Thermodynamic modeling and optimization of a combined biogas steam reforming system and organic Rankine cycle for coproduction of power and hydrogen

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1. Introduction

Nowadays, most countries throughout the world encourage renewable and clean energies utilizations in order to decrease their dependency over fossil fuels. This is mainly due to the fossil fuels shortages and their exhaust adverse effects on the environment. It is predicted that the energy production throughout the world using renewable energy resources will be tripled from 2010 to 2035 which will constitute 31% of all energies [1]. To this end, biogas is used as the most practical renewable energy source in place of fossil fuels for power and hydrogen productions which has a main role in minimization of global warming [2]. Biogas can be achieved by biomass anaerobic fermentation and decomposition which itself is composed of different organic materials, namely, 60–70% methane, 30–40% carbon dioxide, and other negligible gases such as hydrogen, nitrogen, oxygen, mono oxide, and hydrogen sulfide [3]. Therefore, due to the high contribution of carbon dioxide and methane (greenhouse gases) in biogas mixture, one can effectively utilize them in various reforming processes to produce hydrogen [4,5].

In recent years, hydrogen as a clean energy has been considered for energy production which is compatible with environment and widely used in chemical and power plant industries [6,7]. In addition, hydrogen can be effectively converted to electricity by fuel cell systems with negligible greenhouse effects, or vice versa [8,9]. With this regard, Taner [10] investigated on the performance...
of a proton exchange membrane (PEM) fuel cell in terms of pressure and voltage parameters to improve its efficiency, experimentally. He found that if the voltage is controlled by the PEM fuel cell, the wastewater system could be managed easily. Nowadays, 50% of hydrogen is predominantly produced by natural gas steam reforming processes, while 30% produced by oil refineries, 16% produced by coal gasification process, and only 4% is produced by water electrolysis [11]. But, due to the fossil fuels limitations as well as climate changes caused by carbon dioxide leakage and other contaminants, utilization of renewable and clean energies is highlighted. Among all various reforming processes like partial oxidation, auto-thermal reforming, and steam reforming, hydrogen production rate of steam reforming is relatively high [12]. One of the main characteristics of biogas steam reforming systems (70% natural gas) is that they are strongly endothermic and occur at low pressures (< 1 atm) and high temperatures (800–1200 K) which require an external heat source, and hence the system's products temperature is very high [13]. As a result, to recover waste heat of products and enhance the performance of systems (for coproduction of power and hydrogen), integration of this system with cycles that require low-temperature heat source for power production can be taken into account. One of the valuable studies in recent years on the steam reforming catalyst is the experimental investigation of Yang [14] which is carried out on the deactivation and regeneration of this process. The effectiveness and the deactivating behavior of a Ni-based catalyst were studies by this scholar in the presence of methane with different levels of H2S during the steam reforming to find the influence of the sulfur poisoning and physical properties of the samples. They found that the deactivating behavior of the catalyst depends on the operating temperature and the H2S concentration.

In recent studies, organic Rankine cycle (ORC) as an interesting cycle with a high performance as well as a mid-temperature heat source user (150–300 °C) is utilized as a bottoming cycle of different systems such as water electrolyzer, gas turbines, geothermal energy, etc. for co and trigenerations purposes. Performance operation of an ORC is similar to the steam cycle that uses organic working fluids instead of steam. An appropriate working fluid selection for the ORC can improve the performance of this system from thermodynamics and environment viewpoints. This is mainly due to the working fluid thermophysical, safety, and environmental properties which are further discussed in Refs. [15–17].

A comprehensive energy and exergy analysis of the biogas steam reforming system can be a promising way for performance evaluation of power and hydrogen coproduction systems. In accordance with the first-law of thermodynamics, energy analysis of a system calculates the amount of energy (in terms of work and heat) to initiate the predictable thermodynamic processes which is not able to determine the feasibility of these processes. However, exergy analysis as a profitable tool can investigate the quality of available energy and determine the main irreversibility of a system including chemical reactions, mixing process, and heat transfer caused by specific amount of temperature difference [18]. In addition, exergy destruction of different components can be specified leading to provide more suitable thermodynamic condition in order to decrease the system's losses, use energy sources more efficiently, and to enhance the performance of system thereafter [18,19]. In an applicable study, Hamad et al. [20] used biogas as a potential source of renewable energy for hydrogen production from a combined heat, hydrogen, and power (CHHP) system to address the problem of fossil fuel usage at the Missouri University of Science and Technology campus. They showed that their proposed system can reduce the greenhouse gas emissions and used produced hydrogen for different applications of transportations, backup power productions, portable power usages, and other mobility applications. As another application of biogas source, Colmenar-Santos [21] used energy recovery of biogas system from wastewater treatment plant in a Stirling engine from thermodynamics viewpoint. They demonstrated that this treatment leads to sustainable waste management and energy savings in the plant.

In recent years, many investigations in the field of power and hydrogen coproduction systems are conducted. For example, Balta et al. [22] presented energy and exergy analysis of a high temperature system electrolysis (HTSE) for hydrogen production integrating a solar tower, a Brayton cycle, a Rankine cycle, and an organic Rankine cycle. They reported overall energy and exergy efficiencies of 24.7% and 22.36% for power generation section and 87% and 88% for hydrogen production section, respectively. They also found that the hydrogen production rate of the integrated system can be 0.057 kg/s, consuming 1.98 kWh electricity at 230 °C. In another study, Ratlamwala et al. [23] integrated a heliostat field, a steam cycle, an ORC, and an electrolyzer for hydrogen production. They optimized the proposed integrated system based on the first and second laws of thermodynamics, showing that the maximum energy and exergy efficiencies and the rate of hydrogen production can be achieved up to 18.74%, 39.55%, and 1571 L/s, respectively. In addition, parametric study demonstrated that the hydrogen production rate can be increased from 0.606 kg/s to 0.063 kg/s with the increase of heliostat field area from 8000 m² to 50000 m². Alizah-rani et al. [24] proposed an integrated system consisting of a supercritical carbon dioxide Rankine cycle, an ORC, an electrolyzer, and a heat recovery system for power and hydrogen production, medium to high temperature heat source utilization, performance enhancement, and greenhouse gas reduction purposes. Their proposed system could produce 180 kg/h hydrogen for the geothermal mass flow rate of 40 kg/h and temperature of 473 K. Ozcan and Dincer [25] performed thermodynamic analysis of an internal reforming solid oxide fuel cell (IR-SOFC) system with various gasifier products and fuels. They integrated IR-SOFC with an ORC, an absorption refrigeration cycle (ARC) and a water heating unit to produce power, hot water, and cooling output. This integration enhanced energy and exergy efficiencies up to 78% and 50%, respectively. Herdem et al. [26] combined coal gasification and alkaline water electrolyzer system to produce hydrogen with low amount of greenhouse emissivity. The performance of the proposed system was analyzed based on the first- and second-laws of thermodynamics, showing that the overall energy and exergy efficiencies of 58% and 55% can be attained. Ratlamwala and Dincer [27] compared performance of two solar-based heliostat field systems integrated with Cu-Cl cycle and Kalina cycle (case 1) and Kalina cycle and photocatalytic reactor (case 2) for hydrogen production. Exergy assessment revealed that the overall efficiency can be increased from 45.6% to 47.79% for the first case and from 54.94% to 56.41% for the second case, respectively, as solar light intensity increases. Bicer and Dincer [28] developed a hybrid solar-geothermal multigeneration system for hydrogen, cooling, power, and heating productions. They analyzed the performance of the proposed system using energy and exergy concepts and obtained overall energy and exergy efficiencies of 10.8% and 46.3%, respectively for geothermal water temperature of 210 °C. Yilmaz et al. [29] presented a thorough review on hydrogen production methods based on solar energy utilization. They concluded that the solar-based hydrogen production systems can play a significant role in greenhouse gas emissions reduction which offers more sustainability. Rabbani and Dincer [30] presented energy and exergy analysis of a steam reformer coupled with a combined power plant to produce hydrogen from steam and hydrocarbon fuel. They used glycerol as a fuel in steam reformer and presented a comprehensive parametric study, showing that increasing the steam to glycerol ratio increases the hydrogen production, while decreases the
overall efficiency of the system. Cipiti et al. [31] designed a biogas steam reforming reactor in temperature range of 700–900 °C, both theoretically and experimentally. The results of this group demonstrated that increasing temperature and steam to carbon molar ratio in the range of 1–5 increases hydrogen production, where hydrogen molar ratio is obtained 0.45 at temperature of 900 °C and steam to carbon ratio of 3. Hajjaji et al. [32] comprehensively investigated life cycle assessment (LCA) of a hydrogen production system via biogas reforming, showing that the total greenhouse gas emissions of the system can be estimated by 5.59 kg CO2-eq per kg of hydrogen. They concluded that the LCA of the biogas-to-hydrogen system reveals very promising advantages. They also found that the maximum overall efficiency and hydrogen production rate can be achieved at optimum temperature of 800 °C and steam to carbon molar ratio of 3. Ahmed et al. [33] investigated the effect of temperature (590–685) °C, steam to carbon molar ratio (1.28–3.86), and carbon dioxide to methane molar ratio (0.5–1.5) on hydrogen production rate, methane and carbon dioxide conversion ratio, and other equilibrium compounds of biogas steam reforming process. The results demonstrated that the highest methane conversion observed 0.99 at carbon dioxide to methane ratio of 0.98, steam to carbon molar ratio of 3.87, steam to methane molar ratio of 7.64, oxygen to carbon atomic ratio of 4.85, and gas hourly space velocity of 19600 hr⁻¹. Cohce et al. [34] presented a novel biomass-based hydrogen production plant consisting of a biomass gasification, a steam methane reforming, and a shift reaction. Energy and exergy analysis conducted by this group demonstrated that the overall energy and exergy efficiencies of 19% and 22% can be achieved, respectively.

In the previous studies [28,32,33], no comprehensive investigations on effect of different thermodynamic parameters in biogas steam reforming system for hydrogen production rate, energy efficiency, exergy efficiency, and net output power are carried out. To bridge this gap, a comprehensive energy and exergy analysis of a biogas steam reforming system combined with an ORC for power and hydrogen coproduction is performed in this study. Some main objectives of present study are as follows:

- To present a novel form of cogeneration system for power and hydrogen production by integrating a BSR system and an ORC.
- To present a comprehensive thermodynamic modeling of the proposed system based on the first and second laws of thermodynamics.
- To optimize the proposed system by considering energy and exergy efficiencies as objective functions, using GA.

Fig. 1. Schematic diagram of the proposed combined BSR-ORC system.
2. System description

Fig. 1 illustrates schematic of the proposed combined biogas steam reforming (BSR) system and ORC with an IHE. The main purpose of this system is coproduction of power and hydrogen by an appropriate integration of these two systems. In this system, biogas mixture (state 1) enters the system process from right-hand side, while steam (state 3) enters the system process from left-hand side. The existed biogas in storage tank (state 1) is preheated by exhaust gas of steam reforming in methane preheater (state 9), while steam at water tank outlet (state 3) is preheated by the exhaust gas of steam in water preheater (state 10). The preheated streams are mixed together at mixer and then enter the recuperator (state 5). Then, this stream is heated by high temperature of reforming reaction (state 7) in order to be ready for chemical reforming process in reactor. The reaction process inside the reactor can be modeled as below.

In general, biogas steam reforming process in reactor is composed of steam methane reforming (SMR), carbon dioxide methane reforming (CMR), water gas shift (WGS), and methane decomposition (MD) reactions:

**SMR:** \( \text{CH}_4 + \text{H}_2\text{O}(g) = 3\text{H}_2 + \text{CO} \quad \Delta H_{298} = 206.1 \text{ kJ/mol} \) \( (1) \)

**CMR:** \( \text{CH}_4 + \text{CO}_2(g) = 2\text{H}_2 + 2\text{CO} \quad \Delta H_{298} = 247.3 \text{ kJ/mol} \) \( (2) \)

**WGS Reaction:** \( \text{CO} + \text{H}_2\text{O}(g) = \text{H}_2 + \text{CO}_2 \quad \Delta H_{298} = -41.2 \text{ kJ/mol} \) \( (3) \)

**MD Reaction:** \( \text{CH}_4 = 2\text{H}_2 + \text{C} \quad \Delta H_{298} = 74.8 \text{ kJ/mol} \) \( (4) \)

Both SMR and CMR are highly endothermic and are favorable for low pressures (1 atm) and high temperatures (800–1200) K. Therefore, an appropriate heat source for these reactions is very important [13]. WGS reaction is also endothermic and is appropriate for low-temperature heat (500–600) K [35]. The main constraint of CMR is possibility of carbon formation forming (in methane decomposition reaction), which needs a high temperature heat source [36]. In SMR and CMR, one can increase energy efficiency of system and hydrogen production rate and reduce methane forming possibility by adding steam to methane at high temperature. Therefore, optimization of steam to carbon molar ratio and reaction temperature is pronounced to increase hydrogen production rate and reduce carbon forming [5,37].

After considering the above-mentioned reactions, the considered input heat from the heat source is converted to chemical energy in reactor. Then, the exhaust gases flow of reaction in reactor including chemical compounds of hydrogen, carbon monoxide, carbon dioxide, methane, and steam are used for preheating of biogas mixture and system’s inlet steam. The outlet temperature of exhaust gas, which owns high hydrogen molar fraction in comparison with other compounds, is reduced by rejecting its heating capacity to ORC (state 11). Finally, for required hydrogen production and using purification process, hydrogen can be split from synthesis gas (state 13) and stored in hydrogen storage tank for electricity or food productions (state 12).

Due to high temperature of reaction products (state 10) for recovering waste heat of biogas steam reforming system and increasing its performance, ORC with an IHE is used. In ORC, outlet flow of pump first enters the IHE to gain temperature (state 15) and then enters the evaporator to absorb required heating from exhausts gas of biogas steam reforming system (state 16). The saturated vapor then fed to the turbine (state 17) and expanded through it by producing turbine output power. The outlet of turbine then enters IHE to reduce its temperature for regeneration purposes (state 18), and then enters the condenser (state 19) to be condensed to the saturated liquid by rejecting its heating to cold water. The saturated liquid then enters pump, completing ORC operating process.

3. Thermodynamic modeling

In this study, equilibrium compounds in biogas steam reforming system is calculated using Gibbs free energy minimization method in which hydrogen production of steam reforming reactions due to its high molar ratio is paid attention. After that, mass, energy and exergy balance equations for each component and whole system are presented. In addition, the effect of different key parameters on the hydrogen production rate, net output power, energy efficiency, and exergy efficiency of the integrated BSR-ORC system is presented and discussed in detail. For this purposes, EES (Engineering Equation Solver) is used as one of the most robust thermodynamic software.

3.1. Gibbs free energy minimization

Conventionally, Gibbs free energy is used at equilibrium state to calculate molar ratio of chemical compounds in systems that chemical reactions happen [32]. This is mainly because that the Gibbs free energy is reached to its minimum value at chemical equilibrium state. The overall Gibbs free energy of a system at specific temperature and pressure can be expressed as [38]:

\[
G = \sum_{i=1}^{NC} n_i \cdot \mu_i \tag{5}
\]

where, \( n_i \) is the number of equilibrium moles for species \( i \) and \( \mu_i \) is the chemical potential which can be expressed as:

\[
\mu_i = \mu^\circ_i + R_{\text{g}} T \ln \left( \frac{f_i}{f^\circ_i} \right) \tag{6}
\]

where, \( \mu^\circ_i \) is the chemical potential of component \( i \) at reference temperature and pressure, \( f_i \) is the fugacity of the \( i \)th pure component in the reference state and \( f^\circ_i \) is the fugacity of component \( i \) in the mixture. Chemical potential of component \( i \) equals to molar Gibbs free energy which can be expressed as (symbol 0 stands for standard state):

\[
\mu^\circ_i = \frac{f_i^0}{T} = \frac{f_i^0}{T} - TS_i \tag{7}
\]

Fugacity for pure component of \( i \) in the mixture can be obtained as:
\[ f_i = \phi_i \cdot y_i \cdot P \tag{8} \]

where, \( y_i \) is the molar fraction of component \( i \) in equilibrium and \( \phi_i \) is the fugacity coefficient of component \( i \) which is very close to one at high temperatures and low pressures. Assuming \( \phi_i = 1 \) and substituting Eqs. (6)–(8) in Eq. (5), Gibbs free energy can be re-written as:

\[
G = \sum_{i=1}^{NC} n_i \left( \mu_i + R_{uni} T \ln \left( \frac{y_i P}{\nu_i P} \right) \right) \tag{9}
\]

In the case that a solid phase such as carbon will be presented in chemical products at chemical equilibrium state, since solid materials do not have vapor pressure, therefore the chemical potential of carbon can be expressed as:

\[
\mu_c = \mu_{c}^{E} = \frac{\mu_c}{R_c} \tag{10}
\]

Substituting Eq. (10) in Eq. (9), the total Gibbs free energy including carbon can be expressed as:

\[
G = \sum_{i=1}^{NC} n_i \left( \mu_i + R_{uni} T \ln \left( \frac{y_i P}{\nu_i P} \right) \right) + n_c \mu_{c}^{E} \tag{11}
\]

where, \( n_c \) presents the equilibrium moles of carbon and \( \mu_{c}^{E} \) is the reference chemical potential of carbon.

Minimization of Gibbs free energy is considered as a common method to compute the equilibrium compositions of the reaction system using Lagrange multiplier method [39]. The main advantage of this method is that it is not required to know reactions at equilibrium state. Thus, it is sufficient to know material compositions at equilibrium state. It has good convergence rate, has no limitation in number of equilibrium reactions, and used for low-temperature (below 700 K) [40]. In addition, since Gibbs free energy reached to its minimum value at equilibrium state, therefore minimum Gibbs free energy at equilibrium state can be calculated by Lagrange multiplier method as [39]:

\[
\sum_{i=1}^{NC-1} n_i \left( \mu_i + R_{uni} T \ln \left( \frac{y_i P}{\nu_i P} \right) \right) + \sum_{k} \lambda_k a_{ik} + n_c \mu_{c}^{E} = 0 \tag{12}
\]

here, \( \lambda_k \) is Lagrange coefficient.

In the Gibbs free energy minimization, two following restrictions are required to be satisfied [38]:

1) Non-negative of moles number:
\[
n_i \geq 0 \quad i = 1, \ldots, NC \tag{13}
\]

where, NC is the number of components.

2) Mass balance of each atom must satisfy the restriction:
\[
\sum_{i} n_i a_{ik} = A_k \quad k = 1, \ldots, NE \tag{14}
\]

where, NE is the number of element.

3.2. Energy analysis

Assuming a steady state condition for each control volume of Fig. 1, mass and energy balance equations for each component of the system can be expressed as:

Mass balance equation:
\[
\sum_{i} \dot{m}_{in} = \sum_{j} \dot{m}_{out} \tag{15}
\]

Energy balance equation:
\[
\sum_{i} \dot{E}_{in} = \sum_{j} \dot{E}_{out} \tag{16}
\]

where, \( \dot{E}_{in} \) and \( \dot{E}_{out} \) are the energy values at inlet and outlet of control volume, respectively.

3.2.1. Biogas steam reforming system

To determine methane and carbon dioxide conversions and hydrogen production rate in each mole of methane, Eqs. (17)–(19) are employed [41]:

Steam to carbon molar ratio at beginning of reaction:
\[
S_c = \left( \frac{n_{H_2} O}{n_{CH_4}} \right)_{in} \tag{17}
\]

Carbon dioxide to methane molar ratio in biogas mixture:
\[
C_m = \left( \frac{n_{CO_2}}{n_{H_2} O} \right)_{in} \tag{18}
\]

Methane and carbon dioxide conversions in each mole of methane:
\[
CH_4 \text{ conversion} = \left( \frac{(n_{CH_4})_{in} - (n_{CH_4})_{out}}{(n_{CH_4})_{in}} \right) \times 100 \tag{19}
\]
\[
CO_2 \text{ conversion} = \left( \frac{(n_{CO_2})_{in} - (n_{CO_2})_{out}}{(n_{CO_2})_{in}} \right) \times 100 \tag{20}
\]

Hydrogen production per methane mole:
\[
\text{Produced hydrogen} = \left( \frac{(n_{H_2})_{out}}{(n_{CH_4})_{in}} \right) \tag{21}
\]

where, \((n_{H_2})_{out}\) is the hydrogen mole at the outlet of reforming reaction and \((n_{CH_4})_{in}\) is the methane mole at inlet of biogas mixture.

Energy efficiency of biogas steam reforming (BSR) system for hydrogen production can be obtained by:
\[
\eta_{en, BSR} = \frac{m_{H_2} \cdot LHV_{H_2}}{m_{Biogas} \cdot LHV_{Biogas} + Q_{Reac}} \tag{22}
\]

where, \( m_{H_2} \) is hydrogen production rate, \( LHV_{H_2} \) is hydrogen lower heating value, \( m_{Biogas} \) is biogas mixture primary mass flow rate at state 1 (mixture of carbon dioxide and methane), \( LHV_{Biogas} \) is biogas lower heating value, and \( Q_{Reac} \) is the required heating capacity for reaction in reactor.

3.2.2. ORC with an IHE

Net output power of ORC can be obtained by subtracting pump consumed power from turbine output power. In this case, ORC net output power can be expressed as:
\[
W_{net, ORC} = W_{Tur} - W_{Pum} \tag{23}
\]

The energy efficiency of ORC is defined as ORC net output power to input heat received from the evaporator during recovery process:
\[ \eta_{en,\text{ORC}} = \frac{W_{\text{net,ORC}}}{Q_{\text{net}}} \]  \hspace{1cm} (24)  

3.2.3. Combined BSR-ORC system

The overall net output power of the combined BSR-ORC system can be expressed as:

\[ W_{\text{net}} = W_{\text{net,ORC}} \] \hspace{1cm} (25)

In addition, energy efficiency of the combined BSR-ORC system for power and hydrogen coproduction can be given as follows:

\[ \eta_{en} = \frac{\dot{m}_H_2 \cdot \text{LHV}_{H_2} + W_{\text{net}}}{\dot{m}_{\text{Biogas}} \cdot \text{LHV}_{\text{Biogas}} + Q_{\text{Reac}}} \] \hspace{1cm} (26)

3.3. Exergy analysis

Exergy of stream is defined as the maximum attainable theoretical work when this stream is in close heat exchange with its environment to reach an equilibrium state at environment temperature and pressure \[42\]. Neglecting potential and kinetic energies of stream, physical and chemical exergies of each stream can be obtained respectively as:

\[ E^{\text{ph}} = \dot{m}(h - h_0 - T_0(s - s_0)) \] \hspace{1cm} (27)

\[ E^{\text{ch}} = \dot{m} \left[ \sum_i x_i (e^{\text{ch}}_i - RT_0 \ln x_i) \right] \] \hspace{1cm} (28)

where, 0 refers to the environment condition. Also, \( x_i \) is the substance molar ratio in mixture and \( e^{\text{ch}}_i \) is the standard chemical exergy for each compound that is available in Ref. \[43\].

The overall exergy rate can be expressed as \[44\]:

\[ \dot{E} = \dot{E}^{\text{ph}} + \dot{E}^{\text{ch}} \] \hspace{1cm} (29)

Employing exergy balance equation for each component of the system, exergy destruction rate can be obtained \[44\]:

\[ \dot{E}_D = \dot{E}_F - \dot{E}_P \] \hspace{1cm} (30)

where, \( \dot{E}_F \), \( \dot{E}_P \), and \( \dot{E}_D \) are exergy rate of fuel, product and destruction for each component of system, respectively.

Exergy efficiency for each component of a system can be expressed in terms of product to fuel exergy rates ratio \[44-46\]:

\[ \eta_{ex} = \frac{\dot{E}_P}{\dot{E}_F} \] \hspace{1cm} (31)

In addition, exergy due to heat transfer in reactor can be written as:

\[ \dot{E}_{\text{Q,Reac}} = Q_{\text{Reac}} \left( 1 - \frac{T_0}{T_{\text{HS}}} \right) \] \hspace{1cm} (32)

where, \( T_{\text{HS}} \) is heat source temperature.

3.3.1. Biogas steam reforming system

The exergy efficiency of the biogas steam reforming system can be expressed in the follows form:

\[ \eta_{ex,\text{BSR}} = \frac{\dot{E}_{H_2}}{\dot{E}_{\text{Biogas}} + \dot{E}_{\text{Q,Reac}}} \] \hspace{1cm} (33)

3.3.2. ORC with an IHE

The exergy efficiency of the organic Rankine cycle (ORC) can be calculated as follows:

\[ \eta_{ex,\text{ORC}} = \frac{W_{\text{net,ORC}}}{E_{10} - E_{11}} \] \hspace{1cm} (34)

3.3.3. Combined BSR-ORC system

The overall exergy efficiency of the proposed combined BSR-ORC system can be written as:

\[ \eta_{ex} = \frac{W_{\text{net}} + \dot{E}_{H_2}}{E_{\text{Biogas}} + E_{Q,\text{Reac}}} \] \hspace{1cm} (35)

Table 1 listed some required energy and exergy balance equations for each component of the proposed combined BSR-ORC system.

4. Multi-objective optimization

In thermal system design, optimization is carried out to maximize the thermodynamic efficiency and the exergy efficiency based on the thermodynamics viewpoint. This can be performed by several methods, depending on objective demands. Several applicable optimization methods are available in the EES software such as variable metric method, direct algorithm, conjugate directions method, genetic algorithm (GA), etc. In this study, GA method is used which is proven to be the most applicable method in comparison with other methods \[44\]. The assumed responsible parameters for GA optimization is given in Table 2 which are selected based on our previous study \[44\].

Two output design parameters, namely, the energy and exergy efficiencies are considered as objective functions, while reactor temperature \( T_{Reac} \), reaction pressure \( P_{Reac} \), steam to carbon dioxide to methane molar ratio \( S_c \), carbon dioxide to methane molar ratio \( C_m \), pump pressure ratio \( PPR \) and pinch point temperature difference of IHE \( \Delta T_{PP,IHE} \) are specified as the decision variables. Obviously, the main purpose of this optimization is the maximization of the energy and exergy efficiencies which is considered here by multi-objective optimization method. The appropriate range of the constrained decision variables for optimization is listed in Table 3.

For the multi-objective optimization, the Pareto approach is not the only appropriate method to be considered. One alternative method is to weight each function separately and add them all together \[44\]. In this case, different optimal solution of the Pareto front can be obtained by altering these implemented weight coefficients. Multi-objective function (MOF) is defined by weighting each function and summing them all together in this function. After all, the main purpose is to maximize the proposed function.

For the proposed combined BSR-ORC system, the multi-objective function (MOF) can be defined as follows:

\[ \text{Max}(\text{MOF}) = w_1 \times \eta_{en} + w_2 \times \eta_{ex}, \hspace{0.5cm} 0 \leq w_1, w_2 \leq 1 \] \hspace{1cm} (36)

where, \( w_1 \) and \( w_2 \) are the weight coefficients for the energy efficiency and exergy efficiency of the combined BSR-ORC system, respectively.
5. Results and discussions

5.1. Thermodynamic assumptions and input parameters

Biogas mixture compound at inlet of system (at environment temperature of 25°C) made up of 67% methane and 33% carbon dioxide. Steam with molar ratio of 2 per each methane mole ($S_t = 2$) enters the system at environment temperature. Some input parameters for thermodynamic simulation of the proposed combined BSR-ORC system are given in Table 4.

In addition, some assumptions for exergy analysis of the proposed system are taken into account which are:

- All components of system operate at steady state condition.
- Heat losses and pressure drops at all heat exchangers of the integrated system are neglected through thermodynamic modeling.
- Kinetic and potential energies are neglected throughout the simulation.
- Due to high temperature of reactor, carbon forming at biogas steam reforming process is neglected.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Reference pressure, $P_0$(bar)</td>
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<td>Biogas temperature, $T_{biogas}$(K)</td>
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<td>Biogas pressure, $P_{biogas}$(bar)</td>
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<td>Heat source temperature, $T_{h0}$(K)</td>
<td>1073.15</td>
</tr>
<tr>
<td>Pump pressure ratio, $P_{pr}$</td>
<td>5</td>
</tr>
<tr>
<td>Pinch point temperature difference of IHE, $\Delta T_{IHE}$(K)</td>
<td>4</td>
</tr>
<tr>
<td>Cold water temperature difference in condenser, $\Delta T_{cond}$(K)</td>
<td>10</td>
</tr>
<tr>
<td>Pump isentropic efficiency $\eta_{is}(%)$</td>
<td>85</td>
</tr>
<tr>
<td>Turbine isentropic efficiency $\eta_{i}(%)$</td>
<td>85</td>
</tr>
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</table>
Table 5
Model validation of methane steam reforming cycle between present work and Refs. [33,48].

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Parameter</th>
<th>Present work</th>
<th>Literature Relative error Ref. [33] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSR system</td>
<td>CH₄ conversion (%)</td>
<td>91.8</td>
<td>91.2 0.65</td>
</tr>
<tr>
<td></td>
<td>CO₂ conversion (%)</td>
<td>-5.47</td>
<td>-5.41 1.1</td>
</tr>
<tr>
<td></td>
<td>Product hydrogen</td>
<td>2.76</td>
<td>2.79 1.07</td>
</tr>
<tr>
<td>ORC</td>
<td>Working fluid</td>
<td>R113</td>
<td>R113 -</td>
</tr>
<tr>
<td></td>
<td>Evaporator load Qₑᵥₑ (kW)</td>
<td>252</td>
<td>252 0</td>
</tr>
<tr>
<td></td>
<td>Condenser load Qₑₜₜ (kW)</td>
<td>199.2</td>
<td>196 1.5</td>
</tr>
<tr>
<td></td>
<td>Pump power Wₑₑₑₑ (kW)</td>
<td>2.25</td>
<td>2.2 2.27</td>
</tr>
<tr>
<td></td>
<td>IHE load Qₑₑₑₑ (kW)</td>
<td>31.64</td>
<td>30.5 3.73</td>
</tr>
<tr>
<td></td>
<td>Turbine power Wₑₑₑₑ (kW)</td>
<td>55.79</td>
<td>56.5 1.25</td>
</tr>
<tr>
<td></td>
<td>Net produced power</td>
<td>53.54</td>
<td>54.3 1.4</td>
</tr>
<tr>
<td></td>
<td>Wₑₑₑₑ (kW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mass flow rate (kg/s)</td>
<td>1.164</td>
<td>1.15 1.2</td>
</tr>
<tr>
<td></td>
<td>Energy efficiency ηₑₑₑₑ (%)</td>
<td>21.2</td>
<td>21.5 1.39</td>
</tr>
<tr>
<td></td>
<td>Exergy efficiency ηₑₑₑₑ (%)</td>
<td>33.32</td>
<td>33.24 0.24</td>
</tr>
</tbody>
</table>

Table 6
Model validation of methane steam reforming cycle between present work (A) and Ref. [47] (B).

<table>
<thead>
<tr>
<th>Points</th>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
<th>Enthalpy (kJ/kg)</th>
<th>Exergy (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A)</td>
<td>(B)</td>
<td>(A)</td>
<td>(B)</td>
</tr>
<tr>
<td>1</td>
<td>298.15</td>
<td>298.15</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>2</td>
<td>367.05</td>
<td>367.05</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>3</td>
<td>298.15</td>
<td>298.15</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>4</td>
<td>437.55</td>
<td>437.55</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>5</td>
<td>412.95</td>
<td>418.75</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>6</td>
<td>922.85</td>
<td>922.85</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>7</td>
<td>971.55</td>
<td>967.15</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>8</td>
<td>442.65</td>
<td>418.75</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>9</td>
<td>378.35</td>
<td>372.05</td>
<td>6.895</td>
<td>6.895</td>
</tr>
<tr>
<td>10</td>
<td>368.85</td>
<td>369.95</td>
<td>6.895</td>
<td>6.895</td>
</tr>
</tbody>
</table>

- The outlet flow stream of evaporator, condenser and preheaters are saturated.

5.2. Model verification

To verify the accuracy of the present study, simulations are conducted to each sub-system and the results are compared with literature [33,48]. Comparison of calculated results for biogas steam reforming system with those of Ahmed et al. [33] and ORC with those of Safarian and Aramoun [48] demonstrated that the present theoretical work is in a good agreement with literature (Table 5).

In addition, since the main contribution of the proposed combined BSR-ORC system stems from the BSR system, therefore another benchmark test case is selected (Ref. [47]). With this regard, thermodynamic properties including temperature, pressure, enthalpy, and exergy flow rate at each state of methane steam reforming (MSR) system is calculated and compared with this literature (Table 6). Moreover, fluid stream composition for MSR system is also computed and compared with this reference and the results are reported in Table 7. Under the same conditions, it can be said that the developed mathematical procedure for the selected test cases is in quite good agreement with literature.

5.3. Working fluid selection for ORC

Even though some class of working fluids has favorable performance and/or environmental aspects, but none provides a perfect solution. The main problems with natural working fluids include flammability, toxicity, high pressure, or in some cases, a lower efficiency. A refrigerant must satisfy some basic requirements related to safety, environmental properties, chemical stability, thermodynamic properties, and so on. There is no set of optimum characteristics, and hence a tradeoff must be considered.

An earlier utilization of the chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) had resulted in phasing out these group working fluids utilization under Montreal Protocol due to their adverse environmental impacts related to ozone depletion. Properties of CFCs and HCFCs make them a main contributor to ozone depletion, since they contain chlorine. They are relatively inexpensive chemicals and have significant atmospheric life-times [49]. Meanwhile, isobutane (R600) introduced in Europe in 1992 and now accounts for more than one-third of global production [49].

In this paper, four working fluids, i.e., R113, R123, R245fa and R600 are examined and suggested based on their thermophysical, safety, and environmental properties as well as energy and exergy efficiencies. Table 8 listed some useful thermophysical, safety, and environmental data for suggested working fluids. From the environment viewpoint, among all proposed working fluids, R600 is highly recommended due to its low value of GWP. In addition, it will be shown that using R600 in ORC of the proposed integrated system will reveal the highest energy and exergy efficiencies, too (see section 5.5).

5.4. Parametric study

5.4.1. The effect of reactor temperature on the system (Tₑₑₑₑₑₑₑₑ)

Fig. 2 is plotted to show variation of the net output power, hydrogen production rate, energy efficiency and exergy efficiency with various reactor temperatures, using R600 as working fluid. As shown in this figure, an increase in the reactor temperature increases the net output power. The main logical reason behind this phenomenon is that an increase in the reactor temperature increases the turbine output power and pump consumed power, simultaneously. This can be interpreted by the fact that the mass
flow rate of organic working fluid inside the ORC is increased with reactor temperature augmentation, while the energy difference (enthalpy difference) through the turbine and pump is remained constant. Since the turbine output power augmentation rate is considerably higher than the pump consumed power one, thus the net output power of the system will increase with an increase in the reactor temperature (Fig. 2(a)). Due to the high restriction in increase of the reactor temperature in BSR system, there must be an optimum range where reactor temperature can be set. With this regard, it is observed that the hydrogen production rate, energy efficiency and exergy efficiency of the overall BSR-ORC system can be maximized with reactor temperature. Therefore, to attain a higher value of hydrogen production rate along with energy and exergy efficiencies, reactor temperatures fallen into the range of 650–750 °C are recommended. It will show later that the optimum value of reactor temperature based on the first and second laws of thermodynamics is observed in this range, as shown by the base and optimum lines in Fig. 2.

5.4.2. The effect of reaction pressure on the system ($P_{React}$)

To show how the reaction pressure affects the performance of the proposed combined BSR-ORC system, Fig. 3 is presented. As Fig. 3(a) indicates, an increase in the reaction pressure decreases the net output power of the system, since both turbine output power and pump consumed power are decreased throughout this variation. However, the pump consumed power reduction rate is negligible, and hence the net output power will be affected only by turbine output power. Actually, reduction in the net output power of the overall system is due to the low temperature of the products released from the reforming reaction. In other word, as the reaction pressure increases, the products temperature at the inlet of evaporator (state 10) is slightly decreased. This will result in less mass flow rate supplied to the ORC, and hence the turbine output power will be decreased.

In addition, it can be figured out from Fig. 3(a) that at lower reaction pressures a large amount of hydrogen can be produced. This is due to the fact that in an equilibrium system with the number of unequal gas molecules on the side of reaction (Eqs. (1) and (2)), when pressure increases, equilibrium must be reversed in direction of the reactants, and hence the number of gas moles products is reduced, which is consistent with the Le Chatelier’s Principle [50]. Consequently, the amount of hydrogen produced per mole of methane will be decreased based on Eqs. (1) and (2). As a result of these variations it can be concluded that the overall energy and exergy efficiencies of the combined BSR-ORC system will be decreased as reaction pressure increases (Fig. 3(b)).

5.4.3. The effect of carbon dioxide to methane molar ratio on the system ($C_m$)

The effect of the carbon dioxide to methane molar ratio on the net output power, hydrogen production rate, energy efficiency and exergy efficiency of the combined BSR-ORC system is presented in Fig. 4. This figure illustrates that an increase in the carbon dioxide to methane molar ratio decreases both net output power and hydrogen production rate so slightly. However, there is a minimum value for net output power with respect to the carbon dioxide to methane molar ratio. This is mainly due to the fact that an increase in the carbon dioxide to methane molar ratio will result in a minimum point for the mass flow rate variation of organic fluid, while enthalpy difference through the pump and turbine will not be affected through this variation. Thus, the net output power will decrease with augmentation of the carbon dioxide to methane molar ratio at first and then increase (Fig. 4(a)). In addition, reduction in the hydrogen production rate with augmentation of the carbon dioxide to methane molar ratio can be justified by the
following fact. By increasing the amount of carbon dioxide in the biogas mixture, the methane conversion rate (CMR) is increased which has a positive effect on increase of the hydrogen mole production. But, on the other hand, the WGS (Eq. (3)) has progressed in the reverse direction of equilibrium, resulting in hydrogen molecule consumption which has a negative effect on the hydrogen molecule production based on the Le Chatelier’s Principle [50]. As a result, the effect of Eq. (2) is overcome by Eq. (3), and hence hydrogen production will be reduced (Fig. 4(a)). Considering variations of the net output power and hydrogen production rate with carbon dioxide to methane molar ratio, it can be expected that energy and exergy efficiencies will be decreased with augmentation of the carbon dioxide to methane molar ratio (Fig. 4(b)).

5.4.4. The effect of steam to carbon molar ratio on the system

Fig. 5 presents variation of the net output power, hydrogen production rate, energy efficiency and exergy efficiency of the system with various steam to carbon molar ratios. Increasing of the steam to carbon molar ratio increases the net output power and hydrogen production rate, simultaneously. This is mainly due to the fact that an increase in the steam to carbon molar ratio will increase the turbine output and pump consumed powers, since the mass flow rate of the organic working fluid in ORC is increased, while enthalpy difference through turbine and pump is remained constant. However, due to the negligible variation in the pump consumed power compared to the turbine output power increment, the net output power will increase as steam to carbon molar ratio increases (Fig. 5(a)). This figure also depicts that the energy and exergy efficiencies are increased as steam to carbon molar ratio increases due to the output commodities augmentation rate (power and hydrogen) with steam to carbon molar ratio increment under constant input parameters (Fig. 5(b)).
5.4.5. The effect of pump pressure ratio on the system (PPR)

The effect of pump pressure ratio (PPR) on the net output power, hydrogen production rate, energy efficiency and exergy efficiency of the system is presented in Fig. 6. The figure illustrates that an increase in PPR increases the net power output, while has no effect on the hydrogen production rate. This behavior can be explained as follows. An increase in PPR increases enthalpy difference through turbine, while decreases mass flow rate of ORC. However, the mass flow rate decrement is considerably lower than the enthalpy difference increment throughout this variation. Therefore, turbine extracts more power as PPR increases. In addition, enthalpy difference through pump will also be increased as PPR increases, where its augmentation rate overcomes the mass flow rate reduction of ORC. As a result, the pump consumed power will be increased as PPR increases. Since augmentation rate of the pump consumed power is dominated by the turbine output power augmentation rate, thus the net output power will increase as PPR increases (Fig. 6(a)). On the other hand, since hydrogen production rate is independent from ORC’s behavior, thus the hydrogen production rate will remain constant throughout the variation of PPR (Fig. 6(a)). These two variations will affect the energy and exergy efficiencies directly by increasing their values as PPR increases (Fig. 6(b)).

5.4.6. The effect of pinch point temperature difference of IHE on the system \((\Delta T_{PP,IHE})\)

Fig. 7 shows the effect of pinch point temperature difference of IHE on the net output power, hydrogen production rate, energy efficiency and exergy efficiency of the proposed combined BSR-ORC system. As figure indicates, increasing of the pinch point temperature difference of IHE results in the decrease of net output power of the system. This can be contributed to the fact that an increase in the pinch point temperature difference of IHE increases outlet energy of turbine, and hence enthalpy difference through turbine decreases, while the mass flow rate of organic working fluid is
remained constant throughout this variation. Therefore, the output power of the turbine will be decreased as pinch point temperature difference of IHE increases. In addition, the pump consumed power is also decreased as pinch point temperature difference of IHE increases, since the enthalpy difference through this component is decreased, too. As a result of these variations (reduction of the

Fig. 7. The effect of pinch point temperature difference of IHE ($\Delta T_{pp, IHE}$) on the: (a) hydrogen production and net output power and (b) overall energy and exergy efficiencies, using R600.
ference of IHE will not affect the topping cycle concept. With this regard, optimum values of the decision variables (MOOD) mode is presented based on genetic algorithm (GA) combined BSR-ORC system, a multi-objective optimization design.

5.5. Optimization results

Table 10
Thermodynamic properties of streams for the optimal mode, using R600.

<table>
<thead>
<tr>
<th>State</th>
<th>Fluid</th>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$h$ (kJ s$^{-1}$)</th>
<th>$s$ (kJ s$^{-1}$K$^{-1}$)</th>
<th>$m$ (kg s$^{-1}$)</th>
<th>$E_{ph}$ (kW)</th>
<th>$E_{ch}$ (kW)</th>
<th>$E$ (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Biogas</td>
<td>298.2</td>
<td>6.895</td>
<td>–1089</td>
<td>1.077</td>
<td>0.1526</td>
<td>28.76</td>
<td>3367</td>
<td>3395</td>
</tr>
<tr>
<td>2</td>
<td>Biogas</td>
<td>367.1</td>
<td>6.895</td>
<td>–1073</td>
<td>1.125</td>
<td>0.1526</td>
<td>30.35</td>
<td>3367</td>
<td>3397</td>
</tr>
<tr>
<td>3</td>
<td>Water</td>
<td>298.2</td>
<td>6.895</td>
<td>–2898</td>
<td>2.05</td>
<td>0.2159</td>
<td>57.36</td>
<td>113.8</td>
<td>171.16</td>
</tr>
<tr>
<td>4</td>
<td>Water</td>
<td>437.6</td>
<td>6.895</td>
<td>–2841</td>
<td>2.204</td>
<td>0.2159</td>
<td>67.6</td>
<td>113.8</td>
<td>181.5</td>
</tr>
<tr>
<td>5</td>
<td>Reactants</td>
<td>411.2</td>
<td>6.895</td>
<td>–3914</td>
<td>3.331</td>
<td>0.3685</td>
<td>97.27</td>
<td>3480</td>
<td>3578</td>
</tr>
<tr>
<td>6</td>
<td>Reactants</td>
<td>523.2</td>
<td>6.895</td>
<td>–3521</td>
<td>3.917</td>
<td>0.3685</td>
<td>308.4</td>
<td>3480</td>
<td>3789</td>
</tr>
<tr>
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<td>6.895</td>
<td>–2619</td>
<td>4.845</td>
<td>0.3685</td>
<td>413.3</td>
<td>4014</td>
<td>4428</td>
</tr>
<tr>
<td>8</td>
<td>Products</td>
<td>541.6</td>
<td>6.895</td>
<td>–3012</td>
<td>4.331</td>
<td>0.3685</td>
<td>178.2</td>
<td>4014</td>
<td>4192</td>
</tr>
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<td>9</td>
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<td>6.895</td>
<td>–3028</td>
<td>4.302</td>
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<td>171.3</td>
<td>4014</td>
<td>4186</td>
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<td>0.3685</td>
<td>149.2</td>
<td>4014</td>
<td>4163</td>
</tr>
<tr>
<td>11</td>
<td>Products</td>
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<td>3.893</td>
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<td>124.8</td>
<td>4014</td>
<td>4139</td>
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<td>12</td>
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<td>328.6</td>
<td>6.895</td>
<td>880.9</td>
<td>117.4</td>
<td>0.02529</td>
<td>60.58</td>
<td>2962</td>
<td>3023</td>
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<td>13</td>
<td>Exhaust gases</td>
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<td>6.895</td>
<td>–1645</td>
<td>1.251</td>
<td>0.3432</td>
<td>64.18</td>
<td>1052</td>
<td>1116</td>
</tr>
<tr>
<td>14</td>
<td>R600</td>
<td>303.2</td>
<td>2.839</td>
<td>65.53</td>
<td>0.301</td>
<td>0.2412</td>
<td>8.756</td>
<td>–</td>
<td>8.756</td>
</tr>
<tr>
<td>15</td>
<td>R600</td>
<td>304.7</td>
<td>2.839</td>
<td>66.41</td>
<td>0.3014</td>
<td>0.2412</td>
<td>9.507</td>
<td>–</td>
<td>9.507</td>
</tr>
<tr>
<td>16</td>
<td>R600</td>
<td>315.6</td>
<td>2.839</td>
<td>73.2</td>
<td>0.3233</td>
<td>0.2412</td>
<td>9.765</td>
<td>–</td>
<td>9.765</td>
</tr>
<tr>
<td>17</td>
<td>R600</td>
<td>388.8</td>
<td>2.839</td>
<td>177.8</td>
<td>0.6057</td>
<td>0.2412</td>
<td>30.19</td>
<td>–</td>
<td>30.19</td>
</tr>
<tr>
<td>18</td>
<td>R600</td>
<td>324.7</td>
<td>2.839</td>
<td>161</td>
<td>0.6149</td>
<td>0.2412</td>
<td>10.66</td>
<td>–</td>
<td>10.66</td>
</tr>
<tr>
<td>19</td>
<td>R600</td>
<td>309.9</td>
<td>2.839</td>
<td>154.2</td>
<td>0.5935</td>
<td>0.2412</td>
<td>10.25</td>
<td>–</td>
<td>10.25</td>
</tr>
<tr>
<td>20</td>
<td>Water</td>
<td>295</td>
<td>1</td>
<td>563.8</td>
<td>1.983</td>
<td>0.15</td>
<td>0.4311</td>
<td>–</td>
<td>0.4311</td>
</tr>
<tr>
<td>21</td>
<td>Water</td>
<td>305</td>
<td>1</td>
<td>821.1</td>
<td>2.841</td>
<td>0.15</td>
<td>1.994</td>
<td>–</td>
<td>1.994</td>
</tr>
</tbody>
</table>

Moreover, since variation of the pinch point temperature difference of IHE will not affect the topping cycle’s behavior (BSR system), thus the hydrogen production rate is remained constant with any variation in the pinch point temperature difference of IHE (Fig. 7(b)). As a result of these variations (hydrogen production rate and net output power), the energy and exergy efficiencies are decreased slightly as pinch point temperature difference of IHE increases (Fig. 7(b)).

5.5. Optimization results

To present more efficient performance of the proposed combined BSR-ORC system, a multi-objective optimization design (MOOD) mode is presented based on genetic algorithm (GA) concept. With this regard, optimum values of the decision variables along with objective functions are determined for different applied working fluids. For this purpose, optimum thermodynamic properties at each flow stream including temperature, pressure, enthalpy, entropy, mass flow rate and exergy flow rate are presented in Table 9. It is believed that these thermodynamic properties could give more useful information from behavior of the proposed integrated system for designers. In addition, these properties are used to conduct energy and exergy analysis of the proposed system based on the classical laws for each working fluid. Based on these data, the optimum values of decision variables and objective functions for each working fluid are calculated and compared with those values of base mode (Table 10).

According to Table 10, the net output power of the combined BSR-ORC system is increased by 55.27%, 47.66%, 36.67% and 21.58% when R600, R245fa, R123, and R113 are used as working fluid in ORC, respectively, compared to the base mode. Thus, the conducted optimization has more effect on the value of net output power when R600 is used in ORC. In addition, the maximum optimum value of net output power is obtained 15.9 kW, when R600 is used in ORC.

Table 10
Optimum values of decision variables and objective functions.

<table>
<thead>
<tr>
<th>Decision variables/objective functions</th>
<th>R600</th>
<th>R245fa</th>
<th>R123</th>
<th>R113</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_C$</td>
<td>2</td>
<td>2.998</td>
<td>2</td>
<td>2.999</td>
</tr>
<tr>
<td>$P_C$</td>
<td>0.65</td>
<td>0.5021</td>
<td>0.65</td>
<td>0.5004</td>
</tr>
<tr>
<td>$P_{base}$ (bar)</td>
<td>1.5</td>
<td>1.004</td>
<td>1.5</td>
<td>1.006</td>
</tr>
<tr>
<td>$T_{base}$ (K)</td>
<td>967.15</td>
<td>978.85</td>
<td>967.15</td>
<td>977.35</td>
</tr>
<tr>
<td>PPR</td>
<td>5</td>
<td>7.21</td>
<td>5</td>
<td>6.56</td>
</tr>
<tr>
<td>$\Delta T_{Pr,red}$ (K)</td>
<td>4</td>
<td>5.446</td>
<td>4</td>
<td>5.12</td>
</tr>
<tr>
<td>$Q_{base}$ (kW)</td>
<td>834.1</td>
<td>902.1</td>
<td>834.1</td>
<td>897.3</td>
</tr>
<tr>
<td>$Q_{fuel}$ (kW)</td>
<td>78.75</td>
<td>104.3</td>
<td>78.75</td>
<td>102</td>
</tr>
<tr>
<td>$Q_{fuel}$ (kW)</td>
<td>68.51</td>
<td>88.72</td>
<td>69.84</td>
<td>88.81</td>
</tr>
<tr>
<td>$W_{hum}$ (kW)</td>
<td>0.4433</td>
<td>0.8831</td>
<td>0.2295</td>
<td>0.403</td>
</tr>
<tr>
<td>$W_{fuel}$ (kW)</td>
<td>10.68</td>
<td>16.78</td>
<td>9.134</td>
<td>13.55</td>
</tr>
<tr>
<td>$W_{net}$ (kW)</td>
<td>10.24</td>
<td>15.9</td>
<td>8.905</td>
<td>13.15</td>
</tr>
<tr>
<td>$m_{hydrogen}$ (kg s$^{-1}$)</td>
<td>0.02139</td>
<td>0.02529</td>
<td>0.02139</td>
<td>0.02526</td>
</tr>
<tr>
<td>$\eta_{ex}$ (%)</td>
<td>33.86</td>
<td>45.63</td>
<td>33.84</td>
<td>45.61</td>
</tr>
<tr>
<td>$\eta_{en}$ (%)</td>
<td>63.8</td>
<td>74.89</td>
<td>63.77</td>
<td>74.84</td>
</tr>
</tbody>
</table>

Another implication of Table 10 is significant enhancement of hydrogen production rate of the proposed integrated system through the conducted optimization. As it can be figured out, the hydrogen production rate is increased 18.23%, 18.09%, 18.13% and 18.18% when R600, R245fa, R123 and R113 are used in ORC, respectively. Therefore, optimization of the proposed combined BSR-ORC system based on the MOOD mode for resulting maximum hydrogen production rate is highlighted when R600 is used in ORC. Considering this fact on the ground, the maximum hydrogen production rate is obtained 0.02529 kg s$^{-1}$ when R600 is employed in ORC.

Table 10 also listed the optimum and base values of energy and exergy efficiencies of the proposed integrated system for different employed working fluids. As shown in this table, the energy efficiency is increased 34.76%, 34.78%, 34.83% and 34.92% when R600, R245fa, R123 and R113 are employed in bottoming cycle, respectively. As a result of the proposed optimization, the maximum energy efficiency is obtained 45.63% when R600 is used in ORC. The results of conducted multi-objective optimization also reveal a satisfactory improvement in performance of the system based on the second-law of thermodynamics. According to Table 10 it can be concluded that the exergy efficiency of the combined BSR-ORC system is increased 17.38%, 17.35%, 17.34% and 17.4% when R600, R245fa, R123 and R113 are employed in organic Rankine cycle, respectively. As a result, the employed MOOD mode of optimization can result in the maximum exergy efficiency of 74.89% when R600 is used in organic Rankine cycle.

Based on these results it can be said that working fluid selection based on the efficiency criterion has not a considerable effect on optimization results, nevertheless its effect on the environment is discussible. According to the working fluid’s properties presented in Table 8 and the obtained results in Table 10, R600 is recommended to be used in ORC of the proposed combined BSR-ORC system due to its high efficiency as well as environment benefits.

Table 11 presents some significant exergy factors including exergy rate of fuel, exergy rate of product, exergy destruction rate, exergy destruction ratio, and exergy efficiency for different components of the proposed system based on the optimal mode (MOOD mode). As this table indicates, among all components recuperator and reactor account for the highest exergy losses through the system by 23.95 kW (32.28%) and 23.82 kW (32.1%), respectively. Therefore, significant improvement of the proposed system efficiency is attainable when the performance of these two components is improved.

### 6. Conclusion

In this paper, a combined BSR-ORC system is proposed and its feasibility is investigated based on the first- and second-laws of thermodynamics. The proposed system can produce power and hydrogen, simultaneously. In addition, the performance of the proposed system is optimized by considering energy and exergy efficiencies as objective functions and reactor temperature ($T_{Reac}$), reaction pressure ($P_{Reac}$), steam to carbon molar ratio ($S_c$), carbon dioxide to methane molar ratio ($C_{m}$), pump pressure ratio ($PPR$) and pinch point temperature difference of IHE ($\Delta TPP_{IHE}$) as decision variables. Four different working fluids of R600, R245fa, R123, and R113 are used in ORC, where among all of them R600 is recommended due to its high performance and environment benefits. Using R600 as working fluid in ORC, the optimum net output power, hydrogen production rate, energy efficiency and exergy efficiency are obtained 15.9 kW, 0.02529 kg s$^{-1}$, 45.63% and 74.89%, respectively, as steam to carbon molar ratio, carbon dioxide to methane molar ratio, reaction pressure, reactor temperature, pump pressure ratio and pinch point temperature difference of IHE are set into 2.99, 0.502, 1.004 bar, 998.85 K, 7.21 and 5.44 K, respectively. Moreover, the results of exergy analysis indicated that among all components, recuperator and reactor are accountable for the highest exergy destruction through the proposed combined BSR-ORC system by 23.95 kW (32.28%) and 23.82 kW (32.1%), respectively. Therefore, significant improvement of the proposed system performance can be obtained as these two components are redesigned.

At last, a comprehensive parametric study is carried out based on the four key performance criteria, namely, net output power, hydrogen production rate, energy efficiency and exergy efficiency. According to the conducted parametric study it can be concluded that the net output power can be increased by increasing reactor temperature, steam to carbon molar ratio, and pump pressure ratio or decreasing reaction pressure and pinch point temperature difference of IHE. Also, the hydrogen production rate can be increased by increasing steam to carbon molar ratio or decreasing reaction pressure and carbon dioxide to methane molar ratio. In addition, the energy and exergy efficiencies of the combined BSR-ORC system can be increased by increasing steam to carbon molar ratio and pump pressure ratio or decreasing reaction pressure, carbon dioxide to methane molar ratio and pinch point temperature difference of IHE. Last but not the least, it is found that the performance of the proposed integrated system can be maximized based on the reactor temperature.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSR</td>
<td>Biogas steam reforming</td>
</tr>
<tr>
<td>$C_{m}$</td>
<td>Carbon dioxide to methane molar ratio</td>
</tr>
<tr>
<td>CMR</td>
<td>Carbon dioxide steam reforming</td>
</tr>
</tbody>
</table>


