Thermodynamic Performance Comparison of some Renewable and Non- Renewable Hydrogen Production Processes

M. Tolga Balta, A. Hepbasli, I. Dincer

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M. Tolga Balta, Arif Hepbasli, Department of Mechanical Engineering, Faculty of Engineering, Ege University, 35100 Bornova, Izmir, Turkey
Ibrahim Dincer, Faculty of Engineering and Applied Science, University of Ontario Institute of Technology (UOIT), Oshawa, Canada

Abstract

This paper compares thermodynamic performance, through energy and exergy efficiencies, of the some renewable-based (e.g. geothermal) and non-renewable-based hydrogen production processes, namely: (1) steam methane reforming (SMR), (2) hybrid copper–chlorine (Cu–Cl) supplied by geothermal heat and electricity from a geothermal power plant, (3) high temperature steam electrolysis (HTSE) supplied by geothermal heat and electricity from a geothermal power plant. These processes are essentially driven by two different sources such as fossil fuel and geothermal. The results show that energy and exergy efficiencies during hydrogen production range from 65-89% and 63-80% for the SMR. The efficiencies of geothermal-based hydrogen production processes seem to be a bit lower than that of SMR. However, these processes can drastically reduce the GHG emissions compared to non-renewable energy based ones, e.g., SMR process.

Keywords: SMR, Thermochemical, Hybrid, Electrolysis, Energy, Exergy, Efficiency.

1   Introduction

Currently more than 80% of the world's energy supply comes from fossil fuels. As everyone knows, fossil fuel reserves are diminishing rapidly across the world. Beside of this, utilization of fossil fuels emits greenhouse gases, like carbon dioxide, which cause global warming to the environment and hence it is crucial to find alternative, emerging energy solutions that can help reduce greenhouse gas (GHG) emissions as soon as possible. Hydrogen is widely believed to be world's next-generation fuel, because of its reduced environmental impact, more significantly reduced greenhouse gas emissions. In this regard, hydrogen is seen as a sustainable energy carrier which can serve as a potential solution to the current environmental problems since it is a clean energy carrier that is environmentally-benign and sustainable, compared to fossil fuels [1-3].

Hydrogen, which does not exist alone in nature, can be produced from a variety of feedstocks; from fossil resources such as natural gas and coal and from renewable resources. It is always found in the form of compounds and high value energy needs to be consumed for its production. All hydrogen production processes are based on the separation of hydrogen from hydrogen containing compounds from either fossil fuels or water. Recently, further studies have been conducted to develop techniques/technologies for global-scale hydrogen production, in the short-term production of hydrogen from fossil fuels (mainly

natural gas), and in the long-term, hydrogen will be produced from renewable energy. Fig. 1 is a pie chart, showing that 96% hydrogen is currently produced directly from fossil fuels, while about 4% is produced indirectly by electricity utilization.

Although, some of hydrogen production methods, such as steam methane reforming (SMR), are well developed and established for commercial use, it has some disadvantages, such as using extensive amount of electricity and releasing high levels of CO_2. On the other hand, fossil fuel prices are anticipated to increase. Clearly, there is a strong and urgent need to find alternative, environmentally benign ways for hydrogen production. There are limited options for affordable environment friendly hydrogen production. Many researches conduct extensive research on "new technologies for producing hydrogen" that are more cost effective, without greenhouse gas emissions. Alternative clean and efficient pathways for the production of pure hydrogen are water electrolysis and thermochemical water-splitting cycles with renewable energy sources, e.g., solar energy, wind energy, hydropower, biomass and geothermal. These methods are considered the most promising processes for hydrogen production in the future hydrogen economy. Reducing the cost and environmental impact of hydrogen production is a key challenge facing the future transition to a hydrogen economy [5].
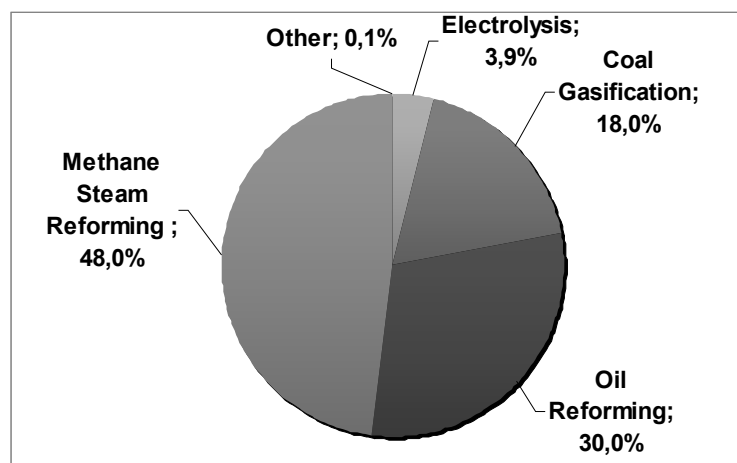

Figure 1:   Feedstock used in the present global hydrogen production (data taken from Ref. [4]).

When considering the use of renewable energy for hydrogen production, geothermal resources seem to be an important and attractive option. In countries with abundant amounts of geothermal energy, certainly geothermal-based hydrogen production will become a major player in hydrogen economy. This can be done in two ways: namely i) by using both geothermal heat and electricity for high temperature steam electrolysis and/or hybrid processes, ii) by using the heat available from geothermal resource in thermochemical processes, of which has been identified in more detail [6-8]. These production methods are still in the developmental stage for commercial applications and require further research and development.

Although numerous studies have been conducted on non-renewable-based hydrogen production processes in the open literature [e.g., 9-15], very few papers and reports are available on hydrogen production from geothermal resources [e.g., 6-8, 16-18]. To the best knowledge of the authors, no studies have been undertaken to compare the performances of some renewable-based (e.g. geothermal) and non-renewable-based (e.g., SMR) hydrogen production processes through exergy analysis. In this study, a geothermal-based (and non-renewable-based hydrogen production processes, namely: (1) steam methane reforming (SMR), (2) hybrid copper–chlorine (Cu–Cl) supplied by geothermal heat and electricity from a geothermal power plant, (3) high temperature steam electrolysis (HTSE) supplied by geothermal heat and electricity from a geothermal power plant compared thermodynamically through energy and exergy efficiencies. Moreover, sustainability index and environmental impact ratios of the considered processes are compared each other.

2   Description of Processes

Here, energy and exergy efficiencies of some renewable-based (e.g. geothermal) and non-renewable-based hydrogen production processes are compared for: (1) steam methane reforming (SMR), (2) hybrid copper–chlorine (Cu–Cl) driven by geothermal heat and electricity from a geothermal power plant, (3) high temperature steam electrolysis (HTSE) driven by geothermal heat and electricity from a geothermal power plant.

Steam methane reforming (SMR): This is the most common method of producing hydrogen. Fig. 2 shows a simplified schematic diagram of a SMR system. Here, the required heat is obtained from an external energy source. Also, it can be provided through combustion of additional methane and/or from using the available energy in the separated exhaust stream through combustion or simple heat exchange [15].
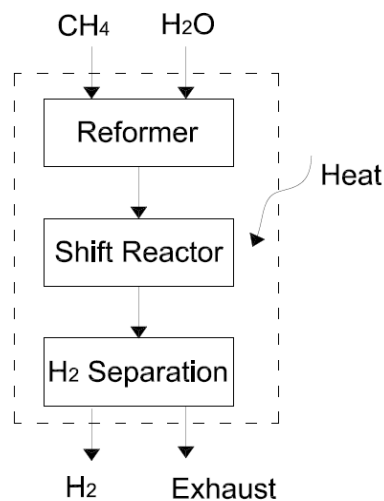

Figure 2:   **Simplified schematic diagram of an SMR process. (adopted from Ref. [15])**

In this process, methane and steam react over a high-temperature catalyst.

$$CH_4 + H_2O \text{ (g)} \rightarrow CO + 3H_2 \tag{1}$$

The reaction is endothermic. And then syngas exiting the reformer is passed through a reactor that converts the CO in the syngas to CO_2 and H_2 using the available H_2O in the syngas or additional H_2O to system.

$$CO + H_2O \text{ (g)} \rightarrow CO_2 + H_2 \tag{2}$$
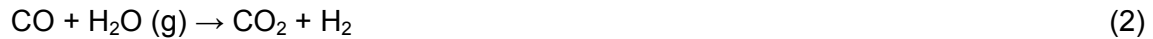
which is exothermic, but the overall reactions in Eqs. (1) and (2) are endothermic. The last step of the SMR process is the separation of the hydrogen from the syngas exiting the reactor, which is mostly H_2, H_2O, and CO_2 [15].

Simpson et al. [15] evaluated the performance of hydrogen production via steam methane reforming (SMR) process using exergy analysis to study both energy and exergy efficiencies. This comparison is given in Table 1. As can be seen in this table, the efficiencies during hydrogen production range between 65-89% for energy efficiency and 62-80% for exergy efficiency.

Table 1:   Comparison of SMR energy and exergy efficiencies. (Adopted from Ref. [15])

References	η (%)	ψ (%)	Notes
Rosen [9]	86	78.5	Detailed system analysis with heat-integration. Uses global reformation model with PSA CO_2 separation and methanation.
Lambert et al. [10]	-	76.62[a]	Purpose of paper was to analyze SMR with oxygen enriched combustion. Uses equilibrium reformer model. Separation method is not described.
Sorin et al. [11]	-	79.88	Only analyzes natural gas reformation to syngas. Reformation heat is provided by combustion of extra fuel.
Simbeck [12]	65.3 , 76.2	-	Purpose of paper was to determine hydrogen production costs. Details of SMR were not described.
Lutz et al. [13]	89[b], 81[c]	-	First law based analysis. Analyzes both a global and equilibrium reformer. Reformer heat is provided by combustion of retentate stream exiting membrane. Does not use detailed heat-integration.
Bargigli et al. [14]	77[d]	71[d]	Purpose of paper was to use a multi-criteria approach to compare hydrogen production pathways through energy, exergy, and emergy analysis.
Simpson et al. [15]	66.7	62.7	Purpose of paper is to apply exergy analysis to the production of hydrogen via natural gas SMR. In this study, the reformer operates at 6.8 bar.
a Uses slightly different exergy efficiency definition.			
b Maximum energy efficiency using global reaction model going to equilibrium.			
c Maximum energy efficiency using equilibrium reformer model.			
d Values taken from National Renewable Laboratory report.			

Hybrid copper–chlorine (Cu–Cl) cycle: This cycle was originally proposed in the 1970s and has recently been proven at laboratory level. It is a hybrid cycle using mainly heat and some electricity to disassociate water into hydrogen and oxygen at a maximum process

temperature of 550°C. In the literature, numerous studies on hydrogen production using Cu-Cl cycles have recently been carried out by many researchers. For example, the steps of the Cu–Cl cycle for nuclear-based hydrogen production have been examined in detail by Orhan et al. [19–23] using exergy analysis approach. Naterer et al. [24] have analyzed the heat requirements for the steps and studied the ways to recover heat in order to minimize the net heat supply for the overall cycle which will improve its overall efficiency. Lewis et al. [25, 26] have studied the Cu-Cl cycle's performance and extended the study for hydrogen production costs. A simple conceptual layout of the Cu-Cl cycle is shown in Fig. 3. It basically consists of five main steps:

(i) $HCl_{(g)}$ production step,

(ii) O_2 production step,

(iii)   Cu production step,

(iv)   drying step, and

(iv)   hydrogen production step.

A chemical reaction takes place in each step, except the drying step. These chemical reactions form a closed internal loop that recycles all of the copper–chlorine compounds on a continuous basis, without emitting any greenhouse gases externally to the atmosphere [27].

Balta et al. [8] analyzed the performance of low temperature thermochemical cycles through energy and exergy efficiencies. The energy and exergy efficiencies of the Cu-Cl cycle were calculated as 51% and 65%, respectively, based upon the complete reactions. This cycle was identified as a highly promising cycle for geothermal-hydrogen production.
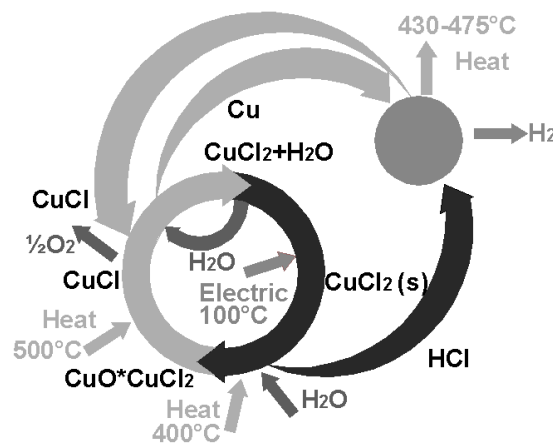

Figure 3:   Simplified schematic diagram of Cu-Cl cycle.

High temperature steam electrolysis (HTSE): In this process, hydrogen production through direct thermal decomposition of water can be done only if the temperature of primary heat source is more than 2500 K. This is not feasible at an industrial level with the present technology. From a thermodynamic viewpoint of water decomposition, it is more advantageous to produce hydrogen if the energy is supplied in mixed form of electricity and heat. Geothermal heat and electricity can be used in HTSE. Balta et al. [6, 7] investigated the thermodynamic performance, through energy and exergy efficiencies, of the HTSE process

coupled with and powered by a geothermal source. The energy and exergy efficiencies at a temperature range of 473 K to 1173 K were found to be from 80% to 87% and from 79% to 86%, respectively.

3 Analysis

In the analysis, the following parameters are studied and the compared with each other.
Exergy efficiency and sustainability index

Sustainable development requires not only that the sustainable supply of clean and affordable energy resources be used, but also the resources should be used efficiently. Exergy methods are very useful tools for improving efficiency, which maximize the benefits and usage of resources and also minimize the undesired effects (such as environmental damage). Exergy analysis can be used to improve the efficiency and sustainability [24].

The relationship between exergy efficiency (ψ) and the sustainability index (SI), as given in [7], is modified here for this application:

$$\psi = 1 - \frac{1}{SI} \tag{3}$$

where

$$SI = \frac{1}{D_P} \tag{4}$$

Here, D_P is the depletion factor defined by Connelly and Koshland [28] as the ratio of exergy destruction rate to the input exergy rate to the system and can be given as,

$$D_P = \frac{\dot{Ex}_D}{\dot{Ex}_{in}} \tag{5}$$

Exergy and Environmental Impact Factor

Many researchers have suggested that the most proper method to reduce the environmental impact is through exergy because it is a measure of the departure of the state of a system from that of the environment [29-32]. Thus, exergy has an important role to play in providing better environment. Environmental impact can be reduced by the increasing the energy and exergy efficiency. Increased efficiency also reduces the exergy losses.

Environmental Impact Ratio

The concentrations of most of greenhouse gases have increased drastically since the industrial revolution. One of the most important greenhouse gases is CO_2. The emissions of CO_2 play a crucial role in climate change. Greenhouse effect increases with the increase of the amounts of CO_2 in the atmosphere. Actually, all resource use leads to some degree of environmental impact. In this context, environmental impact ratio can be given as

$$EIR = \frac{CO_{2_{es}} \; (g \, / \, kWh)}{CO_{2_{coal}} \; (g \, / \, kWh)}$$

(6)

which is defined as ratio of CO_2 emission by a particular renewable/non-renewable technology to CO_2 emission by coal based technology. In other words, the environmental impact ratio is a fraction of CO_2 emitted by a renewable/non-renewable technology as compared to coal based technology.

4   Results and Discussion

The exergy efficiencies of various processes are shown in Fig. 4, as studied earlier by Refs. [6, 8, 9-11, 14, 15]. The overall exergy efficiency of the HTSE becomes 79% [6], and for Cu-Cl cycle it becomes 65% [8], and for SMR process it varies from 63% to 80% [9-11, 14,15]. As can be seen in this figure, the exergy efficiency of the HTSE system is nearly same as SMR process. Note that the overall electrolyser system efficiency is always less as compared to the electrolysis process efficiency due to some various irreversibilities and losses taking place in various components, including coupling pumps, turbines etc. Since some energy losses may occur if such devices are used. In this regard HTSE exergy efficiency may lower than 79%.
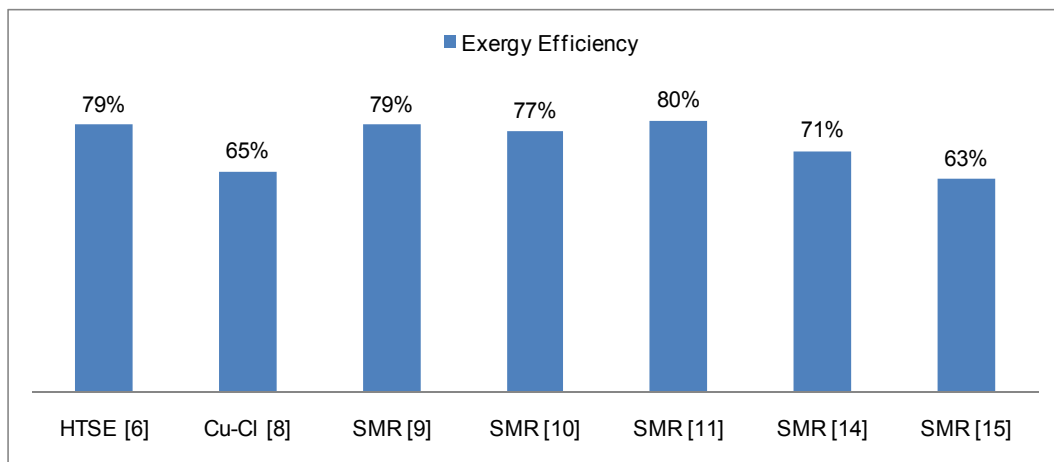

Figure 4:   Exergy efficiencies of various hydrogen production processes.

Figure 5 shows the corresponding sustainability index for the processes considered for hydrogen production respectively. The sustainability index for the HTSE process of Balta et al. [6] is 4.76 and for the Cu-Cl cycle of Balta et al. [8] is 2.86 and for SMR process [9-11, 14,15] it varies from 2.70 to 5.00. A higher sustainability index shows better sustainability of the process.
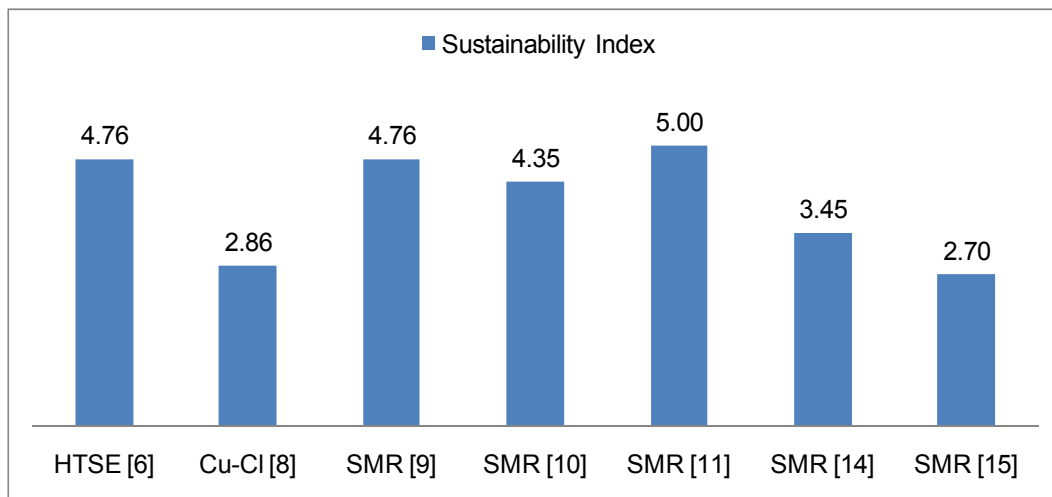
Figure 5:   **Sustainability Index values of various hydrogen production processes.**

Increasing greenhouse gas emissions, particularly CO_2 is a potential environmental impact and affects sustainability of energy usage, generation and transportation. Here, we calculate the environmental impact ratio of some energy technologies based on CO_2 emissions. In this regard, Fig. 6, shows the environmental impact ratio of coal, natural gas and geothermal options for hydrogen production (using the data taken from Refs. [33,34]). Geothermal plants emit typically only 25-30% of the total CO_2 emitted by a coal or natural gas plant, per kWh. Geothermal based emissions vary significantly depending on the technology chosen [35] and may vary from one region to another.
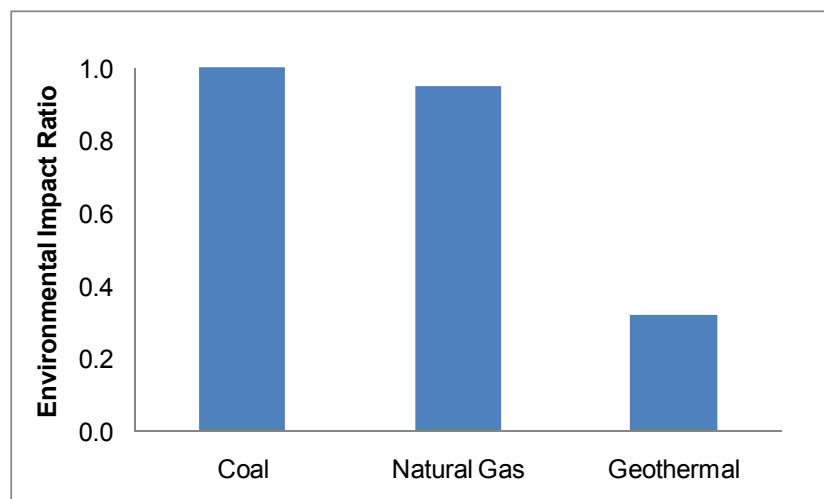

Figure 6:   **Environmental impact ratios of various energy options.**

5   Conclusions

In this paper, we have studied and compared various hydrogen production methods, namely: (1) steam methane reforming (SMR), (2) hybrid copper–chlorine (Cu–Cl) driven by

geothermal heat and electricity from a geothermal power plant, (3) high temperature steam electrolysis (HTSE) driven by geothermal heat and electricity from a geothermal power plant thermodynamically through energy and exergy efficiencies. Moreover, sustainability index and environmental impact ratios of these processes are studied and compared to each other. Since geothermal based hydrogen production processes are essentially at developmental stage, there is a need for further research and development for better design, analysis and performance assessment. The following main conclusions are drawn from the main results of the present study:

The exergy efficiencies of the SMR processes vary from 63% to 80% while it is 79% for the HTSE and 65% for a Cu-Cl cycle.

The sustainability index for the SMR process varies from 2.70 to 5.00 while it is 4.76 for the HTSE and 2.86 for a Cu-Cl cycle.

Using geothermal-based hydrogen production via either HTSE or Cu-Cl cycle reduces the CO_2 emissions by about 70%-75% compared to other options.

Geothermal-based hydrogen production methods, particularly by the thermo-chemical cycles, offer opportunities for better environment and sustainability.

Acknowledgements

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