PROCESS SIMULATION OF NUCLEAR-BASED THERMOCHEMICAL HYDROGEN PRODUCTION WITH A COPPER-CHLORINE CYCLE

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Abstract

Thermochemical processes for hydrogen production driven by nuclear energy are promising alternatives to existing technologies for large-scale commercial production of hydrogen without fossil fuels. The copper-chlorine (Cu-Cl) cycle, in which water is decomposed into hydrogen and oxygen, is promising for thermochemical hydrogen production in conjunction with a Supercritical Water Cooled Reactor. Here, the cycle efficiency is examined using the Aspen Plus process simulation code. A successful simulation of the process is achieved, and possible efficiency improvements are discussed. The results are expected to assist the development of a lab-scale cycle demonstration, which is currently being undertaken at University of Ontario Institute of Technology in collaboration with numerous partners.

1. Introduction

As the world's oil and gas reserves approach and reach a peak production capacity and environmental concerns increase, there is an urgent need to develop alternative energy sources that can continue to power the world's economy. Hydrogen is a promising and clean energy carrier. If effectively utilized, it can help facilitate the use of alternative energy resources to meet present and future energy requirements of society and industry. Hydrogen has an inherent advantage compared to other energy carriers, due to its energy density and environmentally benign nature. At present, tens of millions of tons of bulk industrial hydrogen are produced annually by steam-methane reforming (SMR), the reforming of methane from methane-rich fossil fuels.

Water consists of hydrogen and oxygen bonded together, which can be decomposed to produce hydrogen. Direct and indirect decomposition of water into its constituents is a challenge for various reasons, such as material requirements to withstand the high temperatures and pressures involved in direct water splitting and in thermochemical cycles. In Canada, hydrogen is expected to have an increasingly significant role in the future in the overall energy mix of the country, not only as a transportation fuel but also in the oil and gas industry. For instance, hydrogen is heavily used in Alberta's oil sands for upgrading bitumen to synthetic crude oil.

Due to the difficulties of direct thermal splitting of water to produce hydrogen with present technology, several alternative processes have been identified to produce hydrogen, in two or more steps, including efforts to split water at relatively lower temperatures. The net inputs for such processes are water and heat, while hydrogen and oxygen are produced, and other components recycled. The only emissions are associated with the source of heat to drive the process, and for many sources there are no emissions to the environment. These processes usually require high temperatures, over 450^oC.

Steinfeld [1] and Tamaura et al. [2] have proposed thermochemical processes utilizing solar energy to supply the required heat at up to 800^oC. Many researchers have examined nuclear power as a promising steady supply of high-temperature heat in large capacities, e.g., Mathias et al. [3], Wu et al. [4], Brown et al. [5], Suppiah et al. [6], Ryland et al. [7], Teo et al. [8], Lewis [9,10,11], Wang et al. [12], Li [13], Law et al. [14] and others. While many have adopted nuclear energy as the source of process heat for the reactions, different routes are being investigated. Rosen [15] performed a thermodynamic analysis of hydrogen production by thermochemical water decomposition using the Ispra Mark-10 cycle, while Granovskii et al. [16] carried out a thermodynamic analysis of the use of a chemical heat pump to link a supercritical water-cooled nuclear reactor (SCWR) and a thermochemical water splitting cycle for hydrogen production.

Teo et al. [8], for example, are investigating a UT-3 cycle developed at the University of Tokyo, requiring three steps that involve Ca, Br and Fe. This process requires heat at 750^oC in one of the steps. Several researchers [3,4,5,6,7] are investigating the sulphur-iodine cycle, developed by General Atomics. Like UT-3, the process requires temperatures up to 850^oC in one of the steps. It may be suitable to link such a thermochemical process with a high-temperature gas-cooled reactor, or the Generation IV nuclear reactors under development by several countries around the world.

University of Ontario Institute of Technology (UOIT), Atomic Energy of Canada Ltd. (AECL), Argonne National Laboratory (ANL), partner universities across Ontario and abroad and other collaborators are investigating an alternative cycle for thermochemical production of hydrogen, based on the copper-chlorine (Cu-Cl) cycle [9,10,11,12,13,14]. This cycle has four reaction steps and has advantages over other thermochemical cycles, including the requirement for relatively low-temperature heat. The highest temperature needed for the steps copper-chlorine thermochemical cycle for hydrogen production is less than 550^oC.

ANL has experimentally verified with laboratory proof-of-principle demonstrations all of the steps [9] and a UOIT-led team is currently developing a lab-scale demonstration at higher flow capacities. AECL is also investigating an alternative route by combination of two of the process steps, involving electrolytic production of solid copper. Past AECL studies have successfully combined the first two steps of the process in a high-temperature electrolytic process, which eliminates solids handling and the drying of copper dendrites, where particle size is crucial. Proof-of-principle demonstrations have been made at a small scale [13]. This article focuses on a four-step cycle being developed at UOIT in collaboration with partners. The aim is to simulate a nuclear-based hydrogen production using the copper-chlorine thermochemical cycle, and thereby to improve understanding of the cycle so as to allow it to be scaled to a larger size and to be improved. The simulation is carried out with the Aspen Plus process-simulation code.

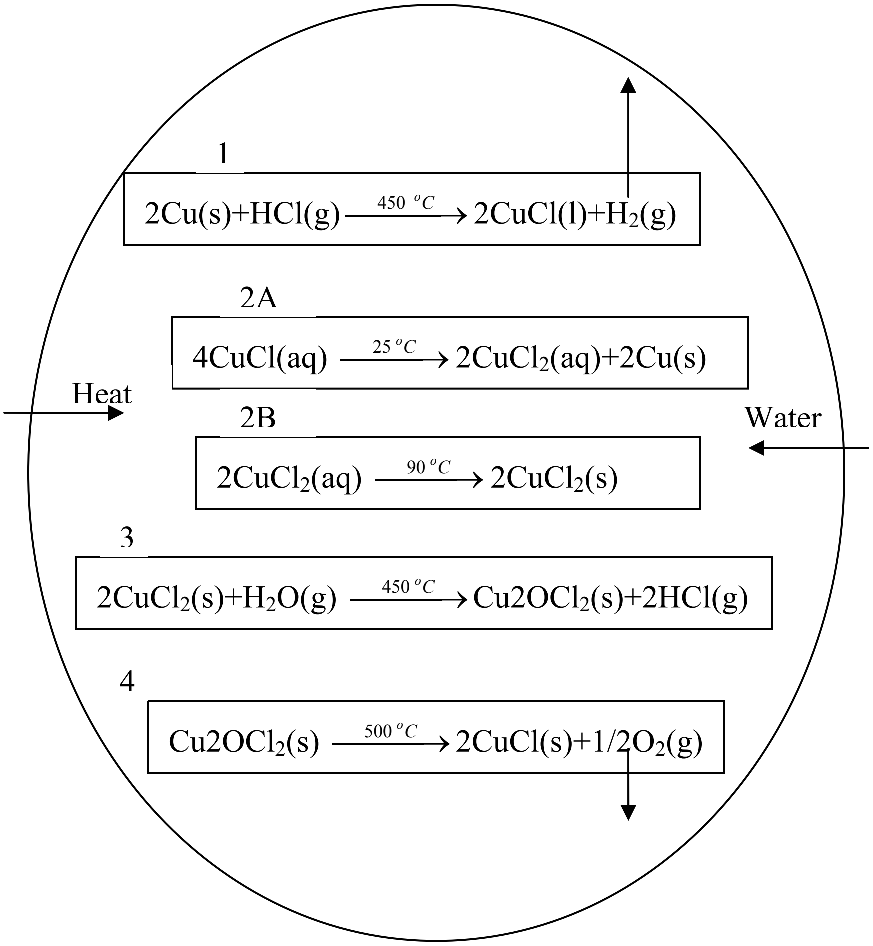

Figure 1: Process schematic of the Cu-Cl thermochemical cycle for hydrogen production.

2. Thermodynamic energy balances for the Cu-Cl cycle

The four-step cycle considered here for thermochemical hydrogen production using the copper-chlorine cycle is illustrated in Figure 1. The overall reaction for the process of thermochemical water splitting is observed in this Figure to be: $H_2O \Rightarrow H_2 + 1/2O_2$. ANL has successfully carried out laboratory experiments [9] that confirm the feasibility of the four steps being investigated at UOIT. Wang et al. [12] have extensively analyzed the energy balances for the different steps. Thermodynamic energy balances for the reactions and processes in the Cu-Cl cycle for hydrogen production are shown in Table 1. The basis for the calculations is 1 mol of H_2O to produce 1 mol H_2 and ½ mol of O_2. The heat balance in the reactions is equal to the change in enthalpy of the reactions, ΔH. The total heat released by the exothermic reactions is 290.1 kJ. Assuming some of the reaction heat has a low quality and temperature, rendering it difficult to recover, a heat exchanger effectiveness of 50% is assumed. In this assumption, 145 kJ of heat is recovered from the reaction heat.

Table 1: Thermodynamic data for reactions in the Cu-Cl cycle and energy balances

Process Reactions	**T (in)**	**T (out)**	**ΔH**
	^oC	**^oC**	**KJ**
Exothermic Reactions			
$H_2(g, 450^oC) \rightarrow H_2(g, 25^oC)$	450	25	-12.2
$1/2O_2(g, 500^oC) \rightarrow 1/2O_2(g, 25^oC)$	500	25	-7.3
$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$	450	450	-46.8
$2CuCl(l, 450^oC) \rightarrow 2CuCl(s, 25^oC)$	450	25	-80.8
H_2O (g, 100^{o}C) → H2O(l, 25^{o}C) (from Cu slurry and CuCl2 solution)	100	25	-58
$2CuCl(l, 500^oC) \rightarrow 2CuCl(s, 25^oC)$	500	25	-84.8
Total theoretical heat recovered from process			-290.1
Total theoretical recovered heat (at 50% heat exchanger effectiveness)			-145
Endothermic Reactions			
$2Cu(s, 25^oC) \rightarrow 2Cu(s, 450^oC)$	25	450	23.4
H_2O in Cu slurry (l, 25^{o}C) → vapor (g, 100^{o}C)	25	100	29
$CuO*CuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$	500	500	129.1
$2CuCl_2(s) + H_2O(g) \rightarrow CuO*CuCl_2(s) + 2HCl(g)$	400	400	116.6
$2HCl(g, 400^oC) \rightarrow 2HCl(g, 450^oC)$	400	450	3
$H_2O(l, 25^oC) \rightarrow H_2O(g, 400^oC)$	25	400	57.7
$2CuCl_2(s, 25^oC) \rightarrow 2CuCl_2(s, 400^oC)$	25	400	54.1
$2CuCl_2(aq, 25^oC) \rightarrow 2CuCl_2(s, 25^oC)$ (with spray drying at 60^{o}C)	25	70	83.1
H_2O in $CuCl_2$ solution (l, 25^{o}C) → vapor (g, 100^{o}C)	25	100	29
Total endothermic reaction heat required (excluding drying heat)			442.1
Minimum heat required by cycle (ΔH_{net})			297.1

The reaction heat for the endothermic processes is found to be 442 kJ, and the net process heat required for the reactions 297.1 kJ. Since one of the steps involves electrolysis, the electrolytic power requirement is calculated using the Nernst equation as follows:

$$\Delta G = nFE \qquad (1)$$

Here, F denotes Faraday's constant (96454.56), E the cell potential of the cells and n the number of transferred electrons. Lewis et al. [11] and Li [13] have shown that a voltage of 0.5 V can be assumed for the electrolysis step, although the current density is low at this voltage. Research [14] on this electrolysis step is ongoing to keep the current density as high as possible, with a low voltage, to reduce energy consumption. The electrochemical work is 192.6 kJ (for 50% conversion efficiency).

About 38 kJ of work is assumed input to the auxiliary equipment. This is the work required to operate pumps, compressors and so forth. The total theoretical energy required for the process is 527.7 kJ. The cycle energy efficiency η can be expressed as:

$$\eta = \frac{\Delta h_f^o \mathrm{H_2O}(25^o C)}{Q + e + W} \tag{2}$$

where Δh_f^o denotes the standard enthalpy of formation of water, Q the process heat required for the reaction, e the electrical work required for the reaction, and W the auxiliary work required by the pumps. The efficiency of the cycle using the higher heating value (HHV) becomes 52.6 %.

3. Process simulation of the Cu-Cl cycle

The Aspen Plus process simulator is applied to the Cu-Cl cycle. Aspen Plus predicts the behavior of process reactions and steps using standard engineering relationships, mass and energy balances, as well as phase and chemical equilibrium data. Thermodynamic data for this simulation is obtained from experimental studies at ANL [9,10,11]. Properties and conditions are estimated where experimental data are not available. An "Electrolyte Non Random Two Liquid" (ELECNTRL) activity coefficient model is used for modeling of the electrolyte step in the stoichiometry reactor. The Soave-Redlich-Kwong (SRK) cubic equation of state is used to evaluate component properties and phase equilibra in the steps that involve vapor-liquid phase change. The above method have the advantage of being able to handle supercritical components of the cycle that do not form liquid, thereby handling both vapor-liquid phases for large ranges of temperature. The methods determine the critical point for the mixture and also have the advantage of generating thermodynamic properties in a consistent manner [17]. The liquid phase equilibrium in the unit operation models manages physical property and phase equilibrium calculations. Mathias [18] has shown that molten CuCl, an important component of the process, undergoes phase transition from cubic to beta-hexagonal structures at 412^{o}C, then to liquid at 423^{o}C. A detailed understanding of this transition is crucial in accurately estimating the thermodynamic properties, enthalpy and free energy, at various states, and variations in specific heats. Aspen Plus has the capability of estimating physical property parameters for components that are not present in the Aspen Plus database, based on a combination of experimental data and molecular formulae. A process flow sheet for the simulation is shown is Figure 2.

In the process flow diagram in Figure 2, stoichiometry reactors (RStoic in Aspen Plus terminology) B11, B62 and B71 are used to simulate the chemical reactions in the process, while B91 is used in the drying step of the process. This is done to handling these reactions that occur independently in a series of reactors. We also calculated the heat of reactions at the specified reference conditions based on consumption of a unit mole or mass of the reference reactant selected for each reaction. A heat balance is performed on the heat exchangers in Figure 2 using the enthalpy of reactions for the process steps.

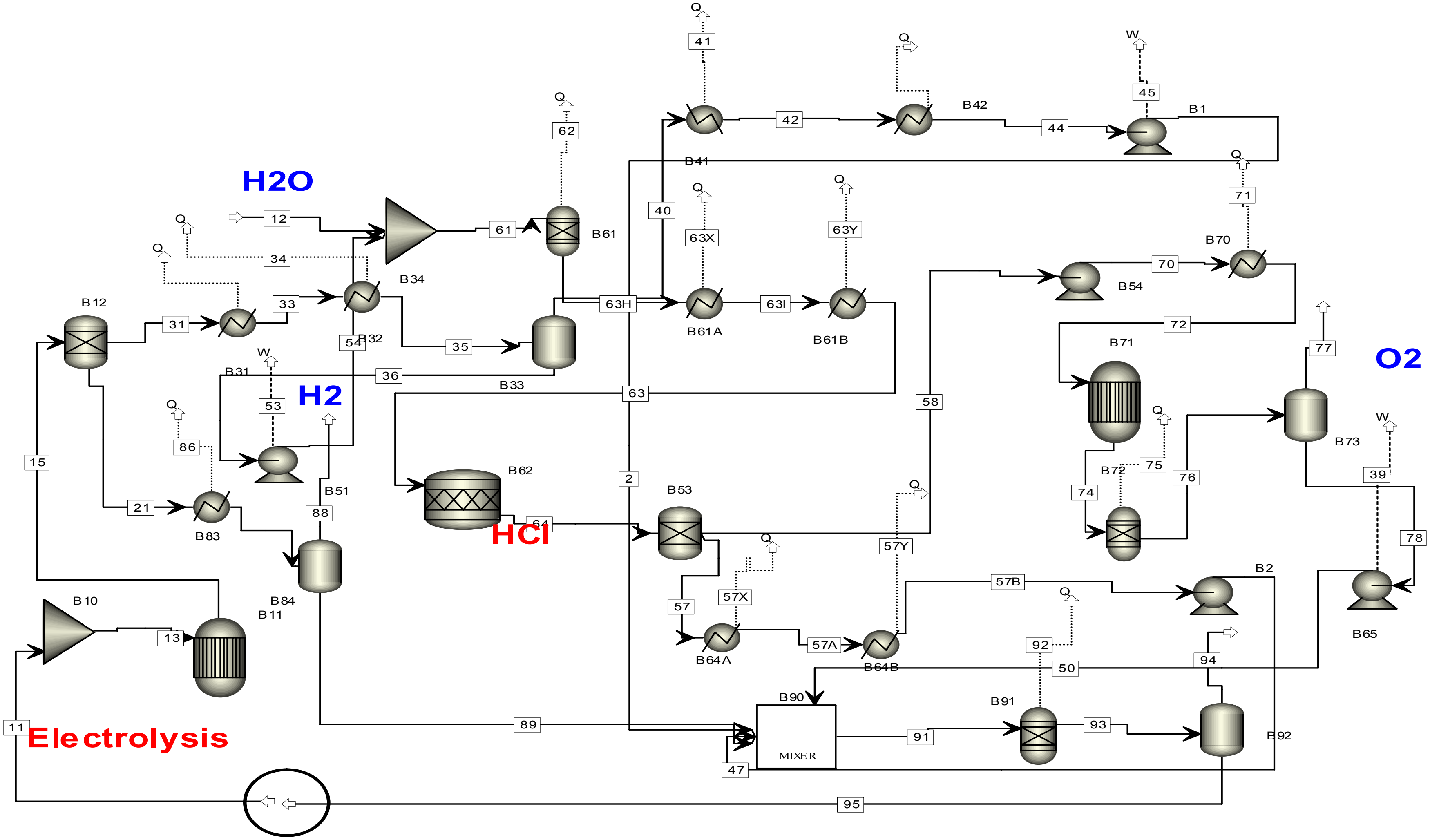

Figure 2: Process flow sheet for thermochemical hydrogen production

4. Results and discussion

The results of the simulation of the process in the flowsheet in Figure 2 are presented and discussed. An input of 100 mol of water yields 100 mol of hydrogen and 50 mol of oxygen. The corresponding energy requirements, input and output temperatures, and other data for the process conditions at various transfer points are shown in Table 2.

Table 2 shows the input and output temperatures associated with various heat transfers and the corresponding heat duty at each point. Using thermodynamic heat balances, the efficiency of the process cycle is calculated. The heat flow for the cycle per mol of hydrogen is about 517.3 kJ. The auxiliary work required to drive the pumps is 26.4 kJ. The total heat required to produce 1 mole of hydrogen using the Cu-Cl cycle is about 543.7 kJ. The energy efficiency of the cycle, following Eq. (2), is determined to be 52.57% based on the higher heating value (HHV). As expected, the largest energy input from this preliminary result using an Aspen Plus simulation occurs in heating of cupric dendrites. This calculation does not take into consideration the actual value of the electrochemical energy input for the cycle as experimental values are not available for the calculations.

Table 2: Process flow diagram heat balance

Heat Exchangers	**Q (kJ)**	**T (in) (^{o}C)**	**T (out) (^{o}C)**
32	7,494.4	25	100
34	24,409.2	100	116
41	-23,186.0	116	105
43	-2,833.6	105	25
57X	-10,736.5	400	90
57Y	32,092.3	90	90
62	-1,552.6	113	90
63X	-9,697.0	90	27
63Y	55,382.1	27	425
71	559.7	425	550
75	-2,718.9	550	25
86	35.10	25	25
92	-17,513.4	117	25
Process heat flow for cycle	51,734.0		
Process heat flow/mol H_2	517.0		
Auxiliary (pump) work	26.4		
Total heat flow for Cu-Cl cycle	543.0		

The predicted cycle efficiency agrees well with past results obtained by Rosen and Scott [19], Yildiz and Kazimi [20] and Rosen [21]. At present, thermochemical hydrogen production has lower energy efficiency than the predominant technology of SMR [20,21]. However, thermochemical hydrogen production has promising potential because it has the potential to eliminate greenhouse gas emissions and utilizes waste heat from nuclear reactors. Eventually, the process may significantly reduce the costs of hydrogen production compared to other methods.

Further optimization and effective heat matching with pinch analysis and better design of various steps within the Cu-Cl cycle are expected to lead to efficiency improvements. Exergy analysis is also expected to improve understanding and improvement possibilities for the process, and is the subject of ongoing research.

5. Conclusions

This simulation of a themochemical hydrogen production with a Cu-Cl cycle at relatively low temperatures has demonstrated that the process is a feasible and promising pathway to sustainable production of hydrogen with Canada's possible future nuclear reactors, namely the SCWR. The utilization of nuclear waste heat, in addition to process heat, improves the overall efficiency of the cycle. A successful simulation of the process has been achieved, and should prove useful in subsequent investigations. Further modifications are expected to yield more efficiency improvements, such as the combination of different steps that could eliminate solids handling.

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