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Thermoeconomic Analysis of a Copper-Chlorine Thermochemical Cycle for Nuclear-Based Hydrogen Production

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Abstract

Thermochemical water splitting with a copper–chlorine (Cu-Cl) cycle is a promising process that could be linked with nuclear reactors to decompose water into its constituents, oxygen and hydrogen, through intermediate copper and chlorine compounds. In this paper, a comprehensive exergoeconomic analysis of the Cu-Cl cycle is reported to evaluate the production costs as a function of the amount and quality of the energy used for hydrogen production, as well as the costs of the exergy losses and the exergoeconomic improvement potential of the equipment used in the process. An additional objective is to determine changes in the design parameters of the Cu-Cl cycle that improve the cost effectiveness of the overall system.

Keywords: Hydrogen, thermochemical water decomposition, nuclear, economic analysis, cost, thermoeconomic analysis, copper-chlorine cycle

1 Introduction

Energy consumption growth is closely related to population growth, although changes in life styles and efficiency improvement have a substantial influence on the per capita annual consumption. As a result of the worldwide increasing energy consumption due to increasing population and rising living standards, the world faces problems with depleting energy resources and the impairing impact of present energy consumption patterns on the global climate and consequently on humanity and the environment. The concerns regarding global climate change are significant and have resulted in extensive R&D on alternative, clean energy sources.

There are various alternative energy options to fossil fuels, including solar, geothermal, hydropower, wind and nuclear energy. While many of the available natural energy resources are limited due to their reliability, quality, quantity and density, nuclear energy has the potential to contribute a significant share of energy supply without contributing to climate change. Nuclear energy has in the past been used almost exclusively for electric power generation, but the direct utilization of nuclear thermal energy for other purposes has the potential to increase efficiency and thereby facilitate energy savings. Hydrogen production via thermochemical water decomposition is a potentially important process for direct utilization of nuclear thermal energy.

Thermochemical water splitting with a copper–chlorine (Cu-Cl) cycle is a promising process that could be linked with nuclear reactors to decompose water into its constituents, oxygen and hydrogen, through intermediate copper and chlorine compounds. The cycle consists of five reaction main steps. Heat is transferred between various endothermic and exothermic reactions in the Cu-Cl cycle, through heat exchangers that supply or recover heat from individual processes.

Studies on the Cu-Cl cycle and its analyses have increased recently. Several studies of the Cu-Cl cycle have been carried out that aim to improve its overall efficiency. For example, the main steps of the Cu-Cl cycle have been assessed thermodynamically by Orhan et al. [1-5], using energy and exergy methods and considering relevant chemical reactions. Energy and exergy efficiencies of the steps in the cycle have been evaluated and parametric studies have been carried out on energetic and exergetic aspects considering variable reaction and reference-environment temperatures [1-5].

Heat is transferred between various endothermic and exothermic reactors in the Cu–Cl cycle, through heat exchangers that supply or recover heat from individual processes. Naterer et al. [6] have examined the heat requirements of these steps, in efforts to recover heat and minimize the net heat supply to the cycle, thereby improving its overall efficiency [6].

Naterer et al. [7] have examined the evaporative drying of aqueous cupric chloride ($CuCl_2$) droplets in the copper-chlorine (Cu-Cl) thermochemical cycle of hydrogen production. Analytical solutions have been developed for the cupric chloride spraying and drying processes, including empirical correlations for heat and mass transfer, based on a single droplet of aqueous $CuCl_2$ solution [7]. Selected design issues associated with reactor scale-up in the thermochemical copper–chlorine (Cu–Cl) cycle for hydrogen production have been studied by Wang et al. [8], focusing on the hydrogen, oxygen and hydrolysis reactors [8].

Orhan et al. [9] have performed an economic analysis of a Cu–Cl pilot plant with an associated parametric study. The analysis takes into account the different types of costs such as energy, operation and maintenance costs, fixed charges on capital investment, etc. The costs with their percentage ranges and factors that affect accuracy and scaling have been examined. Through this scaling method, the total capital investment and total cost of a Cu–Cl pilot plant have been estimated by scaling against the corresponding costs of a sulphur-iodine (S-I) thermochemical water decomposition plant for hydrogen production. The sensitivity studies show that costs vary significantly with the pilot plant capacity, breakdowns of cost components and the capacity factor. Parametric studies with variable plant capacities, approximations and capacity factors have been performed [9].

Although technical studies of the Cu-Cl cycle have been reported, there is a need to understand the potential economics of the cycle, to facilitate eventual commercialisation. Such economic assessments are lacking, especially utilizing advanced tools linked to thermodynamics. Thermoeconomics combines energy (and/or exergy) analysis and economic principles to provide the system designer or operator with information not available through conventional energy analysis and economic evaluations, but useful to the design and operation of a cost-effective system.

In this paper, principles of thermoeconomics are used to evaluate the production costs as a function of the amount and quality of the energy used for hydrogen production, as well as the costs of the exergy losses and the exergoeconomic improvement potential of the equipment used in the process. An additional objective is to determine changes in the design parameters of the Cu-Cl cycle that improve the cost effectiveness of the overall system. The methodology used provides a plausible exploratory approach for improving the cost effectiveness of the Cu-Cl cycle.

2 System Description

Most thermochemical cycles require process heat at high temperatures, exceeding 850°C-900°C. However, existing nuclear power plants typically operate at 250°C-500°C. Recently, Atomic Energy of Canada Limited and Argonne National Laboratory in the U.S. have been developing low-temperature thermochemical cycles designed to accommodate heat sources around 500°C-550°C. Such cycles can be more readily integrated with nuclear reactors. For this temperature range, the copper-chlorine (Cu-Cl) cycle is one of the most promising. Several Cu-Cl cycles have been examined in the laboratory and various alternative configurations identified. Proof-of-principle experiments that demonstrate the feasibility of the processes have been undertaken and a preliminary assessment of the cycle efficiency has demonstrated its potential.

The Cu-Cl cycle consists of a set of reactions to achieve the overall splitting of water into its constituents, hydrogen and oxygen. The overall net reaction is H_2O (g) → H_2 (g) + $1/2O_2$ (g). The Cu-Cl cycle uses a series of intermediate copper and chloride compounds. These chemical reactions form a closed internal loop that recycles all chemicals on a continuous basis, without emitting any greenhouse gases.

The Cu-Cl cycle has been shown [1-9] to be a potentially attractive option for generating hydrogen from nuclear energy. Compared with other hydrogen production options, the thermochemical Cu-Cl cycle is expected to have a higher efficiency, to produce hydrogen at a lower cost, and to have a smaller impact on the environment by reducing airborne emissions, solid wastes and energy requirements.

It can be observed in Fig. 1 that only water and nuclear-derived heat enter the Cu-Cl cycle and only H_2 and O_2 are produced, while greenhouse gas emissions are avoided. In the first step of the cycle (S1), steam at 400°C and solid copper chloride ($CuCl_2$) at 400°C from the dryer enter the fluidized bed, where an endothermic chemical reaction occurs that yields hydrochloric gas (HCl) and Cu_2OCl_2. The hydrochloric gas is compressed and the Cu_2OCl_2 is transferred to another process step after its temperature is increased to the oxygen production reaction temperature of 500°C. In the second (oxygen production) step (S2) an endothermic chemical reaction takes place in which Cu_2OCl_2 is heated and O_2 and copper monochloride (CuCl) are produced. Liquid copper monochloride is solidified by cooling it to 20°C, after which it enters the third (copper production) step (S3) together with the solid copper monochloride from the fifth step (S5). In the third step, solid copper monochloride and water interact endothermically at 20°C. The water acts as a catalyst in this reaction, and does not react with the other elements or compounds. The third reaction involves an electrolysis step, which makes it the most expensive step depending on the price of electricity. In this reaction, solid copper and a copper chloride-water solution are produced. A mixture of copper chloride and water is transferred to the dryer (S4), and solid copper enters the fifth step after its temperature is increased to that step's operating temperature. In the fifth (hydrogen production) step, hydrochloric gas and copper enter and are converted to hydrogen gas (H_2) and solid copper monochloride (CuCl) in a steady-state reaction at 450°C.

Three different variations of the Cu-Cl cycle are currently under investigation: 3-step, 4-step and 5-step cycles.

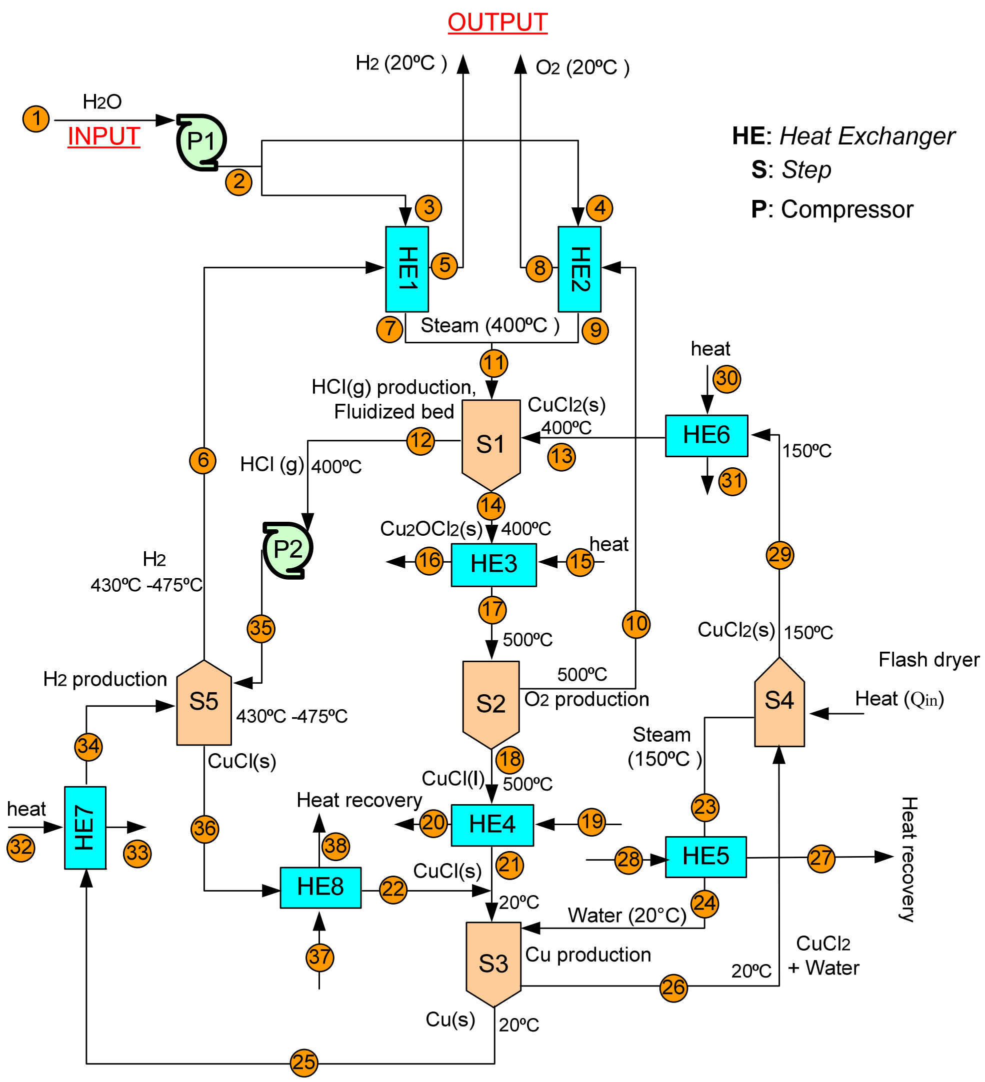

Figure 1: Conceptual layout of a thermochemical Cu-Cl hydrogen production cycle.

3 Analysis

The overall energy efficiency of the Cu-Cl cycle, η_e, can be expressed as the ratio of energy content of hydrogen based on lower heating value (*LHV*) to energy supplied. That is,

$$\eta_e = \frac{L\dot{H}V_{H_2}}{\dot{E}_{in}} \tag{1}$$

An exergy balance can be used in formulating an exergy efficiency for the reacting system; at steady state, the rate at which exergy enters the reacting system equals the rate at which exergy exits plus the rate at which exergy is destroyed within the system. The overall exergy efficiency can be written as

$$\eta_{ex} = \frac{\dot{E}x_p}{\dot{E}x_{in}} = \frac{\dot{E}x_{H_2}}{\dot{E}x_{in}} \tag{2}$$

where $\dot{E}x_{in}$ and $\dot{E}x_p$ are the exergy content of entering and exiting (with products) flows, respectively. Using the exergy balance for the reacting system, the exergy efficiency expression can be written alternatively as

$$\eta_{ex} = 1 - \frac{\dot{E}x_{loss}}{\dot{E}x_{in}} \tag{3}$$

The total cost to produce the exiting streams (hydrogen) equals the total cost of the entering streams plus the cost of owning and operating the cycle. This is expressed by the following cost rate balance for the cycle:

$$\dot{C}_{H_2} = \dot{C}_{in} + \dot{Z} \tag{4}$$

where $\dot{C}$ is the cost rate of the respective stream and $\dot{Z}$, accounts for the cost rate associated with owning and operating the cycle (each in $ per hour, for example). This equation simply states that the total cost of the exiting exergy streams equals the total expenditure to obtain them: the cost of the entering exergy streams plus the capital and other costs. Although the cost rates denoted by in Eq. (4) are evaluated by various means in practice, the present discussion features the use of exergy for this purpose. Since exergy measures the true thermodynamic values of the work, heat, and other interactions between a system and its surroundings as well as the effect of irreversibilities within the system, exergy is a rational basis for assigning costs. With exergy costing, each of the cost rates is evaluated in terms of the associated rate of exergy transfer and a unit cost. Thus, for an entering or exiting stream, we write

$$\dot{C} = c\dot{E}x \tag{5}$$

where *c* denotes the cost per unit of exergy (in cents per kWh, for example) and $\dot{E}x$ is the associated exergy transfer rate. In exergy costing, a cost is associated with each exergy stream. Rewriting Eq. (4),

$$c_{H_2} = \frac{c_{in}}{\eta_{ex}} + \frac{\dot{Z}}{\dot{E}x_{H_2}} \tag{6}$$

4 Results and Discussion

Energy and exergy efficiencies of the Cu-Cl cycle are shown in Fig. 2. The energy efficiency is 0.43 while exergy efficiency is 0.13. The variation of the cost of hydrogen produced with respect to the efficiencies of the Cu-Cl cycle is shown in Fig. 3. This graph is obtained using Eq. (6). The cost of hydrogen decreases by improving the energy or exergy efficiency of the cycle. This is because as efficiencies increase, the destruction cost, which represents the cost that been lost by exergy destruction, decreases.

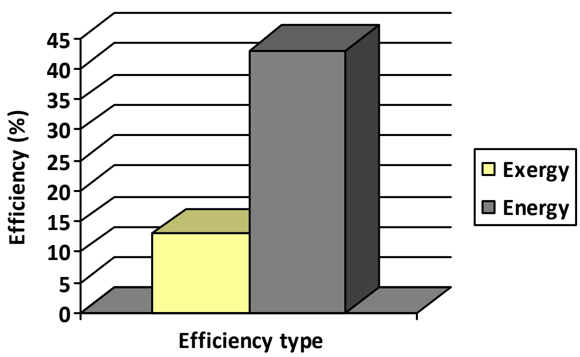

Figure 2: Energy and exergy efficiencies of the Cu-Cl thermochemical cycle.

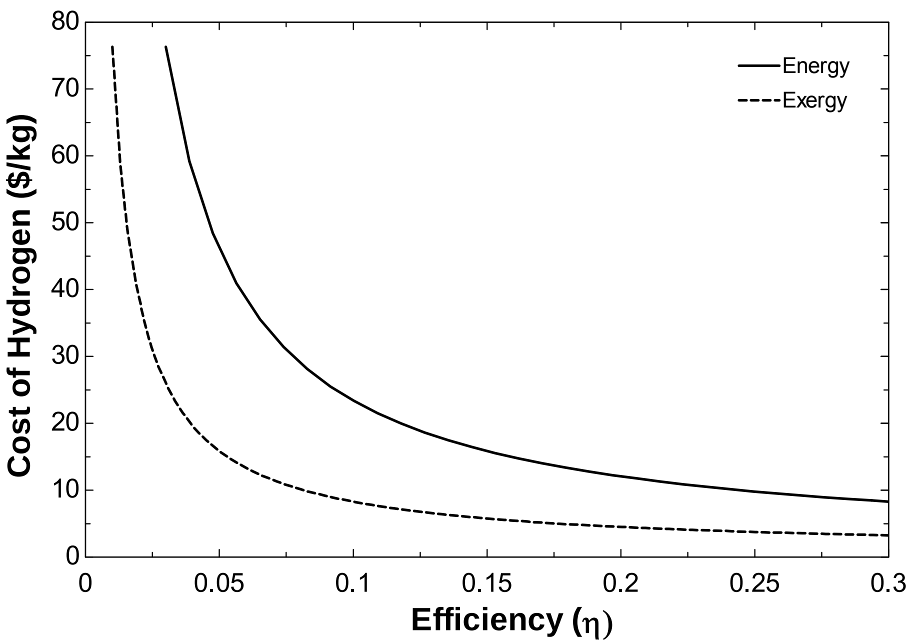

Figure 3: Variation of the cost of hydrogen produced with the efficiencies of the Cu-Cl cycle.

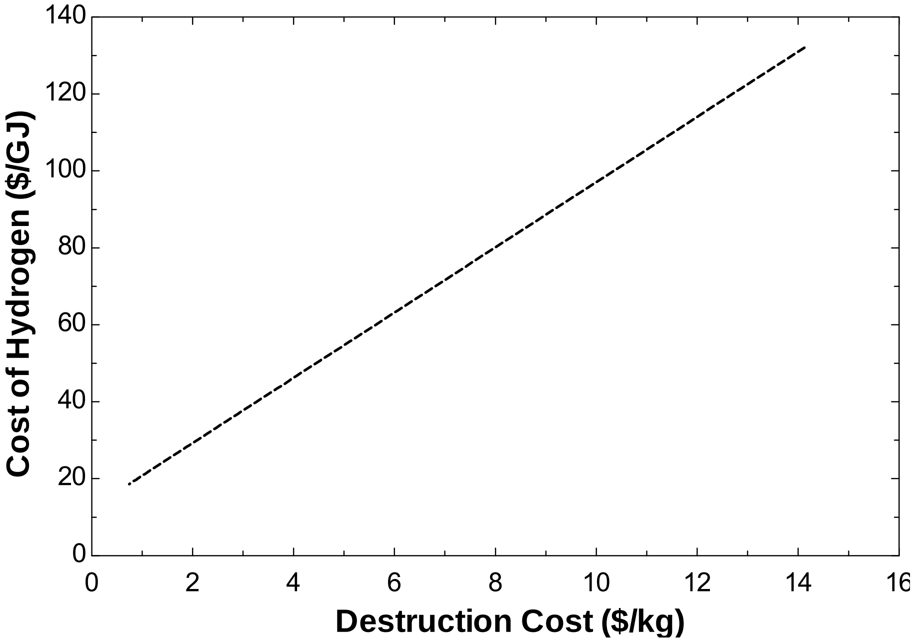

Figure 4: Variation of the cost of hydrogen produced with the cost of destruction in the Cu-Cl cycle.

The effect of the cost of destruction on the unit cost of hydrogen can be seen more clearly in Fig. 4. The cost rate of exergy destruction varies between $1 and $15 per kilogram of hydrogen while the cost of hydrogen rises from $20 to $140 per GJ of hydrogen energy. In Fig. 3, the cost of hydrogen is seen to be highest when the exergy efficiency approaches zero and it decreases as the exergy efficiency increases. The effect of exergy efficiency on the cost of hydrogen is very high in the efficiency range of 5 to 15% and very low in the efficiency range of 15 to 30%. The hydrogen cost approaches its lowest value and becomes roughly constant above an exergy efficiency of 30%. Clearly, an efficiency improvement measure should be evaluated carefully to determine whether it is economically worthwhile.

5 Conclusions

The Cu-Cl cycle has been shown to be a potentially attractive option for generating hydrogen from nuclear energy. Compared with other hydrogen production options, the thermochemical Cu-Cl cycle is expected to have a higher efficiency, to produce hydrogen at a lower cost, and to have a smaller impact on the environment by reducing airborne emissions, solid wastes and energy requirements.

This paper shows how exergy-related variables can be used to minimize the cost of a thermal system. The exergoeconomic analyses of the process reported in this paper for a Cu-Cl thermochemical water decomposition cycle for hydrogen production has allowed several findings. It identifies and evaluates the real energy waste and the real cost sources in the Cu-Cl cycle. The variations of hydrogen cost with parameters like energy and exergy efficiencies, exergy destruction and energy losses have been quantified and characterized. In particular, a parametric study is reported of how the unit costs of hydrogen and the cost rate of exergy destruction of the Cu-Cl cycle vary with the efficiency. This information should assist efforts to understand the thermodynamic losses in the cycle, and to improve its efficiency and cost effectiveness.

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