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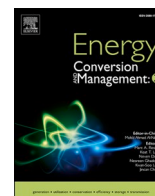
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Optimizing industrial Energy: An Eco-Efficient system for integrated Power, Oxygen, and methanol production using coke plant waste heat and electrolysis

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ABSTRACT

This research presents a novel, eco-efficient hybrid system designed for the simultaneous production of power, oxygen, and methanol. It utilizes energy from coke plants and incorporates state-of-the-art waste heat recovery processes (WHRPs). The system effectively merges electricity and methanol production with WHRPs, improving both environmental sustainability and economic feasibility in industrial energy transformation. It consists of a fuel reforming and combustion unit, a waste heat recovery unit, a unit for hydrogen gas production through water electrolysis, and a methanol synthesis module. This configuration enables the production of 12.72 MW of electricity, 0.51 kg/s of oxygen, and 0.53 kg/s of methanol, achieving an energy productivity of 46.8 % and an exergy efficiency of 85.13 %. The economic analysis indicates competitive costs of \$0.099 per kWh for electricity and \$0.56 per kg for methanol. The system surpasses current technologies in thermodynamic efficiency, operational and product costs, and reduced CO₂ emissions, demonstrating its potential as a sustainable and economically sound solution for industrial energy challenges. It supports global sustainability initiatives and fits within the circular economy concept.

1. Introduction

Recently, the societies demands for energy has seen a notable increase, mainly due to a growing population, the expansion of industry, and the development of urban areas. Fossil fuels, comprising about 80 % of the global energy market, are central to this scenario. Facilities that produce energy using these fossil fuels are crucial for improving energy security and promoting sustainability [1,2]. Nonetheless, the reliance on fossil fuels encounters critical challenges, including the depletion of reserves, geographical constraints, and various geopolitical complications. Additionally, the combustion of fossil energies causes serious damage to the health of society and the ecosystem [3,4]. Energy scientists believe that both the environmental and thermodynamic performances of existing power plants should be improved or new and clean

resources and technologies should be developed [5,6]. However, some other scientists suggested that both approaches to improve energy problems can be implemented simultaneously [7,8]. As for the initial strategy, methods exist to decrease the hazard impacts of pollutants from the exhaust of fossil fuel energy systems [9]. These methods not only lessen the environmental impact but can also enhance the operational efficiency of the plant [10,11]. The use of exhaust waste heat of power plants and industrial wastes in different bottoming cycles and units to design a cascade energy conversion system is one of the most known attractive and fruitful approaches [12,13].

Coke oven gas is one of the valuable industrial wastes that can be extracted from during the synthesis process of coke. The treated coke oven gas can be utilized as a fuel gas or as a feedstock for the chemical products production [14,15]. Coke oven gas can be considered as a hydrogen-rich fuel; because gas of coke oven contains about 60 %

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Nomenclature		Comp	compressor
A	Area (m ²)	ch	chemical
C	Cost (US\$)	en	energy
\dot{E}	Exergetic rate (kW)	Fa	Faraday
\dot{E}_d	Destructed exergy (kW)	HX	heat exchanger
\dot{E}_Q	Thermal exergy (kW)	KC	Kalina cycle
ex	Specific exergy (kW/kg)	rev	reversible
ex ⁰	Specific chemical exergy	ph	physical
F	Faraday constant (C/mol)	Turb	turbine
h	Specific enthalpy (kJ/kg)	tot	total
I	Electric current (A)	<i>Abbreviations</i>	
LHV	Lower heating value (kJ/kg)	AE	Alkaline electrolyzer
\dot{m}	Mass flow rate (kg/s)	CH ₃ OH	Methanol
P	Power (kW)& Pressure (bar)	CO ₂	Carbon Dioxide
\dot{Q}	Heat transfer rat (kW)	DER	Destructed Exergy Rate
s	Specific entropy (kJ/kg. °C)	FRCU	Fuel Reforming And Combustion Unit
T	Temperature (°C)	H ₂ -GU	Hydrogen Generation Unit
V	Electric voltage (V)	H ₂ O	Water
\dot{W}	Electric Power (kW)	LNG	Liquified Natural Gas
x	Mole fraction	MGU	Methanol Generation Unit
Z	Investment cost (US\$)	MOF	Multi-Objective Function
<i>Subscripts</i>		NH ₃	Ammonia
AC	Ammonia cycle	PEM	Proton Exchange Membrane
		WHRP	Waste Heat Recovery Process

hydrogen gas [16]. Therefore, coke oven gas-to-fuel processes in the form of the WHRPs can address an effective and eco-friendly energy conversion system. Indeed, coke oven gas can be converted into valuable fuel for energy generation cycles in the WHRP units instead of being released into the atmosphere and emitting environmental pollutants. This means reducing greenhouse gas emissions [17]. In this regard, downstream cycles and units can be designed for various purposes such as electricity production, cooling and heating capacities, methanol synthesis process, hydrogen fuel, etc. [18,19]. Such cascading processes can address significant benefits such as improved operational efficiency [20], production of diverse and valuable products, reduction of released environmental pollutants, etc. [21]. For instance, it was reported that the use of coke oven gas in a methanol synthesis and ammonia and hydrogen generation processes can result in notable energy savings and a reduction in carbon emissions [22]. Methanol is a valuable chemical product that can have various applications in the textile industry, pharmaceutical industry, agricultural sector, etc. [23,24]. In addition, methanol can be utilized as an environmentally sound energy carrier in industrial and power plant processes. Accordingly, methanol production through eco-friendly approaches can promise an efficient and modern energy conversion system to the energy markets [25]. According to the literature, the production of methanol from coke oven gas instead of using fossil fuel-based routes can be more efficient from the points of view of cost and environment [14,26].

On the other hand, electricity, as the main energy demand, can be produced through power generation cycles coupled with the reforming and combustion processes of coke oven gas. In such processes, the produced combusted gas can supply the thermal duty of the power generation cycle [27]. Indeed, such energy conversion systems are an integration of WHRPs, coke oven gas-based combustion process, and energy production cycles. By designing these energy conversion systems simultaneously, thermodynamic and environmental benefits can be achieved [28]. In the coke oven gas-based energy processes, the thermal energy obtained from the reforming and combustion process can be utilized in electricity generation cycles. Besides that, the available carbon dioxide (CO₂) can be utilized in the methanol synthesis process. The

hydrogenation of carbon dioxide is a widely recognized reaction utilized in the production of methanol [29]. Jouybari et al. [30] introduced a cycle for coke oven gas liquefaction assisted by solar energy, coupled with post-combustion CO₂ capture, aimed at producing methanol and liquefied natural gas (LNG). This approach included a thorough thermo-economic analysis and optimization. In their system, the purified hydrogen and CO₂ were employed in the methanol production process. Their findings indicated an increase in efficiency and a rise in the prime cost of the product when the hydrogen content in the fuel was reduced. Guo et al. [31] observed that the escalating prices of carbon and the growing demand for hydrogen, particularly in the pursuit of carbon neutrality, may present significant opportunities for the broader implementation of the aforementioned technology. Shamsi et al. [27] reported that the WHRP integrated with the coke oven gas combustion process could significantly improve the electricity generation rate and have zero indirect carbon emissions. Ren et al. [32] showcased the thermodynamic and environmental advantages of reforming converter gas with coke oven gas, specifically for thermochemical energy storage in the context of steel production.

As mentioned, it is possible to produce methanol through carbon dioxide hydrogenation reaction. During this reaction, carbon dioxide gas combines with hydrogen and produces methanol and water vapor. The carbon dioxide needed in the reaction can be supplied from the exhaust gases of the reforming and combustion process as well as power generation cycles [33]. However, the supply of hydrogen needed to carry out this reaction is one of the key challenges in the methanol synthesis process [34,35]. Hydrogen derived from the water electrolysis process presents a compelling and environmentally friendly alternative. Electrolyzers are capable of producing hydrogen gas with a purity exceeding 99 %, achieving efficiencies around 80 % [36]. Electricity supply is the only major challenge in the implementation of water electrolysis units. When using renewable electricity, the electrolysis process can be the cleanest approach to produce green hydrogen. In addition, electrolyzer units can be integrated more reliably in electrical self-sufficient energy systems [37,38]. The integration of water electrolysis units in hybrid energy conversion systems had been evaluated by

researchers from different perspectives. Most of the reports indicate the reliability of the water electrolysis process in the production of green hydrogen [39–41].

Integrated energy conversion systems for electricity and methanol production (or other products) had been reported in some literature. It was reported that methanol synthesis based on hydrogenation reaction can be more suitable for long-term purposes compared to reforming methods [42]. Nazerifard et al. [43] developed a methanol, hydrogen and power trigeneration system coupled with a carbon capture unit. The energy and exergy efficiencies of around 67 % and 55 % were achievable for that system. Further, the inlet temperature of methanol synthesis reactor had a great influence on its behavior. Yousaf et al. [44] suggested that advancements in hydrogen production technologies, particularly through the development of high-performance materials and the commercialization of electrolyzers, could lead to further cost reductions in methanol synthesis via the hydrogenation process. Lin et al. [45] introduced a system for the simultaneous production of electricity and methanol, incorporating landfill gas reforming, a gas-steam cycle power plant, a methanol synthesis unit, and an alkaline electrolyzer. They reported energy and exergy efficiencies of 48.7 % and 53.6 % respectively, with the total cost of produced methanol being 0.362 US\$/kg.

Liu et al. [46] proposed a glycerol-fed polygeneration system under a glycerol steam reforming cycle, two power generation cycles, a chilled water unit, a water desalination process, and a methanol synthesis process. The energy and exergy efficiencies and total cost of produced methanol were around 35.6 %, 68.8 %, and 0.214 US\$/kg, sequentially. Perng et al. [47] developed the potential to improve the performance of a proton exchange membrane (PEM) fuel cell integrated with a methanol steam reforming process. The highest hydrogen output, methanol conversion, and net electricity were almost 92.5 %, 0.012 kmol/m³, and 134 W, respectively. Mousavi Rabeti et al. [48] evaluated a poly-generation system under a WHRP integrated with the Brayton, Rankine, organic Rankine, and Kalina cycles. In that system, methanol and hydrogen were, respectively, supplied through the CO₂ capturing from the exhaust gases and the PEM electrolyzer. They reported that the methanol generation could be higher via municipal solid waste fuel than other fuels. Further, date palm waste had the lowest environmental impacts than other fuels. Chen et al. [49] proposed a trigeneration system combining a biogas upgrading unit, an ammonia Rankine cycle, and a thermal desalination unit. This system simultaneously produces electricity, methanol, and desalinated water. Their results showed energy and exergy efficiencies of 51.5 % and 87.4 %, respectively, and the total production cost of methanol was calculated at 0.21 \$/kg. Kim et al. [26] developed a multi-generation system for methanol, power, and heat generation from coke oven gas, showcasing an energy efficiency improvement of 38 % compared to a baseline system and a methanol selling price range of 0.23–0.29 US\$/kg. Zhao et al. [28] achieved an energy efficiency of approximately 54.4 % for a system utilizing pulverized coke in a chemical looping process for hydrogen generation, assisting in the conversion of coke-oven gas to methanol and ammonia. Kim and Kim [50] conducted a techno-economic analysis of a methanol production cycle that utilizes a mixture of hydrogen-rich coke oven gas and carbon-rich Linz-Donawitz gas. Their study highlighted that balancing the optimal hydrogen and carbon equilibrium is crucial for producing methanol that is both environmentally friendly and economically feasible.

An in-depth review of the current literature indicates that systems designed for simultaneous generation of electricity and methanol, using coke oven gas as the main energy source, have not been extensively explored. Moreover, there have been instances where coke oven gas-fueled energy conversion systems have been combined with fuel cells. While fuel cells offer an efficient and environmentally friendly method of energy conversion, their adoption is hindered by high initial costs attributed to their developmental stage. Conversely, in several other studies, the production of methanol is primarily focused on the

reforming process. According to studies [42], methanol synthesis process under a CO₂ hydrogenation reaction can be more suitable for long-term purposes compared to reforming methods. Furthermore, the hydrogen needed for the aforementioned reaction is supplied to the system through storage tanks. It was reported that on-site hydrogen production can improve the reliability of the energy conversion system [36]. This study aims to fill the identified gaps in existing research by undertaking an exhaustive investigation that includes thermodynamic and environmental assessments, cost analysis, and optimization of an innovative coke oven gas-powered hybrid system for generating electricity, oxygen, and methanol. This novel system comprises four key elements: a fuel reforming and combustion unit utilizing coke oven gas, a Waste Heat Recovery Unit (WHRU), a hydrogen production unit via water electrolysis, and a methanol synthesis mechanism. The WHRU incorporates a dual-method strategy, combining a Kalina cycle-based system with an ammonia-based steam power generation cycle. This unique energy conversion system, with its distinctive structure and setup, is unprecedented in existing scholarly literature. The evaluation focuses on its thermodynamic efficiency, yearly expenditures, cost-effectiveness of the products, and CO₂ emissions, showcasing its potential to outperform and offer competitive benefits compared to current technologies. The objectives and contributions of this paper are recapitulated as follows:

- Introducing a state-of-art hybrid plant driven by coke oven gas for the production of electricity, oxygen, and methanol, featuring a unique structure and configuration;
- Conducting an inclusive evaluation of the thermodynamics and environmental impact, along with cost estimation and optimization of the proposed system;
- Employing waste heat from industrial coke production in bottoming cycles to boost the productivity and decrease pollutant emissions of the energy system;
- Achieving self-sufficiency in electricity for the system's operations and the additional capability to power an electrolyzer unit;
- Implementing a scrubber column using water as a solvent to decrease methanol loss through thermal integration;
- Demonstrating the system's superior and competitive benefits in terms of thermodynamic efficiency, overall annual costs, product cost-effectiveness, and CO₂ emission rates when compared with other existing technologies.

2. Methodology

As mentioned the current investigation an innovative hybrid system for power and methanol production, which has been thoroughly assessed in terms of its thermodynamic efficiency, environmental impact, and cost estimation aspects. In this section, the structure overview and process and configuration descriptions of the studied hybrid system are described.

2.1. Structure overview of the studied hybrid system

The planned system is comprised of four main units: a coke oven gas-driven fuel reforming and combustion unit (FRCU), a WHRU (for power generation), a hydrogen gas generation unit (H₂-GU, based on a water electrolysis process), and a methanol generation unit (MGU, based on a methanol synthesis process). The WHRU is based on two power generation units (a Kalina cycle-based and an ammonia-driven steam power generation cycles) that use the flue gas of the FRCU to generate power. In addition, the MGU produces methanol under a methanol synthesis process. In this unit, FRCU the exhaust gas of the FRCU and hydrogen gas produced by the H₂-GU are utilized to produce methanol. The planned hybrid system has been conceptually designed under a new structure and configuration that is capable of producing power and methanol. In addition, the utilized hydrogen gas in the synthesis process

is produced through the process itself and there is no need to inject external hydrogen. The H₂ generated from the electrolysis process is generated under a green cycle [51]. Moreover, the oxygen gas produced from the electrolyzer unit can be considered as a useful product. Note that, the water electrolysis process works under an alkaline electrolyzer stack whose electricity consumption is supplied by the planned cycle itself. Further, the Kalina cycle operates under a mixed fluid (ammonia-water). The design and configuration of the hybrid system under study are illustrated in Fig. 1.

The central component of the envisaged framework is the Fuel Reforming and Combustion Unit (FRCU), which serves a dual role: it not only generates electrical energy but also supplies the motive force for supplementary bottoming cycles and units. The operational feed for the FRCU is sourced by converting coke oven gas through a reforming procedure, positioning this gas as the foundational fuel within the conceptualized hybrid architecture. Note that, the inlet coke oven gas is a mixture of 39 % methane, 3 % carbon monoxide, 55 % H₂, and 3 % nitrogen. The ignition of this fuel in the combustion chamber achieves a twofold outcome: it leads to the creation of flue gas and simultaneously provides the thermal energy indispensable for the process of fuel reforming. The resultant flue gas from the dual processes of reforming and combustion of the coke oven gas acts as the propellant for the heat recovery mechanism, an essential component of both the electricity generation cycles and the cycle for methanol production. Additionally, the process of methanol synthesis necessitates hydrogen, which is procured through the mechanism of an alkaline electrolyzer.

2.2. Process and configuration descriptions of the studied hybrid system

The start of the thermodynamic cycle for the hybrid system is based on the reforming and combustion processes of the fuel. In this context, the initial step involves passing the selected fuel, a mix of methane,

carbon monoxide, hydrogen, and nitrogen (at 25 °C and 1.013 bar), through a heat exchanger (HX-1) to raise its temperature. Simultaneously, water under standard thermodynamic conditions (25) °C and 1.013 bar) is processed through another heat exchanger (HX-2), where its temperature is raised until it becomes water vapor (reaching point 7). Then the fuel and water vapor are directed to a reformer after being mixed by a mixer (point 12). At this stage, a part of the reformed fuel in the reformer (~28 %) is also mixed (recirculated) with the mixture of water vapor and coke. The result of this mixing is directing a stream at a temperature of around 514 °C to the reformer. Two reactions of methane-water vapor reforming and water-gas shift occur inside the reformer (see Table 1) to obtain reformed fuel (point 13). The remaining part of the reformed fuel (~72 %) is passed through heat exchangers HX-1 and HX-2 to provide heat for these exchangers. Afterwards, the fuel is sent to the combustor (point 10 at 45.6 °C) so that the combustion

Table 1
Chemical reactions happening in the energy procedure [53–55].

Eq. no	Process	Description	Equation
Eq. 1	Reforming	Water-gas shift	$CO + H_2O \leftrightarrow H_2 + CO_2$
Eq. 2		Steam-methane reforming	$H_2O + CH_4 \leftrightarrow 3H_2 + CO$
Eq. 3	Combustion	Combustion reaction	$2O_2 + CH_4 \rightarrow 2H_2O + CO_2$
Eq. 4		Combustion reaction	$CO + 1/2O_2 \rightarrow CO_2$
Eq. 5	Methanol synthesis	CO ₂ Hydrogenation	$3H_2 + CO_2 \rightarrow H_2O + CH_3OH$
Eq. 6	Water electrolysis	Oxidation of hydroxyl ion	$2 OH^- \rightarrow 0.5 O_2 + H_2O + 2e^-$
Eq. 7		Reduction of water	$2 H_2O + 2e^- \rightarrow H_2 + 2 OH^-$
Eq. 8		Overall reaction	$H_2O \rightarrow H_2 + 0.5 O_2$

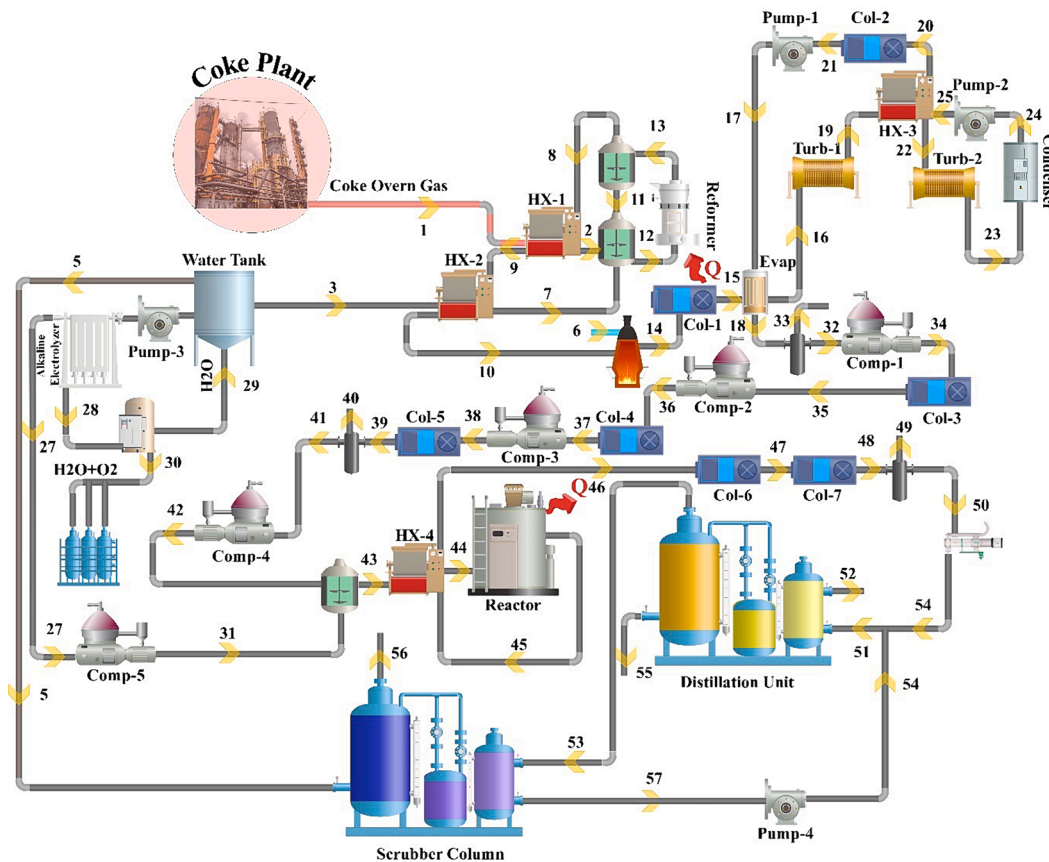


Fig. 1. Proposed structure and layout for the studied hybrid system.

reaction takes place along with the air (at reference thermodynamic conditions). Combustion reactions are processes that occur inside the combustor (see Table 1), during which a very large amount of energy can be released. During the combustion reaction, carbon monoxide combines with air oxygen and produces carbon dioxide (CO₂). As such, carbon dioxide represents the sole emission resulting from the reforming and combustion of coke oven gas. The flue gas, emerging as the byproduct of the Fuel Reforming and Combustion Unit (FRCU) process at point 14, serves as the propellant for the bottoming units/cycles. It is important to highlight that this stream initially fulfills the energy requirements for the reforming process before being channeled to the subsequent cycles. Note that, the LMTD of HX-1, HX-2, HX-3, and HE-4 are 282.5, 101, 18.8, and 109 °C, respectively.

WHRU is a downstream cycle embedded in the studied hybrid system, which is subjected to a thermodynamic cycle of power generation and a methanol synthesis cycle. Ammonia-based steam and Kalina power generation cycles are two embedded thermodynamic cycles for electricity generation purposes. Kalina cycle and ammonia-based steam cycle are coupled with the output of the FRCU process and Kalina cycle, respectively; such that, the flue gas output from the FRCU process is recovered by power generation processes during two stages. Superior thermodynamic and environmental benefits can be expected from multi-level flue gas recovery processes [52]. In the Kalina cycle, thermal energy is converted into power under a steam thermodynamic process. Ammonia-water mixture is considered as heat transfer fluid in this cycle. This system consists of two heat exchangers (with one functioning as an evaporator and the other as a condenser), an intercooler, a steam turbine, and a pump. The heat transfer medium transitions from a liquid to a saturated vapor phase via heat exchange with the flue gas in the evaporator. Furthermore, the turbine's output stream is reconverted to a liquid phase through the condenser and the intercooler. The exit flow from the Kalina cycle is then channeled to the ammonia-based steam cycle for further flue gas heat recovery. Within the ammonia-based power cycle, the transformation of the heat transfer fluid phase is facilitated by heat from the Kalina turbine. This cycle also incorporates a steam turbine, a pump, and a condenser.

The MGU represents an additional bottoming cycle aimed at recuperating flue gas from the coke oven gas reforming and combustion process. Methanol is synthesized within this unit using a fixed bed catalytic reactor through the hydrogenation of carbon dioxide. The reactor's operation for methanol synthesis is modeled using a sophisticated heterogeneous catalytic model within the software. Crucially, flue gas and hydrogen act as the primary inputs for this unit, supplied by the FRCU (at point 18) and H₂-GU (at point 27) units, respectively. The flue gas, emerging from the FRCU process near reference pressure, is subjected to pressure enhancement up to approximately 48 bar (at point 42) using four compressors, with three intercoolers in series to lower the temperature of the compressed gas. Additionally, condensed water is extracted from the flue gas via two separators. Concurrently, hydrogen from the H₂-GU is pressurized using a compressor. The compressed hydrogen and flue gas are then combined in a mixer, heated, and conveyed to a reactor (stream 44) for the hydrogenation of carbon dioxide reaction (refer to Table 1). The reactor's exit fluid first exchanges heat with the incoming stream, then proceeds to the reboiler of the distillation column (point 46). This stream initially imparts heat to the reboiler, followed by cooling to 30 °C (point 48) through an intercooler, before undergoing separation, where crude methanol (point 148) is isolated from the vapor. The subsequent step involves distillation to segregate vapor and liquid phases. The resulting vapor (point 150) is channeled to the lower section of the scrubber column, while water, serving as a solvent, is introduced at the top to extract methanol. This process substantially mitigates methanol losses, with methanol being redirected to the distillation column for further separation. The vapor, predominantly comprising nitrogen, is then released into the atmosphere from the top of the scrubber column. Through this cycle, methanol of 99.9 % purity is attainable.

In the context of this research, the hydrogen necessary for methanol synthesis is generated in-situ via water electrolysis using an alkaline electrolyzer, thus obviating the requirement for an external hydrogen source. This method entails the electrochemical transformation of water into hydrogen (H₂) and oxygen (O₂) within the electrolyzer. Such production of H₂ can be categorized as a green hydrogen generation method. To facilitate this, water at standard thermodynamic conditions is conveyed to the electrolyzer stack via a pump. The electrolyzer comprises two electrodes, an anode and a cathode, which are instrumental in dissociating water molecules. Consequently, the hydrogen thus produced is channeled into the methanol synthesis process, while the resultant oxygen is stored in an oxygen tank, ready for various oxygen-dependent applications. The specific reactions involved in this electrolysis process are detailed in Table 1.

3. Simulation of the studied hybrid plant

The simulation and assessment of the hybrid system under study are conducted using the principles of the 1th and 2th rules of thermodynamics, along with environmental impact and cost estimation analyses. This evaluation is carried out using Aspen and MATLAB software [56,57].

3.1. Energetic and exergetic assessment

The energy and exergy analyze have been provided under the aforementioned laws. In addition, the simulation of the hybrid system is based on Peng-Robinson formulas of state [58,59]. According to the first law of thermodynamics, we can write [60]:

$$\begin{cases} \text{(a): } \sum \dot{m}_{inlet} = \sum \dot{m}_{outlet} \\ \text{(b): } \sum \dot{m}_{inlet} \cdot h_{inlet} - \dot{W} = \sum \dot{m}_{outlet} \cdot h_{outlet} - \dot{Q} \end{cases} \quad (9)$$

Equations 1(a) and 1(b) represent the mass and energy balance formulas, respectively, where, \dot{m} , h , \dot{W} , and \dot{Q} are the mass flow rate, specific enthalpy, power (work), and heat transfer rate, respectively. Based on these mathematical relationships, the equations related to power and heat transfer calculations in different components can be summarized in Table 2.

As mentioned, the hydrogen required for the methanol synthesis process is produced through an alkaline electrolyzer. The power of the electrolyzer is generated through the power generation cycles embedded in the studied hybrid system. Alkaline electrolyzer can be cheaper compared to other available electrolyzers [63,64]. In addition, the most mature and oldest water electrolysis technology is related to this type [21]. The operating efficiency of this electrolyzer is lower than the proton-exchange membrane (PEM) electrolyzer, but its cost is lower compared to the PEM electrolyzer and its operation is easier. Moreover, the longevity, durability, reliability and security of alkaline electrolyzers are higher [65]. Accordingly, alkaline electrolyzers are widely used on large-scales plants. Indeed, the potential of this electrolyzer in scale-up to production capacities in the megawatt range is one of their most significant advantages. The utilized electrolyte in these electrolyzers is alkaline type (sodium hydroxide or potassium hydroxide) at a concentration of 20–40 wt% [17]. The analysis of the alkaline electrolyzer is

Table 2

Equations related to power and heat transfer calculations in different components [51,61,62].

Eq. no	Description	Equation
Eq. 10	Turbine output power	$\dot{W}_{Turbine} = \dot{m} \times (h_{inlet} - h_{outlet})$
Eq. 11	Compressor power consumption	$\dot{W}_{Comp} = \dot{m} \times (h_{outlet} - h_{inlet})$
Eq. 12	Pump power consumption	$\dot{W}_{Pump} = \dot{m} \times (h_{outlet} - h_{inlet})$
Eq. 13	Condenser heat transfer rate	$\dot{Q}_{Cond} = \dot{m} \times (h_{inlet} - h_{outlet})$

based on determining the voltage-current ($V_{AE} - I_{AE}$) characteristic curve as [66]:

$$V_{AE} = \frac{I_{AE}}{A} \times (r_2 T_{AE} + r_1) + V_{rev} + \left[\log \left(\frac{I_{AE}}{A} \cdot (t_1 + t_2/T_{AE} + t_3/T_{AE}^2) + 1 \right) \times s \right] \quad (14)$$

where, A and V_{rev} are the active area and the reversible voltage, respectively. The fixed parameters are described in reference [66]. Further, the hydrogen output is formulated by [67]:

$$\dot{m}_{H_2} = \frac{\eta_{Fa}}{2F} \times I_{AE} \quad (15)$$

where, η_{Fa} is the Faraday efficiency. Further, the power consumption of the electrolyzer can be formulated as follows [68]:

$$\dot{W}_{AE} = V_{AE} \times I_{AE} \quad (16)$$

The output power of the studied hybrid system can be measured as follows:

$$\dot{W}_{net} = \dot{W}_{KC} + \dot{W}_{AC} - \dot{W}_{AE} \quad (17)$$

where, \dot{W}_{KC} and \dot{W}_{AC} are the power outputs of the Kalina and ammonia power generation cycles, respectively. Besides that, the overall energy efficiency is:

$$\eta = \frac{\dot{W}_{net} + (\dot{m}_{CH_3OH} \times LHV_{CH_3OH})}{LHV_{fuel} \times \dot{m}_{fuel}} \quad (18)$$

where, LHV denotes the lower heating value.

Exergy analysis forms a crucial aspect of thermodynamic evaluation, serving to identify inefficiencies within a system component due to irreversibilities. In line with the second law of thermodynamics, the exergy balance equation is articulated as follows [69,70]:

$$\sum \dot{E}_{inlet} - \sum \dot{E}_{outlet} - \dot{E}_d = (\dot{W}_{outlet} - \dot{W}_{inlet}) + (\dot{E}_{Q,outlet} - \dot{E}_{Q,inlet}) \quad (19)$$

where, \dot{E} , \dot{E}_d , and \dot{E}_Q represent the exergy flow, destructed exergy rate (DER), and thermal exergy, respectively. The four exergy components of a flow are: kinetic exergy, chemical exergy, physical exergy, and potential exergy. For the energy conversion system, the first and last terms cannot be considered in the calculations. Therefore, the specific exergy of i -th flow can be written as follows [71]:

$$ex = ex_{ch} + ex_{ph} \quad (20)$$

where,

$$\begin{cases} ex_{ch,i} = RT_0 \times \left(\sum x_i \cdot \ln x_i \cdot \gamma \right) + \sum x_i \cdot ex_i^0 \\ ex_{ph,i} = (h_i - h_0) - T_0 \times (s_i - s_0) \end{cases} \quad (21)$$

where, 0 refers to the reference thermodynamic conditions, and ex^0 , s , γ , and x are the specific chemical exergy, specific entropy, activity coefficient, and mole fraction, respectively. The overall value of DER for the studied hybrid system can be calculated as follows [72]:

$$\dot{E}_{d,tot} = \sum \dot{E}_{d,i} \quad (22)$$

where, $\dot{E}_{d,i}$ represents the value of DER for the i -th component. The DER values for different components can be determined by the mathematical relations mentioned in Table 3. In addition, the overall exergy efficiency is formulated as follows:

Table 3

General exergetic balance relations [35,73].

Element	Exergetic balance	Element	Exergetic balance
Turbine	$\dot{E}_{inlet} - \dot{E}_{outlet} - \dot{W}_T$	Compressor	$\dot{E}_{inlet} - \dot{E}_{outlet} + \dot{W}_{Comp}$
Inter cooler	$\dot{E}_{inlet} - \dot{E}_{outlet}$	Reformer& Reactor	$\dot{E}_{inlet} - \dot{E}_{outlet} + \dot{E}_Q$
Heat exchanger	$\dot{E}_{inlet} - \dot{E}_{outlet}$	Combustor	$\dot{E}_{inlet} - \dot{E}_{outlet}$
Pump	$\dot{E}_{inlet} - \dot{E}_{outlet} + \dot{W}_P$	Column	$\dot{E}_{inlet} - \dot{E}_{outlet}$
Electrolyzer	$\dot{E}_{inlet} - \dot{E}_{outlet} + \dot{W}_{AE}$	Separator	$\dot{E}_{inlet} - \dot{E}_{outlet}$

$$\varepsilon = 1 - \frac{\dot{E}_{d,tot}}{\dot{E}_{inlet,tot}} \quad (23)$$

3.2. Cost estimation

The purpose of the cost analysis for the hybrid system under study is to calculate the initial capital investment, the total annual operating costs, and the per-unit costs of the produced outputs. A large percentage of the production power in the planned hybrid system is consumed for hydrogen production and methanol synthesis. Besides, the components embedded in the methanol synthesis process (especially compressors) have a relatively high initial investment costs. Accordingly, it is expected that the electricity product cost is relatively high compared to other electricity generation technologies. Therefore, there is more focus on the main goal (i.e., the methanol product cost). The total annual cost is expressed as [74]:

$$C_{tot} = C_{en} + Z_{tot} \quad (24)$$

In the above relation, C_{en} refers to the energy cost, is the sum of fuel, cooling water and electricity costs. The power consumption of the studied hybrid system is supplied by the system itself. Therefore, no fee is paid for supplying electricity from the grid, and the hybrid system is self-sufficient from the point of view of supplying electricity. Moreover, in equation (24), Z_{tot} is the initial investment cost. To estimate the initial investment costs for different components, the mathematical equations stated in Table 4 can be used: Further, the methanol and power products costs are expressed by [62]:

$$C_{CH_3OH} = \frac{C_{tot}}{\dot{m}_{CH_3OH} \times \tau} \quad (25)$$

$$C_{Power} = \frac{C_{tot}}{\dot{W}_{net} \times \tau} \quad (26)$$

where, \dot{m}_{CH_3OH} and τ denote the annual methanol production rate and annual running hours, respectively.

3.3. Environmental modeling

One of the primary objectives in developing and utilizing new energy conversion systems is to minimize the emission of environmental pollutants, aiming for low-carbon or carbon-neutral solutions. In this regard, the energy conversion system under the best thermodynamic and

Table 4

Initial investment costs for different elements [21,24,42].

Element	Capital investment cost	Component	Capital investment cost
Turbine	$C_T = 4405 \times \dot{W}_T^{0.7}$	Compressor	$C_{Comp} = 742.9 \times \dot{W}_T^{0.82}$
Heat exchangers	$C_{EVP} = 588 \times A_{HX}^{0.8}$	Drum& Reactor	$C = 17640 \times L^{0.802} \times D^{1.06}$
Pump	$C_P = 1120 \times \dot{W}_T^{0.8}$	Electrolyzer	$C_{AE} = 450 \times \dot{W}_{AE}^{0.92}$

environmental performances will have the potential to be exploited on a plant-scale [75]. CO₂ is the main species in the emission of environmental pollutants from an energy conversion system, so for environmental assessment, the equivalent amount of emitted CO₂ is considered [76]. In an energy conversion system, CO₂ can be emitted directly (through the streams of process) or indirectly (through the power and thermal utilities). Hence, the total amount of emitted CO₂ from the studied hybrid energy system is expressed by [36]:

$$\Psi_{CO_2,tot} = \Psi_{CO_2,direct} + \Psi_{CO_2,indirect} \quad (27)$$

All the consumed power and heat in the studied hybrid energy system is supplied through the process itself. Accordingly, indirect emissions can be considered null [74]. In addition, the steam streams of the embedded separator and scrubber column in the methanol synthesis unit contain carbon dioxide. Based on this, the direct emission of CO₂ in the studied hybrid energy system cannot be ignored. Consequently, the following equation is used to quantify the amount of carbon dioxide emissions from the energy system [77]:

$$\Psi_{CO_2} = \frac{\dot{m}_{CO_2}}{\dot{m}_{CH_3OH}} \text{ or } \Psi_{CO_2} = \frac{\dot{m}_{CO_2}}{\dot{W}_{net}} \quad (28)$$

3.4. Bi-objective optimization

Utilization of optimization algorithms plays a pivotal role in identifying the optimal design conditions and outcomes for an energy conversion system. These algorithms are designed to pinpoint the most efficient operating conditions (defined as the optimization objective function(s) of the energy system, taking into account variations in certain independent variables within permissible ranges (which act as the problem constraints). Optimization algorithms can be implemented for single-function or multi-function objectives [11]. According to the literature [75], multi-function optimization objectives can provide more suitable decision making conditions. This article employs a bi-objective optimization approach for the hybrid energy system under consideration, focusing on both exergetic and environmental objectives. Specifically, the optimization aims to achieve the highest possible exergy efficiency while simultaneously minimizing the rate of CO₂ emissions. To achieve this, the Genetic Algorithm, renowned for its evolutionary approach and effectiveness, is employed to identify the optimal design parameters for the hybrid energy system under investigation. Additionally, the allowable ranges for the decision variables involved in the optimization are specified in Table 5.

In case of multi-objective function (MOF), Pareto approach is mainly employed for this aim. Nevertheless, another method deals with the multi-objective techniques, where weighing coefficient (ω) is assigned to all objectives, formulated by [78]:

$$\begin{aligned} \text{Max}(MOF) &= (\omega_1 \cdot \varepsilon) + (\omega_2 \cdot (1 - \Psi_{CO_2})) \\ \text{where, } &\begin{cases} 0 \leq \omega_1, \omega_2 \leq 1 \\ \omega_1 + \omega_2 = 1 \end{cases} \end{aligned} \quad (29)$$

Fig. 2 in the paper provides a visual representation of the evaluation structure for the hybrid energy system being studied. Additionally, several assumptions have been made to simplify the simulation process:

- The hybrid energy system being analyzed functions in a steady-state mode.
- The temperature of the combustion reaction is assumed to be constant.
- Heat losses in pipelines and heat exchangers are ignored.
- The electrical elements of the system maintain a constant isentropic efficiency throughout their operation.
- Separation operations (in separators and columns) occur under adiabatic processes.
- The outlet streams from the evaporator condenser are assumed to be saturated vapor and saturated liquid, respectively.
- Other working conditions are given in Table 6.

4. Verification of conducted modeling

Verifying the model is essential to ensure the accuracy of the simulation for reliable results. Given that the design of the studied energy system incorporates a novel configuration, the validation of the model for different components has been conducted separately. Consequently, the models for the Kalina cycle, alkaline electrolyzer, and methanol synthesis process were validated against existing reports in authoritative literature. Accordingly, the available reports and data in [80] were employed to model verification of the Kalina-power generation cycle. In [80], an evaluation of a storage system integrated with Kalina and organic Rankine cycles was presented. Electricity generation in Kalina cycle was based on ammonia-water heat transfer fluid. In addition, saturated steam at 45 bar and 133.5 °C flowed into the turbine. The model verification of the Kalina-power generation cycle is established under the comparing the net electricity and thermodynamic efficiencies of the reported and obtained results (see Table 7 (a)). The calculated deviations for net electricity, energy efficiency, and exergy efficiency are 0.98 %, 1.07 %, and 1.16 %, respectively. Therefore, the model of the Kalina-power generation cycle can be acceptable and believable.

The available reports and data in [66] were employed to model verification of the alkaline electrolyzer. In [66], an analysis of an alkaline electrolyzer under prediction of Faraday efficiency, voltage versus current curve, and gas impurities was reported. In that study, the electrolyte was based on potassium hydroxide with 30–40 % wt. The model verification was carried out at a temperature of 80 °C and a pressure of 7 bar. The model verification of the alkaline electrolyzer is established under the comparing the voltage-current density curve of the reported and obtained results (see Fig. 3). As determined, the calculated deviation for voltage is 1.18 %. Hence, the model of the alkaline electrolyzer can be acceptable and believable. Finally, the available reports and data in [81] were employed to model verification of the methanol synthesis process. In [81], an optimization for a Lurgi methanol synthesis reactor was developed under a steady-state model. The syngas inlet temperature and feed mass flow rate were assumed to be 225 °C and 15.91 kg/s, respectively. The model verification of the methanol synthesis process is established under the comparing the mass flow rates of compounds of the reported and obtained results (see Table 7(b)). As determined, the maximum calculated deviation for the mass flow rates of compounds is 1.12 %. Accordingly, the model of the methanol synthesis process can be acceptable and believable.

5. Results and discussion

In this segment, a comprehensive evaluation is presented, encompassing energy and exergy analyses, estimations of cost, assessments of environmental repercussions, and studies aimed at optimization. Moreover, the outcomes derived from this research are juxtaposed with findings from parallel inquiries, underscoring the enhanced efficacy of the advocated hybrid energy framework. This comparative analysis serves not only to showcase the superior functionality of the proposed system but also to validate the dependability of the results acquired.

Table 5
Predefined boundaries of decision variables for optimization.

Variable	Lower range	Upper range
Hydrogen concentration rate, %	28 %	72 %
H ₂ to CO ₂ ratio	1	3
Steam-to-methane ratio	1	3
Turbine-1 inlet pressure, bar	120	240
AE current density, A/m ²	1200	2000

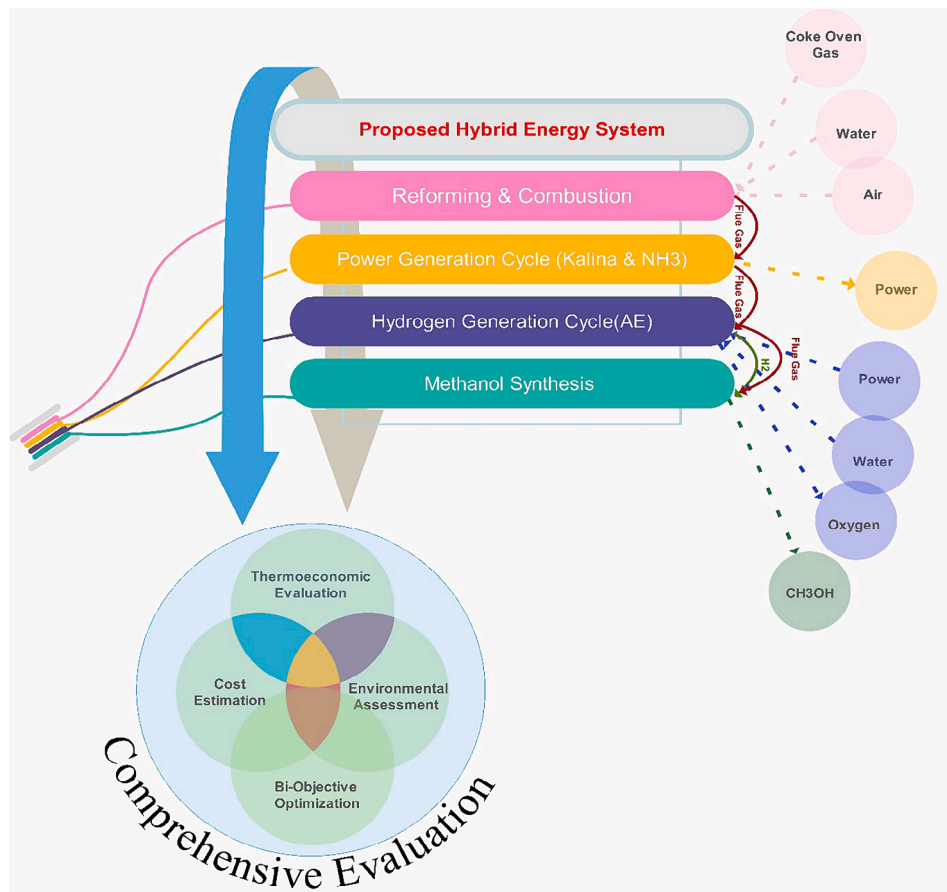


Fig. 2. Evaluation structure of the studied hybrid energy system.

Table 6
Working conditions and design data of the studied energy system [11,53,79].

Parameter	Value	Parameter	Value
Ambient temperature	25 °C	Hydrogen pressure	48 bar
Ambient pressure	1.013 bar	Kalina cycle fluid	Ammonia-water
Combustion temperature	1250 °C	Isentropic efficiency	85 %
Electrolysis temperature	80 °C	Reactor diameter	5.5 m
Inlet air temperature	25 °C	Reactor length	10 m
Inlet water temperature	25 °C	Air composition	21 % O ₂ & 79 % N ₂
Temperature of the methanol reactor on the copper catalyst	300 °C	Void fraction of reactor	40 %
Inlet temperature of syngas to the methanol reactor	190 °C	Adiabatic efficiency of compressors	85 %
Pressure of the methanol reactor on the copper catalyst	50 bar	Annual running hour	8300 h

5.1. Energy and exergy outcomes

The thermodynamic analysis and simulation conducted for the study have established the working conditions at different points, detailed in Table 8. Fig. 4 illustrates the results of the energy analysis. The energy system studied produces three main outputs: electricity, oxygen, and methanol. Additionally, it generates hydrogen gas and thermal energy, which are utilized in various internal processes. Notably, the net outputs of electricity, oxygen, and methanol are 12.72 MW, 0.51 kg/s, and 0.53 kg/s, respectively. It was found that the total electricity generated amounts to 45.3 MW, with approximately 72 % being consumed by the pumping, compression, and water electrolysis processes. In the

Table 7
Model verification results. (a): Model verification of the Kalina-power generation cycle [80].

Variable	Literature	Simulation	Deviation
Turbine inlet temperature, °C	133.50	133.50	0.00 %
Turbine inlet pressure, bar	45.0	45.0	0.00 %
Net electricity, kW	89.30	90.18	0.98 %
Energy efficiency, %	13.0	13.14	1.07 %
Eergy efficiency, %	55.27	55.91	1.16 %

(b): Model verification of the methanol synthesis process [81]

Compounds, mass flow rate (kg/s)	Literature	Simulation	Deviation
Water	0.637	0.631	0.95%
Hydrogen	2.226	2.251	1.12%
Carbon dioxide	5.097	5.147	0.98%
Methanol	3.134	3.10	1.09%
Carbon monoxide	1.360	1.345	1.11%

electricity production, the Kalina and ammonia power generation cycles contribute 60.4 % and 39.6 %, respectively. Furthermore, the electricity consumption shares for pumping, compression, and water electrolysis are 32.5 %, 57.9 %, and 9.6 %, respectively. The water electrolysis process, in particular, uses a significant portion of the plant’s electricity. Thus, if the electricity for the electrolysis process could be sourced from renewable energy, it would not only facilitate the production of green hydrogen but also significantly enhance the net electricity output of the plant.

Under the considered design and operational conditions, the energy system can acquire an energy efficiency of 46.8 %. Zhou et al. [74]

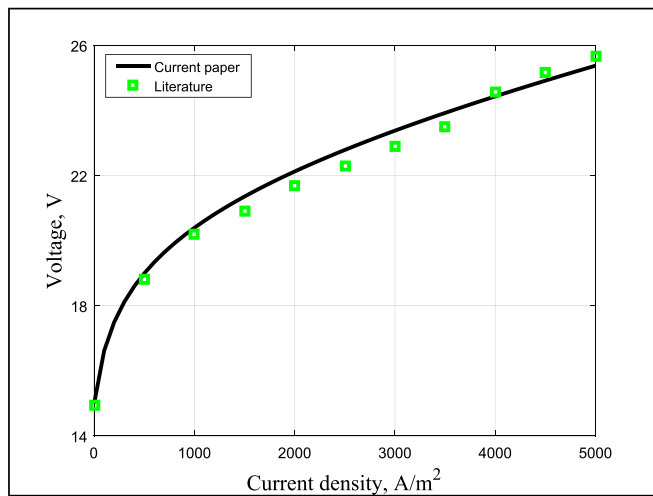


Fig. 3. Model verification of the alkaline electrolyzer [66].

reported an energy efficiency of around 31.4 % for a waste heat recovery system integrated with a desalination unit, two ammonia and ammonia-water based power generation units, and a carbon dioxide separation and liquefaction process. In [82], a solar-powered ammonia-water Rankine cycle, combined with an LNG-cold energy recovery cycle, achieved an energy efficiency of about 13 %. Xu et al. [14] observed an energy efficiency of approximately 53.5 % in a cogeneration plant producing power and methanol, which integrated coke oven gas and blast furnace gas with a methanol synthesis reactor. Zhao et al. [28] achieved an energy efficiency near 54.4 % in a system employing pulverized coke for chemical looping in hydrogen production, supplemented by coke-oven gas for synthesizing methanol and ammonia. By contrast, the energy efficiency of the hybrid system in this study is deemed competitive when compared with other systems documented in the literature. The comparatively modest energy efficiency of the system under investigation is primarily due to the electrical requirements of the electrolysis process. Fig. 5 illustrates a comparative analysis of the energy efficiency of the hybrid energy system under review against those reported in other studies.

Exergy analysis is instrumental in minimizing irreversibilities and enhancing the efficiency of energy conversion processes. It serves as a robust tool for establishing realistic benchmarks for achieving near-ideal performance levels. Unlike energy analysis, exergy analysis provides a more precise identification of the causes and locations of

thermodynamic losses. In this paper, exergy analysis is conducted for various processes and components. In this context, the Destroyed Exergy Rate (DER) for different components and units is calculated, and their contributions to the total destroyed exergy are assessed. The overall DER value for the entire hybrid energy system under study is found to be 160.61 MW. To improve the system’s overall thermodynamic performance, focusing on components with high DER values is crucial. Fig. 6 displays the contribution of each unit in the hybrid system to the DER value. The three primary causes for a high DER value in a component are: the occurrence of irreversible chemical reactions, a significant temperature difference between inlet and exit points, and substantial thermodynamic losses due to low operational efficiency. Therefore, units containing such components will inherently exhibit high DER values.

Fig. 6 indicates that the largest portion of exergy loss in the system, approximately 45.4 %, is attributed to the coke oven gas reforming and combustion unit. This substantial exergy destruction primarily arises from the significant Destruction of Exergy Rate (DER) observed in both the reformer and combustor. Further detailed in Fig. 7, these two components collectively contribute to over 39 % of the total DER of the system. The heightened DER in the reformer and combustor results from the non-reversible chemical reactions occurring within these units. Moreover, the elevated DER value associated with the electricity production unit is linked to the performance of the evaporator (EVP). In the evaporator, the transfer of thermal energy necessary for the phase change of the heat transfer fluid, via heat exchange, is a major contributor to its high DER value.

As mentioned, the components whose inlet and outlet points have a high temperature difference have a greater share in the value of DER. Fig. 7 points out that more than 22 % of the total value of DER is related to the evaporator. In addition, about 12.5 % of the total value of DER is related to two distillation and scrubber columns. However, the share of the distillation column is significantly higher than that of the scrubber column (99 % vs. 1 %). Indeed, the distillation column is in the second rank of the component with the highest DER value. Under the developed exergy analysis, the studied energy system can acquire an exergy efficiency of 85.13 %.

The exergy efficiency is a pivotal metric in the design and deployment of energy conversion systems. Essentially, it significantly influences the thermodynamic efficiency of an energy system or power plant. Systems with higher exergy efficiencies, in comparison to their counterparts, are more likely to be scaled up to plant-level operations. To this end, a comparative analysis of exergy efficiency with other energy conversion processes suggested in academic literature is compiled in Table 9. This extensive comparison demonstrates that the hybrid

Table 8 Working conditions of different points.

Point	T, °C	P, bar	Point	T, °C	P, bar	Point	T, °C	P, bar
1	25.0	1.013	20	62.9	4.5	39	30.0	15.8
2	600.0	1.013	21	25.0	4.5	40	30.0	15.8
3	25.0	1.013	22	114.7	88.0	41	30.0	15.8
4	25.0	1.013	23	25.2	9.8	42	163.0	48.0
5	25.0	1.013	24	25.0	9.8	43	146.3	48.0
6	25.0	1.013	25	27.2	88.0	44	185.2	48.0
7	205.2	1.013	26	25.1	28.0	45	295.2	48.0
8	745.4	1.013	27	80.0	28.0	46	254.7	48.0
9	528.8	1.013	28	80.0	28.0	47	102.2	48.0
10	45.6	1.013	29	80.0	28.0	48	30.0	48.0
11	745.4	1.013	30	80.0	28.0	49	30.0	48.0
12	513.9	1.013	31	82.72	48.0	50	30.0	48.0
13	745.4	1.013	32	30.0	1.013	51	31.5	1.2
14	1250.0	1.013	33	30.0	1.013	52	59.3	1.013
15	1050.0	1.013	34	154.5	2.8	53	59.3	1.013
16	325.1	198.0	35	50.9	2.8	54	81.7	1.013
17	26.4	198.0	36	150.5	6.8	55	100.0	1.2
18	30.0	1.013	37	69.1	6.8	56	90.6	1.013
19	128.0	4.5	38	170.9	15.8	57	81.7	1.013

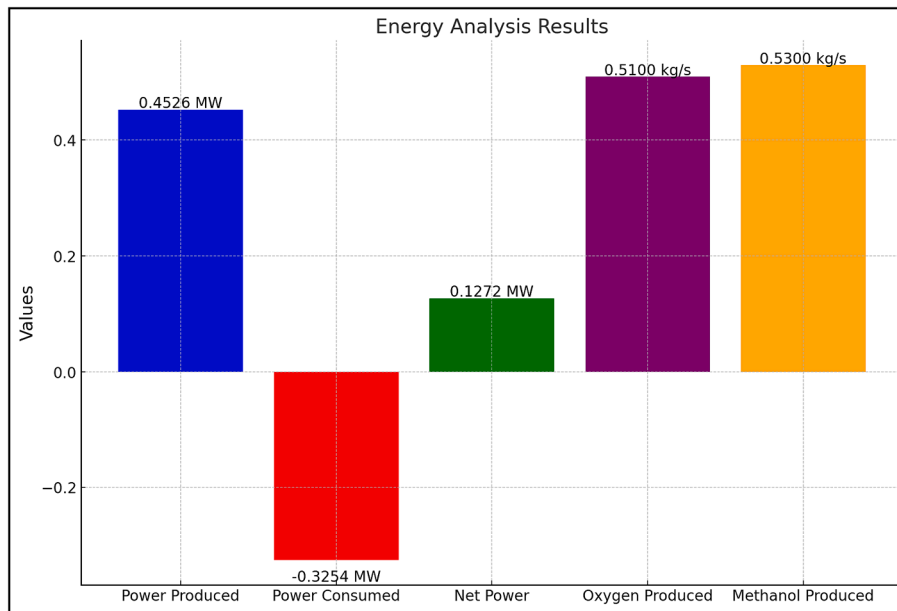


Fig. 4. Results of energy analysis.

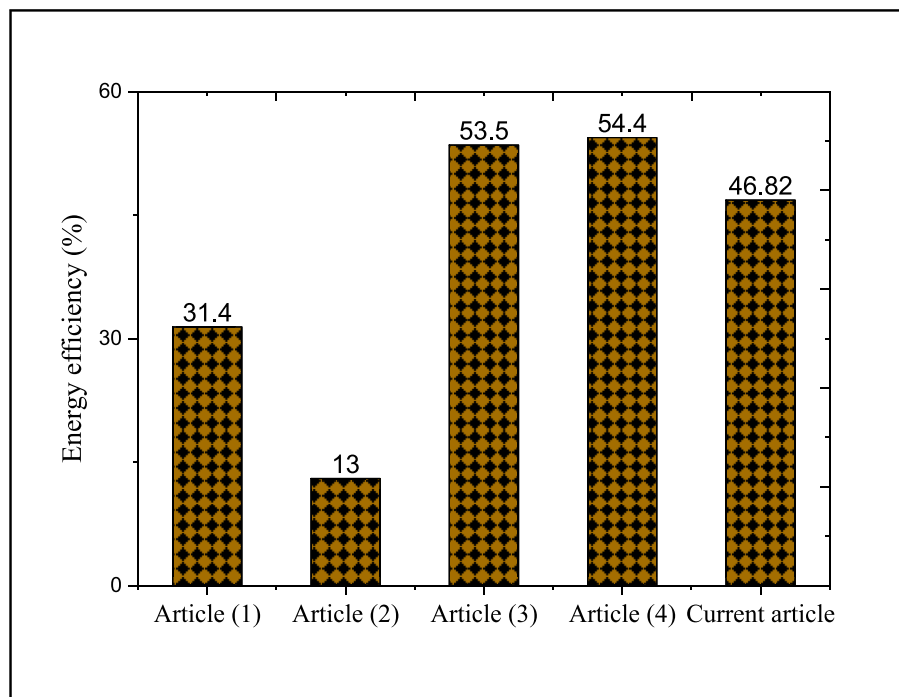


Fig. 5. Comparison of the energy efficiency of the studied hybrid energy system with other systems reported in the publications: article (1) [74], article (2) [82], article (3) [14], and article (4) [28].

energy system under study, which generates electricity and methanol through coke oven gas reforming and combustion, exhibits outstanding exergetic performance relative to various existing technologies. Furthermore, it stands as a close competitor to some of the other documented technologies.

5.2. Cost estimation results

Cost estimation is a vital factor in the decision-making process for implementing new energy conversion systems. Investors prioritize systems with reasonable initial investment and product costs. In this

context, the cost estimation for the hybrid system under study aims to determine the initial investment cost, the total annual cost, and the unit costs of the output products. According to the cost estimation results, the total initial investment and annual costs of the energy system are approximately 19.92 million and 10.51 million US dollars, respectively. Fig. 8 presents the breakdown of the initial investment cost across different units of the hybrid energy system. The electricity production unit demands the highest initial investment, accounting for over 40 % of the system's total initial costs. This high cost is mainly due to the expensive purchase price of turbines. Fig. 9 further details the contribution of each component in the hybrid system to the initial investment

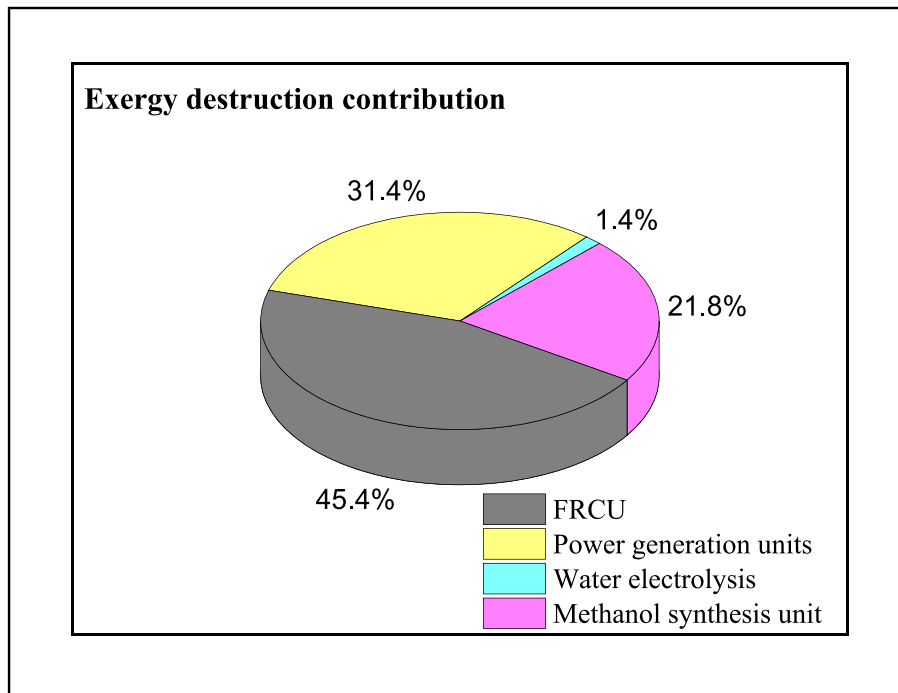


Fig. 6. Contribution of each unit of the studied hybrid energy system in the DER value.

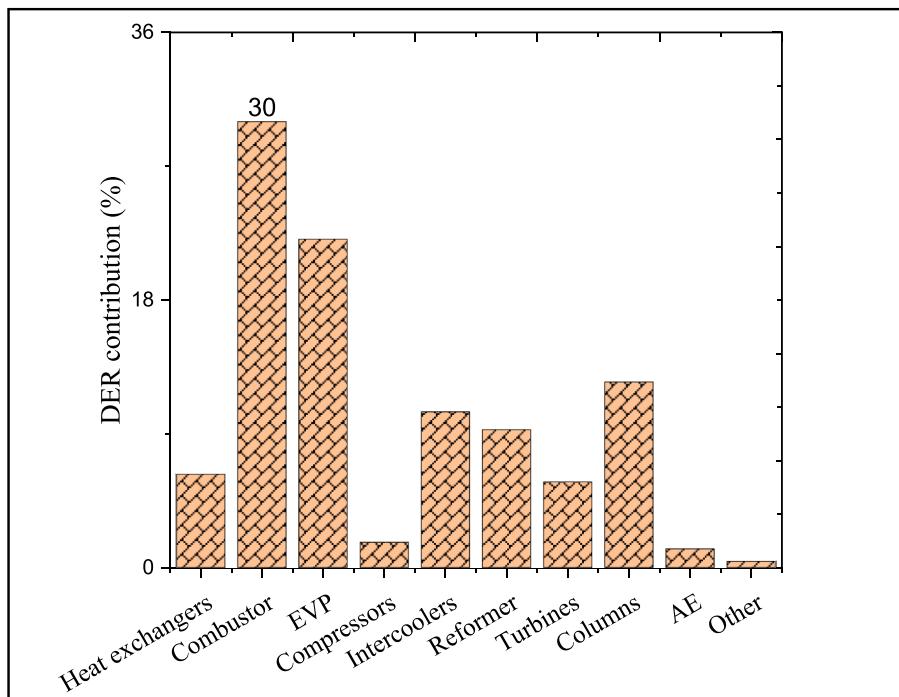


Fig. 7. Contribution of each components of the studied hybrid energy system in the DER value.

cost, highlighting that turbines alone constitute about 30 % of the total initial investment cost.

The acquisition cost of a turbine is closely linked to its operational efficiency. A more efficient turbine comes with a higher purchase price. Opting for a less efficient turbine might lower the initial capital outlay for the energy system, but this can adversely impact its thermodynamic performance. Thus, optimizing both the thermodynamic and cost aspects of the turbine is crucial in the decision-making process. The Methanol synthesis unit ranks second, accounting for approximately 36

% of the highest initial investment costs among various units. Compressors command over 19 % of the total initial investment cost of the energy system, contributing to the significant initial expense of the methanol synthesis unit. The cost of a compressor, similar to that of a turbine, is dependent on its operational efficiency. As noted in the literature, compression is inherently a costly process. The substantial investment required for the hydrogen production unit is primarily due to the electrolyzer’s purchase cost, constituting about 99 % of this unit’s total initial investment. However, hydrogen production through this

Table 9
Comparison for the exergy efficiency of the studied hybrid energy system with other energy conversion processes proposed by the scholars.

Ref.	Energy system structure	Exergy efficiency
[83]	A methanol-electricity polygeneration system under a staged coal gasification process	65.2 %
[28]	A pulverized coke-fueled chemical looping of hydrogen generation assisted coke-oven gas to methanol and ammonia	78.7 %
[84]	A full-spectrum solar-based methanol hybrid energy system to generate electricity, methanol, and cooling and heating capacities	33.3 %
[85]	A cogeneration system (bio-methane and bio-methanol) under an ORC system, An alkaline electrolyzer, and an absorption refrigeration unit integrated with a parabolic trough collector-driven solar unit	45.9 %
[14]	A power and methanol cogeneration plant under coke oven gas and blast furnace gas integrated with a methanol synthesis reactor	26 %
[43]	A trigeneration system (electricity, hydrogen, and methanol) based on a direct methanol fuel cell, an ORC system, a PEM electrolyzer, and a methanol synthesis unit integrated with a carbon capture unit	55.1 %
[86]	An integrated system under an ORC system, a methanol synthesis process, and solar dish collector-driven unit to produce crude helium gas, liquefied natural gas, and liquid methanol	93.8 %
[30]	A solar-based plant for methanol production integrated with a coke oven gas liquefaction process and post-combustion CO ₂ capture	68.72 %
[87]	A methanol production route based on biomass through direct chemical looping (hydrogen production or gasification) processes	60 %
This article	A power, oxygen, and methanol production hybrid system under a coke oven gas-driven fuel reforming and combustion unit, a power generation unit (based on a Kalina cycle and an ammonia-based steam cycle), an alkaline electrolyzer, and a methanol synthesis process	85.13 %

method is considered environmentally friendly. Moreover, this approach eliminates the challenges associated with hydrogen transport and storage.

The cost estimation results also indicated that the electricity product cost and methanol product cost in the studied energy system are 0.099 US\$/kWh and 0.56 US\$/kg, sequentially. Electricity is the main energy requirement of societies and industries. Therefore, the cost of electricity generation is the most critical criterion for comparing electricity generation technologies. Accordingly, a comparison for the electricity product cost in the studied hybrid energy system with other energy conversion processes proposed by the scholars is tabulated in Table 10. According to the comparison, it can be concluded that the studied energy system from the point of view of the electricity product cost can provide an acceptable and competitive result compared to other reported technologies. In addition, the electricity product cost in the offered system has been compared under three different scenarios. Fig. 10 demonstrates the result of comparing the electricity product cost under three hypothetical scenarios. The initial scenario explores the cogeneration of electricity and methanol within the proposed energy system, resulting in an estimated electricity production cost of 0.099 US\$/kWh. The second scenario considers the energy system functioning solely for electricity generation, excluding the hydrogen production and methanol synthesis units. In this case, the cost of producing electricity is calculated to be 0.021 US\$/kWh. The third scenario examines the combined production of electricity and hydrogen, without the methanol synthesis unit, with an estimated electricity cost of 0.032 US\$/kWh. Hence, in the second (excluding hydrogen production and methanol synthesis units) and third (excluding methanol synthesis unit) scenarios, the energy system demonstrates a markedly reduced cost of electricity production, showcasing a significant advantage over other technologies, as detailed in Table 10.

Gu et al. [94] documented the cost of methanol production at 0.73 US\$/kg in a system where CO₂ from flue gas is harnessed in a cogeneration setup employing an alkaline reactor and an Organic Rankine Cycle (ORC) system. Sollai et al. [95] indicated the cost of producing methanol to be approximately 1.06 US\$/kg, utilizing a system that converts power to renewable methanol via water electrolysis and leverages flue gas for heat recovery. Hou et al. [96] detailed the methanol

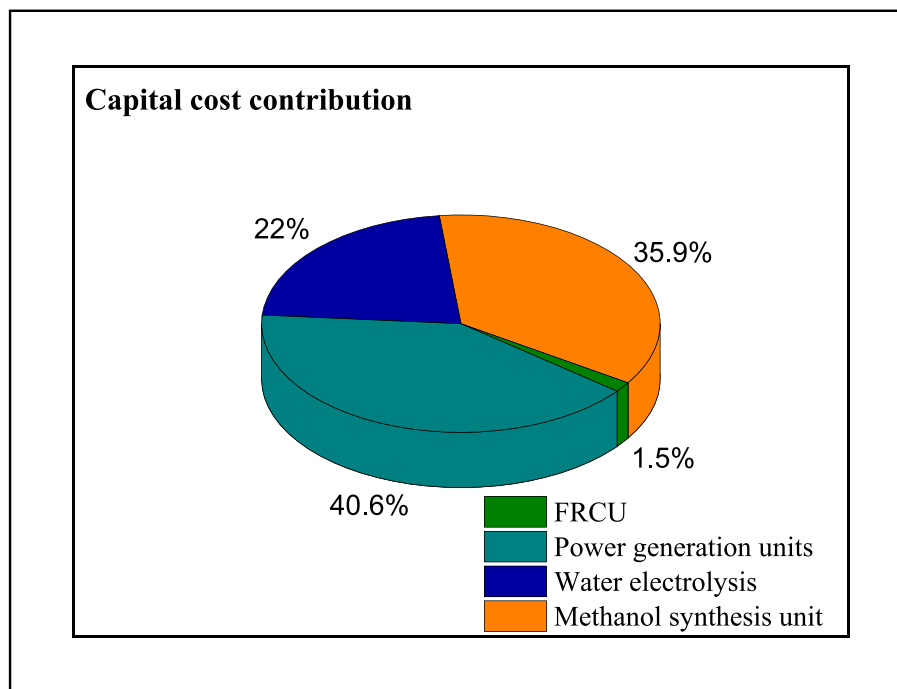


Fig. 8. Contribution of each unit of the studied hybrid energy system in the initial investment cost.

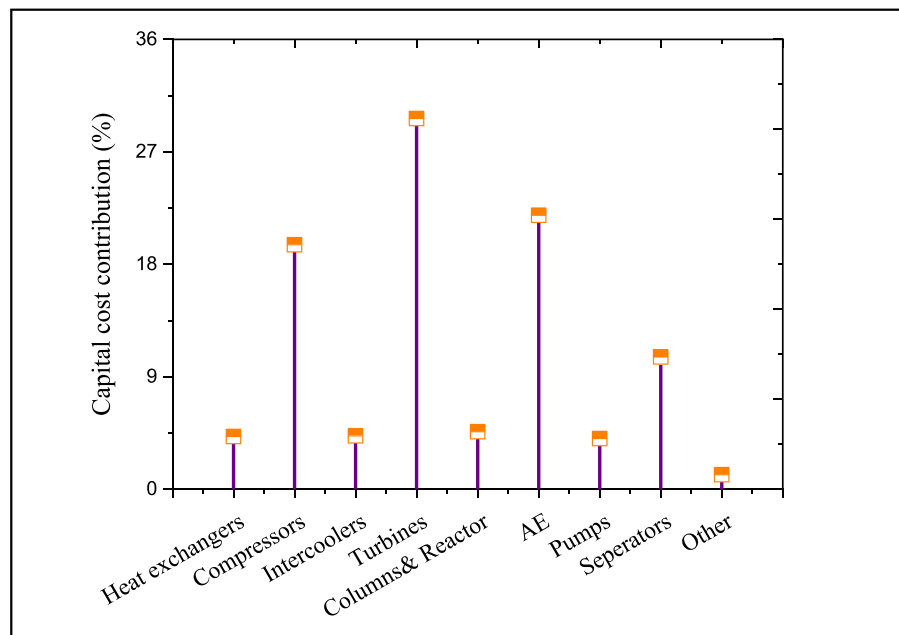


Fig. 9. Contribution of each components of the studied hybrid energy system in the initial investment cost.

Table 10

Comparison for the electricity product cost in the studied hybrid energy system with other energy conversion processes proposed by the scholars.

Ref.	Energy system structure	Electricity product cost, US \$/kWh
[88]	A combined cooling and power under a natural gas-biomass dual fuel gas turbine, an ORC system, and absorption refrigeration unit	0.0761
[74]	A multigeneration framework under two power generation cycle, a fuel gas-waste heat recovery unit, a CO ₂ separation and liquefaction unit, and a desalination unit	0.048
[89]	A solar dish power plant under Egypt desert weather condition	0.134
[90]	A thermal cycle for renewable production of electricity and desalinated water based on biomass gasification technology	0.11
[91]	An integrated system under a waste-to-energy power plant combined with an ORC system	0.088
[92]	A power generation cycle based on a PEM fuel cell and PEM electrolyzer	0.45
[93]	A methanol utilization technology for power generation under a solid oxide fuel cell, a PEM fuel cell, and a gas processing unit Northwest China	0.078
This article	A power, oxygen, and methanol production hybrid system under a coke oven gas-driven fuel reforming and combustion unit, a power generation unit (based on a Kalina cycle and an ammonia-based steam cycle), an alkaline electrolyzer, and a methanol synthesis process	0.099

production cost at 0.23 US\$/kg in a cogeneration framework integrating a biogas upgrading cycle, a natural gas reforming and synthesis unit, and a methanol separation process. Palone et al. [97] noted the cost of methanol production at 0.84 US\$/kg, employing a process generating methanol and ammonia, facilitated by chemical looping gases. Sun and Aziz [87] recorded a production cost of 0.48 US\$/kg for methanol synthesized from biomass through direct chemical looping, including hydrogen production and gasification processes. Nizami et al. [98] cited methanol production costs of 1.04 and 1.67 US\$/kg, utilizing synthesis based on CO₂ hydrogenation, powered respectively by a photovoltaic array-driven electrolyzer and a natural gas process. Wu et al. [93] identified the cost of methanol production at 0.34 US\$/kg in a plant combining methanol steam reforming with a Proton Exchange Membrane (PEM) fuel cell. Fig. 11 delineates the cost comparison of methanol production, from which it can be inferred that the energy system under study offers a competitive and satisfactory methanol production cost when juxtaposed with other documented technologies.

5.3. Environmental analysis outcomes

As indicated, the entire requirement of power and heat in the examined hybrid energy system is self-sustained, derived internally from the system's processes. This setup effectively reduces indirect emissions to negligible levels. Nonetheless, it's noteworthy that the vapor

emissions from the separator and the scrubber column, integral components of the methanol synthesis unit, do contain CO₂. Accordingly, the direct emission of CO₂ in the studied hybrid energy system cannot be ignored. Since methanol and electricity are two useful products of the studied energy system, therefore environmental analysis has been done from two perspectives of electricity and methanol production. According to calculations, the value of released CO₂ from the system was equal to 0.0961 kgCO₂/kWh (or 0.639 kgCO₂/kgMeOH). Environmental analysis has been reported in some studies for different energy conversion systems. Therefore, a comparison between the developed environmental assessments in the present research and the reported by the researchers is stated in Table 11. In addition, the released CO₂ from the natural gas, petroleum, and coal-based plants were reported as 0.53, 0.85, and 1.18 kgCO₂/kWh, sequentially [99]. According to the comparison, it can be concluded that the studied energy system from the point of view of the released CO₂ rate can provide an acceptable and competitive result compared to other reported technologies.

5.4. Parametric analysis

Parametric analysis scrutinizes the relationship between independent variables and the performance metrics of an energy conversion system, offering insights crucial for optimizing system design and functionality. In the context at hand, this analysis probes the influence of

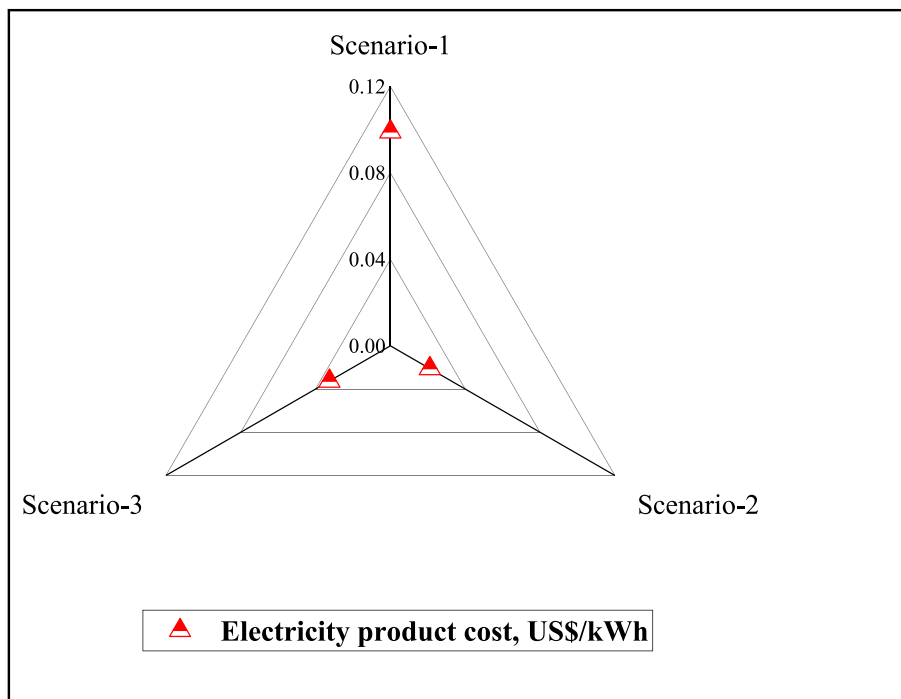


Fig. 10. Result of comparing the electricity product cost under the three hypothetical scenarios.

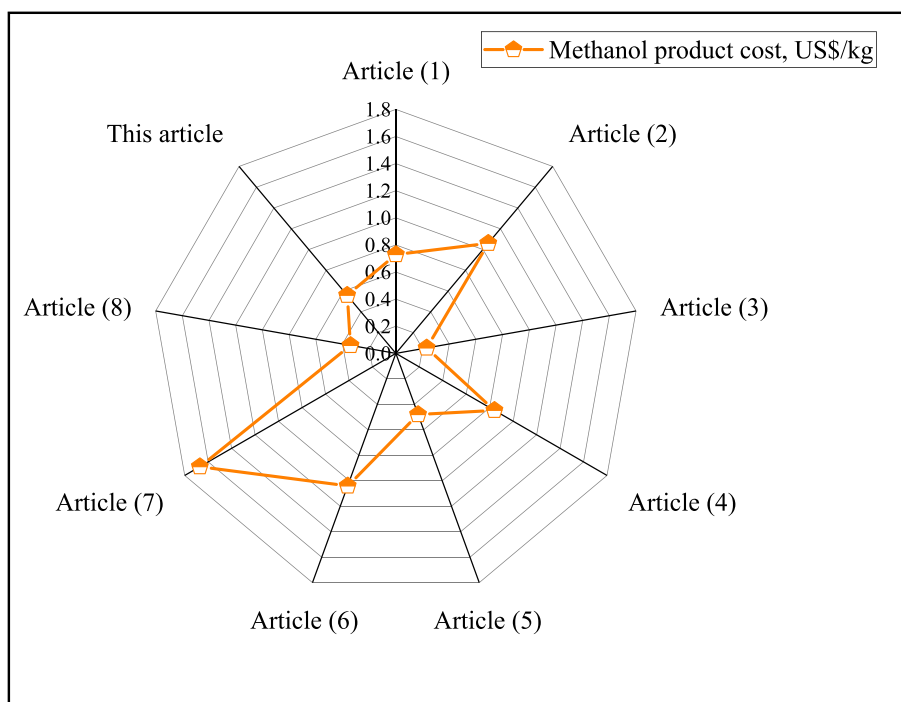


Fig. 11. Comparison of the methanol product cost: article (1) [94], article (2) [95], article (3) [96], article (4) [97], article (5) [87], article (6) [98], article (7) [98], and article (8) [93].

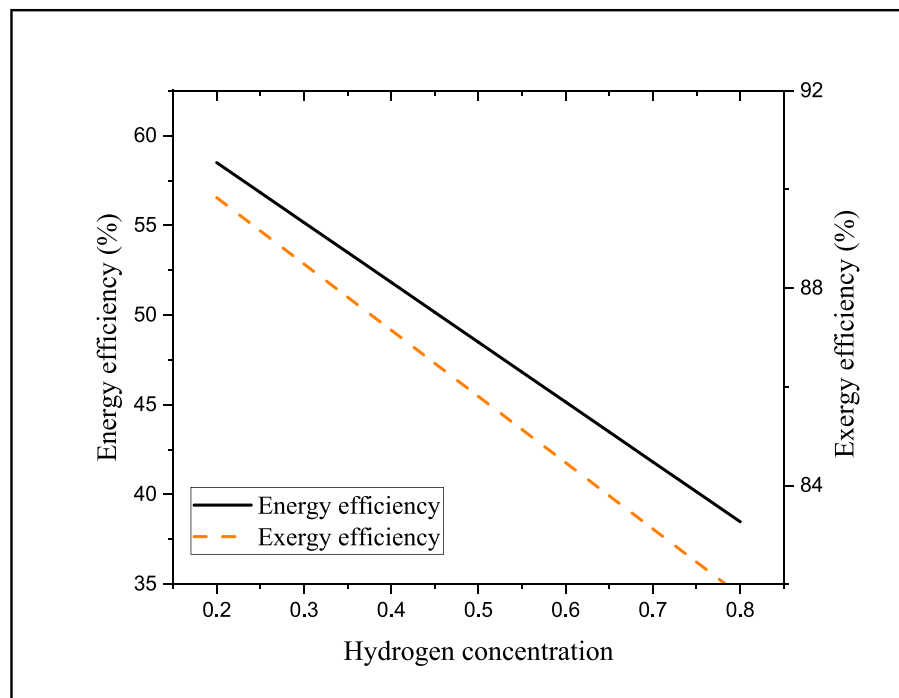
various independent variables – namely, the hydrogen concentration in the input fuel, the hydrogen to carbon dioxide ratio, and the pressure within the Kalina cycle – on the system’s operational efficiency. As depicted in Fig. 12, augmenting the hydrogen concentration in the input fuel correlates with a decline in the system’s thermodynamic efficiencies. This downtrend is primarily attributed to a diminished rate of methanol production, a consequence of the escalated hydrogen concentration. Elevated hydrogen levels correspond with diminished

concentrations of methane and carbon monoxide, thereby leading to a reduced presence of carbon dioxide in the flue gas emitted from the fuel reforming and combustion process. This scenario culminates in a scarcity of thermal energy for the subsequent cycles, adversely impacting the output of electricity and methanol in the power generation and methanol synthesis units. To preserve the balance of the reaction, it becomes necessary to curtail the production rate of hydrogen via the electrolyzer. Despite the reduction in power requirements for compressors, pumps,

Table 11

Comparison between the developed environmental assessments in the present research and the reported by the researchers.

Ref.	Energy system structure	Released CO ₂ rate
[100]	A geothermal-based hybrid system coupled with a fuel cell and a desalination unit	0.124 kgCO ₂ /kWh
[94]	A flue gas's captured CO ₂ -driven cogeneration system based on an alkaline reactor and an ORC system	0.9 kgCO ₂ /kgMeOH
[97]	A methanol and ammonia production process under a chemical looping gases	0.24 kgCO ₂ /kgMeOH
[101]	A biomass gasification-driven fuel cell integrated and an ignition engine	0.5 kgCO ₂ /kWh
[14]	A power and methanol cogeneration plant under coke oven gas and blast furnace gas integrated with a methanol synthesis reactor	1.563 kgCO ₂ /kgMeOH
[102]	A approach to the environmental and enviro-economic analysis of an SI engine at various loads using different fuel blends (methanol-gasoline and hydrogen-methanol-gasoline)	0.279 kgCO ₂ /kWh
[46]	A system based on a glycerol steam reforming cycle, two power generation cycles, a chilled water unit, a water desalination process, and a methanol synthesis process	0.1943 kgCO ₂ /kgMeOH
[103]	A heliostat field-driven solar-boosted energy system integrated with a gas turbine cycle to produce power, water, and methanol	2088 kgCO ₂ /h
[104]	A polygeneration system under three Transcritical CO ₂ , Kalina, and gas turbine power cycles, a water desalination unit, a chiller, and a methanol synthesis process	0.75 kgCO ₂ /kgMeOH
[27]	A power and LNG cogeneration plant under coke oven gas integrated with a LNG recovery process and an ORC system	0.406 kgCO ₂ /kWh
[105]	Sustainable bio-methanol generation under a landfill gas valorization approach	0.605–2.36 kgCO ₂ /kgMeOH
[77]	Different technologies for conversion of CO ₂ from industrial flue gas streams into methanol	0.131–3.11 kgCO ₂ /kWh
[106]	Sustainable catalytic hydrogenation of CO ₂ to methanol using Cu/ZnO/Al ₂ O ₃ catalyst	0.226 kgCO ₂ /kgMeOH
[107]	A systematic sludge-to-methanol process	3.21 kgCO ₂ /kgMeOH
[42]	Methanol production from captured CO ₂ utilizing reforming and hydrogenation processes	1.44 kgCO ₂ /kgMeOH
This article	A power, oxygen, and methanol production hybrid system under a coke oven gas-driven fuel reforming and combustion unit, a power generation unit (based on a Kalina cycle and an ammonia-based steam cycle), an alkaline electrolyzer, and a methanol synthesis process	0.0961 kgCO ₂ /kWh or 0.639 kgCO ₂ /kgMeOH

**Fig. 12.** Effect of hydrogen concentration rate in the input fuel on the thermodynamic efficiencies of the studied energy system.

and electrolyzers owing to higher hydrogen content in the input fuel, the overarching energy efficiency of the system suffers due to the lowered output rates of electricity, methanol, and thermal energy. Additionally, the system's exergy efficiency experiences a downturn, a consequence of the decreased exergy rates of the generated products. The overarching inference from this analysis is that elevating the hydrogen content in coke oven gas inversely affects the thermodynamic efficiencies of the energy conversion system. Consequently, it's imperative to meticulously calibrate the hydrogen production rate in the synthesis process during the design phase of the thermodynamic process to optimize the overall system efficiency.

The hydrogen to carbon dioxide ratio is a critical factor that influences the thermodynamic and environmental performance of an energy system. Fig. 13 demonstrates the impact of this ratio on the

thermodynamic efficiencies and CO₂ emission rate of the examined energy system. An increase in the hydrogen to carbon dioxide ratio implies a higher conversion ratio in the reactor of the methanol synthesis unit. A higher ratio allows for more carbon dioxide to be injected into the reactor, enhancing the hydrogenation of carbon dioxide reaction and thereby increasing methanol production. Since the power consumption of compressors, pumps, and the electrolyzer remains constant, the energy efficiency improves due to the increased production of methanol, a valuable output. Similarly, the enhanced exergy rate of the product leads to improved exergy efficiency. Fig. 13 shows that increasing the hydrogen to carbon dioxide ratio from 1 to 2.5 leads to an improvement in thermodynamic efficiencies by 152 % and 23.62 %, respectively. The increase in energy efficiency is more pronounced than the increase in exergy efficiency. This discrepancy arises because a

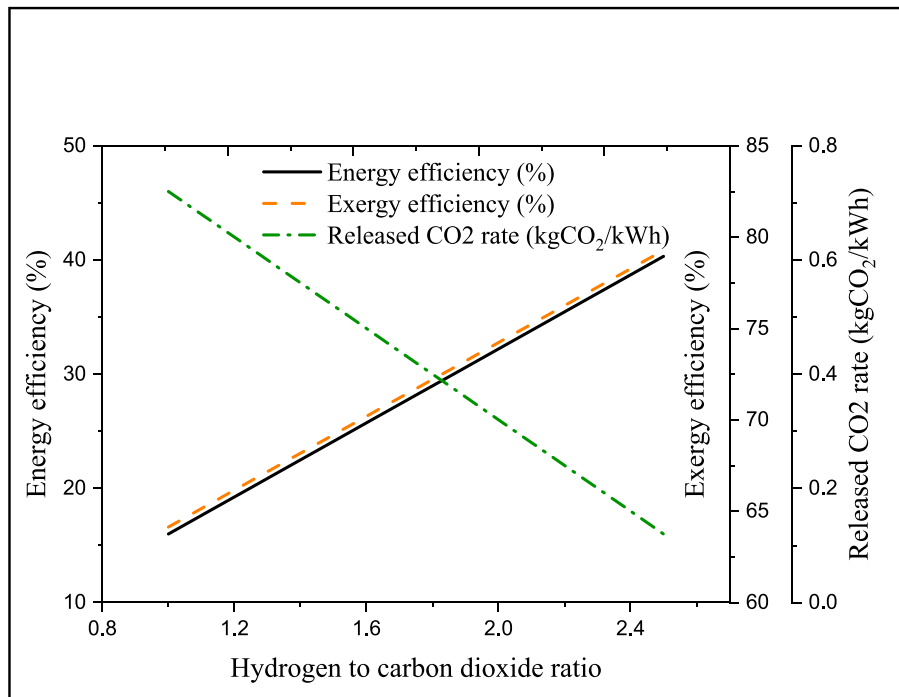


Fig. 13. Effect of hydrogen to carbon dioxide ratio on the thermodynamic efficiencies and released CO₂ rate of the studied energy system.

higher hydrogen to carbon dioxide ratio increases the thermal duty rate of the boiler, which in turn decreases the thermal exergy of the system. However, the overall exergy output remains higher than the input exergy, resulting in an improvement in exergy efficiency. Moreover, the figure illustrates that increased hydrogen to carbon dioxide ratio reduces CO₂ emissions. This reduction occurs as the rate of the chemical reaction inside the scrubber column increases, leading to a decrease in CO₂ release, which in turn mitigates the overall environmental impact of the energy system. An increase in the ratio from 1 to 2.5 results in an

83.3 % reduction in released CO₂. In conclusion, enhancing the hydrogen to carbon dioxide ratio is a vital strategy for improving both the thermodynamic and environmental performances of the studied system.

The inlet flow pressure to turbine 1, a component of the Kalina cycle, stands as a pivotal factor impacting the system's net electricity output and, by extension, its thermodynamic efficiencies. As illustrated in Fig. 14, alterations in this pressure exert a significant influence on both the thermodynamic efficiencies and the CO₂ emission rates of the energy

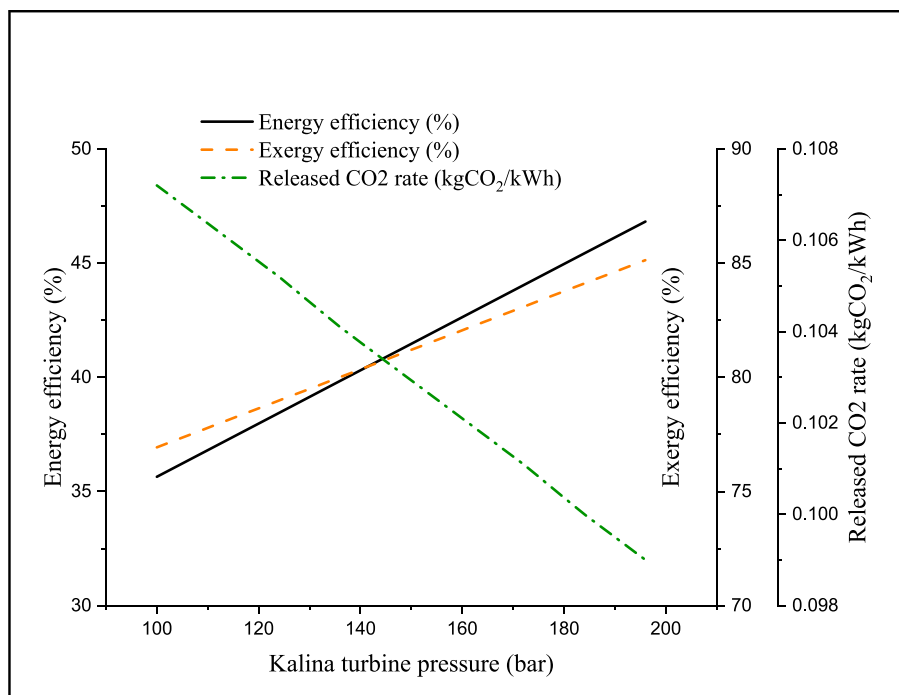


Fig. 14. Effect of pressure of the inlet flow to turbine 1 on the thermodynamic efficiencies and released CO₂ rate of the studied energy system.

system. Elevating the inlet flow pressure to turbine 1 bolsters its power generation capabilities, which, under a regime of constant system parameters, culminates in an augmented net electricity production. This enhancement in electricity generation inherently boosts the energy efficiency of the system, showcasing the critical role of inlet flow pressure in optimizing the system's performance metrics. Additionally, this design results in increased exergy output (with constant input exergy), improving exergy efficiency. Similarly, a higher pressure can diminish CO₂ emissions, as confirmed by Fig. 14, which shows that raising the inlet flow pressure to turbine 1 from 100 to 200 bar enhances thermodynamic efficiencies by 31.3 % and 10.72 %, respectively. Concurrently, CO₂ emissions decrease by 7.6 % owing to the rise in electricity production rate. Thus, elevating the inlet flow pressure to turbine 1 in the Kalina cycle emerges as a crucial factor for augmenting both thermodynamic and environmental performance of the investigated system.

5.5. Optimum design of energy system

Herein, this study also focuses on optimizing an energy conversion system to maximize exergy efficiency while minimizing the rate of CO₂ release. Utilizing a weighting coefficient approach, akin to the Pareto method, the study aims to identify optimal operational conditions [62]. The results, summarized in Table 12, indicate that optimal performance can be achieved under specific design conditions for independent input parameters. Under these optimal conditions, the energy system can potentially increase its exergy efficiency by about 3 % and reduce its CO₂ emission rate by approximately 15 %. To realize this optimized performance, several adjustments in the energy system's parameters are necessary. Firstly, the hydrogen concentration rate in the input fuel and the pressure of the input flow to turbine 1 should be decreased by 32.6 % and 14.6 bar, respectively. Additionally, the ratios of hydrogen to carbon dioxide and steam to methane, along with the current density of the electrolyzer, need to be reduced by 13.3 %, 17.3 %, and 120 A/m², respectively. However, the study suggests that a comprehensive estimation of the optimal cost for this energy system should be considered in future research endeavors, to further enhance the system's efficiency and environmental sustainability.

6. Conclusions

This paper meticulously examines the thermodynamic performance, ecological considerations, cost projections, and optimization approaches associated with a pioneering energy system. This system adeptly capitalizes on coke oven gas to facilitate the production of electricity, oxygen, and methanol, and is characterized by a quartet of integral components: a Fuel Reforming and Combustion Unit that processes coke oven gas, a Waste Heat Recovery Unit (WHRU), an apparatus dedicated to generating hydrogen gas via the electrolysis of water, and a setup designed for the synthesis of methanol. The WHRU is specially outfitted with two distinctive cycles - the Kalina cycle and an ammonia-based power generation cycle, which collectively bestow this energy conversion system with a unique architectural identity, thereby enriching the spectrum of contemporary scholarly discourse in this field. The system's

Table 12
Optimal design of the studied energy system.

Variable	Not optimized	Optimized
Inputs		
Hydrogen concentration rate, %	50	33.7
H ₂ to CO ₂ ratio	3	2.6
Steam-to-methane ratio	3	2.48
Turbine-1 inlet pressure, bar	200	185.4
AE current density, A/m ²	1500	1380
Outputs		
Exergy efficiency, %	85.13	87.72
Released CO ₂ rate, kgCO ₂ /kWh	0.0961	0.0818

operational outcomes are notably impressive, with a production output of 12.72 MW of electricity, 0.51 kg/s of oxygen, and 0.53 kg/s of methanol. Furthermore, it records substantial energy and exergy efficiencies, calculated to be 46.8 % and 85.13 % respectively, underscoring the system's adeptness in energy conversion and its potential for fostering sustainable resource management. The study's cost analysis shows that the production costs for electricity and methanol are 0.099 US\$/kWh and 0.56 US\$/kg, respectively, emphasizing the system's operational efficiency and potential for economic viability. These findings highlight the system's efficiency and economic feasibility, marking significant contributions to the field of energy conversion and sustainable resource utilization:

- (1) The water electrolysis process, pivotal for hydrogen production, accounts for a considerable portion of the plant's electricity consumption. Consequently, if the electricity required for this electrolysis could be sourced from renewable energy, it would not only foster the creation of green hydrogen but also substantially enhance the net electricity output of the plant. By integrating renewable energy sources into the electrolysis process, the plant's overall energy efficiency could be significantly improved, aligning with sustainability objectives and reducing reliance on non-renewable resources.
- (2) The Dispersed Exergy Rate (DER) for the entire hybrid energy system under study was quantified at 160.61 MW. Within this setup, the coke oven gas-reforming and combustion unit registers the highest exergy destruction, accounting for approximately 45.4 % of the total. This significant exergy destruction is predominantly attributed to the elevated DER values inherent in the reformer and combustor components. Together, these two units are responsible for more than 39 % of the total DER value of the energy system. The primary factor contributing to the high DER values is the occurrence of irreversible chemical reactions within the reformer and combustor, which inherently lead to increased exergy destruction. Addressing these inefficiencies could potentially result in enhanced overall system performance and exergy conservation.
- (3) The cost estimation findings reveal that the total initial capital investment and the total annual operational costs for the scrutinized energy system stand at approximately 19.92 million US\$ and 10.51 million US\$, respectively. Of all the components within the energy system, the electricity production unit demands the highest share of initial investment, accounting for over 40 % of the entire system's initial capital outlay. This substantial financial requirement is primarily due to the significant acquisition costs associated with the turbines, which form a crucial part of the electricity production infrastructure. Consequently, the high expenditure on turbines substantially influences the overall initial investment cost of the electricity production unit within the energy system.
- (4) The considerable investment cost for the hydrogen production unit within the energy system is predominantly attributed to the procurement of the electrolyzer, which constitutes about 99 % of the unit's total initial investment cost. Despite this substantial financial commitment, the hydrogen generated via this method is recognized as a product of a green process, adhering to environmental sustainability standards. Moreover, adopting this approach effectively addresses the challenges typically associated with the transportation and storage of hydrogen. By producing hydrogen on-site through electrolysis, the system circumvents the logistical and infrastructural complexities often linked with the external supply and handling of hydrogen, offering a more streamlined and sustainable operational model.
- (5) Introducing extra hydrogen into coke oven gas negatively impacts the thermodynamic efficiencies of the energy system under examination. Therefore, it is advisable to tailor the design of the

thermodynamic process to align with the hydrogen production rate inherent in the synthesis process, ensuring optimal efficiency. Additionally, adjusting the hydrogen to carbon dioxide ratio presents a significant opportunity to enhance both the thermodynamic and environmental performances of the system. By fine-tuning this ratio, the system can potentially achieve a more balanced and efficient operation, leading to improved energy output and a reduced environmental footprint, making it a crucial aspect in the design and optimization of the energy system.

- (6) In optimal design conditions of the energy system, the exergy productivity can be about 3 % higher. At the same time, the released CO₂ rate can be around 15 % lower.

The power requirements of the hybrid system under study are entirely self-sustained, eliminating the need for external electricity from the grid and ensuring the system's self-sufficiency in terms of power supply. This energy system demonstrates superior capabilities in terms of thermodynamic performance, annual costs, product cost efficiency, and reduced CO₂ emissions, making it highly competitive compared to other technologies in the field. However, it is advisable to conduct life cycle and techno-economic analyses, as well as experimental investigations on a smaller scale, to uncover any practical operational limitations. Furthermore, the integration of high-temperature fuel cells and renewable energy sources like wind power and solar photovoltaic arrays, could further enhance the system's appeal. Additionally, assessing the social impacts and potential for job creation associated with the deployment of this energy system could provide valuable insights into its broader societal benefits.

CRedit authorship contribution statement

Amir Ghasemi: Writing – review & editing, Software, Formal analysis. **Hima Nikafshan Rad:** Writing – original draft, Methodology, Data curation. **Nima Izadyar:** Resources, Software, Writing – review & editing. **Mohammad Marefati:** Writing – original draft, Project administration, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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