Efficient Utilization of Industrial Waste Heat for Hydrogen Production via Cu-Cl Thermochemical Water Splitting Cycle

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Hydrogen production through water splitting involves separating hydrogen and oxygen using different technologies. The copper-chloride (Cu-Cl) cyclic reaction is a promising method of hydrogen production due to its low operating temperature, which allows it to use low-grade waste heat from industries, leading to reduced heat discharge to the environment. The process forms a closed loop, with all intermediate chemicals being recycled. All of the chemical and electrochemical reactions can be carried out at temperatures that do not exceed about 530 °C. The heat requirement of this process can be satisfied by an intermediate temperature. This study aims to assess the energy efficiency of an integrated system comprising a chemical heat pump as a heat recovery unit and copper-chloride thermochemical cycle water splitting for hydrogen generation. The simulation is conducted using Aspen Plus software to analyze the energy and mass balance of each stream in the process. The results indicate that the Cu-Cl cycle alone has an energy efficiency of 41.14 % and an internal heat recovery ratio (IHRH) of 72 %. Integrating the Cu-Cl cycle with two chemical heat pump hierarchies could enhance the overall process efficiency to 48.14 %.

1. Introduction

Hydrogen (H\textsubscript{2}) has been recognized as a potential energy carrier for the future due to its advantageous characteristics, including high energy density, abundance, the production of only H\textsubscript{2}O upon combustion, and a wide variety of production methods, particularly with the increasing demand for reducing carbon emissions (Dutta, 2014). The widespread integration of hydrogen across various industries holds the potential to decrease greenhouse gas emissions considerably (Aziz et al., 2021). In various industries, hydrogen finds application in oil refining, ammonia production, methanol production, and steel production. Also, hydrogen-based fuel remains the aerospace industry’s primary propellant for rocket propulsion systems (Acar and Dincer, 2020). In power generation, hydrogen and ammonia can increase gas turbines’ flexibility. However, most commercial hydrogen production currently relies on fossil fuels, particularly natural gas. Most hydrogen is generated through steam-methane reforming (SMR) using natural gas (NG) as the primary feedstock, releasing significant quantities of CO\textsubscript{2} and leading to environmental degradation. Alternatively, renewable energy sources can be utilized for hydrogen production through various methods such as biomass gasification, pyrolysis, co-pyrolysis, aqueous phase reforming, electrolysis, photo-electrolysis, and thermochemical water splitting. Thermochemical water splitting, a promising and emerging technology, involves utilizing high-temperature heat (500 °C – 2,000 °C) to drive a sequence of chemical reactions that result in hydrogen production. This process is designed to reuse the chemicals involved in each cycle, creating a closed loop that solely requires water and produces hydrogen and oxygen (Gorensek et al., 2022). The sulfur-iodine (S-I) and copper–chlorine (Cu–Cl) cycles are two examples of thermochemical cycles. The Cu–Cl cycle, which operates at lower temperatures (up to 550 °C), requires less heat input to generate hydrogen than the S-I cycle (up to 825 °C – 900 °C) (Naterer et al., 2013). Chemical heat pumps can also be utilized and investigated for heat upgrading due to their high storage capacity and heat of reaction (Odukoya and Naterer, 2014a). However, handling highly corrosive HCl
at high temperatures is a major challenge. Although the process is not very catalyst dependent, it requires thermal energy to drive the process. Various heat sources, including nuclear reactors, concentrated solar plants, electricity, photonic energy, and industrial waste heat, can generate the heat needed (Gorensek et al., 2022). In the upcoming years, thermochemical water splitting cycles and high-temperature (steam) electrolysis stand out as the primary contenders for hydrogen generation (Xu et al., 2017). The Cu-Cl cycle is a lucrative method used for hydrogen production since it works at a low temperature, requires low voltage, and allows heat to directly utilize to produce hydrogen rather than producing electricity in prior. By employing heat recovery techniques and optimizing the process design, it is possible to extract the maximum energy from low-grade heat sources and enhance the overall efficiency of the Cu-Cl thermochemical water splitting cycle. This can help make the cycle more economically viable and environmentally friendly for hydrogen production. This research aims to perform a simulation of the Cu-Cl thermochemical water splitting hydrogen production with the possibility of low-grade heat waste utilization from industrial plants. The results will then be compared to the existing five-step copper-chlorine cycle according to multiple studies that are available in the literature.

2. Research methodology

2.1. Proposed integrated system

The main concept is to combine thermochemical water splitting for hydrogen production with low-grade waste heat from industrial plants. To convert industrial waste heat into useful energy, a chemical heat pump is selected for heat recovery. The recuperated heat will be integrated into Cu-Cl thermochemical water splitting by using the hydrolysis reaction and copper oxychloride decomposition, as illustrated in Figure 1. By employing heat recovery techniques and optimizing the process design, the maximum energy from low-grade heat sources and the overall efficiency can be enhanced. Prior to the simulation, the process flow diagram must be made and will require multiple entry data, which originate from literature sources such as books, journal articles, or patents, to complete the drawing and be ready for simulation. The energy efficiency of the system is defined as the ratio of energy out and energy in. Based on the low heating value for hydrogen, the efficiency can be defined by:

$$\eta_e = \frac{LHV_{H_2}}{Q_{net} + W}$$

Where LHV is the lower heating value of hydrogen (244 kJ/mol H$_2$), W is the electrical work required for the electrolyzer, and $Q_{net}$ is the net heat requirement for endothermic processes, after subtracting with the recoverable heat to produce an amount of unit hydrogen. The simulation of the integrated CHP and Cu-Cl thermochemical cycle will be run by Aspen Plus software as it can generate the result of energy and mass balance of each stream along the process. Losses are negligible as the software provides an ideal condition. The simulation generated by Aspen Plus provides the production rates from the reaction as well, such that manual calculation is not needed. The data used as the input parameter refer to scientific journals, books, and other sources. Based on the process flow diagram, we can calculate mass balance both on the Cu-Cl thermochemical cycle and the magnesium oxide chemical heat pump. The mass and balance for each process are derived by calculating the mass flow in and out of each component in the stream that gets in and out from each piece of equipment.

Figure 1: Schematic diagram of proposed integrated CHP And Cu-Cl thermochemical cycle
The initial conditions for this simulation were 400 °C and 0.5 bar of pressure, while the flowrates of H₂O and solid copper (II) chloride were set at 100 kmol/h and 200 kmol/h. Within the hydrogen production section, a reactor is employed to bring solid copper particles into contact with hydrogen chloride, resulting in the production of an impure hydrogen product and cuprous chloride. In an industrial setting, this reaction can take place either in a fixed bed reactor or a fluidized bed reactor. However, fluidized bed reactors may encounter challenges such as entrainment loss due to the size of the copper particles used. Consequently, the fixed bed reactor appears to be a more suitable option. Within the simulation, the reactor was represented by two essential components: a stoichiometric reactor and a phase separator.

Copper oxychloride decomposition was modeled at 500 °C and 1 bar. The reactor used was a stoichiometric reactor, and the steps comprised a heater prior to the reactor and a phase separation for liquid copper chloride and gaseous O₂. The O₂ product will then cool down to 20 °C under 1 bar pressure. For the four and five-step cycles, the disproportionation reaction is an electrochemical reaction where copper (I) chloride is transformed into copper (II) chloride and elemental copper. The heat from both H₂ production (step 5) decomposition reaction (step 2) is recovered by channeling the molten CuCl stream directly into a heat exchanger before mixing it together in a mixer reactor. Theoretically, an electrolysis cell would have been included in the electrolyzer. In this simulation, however, it was modeled using the stoichiometric reactor.

Hydrogen production is the last step in this cycle and the only exothermic process out of the five. In the four and five-step cycles, hydrogen is produced in the hydrogen reactor by reacting copper granules with hydrogen chloride according to the reaction,

\[ 2Cu(s) + 2HCl(l) \rightarrow 2CuCl(l) + H_2(g) \]  

The hydrogen chloride and copper are contacted counter currently, with the gas coming from below and the solids trickling from above. In a hydrogen production reaction, the conversion generally increases with an increase in temperature and decreases with increasing pressure. Due to this, conditions for the reactor were chosen to have the lowest pressure practically possible and the highest economic temperature. In this simulation, the hydrogen production step was modeled using a stoichiometric reactor under the operating condition of 450 °C temperature and 1 bar pressure. The solid copper chloride is sent back for the electrolysis step, and the hydrogen product will be cooled down from a very high temperature to 25 °C. Since this reaction occurs at exothermic conditions, the released heat could be utilized for another process to increase energy efficiency.

### 2.2. Waste heat recovery and chemical heat pump utilization

Since most of the wasted energy is discharged in the form of low-grade temperature gas, the recovery of this heat becomes a very challenging task. Low-grade heat refers to heat sources with relatively low temperatures, such as waste heat from industrial processes or solar thermal energy. To efficiently utilize low-grade heat in the Cu-Cl cycle, a multi-stage system with heat recovery can be implemented. In such a system, different stages of the cycle can operate at different temperature ranges, with heat recovered from one stage being used to drive the subsequent stage. For example, waste heat at a temperature range of 300-400 °C can be used for the CuCl₂ production stage. The heat released during the CuCl₂ decomposition stage at 400-800 °C can then be recovered and utilized in the subsequent water-splitting stage at 800-900 °C. By employing heat recovery techniques and optimizing the process design, it is possible to extract the maximum energy from low-grade heat sources and enhance the overall efficiency of the Cu-Cl thermochemical water splitting cycle. This can help make the cycle more economically viable and environmentally friendly for hydrogen production.

A chemical heat pump is a technology that utilizes chemical reactions to store thermal energy, such as waste heat and solar heat, and then releases it to provide heat for heating, cooling, or refrigeration (Lai et al., 2020). The technology involves a chemical reaction that absorbs heat when it occurs and releases heat when it is reversed (Gupta et al., 2021), as shown in Figure 2. Calcium oxide and calcium sulfate are examples of materials that can be used in chemical heat pumps (Gupta et al., 2021). The cycle characteristics of a chemical heat pump utilized for heat upgrading were investigated by harnessing the hydration reaction of calcium sulfate (Shiren et al., 2020). After performing calculations for the coefficient of performance (COP) and hourly heat output using the reactor module model, it was found that the heat upgrading cycle achieves a maximum COP value of 0.57. According to Naterer's study (Naterer, 2008), low-grade waste heat can be upgraded using magnesium oxide (MgO) or vapor chemical heat pump (CHP) and exothermic reactors of salt or ammonia to release heat at a higher temperature. The integration of CHP with the Cu-Cl cycle involves two steps in the overall process. The first step is the endothermic hydrolysis stage, where the supplied heat is upgraded by MgO/vapor CHP, and the exothermic decomposition of copper oxychloride (CuO·CuCl₂) is supplied with heat separately from salt/ammonia CHP. Another study by Odukuoya and Naterer (2014b) suggests using Calcium Oxide (CaO)/vapor in a chemical heat pump instead of MgO. The research demonstrates that the CaO/vapor chemical heat pump has a higher efficiency than MgO/vapor pump, with a coefficient of performance (COP) comparison of 4.6 and
2.75. However, this paper will use MgO/vapor for integration with the hydrolysis steps in the Cu-Cl cycle. The CHP operates in two modes: heat storage and heat supply, with solid products from each reactor serving as solid feed to the other.

![Diagram](image)

Figure 2: The principle underlying the chemical heat pump: (a) heat storage mode, (b) heat output mode (Kato et al., 2005)

### 3. Result and discussion

The study indicates that the endothermic processes necessitate a total heat input of 1,247.65 kJ, while the exothermic processes recover 1,017.29 kJ of heat per mole of hydrogen. With an assumed heat recovery ratio of 72 %, the highest recoverable heat that can be furnished to the endothermic processes is 732.45 kJ, resulting in a net heat requirement of 515.2 kJ. The electrolyzer and dryer reactor need electrical energy to function, and assuming a conversion efficiency of 40 %, the total electricity requirement for this cycle is 68.11 kJ/mol of hydrogen produced.

The efficiency of the simulated system shows a similar result to the study of a five-step Cu-Cl cycle that is done by Mapamba, 2011 which is 41.42 %. The cycle efficiency is directly associated with the overall energy requirements since the efficiency is the ratio of heat of formation of hydrogen with respect to the energy requirement of the cycle. The overall heat requirement is the denominator in calculating energy efficiency, making these two values inversely proportional. That being said, the higher the heat requirement the cycle needs, the lower efficiency it generates. Among the five steps, hydrolysis and decomposition have the highest energy requirement. The higher heat input of both hydrolysis and decomposition reactors is because the processes are maintained at a higher temperature for the chemical reaction to take place.

<table>
<thead>
<tr>
<th>Hierarchy</th>
<th>Heat duty</th>
<th>Heat out</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cl TCWS</td>
<td>1,315.76</td>
<td>Recoverable heat (IHRR = 72 %)</td>
</tr>
<tr>
<td>Salt/Ammonia CHP</td>
<td>0</td>
<td>-62.64</td>
</tr>
<tr>
<td>MgCl/vapor</td>
<td>0</td>
<td>-22.57</td>
</tr>
<tr>
<td>Total $Q_{in}$</td>
<td>1,315.76</td>
<td>-817.65</td>
</tr>
<tr>
<td>$Q_{net}$ (kJ/mol H2)</td>
<td>498.10</td>
<td></td>
</tr>
</tbody>
</table>

It is shown that the efficiency of the hydrogen production system is escalated from 41.14 % to 48.18 %, which means that integrating two hierarchies of the chemical heat pump into the sole Cu-Cl cycle can increase the overall energy efficiency by 7 %. Sensitivity analysis is a method for evaluating how a process responds to various primary operating and design variables. It is performed in several steps of the Cu-Cl cycle to see how it varies as the specified parameters are modified. The drying process takes place at 80-150 °C. The varying parameter of sensitivity analysis conducted for this process is reaction temperature, while the defined parameter
is the yield percentage of solid CuCl₂. Based on the sensitivity analysis illustrated in Figure 3, the 93 % yield of solid CuCl₂ from the aqueous state could be reached starting from 125 ºC. After 125 ºC, increasing the temperature no longer has an effect on the product of solid CuCl₂. As it is known that increasing temperature could lead to the heat requirement of the process, setting the temperature at where the maximum yield is started to achieve would allow a maximum conversion with a minimum heat requirement.

Figure 3. Variation of drying temperature to the yield of solid CuCl₂

4. Conclusions

By utilizing methods to recover heat and optimizing the design of the process, it becomes feasible to extract the highest amount of energy from low-grade heat sources and improve the overall effectiveness of the Cu-Cl thermochemical water splitting cycle. This advancement has the potential to make the cycle economically feasible and environmentally sustainable for the production of hydrogen. Based on the simulation of the thermochemical water splitting using the Cu-Cl cycle for hydrogen production, several conclusions. The system yields hydrogen at 11.9 % with the amount of approximately 200 kg for every 1,800 kg/h water with oxygen as the side product. The initial amount of CuCl₂ needed for circulating within the system is 28,690 kg/h. It is known that among the five reactions, hydrolysis of CuCl₂ and decomposition of CuO.CuCl₂ is the two that require the most input heat. Outside the reactions, some heater also requires a large amount of heat for prior conditioning of the material. Integrating the Cu-Cl cycle with two chemical heat pump hierarchies could improve the efficiency of the overall cycle by up to 48.14 %.

References


