Process Integration of Material Flows of Copper Chlorides in the Thermochemical Cu-Cl Cycle

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ABSTRACT

The copper-chlorine (Cu-Cl) thermochemical hydrogen production cycle consists of three chemical reactions, i.e., electrolyisis of copper (I) chloride (CuCl) and hydrogen chloride (HCl), hydrolysis of copper (II) chloride ($CuCl_2$), and thermolysis of copper oxychloride (Cu_2OCl_2). The outlet stream of the electrolysis includes aqueous $CuCl_2$, CuCl, and HCl. The $CuCl_2$ product of the electrolysis is the reactant of downstream hydrolysis. In this paper, three integration pathways for the copper chloride flows between electrolysis and hydrolysis reactors are investigated in terms of energy saving and reduction of auxiliary operations for the processing of the flows. The integration pathways include solid precipitation of $CuCl_2$ using a crystallization process, water vaporization in the hydrolysis reactor by introducing the electrolyzer outlet stream directly to the reactor, and vaporization in an intermediate spray dryer.

Keywords: hydrogen production, Cu-Cl cycle, energy efficiency, process integration

1. INTRODUCTION

As energy demand grows, the reliance on fossil fuels to fulfill energy requirements will cause substantial environmental consequences. To meet the increasing demand while reducing GHG emissions, renewable energy systems and fuels have been sought as an alternative to combusting fossil fuels. Hydrogen has been viewed as a promising fuel with a combustion product of clean water. It can fuel specially designed internal combustion engines or fuel cells for a variety of energy needs [1].

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However, due to its high reactivity, hydrogen gas does not naturally exist and is typically part of larger molecules, such as water (H_2O) or methane (CH_4). Currently, hydrogen is primarily derived from fossil fuels: 48% from steam methane reforming (SMR), 30% from refinery / chemical off-gases, and 18% from coal gasification (water electrolysis produces less than 4% of the total hydrogen production) [2, 3]. The environmental benefits of using hydrogen in a vehicle could be significant, but is dependent on the source of the hydrogen. Producing hydrogen from fossil fuels consumes finite natural resources and releases large quantities of GHG emissions which is unsustainable. Alternative methods for hydrogen production that avoid or limit using fossil fuels and reduce GHG emissions are needed.

One method for hydrogen production uses electrolysis to split water molecules into constituent hydrogen and oxygen molecules, and the electricity for the electrolysis could be generated from nuclear or solar thermal energy. However, there is a significant energy loss when the thermal energy is converted to electricity. If the thermal energy can be used to split water into hydrogen and oxygen thermally, the production efficiency can be substantially increased. However, direct splitting of 35% water vapour requires a temperature of at least 3,000ºC [4], which is a very challenging temperature for industrial processes. To overcome this temperature issue, many investigators are developing indirect thermal decomposition cycles, which are termed as thermochemcial cycles. In a thermochemical cycle, water molecules first associate with auxiliary chemicals to form intermediate compounds, and then these compounds release hydrogen and oxygen. In the overall reaction, water is the only reactant entering the cycle that consists of several auxiliary and intermediate processes, and hydrogen and oxygen are the only products out of the cycle.

Approximately two hundred thermochemical cycles have been reported [5 - 7], among which the copper-chlorine (Cu-Cl) cycle is a promising method of hydrogen production. The Cu-Cl cycle is a hybrid cycle consisting of three chemical reactions, i.e., electrolysis of aqueous CuCl and HCl for hydrogen and $CuCl_2$ production, hydrolysis of $CuCl_2$ with steam for the production of Cu_2OCl_2, which releases oxygen in its downstream thermolysis reaction. The three reactions are listed as follows:

$2CuCl(aq) + 2HCl(aq) = H_2(g) + 2CuCl_2(aq)$, 70-100ºC (Electrolysis of CuCl and HCl) (1)

$2CuCl_2(s) + H_2O(g) = Cu_2OCl_2(s) + 2HCl(g)$, 360-390ºC (Hydrolysis of $CuCl_2$) (2)

$Cu_2OCl_2(s) = 2CuCl(l) + 1/2O_2(g)$, 360-390ºC (Thermolysis of Cu_2OCl_2) (3)

where aq, g, l, and s in brackets represent aqueous, gaseous, liquid, and solid, respectively. The liquid subscript indicates a molten state of the salt rather than aqueous, although aqueous solution exists in liquid form. The Cu-Cl cycle can form a closed loop with the CuCl - HCl electrolyzer to produce hydrogen without external emissions to the atmosphere. Advantage of this cycle is as follows. Temperature of the heat for the cycle is significantly lower than that for many other cycles. Also, the Cu-Cl cycle has considerably lower electrical power requirement, compared to typical water electrolysis, by using a CuCl - HCl electrolyzer.

The Cu-Cl cycle for hydrogen production [8], which consists of 3 chemical reactions and auxiliary physical processes. A closed cycle can be formed in a variety of ways and there are different variations of the Cu-Cl cycle [9], but the linkage of the copper (II) chloride ($CuCl_2$) in the outlet stream from the CuCl - HCl electrolyzer (reaction 1) with the reactant flow of the $CuCl_2$ hydrolysis (reaction 2) is always required in different variations, and there are different linkage options which may influence the energy requirement and number of auxiliary unit operations.

In this paper, integrating the electrolyzer and hydrolysis reactors in the Cu-Cl cycle is investigated in terms of the number of auxiliary operations, energy requirement, and mass flows to evaluate the feasibility of three integration pathways, including (i) vaporizing the electrolyzer's outlet stream in the hydrolysis reactor, (ii) vaporizing excess H_20 in a spray dryer before the hydrolysis reactor, and (iii) crystallizing $CuCl_2$ by using solubility changes at different temperatures to remove excess water before the hydrolysis reactor. The study of different pathways can provide valuable information for a compact and energy efficient method to integrate the processes of the Cu-Cl cycle.

2. LINKAGE COMPLEXITY AND NUMBER OF MAJOR AUXILIARY OPERATIONS

To directly link the electrolysis (reaction 1) and hydrolysis (reaction 2) reactors, the H_2O content of the aqueous solution can be directly used as the reactant in the hydrolysis reaction, as illustrated in Figure 1. However, according to past studies [10, 11], the water content in the solution is several times higher than required by the downstream hydrolysis reaction. Numerous interconnected variables affect the water content quantities in the electrolyzer outlet and hydrolysis inlet and optimal quantities are not fully determined in previous research. In this paper, ranges of water content (based on previous research) are investigated to help identify optimal operating conditions and integration techniques. An additional vaporization requirement is introduced into the hydrolysis reactor and additional steam-HCl separation processes are required downstream of the hydrolysis reactor. Detailed studies on the conversion extent of the solid hydrolysis reactant predict an optimal steam conversion of 4 to 15 mol of H_2O per mol of HCl produced [12]. To reduce the vaporization load of the hydrolysis reaction and improve the thermal efficiency of the Cu-Cl cycle, the water in the aqueous solution must be significantly reduced in the $CuCl_2$ solution before entering the hydrolysis reactor. This introduces some engineering challenges into the process integration of reactions (1) and (2), including the selection of a technology to obtain $CuCl_2$ solid from its aqueous solution and a method to remove the water content at a low cost. This optimum H_2O amount for the hydrolysis reaction requires much heat for H2O vaporization. Optimization of H_2O amount is required considering these factors.

In the CuCl electrolyzer of reaction (1), recent estimations from experimental results suggest a practicable conversion extent (with high efficiency) of 50 - 65% [13, 14], which indicates that unreacted CuCl will be in the outlet stream of the electrolyzer. This complicates reactor integration, requiring $CuCl_2$ and CuCl separation. Furthermore, altered conversions will change the outlet stream compositions and complicate the concentrating process.

A spray dryer which extracts solid $CuCl_2$ from aqueous solution from electrolysis is the second option. A spray dryer is a common method to produce powder from slurry. Figure 2 illustrates the schematic of this linkage pathway. To operate the spray drying process, a drying gas is needed. Air is easy to obtain and can be operated at a lower cost than other pure gases. However, the oxygen in air will oxidize CuCl entrained in the $CuCl_2$ aqueous solution, therefore, an inert gas must be used to vaporize the water in the $CuCl_2$ aqueous solution. After drying, the gaseous HCl and H_2O must be recovered, which requires a recovery unit to separate the drying gas from gaseous HCl and H_2O. For full recovery, the H_2O must be fully condensed to absorb HCl to form aqueous HCl, which requires a condenser or vapour liquefaction system. To completely remove toxic gaseous HCl from the drying gas is energy intensive, and the inert drying gas is more expensive than air, requiring the drying gas to be recycled. Numerous energy intensive operations are needed to use spray drying as the linkage pathway for the copper chloride flows.

Figure 3 illustrates a third integration option that crystallizes the electrolyzer's outlet stream before the hydrolysis reactor. The outlet stream flows into a heat exchanger, i.e., a cooler, and then a portion of solid crystalline $CuCl_2$ and CuCl precipitates out of the aqueous solution due to the solubility change at different temperatures. The residual clear solution of the crystallizer is pumped back to the electrolyzer and the precipitated solids ($CuCl_2$ and CuCl) are conveyed into the hydrolysis reactor. Compared with spray drying, crystallization requires less auxiliary operations, as well as preventing HCl from entering the hydrolysis reactor, which will improve the reactant extent, as presented in Eq. (2). Reducing the excess steam in the hydrolysis reactor simplifies integrating HCl in the hydrolyzer outlet stream with HCl in electrolyzer influent, by preventing an additional concentration process.

A compact cycle with fewer processes is typically preferred for operational simplicity and cost. The integration complexity is reflected by the number of major auxiliary processes needed to conduct the copper chloride flows to the desired chemical reactors. In addition to the number of major auxiliary processes that are needed to conduct the flows to the desired chemical reactors, energy requirement is a more significant consideration. It is preferred that the energy saving pathway is selected for the linkage. The following sections calculate the energy requirement for the three pathways.

3. FORMULATION OF ENERGY REQUIREMENTS OF CU-CL CYCLE INTEGRATION

In this section, the thermodynamic formulation for integrating the electrolyzer and hydrolysis reactor is presented. In the Cu-Cl cycle, achieving complete conversion is difficult and is a challenge to process integration by significantly reducing the thermodynamic efficiency of the cycle as chemical conversion effectiveness reduces as the reactants are consumed [15]. The heat input is calculated in the following way. The minimum thermal energy input to integrate the electrolyzer and hydrolysis reactor can be represented by

$$\Delta H_T = f(\Delta H_{Cp,water}, \Delta H_{Cp,steam}, H_{latent,H_2O}, \Delta H_{Cp,CuCl_2}, \Delta H_{Cp,CuCl}, \Delta H_{Cp,HCl}, \Delta H_{r,CuCl_2 \bullet H_2O}) \quad (4)$$

where $H_{Cp,water}, H_{Cp,steam}, H_{latent,H_2O}, H_{Cp,CuCl_2}, H_{Cp,CuCl}, \Delta H_{Cp,HCl}$ and $\Delta H_{r,CuCl_2 \bullet H_2O}$ represent the energy requirement to elevate the water temperature, to elevate the steam temperature, to convert water to steam, to elevate the $CuCl_2$ temperature, to elevate the CuCl temperature, to elevate the HCl temperature and to hydrated $CuCl_2$.

The thermal input for temperature elevation can be represented by

$$Q = nC_p\Delta T \tag{5}$$

where n, C_p, and ΔT represent the mole number, the heat capacity and the temperature change. H_2O phase change can be represented by

$$H_{latent} = n\beta \tag{6}$$

where β represents the enthalpy of vaporization coefficient. The crystallization process is represented by

$$CuCl_2(aq) + (n_w + m_w)H_2O(l) = CuCl_2 \bullet n_wH_2O(s) + m_wH_2O(l), \text{ below } 60^oC \tag{7}$$

where $n_w + m_w$, represents the total number water molecules, per mole of $CuCl_2$, in the aqueous solution. On the right-hand-side of Eq. (7), n_w represents the number of water molecules that are in a crystallized form with $CuCl_2$ to form copper (II) chloride hydrate, the magnitude of n_w can be from 0 - 4, depending on the temperature [16 - 20] and it can be a non-integer if the crystallization final state does not reach equilibrium [21]. The crystallization effectiveness is calculated by

$$\zeta_{s,i^oC} = \frac{n_{s,80^oC} - n_{s,i^oC}}{n_{s,80^oC}} \tag{8}$$

where n_s represents the molar quantity of $CuCl_2$ in solid phase. The subscript $i°C$ represents the output temperature of the crystallizer. The steam requirement (ξ) in the hydrolysis reactor can be defined by

$$\xi = \frac{n_{H_2O}}{n_{CuCl_2}} \tag{9}$$

where the stoichiometric minimum value for ξ is 0.5. Material flows are determined from previous research and experimental data. Recent experiments [22] and thermodynamic analysis [23, 24] suggest an optimal temperature of the hydrolysis reactor to be approximately 375°C. In this paper, the calculations are conducted in Microsoft Excel, and all pressures are maintained at ambient.

4. RESULTS AND DISCUSSION

4.1 Effects of electrolysis extent and outlet stream composition on the energy requirements.

In this section the results of the thermodynamic analysis of integrating the electrolysis and hydrolysis reactors is presented. In Table 1, the crystallization properties of a $CuCl_2$-CuCl-HCl solution are presented for 1 litre of solution between 20°C and 80°C on the basis of the assumption is that crystallization operates on the solubility curve, i.e., the operation line obeys the solubility curve, which will be discussed later in this paper.

Figure 4 [25] illustrates the solubility curve and operation line of the crystallization in a ternary system of $CuCl_2$, HCl, and water, where the HCl concentration is 2M. Crystallization experiments were performed at the Clean Energy Research Laboratory (CERL) of the University of Ontario Institute of Technology (UOIT) to examine the repetition assumption. The solubility data was collected from previous studies [26, 27]. The solubility data at 80ºC was not found in published literature. However, the starting temperature of crystallization was performed from 80ºC to include the temperature of the electrolyzer's outlet stream.

For each temperature, the solution at the inlet of the crystallizer was selected based on the ratio of $CuCl_2$-CuCl-HCl in the solution to best match the concentration of the electrolyzer outlet stream (between 50% and 65% conversion of CuCl to $CuCl_2$).

In Figure 5 the crystallization effectiveness (ξ) is calculated by Eq. (8) and the amount of solids are determined by the product of crystallization effectiveness and molar input. As presented in Figure 5, the crystallization of CuCl is negligible between 80°C and 60°C temperature of 18% of $CuCl_2$ crystallization. However, as presented in Table 1, the HCl concentration is increased from 6.09 M to 8.55 M from 80°C to 60°C, which will contribute to the relative quantities of CuCl and $CuCl_2$ solids. Future experiments will determine the relative impacts of HCl on the solubility of CuCl and $CuCl_2$ for limiting the crystallization of CuCl. Adding HCl to the solution will improve crystallization properties.

When crystallization temperature is below 60°C, $\xi CuCl_2$ is higher. However, $\xi CuCl$ also increases in the product. A crystallization solid output with a high concentration of $CuCl_2$ will supply the hydrolysis reactor with a more pure reactant and enable higher hydrolysis efficiencies. However, CuCl will precipitate out of the solution (with $CuCl_2$), which will reduce the purity of the hydrolysis reactant. Furthermore, higher conversion extents in the electrolyzer also increase the electricity consumption of the electrolytic process. To achieve high thermal efficiency in the Cu-Cl cycle, an optimal balance between conversion extent as well as thermal and electrical energy input needs to be determined. Reducing the temperature to 20°C increases the solid fraction of $CuCl_2$ to 42%, with 31% CuCl.

As presented in Figure 6, a significant portion of the energy input to the hydrolysis reactor is used to convert water to steam, particularly when the steam requirement (ξ, steam to copper (II) chloride ratio) is high. If the outlet stream of the electrolyzer is introduced directly into the hydrolysis reactor, the steam to copper (II) chloride ratio will be in the range of 17 - 34 and require significant thermal input due to the high water vaporization load. This result highlights the importance of concentrating the electrolyzer outlet stream before it is directed to the hydrolysis reactor (i.e., the option shown in Figure 1, has a low thermal efficiency).

The hydrolysis energy requirement (E) is linearly dependent on the steam requirement of the reactor, which can be represent by (at a reaction temperature of 375^{o}C)

$$E = 61.587\xi + 14.784 \tag{10}$$

where ξ represents the steam requirement. An excess steam requirement of 8 mol H_2O per mol of $CuCl_2$ will require a minimum energy input of 507 kJ/mol. However, 17 mol H_2O and 34 mol H_2O per mol of $CuCl_2$ will require a minimum energy input of 1062 kJ/mol and 2109 kJ/mol, respectively. An excess steam requirement of 8 mol H_2O per mol of $CuCl_2$ has been chosen because it is a balance between estimated values based on previous experimental research [12, 15].

Cooling the electrolyzer outlet stream, as needed for the crystallization process, will dissipate thermal energy from the cycle. The depleted thermal energy is low grade and cannot be easily recaptured for useful processes. In Figure 7, the thermal energy depleted in the crystallizer is presented for 3 conversion extents of the electrolyzer: 25%, 50%, and 65%. As presented in the right half of Table 1, each conversion extent has a different concentration of outlet stream compounds. The lower concentration of $CuCl_2$ (corresponding to lower conversion extents in the electrolyzer) produce a more dilute solution in terms of $CuCl_2$, thus increasing the energy lost in the crystallizer, primarily due to thermal energy lost by cooling a greater quantity of H_2O. As indicated in Equation (7), a portion of the water exists in different forms before and after crystallization, so there is an enthalpy change accompanying the process. If the magnitude of n_w is two (a likely result), the dehydration of $CuCl_2{\bullet}2H_2O$ at 127°C has an enthalpy change of 117 kJ/mol [28]:

$CuCl_2{\bullet}2H_2O(s) = CuCl_2\,(s) + 2H_2O(g)$, $\Delta H_r = 117$ kJ/mol at 127°C (11)

The positive value of ΔH in equation (11) indicates an endothermic dehydration process and its reverse process (i.e. hydration) is an exothermic, which leads to an additional thermal energy loss. Temperature has a negligible effect on enthalpy change in the range of 0 - 127°C, suggesting the magnitude can be approximated by the hydration enthalpy change. Hydration starts from an initial state of liquid rather than gas and the vaporization enthalpy change of water is:

$2H_2O(g) = 2H_2O(l)$, $\Delta H_{\text{latent, }H_2O} = -78$ kJ/mol at 127°C

(12)

The sum of equations (11) and (12) indicates an enthalpy of dehydration of $CuCl_2{\bullet}2H_2O$:

$CuCl_2{\bullet}2H_2O(s) = CuCl_2\,(s) + 2H_2O(l)$, $\Delta H_{\text{dehydration}} = 39$ kJ/mol at 127°C

(13)

The reverse process of equation (13) provides a hydration enthalpy of copper (II) chloride hydrate of

$\Delta H_{r,CuCl_2{\bullet}2H_2O} = -39$ kJ/mol:

$CuCl_2\,(s) + 2H_2O(l) = CuCl_2{\bullet}2H_2O(s)$, $\Delta H_{r,CuCl_2\cdot 2H_2O} = -39$ kJ/mol at 127°C

(14)

As illustrated in Figure 8, the quantity of H_2O in the electrolyzer outlet stream rises significantly with reduced conversion extents. An input electrolyte solution of 2 M CuCl and 6 M HCl, and a 50% conversion in an electrolyzer will produce an outlet stream of 1 mol $CuCl_2$ and 42.7 mol of H_2O. This is a significantly higher quantity of H_2O than is likely required by the hydrolysis reactor [15, 29, 30] and the excess water will require a significant quantity of thermal energy to heat to the required hydrolysis reaction temperature, increasing the minimum thermal energy requirement of the hydrolysis reactor to 2,940 kJ per mol of $CuCl_2$, if the outlet stream is directly introduced to the hydrolysis reactor to provide the steam and $CuCl_2$ reactants.

Utilizing a crystallizer in the temperature range of 80°C to 60°C, will lose 85 kJ/mol into the crystallizer, to produce 0.18 mol of $CuCl_2$ solids. To produce 1 mol of $CuCl_2$ solids will lose 480 kJ/mol of thermal energy contained in the solution (a comparable value in magnitude to the minimum energy requirement of the hydrolysis reactor with an excess steam requirement of 8 (507 kJ/mol of $CuCl_2$). The crystallizer offers appreciable advantages to the thermal efficiency of the Cu-Cl cycle (the pathway illustrated in Fig. 1).

As presented in Table 2, a comparative energy requirement of the three integration pathways identifies crystallization as the preferred pathway to limit energy use in the cycle. The calculated minimum energy requirement of a hydrolysis reactor and crystallizer for several quantities of excess steam, ranges from 649 to 3,574 kJ/mol, for ξ of 2.5 to 50, respectively. A 65% conversion extent is maintained in the electrolyzer. The calculated minimum energy requirement of a hydrolysis reactor when directly connected to the electrolyzer for several conversion extents in electrolyzer, ranges from 1727 to 17,136 kJ/mol, for electrolyzer conversion extents of 1 to 0.1, respectively.

4.2 Preferred operation of crystallization

In Section 4.1, the energy requirement estimation is based on the assumption that the operation line of crystallization will obey the solubility curve.

It can be observed that the experimental operation line for the crystallization is below the solubility curve. This indicates more $CuCl_2$ precipitated out of its aqueous solution in practical operations. The phenomenon does not mean the thermodynamic limit, i.e., solubility, was violated because when temperature decreases and $CuCl_2$ crystallizes, some water will attach to the $CuCl_2$ molecules in the form of hydrated water, as indicated in equation (7). The formation of hydrated water will reduce the amount of free water in the clear solution and further saturate the clear solution, consequently more $CuCl_2$ will crystallize until a new equilibrium is reached. The phenomenon was also observed in the binary system of $CuCl_2$ and water. Figure 9 illustrates the solubility curve and operation line of the crystallization in the binary system of $CuCl_2$ and water. In the Figure, the solubility data was also collected from previous studies [31, 32], and the crystallization was started at 80ºC and stopped at different lower temperatures. In the crystallization experiments (binary and ternary systems), a final temperature of approximately 20ºC was examined to investigate using a fluid at ambient temperature, such as air or water, to remove heat from the crystallizer and avoid additional energy requirements. Also, the crystallization runtime (final temperature ≥ 20ºC) in Figures 4 and 9 was less than 120 minutes to ensure a manageable operating time in scaled up units.

In summary, the energy requirement estimation can be conservatively based on the assumption that the operation line of the crystallization of $CuCl_2$ will obey the solubility curve for both the binary and ternary systems of $CuCl_2$-water and $CuCl_2$- HCl-water, respectively. The repetition may make the linkage of $CuCl_2$ flows more compact and energy saving because it will reduce the size of the crystallization vessel and number of crystallization stages compared with otherwise the crystallization line is located above the solubility curve in Figures 4 and 9.

As discussed previously, the electrolyzer's outlet stream also includes CuCl if its conversion to $CuCl_2$ is incomplete. As the formation of hydrated water caused by crystallization of $CuCl_2$ will reduce the free water amount in the solution, it is expected that this concentrating effect may also facilitate the precipitation of CuCl. Further investigations are needed to examine the operation line for the precipitation of CuCl.

5. CONCLUSIONS

This paper performed a thermodynamic analysis on the electrolysis and hydrolysis reactions of the Cu-Cl thermochemical hydrogen production cycle with an emphasis on linking the energy and mass flows. The following three integration methods were examined: directly introducing the aqueous outlet stream of the electrolyzer to the hydrolysis reactor, adopting an intermediate crystallizer to separate solid $CuCl_2$ from the influent stream of the hydrolysis reactor, and vaporizing excess H_2O before the hydrolysis reactor by using a spray dryer. Ongoing experiments are investigated the parameters of the electrolyzer operation.

Spray drying has the highest energy intensity of the three methods analyzed in this paper. Directly feeding the electrolyzer's outlet stream into the hydrolysis unit provides the most intensified integration design of the copper chloride flows. However, crystallization requires less energy input. High conversion of CuCl to $CuCl_2$ in the electrolyzer is important, as well as low steam requirement in the hydrolysis reactor. A crystallizer can be a compact integration pathway to link the electrolyzer and hydrolysis reactor, by separating a portion of the $CuCl_2$ and CuCl solids from the aqueous solution, as well as recycling the residual solution to the electrolyzer inlet. Electricity input to the CuCl electrolysis and heat input to the thermolysis will be investigated in future to evaluate clearly which options is most efficient to produce hydrogen.

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NOMENCLATURE

H	enthalpy, kJ/mol
C_p	specific heat, kJ/mol · K
E	energy, kJ/mol
n, m	number of moles
Q	thermal energy, kJ/mol
T	Temperature, K

Greek Letters

ξ	steam requirement (steam to copper (II) chloride ratio)
β	enthalpy of vaporization, kJ/mol

Subscripts

T	total
w	water
s	solid
r	reaction
$i^\circ C$	output temperature of crystallizer
latent	latent heat of vapourization
dehydration	enthalpy of dehydration

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Table 1: Solubility of CuCl, CuCl$_2$ and HCl

	Saturated solubility for 1 litre of solution [mol]			Saturated solubility for 1 litre of solution normalized to a constant quantity of HCl [mol]		
T [^{o}C]	CuCl	CuCl$_2$	HCl	CuCl	CuCl$_2$	HCl
20	1.46	2.31	8.66	1.03	1.63	6.09
40	1.68	3.06	9.73	1.05	1.92	6.09
60	2.08	3.26	8.55	1.48	2.32	6.09
80	1.48	2.82	6.09	1.48	2.82	6.09

Table 2: Comparative energy requirement of three integration pathways

Hydrolysis and crystalization with 65% conversion extent in electrolyzer			Hydrolysis reactor for direct connection to electrolyzer			Hydrolysis and spray drying	
Excess steam required in hydrolysis	Energy required [kJ/mol]		Conversion extent in electrolyzer	Energy required [kJ/mol]			Energy required [kJ/mol]
50	3574		0.1	17136			
25	2034		0.25	6851			
8	987		0.5	3432			
2.5	649		0.65	2940			
			1	1727			

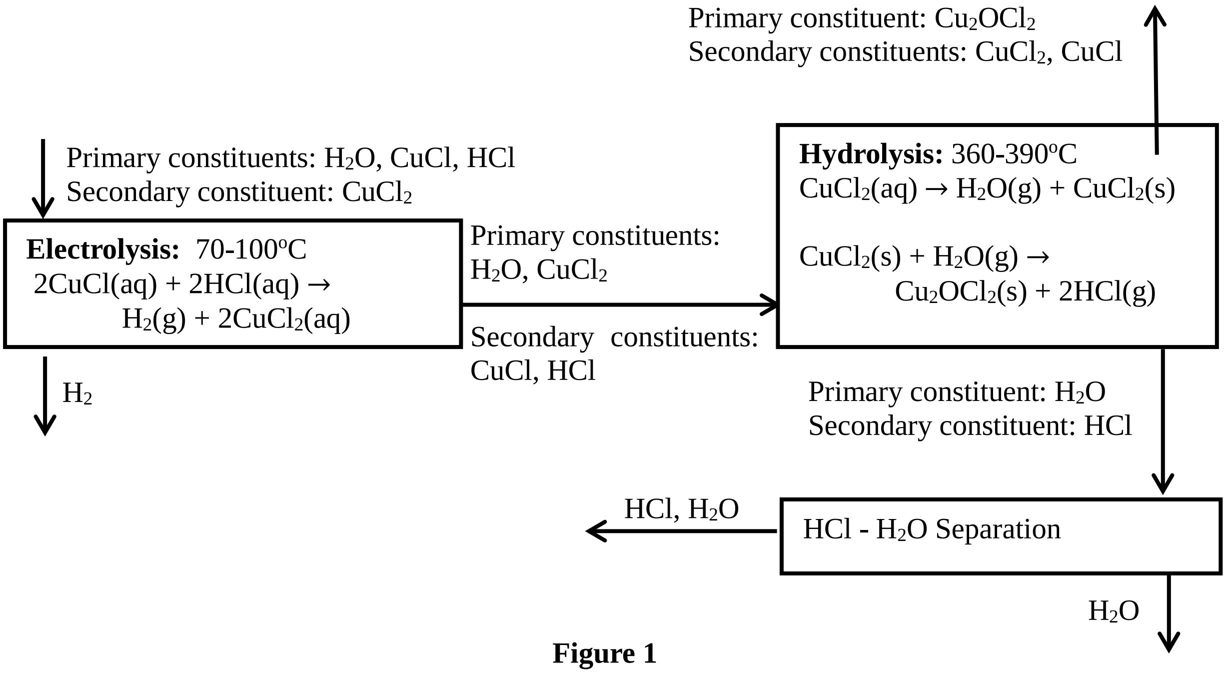
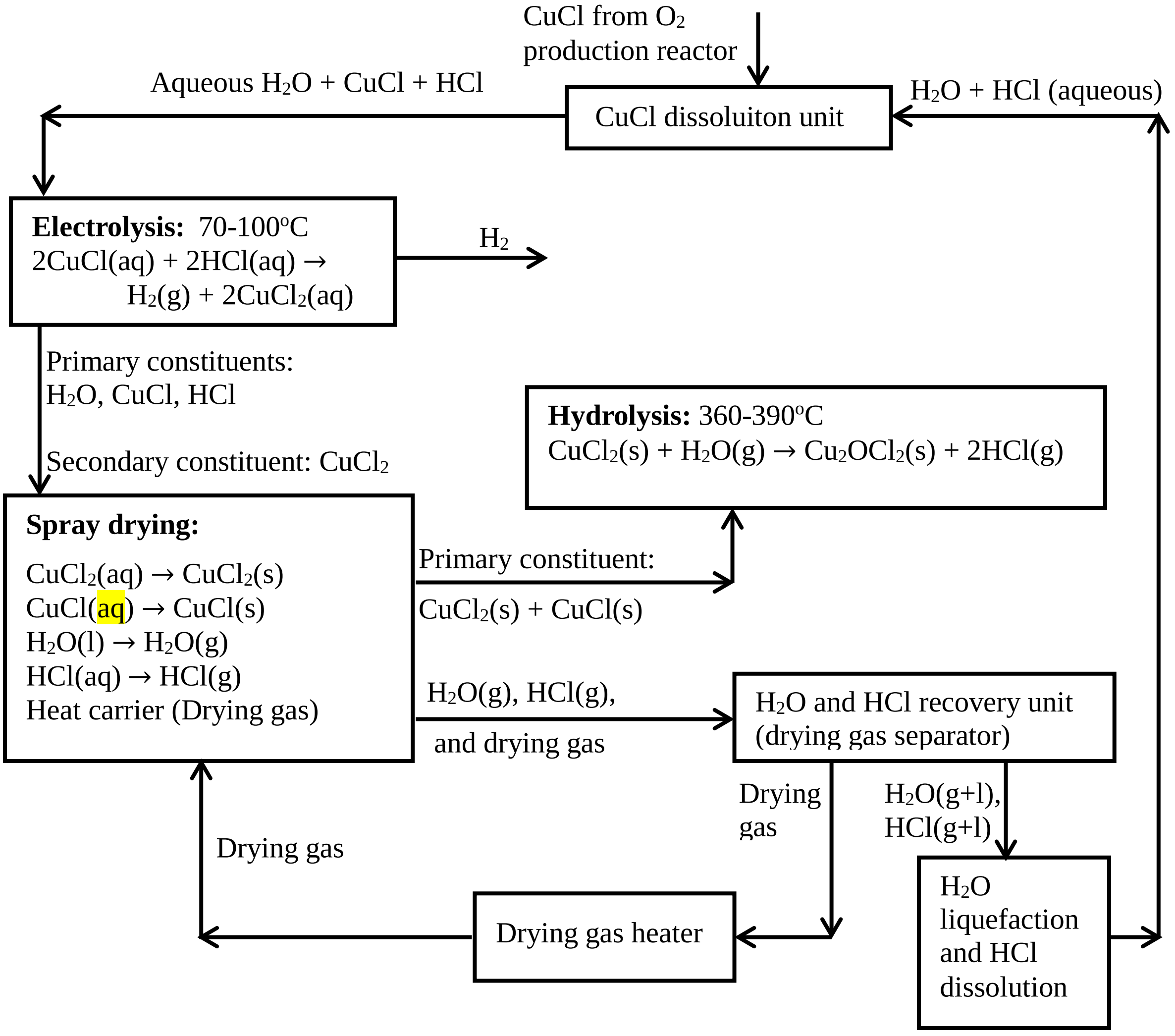

Primary constituent: Cu_2OCl_2
Secondary constituents: $CuCl_2$, CuCl
Primary constituents: H_2O, CuCl, HCl
Secondary constituent: $CuCl_2$
Electrolysis: 70-100°C
$2CuCl(aq) + 2HCl(aq) \rightarrow H_2(g) + 2CuCl_2(aq)$
H_2
Primary constituents: H_2O, $CuCl_2$
Secondary constituents: CuCl, HCl
Hydrolysis: 360-390°C
$CuCl_2(aq) \rightarrow H_2O(g) + CuCl_2(s)$
$CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2(s) + 2HCl(g)$
Primary constituent: H_2O
Secondary constituent: HCl
HCl, H_2O
HCl - H_2O Separation
H_2O

Figure 1



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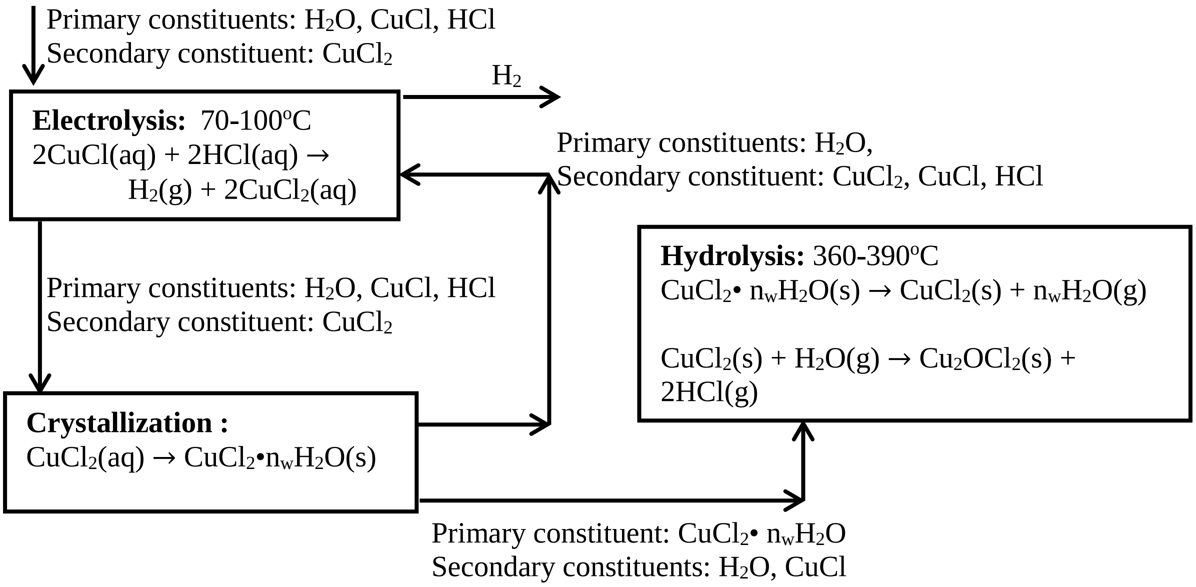

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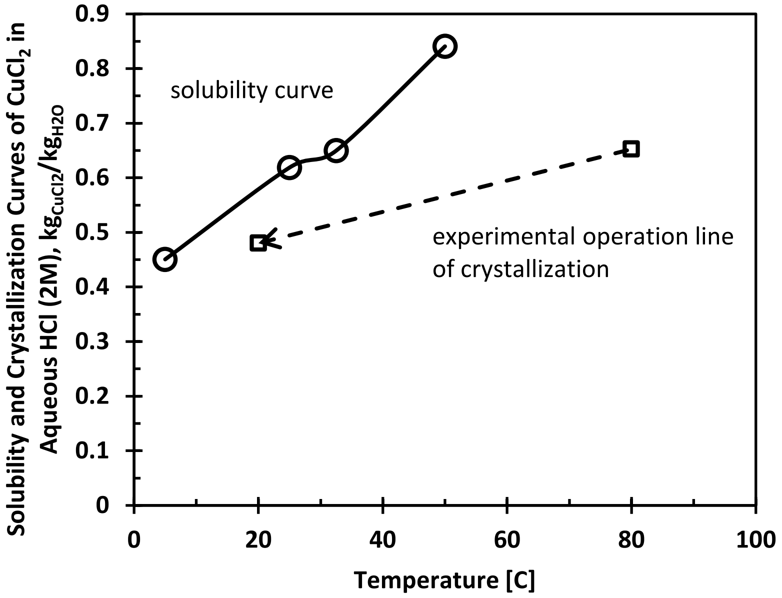

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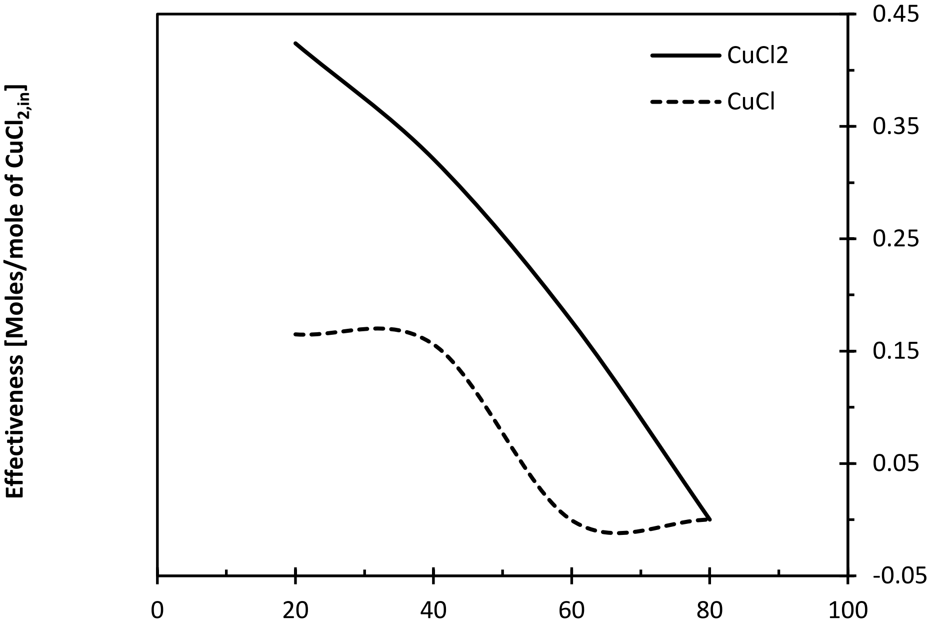

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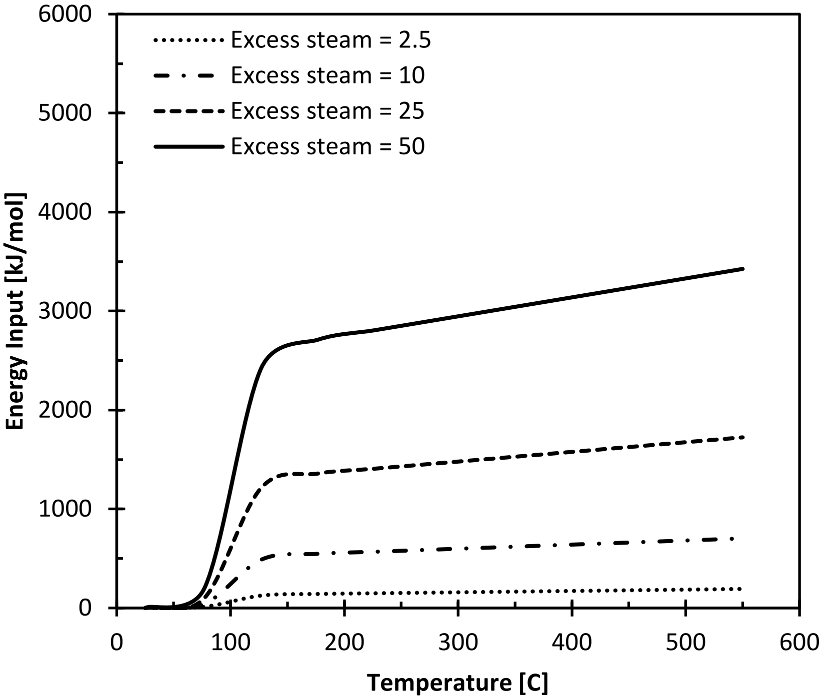

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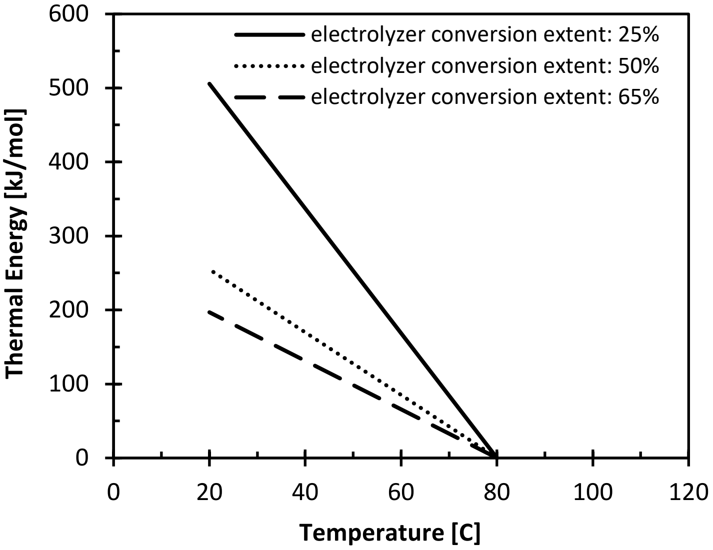

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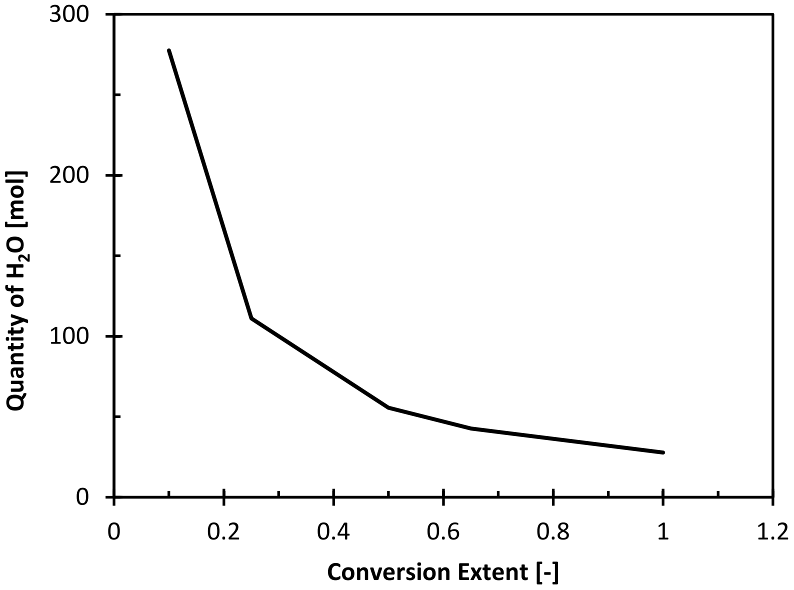

Figure 8

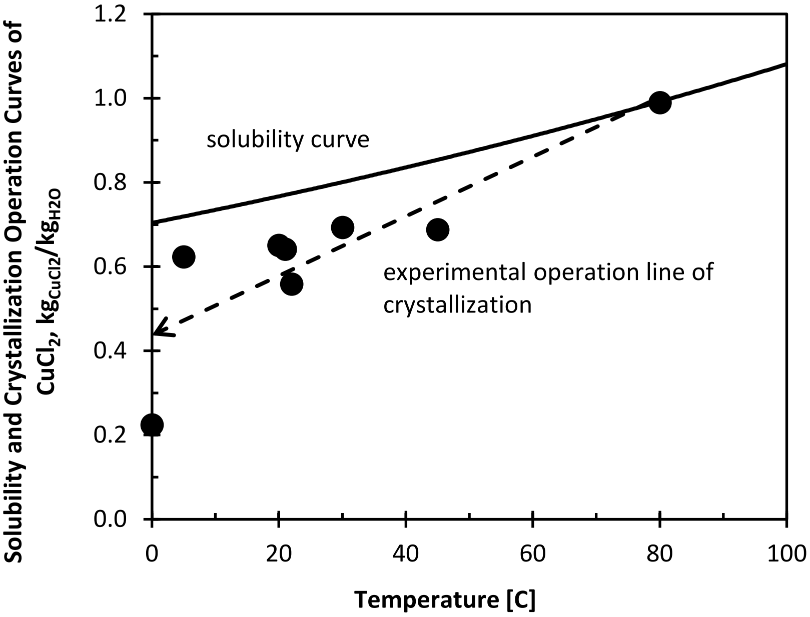

Figure 9