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Multi-Objective Optimization of a Vanadium Chloride Thermochemical Cycle Integrated with Solar Power Plant for Hydrogen Production

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ABSTRACT

Global warming and climate change, primarily driven by greenhouse gas emissions, present significant global challenges. Addressing these issues requires substantial reductions in greenhouse gas emissions. This study provides a technical and economic evaluation of hydrogen production from solar energy, utilizing a proton exchange membrane (PEM) electrolyzer and the vanadium chloride (V-Cl) thermochemical cycle. The solar power tower unit supplies the necessary energy to drive a cascaded Organic Rankine Cycle (CORC) for power generation, as well as a thermochemical hydrogen production unit, enabling the cogeneration of electricity and hydrogen. All power generated by the CORC is directed to the PEM electrolyzer for hydrogen production, resulting in dual hydrogen production capabilities within the system. Feasibility assessments are conducted using thermodynamic principles and exergy-based analyses, while economic evaluations gauge the system's performance. Moreover, multi-objective optimization is employed to determine the optimal operational conditions of the system. At the optimal point, the system achieves a hydrogen production rate of 125.029 kg/h, an energy efficiency of 39.66%, and an overall cycle cost rate of 120.937 \$/h.

Keywords: Hydrogen production, Proton exchange membrane electrolyzer, Vanadium chloride cycle, Cascaded organic rankine cycle

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بهینه‌سازی چند هدفه چرخه ترموشیمیایی و انادیوم کلرید یکپارچه با نیروگاه خورشیدی برای تولید هیدروژن

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چکیده

گرمایش جهانی و تغییرات اقلیمی که عمدتاً ناشی از انتشار گازهای گلخانه‌ای هستند، از چالش‌های اساسی در مقیاس جهانی به‌شمار می‌آیند. مقابله مؤثر با این معضل مستلزم کاهش چشمگیر انتشار گازهای گلخانه‌ای است. در این پژوهش، ارزیابی فنی و اقتصادی تولید هیدروژن از انرژی خورشیدی با بهره‌گیری از الکترولیزر غشای تبادل پروتون و چرخه ترموشیمیایی و انادیوم-کلراید ارائه شده است. در این سامانه، واحد برج خورشیدی انرژی مورد نیاز برای راه‌اندازی یک چرخه رانکین آلی آبشاری به‌منظور تولید توان و همچنین واحد تولید هیدروژن ترموشیمیایی را تأمین می‌کند؛ به‌گونه‌ای که امکان تولید همزمان برق و هیدروژن فراهم شود. کل توان تولیدی در چرخه رانکین آلی آبشاری به الکترولیزر غشای تبادل پروتون اختصاص می‌یابد و بدین ترتیب، سیستم از قابلیت تولید دوگانه هیدروژن برخوردار می‌گردد. ارزیابی امکان‌پذیری سامانه بر پایه اصول ترمودینامیکی و تحلیل‌های مبتنی بر انرژی انجام شده و عملکرد اقتصادی آن نیز مورد بررسی قرار گرفته است. افزون بر این، به‌منظور تعیین شرایط بهره‌برداری بهینه، از بهینه‌سازی چندهدفه استفاده شده است. نتایج نشان می‌دهد که در نقطه بهینه، نرخ تولید هیدروژن برابر با ۱۲۵/۰۲۹ کیلوگرم بر ساعت، بازده انرژی ۳۹/۶۶٪ و نرخ هزینه کل چرخه ۱۲۰/۹۳۷ دلار بر ساعت حاصل می‌شود.

کلیدواژه‌ها: تولید هیدروژن، الکترولیزر غشای تبادل پروتون، چرخه ترموشیمیایی و انادیوم-کلراید، چرخه رانکین آلی آبشاری

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1- Introduction

In today's world, population growth and industrial development have created an increasing demand for sustainable and clean energy resources [1]. This scenario has driven researchers to explore alternative renewable energy sources such as wind, solar, geothermal, tidal, and hydropower, which are pivotal in transitioning to a more sustainable energy future [2]. However, the inherent intermittency and unpredictability of renewable resources underscore the critical need for reliable energy storage systems. Among the technologies addressing this challenge, heliostat systems stand out for their ability to capture and concentrate solar energy to produce thermal energy [3]. This thermal energy can be effectively utilized in various thermodynamic cycles to generate electricity, heat, or clean fuels like hydrogen. Hydrogen, as a promising energy carrier, offers high energy density and compatibility with renewable energy storage [4]. One of the prominent technologies for hydrogen production is the PEM electrolyzer, which has gained significant attention due to its high efficiency and ability to operate at high energy densities. However, there are several other methods for hydrogen production, including Alkaline electrolyzers and solid oxide electrolyzers (SOEC). Additionally, thermochemical methods like the V-CL cycle, which utilizes heat to dissociate water into hydrogen and oxygen, are also among the noteworthy technologies in this field.

The production of hydrogen in an economically viable and sustainable manner remains one of the fundamental challenges in this field. However, integrating solar technologies with the vanadium-chloride thermochemical cycle provides a novel and efficient solution to these challenges, paving the way for cleaner hydrogen production. Hydrogen production via thermochemical cycles is a promising option for large-scale green hydrogen production with much lower global warming potential (GWP) where the energy drives the process to be carbon neutral. In such cycles, water undergoes a series of chemical reactions with presence of chemical compounds with oxygen and hydrogen as only products where other compounds are recycled within the cycle [5]. Tolga et al. [6] performed a comparative analysis of V-Cl, Cu-Cl, Mg-Cl, and Fe-Cl cycles, concluding that the V-Cl cycle, with an efficiency exceeding 40%, represents one of the most promising options among low-temperature thermochemical cycles. Mohammadi et al. [7] studied solar-powered hydrogen production using the V-CL thermochemical cycle in a Shiraz building, finding that with 70 m² of collectors and 345 kW fuel cells, CO₂ emissions were reduced to 10.31 tons per year, with a cost of \$4.915 per hour.

Rashidi et al. [8] studied a thermodynamically modeled microturbine-based multigeneration energy system is optimized using a novel multi-objective firefly algorithm to maximize exergy efficiency and minimize total cost rate, achieving up to 69% efficiency and \$572/h cost, with results validated against other optimization methods. Ghavami et al. [9] studied a novel gas turbine–helium reactor multigeneration system with hydrogen, cooling, and desalination units is modeled and optimized, achieving 74.4% energy and 50.2% exergy efficiency.

Given the critical importance of solar energy and the increasing demand for green hydrogen production methods, this research introduces an innovative system for the co-production of power and hydrogen utilizing a heliostat field. In this system, a central receiver provides high-temperature heat to drive a V-Cl thermochemical cycle unit for hydrogen production. Simultaneously, a cascaded organic Rankine cycle uses the thermal energy from the exiting solar salt of the hot storage tank to generate electricity. The proposed design is analyzed based on comprehensive thermodynamic and economic evaluations and achieves its optimal operating point through a parametric analysis followed by a three-objective optimization based on maximizing the hydrogen production rate and efficiency while

minimizing the total cost rate. The main contributions of the present article are outlined in the following bullet points:

- Environmentally friendly power and hydrogen production systems are being proposed, utilizing various methods such as PEM electrolysis and the vanadium chloride thermochemical cycle, integrated with cascaded organic rankine cycles for power generation.
- The optimal points of the system are determined by employing an Artificial Neural Network (ANN) and the NSGA-II algorithm to establish a trade-off between energy efficiency, total cost rate, and total hydrogen production.
- A comprehensive analysis of the proposed system is conducted from the perspectives of energy, exergy, and economic (3E) considerations, along with a parametric study of the system.

2- System description

Figure 1 illustrates a schematic representation of a solar-powered hydrogen and electricity generation system. As depicted in the figure, the system incorporates a solar heliostat field to supply the thermal energy required for the operation of the power plant. Two technologies, namely the PEM electrolyzer and the V-CL cycle, have been employed for hydrogen production. The V-CL cycle relies on thermal energy for hydrogen production, which is supplied by the heliostat system. In contrast, the PEM electrolyzer requires electrical energy, provided by a power generation cycle incorporating a cascade organic rankine cycle. The working fluids for the two distinct ORCs are selected to maximize power output. All the electricity generated by the CORC cycle is directed to the PEM electrolyzer, while the hydrogen produced is stored in a hydrogen storage tank.

3- System modeling

Based on the first law of thermodynamics, mass and energy conservation equations were established for each individual component of the system. Assuming minimal changes in kinetic and potential energy, these equations simplified as follow [10]:

$$\sum \dot{m}_i - \sum \dot{m}_e = \frac{dm_{cv}}{dt} \tag{1}$$

$$\dot{Q} - \dot{W} + \sum_{inlets} \dot{m} h_i - \sum_{outlets} \dot{m} h_e \tag{2}$$

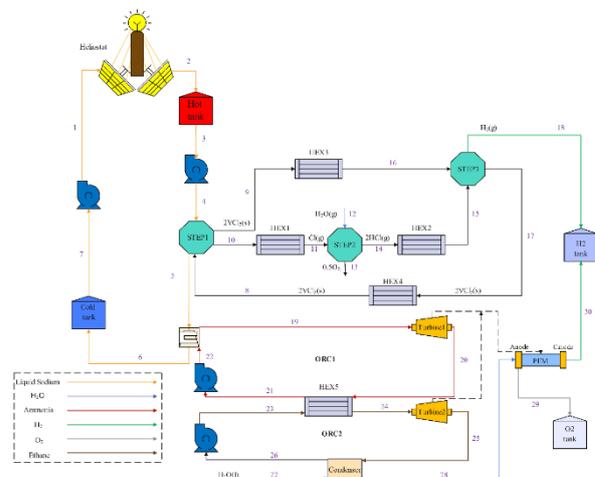


Fig.1 .The schematic diagram of the proposed integrated energy system based on Heliostat/CORC/PEM/V-CL.

Within these equations, 'h' represents the flow enthalpy. The subscript 'i' denotes input values, while 'e' represents output values.

The exergy balance equation is typically expressed as follows [11]:

$$\dot{E}x_Q + \sum_{inlets} \dot{m}_{in} ex_{in} = \sum_{outlets} \dot{m}_{out} ex_{out} + \dot{E}x_W + \dot{E}x_D \quad (3)$$

The exergy of heat within the system and the exergy of work are defined as follows [11]:

$$\dot{E}x_Q = \left(1 - \frac{T_0}{T}\right) \dot{Q} \quad (4)$$

$$\dot{E}x_W = \dot{W} \quad (5)$$

The overall exergy of each stream includes both physical and chemical exergy.

$$ex_i = ex_{p,hi} + ex_{ch,i} \quad (6)$$

Physical and chemical exergy are calculated by comparing the properties of the stream to those of the reference environment, using the following formula [11]:

$$ex_{p,h} = \sum \left[(h_i - h_0) - T_0 (s_i - s_0) \right] \quad (7)$$

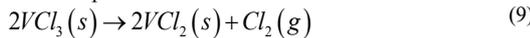
$$ex_{ch} = \sum x_i ex_{ch,i}^0 + RT_0 \sum x_i \ln(x_i) \quad (8)$$

3-1- Heliostat solar field

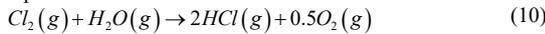
The solar subsystem relies on a heliostat field to act as the primary concentrator. This field consists of an array of mirrors arranged to focus incident solar radiation onto a central receiver located at the top of a tower, thereby generating high-grade thermal energy. To effectively drive the Cascade Organic Rankine Cycle, a working fluid with exceptional thermal stability is required. Liquid sodium is selected for this role due to its high boiling point (1155 K) and favorable heat transfer characteristics. These properties allow the system to achieve the necessary high temperatures without the safety risks and complexities associated with high-pressure operations. The mathematical model utilized in this study calculates the thermal power delivered to the receiver by considering optical losses and efficiency factors. For a complete breakdown of the governing equations and validation of the solar field model, readers are referred to Ref.[3].

3-2- Vanadium-chloride cycle

As illustrated in Figure 2, the V-CL cycle primarily consists of three chemical reactions occurring at low, medium, and high temperatures. In the first reaction, which takes place at a temperature of 798 K, V-CL3 decomposes into V-CL2 and Cl2.



Subsequently, the Cl2 gas produced in the previous reaction reacts with H2O to generate O2 and HCl. This reaction occurs at a temperature of 373 K.



In the final stage of this cycle, HCl (g) and V-CL2 (s) combine to produce hydrogen and V-CL3. This reaction occurs at a temperature of 573 K. The mathematical modeling of the V-CL cycle is thoroughly detailed in Ref.[12].

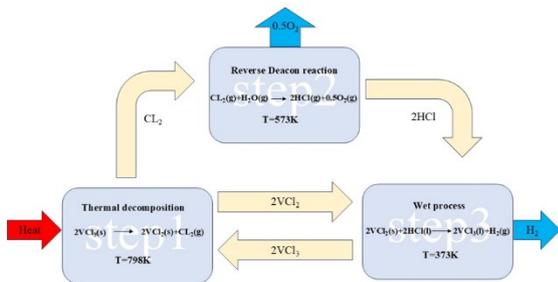


Fig.2 Schematic of a three-step V-Cl thermochemical cycle for hydrogen production.

3-3-Cascaded Organic Rankine cycles

The use of a Cascaded Organic Rankine Cycle (CORC) with ammonia as the working fluid provides notable advantages [13]. Solar energy serves as the primary heat source for the CORC, driving the evaporation of the working fluid in evaporator 1. In the second ORC, organic fluids such as ethane can be employed. A heat exchanger, labeled as HX5, connects the first ORC to the second ORC unit, enabling integration despite the differences in working fluids.

4- Economic analysis

In economic modeling, calculating a system's total cost requires defining cost functions for each component. These functions estimate equipment costs based on design parameters, dimensions, and specified criteria [14].

$$\dot{Z}_k = \frac{Z_k \times CRF \times \phi}{N \times 3600} \quad (11)$$

In this equation, the acquisition cost of component k is represented by Z_k , while N denotes the annual operating hours for the unit. Additionally, the maintenance factor ϕ , which is typically set at 1.06, accounts for maintenance costs. The capital recovery factor (CRF) is calculated as follows [14]:

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (12)$$

In this equation, i represents the interest rate, and n denotes the expected service life of the components. Equation (14) is used to adjust the cost of each equipment unit from its original year to the current year, using the equipment cost index.

$$cost \text{ at present year} = original \text{ cost} \times \frac{cost \text{ index of the present year}}{cost \text{ index of the base year}} \quad (13)$$

$$Z_{2024} = Z \frac{CI_{2024}}{CI_{reference}} \quad (14)$$

Where $CI_{reference}$ represents the cost index of the reference year, and CI_{2024} is the cost index of the current year.

Evaluating financial factors requires examining the costs, benefits, and overall economic viability of energy technologies. This evaluation includes upfront investment, ongoing operational costs, and the expected lifetime of the energy infrastructure. By considering these elements, researchers can assess the economic feasibility of energy alternatives and compare their cost-effectiveness and sustainability. In financial modeling, defining the cost function for each component is essential for determining the total system cost. The costs associated with different system components are summarized in Table 1.

5- Performance indicators

One method to assess the energy efficiency of this cycle is by calculating the ratio of the input energy that is ultimately converted into hydrogen's energy content, considering its lower heating value [15].

$$\eta_{overall} = \frac{\dot{m}_{H_2} LHV_{H_2}}{\sum Q_{in}} \quad (15)$$

where Q_{in} represents the amount of heat supplied to the cycle. The exergy efficiency can also be expressed as follows:

$$\eta_{ex,overall} = \frac{\sum Ex_{H_2}}{\sum Ex_{in}} \quad (16)$$

where Ex_{H_2} represents the total exergy content of the hydrogen produced by the cycle, and Ex_{in} represents the input exergy to the cycle.

6- Results and discussion

The proposed system has been developed using MATLAB software. Multi-objective optimization is conducted to determine the optimal conditions for proposed system using Artificial Neural Networks and Genetic Algorithms within MATLAB software.

7- Model validation

Each component of the proposed system is validated separately in this section. First, the PEM electrolyzer is validated using the experimental data from [12], as shown in Fig. 3. The V-CL thermochemical cycle is validated using the data provided by [6] as in Table 2.

Table1. Formulas for estimating costs associated with individual components of a cycle.

Component	Purchase equipment cost (PEC)
CORC:	
ORC 1:	
Evaporator	$Z_{Eva,ORC1} = 309.14(A_{Eva})^{0.85}$
Turbine	$Z_{T,ORC1} = 4750(\dot{W}_T)^{0.75}$
Pump	$Z_{P,ORC1} = 200(\dot{W}_P)^{0.65}$
Condenser	$Z_{Con,ORC1} = 516.62(A_{Con})^{0.6}$
ORC 2:	
Evaporator	$Z_{Eva,ORC2} = 309.14(A_{Eva})^{0.85}$
Turbine	$Z_{T,ORC2} = 4750(\dot{W}_T)^{0.75}$
Pump	$Z_{P,ORC2} = 200(\dot{W}_P)^{0.65}$
Condenser	$Z_{Con,ORC2} = 516.62(A_{Con})^{0.6}$
Solar:	
Heliostat	$Z_{heliostat} = 150A_{helio}N_{helio}$
PEME:	
Electrolyzer	$Z_{elec} = 1000\dot{W}_{elec}$
Preheater	$Z_{pre} = 130\left(\frac{A_{pre}}{0.093}\right)^{0.78}$
VCl:	
	$Z_{VCl} = 0.125\dot{m}_{H_2}LHV_{H_2}$

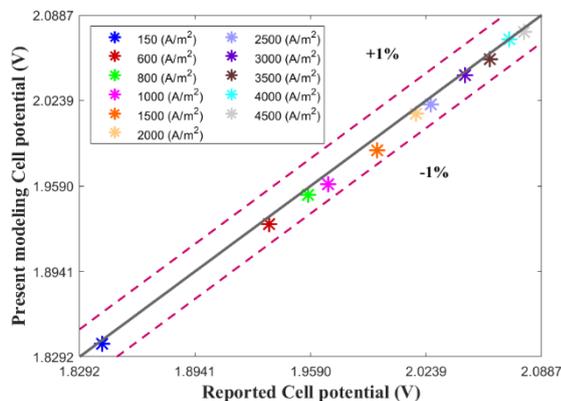


Fig.3 Validation of the PEM model with experimental data [12].

Table2.Validation of the V-CL thermochemical cycle [6].

	beta et al.[4]			
	Q	Inlet Exergy	Outlet Exergy	Exergy destruction
step1	349.6	1174	1053	121
step2	70.77	183.9	172	11.9
step3	-88.72	1061.09	1004	57.09
current study				
	Q	Inlet Exergy	Outlet Exergy	Exergy destruction
step1	346.23	1074	1042.60	31.65
step2	71.43	173.03	172.03	3.00
step3	-87.98	1065.10	1003.70	61.42

8- Parametric study

Figure 4 illustrates the variations in energy and exergy efficiency, the total hydrogen production, and the cost rate as a function of the heat input to the system. Increasing the heat input to the vanadium-chloride (V-CL) cycle enhances hydrogen production, thereby improving energy and exergy efficiencies. However, providing additional heat to the V-CL cycle leads to higher costs. Specifically, increasing the heat input from 3500 kW to 7000 kW raises the cost rate from \$119 per hour to \$122 per hour, thereby increasing the total cost rate. Increasing the heat input to the V-CL presents a clear trade-off between initial investment and long-term economic benefits. As the heat input increases, the LCOH decreases, indicating that higher initial costs lead to more efficient energy production in the long run, making the system economically viable over time.

In Figure 5, it is observed that increasing the number of heliostat mirrors from 150 to 500 results in a reduction in hydrogen production from 100 kg/h to 96 kg/h, while the energy and exergy efficiencies drop from 39.7% to 39.1%. Naturally, the cost rate also increases as the number of mirrors rises. These changes are attributed to the reduction in flow rate with the increasing number of heliostat mirrors. The reduced flow rate decreases the heat input to the Vanadium-Chloride (V-CL) cycle, leading to a decline in hydrogen production. This reduction in hydrogen production, in turn, causes a drop in energy and exergy efficiencies.

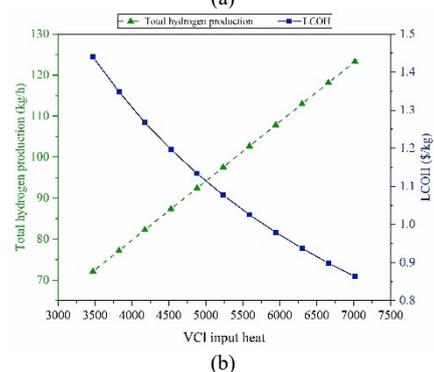
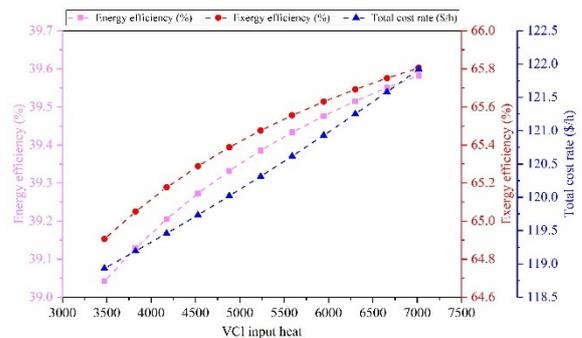


Fig.4 The effect of V-Cl heat load on performance variables.

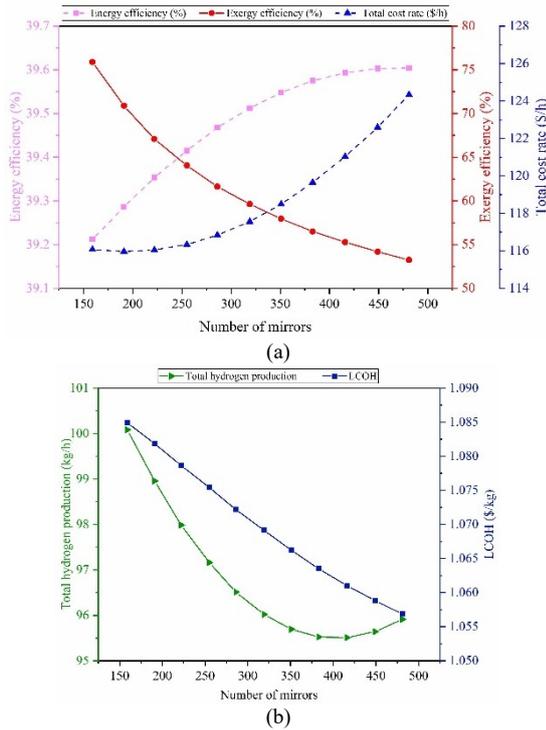


Fig.5 The Effect of the Number of Mirrors on Performance Variables.

Furthermore, the increased number of heliostat mirrors contributes to a higher total cost rate. As the number of heliostat mirrors increases from 160 to 480, the LCOH decreases from 1.084 to 1.056.

8- Optimization results

The integrated system was optimized using the NSGA-II algorithm to enhance hydrogen production, energy efficiency, and cost rate. The Pareto front generated from the optimization is illustrated in Fig. 6. Based on Fig. 6, the optimal values for the system are identified as an energy efficiency of 39.66%, a total hydrogen production of 125.029 kg/h, and a total cost rate of 120.937 \$/h.

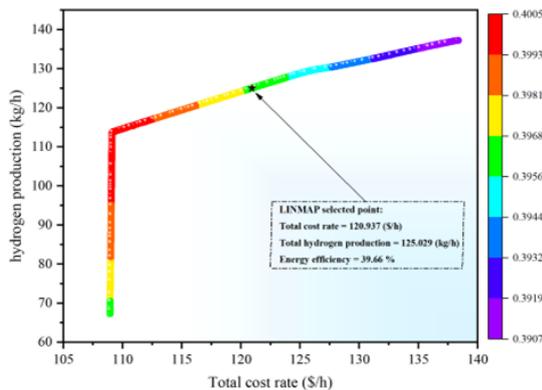


Fig.6 Three Objective Pareto Frontiers of Total Cost Rate, Total Hydrogen Production, and Energy Efficiency.

Table3. Optimal points and their associated decision variables.

Item	Optimum value
V-CL heat load (kW)	7148.70
Liquid-sodium mass flow rate (kg/s)	33.40
Number of mirrors	480
Energy efficiency (%)	39.66
Total cost rate (\$/h)	120.937
Total hydrogen production (kg/h)	125.029

8- Conclusions

In this research, a novel solar-driven integrated system comprising a heliostat field, a Vanadium-Chlorine thermochemical cycle, and a Cascaded Organic Rankine Cycle was modeled and optimized. The study focused on the techno-economic feasibility of co-producing hydrogen and electricity. The key findings are summarized as follows:

- Through multi-objective optimization using the NSGA-II algorithm, the optimal operating point was identified. At this point, characterized by 480 heliostats and a V-Cl heat load of 7148.70 kW, the system achieves a total hydrogen production rate of 125.029 kg/h, an energy efficiency of 39.66%, and a total cost rate of 120.937 \$/h.
- The parametric study reveals that increasing the heat input to the V-Cl cycle significantly enhances the system's performance. Specifically, higher heat loads lead to increased hydrogen production and improved energy and exergy efficiencies, although this comes with a corresponding rise in the total cost rate.
- The analysis indicates a direct correlation between the solar field size and economic factors. Increasing the number of heliostat mirrors results in a higher total cost rate due to the increased capital investment required for the additional collectors.
- Despite the increase in the total cost rate with larger system scales, the Levelized Cost of Hydrogen (LCOH) demonstrates a decreasing trend as the heat input increases. This suggests that higher initial investments can lead to more efficient energy production in the long run, making the system more economically viable over time.

Ethical Statement

The content of this manuscript is original, based on the authors' research, and has not been published or submitted elsewhere, either in Iranian or international journals

Conflict of interest

The authors declared that they have no conflicts of interest to this work.

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