Thermochimica Acta 497 (2010) 60–66

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Exergoeconomic analysis of a thermochemical copper–chlorine cycle for hydrogen production using specific exergy cost (SPECO) method

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ARTICLE INFO

Article history:
Received 6 June 2009
Received in revised form 1 August 2009
Accepted 21 August 2009
Available online 31 August 2009

Keywords:
Hydrogen
Thermochemical water decomposition
Nuclear
Cost analysis
Energy
Exergy
Exergoeconomics
Specific exergy cost

ABSTRACT

The manner is investigated in which exergy-related parameters can be used to minimize the cost of a copper–chlorine (Cu–Cl) thermochemical cycle for hydrogen production. The iterative optimization technique presented requires a minimum of available data and provides effective assistance in optimizing thermal systems, particularly in dealing with complex systems and/or cases where conventional optimization techniques cannot be applied. The principles of thermoeconomics, as embodied in the specific exergy cost (SPECO) method, are used here to determine changes in the design parameters of the cycle that improve the cost effectiveness of the overall system. The methodology provides a reasonable approach for improving the cost effectiveness of the Cu–Cl cycle, despite the fact that it is still in development. It is found that the cost rate of exergy destruction varies between \$1 and \$15 per kilogram of hydrogen and the exergoeconomic factor between 0.5 and 0.02 as the cost of hydrogen rises from \$20 to \$140 per GJ of hydrogen energy. The hydrogen cost is inversely related to the exergoeconomic factor, plant capacity and exergy efficiency. The results are expected to assist ongoing efforts to increase the economic viability and to reduce product costs of potential commercial versions of this process. The impact of the results are anticipated to be significant since thermochemical water splitting with a copper–chlorine cycle is a promising process that could be linked with nuclear reactors to produce hydrogen with no greenhouse gases emissions, and thereby help mitigate numerous energy and environment concerns.

1. Introduction

Increasing demand for energy, combined with diminishing fossil-fuel resources and concerns about greenhouse gas emissions, have increased the interest in the efficient and cost effective generation and use of hydrogen. Interest has also increased on the development of fossil-fuel-fired “zero-emission” power plants [1].

The design of thermal systems requires the explicit consideration of engineering economics, as cost is always an important consideration. Thermoeconomics (also known as exergoeconomics) is the branch of engineering that combines exergy analysis and economic principles to provide information useful for designing a system and optimizing its operation and cost effectiveness, but not available through conventional energy analysis and economic evaluation. A plant owner wants to know the true cost at which each of the utilities is generated; these costs are then charged to the appropriate final products according to the type and amount of each utility used to generate each final product. Accordingly, the objectives of thermoeconomic analysis include one or more of the following: (a) to calculate separately the costs of each product generated by a system having more than one product, (b) to understand the cost formation process and the flow of costs in the system, (c) to optimize specific variables in a single component, and (d) to optimize the overall system [2,3].

Another important aspect of thermoeconomics is the use of exergy for allocating costs to the products of a thermal system. This involves assigning to each product the total cost to produce it, namely the cost of fuel and other inputs plus the cost of owning and operating the system (e.g., capital, operating and maintenance costs). Such costing is a common problem in plants where utilities such as electrical power, chilled water, compressed air and steam are generated in one department and used in others. The plant operator needs to know the cost of generating each utility to ensure that the other departments are charged properly according to the type and amount of each utility used. Common to all such considerations are fundamentals from engineering economics, including procedures for annualizing costs, appropriate means for allocating costs and reliable cost data [4].

The total cost is the sum of the capital cost and the fuel and other operating costs. A simple example of optimizing design variables is shown in Fig. 1, where the total cost curve exhibits a minimum at the point labelled a. Note that the curve is relatively flat in the neighbourhood of the minimum, so there is a range of design

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doi:10.1016/j.tca.2009.08.008

Nomenclature

c	cost per unit of exergy ($/GJ)
$\dot{C}$	cost rate ($/kg)
E	energy
$\dot{E}$	energy rate (GJ/kg)
$\dot{E}x$	exergy rate (GJ/kg)
f	exergoeconomic factor
Q	thermal energy
RCD	relative cost difference
T	temperature (°C)
$\dot{Z}$	cost rate of owning and operating the cycle ($/kg)
η	efficiency

Subscipts

e	electrical
ex	exergetic
f	fuel
in	inlet
out	outlet
p	products
0	reference state
dest	destruction

variables that could be considered nearly optimal from the standpoint of minimum total cost. If reducing the fuel cost were deemed more important than minimizing the capital cost, we might choose a design that would operate at point a′. Point a″ would be a more desirable operating point if capital cost were of greater concern. Such trade-offs are common in design situations [4].

The actual design process can differ significantly from the simple case considered above. For instance, costs cannot be determined as precisely as implied by the curves in Fig. 1. Fuel prices may vary widely over time, and equipment costs may be difficult to predict as they often depend on a bidding procedure. Equipment is manufactured in discrete sizes, so the cost also does not vary continuously as shown in the figure. Furthermore, thermal systems usually consist of several components that interact. Optimization of components individually usually does not guarantee an optimum for the overall system. Finally, a general system involves numerous design variables must be considered and optimized simultaneously [4].

The development and application of exergoeconomics has provided a theoretical basis for designing efficient and cost effective energy systems. Since the 1950s, exergoeconomics has been described in various studies and applied to numerous technologies and processes [5–19]. For example, Hua et al. [8] presented a new exergoeconomic approach to optimize energy systems in which, after tracing the energy evolution and degradation within a system, a binary subsystem model was proposed and optimization strategies introduced.

Exergonomics mirrors ordinary economics, using exergy expenditures instead of monetary ones. Some examples of optimization by a simple relation of invested exergy and current exergy expenditures, including heat transfer through a wall, an electrical conductor and a thermal insulating wall, have been recommended for educational purposes by Yantovski [9]. The progress of a systematic exergoeconomic methodology for analysis and optimization of process systems has been described by Zhang et al. [10]. Based on a three-link-model, by applying a reversed exergy costing method to process systems, a hierarchical exergoeconomic model has been developed and the decomposing-coordinating optimization strategy has been introduced to analyze and optimize the total process or system. A retrofit of an aromatic separation system has been used to illustrate this method [10].

A combination of exergy and economic analysis for complex energy systems has been proposed by Kim et al. [11]. A general cost-balance which can be applied to any component of a thermal system has been derived. In the study, the exergy of material streams is decomposed into thermal, mechanical and chemical exergy flows and an entropy-production flow. A unit exergy cost is assigned to each disaggregated exergy in the streams at any state. The methodology results in a set of equations for the unit costs of various exergies by applying the cost-balance to each component of the system and to each junction. The monetary evaluations of various exergy costs (thermal, mechanical, etc.), as well as the production cost of electricity for the thermal system, have been obtained by solving the set of equations. The lost costs of each system component can also be obtained by this method. The proposed exergy costing method has been applied to a 1000-kW gas turbine cogeneration system [11].

Tsatsaronis and Moran [12] have studied exergy-aided cost minimization, which shows how exergy-related variables can be used to minimize the cost of a thermal system. These variables include the exergy efficiency, the rates of exergy destruction and exergy loss, an exergy destruction ratio, the cost rates associated with exergy destruction, capital investment and operating and maintenance, a relative cost difference of unit costs and an exergoeconomic factor. A simple cogeneration system is used as an example

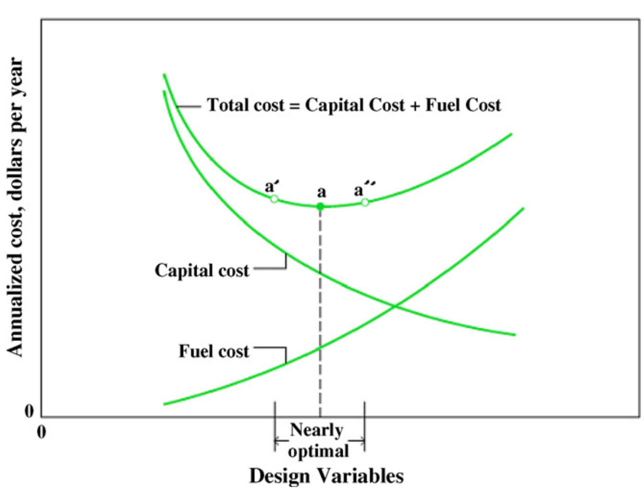

Fig. 1. Optimizing a design parameter based on total annualized cost [4].

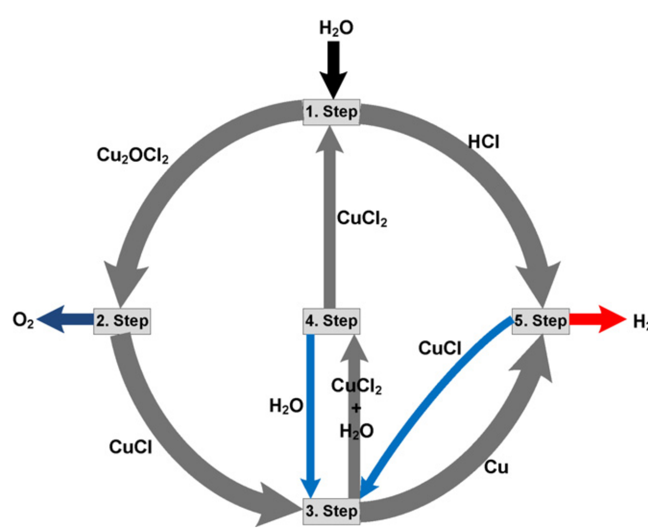

Fig. 2. Cu–Cl thermochemical cycle for hydrogen production.

Table 1
Main steps in the Cu–Cl cycle with their corresponding reactions.

Step	Reaction	Temperature range (°C)	Pressure (kPa)	Feed/output[a]	
1	$2CuCl_2(s)+H_2O(g) \rightarrow CuO^*CuCl_2(s)+2HCl(g)$	400	101	Feed: Output:	$CuCl_2(s)+H_2O+Q$ $CuO^*CuCl_2(s)+HCl(g)$
2	$CuO^*CuCl_2(s) \rightarrow 2CuCl(l)+(1/2)O_2(g)$	500	101	Feed: Output:	$CuO^*CuCl_2(s)+Q$ Molten CuCl salt + O_2
3	$4CuCl(s)+H_2O \rightarrow 2CuCl_2(aq)+2Cu(s)$	25–80	101	Feed: Output:	CuCl and H_2O+E_e Cu and slurry
4	$CuCl_2(aq) \rightarrow CuCl_2(s)$	>100	101	Feed: Output:	$CuCl_2(aq)+Q$ $CuCl_2+H_2O$ vapors
5	$2Cu(s)+2HCl(g) \rightarrow 2CuCl(l)+H_2(g)$	430–475	101	Feed: Output:	Cu + HCl H_2 + CuCl(l) salt + Q

[a] Q denotes thermal energy and E_e electrical energy.

to demonstrate the application of an iterative exergy-aided cost minimization method [12].

A comprehensive methodology for the analysis of systems and processes, based on the quantities exergy, cost, energy and mass, and referred to as EXCEM analysis, was developed by Rosen and Dincer [13]. The first law of thermodynamics embodies energy analysis, which identifies only external energy wastes and losses. Potential improvements for the effective use of resources are not consistently evaluated with energy, e.g., for an adiabatic throttling process. However, the second law of thermodynamics, which can be formulated in terms of exergy, takes entropy into consideration and accounts for irreversibilities. Economics, which are also important, are incorporated in EXCEM analysis through costs.

An EXCEM analysis of a copper–chlorine (Cu–Cl) thermochemical cycle for hydrogen production has been reported [20]. The current study continues that work by discussing how exergy-related parameters can be used to minimize the cost of a thermal system in general and the Cu–Cl cycle in particular. In this paper, principles of thermoeconomics, as embodied in the specific exergy cost (SPECO) method, are used to determine changes in the design parameters of the cycle that result in an improvement of the cost effectiveness of the overall system. We also present an exergy analysis of the Cu–Cl cycle and its 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 all equipment in the process. The methodology used provides an exploratory approach for improving the cost effectiveness of the Cu–Cl cycle, which is reasonable since the process is still in development.

2. The copper–chlorine (Cu–Cl) cycle

A conceptual layout of a Cu–Cl plant for thermochemical water decomposition is illustrated in Fig. 2. The cycle, potentially driven by nuclear heat, splits water into hydrogen and oxygen through intermediate copper and chlorine compounds. This cycle includes three thermochemical reactions and one electrochemical reaction.

The cycle involves five steps (Table 1):

1. HCl(g) production, using such equipment as a fluidized bed,
2. oxygen production,
3. copper (Cu) production,
4. drying, and
5. hydrogen production.

A chemical reaction takes place in each step, except drying. The chemical reactions form a closed internal loop that recycles all of the copper–chlorine compounds on a continuous basis, without emitting greenhouse gases externally to the atmosphere. The Cu–Cl cycle thus represents a promising method to produce hydrogen efficiently and environmentally benignly.

Many studies (e.g., [20–29]) of the Cu–Cl cycle have shown that it offers 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.

3. Analysis

A comprehensive exergoeconomic analysis of the Cu–Cl cycle consists of (a) an exergy analysis [21–25], (b) an economic analysis [26,27], (c) exergy costing, and (d) an exergoeconomic evaluation [20]. In the exergy analysis, we evaluate the exergy of all streams in the cycle as well as the rate of exergy destruction, $\dot{E}x_{dest}$, and the exergy (second law) efficiency η_{ex} for each plant component.

In an economic analysis of thermal systems, the annual values of carrying charges, fuel costs, raw water costs, and operating and maintenance expenses $\dot{Z}$ supplied to the overall system are necessary inputs. However these cost components may vary significantly over their economic lives. Therefore, levelized (annualized) values for all cost components are typically used in the economic analysis and evaluations of the overall system.

Several thermoeconomic approaches are reported in the literature. One, the specific exergy costing (SPECO) method [12] is used throughout this study. This method is based on specific exergies and costs per exergy unit, exergy efficiencies, and the auxiliary cost-

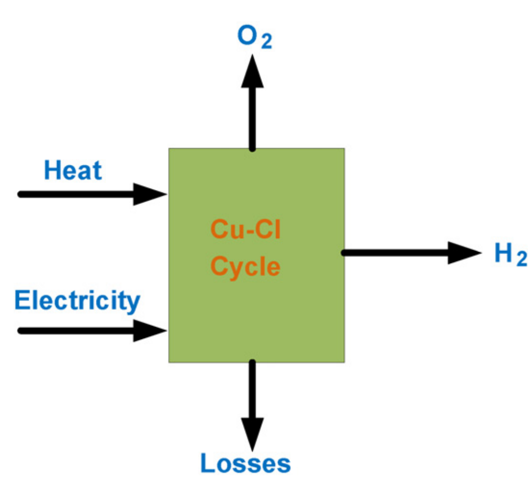

Fig. 3. Inlet and outlet streams of the Cu–Cl thermochemical cycle.

ing equations for system components. The method consists of the following three steps: (i) identification of exergy streams, (ii) definition of fuel and product for each system component and (iii) allocation of cost equations. For the exergoeconomic analysis, it is helpful to define a fuel and a product for the Cu–Cl cycle (see Fig. 3).

The SPECO methodology [12] can be used as an exploratory approach aimed at improving the cost effectiveness of a thermal system, and involves the following steps:

- Rank the components in descending order of cost importance using the sum $(\dot{Z}+\dot{C}_{dest})$.
- Consider design changes initially for components for which the value of this sum is high.
- Pay particular attention to components with a high relative cost difference (*RCD*), especially when the cost rates $\dot{Z}$ and $\dot{C}_{dest}$ are high.
- Use the exergoeconomic factor *f* to identify the major cost source (capital investment or cost of exergy destruction):
  - if *f* is high, investigate whether it is cost effective to reduce the capital investment for the *k*th component at the expense of component efficiency; and
  - if *f* is low, try to improve the component efficiency by increasing the capital investment.
- Eliminate any subprocesses that increase the exergy destruction or exergy loss without contributing to the reduction of capital investment or of fuel costs for other components.
- Consider improving the exergy efficiency of a component if it has a relatively low exergy efficiency or relatively large values of exergy destruction, exergy destruction ratio, or exergy loss ratio.

When applying this methodology, it is important to recognize that the values of all thermoeconomic variables depend on the component types (heat exchanger, compressor, pump, chemical reactor, etc.). Accordingly, whether a particular value is judged to be high or low can be determined only with reference to a particular class of components. It is also important to consider the effects of contemplated design changes in one component on the performance of the remaining components. These effects may be determined either by inspection of the system flowsheets or by using a simulation program, which is the subject of ongoing research by the authors.

The methodology introduced above is now applied to the Cu–Cl cycle, in order to identify the effects of the design variables on the costs and suggest modifications to the design variables that can make the system more cost effective.

The total cost to produce the exiting streams (hydrogen and losses) equals the total cost of the entering streams plus the cost of owning and operating the cycle. Here we treat oxygen as a waste, although it is also a potential by-product. The following cost rate balance can be expressed for the cycle:

$$\dot{C}_{H_2}+\dot{C}_{O_2}+\dot{C}_{\text{Losses}}=\dot{C}_{\text{Heat}}+\dot{C}_{\text{Electricity}}+\dot{Z} \tag{1}$$

where $\dot{C}$ denotes the cost rate of the respective stream and $\dot{Z}$ the cost rate associated with owning and operating the cycle. The cost rates are expressed in units like $/h, for example. Eq. (1) 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. Since we treat oxygen and heat losses from the cycle as wastes, we can assume the unit costs $\dot{C}_{O_2}$ and $\dot{C}_{\text{Losses}}$ are both zero. Thus, Eq. (1) simplifies to

$$\dot{C}_{H_2}=\dot{C}_{\text{Heat}}+\dot{C}_{\text{Electricity}}+\dot{Z} \tag{2}$$

In the present discussion, the cost rate $\dot{Z}$ is presumed known from a previous economic analysis [26,27]. Although the cost rates denoted in Eq. (1) 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 can write

$$\dot{C}=c\dot{E}x \tag{3}$$

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. Exergy cost rates associated with matter, electricity and heat flows may be written respectively as

$$\dot{C}_{\text{matter}}=(c\dot{E}x)_{\text{matter}} \tag{4}$$

$$\dot{C}_{\text{Electricity}}=(c\dot{E}x)_{\text{Electricity}}=(c\dot{E})_{\text{Electricity}} \tag{5}$$

$$\dot{C}_{\text{Heat}}=(c\dot{E}x)_{\text{Heat}}=\left[c\left(1-\frac{T_0}{T}\right)\dot{E}\right]_{\text{Heat}} \tag{6}$$

Thus Eq. (2) can be expressed as follows:

$$(c\dot{E}x)_{H_2}=(c\dot{E}x)_{\text{Heat}}+(c\dot{E}x)_{\text{Electricity}}+\dot{Z} \tag{7}$$

Solving for the unit cost of hydrogen c_{H_2} yields

$$c_{H_2}=\frac{c_{\text{in}}(\dot{E}x_{\text{Heat}}+\dot{E}x_{\text{Electricity}})+\dot{Z}}{\dot{E}x_{H_2}} \tag{8}$$

where c_{in} is the unit cost of exergy. Introducing the cycle exergy efficiency η_{ex} as

$$\eta_{\text{ex}}=\frac{\dot{E}x_{\text{out}}}{\dot{E}x_{\text{in}}}=\frac{\dot{E}x_{H_2}}{\dot{E}x_{\text{Heat}}+\dot{E}x_{\text{Electricity}}} \tag{9}$$

we can combine Eq. (8) with Eq. (9) to obtain

$$c_{H_2}=\frac{c_{\text{in}}}{\eta_{\text{ex}}}+\frac{\dot{Z}}{\dot{E}x_{H_2}} \tag{10}$$

When the SPECO method is applied, the performance of a component can be defined and the cost flow rates through components associated with the exergy loss are calculated using the cost history of the plant. This is provided by the exergoeconomic factor *f* defined as

$$f=\frac{\dot{Z}}{\dot{Z}+c_{\text{in}}\dot{E}x_{\text{dest}}} \tag{11}$$

Here, $\dot{E}_{\text{dest}}$ is the corresponding exergy destruction of the cycle. Another useful variable in thermoeconomic evaluations is the relative cost difference (*RCD*), which measures the relative increase in the average cost per exergy unit between fuel and product of the component. The relative cost difference for the cycle can be written as

$$RCD=\frac{c_p-c_f}{c_f} \tag{12}$$

where c_p is the unit exergetic cost of the product of the system and c_f is the unit exergetic cost of the fuel used. For the Cu–Cl cycle,

$$RCD=\frac{c_{H_2}-c_{\text{in}}}{c_{\text{in}}} \tag{13}$$

The relative cost difference is a useful variable for evaluating and optimizing a system component. Finally, the cost rate of exergy destruction is defined as

$$\dot{C}_{\text{dest}}=c_{\text{in}}\dot{E}x_{\text{dest}} \tag{14}$$

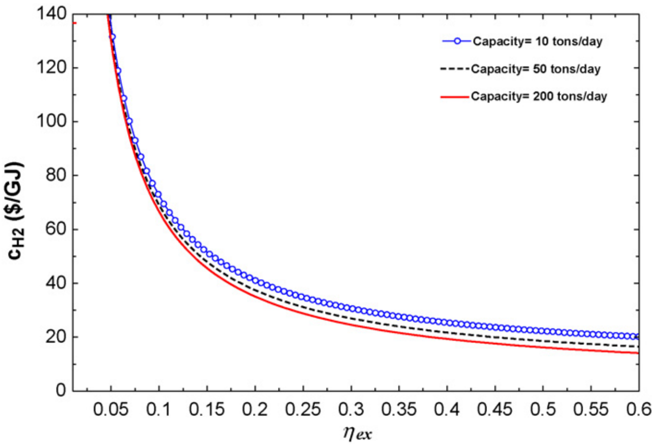

Fig. 4. Variation of the unit cost of hydrogen with exergy efficiency of the Cu–Cl cycle, for several hydrogen production capacities.

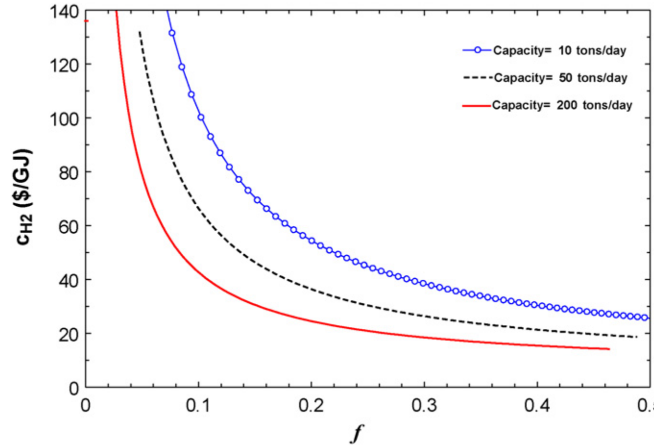

Fig. 7. Relation between the unit cost of hydrogen and exergoeconomic factor *f*, for several hydrogen production capacities.

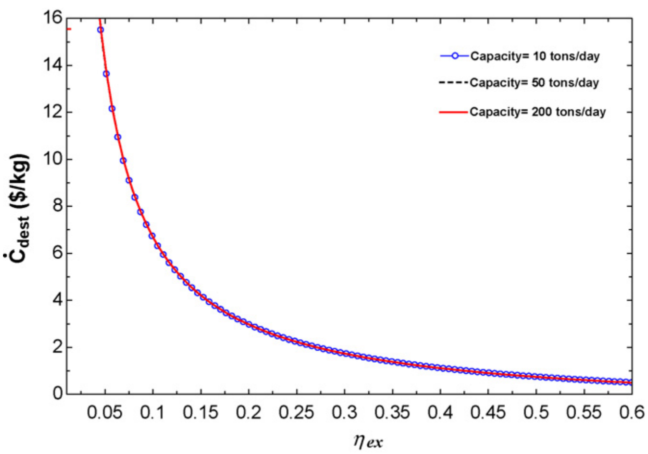

Fig. 5. Relation between cost rate of exergy destruction and exergy efficiency, for several hydrogen production capacities.

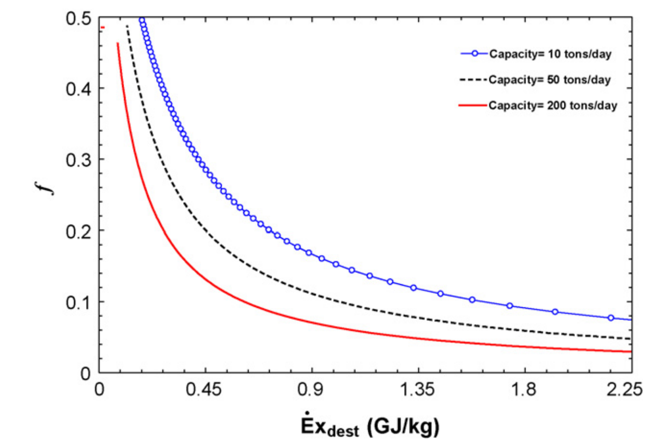

Fig. 8. Variation with exergy destruction rate of the exergoeconomic factor, for several hydrogen production capacities.

4. Results and discussion

Exergoeconomic analyses consider the quality of energy, as measured by exergy, in allocating the costs of a process to its products. It is important to determine the critical points in the unit from the exergy viewpoint and to properly allocate the total cost to the product streams, to determine the monetary flows through the cycle, and to state the relevance in economic terms of the exergy losses of each component.

The variation of the unit cost of hydrogen with respect to the exergy efficiency of the Cu–Cl cycle is shown in Fig. 4. This graph is obtained using Eq. (10) for three plant capacities (10, 50 and 200 tons/day). These capacities represent typical industrial-scale

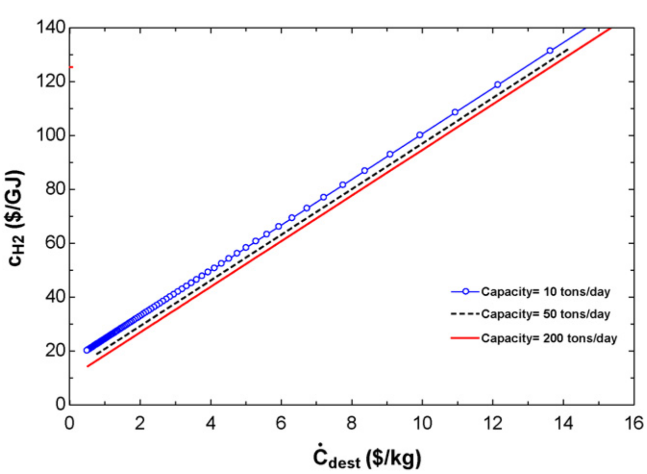

Fig. 6. Variation of the unit cost of hydrogen with the cost rate of exergy destruction, for several hydrogen production capacities.

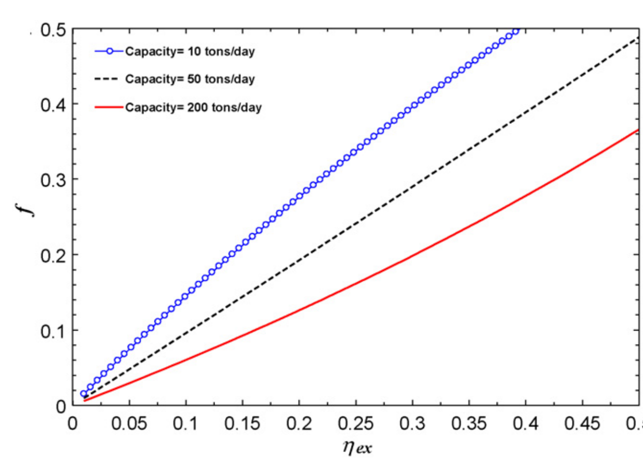

Fig. 9. Variation of exergoeconomic factor with cycle exergy efficiency, for several hydrogen production capacities.

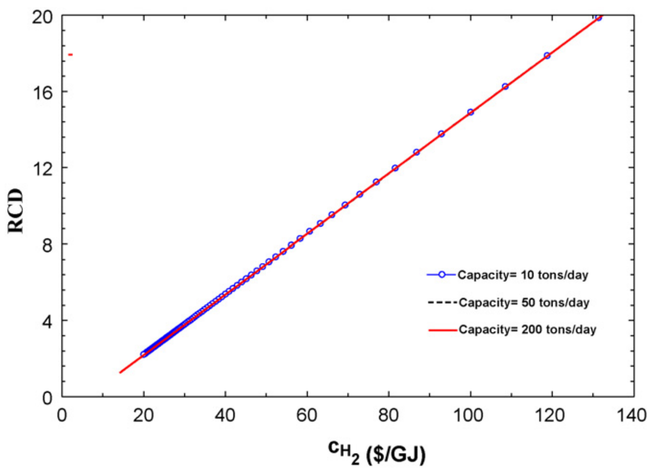

Fig. 10. Variation of the relative cost difference (*RCD*) with the unit cost of hydrogen, for several hydrogen production capacities.

values for gas production processes, and are used to determine the effect of plant capacity on hydrogen cost. It can be seen from the figure that a larger plant capacity leads to a lower unit cost of hydrogen since the capital and operating costs of the cycle ($\dot{Z}$) per unit mass of hydrogen is smaller for a larger capacity plant. The cost of hydrogen decreases also by improving the exergy efficiency of the cycle. This is because as exergy efficiency increases, the exergy destruction cost ($\dot{C}_{dest}$), which represents the cost that been wasted by exergy destruction, decreases. The inversely proportional relation between the cost rate of exergy destruction and exergy efficiency is illustrated in Fig. 5. The cost rate of exergy destruction continually increases as the exergy efficiency approaches zero, and approaches zero as the exergy efficiency approaches unity. It is observed in the figure that the capacity of the plant does not affect the relation between cost rate of exergy destruction and efficiency. The effect of the cost rate of exergy destruction on the unit cost of hydrogen can be seen more clearly in Fig. 6. 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. 4, 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 efficiency on the cost of hydrogen is very high in the efficiency range of 5–30% and very low in the efficiency range of 30–60%. The hydrogen cost approaches its lowest cost and becomes roughly constant above an exergy efficiency of 60%.

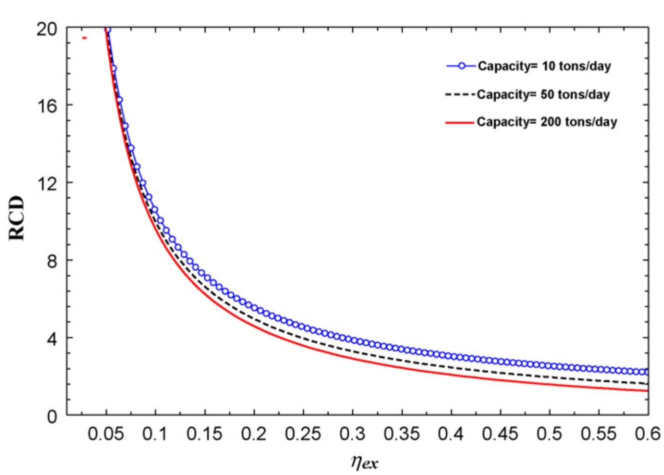

Fig. 11. Variation with exergy efficiency of the relative cost difference (*RCD*), for several hydrogen production capacities.

Clearly, an efficiency improvement measure should be evaluated carefully to determine whether it is economically worthwhile.

The relation between the unit cost of hydrogen and exergoeconomic factor *f* is presented in Fig. 7. The exergoeconomic factor varies between 0.02 and 0.5 while the hydrogen cost varies from $20/GJ to $140/GJ. The hydrogen cost is inversely proportional to the exergoeconomic factor, mainly because by improving the exergoeconomic factor, the exergy destruction rate decreases and hence the exergy efficiency increases. The effect on the exergoeconomic factor of exergy destruction and exergy efficiency is shown in Figs. 8 and 9, respectively.

Fig. 10 shows the variation of the relative cost difference (*RCD*), the relative increase in the average cost per exergy unit between fuel (inlet energy) and product (hydrogen), with the unit cost of hydrogen. Increasing the relative cost difference raises the cost of hydrogen linearly since it is inversely proportional to exergy efficiency (see Fig. 11).

5. Conclusions

Results are presented of the thermodynamic simulation, economic and exergoeconomic analyses of the copper–chlorine (Cu–Cl) thermochemical cycle for hydrogen production, including estimates of product costs. The exergoeconomic analysis identifies and evaluates the actual energy losses and the real cost sources in the Cu–Cl cycle. This analysis is a useful tool in evaluating the potential for improving the cycle efficiency and cost effectiveness. With the aid of this analysis, cost parameters can be approximated, even without the existence of designs for the total cycle.

This paper demonstrates also how exergy-related parameters can be used to reduce the cost of a thermal system and possibly minimize it. These parameters include the exergy efficiency, rates of exergy destruction and exergy loss, the exergy destruction ratio, cost rates associated with exergy destruction, capital investment and operating and maintenance costs, the relative cost difference of unit costs, and an exergoeconomic factor.

The iterative technique presented here requires a minimum of available data and provides effective assistance in improving and optimizing thermal systems, particularly when they are complex and/or in cases where conventional optimization techniques cannot be applied in system optimization.

Acknowledgement

The authors gratefully acknowledge the financial support provided by the Ontario Research Excellence Fund.

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