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Research Paper

Tapping the benefits of using geothermal energy and absorption refrigeration system in the precooling part of a hydrogen liquefaction cycle

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Abstract: Given the importance of using renewable energy sources in industries, using methods of energy storage is a crucial topic. The use of renewable energy sources and water electrolysis for the production of power and hydrogen gas has received much attention in recent years, therefore, in this method, hydrogen gas and oxygen are separated from water without any pollution, hydrogen production in processes with zero carbon emission is known as green hydrogen, which is used in this research. Geothermal energy is used to precool the hydrogen gas. The innovation of this research is to propose an idea to integrate geothermal energy into a hydrogen liquefaction cycle which is fed by solar energy. Solar arrays have been used to power proton membrane electrolyzers and liquefaction sections, and Bandar Abbas City has been considered for implementing the proposed system. The power generation capacity of solar arrays is 6000 kilowatts, while the separation capacity of the electrolyzer is 435 kg/hour of oxygen gas and 55 kg/hour of hydrogen gas. The specific energy consumption of the liquefaction cycle is 4.97 kWh per kilogram of liquid hydrogen, and the most exergy destruction is related to the electrolyzer and the heat exchangers. The hydrogen liquefaction cycle with and without the geothermal and absorption refrigeration system is evaluated.

keywords: Hydrogen, Geothermal, Solar energy, PEM, Water-ammonia absorption.

Highlights

- Tapping the benefits of using geothermal energy source in hydrogen liquefaction cycle.
- Pre-cooling part of a hydrogen liquefaction cycle is integrated into an absorption refrigeration system.
- Geothermal and solar renewable energy sources are used to precool the hydrogen gas and generate power, respectively.
- Exergy analysis is utilized to achieve a better performance of the proposed system.

1 Introduction

One of the methods of sustainable energy production is the use of renewable solar energy to power various systems. In addition, hydrogen is used in various industries (Ghorbani et al. 2019). Due to the importance of saving the environment and the need to reduce greenhouse gases in various processes, including the hydrogen production process, the use of electrolyzers and solar energy to produce hydrogen as a process with zero carbon output has received much attention in recent years. According to technological progress related to green systems, the cost of hydrogen production using this method has decreased in recent years, and as a result, hydrogen production using solar energy and electrolyzers is economically competitive with other methods of hydrogen production (Rahman and Wahid 2021). The clean production of hydrogen is divided into two branches, green hydrogen, and blue hydrogen, in such a way that the hydrogen produced in the set of processes that have zero carbon output is called green hydrogen Faramarzi et al. (2021), but if the hydrogen production processes have carbon output which is captured by a carbon capture system, the product is called blue hydrogen. In this research, according to the use of solar energy, the product is green hydrogen, which is the cleanest method of hydrogen production (Ghorbani et al. 2020).

Using solar and geothermal energy to supply the

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consumption power of hydrogen production units has been of interest in the past years. In the work of Bicer and Dincer (2016), a multi-generation renewable system was investigated based on the integration of a power generation system based on solar and geothermal energy systems using the organic Rankine cycle and solar arrays, from an air circulation system. Photovoltaic modules were used to transfer more heat to the air, and the exergy efficiency of the cycle was 28%. The results showed that the evaporator in the organic Rankine cycle had the highest exergy destruction, which was about 37% of the total exergy destruction of the entire system. Aasadnia, Mehrpooya, and Ansarinasab (2019) investigated the use of solar energy in combination with an absorption refrigeration cycle to reduce the temperature of the hydrogen liquefaction cycle. Rankine cycle and pre-cooling and low-temperature units were considered in the studied process. Yuksel, Ozturk, and Dincer (2019) investigated the use of solar and geothermal energy to produce power and hydrogen. Proton exchange membrane electrolyzers are considered a clean and highly efficient technology. The production of hydrogen from water electrolysis, which splits water molecules into hydrogen and oxygen using electricity, can be very useful when combined with other technologies. When the electricity generated by various cycles is used for water electrolysis, hydrogen stores unused energy for future use and can be considered as a fuel and energy source for transportation and energy sectors. Some advantages of proton exchange membrane electrolyzers over other electrolyzers that led to their selection in this study include high performance, high voltage efficiency, quick system response, and compact cell design. However, some of its disadvantages are high component costs, corrosive acid components, and relatively low durability. Compared to other types of electrolyzers, the proton membrane electrolyzer has the advantages of low working temperature, smaller design, the ability to occupy less space, and the ability to work at high current density. Production rate of 99.99 % of hydrogen and oxygen, high efficiency (8%0 to 90%), and fast response (Shiva Kumar and Himabindu 2019). Moradi Nafchi et al. (2018) used solar energy to supply the required power of a PEM. The effect of different variables on system performance was investigated. The efficiency of their proposed cycle had an exergy efficiency of 41.25%. El-Emam and Dincer (2018) used solar energy to produce hydrogen from water using a PEM, the capacity of the proton membrane electrolyzer was 1.25 kg/h. Electrolysis of water for hydrogen production has been studied in many researches, but its combination with power supply units from renewable sources as well as hydrogen liquefaction is one of the issues that has received less attention and is also studied in this research. Nouri et. al (2020) proposed a cycle to convert production power into liquid hydrogen and carbon dioxide. The proposed cycle consisted of five sub-systems, which included photovoltaic power generation systems, an electrolyzer for separating hydrogen and oxygen from water, an absorption cooling cycle for the liquefaction of carbon dioxide, a power generation unit with oxygen fuel, and a hydrogen liquefaction cycle. The proposed cycle had a capacity of 3.3 kg/s of liquid hydrogen and 10 kg/s of carbon dioxide. The exergy efficiency of the cycle is 95% and its specific energy consumption is 3.359. Ranjbar et al. (2017) investigated a Matiant cycle and the organic Rankine cycle with a PEM for the simultaneous production of power and hydrogen. R123 working fluid was used in the Rankine cycle. The organic Rankine cycle supplied the power required by the electrolyzer. Water with the ambient temperature entered the heat exchanger where its temperature rose to the temperature of the electrolyzer. After leaving the cathode, the produced hydrogen gave its temperature to the environment and became the same temperature as the environment. The electrolyzer converted power, heat and water into hydrogen and oxygen. One of the main applications is to use an electrolyzer to produce hydrogen using solar electricity, in order to convert the power of the sun's renewable energy into hydrogen to enable the storage and transmission of solar electricity, in addition, this process is completely compatible with the environment (Moradi and Groth 2019). Ginsberg et al. (2022) examined polymer electrolyte membranes to estimate temperature and pressure changes for hydrogen production using water electrolysis and found that at high pressures, voltage is significantly affected by temperature changes, and higher temperatures result in decreased voltage. Additionally, voltage is proportional to pressure, and higher pressures require higher voltages. Fakourian and Alizadeh (2023) combined multi-purpose solar cells with proton exchange membrane electrolyzers. They experimentally measured the efficiency of hydrogen production for six modules and found a maximum of 16.8% for one module. They also investigated the effect of temperature on the performance of proton exchange membrane electrolyzers and current-voltage characteristics. Their proposed design's main advantage was higher current at lower voltage, leading to a significantly increased system efficiency. Lin et al. (2022) investigated j-v parameters of proton exchange membrane electrolyzers for hydrogen production from water and developed an electrochemical model for use in high capacity activation. Sensitivity analysis also showed that the higher the operational temperature, the lower the cell potential, and the high capacity activation of the anode, the main source of voltage drop.

Faramarzi et al. (2021) proposed a hydrogen liquefaction cycle that included two stages of pre-cooling and low-temperature cooling. The combined refrigerant was used to reduce the work consumed in the compression units. The use of ortho-to-para converters and the selection of appropriate equations of state for hydrogen at very low temperatures were also investigated, and the result was that the appropriate equation of state for pure hydrogen gas at low temperatures was modified by Bendick-Webb-Robin and for mixed refrigerant flows. was Peng-Robinson. The exchanger of the pre-cooling section had the highest exergy destruction and the specific energy consumption of the whole cycle was 8.85 kWh per kilogram of liquid hydrogen production. Neon, helium, and hydrogen refrigerants were used in the low-temperature cooling section and nitrogen refrigerants and hydrocarbon derivatives were used in the pre-cooling section. Energy, exergy, and economic analyses were used by Nourbakhsh et al. (2021) to study a mixed refrigerant liquefaction cycle which was integrated into a natural gas liquefaction cycle. Rezaie Azizabadi et al. (2021) studied a hydrogen liquefaction cycle integrated into a waste heat system recovery assisted by the absorption process. Using geothermal energy in some studies was integrated with other systems like liquid natural gas systems (Faramarzi and Khavari 2023) and multi-generation systems

(Faramarzi et al. 2023).

Using Electricity and cold energy from renewable energy sources for the water electrolyzer system, the compressors of the compression section of liquefaction, and the precooling part of the hydrogen liquefaction system is one of the topics that has been studied less and is investigated in this research. The novelty of this study is based on using cold energy from geothermal energy which is produced by an absorption system in the precooling part of a hydrogen liquefaction cycle. Solar arrays are used to generate power for the PEM and hydrogen liquefaction cycle. Using renewable energy sources to provide power for the PEM and hydrogen liquefaction cycle means that the proposed cycle has no carbon emission named green hydrogen production system.

2 Methods

The proposed process includes subsystems: the subsystem that converts sunlight into electricity by solar cells, the proton membrane water electrolyzer, the geothermal absorption system, and the hydrogen liquefaction cycle. The hydrogen liquefaction cycle is assisted by a pre-cooling system and a cryogenic mixed refrigerant. In Fig. 1, the diagram of the studied cycle is shown. A set of solar cells generates electricity by using sunlight and the generated electricity is divided into two parts, some of it is transferred to the local power grid and the other amount provides the required power for the electrolyzer unit. The electrolyzer unit separates water from water and produces hydrogen at a temperature of 80 °C and a pressure of 2 kPa. Hydrogen is transferred to the storage tank and it is liquefied by the hydrogen liquefaction unit. The city of Bandar Abbas in Iran is the place of implementation of this plan. The details of the solar arrays used in this study are based on the work of Ghorbani et al. (2020).

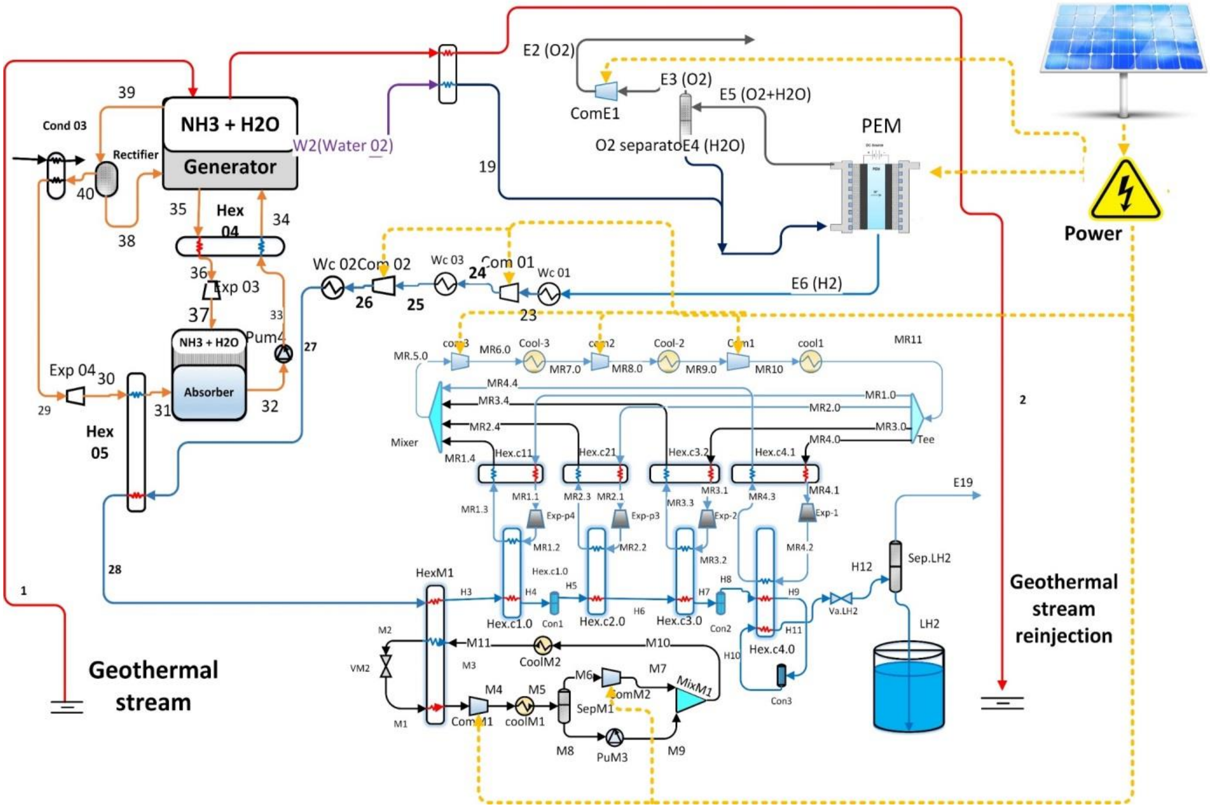

Fig. 1 Flow diagram of the proposed multi-generation system

To supply power with a capacity of 6 MW, a system connected to the solar array network is used, which includes solar panels and direct and alternating current converter units. The specifications of the solar power generation unit are designed based on the information provided in the work of Nouri et al. (Nouri et al. 2020). Twenty thousand single crystal silicon modules are installed in 1819 rows of 11. The angle of the arrays is 28 and the orientation of the arrays is zero. The arrays have an open circuit voltage of 39.7 v and a short circuit current of 9.83 A. The maximum temperature is 45 °C and their efficiency is 15 %. More details of the solar arrays used in this study are available in the work of Nouri et al. (2020). The proton membrane electrolysis unit of this research is considered based on the results of Seyedmatin et al. (2020). The production capacity of the electrolyzer is 55.23 kg/h of hydrogen gas with a temperature of 80 °C. According to Fig. 1, streams E4 and 19, which are water, enter the electrolysis and after separating stream 23, which is hydrogen, leaves the electrolyzer. Another output stream from electrolysis is E5, which consists of oxygen and water, the oxygen output goes to the hydrogen liquefaction cycle, while the water re-enters the electrolysis. The mole fraction of different components in mixed refrigerant streams is based on the work of Faramarzi et al. (2021). The geothermal stream is used in the absorption system to produce cold energy which is utilized in precooling part of the hydrogen liquefaction cycle. In the hydrogen liquefaction cycle, the hydrogen gas is precooled in a heat exchanger, then enters the next heat exchanger where the mixed refrigerant precools the hydrogen gas. After precooling, the hydrogen gas enters the final cooling section where the mixed refrigerant including neon, hydrogen, and helium are used to liquefy the hydrogen. The maximum pressure in the pre-cooling section is 4200 kPa and the minimum pressure is 330 kPa. In the final cooling section, the maximum pressure is 1505 kPa, while the minimum pressure is 101 kPa. The ratio of pressure increase in the pre-cooling section is done in two stages, which are 3.3 and 3.5, while in the final cooling section, three stages of compression are done. In this research, after examining different methods, the Modified Bendick Web Robin (MBWR) equations of state were used to simulate the pure hydrogen flow stream, and the Peng-Robinson (PR) equation of state was used for mixed refrigerant and natural gas flows. Fig. 2 shows the flow chart of the method used in this study. The method used in this study is based on the work of Faramarzi et al. (2021). The properties of the main streams are given in Table 1. Some assumptions are as follows:

- Potential and kinetic energy changes are insignificant (Ghorbani et al. 2020).
- The pressure drop in heat exchangers is 30 kW and it is 50 kW in coolers based on the works of Ranjbar et al. (2022) and Faramarzi et al. (2021b).
- The minimum temperature approach is between 1 °C to 8 °C in heat exchangers Yuksel et al. (2017) and Faramarzi et al. (2021).
- Based on the work of Yin and Ju (2020), the adiabatic efficiency of compressors is 80%, turbine expanders 85%, and pumps 80% (Saadabad et al. 2022).

There are limitations and obstacles to producing liquid hydrogen using renewable energy sources, including:

- Limited availability of renewable energy sources: The availability of renewable energy sources such as solar and geothermal is dependent on weather conditions and geographical location, which can limit their availability and reliability.
- High cost of renewable energy technologies: The initial investment required for installing renewable energy technologies such as solar panels and wind turbines can be high, which can make the production of liquid hydrogen by electrolyzer expensive.
- Energy storage limitations: Renewable energy sources are intermittent, which means that they cannot produce a constant supply of electricity. This can lead to energy storage limitations, which can affect the overall efficiency of the electrolyzer.

The exergy analysis, ignoring the changes of kinetic and potential exergy, has been considered as follows (Faramarzi et al. 2022):

$$e = e^{ph}(h - h_0 - T(S - S_0)) + e^{ch}(\sum_j x_j {e_j}^{ch} + \bar{R}T_0 \sum_j x_j \ln x_j) \qquad (1)$$

$$\dot{Q}_{cv} + \sum \dot{m}_{in} h_{in} = \sum \dot{m}_{out} h_{out} + W_{cv} \qquad (2)$$

$$E_i + E_{Qi} = E_o + E_{Qo} + W_{sh} + I \qquad (3)$$

Exergy efficiency and exergy destruction are calculated for the equipment. The coefficient of performance (COP) and SEC are calculated to compare the hydrogen liquefaction cycle (Nourbakhsh et al. 2021).

$$SEC = \frac{P_{net}}{\dot{m}_l} \qquad (4)$$

$$COP = \frac{Q_c}{P_{net}} \qquad (5)$$

The exergy efficiency of different equipment is calculated as follows (Asadnia and Mehrpooya 2017; Faramarzi, et al. 2021; Serkani and Mafi 2020):

$$\eta_{ex,throttle\ valve} = \frac{e_{out}^{\Delta T} - e_{in}^{\Delta T}}{e_{in}^{\Delta p} - e_{out}^{\Delta p}} \qquad (6)$$

$$\eta_{ex,conversion\ reactor} = \frac{e_{out}}{e_{in}} \qquad (7)$$

$$\eta_{ex,Heat\ exchanger} = 1 - \left\{\frac{\sum_1^n(\dot{m}\Delta e)}{\sum_1^n(\dot{m}\Delta h)}\right\}_{hot} + \left\{\frac{\sum_1^n(\dot{m}\Delta e)}{\sum_1^n(\dot{m}\Delta h)}\right\}_{cold} \qquad (8)$$

$$\eta_{ex,Compressor} = \frac{e_{in} - e_{out}}{W_{com}} \qquad (9)$$

$$\eta_{ex,turbin} = \frac{W_{tur}}{e_{in} - e_{out}} \qquad (10)$$

$$\eta_{ex,PEM} = \frac{\dot{N}_{H_2,out} \times \dot{E}x_{H_2}}{W_{ORCT} + \dot{E}x_{HEX}} \qquad (11)$$

$$\eta_{ex,cycle} = 1 - \frac{I_{total}}{P_{net}} \qquad (12)$$

Table 1 **Thermodynamic properties of the proposed multi-generation system.**

Stream name	$\dot{m}(kg\ s^{-1})$	T (°C)	P (kPa)	Stream Composition
E2	0.12	80	101	Oxygen
E6	0.015	80	101	Hydrogen
MR5.0	0.23	23	101	Mixed refrigerant
MR11	0.6	20	4200	Mixed refrigerant
28	0.0015	-27	2000	Hydrogen
1	100	200	890	Geothermal water
27	0.015	26.9	2000	Hydrogen
LH2	0.015	-251	0.0	Hydrogen

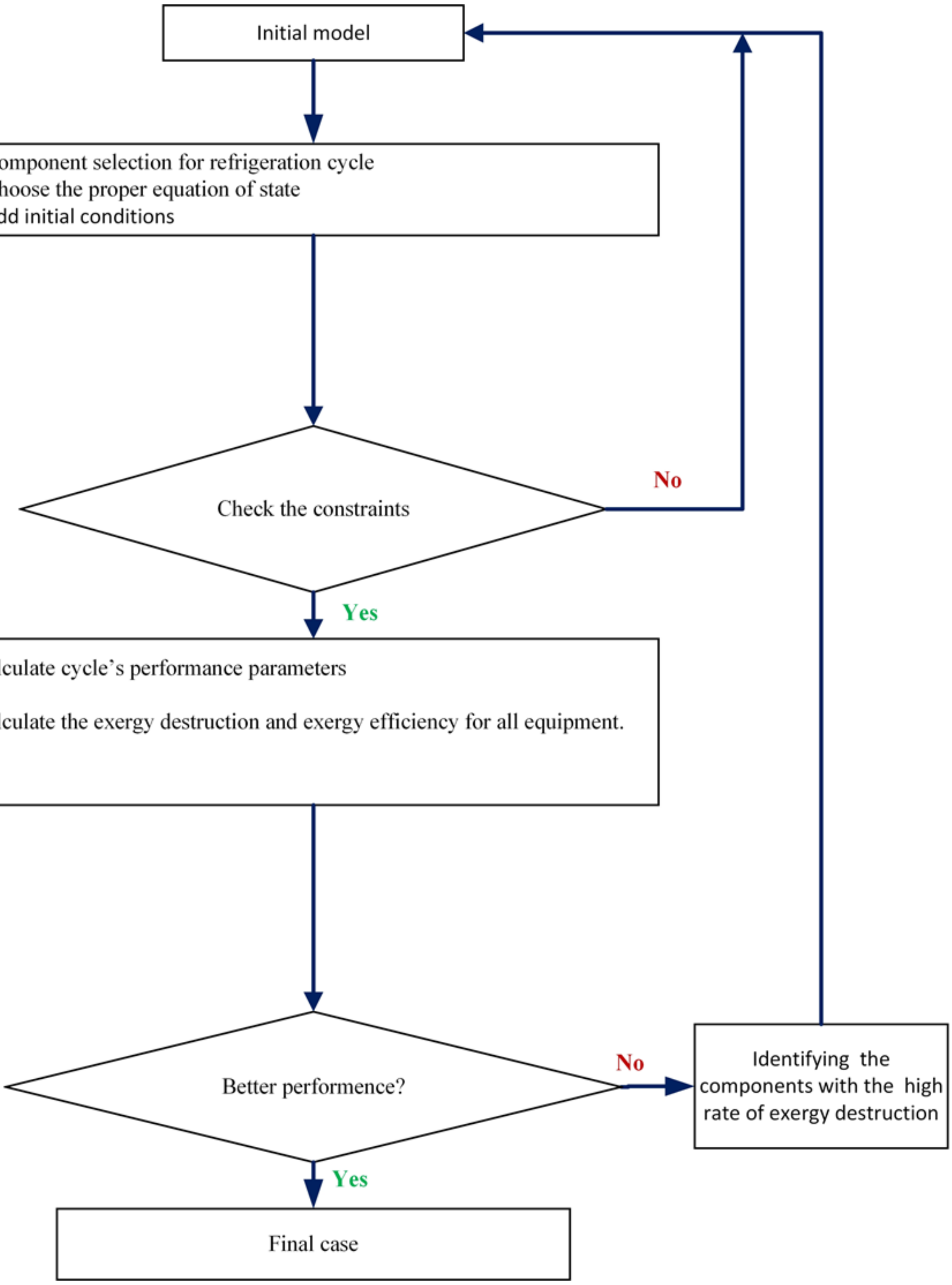

Fig. 2 Flow chart of the method used in the present study.

3 Results

In Bandar Abas, the city studied for the proposed cycle, the highest amount of radiation was observed in May and the lowest amount of radiation was observed in December, while the highest ambient temperature occurred in July and the lowest temperature occurred in January based on the reference of Ghorbani et al. (2020). The performance rate of solar arrays is equal to the ratio of the amount of energy output from the system to the energy that the system can produce. The best performance rate occurs in January and December for Bandar Abas city. The specifications of the proton membrane electrolyzer used in this research are given in Table 2. The design of the electrolyzer used in this research is based on the work of (Nikzad et al. 2023). According to the type of electrolyzer in this research, which is a Fraunhofer ISC type (manufactured by Fraunhofer Institute, manufacturer of hydrogen-producing proton membrane electrolyzers), each cell of the electrolyzer has an active area of 100 square centimeters and a production rate 20 NL/h, the mass of the electrolyzer has 39 cells with a production capacity of 54 kg/h of hydrogen, also for each electrolyzer cell, the maximum voltage of each cell is 2.2 V, the maximum compressive strength is 207 bar, the membrane thickness is 100 micrometers, the activation energy Anode and cathode are 76 and 18 kJ/mol, respectively.

In Table 3 specifications of the heat exchangers of the proposed system are shown. Fig. 3 shows the exergy efficiency of the equipment. The total exergy efficiency is 44% for the hydrogen liquefaction cycle while it is 57 % for the PEM. Fig. 4 shows the exergy destruction for the equipment of the hydrogen liquefaction. In Fig. 4, the exergy destruction of different components is compared with each other. As it is clear, the electrolyzer has the most exergy destruction, while the heat exchangers and coolers also have a high contribution to the exergy destruction of the whole system. Fig. 5 shows the composite curves of hot and cold flows for the heat exchanger namely HexM1. At a minimum temperature difference of 1 ℃, composite curves of cold and hot are closer to each other, leading to a reduction in exergy destruction in the heat exchanger and a need for a larger heat exchanger because of the requirement for a greater heat exchange surface, this results in higher costs for constructing the heat exchanger. Therefore, finding the optimal value for the minimum temperature approach in heat exchanger design is crucial as it directly affects the amount of exergy destruction in the heat exchangers and their construction costs.

Table 2 Thermodynamic properties of the proposed multi-generation system.

Parameters	Value	Parameters	Value
Pressure of the oxygen flow stream	101 kPa	$E_{act,a}$ (kJ/mol)	76
Pressure of the hydrogen flow stream	101 kPa	$E_{act,c}$ (kJ/mol)	18
F (C/mol)	96486	λ_a	14
λ_c	10	ε	0.8
L (μm)	100	$J_a^{ref}\,(\mathrm{A/m^2})$	170000
$J_a^{ref}\,(\mathrm{A/m^2})$	460000		

Table 3 Specification of the heat exchangers

Name of the heat exchanger	LMTD (℃)	Q (kW)	Minimum temperature approach (℃)
HexM1	16.3	72112	1
HexC1.0	5.1	2541	2.1
HexC11	1.2	19490	1
HexC2.0	5.2	1273	3.9
HexC21	2.1	18733	1
HexC3.0	5.1	1268	2.3
HexC31	1.9	1143	1.1
HexC4.0	6.1	269	3
HexC4.1	4.5	9157	3.1

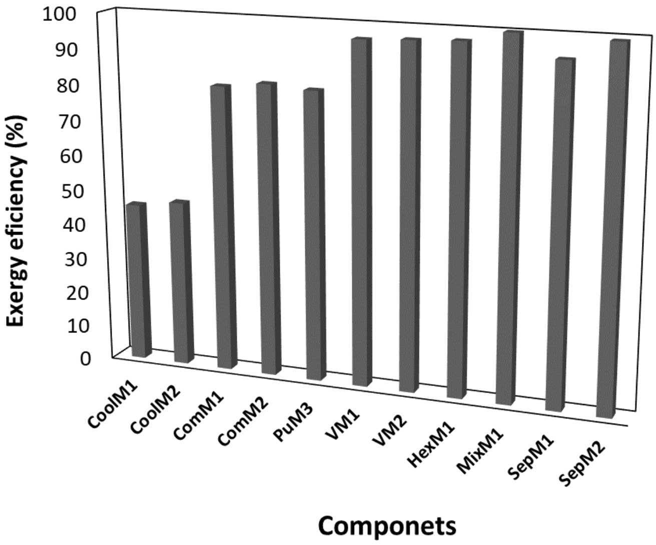

Fig. 3 Exergy efficiency of different components

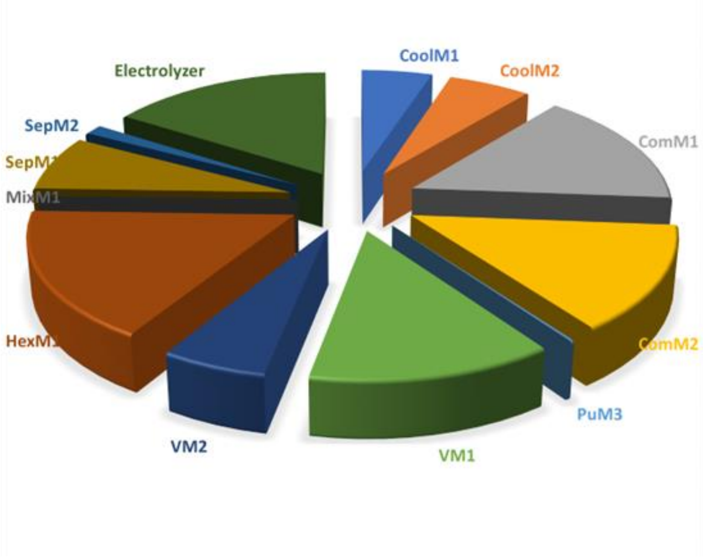

Fig. 4 Exergy destruction percentage of different components

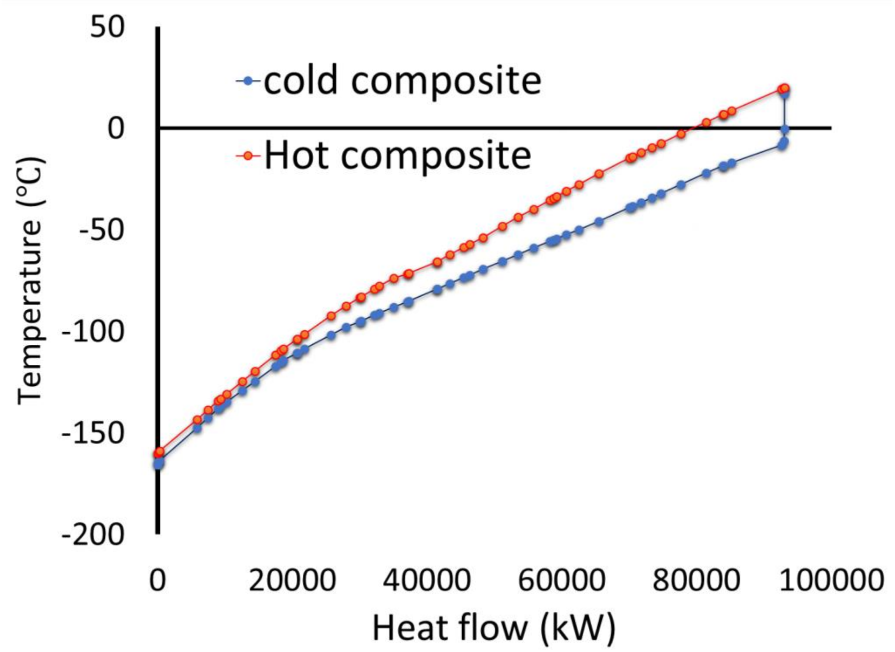

Fig. 5 **Composite curves of the most effective heat exchanger**

In Table 4, the characteristics of the liquefaction cycle examined in this research are compared with the work of Yang et al. (2019) and Nami et al. (2017). In Yang et al. (2019), a nitrogen pre-cooling system and a Brayton cooling system with hydrogen gas as the refrigerant were used, the use of a liquid natural gas recovery system was used to provide part of the cooling of the nitrogen pre-cooling section. The capacity of the cycle proposed by Yang et al. (2019) was 300 TPD of liquid hydrogen with a temperature of -251 ℃ and a pressure of 130 kPa. The liquefaction cycle used in the present study has a SEC of 5.07 for the case without geothermal and absorption refrigeration system while it is 4.97 for the case with absorption refrigeration system, the required power of which is supplied by solar arrays. The cycle proposed by Nami et al. (2017) has a combined process including a power generation unit and an electrolyzer, which does not have a hydrogen liquefaction cycle, and hydrogen gas was its product, and the power produced by the organic Rankine unit was used. In the current research, the output hydrogen is in liquid form and the power produced in the solar array unit has been used in the electrolyzer and compression part of the hydrogen liquefaction cycle.

Table 4 Comparison of the proposed cases with other cycles

Properties of the cycle	(Nami et al. 2017)	(Yang et al. 2019)	Present study (Th case without the absorption refrigeration cycle)	Present study (Th case assisted by the absorption refrigeration cycle)
Specific energy consumption (kWh/kg)	Without LH2 production	11.04	5.07	4.97
Power supply	Organic Rankine Cycle	General power grid	Solar arrays	Solar arrays
Hydrogen Separation System	Proton Membrane Electrolyzer	Steam Methane Reforming	Proton Membrane Electrolyzer	Proton Membrane Electrolyzer
Refrigerant type in LH2 production	Without LH2 production	H2	Mixed refrigerant	Mixed refrigerant
Type of hydrogen production	Green hydrogen	Blue hydrogen (by using carbon capture system)	Green hydrogen	Green hydrogen

4 Conclusion

In this research, the use of solar energy and electrolyzer to produce hydrogen without any pollution has been investigated. The hydrogen liquefaction cycle is assisted by an absorption system that uses the geothermal energy in its generator section.

- The hydrogen liquefaction cycle is examined for the cases with and without the absorption refrigeration cycle assisted by a geothermal energy source. In this study, by combining a hydrogen liquefaction cycle with a green hydrogen production system, the combined process is proposed in which the output product is liquid hydrogen at a temperature of -251 °C and a pressure of 101 kPa, which does not need to be supplied with power from outside the system, and the required power is supplied from the solar array unit. In the liquefaction section, heat exchangers have the highest exergy destruction, while in the whole proposed combined process, the electrolysis unit has the highest exergy destruction.
- The city of Bandar Abbas is investigated and suggested for the implementation of the proposed combined process due to the possibility of providing solar energy and also the water required for the separation and production of hydrogen as well as access to seawater. additionally, the carbon emission of the proposed process in this research is zero.
- A proton membrane electrolyzer with a gas production capacity of 121 gr of oxygen gas and 15 gr of hydrogen gas at a temperature of 80 °C and a pressure of 101 kPa has been used for water separation. The liquefaction unit has a capacity of 1.29 TPD and a specific energy consumption of 4.97 kWh/kgLH2.

5 Recommendations for future works

It is suggested to do economic and exego-economic analyses for the proposed cycle to estimate the cost of hydrogen production and compare it with other methods. Additionally, using other forms of renewable energy sources instead of renewable energy can be studied for the proposed model.

Nomenclature

Symbols

e	Exergy (kW)
E_a	Energy consumption in electrolyzer (kJ/mol)
J	Current density (A/m^2)
F	Faraday constant (c/mol)
h	Specific enthalpy $(\mathrm{kJ}/\mathrm{kg})$
P_{net}	Net power (kW)
s	entropy $(\mathrm{kJ}/\mathrm{kgK})$
I	Exergy destruction (kW)
V	Voltage of electrolyzer (V)
W_{com}	Work of compressor (kW)
Hex	Heat exchanger

Reference

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