temperatures of the hot stream versus the cold stream.

and exergy destruction together. It should also be noted that the above results have showed that the optimal performance characteristics depend on many parameters such as c , ϵ and NTU. These parameters should be considered for the optimal design of a heat exchanger.

Heaters, coolers and heat exchangers are used to supply or recover heat in each process in the cycle. The corresponding heat requirements, recovered heat and other data for the heat exchangers at various transfer points are shown in Table 2, where results are presented per mole of hydrogen. Based on data given in this table, an energy balance of the cycle and the corresponding efficiency are evaluated. Note that exothermic heat terms are denoted by a negative sign.

Table 2. Energy balance of heat exchangers in the five-step Cu–Cl cycle, at $\epsilon = 0.75$.

| Block | Description | Process | ΔH (kJ/mol H ₂) |
|---|-------------|---|-------------------------------------|
| HE1 | Heater | H ₂ O (25°C) → H ₂ O (400°C) | 80 |
| HE2 | Heater | CuCl ₂ (80°C) → CuCl ₂ (400°C) | 61.3 |
| HE3 | Heater | Cu ₂ OCl ₂ (400°C) → Cu ₂ OCl ₂ (500°C) | 20.8 |
| HE4 | Heater | HCl (400°C) → HCl (450°C) | 4.0 |
| HE5 | Heater | CuCl ₂ /H ₂ O (25°C) → CuCl ₂ /H ₂ O (80°C) | 57.6 |
| HE6 | Cooler | H ₂ O (80°C) → H ₂ O (25°C) | −30 |
| HE7 | Cooler | CuCl (500°C) → CuCl (25°C) | −64 |
| HE8 | Cooler | CuCl (450°C) → CuCl (25°C) | −60.6 |
| HE9 | Heater | Cu (25°C) → Cu (450°C) | 32.5 |
| HE10 | Cooler | H ₂ (450°C) → H ₂ (25°C) | −9 |
| HE11 | Cooler | O ₂ (500°C) → O ₂ (25°C) | −5.6 |
| Total heat demand for endothermic heat exchangers | | | 256.2 |
| Total heat recovery from exothermic heat exchangers | | | −169.2 |
| Net heat requirement | | | 87 |

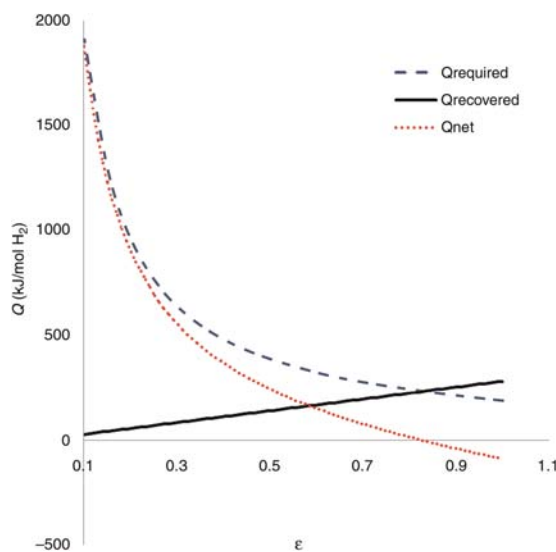


Figure 9. Effect of the heat exchanger effectiveness on heat recovery in the Cu–Cl cycle.

From Table 2, the total heat requirement for endothermic processes is found to be 256.2 kJ/mol of hydrogen and the heat recovery from exothermic processes 169.2 kJ/mol of hydrogen. Using again the recovered heat within the cycle for endothermic processes, the net heat requirement is 87 kJ/mol of hydrogen. Note that in heating and cooling processes (heat recovery) in the cycle, a 75% heat exchanger effectiveness is assumed.

The effect of the heat exchanger effectiveness on thermal management in the Cu–Cl cycle is illustrated in Figure 9. As can be seen, the amount of recovered heat within the cycle can be increased by using heat exchangers with higher effectivenesses. Then, the total heat requirement and consequently the net heat requirement for the cycle is decreased. This reduction is important. At $\epsilon = 0.85$, the total heat demand is equal to the recovered heat and thus the net heat requirement is zero. Beyond that point ($\epsilon > 0.85$), the net heat requirement is negative since the recovered heat is more than the total heat

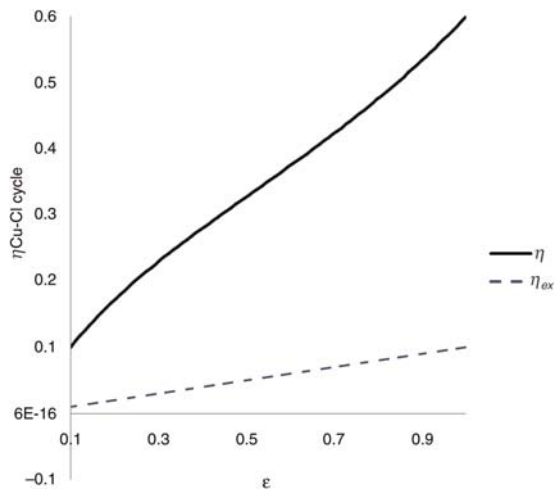


Figure 10. Variation of the Cu–Cl cycle overall efficiencies with the exchanger effectiveness.

demand in the cycle. However, in this calculation, the heat requirement for chemical reactions and the electrical energy needed for electrolysis, pumping and compression are not counted for, as we are only dealing with heat exchangers.

The variation of the overall efficiencies of the Cu–Cl cycle with heat exchangers effectiveness is given in Figure 10. Both energy and exergy efficiencies of the cycle increase using more effective heat exchangers in the cycle. This is because heat exchangers with higher effectiveness result in more heat recovery within the cycle and thus decrease external heat requirements for the cycle.

5 CONCLUSIONS

This study analyzes the heat exchangers in the Cu–Cl thermochemical cycle to improve heat transfer effectiveness and hence improve the overall cycle efficiency. The thermal management and energy handling options within the cycle are studied and heat recovery opportunities are examined. Each heat exchanger in the cycle is examined individually based on the chemical/physical behavior of the process, and the most appropriate options are recommended. A thermodynamic analysis and associated parametric studies are performed for various configurations to contrast their efficiencies and effectivenesses.

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NOMENCLATURE

A Heat transfer area (m^2)
 c Ratio of heat capacity rates

C_p Specific heat at constant pressure (J/kg K)
 \dot{E}_x Exergy rate (W)
 h Specific enthalpy (J/kg)
 \dot{m} Mass flow rate (kg/s)
 NTU Total number of heat transfer units
 \dot{Q} Heat transfer rate (W)
 s Specific entropy (J/kg K)
 T Temperature (K)
 U Overall heat transfer coefficient ($\text{W/m}^2 \text{K}$)

Greek Symbols

ε Effectiveness of the heat exchanger
 η_{ex} Exergy efficiency

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