Exergy analysis for decision making on operational condition of a continuous photobioreactor for hydrogen production via WGS reaction

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A B S T R A C T

In the present study, continuous photobiological hydrogen production from syngas through the water gas shift (WGS) reaction by Rhodospirillum rubrum was thermodynamically scrutinized using both conventional exergy and eco-exergy concepts for the first time. These analyses were applied for decision making on liquid media flow rate and agitation speed with respect to the sustainability and productivity issues. The maximum process exergetic efficiency was found to be 22.27% and 22.09% using the conventional exergy and eco-exergy concepts, respectively, at a liquid media flow rate of 12 mL/min and an agitation speed of 500 rpm as the best operational conditions. In general, the eco-exergetic parameters and their conventional exergy counterparts did not show significant differences due to the slow growth rate of the microorganisms in the bioreactor. However, eco-exergy concept would be strongly recommended to apply for analyzing such renewable fuel production systems containing living organisms. Moreover, this work demonstrated the merits of exergetic indicators based on the second law of thermodynamics over the single process yield in assessing photobiological hydrogen production. The results obtained also showed that exergy analysis could facilitate on-going attempts to increase the sustainability and productivity of large-scale photobiological hydrogen production systems.

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Introduction

Nowadays, global energy consumption has markedly increased due to increasing life standards and world population [1,2]. It is approximated that non-renewable fossil fuels i.e. petroleum, natural gas, and coal contribute 80% of world’s energy supply [3]. However, fluctuating prices of fossil fuels and their rapid depletion as well as the emissions caused by their combustion (i.e. CO₂, SO₅, NOₓ, and particulate matters) have led policymakers and researchers to pay an increasing deal of attention to renewable energy carriers [4–7]. It is fortunate that the continually-replenished renewable energy resources could improve public health and environmental quality and more importantly could enable future generations to minimize the current over-dependence on the fossil fuels.

Hydrogen is considered as one of the most promising candidates to substitute fossil-based fuels owing to the abundance and availability of its feedstock [8]. Hydrogen can be produced from renewable or non-renewable sources [9]. Unfortunately, over 96% of the world’s hydrogen demands are still met by non-renewable fossil fuels through natural gas reforming, oil/naphtha reforming from refinery/chemical industrial off-gases, coal gasification, and water electrolysis [10]. Due to the significant amounts of greenhouse gas emissions generated from non-renewable hydrogen production methods, further development and implementation of green methods like biological pathways for eco-friendly production of hydrogen is crucial. Biological hydrogen or biohydrogen can be produced through various approaches such as biomass gasification, artificial photosynthesis, bio-photolysis, and photo-fermentation [11]. Among various biological pathways, photo-fermentation in the presence of appropriate substrates to support microbial survival and growth, is one of the most promising routes for renewable hydrogen production [9]. Nevertheless, it is constantly necessary to evaluate the available or emerging pathways for biohydrogen production using advanced engineering tools to assess their potential environmental pros and cons more accurately.

In line with that, thermodynamic approaches such as energy and exergy analyses have been proven as valid techniques to quantify both environmental and financial aspects
of various renewable fuels production. However, exergy analysis has the superiority compared to energy analysis in terms of environmentally-conscious decision making because of its unique conceptual features in recognizing the locations, types, sources, and magnitudes of thermodynamic irreversibility or resource destruction [12,13]. Generally speaking, exergy can be defined as the maximum amount of theoretical work that can be achieved by bringing an energy system to equilibrium with its reference environment [14]. Hence, exergy-based analyses have become very popular in recent years for assessing the sustainability and productivity of various energy conversion systems [15–20].

Considerable attempts have also been made to apply exergy-based analysis for hydrogen production from various renewable and non-renewable resources [21–27]. For instance, Neelis et al. [21] successfully analyzed eight different hydrogen production and storage chains for automotive applications using an exergetic well-to-wheels analysis. Later, Maddaloni and Rowe [22] studied the feasibility of electricity generation by various natural gas pressure reduction facilities using an expander and subsequent utilization of the generated power to produce hydrogen using exergy concept. In another study, Cleeton et al. [23] simulated exergetically a chemical looping combustion system in conjunction with a steam-coal gasification process for simultaneous hydrogen and electricity production. In continuation, Orhan et al. [24] applied specific exergy cost technique for exergoeconomic analysis of hydrogen production from thermochemical copper–chlorine cycle. In the same year, Perdikaris et al. [25] also presented exergy analysis of a carbon free solid oxide cells/solid oxide fuel cells system for simultaneous production of hydrogen, electricity, and heat from natural gas. Khila et al. [26] also effectively compared energetic and exergetic performance assessment of three different types of ethanol reforming processes including ethanol steam reforming, partial oxidation, and auto-thermal reforming for hydrogen production. Recently, hydrogen production from poplar lignocellulosic biomass gasification in a low-pressure char indirect gasifier was analyzed based on exergy concept as well [27].

According to the findings of the above-mentioned successful studies, various energy conversion systems can be satisfactorily designed and optimized by means of exergy analysis with respect to the sustainability and productivity issues. Despite of that and although a number of investigations has been performed and published to date on biohydrogen production using various microorganisms [28–30], those surveys were only aimed at investigating the feasibility and modeling features of the studied systems. In better words, to the best of our knowledge, there is no report published on exergy analysis of continuous photobiological hydrogen production from syngas through the water gas shift (WGS) reaction via anaerobic photosynthetic bacteria. Therefore, the main objective of the present survey was set to perform an exergy analysis for photobiological hydrogen production via WGS reaction by *Rhodospirillum rubrum* in a continuous bioreactor using conventional exergy and exo-exergy concepts for the first time. More specifically, these approaches were applied for decision making on liquid media flow rate and agitation speed for achieving the most cost-effective and eco-friendly conditions for biological hydrogen production. The findings of such analyses could provide fruitful information to engineers, researchers, managers, and policymakers involved in design, simulation, optimization, analysis, management, and implementation of industrial-scale photobioreactors for biohydrogen production.

### Materials and methods

#### Biohydrogen production and analyses

Pure culture of *Rhodospirillum rubrum* was obtained from the American Type Culture Collection (ATCC). The microorganism was grown in an enriched ATCC medium under anaerobic condition at 30 °C in the presence of tungsten light. The growth medium used included 2.5 g acetic acid neutralized with sodium hydroxide at pH 6.9, 1.25 g (NH₄)₂SO₄, 1 g yeast extract, 0.9 g K₂HPO₄, 0.6 g KH₂PO₄, 0.2 g MgSO₄·7H₂O, 0.07 g CaCl₂·2H₂O, 0.02 g EDTA, and 0.01 g ferric citrate. Then, 7.5 mL B-Vitamin solution containing 0.4 g thiamine HCl, 0.2 g nicotinamide, 0.2 g nicotinic acid, and 0.008 g biotin was added to the medium. 1 mL trace metal solution elements comprising of 3 g ferric citrate, 0.5 g EDTA, 0.2 g CaCl₂·2H₂O, 0.02 g (NH₄)₆Mo₇O₂₄, 0.02 g MgSO₄·7H₂O, 0.01 g ZnSO₄·7H₂O, 0.01 g H₃BO₃, and 0.01 g CuSO₄·5H₂O was also included into the medium. Moreover, the pH was adjusted to 6.5 adding 0.2 M HCl and base 0.2 M NaOH solutions using peristaltic pumps.

The continuous experiments were performed in a 2 L fermenter in the absence of oxygen with continuous supply of liquid media and syngas at ambient pressure and 30 °C. The syngas mixture included 55% CO, 20% H₂, 15% Ar, and 10% CO₂. The reactor was equipped with temperature, pH, level, and dissolved oxygen sensors. The experimental setup of the continuous bioreactor used in this study is schematically depicted in Fig. 1. In order to maintain the anaerobic conditions, the system was purged with nitrogen. A 5% inoculum was used to eliminate the log phase. Two tungsten lamps (40 W) were used to supply a uniform light intensity of 1500 lux on the fermenter surface throughout the experiments. The outflow stream into the effluent tank was controlled by the level controller.

In order to investigate the effect of syngas flow rate and agitation speed, the bioreactor was operated at various gas flow rates (5–14 mL/min) and agitation speeds (150–500 rpm) within a period of two months continuous process for hydrogen production (at optimum pH of 6.5). Fig. 2 reveals the continuous bioreactor operation at various syngas flow rates and agitation speeds. Unlike the syngas flow rate and agitation speed, the liquid flow rate was maintained at a fixed rate of 0.65 mL/min for the duration of two months. It is worth noting that all the experiments were replicated twice and the average values were used in the energetic calculations.

The gas sampling was carried out routinely and gas compositions were determined by a Perkin Elmer Autosystem XL gas chromatograph (USA) equipped with thermal conductivity detector and a Carboxene 1000 column (Supelco, USA) [31]. Liquid samples (1 mL) for analysis and cell density...
measurements were withdrawn from the bioreactor and were filtered using Whatman 0.45 μm cellulose membrane (England). Cell concentration was determined by measuring optical density at 400 nm using a Cecil 1000 series spectrophotometer (Cecil Instrument, England) and was subsequently converted to cell dry weight values using a previously determined calibration curve. The acetate concentration in the samples was measured using a Perkin Elmer Clarus 500 gas chromatograph (USA) equipped with a flame ionization detector (FID) and a Carbopack B-DA/4% Carbowax 20 M column (Supelco, USA) as described in our previous report [31].

**Theoretical considerations**

Fig. 3 explains a schematic view of the photobioreactor as a control volume considered for exergy analysis with input and output terms.

Based on Fig. 3, the mass and exergy balance equations for the photobioreactor can be expressed as follows:

\[
\frac{m_{MO,at} - m_{MO,at}}{\Delta t} + \left( m_{CM,at} - m_{CM,at} \right) = \left( m_{LM,in} - m_{LM,out} \right) + \left( m_{SC,in} - m_{SC,out} \right) + \left( m_{CW,in} - m_{CW,out} \right) - m_{MO,in}
\]

(1)
where \( m_{\text{MO}} \) and \( m_{\text{CM}} \) denote the masses of microorganisms and culture media, respectively, at times \( t \) and \( t + \Delta t \) accumulated in the bioreactor. \( m_{\text{LM}} \), \( m_{\text{SG}} \), and \( m_{\text{CW}} \) are the mass flow rates of inflow and outflow liquid media, syngas, and cooling water, respectively, and \( m_{\text{MO}}_{\text{out}} \) stands for the mass flow rate of microorganisms leaving the photobioreactor.

Obviously, the inflow and outflow rates of the cooling water are equal; therefore, the above equation could be summarized as follows:

\[
\frac{(m_{\text{MO}}_{\text{in}} - m_{\text{MO}}_{\text{out}})}{\Delta t} = (m_{\text{LM}}_{\text{in}} - m_{\text{LM}}_{\text{out}}) + (m_{\text{SG}}_{\text{in}} - m_{\text{SG}}_{\text{out}}) + m_{\text{MO}}_{\text{out}} \tag{2}
\]

The exergy balance of the photobioreactor could be expressed through the following equation:

\[
\begin{align*}
\frac{\Delta t}{(\text{Ex}_{\text{MO}}_{\text{in}} - \text{Ex}_{\text{MO}}_{\text{out}})} & = (\text{Ex}_{\text{LM}}_{\text{in}} - \text{Ex}_{\text{LM}}_{\text{out}}) + (\text{Ex}_{\text{SG}}_{\text{in}} - \text{Ex}_{\text{SG}}_{\text{out}}) + (\text{Ex}_{\text{CW}}_{\text{in}} - \text{Ex}_{\text{CW}}_{\text{out}}) \\
&+ \text{Ex}_W + \text{Ex}_D - \text{Ex}_{\text{MO.out}} - \text{Ex}_{\text{des}} \tag{3}
\end{align*}
\]

where \( \text{Ex}_{\text{CM}} \) and \( \text{Ex}_{\text{MO}} \) represent the exergetic values of culture media and microorganisms, respectively, at times \( t \) and \( t + \Delta t \) accumulated in the bioreactor, \( \text{Ex}_{\text{LM}} \) shows the exergy rate of inflow and outflow liquid media, \( \text{Ex}_{\text{SG}} \) is the exergy flow rate of syngas, \( \text{Ex}_{\text{CW}} \) denotes the exergy rate of inflow and outflow cooling water, \( \text{Ex}_W \) and \( \text{Ex}_D \) are the exergetic rates of delivered work and light to the culture media from mechanical agitator and tungsten lamp, respectively, \( \text{Ex}_{\text{MO.out}} \) stands for the exergy flow rate of microorganism leaving photobioreactor, and \( \text{Ex}_{\text{des}} \) represents the exergy destruction rate in the photobioreactor.

The following equation was applied to determine the exergetic quantity of the liquid media accumulated in the bioreactor during the fermentation process:

\[
\text{Ex}_{\text{CM}} = \dot{n}_{\text{CM}} \left( \sum_i x_i e_i + \Delta \dot{W}_0 \sum_i x_i \ln(x_i) \right) + m_{\text{CM}} C_{\text{CM}} \left( T_{\text{CM}} - T_0 \right) \\
- T_0 \ln \left( \frac{T_{\text{CM}}}{T_0} \right) \tag{4}
\]

where \( \dot{n}_{\text{CM}} \) denotes the mole number of material amassed in the bioreactor, \( x_i \) is the molar fraction of each component amassed in the bioreactor, \( e_i \) shows the standard chemical exergy of \( i \) th component amassed in the bioreactor, \( R \) is the gas constant (8.314 J/mol K), \( C_{\text{CM}} \) is the specific heat capacity of culture media, \( T_{\text{CM}} \) represents the temperatures of culture media, and \( T_0 \) is the dead state temperature considered to be 25 °C. Moreover, the specific heat capacity of the liquid media was considered to be equal to pure water, since at least 98% of the liquid media composed of pure water. Furthermore, the exergetic rates of inflow and outflow liquid media were obtained as follows:

\[
\begin{align*}
\text{Ex}_{\text{LM}} = \dot{n}_{\text{LM}} \left( \sum_j x_j e_j + \Delta \dot{W}_0 \sum_j x_j \ln(x_j) \right) + m_{\text{LM}} C_{\text{LM}} \left( T_{\text{LM}} - T_0 \right) \\
- T_0 \ln \left( \frac{T_{\text{LM}}}{T_0} \right) \tag{5}
\end{align*}
\]

where \( \dot{n}_{\text{LM}} \) and \( m_{\text{LM}} \) are the mole and mass rates of inflow and outflow liquid media, respectively, \( x_j \) is the molar fraction of each component in the inflow and outflow liquid media, \( e_j \) represents the standard chemical exergy of \( j \) th component of the inflow and outflow liquid media, \( C_{\text{LM}} \) is the specific heat capacity of liquid media, and \( T_{\text{LM}} \) is the temperature of inflow and outflow liquid media.

The specific chemical exergies of organic materials utilized in the preparation of culture media were computed using the linear mathematical model suggested by Song et al. [32].

\[
\begin{align*}
\text{ex}_{\text{CM}} &= 363.439 \text{C} + 1075.633 \text{H} - 86.308 \text{O} + 4.14 \text{N} + 190.798 \text{S} \\
&- 21.1 \text{A}
\end{align*}
\]

\[\text{Fig. 3 – Schematic illustration of the continuous photobioreactor for hydrogen production using Rhodospirillum rubrum.}\]
\[ \varepsilon_{\text{OM}} = M_{\text{OM}} \varepsilon_{\text{OM}} \]  
\[ \text{(7)} \]

where C, H, O, N, S and A represent the percentages of carbon, hydrogen, oxygen, nitrogen, sulfur, and ash of an organic material, respectively. Additionally, the standard chemical exergies of the inorganic materials applied in the present study were gathered from the literature [33] (Table 1).

The following equation was applied to obtain the exergy flow rates of the inflow and outflow syngas.

\[ \dot{E}_{\text{SG}} = \dot{n}_{\text{SG}} \left( \sum_{m} X_m \varepsilon_m + \Delta H_0 \sum_{m} X_m \ln(X_m) + \Delta H_0 \ln \left( \frac{P}{P_0} \right) \right) + m_{\text{SG}} C_{\text{SG}} \left( T_{\text{SG}} - T_0 - T_0 \ln \left( \frac{T_{\text{SG}}}{T_0} \right) \right) \]
\[ \text{(8)} \]

where \( \dot{n}_{\text{SG}} \) and \( m_{\text{SG}} \) are the mole rates of inflow and outflow syngases, \( X_m \) shows the molar fraction of each component in the inflow and outflow syngases, \( \varepsilon_m \) is the standard chemical exergy of \( m \)th component of the inflow and outflow syngases, \( P \) and \( P_0 \) are the pressure of syngas and dead state, respectively, and \( T_{\text{SG}} \) is the temperature of inflow and outflow syngases. The dead state pressure was assumed to be 100 kPa.

The specific heat capacity of the inflow and outflow gases was computed using the following equation:

\[ C_{\text{SG}} = \sum_{m} X_m C_n \]
\[ \text{(9)} \]

where \( X_m \) and \( C_n \) are the mass fraction and specific heat capacity of each component of the syngas. The mathematical equations used in the calculation of the specific heat capacities of syngas components together with their standard chemical exergies are given in Table 2.

The following formula was used to calculate the exergy loss rate to the cooling water.

\[ \dot{E}_{\text{CW}} = m_{\text{CW}} C_{\text{CW}} \left( T_{\text{CW}} - T_0 - T_0 \ln \left( \frac{T_{\text{CW}}}{T_0} \right) \right) \]
\[ \text{(10)} \]

where \( m_{\text{CW}} \) is the mass flow rate of cooling water, \( C_{\text{CW}} \) stands for the specific heat capacity of water, and \( T_{\text{CW}} \) denotes the temperature of the cooling water at the inlet and outlet sections.

The chemical exergy of the microorganism accumulated in the photobioreactor at any times was obtained as follows:

\[ \dot{E}_{\text{MO}} = 18.7 m_{\text{MO}} \]
\[ \text{(11)} \]

where 18.7 kJ/g is the chemical exergy content of average detritus [36,37]. Similarly, the chemical exergy of the microorganisms leaving the bioreactor was obtained as follows:

\[ \dot{E}_{\text{MO, out}} = 18.7 m_{\text{MO, out}} \]
\[ \text{(12)} \]

In addition to the conventional exergy approach, eco-exergy theory was also employed in this investigation due to the presence of living microorganisms in the photobioreactor. For this aim, the hypothesis proposed by Jørgensen et al. [36] was applied. They stated that the living organisms carry more work energy than the non-living constituents which only carry chemical energy. This could be ascribed to the large amount of the genetic information embodied in the living organisms. Jørgensen et al. [36] designated this amount of exergy as eco-exergy (\( \Phi \)) and developed the following equations for determining the eco-exergy of living organisms.

\[ \phi \Delta T_0 = 7.34 \times 10^9 E_{\text{MO}} + E_{\text{MO}} \ln(20^{\text{mol}}) \]
\[ \text{(13)} \]

### Table 1 – The standard chemical exergy of materials used for the culture media preparation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Standard chemical exergy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>0.9</td>
</tr>
<tr>
<td>Acetate sodium</td>
<td>NaC₂H₄O₂</td>
<td>873.599</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>C₁₀H₁₄O₅</td>
<td>955.466</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>660.6</td>
</tr>
<tr>
<td>Magnesium sulfate</td>
<td>MgSO₄·7H₂O</td>
<td>87.0</td>
</tr>
<tr>
<td>Calcium chloride dehydrate</td>
<td>CaCl₂·2H₂O</td>
<td>89.7</td>
</tr>
<tr>
<td>Ferric citrate</td>
<td>Fe₂(H₂O)₃</td>
<td>2076.735</td>
</tr>
<tr>
<td>Potassium dihydrogen phosphate</td>
<td>KH₂PO₄</td>
<td>50.07</td>
</tr>
<tr>
<td>Dipotassium hydrogen phosphate</td>
<td>K₂HPO₄</td>
<td>78.32</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C₆H₆N₂O</td>
<td>3143.108</td>
</tr>
<tr>
<td>Thiamine HCl</td>
<td>C₂H₇ClN₂O₅·HCl</td>
<td>7587.879</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>C₁₂H₁₄NO₅</td>
<td>2890.804</td>
</tr>
<tr>
<td>Zinc sulfate heptahydrate</td>
<td>ZnSO₄·7H₂O</td>
<td>88.6</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H₃BO₃</td>
<td>21.97</td>
</tr>
<tr>
<td>Copper sulfate pentahydrate</td>
<td>CuSO₄·5H₂O</td>
<td>91.39</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid (EDTA)</td>
<td>C₁₂H₁₄N₂Oₙ</td>
<td>5006.731</td>
</tr>
<tr>
<td>Ammonium molybdate</td>
<td>(NH₄)₆Mo₇O₂₄</td>
<td>1882.025</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>74.9</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>HCl</td>
<td>84.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Mathematical equation for specific heat calculation  ((\theta = T\text{[kelvin]}/1000))</th>
<th>Standard chemical exergy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H₂)</td>
<td>( C_{\text{H}_2} = 13.46 + 4.60\theta - 6.85\theta^2 + 3.79\theta^3 )</td>
<td>236.1</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>( C_{\text{CO}} = 1.10 - 0.46\theta + 1.00\theta^2 - 0.45\theta^3 )</td>
<td>275.10</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>( C_{\text{CO}_2} = 0.45 + 1.67\theta - 1.27\theta^2 + 0.39\theta^3 )</td>
<td>19.87</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>( C_{\text{Ar}} = 0.52 )</td>
<td>11.69</td>
</tr>
</tbody>
</table>

* Obtained from Wall [33].
* Calculated based on the Eqs. (6) and (7).
* Obtained from [http://www.exergoeconomy.com/][34].
* Since thermodynamic data for these materials were not available, their standard chemical exergy values were calculated for an equimolar mixture of their components.
* Due to the lack of thermodynamic data for ammonium molybdate, its standard exergy was computed using the Eqs. (6) and (7). The error out of this assumption was negligible since its amount in culture media was only 9.81 \times 10^{-7} kg.
\[
\beta = 1 + \frac{\ln(20)(N\overline{N} - NRG)}{3 \times 7.34 \times 10^4}
\]  
(14)

where \(N\overline{N}\) and \(NRG\) denote the number of nucleotides and number of repeating genes, respectively.

Since \(\ln 20 = 3\), therefore, the above equation could be simplified as follows:

\[
\beta = 1 + \frac{N\overline{N}(1 - NRG)}{7.34 \times 10^4}
\]  
(15)

where \(\beta\) is the ratio of the eco-exergy to the chemical exergy accounting for how information is embodied in a given microorganisms. This value \(\beta\) has been reported to be 8.5 for bacteria [36]. In order to approximate the mechanical work delivered to the culture media, the Reynolds number \(Re\) was determined for various agitation speeds using the following well-known equation.

\[
Re = \frac{\rho ND^2}{\mu}
\]  
(16)

where \(\rho\) shows the fluid density, \(N\) represents the impeller speed, \(D\) is the impeller diameter, and \(\mu\) stands for the fluid viscosity. The mechanical work delivered to the culture media is proportional to the Reynolds number and can be computed using the following equation [38]:

\[
W = N\rho ND^2
\]  
(17)

where \(W\) and \(N\) are the mechanical work delivered to the culture media and power number of a given agitation rate, respectively.

The exergy rate of the mechanical work delivered to the culture media was equal to the agitator power.

\[
\dot{E}_{xw} = W
\]  
(18)

Generally, when light travels through the air and intercepts the surface of transparent materials, such as glass, a certain fraction of the light is reflected and the rest is transmitted into the material. In this study, the fermenter body was considered as a transparent material (Borosilicate glass) reflecting a remarkable fraction of the incident light.

According to Fresnel equations, the incidence angle of the light reaching a surface could affect the amount of reflection taking place. Fig. 4 represents schematically the relative angles and other factors affecting the amount of reflection.

The reflection coefficient of the s-polarized and p-polarized incident lights can be obtained using the Fresnel equations as follows [39]:

For s-polarized lights:

\[
R_s = \frac{|n_1 \cos \theta_i - n_2 \cos \theta_r|^2}{|n_1 \cos \theta_i + n_2 \cos \theta_r|^2}
\]  
(19)

And for p-polarized lights:

\[
R_p = \frac{|n_1 \cos \theta_i - n_2 \cos \theta_r|^2}{|n_1 \cos \theta_i + n_2 \cos \theta_r|^2}
\]  
(20)

where \(R_s\) and \(R_p\) are the reflection coefficient of the s-polarized and p-polarized lights, \(n_1\) is the refractive index of the air at standard condition for temperature and pressure (1.00027), \(n_2\) is the refractive index of the fermenter body (1.47, Borosilicate glass), \(\theta_i\) is the angle which the incident light makes to the normal of the interface, and \(\theta_r\) represents the angle which the transmitted light makes to the normal of the interface.

The relationship between the angles and refractive indices was given using the Snell’s law as follows [40]:

\[
\frac{\sin \theta_i}{\sin \theta_r} = \frac{n_2}{n_1}
\]  
(21)

In this case, the tungsten lamp as an incandescent light source produces unpolarized light [41]. According to the Fresnel equations, the reflection coefficient of an unpolarized light \((C_r)\) can be regarded as the average of \(R_s\) and \(R_p\) [40]. It should be noted that the refractive indices of air \((n_1)\) and bioreactor glass \((n_2)\) were extracted from the refractive index database website [42]. In this study, because the light reaches the fermenter surface from various directions, the incidence angle was considered in a variable range from 1 to 90°. Finally, the average of reflections occurred in the incident angles from 1 to 90° by 1° interval for unpolarized light was found to be 0.145. To calculate the delivered light exergy to the fermenter, the exergy balance equation for the tungsten lamp proposed by Asada and Shukuya [43] was used in this study. By means of a schematic illustration (Fig. 5), the main factors including the input and output terms used for writing the exergy balance are shown.
The energy balance equation for the tungsten lamp can be presented as follows:

$$W_d = q_{TL} + L_R$$  \hspace{1cm} (22)

where $W_d$, $q_{TL}$, and $L_R$ are the power supplied to the lamp, heat transferred from the lamp bulb surface to the ambient, and radiation light emitted from the bulb surface, respectively.

In addition, the second law of thermodynamic balance for the lamp used can be written as follows:

$$S_{in} + S_{gen} = S_{rad} + \frac{q_{TL}}{T_{TL}}$$ \hspace{1cm} (23)

where $S_{in}$ denotes the entropy flux accompanied with electricity supply, $S_{gen}$ shows the total entropy generated at the lamp subsystems, $S_{rad}$ stands for the entropy flux accompanied by radiation energy emitted from the lamp surface, and $T_{TL}$ is the temperature of the bulb surface. Furthermore, the value of $S_{in}$ can be considered to be zero since the work is entropy free. Eventually, the exergy balance for the lamp can be obtained using the following equation:

$$E_{xin} = E_{xrad} + \left(1 - \frac{T_0}{T_{TL}}\right)q_{TL} + E_{xdes,TL}$$ \hspace{1cm} (24)

where $E_{xin}$ shows the exergy flux of electrical power, $E_{xrad}$ denotes the exergy flux accompanied with visible radiation emitted by the tungsten lamp, $E_{xdes,TL}$ represent the total exergy destroyed in the tungsten lamp subsystems.

The overall exergy destruction of the tungsten lamp and the exergy flux of visible radiation emitted by the tungsten lamp can be found using the following equations:

$$E_{xdes,TL} = T_0S_{gen}$$ \hspace{1cm} (25)

$$E_{xrad} = L_R - T_0S_{rad}$$ \hspace{1cm} (26)

According to the above mentioned theory, Shukuya [44] found that about 34% of the incident light from an incandescent lamp (tungsten lamp) was useful work or exergy. On this basis, the light exergy delivered to the culture media was obtained using the following equation:

$$E_{xSG} = (1 - \alpha)\alpha A_I_{TL}$$ \hspace{1cm} (27)

where $\alpha$ represents the energy to exergy ratio (0.34), $A_I$ shows the surface area of the photobioreactor receiving the light, and $I_{TL}$ and the light intensity, respectively.

According to the above-mentioned theory and assumptions, the exergetic value of the tungsten light delivered to the culture media was computed to be at 36.61 J/s.

The rational exergy efficiency of the photobioreactor was determined as follows:

$$\eta = \frac{E_{xout}}{E_{xin}}$$

$$= \frac{E_{xMO,1} + E_{xLM,1} + \left(E_{xLM,out} + E_{xSG,out} + E_{xCW,out}\right)\Delta t}{E_{xMO,1} + E_{xLM,1} + \left(E_{xLM,in} + E_{xSG,in} + E_{xCW,in}\right)\Delta t}$$ \hspace{1cm} (28)

In addition to the rational exergy efficiency and for decision making on the syngas flow rate and agitation speed by taking into account the exergy of biohydrogen produced during continuous fermentation, the process exergetic efficiency was also defined as follows:

$$\psi = \frac{E_{xH}_1}{E_{xin}}$$

$$= \frac{E_{xMO,1} + E_{xLM,1} + \left(E_{xLM,out} + E_{xSG,out} + E_{xCW,out}\right)\Delta t}{E_{xMO,1} + E_{xLM,1} + \left(E_{xLM,in} + E_{xSG,in} + E_{xCW,in}\right)\Delta t}$$ \hspace{1cm} (29)

where $E_{xH}_1$ is the chemical exergy rate of the produced hydrogen.

Moreover, the dimensionless normalized exergy destruction was computed using the following equations:

$$N_{ex,des} = \frac{E_{xdes}}{E_{xin}}$$ \hspace{1cm} (30)

### Results and discussions

**Exergy analysis of syngas**

The effect of syngas flow rate and agitation speed on the exergy flow rate of inlet and outlet syngases during 1284 h of continuous CO fermentation are presented in Fig. 6. The exergetic values of the inflow and outflow gases were found to be in the range of 0.67–1.90 kJ/s and 0.41–1.91 kJ/s, respectively. In general, a similar trend was observed between syngas flow rate and its corresponding exergetic inflow rate (compare Figs. 2 and 6). This occurred due to that fact an increase in the flow rate of inlet syngas enhanced the mole flow rate into the bioreactor, which in turn augmented the inflow exergy, based on the Eq. (8). Obviously, the exergy of the outflow syngas was remarkably lower that the inflow syngas for all the syngas flow rates and agitation speeds. This could be attributed to the bioconversion of the harmful carbon monoxide with higher standard chemical exergy into the hydrogen and carbon dioxide with lower standard chemical exergies via the WGS reaction (Table 2). Moreover, the exergy of the outflow syngas followed a similar trend to that observed for the inflow syngas. In better words, the exergy of the outflow syngas was profoundly influenced by the exergy of inflow syngas.

**Exergy analysis of microorganisms**

Fig. 7 shows the exergy and eco-exergy values of the microorganisms accumulated in the bioreactor during 1284 h of continuous fermentation time. The maximum exergetic and eco-exergetic values of the microorganisms accumulated in the bioreactor were found to be 176.57 kJ and 1500.87 kJ, respectively, with the liquid media flow rate of 5 mL/min and agitation speed of 300 rpm. However, both exergy and eco-exergy values of the microorganisms remained almost constant with various agitation speeds and syngas flow rates during CO fermentation process, indicating the stable performance of the bioreactor. Moreover, both accumulated exergy and eco-exergy quantities of the microorganisms fluctuated at lower agitation speeds because of an inadequate mixing process. However, these values reached their stable magnitudes at higher agitation speeds owing to the higher
mass transfer rates. It should also be mentioned that higher agitation speeds could lead to cell damage and insufficient CO uptake and hydrogen production due to the higher shearing force. The most extreme drop was observed in the exergy and eco-exergy values of the microorganisms accumulated in the bioreactor at the end of fermentation time because of the higher shearing force at higher agitation speeds. Additionally, the eco-exergy value of the microorganisms at a given time was considerably higher than its corresponding chemical exergy, since the eco-exergy approach reflects the work of information embedded in the genomes of living organisms in the exergetic computations as well. Nonetheless, both exergy and eco-exergy values of the microorganisms at a given time had a similar tendency because of multiplying the chemical exergy of the microorganisms and weighting factor (β) in measuring the eco-exergy quantity.

The exergy and eco-exergy values of the outflow microorganisms from the bioreactor during 1284 h of continuous fermentation times are manifested in Fig. 8. Both exergetic and eco-exergetic values of the microorganisms leaving the bioreactor had similar trends to those of exergy and eco-exergy of the microorganisms accumulated in the bioreactor. Even though the mass flow rate of the fresh liquid media was constant during this study, it must be noted that its augmentation could have enhanced both exergy and eco-exergy values of the microorganisms exhausting from the bioreactors owing to the unfavorable wash-out phenomenon at higher liquid media flow rates. This could have profoundly diminished the cell population in the bioreactor and subsequently CO uptake and H₂ production.

**Exergy analysis of liquid media**

Fig. 9 explains the exergy rates of inflow and outflow liquid media into/from the bioreactor during 1284 h of continuous CO fermentation. Furthermore, the exergetic value of the culture media is also illustrated in this figure. The exergy of
the liquid media leaving the bioreactor was drastically lower than the exergy of inflow fresh liquid media. This was ascribed to the fact the carbon source and water available in the culture media were consumed during the fermentation process for bacterial growth and hydrogen production, respectively. This in turn lowered the exergy of liquid media exhausting from the bioreactor. Obviously, the exergy of the culture media dramatically dropped at the beginning of fermentation process due to the rapid growth of microorganisms. It could be concluded that the cell growth or exergy of the microorganism was the main factor affecting the exergy magnitude accumulated in the bioreactor.

**Overall exergy analysis of photobioreactor**

Fig. 10 describes the exergy destruction rates in the bioreactor during 1284 h of continuous CO fermentation process using both exergy and eco-exergy concepts. There was no significant difference in the exergy destruction obtained using both approaches possibly due to the sluggish growth of the microorganisms and low volume of the applied bioreactor. Nevertheless, there is no doubt that the eco-exergy approach should be employed for energy conversion systems containing living organisms. The maximum exergy destruction rate was found to be 1.24 kJ/s using both approaches when the agitation speed was set at 500 rpm. The exergy destruction in the bioreactor could be caused by various sources such as intensive chemical and biochemical reactions, rapid heat and mass transfer phenomena, harsh mixing process, substrate consumption by microorganism, as well as bacterial cell growth and death. However, it is interesting to note that the exergy destruction rate of the process increased harmonically with increasing the agitation speed of the impellers. This meant that the exergy destruction rate in the bioreactor was profoundly influenced by the mechanical work delivered to the culture media. It is worth mentioning that the light intensity could also be another important factor influencing the exergy destruction during photobiological processes.
hydrogen production. Therefore, the resource destruction could be avoided during photobiological hydrogen production if one could sustain hydrogen production at the lowest feasible light intensity and agitation speed.

The dimensionless normalized exergy destruction in the bioreactor during 1284 h of continuous fermentation process using both exergy and eco-exergy approaches are depicted in Fig. 11. This indicator by taking into account the exergy of hydrogen produced during fermentation could provide meaningful information compared to those obtained using the formal exergy destruction. The minimum normalized exergy destruction was found to be at 0.40 and 0.27 using exergy and eco-exergy approaches, respectively, at the liquid inflow rate of 14 mL/min and agitation rate of 300 rpm. However, a similar trend was observed for the normalized exergy destruction based on both conventional exergy and eco-exergy concepts, as previously elucidated. In general, this indicator can be effectively utilized for designing and optimizing industrial continuous photobioreactors to simultaneously improve the sustainability and productively of biological hydrogen production.

Fig. 12 exhibits the effect of syngas inflow rate and agitation speed on the rational and process exergy efficiencies using both conventional and eco-exergy concepts. The maximum rational exergy efficiency was found to be 98.21% and 98.79% using conventional exergy and eco-exergy concepts, respectively, at the syngas flow rate of 14 mL/min and agitation speed of 300 rpm. However, the maximum process exergetic efficiency was determined at 22.27% and 22.09 via conventional exergy and eco-exergy approaches, respectively, at the syngas flow rate of 12 mL/min and agitation speed of 500 rpm. This reveals the obvious debility of the rational exergy efficiency in diagnosing the sustainable and productive operational condition during analyzing the energy conversion systems. Therefore, the conceptual indicators like process exergetic efficiency should be considered in evaluating

![Fig. 10](image1.png) The effect of syngas volume flow rate and agitation speed on exergy destruction rate in the bioreactor during 1284 h of continuous fermentation.

![Fig. 11](image2.png) The effect of syngas volume flow rate and agitation speed on dimensionless normalized exergy destruction in the bioreactor during 1284 h of continuous fermentation.
Conclusions

The exergetic performance of a continuous photobioreactor during 1284 h of continuous CO fermentation at various liquid media flow rates and agitation speeds was conducted using both conventional and eco-exergy concepts. The maximum process exergetic efficiency was found to be 22.27% and 22.09, while the system exergetic efficiency was 98.21% and 98.79% using the conventional exergy and eco-exergy concepts, respectively. Obviously, the process exergetic efficiency was remarkably lower than the system exergetic efficiency. However, the process exergetic efficiency could provide meaningful information by creating a conceptual linkage between the exergy of the produced hydrogen and the exergy supplied into the photobioreactor. The results showed that exergy analysis could provide useful insights into the identification and quantification of irreversibilities in photobiological hydrogen production systems. Finally, the application of the detailed exergoeconomic and exergoenvironmental analyses along with advanced optimization techniques for decision making on operational conditions of large-scale continuous photobioreactors for hydrogen production must be taken into account in future studies. Such comprehensive analyses could lead to discounting the thermodynamic inefficiency, the overall cost, and the overall environmental impact of photobiological hydrogen production.

R E F E R E N C E S
