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Thermodynamic viability of a new three step high temperature Cu-Cl cycle for hydrogen production

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ABSTRACT

A new three step high temperature Cu-Cl thermochemical cycle for hydrogen production is presented. The performance of the proposed cycle is investigated through energy and exergy approaches. Furthermore, the effects of various parameters, such as the temperatures of the steps of the cycle and power plant efficiency, on various energy and exergy efficiencies are assessed with parametric studies. The results show that the exergy and energy efficiencies of the proposed cycle are 68.3% and 32.0%, respectively. In addition, the exergy analysis results reveal that the hydrogen production step has the maximum specific exergy destruction with a value of 150.9 kJ/mol. The results suggest that proposed cycle may provide enhanced options for high temperature thermochemical cycles by improving thermal management without causing a sudden temperature jump/fall between the hydrogen production step and other steps.

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Introduction

On earth, hydrogen is available in abundance in the form of H₂O. To consider hydrogen as a fuel and an energy carrier, it is needed as H₂. Currently, 90% of the hydrogen in the world is produced by steam methane reforming (a fossil fuel based hydrogen production method). In order to produce hydrogen on larger scale without causing undue harm to the environment, thermochemical cycles for hydrogen production coupled with renewable energy or nuclear energy can be advantageous [1–8].

McQuillan et al. [9] have reviewed more than 200 thermochemical cycles for hydrogen production. They shortlisted

several cycles based on prospects, such as the hybrid sulfur, sulfur iodine, cadmium sulfate and hybrid copper chlorine (Cu-Cl) cycles. Most of these thermochemical cycles have operating temperatures of more than 800°C, although the hybrid Cu-Cl cycle requires the lowest temperature (550°C). Wang et al. [10] provided the comparison between the two most promising cycles. i.e. Cu-Cl and Sulphur Iodine (SI). They found that the energy requirement for both the cycles was almost the same. However, the Cu-Cl cycle offered a lower operating temperature which is an advantage compared to the SI cycle. They further report that the Cu-Cl cycle has less material issues compared to the SI cycle. There are various options of hybrid Cu-Cl cycles, namely two step, three step,

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Nomenclature

ex	specific exergy (kJ/mol)
h	specific enthalpy (kJ/mol)
LHV	lower heating value (kJ/mol)
P	pressure (kPa)
q	specific heat (kJ/mol)
T	temperature (K)
w	specific work (kJ/mol)

Greek Letters

η	efficiency
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Subscripts

aq	aqueous
ch	chemical
d	destruction
elec	electrical
en	energy
eq	equivalent
ex	exergy
g	gas
l	liquid
max	maximum
ov	overall
ph	physical
pp	power plant
s	solid, source
0	ambient
1,2 ...	step number

Acronyms

AECL	Atomic Energy of Canada Limited
CNL	Canadian Nuclear Laboratories
UOIT	University of Ontario Institute of Technology

four step, and five step. The four step hybrid Cu-Cl cycle has been studied by various institutions, especially by Canadian Nuclear Laboratories (CNL), previously known as Atomic Energy of Canada Limited (AECL), and University of Ontario Institute of Technology (UOIT) [11–13]. Table 1 lists the chemical steps in the four step hybrid Cu-Cl cycle. The maximum temperature required in the cycle is 550°C (see Table 1). The chemical reactions provided in the table form a closed internal loop. Thus, all chemicals are recycled, without causing harm to the environment.

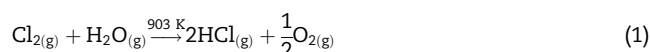
However, there are challenges associated with this four step cycle, such as hindering copper crossover in the electrolyser and difficulty in separation of the spent electrolyte from the aqueous solution [14]. To use this cycle for hydrogen production at a large scale, these challenges need to be

addressed. The introduction of high temperature electrolysis is one option, as it improves integration and thermal management without causing a sudden temperature jump/fall between the hydrogen production step and the other steps. Hence, the main objective of this study is the introduction of a high temperature electrolysis step and proposing a new option of the Cu-Cl cycle based on high temperature electrolysis, while maintaining all the chemicals (products or reactants) except water, hydrogen, and oxygen being recycled. To assess thermodynamic viability, the proposed cycle is analysed with energy and exergy analyses. The effects of various parameters, such as the temperature of each step of the cycle and the power plant efficiency, are determined on various energy and exergy efficiencies via parametric studies.

Cycle description

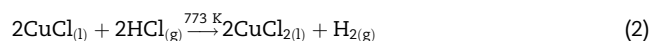
A schematic diagram of the proposed three step Cu-Cl cycle for hydrogen production is shown in Fig. 1. Details on the three steps of the cycle are now provided.

Hydrolysis Step (Step 1):



This step is based on the study conducted by Dokiya and Kotera [15], who showed that hydrolysis step needs to be at over 900 K. Similarly, Gupta et al. [16] showed experimentally for the hydrolysis step that, if carried out at 900 K, an equilibrium conversion around 90% is possible.

Hydrogen Production Step (Step 2):



In this step, the CuCl liquid reacts with HCl gas and is electrolysed to yield liquid CuCl₂ and hydrogen. Various researchers [17–20] have studied this step in the aqueous state, but to the authors' knowledge this study constitutes the first report of this step in the molten state. In order to close the cycle, the produced CuCl₂ liquid from this step can be utilised in the decomposition step.

Decomposition Step (Step 3):



The decomposition step proposed here is based on the study conducted by Gupta et al. [21]. They demonstrated that, if CuCl₂ solid is heated to a temperature above 750 K, it produces solid CuCl and Cl₂ gas. In order to have both CuCl and CuCl₂ in the liquid state, this step needs to be carried out at temperatures above the melting point of CuCl and CuCl₂.

Table 1 – Chemical reaction steps in the four step hybrid Cu-Cl cycle.

Reaction	Operating Temperature (°C)
Step 1: $2\text{CuCl}_{2(s)} + 2\text{H}_2\text{O}_{(g)} \rightarrow 2\text{HCl}_{(g)} + \text{CuO} + \text{CuCl}_{2(s)}$	400
Step 2: $\text{CuO} + \text{CuCl}_{2(s)} \rightarrow 2\text{CuCl}_{(l)} + \frac{1}{2}\text{O}_{2(g)}$	550
Step 3: $2\text{CuCl}_{(aq)} + 2\text{HCl}_{(aq)} \rightarrow \text{H}_{2(g)} + 2\text{CuCl}_{2(aq)}$	25
Step 4: $2\text{CuCl}_{2(aq)} \rightarrow 2\text{CuCl}_{2(s)}$	<100

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