Comparative studies of Cu-Cl Thermochemical Water Decomposition Cyles for Hydrogen Production

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Abstract. This research focuses on thermodynamic analysis of the copper chlorine cycles. The cycles were simulated using Aspen Plus software. All thermodynamic data for all the chemical species were defined from literature and the reliability of other compounds in the simulation were ascertained. The 5-step Cu–Cl cycle consist of five steps; hydrolysis, decomposition, electrolysis, drying and hydrogen production. The 4-step cycle combines the hydrolysis and the drying stage of the 5-step cycle to eliminate the intermediate production and handling of copper solids. The 3-step cycle has hydrolysis, electrolysis and hydrogen production stages. Exergy and energy analysis of the cycles were conducted. The results of the exergy analysis were 59.64%, 44.74% and 78.21% while that of the energy analysis were 50%, 49% and 35% for the 5-step cycle, 4-step cycle and 3-step cycle respectively. Parametric studies were conducted and possible exergy efficiency improvement of the cycles were found to be between 59.57-59.67%, 44.32-45.67% and 23.50-82.10% for the 5-step, 4-step and 3-step respectively. The results from the parametric analysis of the simulated process could assist ongoing efforts to understand the thermodynamic losses in the cycle, to improve efficiency, increase the economic viability of the process and to facilitate eventual commercialization of the process.

1 Introduction

The world faces problems with depleting energy resources resulting from worldwide increasing energy consumption due to increasing population and rising living standards. This is in addition to concerns regarding global climate change accruing from energy related activities. Hence, there have been extensive researches and developments of alternative clean energy sources which can be derived from renewable sources. There are various alternative energy options to fossil fuels, including solar, geothermal, hydropower, wind and nuclear energy. However, Hydrogen is a potential alternative that has been viewed as a promising fuel [1].It has some unique characteristics that makes it an ideal

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energy carrier that can satisfy all energy needs [2]. Hydrogen, though abundant on earth does not exist alone, it is produced from compounds that contains it. There are various ways of generating hydrogen for energy usage. Some of the various processes include; the solar based hydrogen production, electrolysis, biological processes, gasification and the thermochemical water decomposition [3,4] Hydrogen production via thermochemical water decomposition is one of the key potential source of energy.

Thermochemical water splitting with a copper-chlorine (Cu-Cl) cycle is a promising process involving intermediate copper and chlorine compounds with a net input of water and heat and a net output of hydrogen and oxygen [5,6]. These chemical reactions form a closed internal loop that recycles all chemicals on a continuous basis, without emitting any greenhouse gases. Thermochemical water decomposition is an emerging technology for large-scale production of hydrogen. About 200 thermochemical cycles have been identified but the copper–chlorine thermochemical cycle is regarded as one of the most promising approaches. The Cu-Cl thermochemical cycles are of different types. The numbers of steps (3-steps, 4-steps or 5-steps) have influences on the scale-up challenges and overall cycle efficiencies. A 3-step, 4-step and 5-step cycles of Cu-Cl system for thermochemical water decomposition cycles have been studied extensively [7-9] but there is need for comparative studies that can aid in decision making on the most effective and efficient step cycle especially with respect to the second law efficiency of the process [5].

This study presents the simulation, analysis and parametric studies of the 3 step, 4-setp and 5-step Cu-Cl cycles. It is expected that the study will assist ongoing efforts in seeing to the eventual commercialisation of the process.

The study is presented as follows. In section 2, the detail description of each of the step and the analysis procedures is presented. Section 3 gives the results and discussion and section 4 concludes the study.

2 System description, simulation and analysis

2.1 Description of the 3-step Cycle

There are two concepts that can be adapted here. Lewis et al. 2009 [10] has three reactions in sequence- Electrolysis, hydrolysis and decomposition. However, the concept of Wang et al. 2009 [11] is adapted for this study and presented in Table 1

Table 1. Reactions in the 3-step Cu-Cl cycle

Step	Reaction	Temperature(^{o}C)
1	$2CuCl_2(aq)+H2O(g)\rightarrow 2CuCl(l)+2HCl(g)+1/2O_2(g)+H_2O(g)$	400-600
2	$4CuCl(s)\rightarrow 2Cu(s)+2CuCl_2(aq)$	20-80
3	$2Cu(s)+2HCl(g)\rightarrow 2CuCl(l)+H_2(g)$	430-475

2.2 Description of the 4-step cycle

The 4-step cycle combines the processes of hydrolysis of copper and drying step in the 5-step cycle, to produce hydrogen gas and molten CuCl. The 4-step cycle combines these processes together to eliminate the intermediate production and handling of copper solids, through a CuCl/HCl electrolyzer that produces hydrogen electrolytically and aqueous Cu(II) chloride and it has an advantage of requiring less equipment.

The chemical reactions involved in the 4-step Cu-Cl water decomposition as adapted from Wang et al. 2009 [11] are described in the Table 2.

Table 2. Reactions in the 4-step Cu-Cl Cycle

Step	Name	Reaction	Conditions
1	Hydrolysis	$2CuCl_{2(aq)}+2H_2O_{(g)}\rightarrow Cu_2OCl_{2(s)}+2HCl_{(g)}+H_2O_{(g)}$	375 - 400^{0}C
2	O_2 Production	$Cu_2OCl_{2(s)} \rightarrow 1/2O_{2(g)}+2CuCl_{(l)}$	500 - 530^{0}C
3	Electrolyzer	$4CuCl_{(s)} \rightarrow 2Cu_{(s)}+2CuCl_{2(aq)}$	30 -80^{0}C
4	H_2 Production	$2Cu_{(s)}+2HCl_{(g)} \rightarrow 2CuCl_{(l)}+H_{2(g)}$	430 -475^{0}C

2.3 Description of the 5-step cycle

There are 5 steps in this cycle including three thermochemical reactions and one electrochemical reaction. The steps, their reactions and temperature ranges are presented in Table 3.

Table 3. The five steps in the Cu-Cl cycle with their corresponding reactions

Step	Reaction	Temperature Range
Hydrolysis(S1)	$2CuCl_{2(s)}+H_2O_{(g)}\rightarrow CuO*CuCl_{2(s)}+2HCl_{(g)}$	375-400°C
Decomposition (S2)	$CuO*CuCl_{2(s)}\rightarrow 2CuCl_{(l)}+1/2O_{2(g)}$	500°C
Electrolysis (S3)	$4CuCl_{(s)}+H2O\rightarrow 2CuCl_{2(aq)}+2Cu_{(s)}$	25-80°C
Drying (S4)	$CuCl_{2(aq)}\rightarrow CuCl_{2(s)}$	>100°C
Hydrogen production (S5)	$2Cu_{(s)}+2HCl_{(g)}\rightarrow 2CuCl_{(l)}+H_{2(g)}$	430-475°C

2.3 ASPEN-HYSYS Simulation

HYSYS is a process modeling package typically used for steady state simulation, performance monitoring, design, control and optimization of various chemical processes. It predicts the behaviour of chemical reactions using relationships such as mass and energy balances, equilibrium relationships and rate correlations (i.e. reaction and mass/heat transfer). By choosing the appropriate unit operations and thermodynamic models, reliable thermodynamic data and realistic operating conditions, Aspen Hysys uses mathematical models to predict the performance of the cycle and actual plant behavior. The cycles were simulated in HYSYS. The simulation steps are adding appropriate component list, fluid package selection and defining reactions in the basis environment while the streams and unit operations were specified and defined in the simulation environment. The simulation of the steps were carried out with experimental data from previous researches [10-12] and thermodynamic data from literatures.

2.3 Thermodynamic analysis

The physical Exergy of the stream was calculated using:

$$E_{xphy} = \Delta H\text{-}T_o\Delta S \quad (1)$$

Where, ΔH is the change in enthalpy, ΔS is the change in entropy, T_o is the reference temperature.

$$\Delta H = A\times T + \frac{T^2}{2} + C\times\frac{T^3}{3} + D\times\frac{T^4}{4} - E\times\frac{1}{T} + F - H \quad (2)$$

$$S = A\times lnT + B\times T + C\times\frac{T^2}{2} + D\times\frac{T^3}{3} - E\times\frac{1}{2T} + G \quad (3)$$

$$\Delta S = S\text{-}S_0 \quad (4)$$

Where T is 1/1000 of the specified temperature (in K) of the component and A, B, C, D, E, F, G and H are constants.

The chemical exergy is calculated as

$$E_{ch} = (\mu^0\text{-}\mu_0^0) + RT_0 \ln\left(\frac{c}{c_0}\right) \quad (5)$$

$$E_{heat} = \left(1 - \frac{T_0}{T}\right) Q \quad (6)$$

The total exergy of a stream: The total exergy into and out of a unit is calculated using the following equation;

$$E_X = E_{phy} + E_{ch} + E_{heat} \quad (7)$$

The exergy efficiency of each process step is calculated as

$$n = \frac{Total\ output\ exergy}{Total\ input\ exergy} \times 100 \quad (8)$$

3 Results and discussion

The energy efficiency, exergy efficiency and irreversibilities of all steps in each cycle and the overall cycle was conducted. Parametric studies were also conducted for each cycle and the corresponding efficiencies were evaluated. Fig.1 gives the HYSYS simulation of the 3-step cycle.

Energy and exergy efficiency of the five-step Cu-Cl cycle is calculated to be 35.89% and 59.64%, respectively. Exergy efficiency increases with the increase in the reaction temperature of both the hydrogen production and drying steps reactor but decreases in the hydrolysis step as seen in fig. 2. Also optimum temperatures for the exergy efficiency for each step in the cycle was found to be 300^{0}C, 100^{0}C, 20^{0}C 100^{0}C and 350^{0}C for the hydrolysis step , decomposition step, electrolysis step , drying step and hydrogen production step respectively. The exergy efficiency of the cycle is seen to increase with increasing reference temperature too.

The overall energy and exergy efficiencies of the four-step CuCl cycle are obtained as 49.39% and 44.78%, respectively. In a related work, the exergy efficiency was found to be 42% [13] and the energy efficiency was 21.6% [14]. The overall efficiency decreases with increasing reference environment temperature from -5^{0}C to 30^{0}C.

The overall efficiency increases with increased temperature of the hydrolysis reaction step.

The exergy efficiency of the hydrolysis and the hydrogen production steps of the cycle increases with increase in temperature as seen in fig. 3.

The overall exergy efficiency of the three-step Cu-Cl cycle is 78.5%. There is 0.03% decrease in the overall exergy efficiency of electrolysis reaction step as temperature is increased. Variation of feed rate of $CuCl_2$ and H_2O at 2:1 results in exergy efficiency that ranges from 73.9% to 86.2% while ratio 1:1 ranges from 41.96% to 26.66% as seen in fig.4.

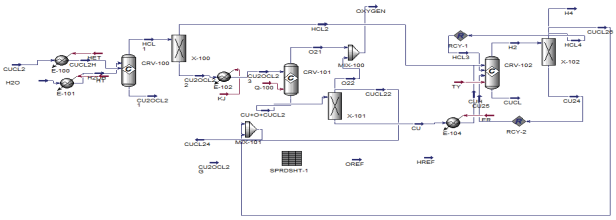

Fig. 1. HYSYS Simulation of the 3-step cycle

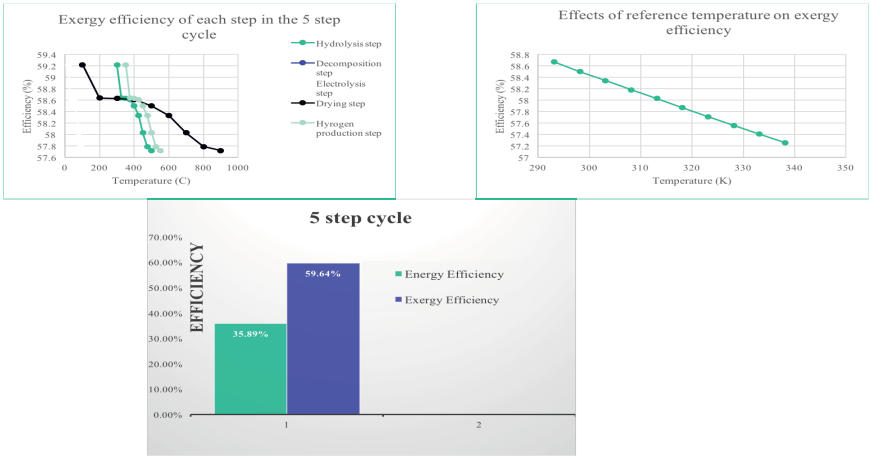

Fig. 2. Parametric studies of the 5-step cycle

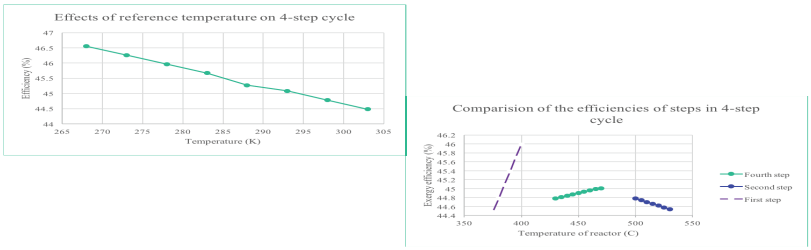

Fig. 3. Parameric studies of the 4-step cycle

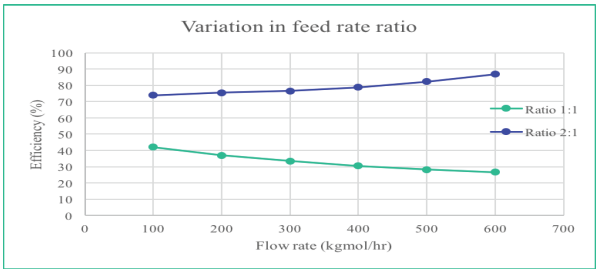

Fig. 4. Parametric study of the 3-step cycle

4 Conclusion

- The results of the exergy analysis gave 59.64%, 44.74% and 78.21% for the 5-step cycle, 4-step cycle and 3-step cycle respectively while that of the energy analysis is 50%, 49% and 35% for the 5-step cycle, 4-step cycle and 3-step cycle respectively.

- Parametric studies were conducted and possible exergy efficiency improvement of the cycles were found to be between 59.57-59.67%, 44.32-45.67% and 23.50-86.2% for the 5-step, 4-step and 3-step respectively.

- The 3-step cycle seems to be the most energy efficient in terms of second law analysis when compared to other steps cycles. It also seems to be the most receptive to parametric variations.

- The most challenging step in the cycle is the electrolyzer design. Simulation of this step will require themodynamic models that will ably depict the actual electrolysis process.

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