



Investigation of an integrated hydrogen production system based on nuclear and renewable energy sources: Comparative evaluation of hydrogen production options with a regenerative fuel cell system

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ABSTRACT

Hydrogen has risen as a sustainable and efficient energy carrier option in reducing environmental pollution, and is seen as a potential solution for the current energy crisis. Hydrogen production via water decomposition is a potential process for direct utilization of nuclear thermal energy to increase efficiency and thereby facilitate energy savings. While many of the available renewable 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 with very limited impacts to climate change. The proposed model in this study is an integrated hydrogen production system combining both nuclear and solar energy sources. This integrated system includes storage of hydrogen and its conversion to electricity by a regenerative fuel cell system when needed. There are many matured water splitting processes that can be linked with the nuclear and solar energy sources to decompose water to its constituents, among which is hydrogen. In this regard, a comparative study is carried out to evaluate an optimal and feasible hydrogen production/storage process with a regenerative fuel cell that can be linked to this integrated system. Studies conducted here on hydrogen production processes show the thermochemical water decomposition to be the better option for producing hydrogen, comparing to electrolysis, due to its high efficiencies and low costs. Energy and exergy efficiencies of various hydrogen production processes, and fuel cell systems are evaluated and compared. Also, a parametric study is conducted on these efficiencies to see the effect of various operating conditions.

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1. Introduction

The increase in energy demand has been an issue since the beginning of modern age. Such an unexpected rise in the energy demand has become a concern for both developing and developed countries for a long time. Developments in power generation technologies have relied mainly on coal, oil and gas or other fossil fuels. The main concern about these technologies is their negative impact on environment due to generation of pollution associated with their usage. Furthermore, the current usage of finite fossil fuels at high rates could lead to a drastic energy crisis in the future. Consequently, civilization is forced to investigate and develop alternative clean energy sources for a brighter future.

Major parts of the world are still dependent on conventional means of producing power and facing an urgent need to shift their power generation technologies to renewables. Greenhouse gases such as carbon dioxide, emitted by fossil fuels combustion, prevent the radiated solar energy from surfaces on the Earth to get transmitted back to space. This results in radiation being trapped within the Earth's atmosphere. This greenhouse effect increases severely in direct relation with pollution, which results in global warming. This in turn causes the melting of the ice caps at the poles, leading to a rise in ocean waters, and thus submerging our precious land.

During the modern age, when new industries were constructed to enhance the standard of living, pollution was not considered as a factor in development. As technology grew and people around the world realized the lethal effects that pollution could cause to our planet, new research and development began to arise. Renewable energy sources are considered to be the future in power generation, since they are abundantly available depending on the geographic conditions and pollution-free.

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Due to many global challenges, potential energy solutions are required to improve sustainability and reduce environmental pollution caused by fossil fuels used in energy generation. Renewable energies have long been considered the viable option due to their ready availability. Renewable energy sources are clean and green but the main drawback is they are not sufficient yet to satisfy the global energy demand. They too have their downsides due to quality, quantity, density, and reliability. Hence, there is a need for an additional sustainable energy source that could provide a large-scale energy supply to complement renewable energy sources. Thus, attempts are being made to combine nuclear energy to back up renewables. Apart from its waste and safety concerns, nuclear energy is clean and does not contribute to any greenhouse gas emissions. Therefore, it can be used as a transition face until renewable sources mature and become sufficient for a fully renewable future.

Due to rise in the global energy demand at an unprecedented rate, it has become very crucial to come up with a system that is energy efficient, environmentally benign, and sustainable at the same time. There are many R&D and ongoing efforts to find a viable energy system that is capable of meeting energy demands. For a long time, hydrogen production has been researched and developed into a large and growing industry. Hydrogen has a variety of uses. It is currently used in processing fossil fuels, producing ammonia, acting as a coolant in electrical generators, serving in manufacturing plants to determine leaks, and serving as a shielding gas in atomic welding. Developing technologies also show its usage in transportation vehicles in the future and in fuel cells to produce electrical power. Hydrogen is not a primary energy source. It is an energy carrier. Hence, it has to be produced. Once manufactured, this gas would serve as a storage medium for energy generated by other means. A large amount of energy is dissipated as heat when hydrogen is burned. The temperature when hydrogen is burned in the air can roughly reach to 2000 °C.

The production of hydrogen from solar energy has long been studied by many scientists [1–5]. For a long time, developments in such systems had decreased due to the low efficiency of PV (photovoltaic) conversion and expensive equipments. But recently, with advancements in the technology, PV efficiencies have increased significantly. Also, the costs of equipment have decreased. Momirlan et al. [6] have presented some methods used in different countries in production of hydrogen from solar energy. Orhan et al. [7], have investigated a nuclear and renewable integrated system to produce hydrogen from water by thermochemical water splitting using a Cu–Cl cycle. Carton et al. [8] have studied renewable hydrogen production opportunities in Ireland. Abanades et al. [3] have screened water-splitting thermochemical cycles potentially attractive for hydrogen production by concentrated solar energy. Guo et al. [4] have examined solar hydrogen production and its development in China. Bozoglan et al. [1] have assessed sustainable solar hydrogen production techniques. Charvin et al. [5] have examined two-step water splitting thermochemical cycle based on iron oxide redox pair for solar hydrogen production.

Ngoh and Njomo [9] have provided an overview of hydrogen gas production from solar energy. They have showed the different methods and available technologies currently used for producing hydrogen using solar energy as the main source. The first reported process is the photochemical process, which utilizes solar light in the hydrolysis of water. There are two sub-procedures known as the photo biological procedure, which uses certain organisms to act as biological catalysts in the production of hydrogen from water, and the photo electrochemical procedure, in which a semiconductor photocatalyzer is submerged in an aqueous electrolyte or in water to decompose them into hydrogen and water. The second process is the thermochemical process, which includes solar cracking of

hydrocarbons, steam reforming of hydrocarbons, and thermochemical transformation of biomass. These procedures use concentrated solar radiations as the main heat source at high temperatures to carry out the endothermic reactions. The last process is the electrochemical process in which electrolysis of water is carried out. This process is the most commonly used and developed method in industries for the production of hydrogen. It is concluded that, from an exergy analysis on these processes, the electrolysis of water is more efficient in areas where strong solar radiation potential is available [9].

Miri and Mraoui [10] have conducted a detailed analysis of an electrolysis process of hydrogen production using solar energy. The electricity supply was done using PV (photovoltaic) cells and water vapor electrolysis was done by a solar concentrating power station at high temperatures. A numerical simulation of hydrogen production was proposed. This analysis was done using values of solar radiation at different sites in Algeria. The conclusions drawn by the researchers were that for the optimal operation of the system, the complete installed system must be located at good climatic conditions. It must be located in localities with strong insulations capable of holding maximum power, taking into account the fact that an increase in temperatures decreases the output of the electric solar power stations.

Kazim and Veziroglu [11] have presented a quantitative study considering the benefits of a solar hydrogen energy system when used in the United Arab Emirates (UAE). Their study indicated that the UAE would fail to meet oil and natural gas market demands in the near future. In order to maintain the country's share in the world energy market, hydrogen was proposed to meet the demands. Certain mathematical models were used in the study to find out the technical and economical feasibility of using solar hydrogen production methods in the UAE. Some of the parameters used in the model calculations were simplified to get a better overview of the energy situation in the country. The author's recommendations were that the UAE should use the barren desert areas for photovoltaic farms. They also recommended that the UAE build pipelines as early as possible, currently for transporting natural gas to other countries and for later stages, when fossil fuels deplete and the hydrogen economy is booming, to transport hydrogen to meet the energy demands. At initial stages, the sales generated from hydrogen would be minimal but then could start increasing to generate the country's income. Future projects could also influence the government's enthusiasm in solar hydrogen production [11].

Negrou et al. [12] have presented a case study of a solar hydrogen production system sited in Algeria. A numerical simulation was conducted for the installed capacity based on the characteristic equations governing the electrolysis of water, solar towers, and hydraulic pumping system. The main aim of the research was to find the most favorable geographic conditions for better production of hydrogen. From their case study, maximum values for the hydrogen production from solar energy were calculated in the southernmost parts of Algeria. The authors also stated that the electricity generated from solar hydrogen production was much cheaper than that of generated by conventional energy [12].

There are several other methods of hydrogen production from solar energy that can be mentioned here. One is studied by Zhang et al. [13] to produce hydrogen from a solar energy-powered supercritical cycle that uses carbon dioxide (CO₂). Supercritical CO₂ was used as the working fluid for a combined production of thermal and hydrogen energy. The proposed system consisted of a heat recovery system, heat pump, power-generating turbine, electrolysis of water, and evacuated solar collectors. CO₂ was efficiently converted into a supercritical state at high temperatures. The high temperatures utilized in the production of electricity and thermal

energy. The benefit of this system is that the generated electricity from inside the supercritical cycle can be directly used to produce hydrogen gas from water [13].

Chen et al. [14] have proposed another method of hydrogen production using solar energy itself by biomass gasification in supercritical water. The proof for this concept was successfully carried out. The real biomass (wheat stalk, corn meal) and model compounds of biomass like glucose were used, and gasified continuously with a novel system to produce hydrogen-rich gas. The results confirmed that a maximal gasification efficiency in excess of 110% was reached, in which the fraction of hydrogen in the gas product approached 50% [14].

Hydrogen production using nuclear energy is also important in this review section due to its applicability in the proposed model. Forsberg [15] has presented a detailed study on the future of hydrogen production using nuclear energy. It is stated that, for generation, storage, and transforming of hydrogen, it must be done on a large scale for economical purposes. Hence, this favors the use of large-scale nuclear systems to produce hydrogen. Also, the store energy in hydrogen enables it to match the variable energy demand when required. Similarly, because of possible transport systems requiring hydrogen, nuclear hydrogen would be the future of transportation [15].

In another study, Forsberg [16] has discussed the progress in future hydrogen markets for large-scale production systems. The cost of hydrogen includes the distribution phase, storage phase, and, mainly, the production phase. To avoid collection costs for hydrogen that occur from distribution sources, large users of energy will favor high-volume, centralized hydrogen production technologies. In the paper, potential hydrogen markets were identified to characterize the favorability of large-scale hydrogen production systems. The most high-volume centralized hydrogen production technologies are nuclear energy and fossil energy with carbon dioxide. The potential for hydrogen in the markets will be in the production of liquid fuels like gasoline, diesel, and others, and mainly in generating electricity. If high hydrogen production becomes possible, it could not only be used for generating electricity, but also for hot water and heating/cooling systems too if economically viable. In order to create viable large-scale hydrogen production systems, developers must have a thorough knowledge of hydrogen technology and strong business partnerships for reducing costs [16].

Balat [17] has studied potential importance of hydrogen as a future solution to environmental and transportation problems. It is concluded in the study that motor vehicles also contribute a significant amount in terms of pollution. Hydrogen is one of the clean fuels that could help in reducing vehicle emissions. Hydrogen has a particular importance in producing low-emission, cleaner, and sustainable energy systems [17].

Due to its importance, hydrogen is studied by researchers around the world, with the parallel development of networks and international partnerships to promote the hydrogen economy. For instance, Ricci et al. [18] have conducted a critical review and a case study to find out the current perceptions and usages of hydrogen. It is concluded that the public awareness and knowledge of hydrogen is very limited, with the exception of a few places where certain demonstration projects and communication campaigns have increased the public interest. It is also stated that there is a positive attitude towards the development of hydrogen, but there are concerns about its storage and safety. However, with advancements in technology, this would not be problem in coming future. By presenting certain key findings, the authors have attempted to show that with a qualitative approach and with first-hand experience, public perceptions towards hydrogen as energy carrier could be tackled effectively [18].

The proposed model in this study is an innovative design that utilizes nuclear and solar energies as the primary energy sources. The coupled nuclear/solar energy sources are then linked with a hydrogen production process to form hydrogen through water splitting processes. Solar energy depends mainly on the sun's radiation. When enough solar radiation is not available, a stable energy source that can provide a continuous flow of energy is required. Nuclear energy serves as a support, make-up and back-up power supplier to complement the renewable solar energy source. This study is of prime importance in the field of energy, since it can provide a clean, sustainable, and long-lasting solution for meeting the energy demands in a fast developing country. The eventual objective of the study is to conduct a complete thermodynamic analysis on the overall system. In this regard, the specific objectives in this paper are to carry out a comparative study to evaluate an optimal and feasible hydrogen production process with a regenerative fuel cell that can be linked to this integrated system. Also, to evaluate and compare energy and exergy efficiencies of various hydrogen production processes and fuel cell systems. Furthermore, to conduct a parametric study on these efficiencies and evaluate the effect of various operating conditions.

2. Outlook and prospects

Energy drives industrial society. It is, therefore, not surprising that many attempts have been made to analyze future needs for energy and the availability of various energy sources. Energy consumption growth is closely linked to population growth, although changes in life styles and efficiency have a substantial influence on the per capita annual consumption. The structure of population and the share between urban and rural populations also affect energy demand [19].

As a result of increasing global energy consumption due to increasing population (as seen in Fig. 1) and rising living standards in developing countries, the world faces problems such as depleting energy resources, and the impairing impact of present energy consumption patterns on the global climate as well as on humanity and the environment [20,21]. Fig. 2 illustrates the causal link in the climate change cycle.

Currently, 90% of the total primary energy demands are met by fossil fuels, the combustion of which emits large amounts of greenhouse gases [22]. This phenomenon can be seen in Fig. 3, where the energy-related CO₂ emissions are shown since 1980 for the OECD, developing countries and transition economies. Also, global CO₂ emissions by fuel type are given in Fig. 4 between 1971 and 2006. The risk of global climate change is of great concern to policy makers and the public. The relation between the energy generation sector and environmental pollution (see Fig. 5) is being scrutinized in industrialized countries. Before implementing any power generation project, extensive studies are normally performed on the impact of the project on the environment, and measures for avoiding climate change and other environmental impacts are considered.

A mismatch often exists between energy production and consumption. Nuclear facilities produce energy at a constant rate, while renewable energy facilities produce energy at a variable rate, and neither matches the demand. Also, day-night and seasonal variations of sunlight cause the typical capacity factor (ratio of actual energy output to energy output at full capacity for a period) of solar to be 18% [15].

Research on clean, economic, and abundant energy can help mitigate global warming and increase energy supplies. Alternative options to fossil fuels are renewable and nuclear energy sources. Global total primary energy supply by fuel type between 1971 and 2006 is presented in Fig. 6. Nuclear energy has been almost

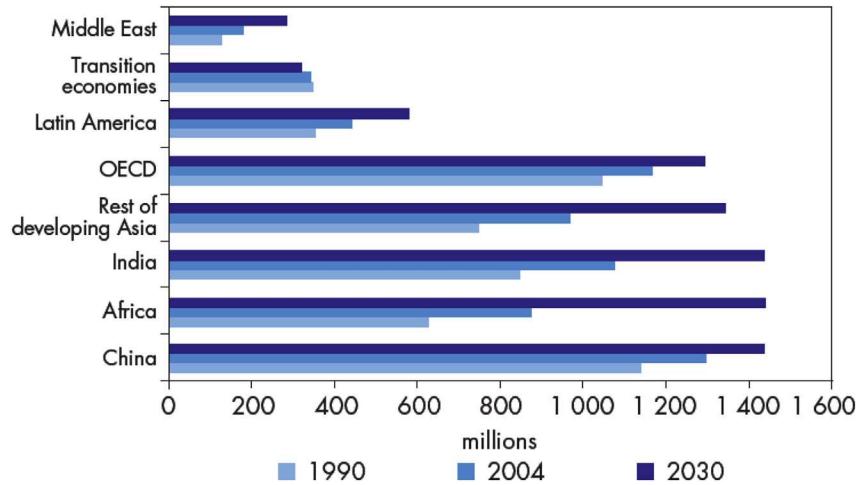


Fig. 1. World population growth by region [20].

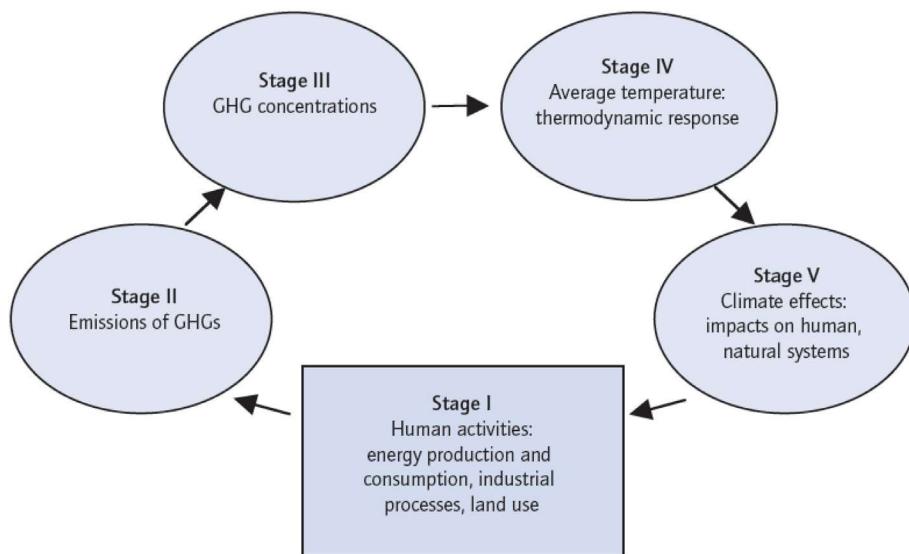


Fig. 2. Causal links in the climate change cycle [20].

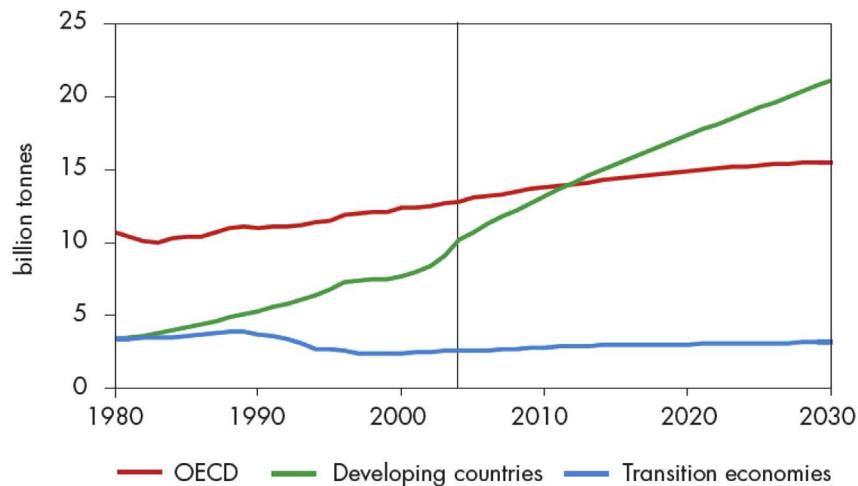


Fig. 3. Energy-related CO₂ emissions by region [20].

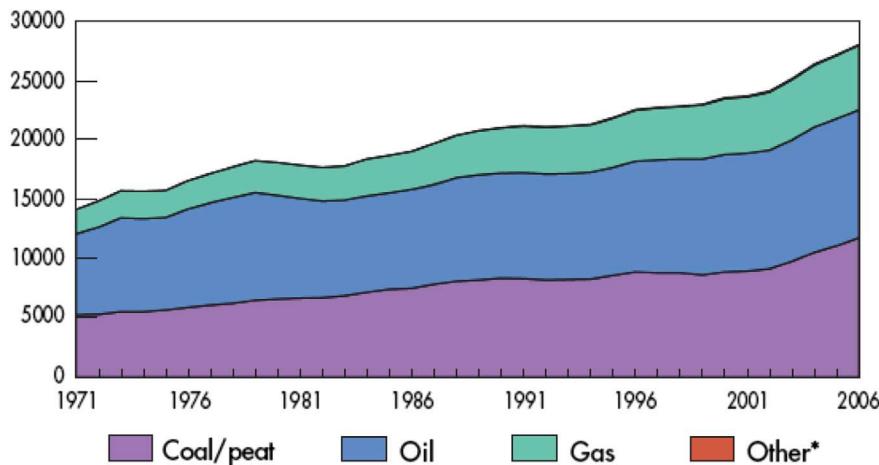


Fig. 4. Global CO₂ emissions by fuel type (Mt of CO₂) for 1971–2006 [20].

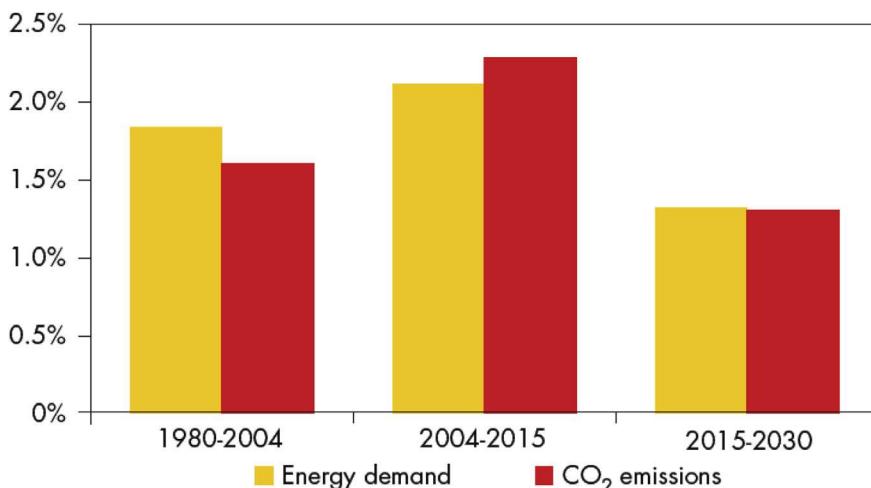


Fig. 5. Average annual growth in global energy-related CO₂ emissions and primary energy demand [20].

exclusively utilized for electrical power generation, but the direct utilization of nuclear thermal energy can be used to increase energy efficiency and thereby facilitate energy savings. Hydrogen production is a key technology for the utilization of nuclear thermal energy [e.g., [23]].

Hydrogen is a useful energy carrier. It can be stored, transported and used as a fuel. It also can be converted to electrical energy by means of fuel cells and other devices. Except for the driving energy source, since hydrogen can be produced from water and, after oxidation, it returns to water, hydrogen is “clean” from the

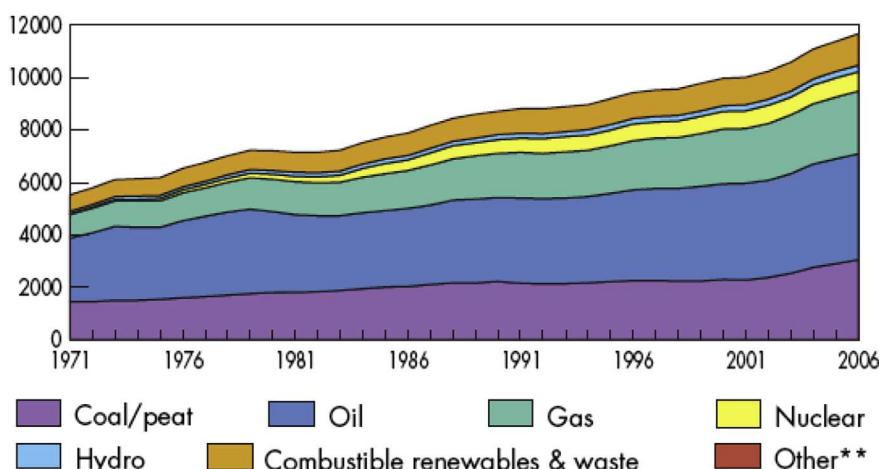


Fig. 6. Global total primary energy supply (excluding electricity) by fuel type (Mtoe) for 1971–2006 [20]. Other includes geothermal, solar, wind and heat.

viewpoint of environmental effects. The “hydrogen economy” where hydrogen and electricity serve as complementary energy carriers has been considered for a long time [24].

Two candidates for large-scale hydrogen production in the near future are nuclear-assisted thermochemical water splitting and natural gas steam reforming. Most of the hydrogen produced worldwide today is from fossil fuels, primarily via steam reforming of natural gas. Fossil-fuel-based hydrogen contributes to climate change. Hydrogen must be produced from water using non-fossil fuels, to avoid the environmental problems and limitations of fossil fuels. The electrolysis of water is a mature technology, but subject to inefficiencies due the conversion of heat to electricity in thermal power stations. This inefficiency can be avoided through thermochemical cycles that consist of a sequence of chemical reactions yielding a net reaction of water decomposition [25].

3. System studied

It was clear from the literature study in the previous section that nuclear and renewable energies are suitable to be coupled in order to address the global energy demand. Until large-scale production capacity of renewable energies become accessible, nuclear energy can serve as a support and back-up power supplier in the transition to an almost complete renewable energy sector. This is shown in the left panel of Fig. 7. The constant bulk part of the power is generated in nuclear base-load stations (full/constant load) and the rest (the variable loading) is covered by renewable energies.

The power generation must be from the flexible sources since the demand is changing daily and seasonally, as shown in right panel of Fig. 7. In many sectors predictably the price of peak electricity is 3–4 times that of off-peak electricity. The renewable sources can fulfill almost the entire fluctuating part of the systems as they consist mainly of flexible technologies that the production capacity can be controlled easily to ramp up and down. Renewable sources are available in an inconsistent and somewhat unpredictable way. Currently, the variable power output of most electrical grids is attained by varying the power output of low-capital-cost fossil fuel powered plants. Now and in the future, however, meeting variable electrical demand economically becomes one of the main challenges since there are constraints on the use of fossil fuels. Therefore, nuclear and renewable coupled hydrogen systems are potential solutions to the challenge of producing peak energy and are also enabling technologies for the large-scale use of renewable energy options such as solar. Without hydrogen, the role of renewable energy sources will be inadequate since there is no any effective method for long-term storage of electricity yet. A more effective method would be the structure of nuclear power plants in

serial operating constantly at full capacity and using extra power that the grid cannot engage for hydrogen production.

The complete schematic diagram of the proposed model is shown in Fig. 8. An effective method to supply any desired/manageable load profile to the grid is to integrate the nuclear and renewable coupled system with an energy storage device, such as a regenerative fuel cell. The regenerative fuel cell is combined with a hydrogen production process along with hydrogen storage, as shown in Fig. 8. The power conditioning and control unit has a very crucial task in this configuration. It must direct the power from the renewable/nuclear-coupled system to either the grid or hydrogen production process, and switch to fuel cell power mode when there is no enough power from the coupled system. Thus, the system operates as a smart grid, in which the energy production capacity can be controlled based on the fluctuation in demand. In addition, the nuclear/renewable-generated hydrogen can be used for other manners, e.g. as a fuel for cooking and heating in residential or commercial buildings, and transportation as an attractive option for rural areas.

4. Hydrogen production processes

Hydrogen economy is considered to be the future of power generation. However, hydrogen is not freely available and needs to be produced. It is thus an energy carrier like a battery, unlike a primary energy source such as coal. It can be produced by many methods such as steam reformation of hydrocarbons, water electrolysis, and thermochemical splitting of water.

Steam reformation is a method of producing hydrogen from hydrocarbon fuels such as natural gas. This procedure is carried out in a processing device called a reformer, which reacts fossil fuels with steam at high temperatures. It is considered as a practical way to provide the required hydrogen for fuel cells. But there are major issues that could be faced while using this reformer-fuel-cell system. As mentioned, this process requires fossil fuel or fuels that involve CO_x emissions that play a major role in global warming. Although there are methods to capture CO₂, it could add a further amount to the cost.

Electrolysis is another procedure that is used to produce hydrogen by using electrical energy. When an electrical current is passed through water, decomposition of water produces hydrogen and oxygen. Two electrodes are taken into which a power source is passed. Hydrogen is produced at the cathode and oxygen will appear at the anode. Direct electrolysis of water requires high amount of energy, as the chemical bonds between hydrogen and oxygen inside the water molecule are strong. Hence, a catalyst like sodium hydroxide (NaOH) or potassium hydroxide (KOH) is used to loosen the bonds.

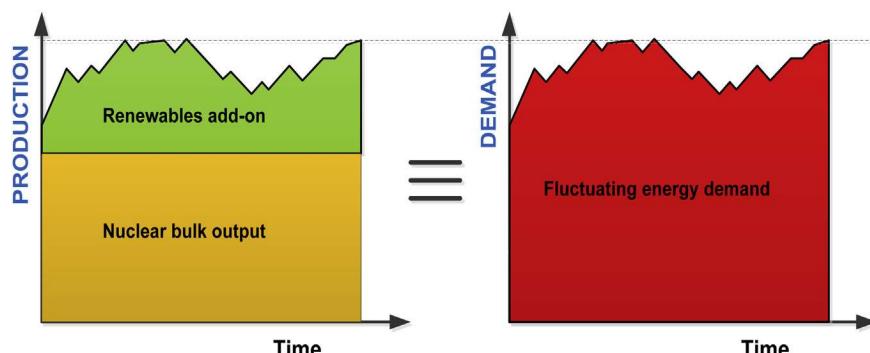


Fig. 7. Renewable energies add-on to nuclear bulk output versus the fluctuating energy demand.

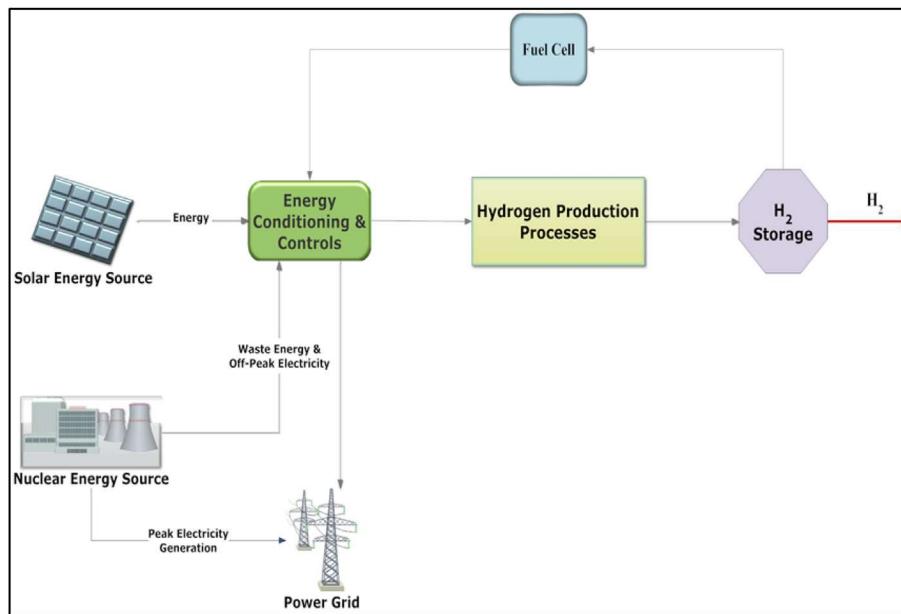


Fig. 8. Integrated hydrogen production process using solar and nuclear energies as the primary sources.

Another method, and the most sought-after, is the thermochemical splitting of water. This method uses thermochemical cycles that adopt heat sources with chemical reactions to split water into hydrogen and oxygen. This option is favorable since the heat required in this process can be obtained from renewable energy sources such as solar. Nuclear energy is also considered a suitable heat provider.

Currently, there are many cycles that can be used for hydrogen production. Although several hundreds of thermochemical cycles are known, research is concentrated only on those that can provide viability and technical feasibility [26]. Certain conditions need to be satisfied before choosing a thermochemical cycle. The selections of the cycles taken in this research were done based on the feasibility of the hydrogen production process for commercial purposes. The following criteria were adopted for selecting the commercial hydrogen production processes [27],

- Process temperature:** Thermochemical cycles operate at a wide range from 400 °C to more than 3000 °C for the decomposition of water. But very high temperatures are very difficult to achieve for commercial applications. Not only the high temperatures are an issue, the materials and the separation of chemicals also become a major challenge.
- Process safety and environment factors:** Some cycles are able to achieve the suitable temperature limit but are still not considered in this study due to their viability. They could be hazardous to the environment due to the type of chemicals utilized. The cycles that use high amounts of mercury, cadmium, and bromine compounds fall under this category.
- Process complexity:** Some cycles proved to be thermodynamically stable, but were eliminated due to high complexities in the processes. The processes that were not taken into consideration involved many complex and difficult gas separation steps. Also, cycles that utilize carbon compounds were eliminated due to difficulties in producing hydrogen free of carbon footprints.
- Process economics:** Even the cycles that had low temperatures were eliminated due to lack of the compounds required in the thermochemical process. The compounds are not abundantly available on the earth's surface, in oceans, or in the atmosphere.

Hence, the required elements for producing hydrogen will not be economically feasible.

Based on the above criteria, only three thermochemical hydrogen production processes are taken into consideration for comparative purposes. The chosen cycles have an operating temperature range that is achievable using the integrated approach of coupling solar and nuclear energy sources. Also, these cycles have better process safety and less complexity in the chemical reactions. Selected cycles are the magnesium chloride (Mg–Cl), copper–chlorine (Cu–Cl) and sulfur–iodine (S–I) cycles. These cycles have many advantages and can be linked with different heat sources. The details of these cycles are given below along with their flow diagrams.

The sulfur–iodine (S–I) cycle is a three-step thermochemical process of splitting water into hydrogen and oxygen. The process flow diagram of S–I cycle is shown in Fig. 9. The net inputs to the cycle are water and energy, while the net outputs are oxygen and hydrogen. The maximum operation temperature of the cycle is about 850 °C, which is attainable by the combined efforts of solar and nuclear energy sources. It is a completely closed system without any by-products that are harmful. Also, all components used are in the fluid state, and therefore could be used for continuous operation. The first step in this cycle is the production of H_2SO_4 and HI [28]. Recycled I_2 from Step 3 and SO_2 from Step 2 react with water for the production of H_2SO_4 in a counter-current reactor. This step occurs at around 120 °C and is also called the Bunsen reaction. Step 2 is the decomposition of H_2SO_4 . It decomposes to H_2O and SO_3 , and the SO_3 is decomposed to SO_2 and O_2 at 850 °C. The SO_2 is then sent back to the first step. Step 2 is the most complicated step among them and also the most technically-demanding. It has been subject to many modifications to decrease the temperatures involved. The final step, Step 3, is the decomposition of HI into I_2 , which is sent back to Step 1 and the required product H_2 is utilized. This reaction occurs at around 450 °C.

The magnesium–chlorine (Mg–Cl) thermochemical cycle is a hybrid process which utilizes heat and electrical energy to split water into hydrogen and oxygen at a maximum process

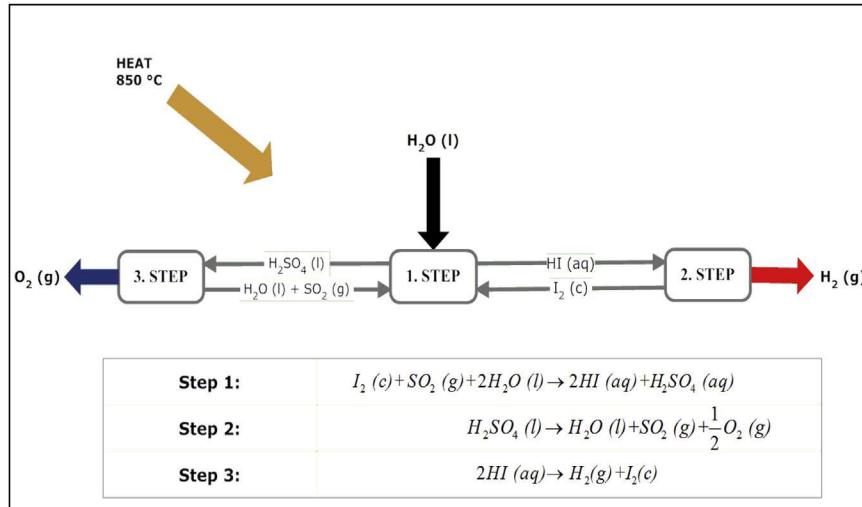


Fig. 9. Process flow diagram of sulfur–iodine cycle.

temperature of 550 °C (see Fig. 10). Literature reviews done on this type of cycle are very few [29]. The low temperature of this type of cycle makes it suitable for this study. The cycle consists of two thermochemical and one electrochemical reaction. The three steps involved in this cycle are hydrolysis, chlorination, and hydrogen production. In the hydrolysis step, a gas reaction takes place in which MgO and HCl are produced by the hydrolysis of MgCl₂. This reaction occurs at a steady state and is a highly endothermic process. The temperature range for this reaction is between 450 °C and 550 °C. This is the reaction in the cycle that requires the highest temperature. The product, MgO, goes to Step 2 where chlorination takes place. In this step, MgO and Cl₂ enter as reactants to form MgCl₂ and oxygen at reaction temperatures of about 400 °C–500 °C. The MgCl₂ produced is then sent back to Step 1. The final step is the hydrogen production process. This step can be done either thermochemically or electrochemically. The thermochemical process for the dissociation of HCl requires a great deal of energy and occurs at a very high temperature. Compared to this approach, the electrochemical process is a low-temperature operation. It occurs at temperatures between 70 °C and 90 °C. Anhydrous HCl

electrolysis is the method used here for dissociation as it requires lower electrical energy than aqueous HCl electrolysis. The products after dissociation of HCl are H₂ and Cl₂. The Cl₂ is then returned back for the chlorination step.

The Copper–Chlorine (Cu–Cl) cycle is currently the most investigated of all the other cycles due to its many merits. This cycle can be classified into three categories: three-step, four-step and five-step Cu–Cl thermochemical water splitting cycles. The difference among these types of cycles is the complexity due to the number of steps involved. A comparative study done on the efficiency of these cycles in Ref. [30] showed that a four-step Cu–Cl cycle has the best efficiency and the lowest fuel consumption rate among the other two types. Also, the four-step process was shown to have less impact on the atmosphere [31]. This is a hybrid process which uses both electrolysis and thermochemical steps as shown in Fig. 11. The maximum temperature requirement in this cycle is 530 °C. The merits of this cycle are that it requires only low temperatures for its operation, and is able to utilize low-grade waste heat to improve the energy efficiency and use lower-cost materials. Also, this cycle requires very low voltages in the electrochemical

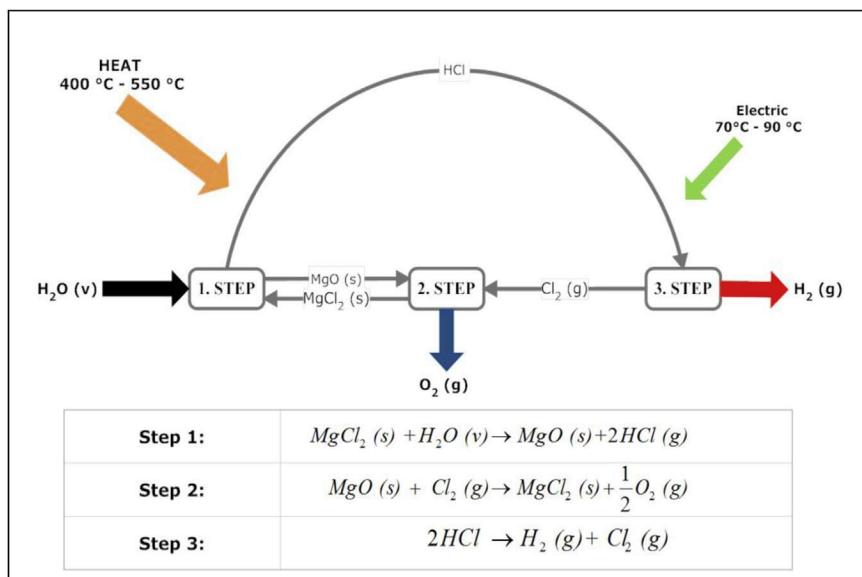


Fig. 10. Process flow diagram of magnesium–chlorine cycle.

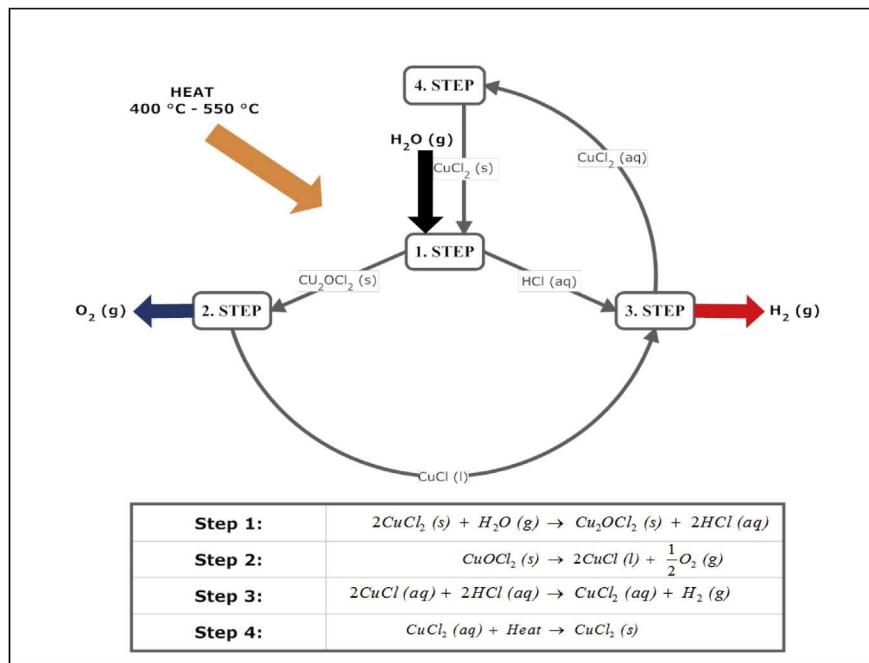


Fig. 11. Process flow diagram of copper–chlorine cycle.

step: between 0.6 V and 1.0 V, or even lower if less current density is achieved. A challenge for this cycle is the solid handling between the processes and corrosive working fluids. The four-step type process used in this study, which consists of hydrolysis, oxygen production, hydrogen production and drying. In the first step of hydrolysis, high temperature steam at 400 °C is added to solid CuCl₂. The products coming out of this hydrolysis step are aqueous HCl and solid Cu₂OCl₂. The second step of this cycle is the oxygen production step. This step is the most energy-consuming step as it requires about 500 °C. In this step, Cu₂OCl₂ is broken down into CuCl and O₂. The CuCl is then used in the next step, the hydrogen production process step, where it reacts with HCl from the first step in an electrolyzer to produce CuCl₂ and H₂ at temperatures as low as 100 °C. The last step is the drying step in which aqueous CuCl₂ is dried in a heat exchanger to form solid CuCl₂ which is then used back in the first step.

5. Hydrogen storage

Many benefits of using hydrogen as an energy carrier in the coming future have already been mentioned. Hydrogen is abundant in the universe, but it is not in the element form. Therefore, it has to be produced. Unlike petroleum, hydrogen can be produced from renewable energy sources and has no pollution, as its by-product is water. But the main issue involved in the usage of hydrogen is its storage. One gram of hydrogen occupies around 11 L of space at atmospheric pressure. So for saving space, the hydrogen gas is pressurized to several hundreds of atmospheric pressures and stored in pressure vessels. There are many methods involved in the storage of hydrogen, which can be on-board in mobile applications such as hydrogen-fueled vehicles, or stationary as in power generation utilization.

5.1. On-board hydrogen storage

On-board storage of hydrogen for vehicles and other mobile applications is considered the most technically challenging barrier for the wide application of hydrogen on a commercial scale. This

type of storage technology can be divided into physical storage, where the hydrogen molecules are stored via compression or liquefaction, and chemical storage where hydrides are stored. Many studies have been conducted focusing on hydrogen as a lightweight energy carrier. The details are given below.

a) *Chemical storage:* Many chemical compound materials are capable of storing hydrogen. The efforts are now towards using metal hydride materials as a method for storing hydrogen. This method has the advantage of being safe due to its large-volume storage capacity for on-board applications. Magnesium-based hydrides show a promising solution for mobile hydrogen storage, with a reversible capacity of 7.6 wt% for hydrogen storage [32]. Boron is another favorable element for hydrogen storage due to its chemical hydrides and nanostructural forms [33].

Another chemical storage is the usage of carbon structures like fullerenes. Fullerenes are a class of carbon compound which shows unusual structural, chemical, and physical properties which lead to unexpected and novel applications [34]. An experimental study on fullerenes showed that more than 6 wt% of hydrogen can be adsorbed by fullerenes at 180 °C and about 25 bar [35]. Graphene is another type of carbon compound, which is composed of pure carbon with atoms arranged in a regular hexagonal pattern and when hydrogen is adsorbed it becomes graphane. This type of carbon material is reported to have a good hydrogen storage capacity.

b) *Physical storage:* In physical storage, hydrogen is stored by compression or liquefaction and in a molecular state. These technologies are well established and commercialized methods. Hydrogen can stay in gaseous state even under considerable amount of pressure. For example, it is compressed to a pressure range of 350 and 700 bars in vehicles. Pressurizing the hydrogen for gaseous storage offers the simplest solution in terms of the infrastructure requirements and is the most popular method of all the storage methods. For hydrogen to be in the liquid state, it needs to be stored in cryogenics. The temperatures need to be

maintained at 20.3 K or slightly above, which needs a lot of efforts and energy to remain in that state. It is reported that hydrogen liquefaction requires about 30%–40% of the LHV (lower heating value) of hydrogen while for hydrogen compression (gaseous storage) it requires only 5%–20% of the LHV [36]. Hence, pressurizing hydrogen seems to be a better solution for storage but other challenges like space and cost must also be taken into consideration.

Another arrangement that is considered a physical storage method of hydrogen molecules is carbon nanotube. Many studies have been conducted [37] evaluating a wide range of temperatures and pressures in order to establish the reliability of this phenomenon as a potential hydrogen storage technique. It is reported to be acceptable for future storage but a conclusion to do further investigation was reached to take into consideration other factors.

5.2. Stationary hydrogen storage

Unlike the mobile hydrogen storage methods, stationary hydrogen storage does not have major issues related to hydrogen density. The hydrogen can be stored in large enclosed areas and kept safely away from any possible dangers. One option of storing hydrogen is underground storage. This type of storage is the practice of employing underground caverns, salt domes, and depleted oil and gas fields. The storage of hydrogen can be done in large capacities by this method and is suitable for grid energy storage. This is essential for a future hydrogen economy.

The concept of storing hydrogen gas underground is inspired by the need to supply energy to consumers during high demands. Geographical formations like salt caverns or salt domes can be used to store the gas. Salt domes are formed when deposits of salts are restricted to a marine basin. When the salt is restricted or unable to move, evaporation occurs resulting in salt domes. Salt caverns are underground caves where excavation of minerals has led to large empty areas. Even depleted oil and gas reservoirs that are deep underground can act as hydrogen gas storage [33,38].

Unlike surface tanks, deep underground storage has the capability to store higher volumes and pressures. Also, other advantages are that underground storage does not require large land and provides higher security against any external influences [38].

Storage options are generally dependent on the geological conditions of the area. Depleted oil and gas reservoirs are especially characterized by the large storage capacities as seen in Fig. 12. These reservoirs are mainly used to meet seasonal demands and have high cushion gas requirements. Cushion gas is the physically unrecoverable natural gas that provides a required pressurization for hydrogen gas [33,38].

6. Fuel cell systems

Fuel cell is an electrochemical energy conversion device that converts the chemical energy of fuels into electrical energy directly, without any intermediate combustion process. Unlike depleting batteries, fuel cells can run continuously as long as the fuel is provided. This fuel can vary in a wide range options such as hydrogen, natural gas, methanol, or biogases. The end products of the electrochemical reaction in the fuel cell are electricity, water and heat.

Fuel cells have many advantages. They produce no emissions or if fossil fuels are used, much lower emissions compared to current power generation technologies. They have relatively higher efficiencies compared to gas or diesel engines. Most fuel cells can work silently and with different types of fuels. The system maintenance in the fuel cells is minimal as there are no moving parts, and they can operate for a very long time.

Fuel cells also have some drawbacks if they are to be employed in very large capacities. The main drawback is that they are not economically feasible yet. The cost to produce and store hydrogen is high, and it might ends up costing more energy than one actually gets out of the fuel cell. Until fuel cell technology reaches a point where it's more economically feasible, this will be the biggest hurdle that must be overcome.

There are many types of fuel cells available in the market [39]. They are mainly differentiated on the type of electrolyte used between the anode and cathode. The cost of fuel cells depend on the

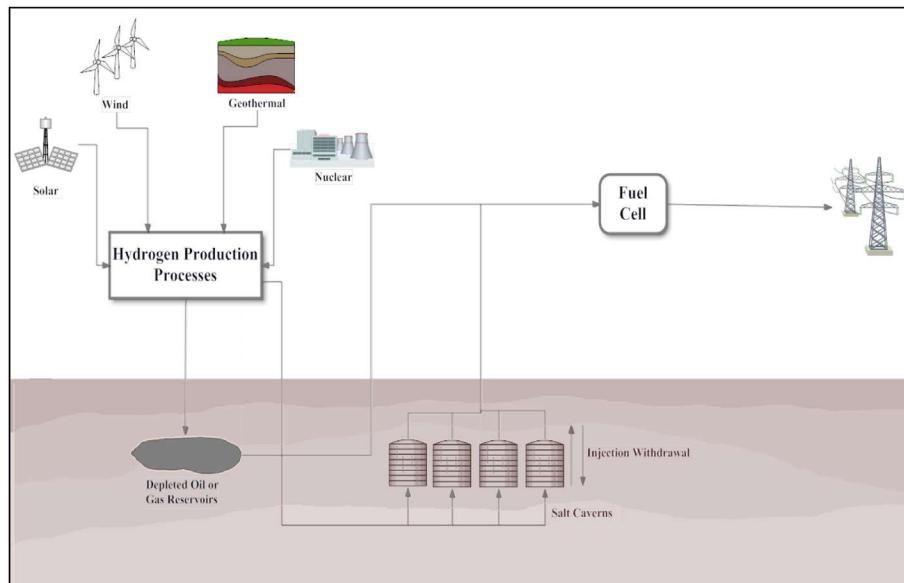


Fig. 12. Schematic view of hydrogen storage in a salt cavern, and depleted oil and gas field.

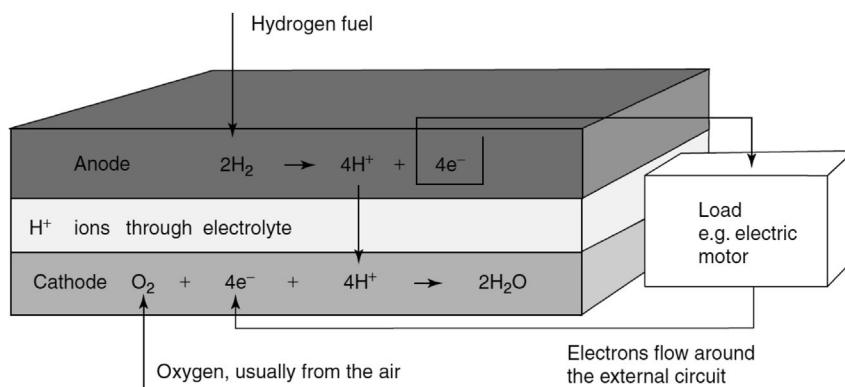
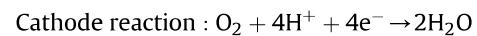
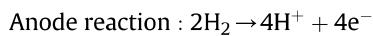


Fig. 13. Phosphoric acid fuel cell (PAFC) schematic diagram [40].

electrolyte used as well. The types of fuel cells utilized in this study are given below with their detailed description.

6.1. PAFC (phosphoric acid fuel cell)

PAFCs are named after their liquid phosphoric acid electrolyte. These were the first to be used for commercial purposes. Fig. 13 shows the schematic diagram of a PAFC. They have an operating temperature range between 150 °C and 200 °C. They are utilized in large capacity power applications, such as buses and buildings. They also have increased tolerance to fuel impurities. The electrolyte is usually a highly concentrated liquid phosphoric acid (H_3PO_4) saturated in a silicon carbide (SiC) matrix [40]. The electrodes are usually made of carbon paper coated with a finely dispersed platinum catalyst, which is the main contributor of the high cost. Also, another disadvantage is that phosphoric acid solidifies below 40 °C, which results in a difficult start-up. Hence, PAFCs need to be restrained above this temperature when not used. In operation, the hydrogen enters through the anode while oxygen enters as a part of the air through the cathode as shown in Fig. 13. The chemical equations involved are as shown below.



6.2. SOFC (solid oxide fuel cell)

SOFCs are named by their solid oxide electrolyte. Fig. 14 shows the schematic diagram of a SOFC. Their usual operating temperatures are about 1000 °C. Many features of this fuel cell technology make it attractive for industry and utility applications. One main advantage is their high tolerances to fuel contaminants. Also, unlike other fuel cells, the individual cells do not have to be constructed in a plate-like configuration. In order to have quick access to the gases, the electrodes are made porous. The charge carrier is the oxygen ion, O^{2-} .

Another advantage of this fuel cell is that it operates at very high temperatures; hence there is no need for an expensive catalyst. They are able to reform fuels internally due to the high temperature, which enables it to use a variety of fuels and reduce costs. Also carbon monoxide (CO) is not poisonous for the fuel cell, hence allowing the usage of gases made from coal.

The disadvantages are that high temperatures can cause slow start-up times (up to 8 h). Hence, thermal shielding to contain the heat is required. The high temperatures also cause durability issues.

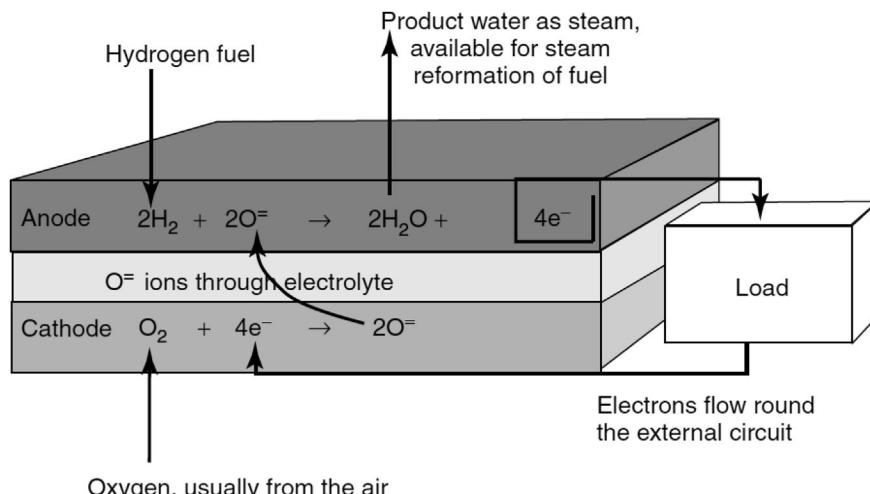
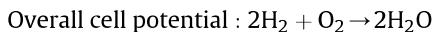
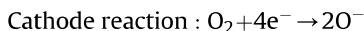
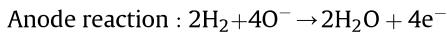


Fig. 14. Solid oxide fuel cell (SOFC) schematic diagram [40].

Currently, research is being conducted to reduce the operating temperatures to 600 °C. The reactions involved in the cathode and anode are as follow.

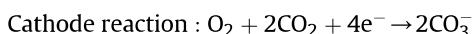


6.3. MCFC (molten carbonate fuel cell)

This type of fuel cell consists of an electrolyte of a molten carbonate salt mixture ($\text{Li}_2\text{CO}_3-\text{K}_2\text{CO}_3$, 62%–38%). The electrolyte is suspended in a porous, chemically inert ceramic matrix. They operate at temperatures of 600 °C and above. These fuel cells can be used in utility and industry applications. Non-precious metals like nickel (Ni) are usually used as catalysts at the cathode and anode. The charge carrier is the carbonate ion CO_3^{2-} . Fig. 15 shows the schematic diagram of a MCFC.

Improved efficiencies of this fuel cell technology is another reason why more focus is drawn to utilizing them for larger capacity requirements. These fuel cells are not poisoned by carbon monoxide (CO) or carbon dioxide (CO_2). Hence, they too can use gases made from coal. Since these fuel cells operate at high temperatures, they don't require any external reformer to convert fuels to hydrogen. If the waste heat is captured and utilized, efficiencies can go much higher.

The main disadvantage of this fuel cell technology is its durability. The fuel cells, as mentioned before, operate at high temperatures and the corrosive electrolyte used causes a breakdown in the components. Further corrosion occurs, decreasing the cell's life. Corrosion-resistant materials are developed to increase cell life without decreasing performance. The anode and cathode reactions are as shown below.



7. Analysis

Efficient use of energy is a substantial contributor to any sustainable system for meeting rising energy requirements. Consequently, it is vital to evaluate alternative technologies for renewable/nuclear-based hydrogen production in terms of their energy and exergy efficiencies. The overall performance of alternative routes for using nuclear energy for this purpose depends on parameters like operating temperature, conversion efficiency of the process, and complexity of the plant and its subsystems. To contribute in process development, we analyze an integrated system in this study by investigating the H_2 production stage of the system, thermodynamically.

All devices incur irreversibilities in any real case application. Thermochemical cycles designed to operate through chemical reactions are not an exception in actual conditions and are also encounter destruction in their process. In addition, they are also subject to other losses associated with their operation. Actual thermodynamic inefficiencies in a thermal system are related to exergy destruction and exergy loss. Exergy analysis identifies the amount, cause and the place of exergy destructions, and hence gives an idea to cure it. However, only a part of the exergy destruction can be avoided in the system and its components. Minimum exergy destruction for each component is imposed by physical, technological and economic constraints. The difference between the total and the unavoidable exergy destruction rate represents the avoidable exergy destruction rate, which provides a realistic measure of the potential for improving the thermodynamic efficiency of a component and consequently the overall system.

In the analysis, all quantities are provided in terms of per kmol of hydrogen produced. Also, we assume that the reference environment temperature (T_0) and pressure (P_0) are 25 °C and 1 atm, respectively. In the chemical reaction, reactants and products are at the reaction temperature and a pressure of 1 atm. The process occurs at steady state, is adiabatic and proceeds to completion.

The principle of conservation of mass indicates that the masses of products and reactants are equal in chemical reactions. A general steady-state mass rate balance can be expressed as follows:

$$\dot{m}_{in} = \dot{m}_{out} \text{ or } \dot{m}_{reactants} = \dot{m}_{products} \quad (1)$$

For a chemical process, a mass balance can be expressed as

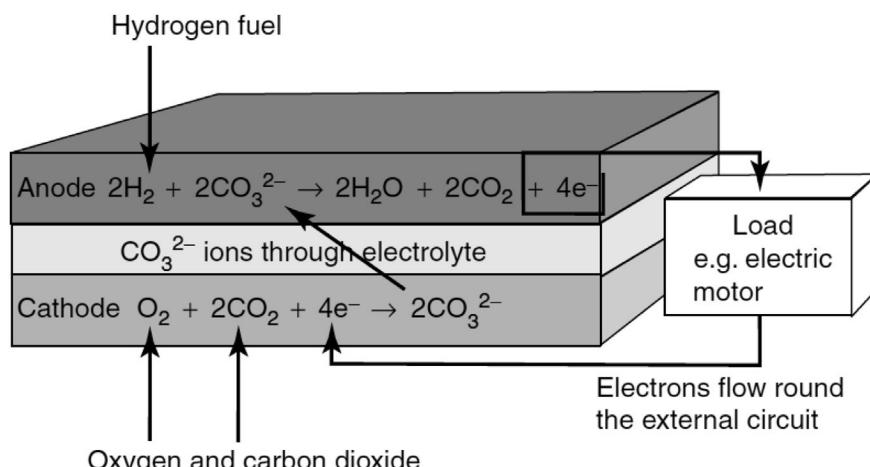


Fig. 15. Molten carbonate fuel cell (MCFC) schematic diagram [40].

$$\sum [n\bar{m}]_{react} \tan ts = \sum [n\bar{m}]_{products} \quad (2)$$

where \bar{m} and n are molar mass and mole number of the compound per cycle, respectively.

The conservation of energy principle applies whether or not a chemical reaction occurs within the system. The heat transfer for a chemical process involving no work interaction W is determined from the energy balance $\dot{E}_{in} - \dot{E}_{out} = \Delta\dot{E}_{system}$ applied to the system with $W = 0$. For a steady state reaction, the energy balance reduces to

$$Q = H_p - H_R = \sum n_p (\bar{h}_t + \bar{h} - \bar{h})_p - \sum n_R (\bar{h}_t + \bar{h} - \bar{h})_R \quad (3)$$

The overall energy efficiency of a hydrogen production process, η_e , can be described as the fraction of energy supplied that is converted to the energy content of H_2 based on its lower heating value

$$\eta_e = \frac{\overline{LHV}_{H_2}}{\overline{Q}_{in} + \overline{Q}_{loss}} \quad (4)$$

where \overline{LHV}_{H_2} is the lower heating value per kmol of hydrogen, \overline{Q}_{loss} is the total heat loss from the process and \overline{Q}_{in} is the total energy used by the process to produce a unit amount of product hydrogen. The lower heating value of hydrogen is 240,000 kJ/kmol H_2 .

Also, the exergy balance for a process involving chemical reactions can be written as

$$\sum Ex_{in} - \sum Ex_{out} - Ex_{destruction} = \Delta Ex_{system} \quad (5)$$

For a steady-state process, ΔEx_{system} is zero. The specific exergy of a flow can be expressed as

$$\underline{Ex} = (\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0) + \frac{V^2}{2} + gz + \overline{Ex}^{ch} \quad (6)$$

Here, the underlined term is the thermomechanical contribution and Ex^{ch} is the chemical contribution, which combines to yield the exergy, associated with a flow at a specified state. Combining Eqs. (5) and (6) for a process involving no work interactions yields

$$\begin{aligned} \underline{Ex}_{destruction} &= \sum n \left[(\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0) + \frac{V^2}{2} + gz + \overline{Ex}^{ch} \right]_{in} \\ &\quad - \sum n \left[(\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0) + \frac{V^2}{2} + gz + \overline{Ex}^{ch} \right]_{out} \\ &\quad + \left(1 - \frac{T_0}{T_{reaction}} \right) Q \end{aligned} \quad (7)$$

where Q , as given in Eq. (3), is the heat flow into the system (negative for exothermic reactions). For the chemical reactions in the hydrogen production processes mentioned in the above sections, it is reasonable to assume the specific kinetic exergy ($V^2/2$) and specific potential exergy (gz) of the flows are equal to zero. Then,

$$\begin{aligned} \underline{Ex}_{destruction} &= \sum n \left[(\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0) + \overline{Ex}^{ch} \right]_{in} \\ &\quad - \sum n \left[(\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0) + \overline{Ex}^{ch} \right]_{out} \\ &\quad + \left(1 - \frac{T_0}{T_{reaction}} \right) Q \end{aligned} \quad (8)$$

The methods used for evaluating the properties differ somewhat

for reacting and nonreacting systems. In thermodynamic property tables for nonreacting system, values for specific internal energy u , enthalpy h , and entropy s are relative to some arbitrary datum state where the enthalpy (or alternatively the internal energy) and entropy are set to zero. This approach is satisfactory for evaluations involving differences in property values between states of the same composition, because then the arbitrary datum cancels. However, when a chemical reaction occurs, reactants change and products are formed, so differences cannot be calculated for all substances involved. For reacting systems, it is necessary to evaluate quantities like h , u , and s so there are no inconsistencies in properties.

With the specific enthalpy and entropy values, we can calculate the specific chemical exergy \overline{Ex}^{ch} value of each compound. Evaluating the thermomechanical contributions can be thought of as bringing the system without change in composition from the specified state to T_0 and P_0 , the condition where the system is in thermal and mechanical equilibrium with the reference-environment. Depending on the nature of the system, this may be a real or hypothetical condition.

The chemical exergy based on a typical exergy reference environment exhibiting standard values of the environmental temperature T_0 and pressure P_0 such as 298.15 K and 1 atm is called standard chemical exergy. To determine the standard chemical exergy of any substance not present in the environment, we consider the reaction of the substance with other substances for which the standard chemical exergies are known, and write

$$\overline{Ex}^{ch} = -\Delta G + \sum_P n \overline{Ex}^{ch} - \sum_R n \overline{Ex}^{ch} \quad (9)$$

where ΔG is the change in Gibbs function for the reaction, regarding each substance as separate at temperature T_0 and pressure P_0 . The other two terms on the right side of Eq. (9) are evaluated using the known standard chemical exergies, together with values of n , which denotes the moles of these reactants and products per mole of the substance whose chemical exergy is being evaluated.

The performance of systems to do work can be expressed as the ratio of the actual work developed to the maximum theoretical work. This ratio is a type of exergy (second law) efficiency. The relatively low exergy efficiency exhibited by many common power-producing devices suggests that thermodynamically more efficient ways of utilizing the fuel to develop power might be possible. However, efforts in this direction must be tempered by the economic imperatives that govern the practical application of all devices. The trade-off between energy savings and the additional costs required to achieve those savings must be carefully weighed.

An exergy balance can be used in formulating 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. We assume the reactor is well insulated, so there is no heat transfer and thus no accompanying exergy transfer. There is also no work \dot{W}_{cv} , so exergy exits only with the reaction products. Exergy efficiency can be written as

$$n_{ex} = \frac{\overline{Ex}_{out}}{\overline{Ex}_{in}} \quad (10)$$

where \overline{Ex}_{in} is the specific exergy that enters with the reactants plus heat (which is non-zero in the case of an endothermic reaction), and \overline{Ex}_{out} is the specific exergy exiting the system with the products plus heat (which is non-zero in the case of an exothermic reaction). Using the exergy balance for the reacting system, the exergy efficiency can be written alternatively as

$$n_{ex} = 1 - \frac{\bar{ex}_{destroyed}}{\bar{ex}_{in}} \quad (11)$$

An analysis is also conducted on the fuel cell part. Efficiency of different types of fuel cells is calculated to determine the optimum option for the integrated system. Thermodynamic analysis of fuel cells require utilizing many essential parameters like the Gibbs's energy, enthalpy and entropy of formation, and the physical and chemical exergies in the cell.

The energy efficiency of fuel cells can be formulated as,

$$\eta_{energy} = \frac{\Delta\bar{g}_f}{\Delta\bar{h}_f} \quad (12)$$

where, $\Delta\bar{g}_f$ is the Gibbs free energy change and $\Delta\bar{h}_f$ is enthalpy of formation change. Gibbs free energy is defined as energy that is available to do external work at a constant temperature and pressure. All work that occurs due to changes in volume is neglected when considering the Gibbs free energy. The Gibbs function of a system can be defined in terms of enthalpy and entropy by the following equation,

$$G = H - T \times S \quad (13)$$

Similarly, the change in molar Gibbs free energy of formation is given as,

$$\Delta\bar{g}_f = \Delta\bar{h}_f - T \times \Delta\bar{s} \quad (14)$$

The enthalpy of formation change, $\Delta\bar{h}_f$, is the difference between \bar{h}_f of the products and \bar{h}_f of the reactants. Thus, for the reaction $H_2 + 1/2O_2 \rightarrow H_2O$, the enthalpy of formation change is,

$$\Delta\bar{h}_f = (\bar{h}_f)_{H_2O} - (\bar{h}_f)_{H_2} - \frac{1}{2}(\bar{h}_f)_{O_2} \quad (15)$$

Also, the change in molar entropy, $\Delta\bar{s}$, is the difference between \bar{s} of the products and \bar{s} of the reactants.

$$\Delta\bar{s} = (\bar{s})_{H_2O} - (\bar{s})_{H_2} - \frac{1}{2}(\bar{s})_{O_2} \quad (16)$$

\bar{h}_f and \bar{s} vary with temperature as can be seen in the following Eqs. (17) and (18). The subscript T of \bar{h} and \bar{s} in these equations is the temperature and \bar{c}_p is the molar heat capacity at a constant pressure. The standard temperature used in this analysis is 298.15 K.

The molar enthalpy of formation at temperature T is given by

$$\bar{h}_T = \bar{h}_{298.15} + \int_{298.15}^T \bar{c}_p dT \quad (17)$$

And the molar entropy is,

$$\bar{s}_T = \bar{s}_{298.15} + \int_{298.15}^T \frac{1}{T} \bar{c}_p dT \quad (18)$$

The values for the molar enthalpy of formation and the molar entropy at a standard temperature of 298.15 K are given in Table 2. Also the values of T for different types of fuel cells are shown in Table 3.

The molar heat capacity at constant pressure, \bar{c}_p , is not constant with respect to temperature, and given in Eqs. (19)–(21). These equations are accurate to a value of 0.6% over a temperature range of 300 K–3500 K.

Table 1
Comparison of thermochemical cycles for hydrogen production.

Parameters	Cu–Cl cycle	S–I cycle	Mg–Cl cycle
No. of chemical steps	4/3/2	3	3
Highest temperature (°C)	530	850	550
Energy efficiency (%)	67	76	64
Exergy efficiency (%)	72	75	35
Energy input (MJ/kg of H ₂ produced)	228	183	265

For steam, constant pressure heat capacity is,

$$\bar{c}_p = 143.05 - 58.040 \times T^{0.25} + 8.2751 \times T^{0.5} - 0.036989 \times T \quad (19)$$

And, for hydrogen, H₂, it is,

$$\bar{c}_p = 56.505 - 22222.6 \times T^{-0.75} + 116,500 \times T^{-1} - 560,700 \times T^{-1.5} \quad (20)$$

Also, for oxygen, O₂,

$$\bar{c}_p = 37.432 + 2.0102 \times 10^{-5} \times T^{1.5} - 178,570 \times T^{-1.5} + 2,368,800 \times T^{-2} \quad (21)$$

Exergy efficiency of a fuel cell system can be stated as the ratio of power output over the difference between exergy of reactants and exergy of products,

$$\begin{aligned} \eta_{exergy} &= \frac{\text{Electrical power output}}{(\text{Exergy})_R - (\text{Exergy})_P} \\ &= \frac{\dot{W}_{elect}}{(\Psi_{air,R} + \Psi_{H_2,R}) - (\Psi_{air,P} + \Psi_{H_2O,P})} \end{aligned} \quad (22)$$

where, \dot{W}_{elect} is the electrical power output in kW and $\Psi_{air,R}$, $\Psi_{H_2,R}$, $\Psi_{air,P}$, $\Psi_{H_2O,P}$ are the total exergies of the reactants air and hydrogen, and the products air and water, respectively.

The total exergy of the reactants and the products can be determined through the following equations,

$$\Psi_{air,R} = \dot{m}_{air,R} \times (ex_{ch} + ex_{ph})_{air,R} \quad (23)$$

$$\Psi_{H_2,R} = \dot{m}_{H_2,R} \times (ex_{ch} + ex_{ph})_{H_2,R} \quad (24)$$

$$\Psi_{air,P} = \dot{m}_{air,P} \times (ex_{ch} + ex_{ph})_{air,P} \quad (25)$$

$$\Psi_{H_2O,P} = \dot{m}_{H_2O,P} \times (ex_{ch} + ex_{ph})_{H_2O,P} \quad (26)$$

where, ex_{ph} is the physical exergy in kJ/kg, ex_{ch} is the chemical exergy in kJ/kg, and \dot{m} is the mass flow rates of the reactants and products in kg/s.

Physical exergy is the work obtained through a reversible process to bring a substance from an initial state (T, P) to the standard environmental condition (T_0, P_0). The physical exergy, also known as thermomechanical exergy, can be stated as,

$$ex_{ph} = (H - H_0) - T_0 \times (S - S_0) \quad (27)$$

Table 2

Enthalpy of formation, molar entropy and standard chemical exergy values of hydrogen.

Substance	Enthalpy of formation, \bar{H}_f (J/mol)	Molar entropy, \bar{s} (J/mol K)	Standard chemical exergy, e_{ch} (J/kg)
H_2O (steam)	-241,827	188.83	50,550
H_2	0	130.59	118,050,000
O_2	0	205.14	124,000
CO_2	-393,500	213.8	454,545

where, H is the standard enthalpy at temperature T in kJ/kg, H_0 is the specific enthalpy at standard condition in kJ/kg, S is the entropy at temperature T in J/kg K, S_0 is the specific entropy at standard temperature T_0 in J/kg K, and T_0 is the ambient standard temperature in K.

Chemical exergy is the maximum possible work obtained when a substance is brought from the environmental state to the dead state. The specific chemical exergy can be formulated as,

$$ex_{ch} = \sum (x_n \times e_{ch}^n) + (R \times T_0 \sum (x_n \times \ln x_n)) \quad (28)$$

where, x_n is the molar fraction of the component, e_{ch}^n is the standard chemical exergy in J/kg, R is the gas constant in J/kg K, and T_0 is the standard temperature taken as 298.15 K.

The mass flow rate values of the reactants and the products in the fuel cell can be calculated in terms of power output \dot{W}_{elect} , voltage V , and the stoichiometry of air, λ . From the reactions involved in the fuel cell, four electrons are transferred for every mole of oxygen. Also the molar mass of oxygen is 32×10^{-3} kg/mol. Therefore, oxygen usage is,

$$\dot{m}_{O_2} = \frac{32 \times 10^{-3} \times \dot{W}_{elect}}{4 \times F \times V_{cell}} = 8.29 \times 10^{-8} \times \left(\frac{\dot{W}_{elect}}{V_{cell}} \right) \quad (29)$$

where, F is Faraday's constant taken as 96,485 J. The molar proportion of air that consists of oxygen can be taken as approximately 0.21, and the molar mass of air as 28.97×10^{-3} kg/mol. Then, the mass flow rate of reactant/inlet air can be formulated as,

$$\begin{aligned} \dot{m}_{air,R} &= \frac{28.97 \times 10^{-3} \times \lambda \times \dot{W}_{elect}}{0.21 \times 4 \times F \times V_{cell}} \\ &= 3.57 \times 10^{-7} \times \left(\frac{\lambda \times \dot{W}_{elect}}{V_{cell}} \right) \end{aligned} \quad (30)$$

The oxygen reacts with hydrogen in the fuel cell will be depleted from the exit air. Then, the mass flow rate of exit air will be the

Table 3

Input data and assumptions for SOFC, MCFC and PAFC.

Section	Values
<i>General data</i>	
Standard pressure (P_0), MPa	0.1
<i>Solid oxide fuel cell (SOFC)</i>	
Operating temperature (T), K	1253
Electric power output (\dot{W}_{elect}), kW	200
Voltage (V), V	480
<i>Molten carbonate fuel cell (MCFC)</i>	
Operating temperature (T), K	923
Electric power output (\dot{W}_{elect}), kW	2800
Voltage (V), V	13,800
<i>Phosphoric acid fuel cell (PAFC)</i>	
Operating temperature (T), K	473
Electric power output (\dot{W}_{elect}), kW	400
Voltage (V), V	480

difference between the mass flow rates of inlet air and the oxygen used, as shown below.

$$\dot{m}_{air,P} = 3.57 \times 10^{-7} \times \left(\frac{\lambda \times \dot{W}_{elect}}{V_{cell}} \right) - 8.29 \times 10^{-8} \times \left(\frac{\dot{W}_{elect}}{V_{cell}} \right) \quad (31)$$

A similar approach to that of oxygen can be followed to determine the mass flow rate for the hydrogen usage, except it must be noted that there are two electrons from each mole of hydrogen. Thus, the hydrogen usage can be calculated as,

$$\dot{m}_{H_2,R} = \frac{2.02 \times 10^{-3} \times \dot{W}_{elect}}{2 \times F \times V_{cell}} = 1.05 \times 10^{-8} \times \left(\frac{\dot{W}_{elect}}{V_{cell}} \right) \quad (32)$$

In a hydrogen-fed fuel cell, the end product is water, which is produced at a rate of one mole for every two electrons. The molar mass of water is 18.02×10^{-3} kg/mol. Then, the mass flow rate of water produced is,

$$\dot{m}_{H_2O,P} = \frac{18.02 \times 10^{-3} \times \dot{W}_{elect}}{2 \times F \times V_{cell}} = 9.34 \times 10^{-8} \times \left(\frac{\dot{W}_{elect}}{V_{cell}} \right) \quad (33)$$

In the case of a MCFC (molten carbonate fuel cell), carbon dioxide is added to the cathode along with the oxidizer as required to produce carbonate ions. The carbon dioxide mass flow rate is,

$$\dot{m}_{CO_2,R} = \frac{44.01 \times 10^{-3} \times \dot{W}_{elect}}{2 \times F \times V_{cell}} = 2.28 \times 10^{-7} \times \left(\frac{\dot{W}_{elect}}{V_{cell}} \right) \quad (34)$$

For a reversible fuel cell system, i.e. no losses, the electrical work is equal to the Gibbs free energy released, $\Delta\bar{g}_f$. Thus, the EMF or the reversible open circuit voltage of a hydrogen fuel cell is,

$$E = \frac{-\Delta\bar{g}_f}{2 \times F} \quad (35)$$

The molar enthalpy of formation, molar entropy, and standard chemical exergy of hydrogen, oxygen, steam, and carbon dioxide at a standard temperature of 298.15 K are given in Table 2. Also, some input data of analysis is given in Table 3.

8. Results and discussion

Table 1 shows the comparison of S-I, Mg-Cl and Cu-Cl thermochemical cycles in terms of number of steps, highest operation temperature, energy and exergy efficiencies, and external energy input. In the table, the total energy input is the heat and electricity demand for producing 1 kg of H_2 .

As mentioned above, the S-I cycle is a process in which hydrogen is produced by decomposing sulfuric acid (H_2SO_4). The process is carried out adiabatically by several subsections, at a maximum pressure of 1.2 MPa. These subsections are (1) sulfuric

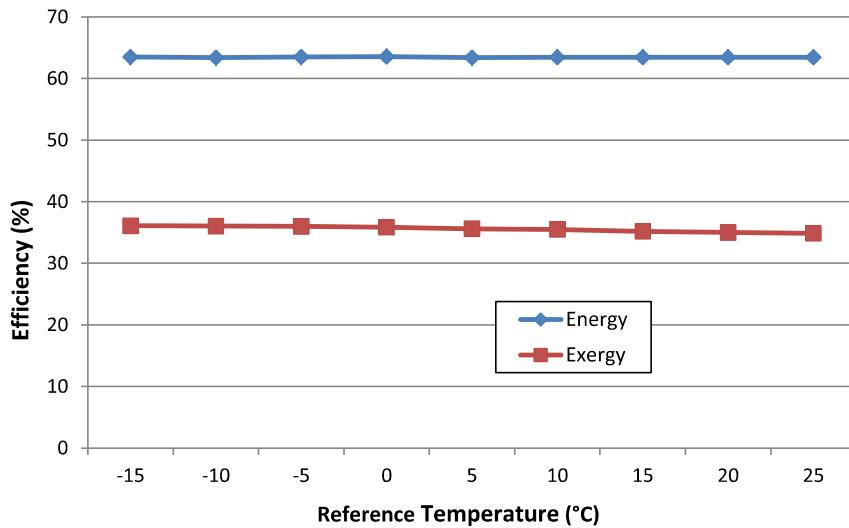


Fig. 16. Variation of energy and exergy efficiencies with the reference environment temperature.

acid concentration, (2) acid evaporation and SO_3 production, and (3) SO_3 decomposition. The energy that is involved in the overall reaction is 278.643 kJ/mol SO_2 . Also, the total thermal energy supplied to the process is 366.747 kJ/mol SO_2 . Therefore, the energy efficiency is calculated to be 76%. The net output exergy of the overall process is 193.653 kJ/mol SO_2 , while the net exergy supplied to the process is 256.015 kJ/mol SO_2 . Hence, the exergy efficiency is determined to be 75.6%.

The Mg–Cl cycle operates on a low process temperature similar to that of the Cu–Cl cycle. Fig. 16 illustrates the variation of energy and exergy efficiencies of the cycle with the reference environment temperature. As can be seen from the figure, the energy efficiency shows nearly no change with the variation of reference temperature. But the exergy efficiency shows a variation from 36.11% to 34.86% with a change in reference environment temperature from $-15\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$. Hence, at a standard reference temperature of $25\text{ }^\circ\text{C}$, the energy and exergy efficiencies are about 64% and 35%, respectively.

The Cu–Cl cycle is currently has gained many interests and investigations due to its several merits as mentioned in the previous sections. The cycle utilized in this study is the four-step process integrated with a Kalina cycle. Heat exchangers are also used to recover the waste heat from the Cu–Cl and maximizing the efficiencies. Therefore, energy and exergy efficiency analysis are performed considering three scenarios; with heat recovery system (w HR), without heat recovery system (w/o HR) and with Kalina cycle integration (w I). The results of these three scenarios are given in Figs. 17 and 18. From the figures, the energy and exergy efficiencies vary quite significantly with the electrolyzer temperature. This effect is due to the fact that electrolyzer temperature determines the amount of energy carried out by the hydrogen and other byproducts leaving the electrolyzer (and eventually the cycle). As shown in Fig. 17, the energy efficiency of the cycle without heat recovery, with heat recovery, and with integration is calculated to vary from 46.94% to 43.68%, 53.35%–49.19%, and 59.15%–49.02%, respectively. Also, from Fig. 18, the exergy efficiency of the system without heat

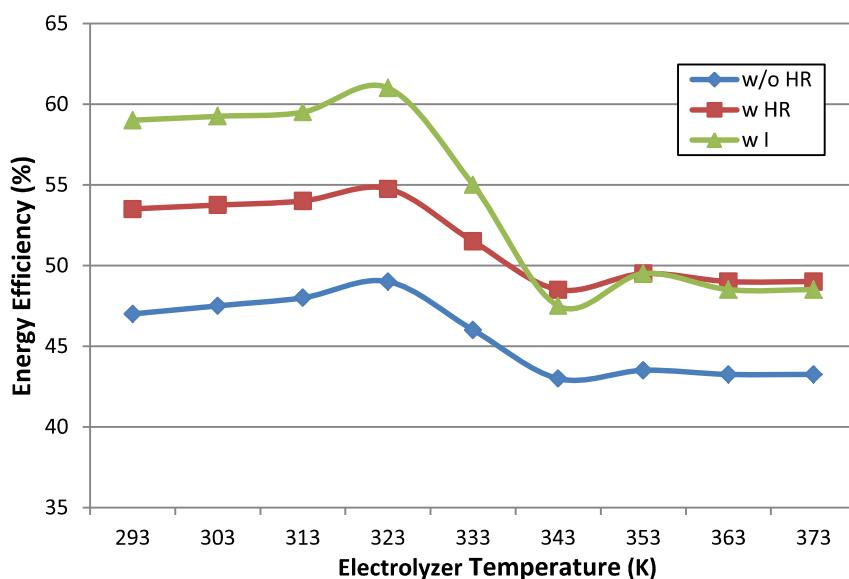


Fig. 17. Effect of the electrolyzer temperature on the energy efficiencies.

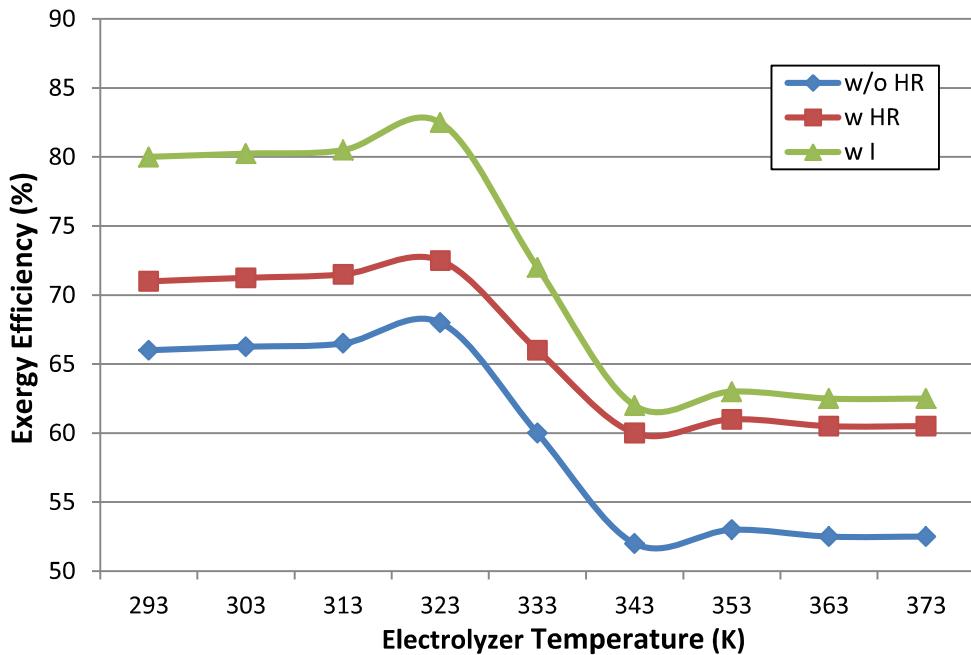


Fig. 18. Effect of the electrolyzer temperature on the exergy efficiencies.

recovery, with heat recovery, and with integration is determined to vary from 65.97% to 52.31%, 70.91%–60.49%, and 80.11%–62.37%, respectively. These results suggest that the optimum operating temperature of the electrolyzer is 328.6 K for a maximum energy and exergy efficiencies of 66.92% and 72.06%, respectively, for overall cycle.

Fig. 19 shows a comparative analysis between three different thermochemical hydrogen production processes. From the figure, the S–I cycle shows a better performance from the efficiency point of view. However, a drawback of this cycle is its high operating temperature of 850 °C. The maximum temperature reached in a water-cooled nuclear reactor is around 350 °C and the rest need to be achieved with the help of the solar energy source. If this high temperature is achieved by combined efforts of the nuclear/solar

coupled system, then S–I can be used. Otherwise, the Cu–Cl cycle should be considered for hydrogen production due to its lower operating temperatures of approximately 550 °C, which is achievable.

Among the three thermochemical hydrogen production cycles presented above, only the S–I cycle has been scaled up sufficiently to the level of industrial equipment and well commercialized. The other two are still at the stage of proof-of-principle, small bench-scale apparatus and individual pilot plants. Thus, there are few previous studies [24–30] on the same subject that the results of this study can be compared with. Nonetheless, to facilitate the validation of the results above, a comparison is made in three stages. First, the results are comforted with the previous thermodynamic analyses to make sure that they are within the boundary

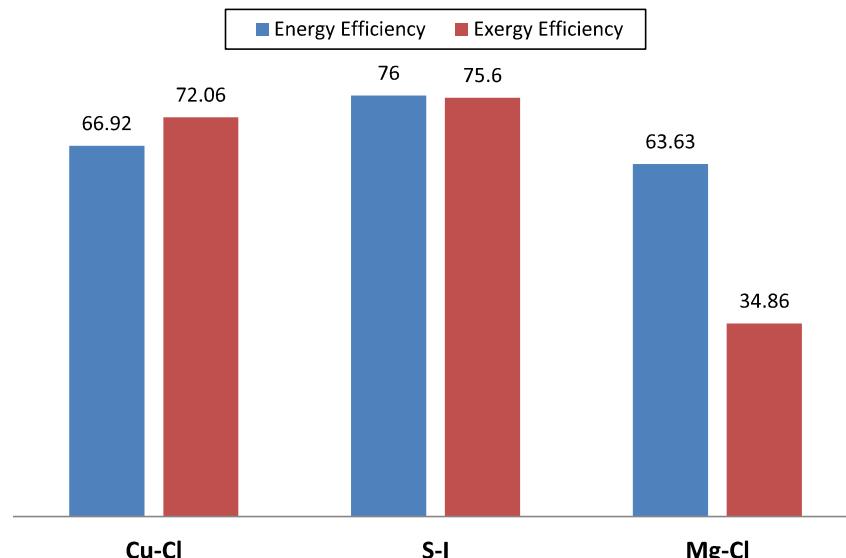


Fig. 19. Efficiency comparison for Cu–Cl, S–I, and Mg–Cl cycles.

Table 4

Complete fuel utilization results for SOFC, MCFC and PAFC.

	Solid oxide fuel cell (SOFC)	Molten carbonate fuel cell (MCFC)	Phosphorous acid fuel cell (PAFC)
Enthalpy of formation, $\Delta \bar{H}_f$ (kJ/mol)	-249237.45	-247311.48	-243568.37
Gibbs free energy, $\Delta \bar{G}_f$, (kJ/mol)	-178568.25	-196924.91	-220426.85
Exergy of reactant air, $E_{air,R}$ (kW)	83.05	563.63	20.43
Exergy of reactant hydrogen, $E_{H_2,R}$ (kW)	457.30	5112.35	565.43
Exergy of product air, $E_{air,P}$, (kW)	6.05	55.18	4.81
Exergy of product water, $E_{water,P}$ (kW)	54.41	417.32	25.23
Exergy of reactant carbon dioxide, $E_{CO_2,R}$ (kW)	0	292	0
EMF, V (V)	0.93	1.02	1.15
Energy efficiency, η_{energy} (%)	62.47	68.89	77.12
Exergy efficiency, η_{exergy} (%)	41.68	50.95	71.96

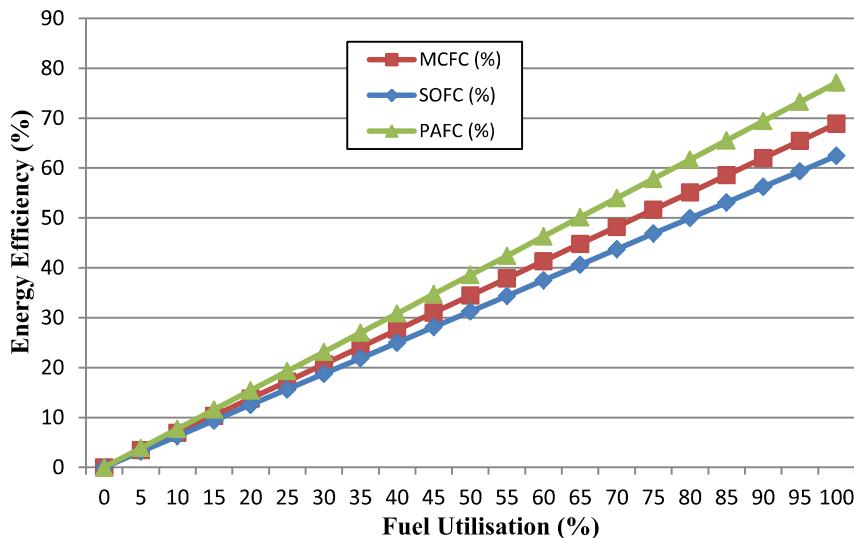


Fig. 20. Energy efficiency variation of fuel cells with respect to fuel utilization.

of thermodynamic laws and logic. Secondly, although the reported experimental studies in the literature are at the level of small bench-scale apparatus and for only individual steps, not the overall cycle, the results here are compared with these experiments to make sure that the trends are conformable. Finally, there are some

theoretical studies in the literature that the results in this study are also validated with.

EMF and energy/exergy efficiencies of fuel cells are illustrated in Table 4. These results are for the ideal case of complete utilization of hydrogen. However, the fuel utilization will vary in working fuel

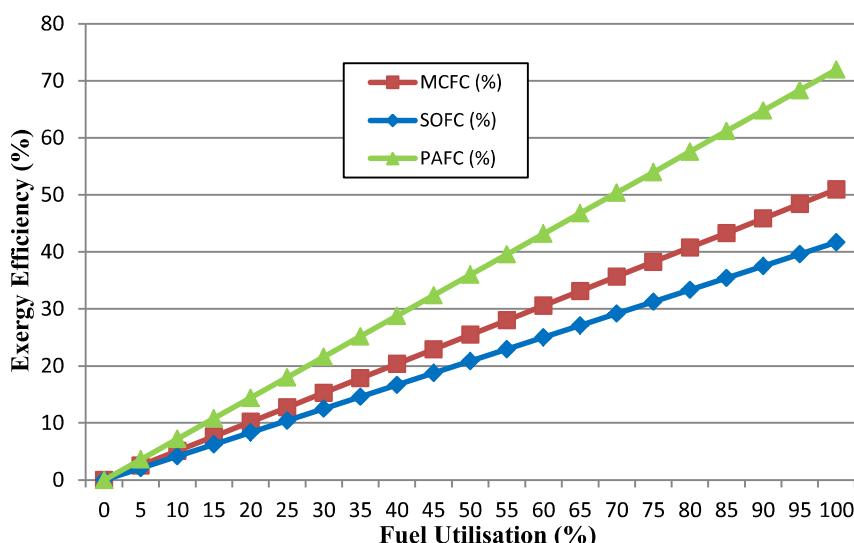


Fig. 21. Exergy efficiency variation of fuel cells with respect to fuel utilization.

cells based on the type of fuel cell. Figs. 20 and 21 show the variation of energy and exergy efficiencies with respect to fuel utilization, respectively. As can be seen from these figures, both energy and exergy efficiencies of all three types of fuel cells have a direct relation with the fuel utilization.

From the results, it can be observed that for ideal conditions, PAFCs have higher energy and exergy efficiency than MCFCs. However, this is not the case in actual conditions. MCFCs operate at much higher temperatures, which results in decrease of theoretical voltage and hence maximum theoretical efficiency. On the other hand, an increase in operating temperatures increases the electrochemical reaction rate, and hence higher current and power output. The net effect is that the real operating voltage in MCFCs is higher than the voltage in PAFCs at the same current density. Hence, due to high operating voltages in MCFCs, more power is available at higher fuel efficiencies than in PAFCs for the same electrode area.

MCFCs do not require any expensive electrodes, unlike PAFCs that require a platinum catalyst. Also, in MCFCs the area required is less due to the reason mentioned. This makes MCFCs more favorable than PAFCs in terms of cost.

Another benefit of the high operating temperature in MCFCs is the possibility of using fossil fuels such as natural gas. The natural gas gets reformed to produce hydrogen that is then utilized in the fuel cell. In this way, when hydrogen is deficient, fossil fuels can be used. The efficiency of MCFCs is higher than that of conventional power generation methods, which is another benefit of utilizing these fossil fuels.

Unlike any other fuel cells currently available, MCFCs require the need of carbon dioxide. At high temperatures, the electrolyte used forms a highly conductive molten salt, along with carbonate ions CO_3^{2-} which are used for reaction in the anode. However, the electrolyte's capability to produce the required ions decreases by time. Hence, carbon dioxide is provided through the cathode along with the oxidizer. In this way, the power produced by fuel cells further reduces carbon dioxide present in the surroundings. The excess carbon dioxide in the anode captured to use back in the cathode. Also, due to this reason, MCFCs are not prone to poisoning.

Due to the fuel cell's high operating temperatures, a large amount of waste heat is produced inside it. This heat could be captured and reused in a steam turbine to further increase efficiency. This approach could potentially increase the efficiency of the MCFCs up to 85%.

9. Conclusions

An integrated hydrogen production system combining both nuclear and solar energy sources is presented. This integrated system includes storage of hydrogen and its conversion to electricity by fuel cells when needed. In this regard, a detailed description of the integrated system is given and its functionality is provided in a smart grid approach. An extensive literature review of hydrogen storage options is also carried out. Furthermore, a comparative study is performed to evaluate an optimal and feasible hydrogen production process that can be linked to this integrated system. Studies conducted here on hydrogen production processes show the thermochemical water decomposition to be a better option for producing hydrogen, comparing to electrolysis, due to its high efficiencies and low costs. Energy and exergy efficiencies of various thermochemical hydrogen production processes and fuel cell systems are evaluated and compared. Also, a parametric study is conducted to evaluate the effect of various operating conditions. The thermodynamic analysis reported in this study has allowed concluding that the S-I cycle shows a better performance from the efficiency point of view.

However, a drawback of this cycle is its high operating temperature of 850 °C. The maximum temperature reached in a water-cooled nuclear reactor is around 350 °C and the rest need to be achieved with the help of the solar energy source. If this high temperature is reached by combined efforts of the nuclear/solar coupled system then S-I cycle can be utilized, otherwise the Cu–Cl cycle should be considered for hydrogen production due to its lower operating temperatures. Also, the energy efficiencies of SOFC, MCFC and PAFC are 62%, 69% and 77%, respectively, while exergy efficiencies are 42%, 51% and 72%, respectively. These results are calculated based on complete fuel utilization. With less fuel utilization inside the fuel cells, the thermodynamic efficiencies tend to decrease. Capturing the waste reaction heat of MCFC and SOFC could lead to a further increase in the efficiencies.

Nomenclature

Ex	exergy, kJ
\bar{ex}^{ch}	specific chemical exergy, kJ/kmol
F	Faraday's constant
G	Gibbs function, kJ
\bar{g}	specific Gibbs free energy, kJ/kmol
H	total enthalpy, kJ
h	specific enthalpy, kJ/kg
\bar{h}	specific enthalpy, kJ/kmol
\bar{h}^0	specific enthalpy at reference state, kJ/kmol
\bar{h}_f^0	specific enthalpy of formation, kJ/kmol
\dot{m}	mass flow rate, kg/s
n	number of moles per cycle, kmol/kmol H ₂
Q	heat, kJ
R	gas constant
s	specific entropy, kJ/kg K
\bar{s}	specific entropy, kJ/kmol K
\bar{s}^0	specific entropy at reference state, kJ/kmol K
$T_{reaction}$	reaction temperature, K
T_0	reference-environment temperature, K
V	velocity, m/s
Z	elevation, m
ΔG	change in Gibbs function for a reaction, kJ

Greek letters

η	energy efficiency
η_{ex}	exergy efficiency
Δ	change
λ	stoichiometric ratio

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