Exergy-based performance analysis of a continuous stirred bioreactor for ethanol and acetate fermentation from syngas via Wood–Ljungdahl pathway

Mortaza Aghbashlo a,*, Meisam Tabatabaei b,c,*, Ali Dadak a, Habibollah Younesi d, Ghasem Najafpour e

a Department of Mechanical Engineering of Agricultural Machinery, Faculty of Agricultural Engineering and Technology, College of Agriculture and Natural Resources, University of Tehran, Karaj, Iran
b Microbial Biotechnology and Biosafety Department, Agricultural Biotechnology Research Institute of Iran (ABRII), P.O. Box 31535-1897, Karaj, Iran
c Biofuel Research Team (BRTeam), Karaj, Iran
d Department of Environmental Science, Faculty of Natural Resources, Tarbiat Modares University, Nour, Mazandaran, Iran
e Faculty of Chemical Engineering, Noshirvani University of Technology, Babol, Iran

HIGHLIGHTS

• Exergy analysis as a decision-making tool for sustainability appraisal of continuous ethanol and acetate fermentation.
• Effect of liquid media and syngas flow rates as well as agitation speed on exergetic performance parameters of the bioreactor.
• 450 rpm agitation speed, 0.55 ml/min liquid media flow rate, and 8 ml/min syngas A flow rate as the best operational condition.
• Potential application of the developed approach to facilitate ongoing attempts to improve the performance of bioreactors.

ABSTRACT

In this work, a thermodynamic framework was proposed to achieve improved process understanding of ethanol and acetate fermentation in a continuous stirred tank bioreactor from syngas through the Wood–Ljungdahl pathway. The bioreactor performance was evaluated using both conventional exergy and eco-exergy principles to identify the effect of different operational parameters i.e. agitation speeds and liquid media flow rates as well as syngas volume flow rates and its composition on the sustainability and renewability of the process. The exergy efficiency of the bioreactor was found to be in the range of 8.14–89.51% and 8.86–89.52% using the conventional exergy and eco-exergy concepts, respectively. The maximum exergetic productivity index was found to be 6.82 and 6.90 using the conventional exergy and eco-exergy concepts, respectively, at agitation speed of 450 rpm, liquid media flow rate of 0.55 ml/min, and syngas volume flow rate of 8 ml/min containing 10% CO2, 15% Ar, 20% H2, and 55% CO. In general, the exergetic performance parameters computed using both concepts under the studied conditions did not display significant differences because of the low volume of the bioreactor and slow growth rate of the microorganisms. The results of the present study showed that exergy concept and its extensions could undoubtedly play a strategic role in assessing biofuel production pathways with respect to the issues currently of major interest in the renewable energy industry, i.e., sustainability and productivity.

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1. Introduction

It is anticipated that the rapid depletion of fossil fuel reserves because of increasing global energy utilization accompanied with increasing population and rising life standards will lead to their shortage and higher prices in the near future (Akia et al., 2014). These problems will become even more serious because of the
detrimental environmental impacts of fossil fuels such as global warming, climate changes, acid rain, and stratrospheric ozone exhaustion (Rahimnejad et al., 2014; Atabani et al., 2014). Within recent decades, carbon neutral biofuels produced from non-edible feed stocks (second generation biofuels) has been taken into account as one of the substitutes for fossil fuels since they do not compete with the food industry over land and water use (Mohammadi et al., 2014). Amongst the second generation biofuels technologies, lignocellulosic biomass gasification and subsequent Fischer–Tropsch synthesis has been shown to be one of the most applicable techniques for converting the non-food crops to more useful forms of energy and organic materials. Recently, conversion of the produced syngas into biofuels and biomaterials by microbial catalysts has received considerable attention compared to chemical catalysts. These natural catalysts can upgrade syngas components into various desired end-products such as acetate, butyrate, ethanol, and buthanol (Elshahed, 2010; Dusséaux et al., 2013). Despite the promising nature of such processes, it is still vital for researchers to find the most sustainable and economical pathways for the development of biofuel industries.

Nowadays, thermodynamic analysis, particularly exergy analysis, has attracted extraordinary interests as a key engineering tool for system design, analysis, and optimization of energy conversion systems (Colak and Hepbasli, 2007; Colak et al., 2008; Icier et al., 2010; Hepbasli et al., 2010). In general, exergy refers to the maximum amount of theoretical work that could be generated by a stream of matter, heat or work as it reaches an equilibrium with a reference state (Aghbashlo et al., 2012a, 2012b; Ofari-Boateng et al., 2012a, 2012b, 2012c; Aghbashlo et al., 2015; Dadak et al., 2015; Hosseini et al., 2015). Unlike energy analysis, exergy analysis has been proved to be an efficient and reliable tool for evaluating various biofuels synthesizing routes especially owing to the ability of determining the value of the thermodynamic irreversibilities.

In this sense, a considerable amount of published papers can be found in the literature on the application of exergy concepts for analyzing available and new pathways proposed for ethanol production (Ofori-Boateng and Lee, 2013; Ofori-Boateng and Lee, 2014; Ortiz and de Oliveira, 2014). For instance, Ojeda and Kafarov (2009) applied exergy concept to assess two kinds of enzymatic hydrolysis reactors operating on lignocellulosic biomass for second generation bioethanol production. Later, Ojeda et al. (2011a) applied both energy and exergy analyses along with process integration methodologies for production of bioethanol from acid-pretreated bagasse using different process configurations including sequential hydrolysis and fermentation, simultaneous saccharification and fermentation, and simultaneous saccharification and co-fermentation. In the same year, Dias et al. (2011) used thermoeconomic analysis for calculating exergy-based costs of electricity and ethanol for a traditional Rankine cycle and biomass integrated gasification combined cycle. Ojeda et al. (2011b) also compared four ethanol production chains through the use of the typical daily amount of residual biomass generated by the sugar industry using exergy concept. In a recent study, exergetic life cycle assessment was employed by Ofori-Boateng and Lee (2014) to evaluate thermo-environmental renewability of an oil palm based biorefinery approaches for mutual production of cellulosic ethanol and phytochemicals from oil palm fronds. Moreover, Ortiz and de Oliveira (2014) evaluated four pretreatment technologies including steam explosion, organosolv, liquid hot water, and steam explosion plus liquid hot water via exergy analysis to prepare lignocellulosic biomass for bioethanol production from sugarcane bagasse.

Although a large number of reports have been published on the production of various biofuels from syngas via natural catalysts (Kundhiyana et al., 2010; Maddipati et al., 2011; Liu et al., 2012, 2014), the exergetic performance of such bioreactors has not yet been investigated, to the best of our knowledge. Therefore, the aim of current survey was to conduct the exergy analysis of a continuous ethanol and acetate fermentation from syngas through the Wood–Ljungdahli pathway at different agitation speeds and liquid media flow rates as well as syngas volume flow rates and its compositions to achieve the optimal conditions. This was the first time that an exergy analysis was performed on a continuous bioreactor used for liquid fuel production from syngas using microbial catalysts. The findings of such a study would be beneficial to policy makers and researchers for identifying the most appropriate conditions to achieve an eco-benign and highly efficient route for biofuels production. In general, exergy analysis could aid to develop strategies and guidelines for more sustainable and effective biofuel production using various routes.

2. Materials and methods

2.1. Microorganism, culture media, and syngas

The detailed information on the continuous ethanol and acetate fermentation via Clostridium ljungdahlii can be found in our previous publications (Younesi et al., 2005; Mohammadi et al., 2012). A pure culture of the bacteria C. ljungdahlii ATCC 55383 used for acetate and ethanol fermentation from syngas was obtained from the American Type Culture Collection (USA). The microbes were grown in a rich ATTC media in an incubator shaker (Barnstead/Lab-Line, MaxQ 4000, USA) at 37 °C anaerobically. For the growth stage, the microbial culture prepared was transferred into Wheaton serum bottles made of Borosilicate glass, containing 50 ml liquid medium of the following compounds: NH4Cl (1 g/L), KCl (0.1 g/L), MgSO4·7H2O (0.2 g/L), NaCl (0.8 g/L), KH2PO4 (0.1 g/L), CaCl2·2H2O (0.02 g/L), yeast extract (1 g/L), NaHCO3 (2 g/L) and fructose (5 g/L). The trace element solution was prepared by mixing the following chemicals (10 mL): Nitriloacetic acid (2 g), MnSO4·H2O (1 g), NaCl (1 g), (NH4)2Fe (SO4)2·6H2O (0.8 g), CoCl2·6H2O (0.18 g), ZnSO4·7H2O (0.2 g), CuCl2·2H2O (0.1 g), NiCl2·6H2O (0.01 g), CuSO4·5H2O (0.01 g), Na2MoO4·2H2O (0.01 g), Na2SeO3 (3 mg) and Na2WO4·2H2O (3 mg). Vitamin solution (10 ml) included: biotin (2 mg), folic acid (2 mg), pyridoxine-HCl (10 mg), thiamine-HCl (5 mg), riboflavin (5 mg), nicotinic acid (5 mg), calcium (–)+ pantothenate (5 mg), cyanocobalamin (0.1 mg), p-aminobenzoic acid (5 mg) and thioctic acid (5 mg). Also, reducing agent was prepared in 100 ml distilled water: NaOH (0.9 g), cysteine HCl (4 g) and Na2S·9H2O (4 g). The reducing agent and fructose were separately autoclaved and added into the media solution.

Fig. 1 schematically represents the experimental set up applied for acetate and ethanol fermentation with automatic temperature and pH controls. The defined medium containing vitamin solution, trace metals, sodium bicarbonate and reducing agent was used to prepare the inocula and for cultivation of the cells in the bioreactor. The medium was reduced by adding 10 mL of Na2S·9H2O solution (10% w/v). Moreover, the bioreactor temperature was kept at a constant temperature of 37 °C. Fig. 2A shows the continuous bioreactor operation at various fresh liquid flow rates and agitation speeds while Fig. 2B shows the variations applied in syngas volume flow rates and its compositions throughout the ethanol and acetate fermentation process. It must be noted that three different compositions of syngas blended for industrial application (Air Products, Malaysia) were used in this study. The syngas A consisted of 10% CO2, 15% Ar, 20% H2, and 55% CO. While the syngas B composed of 15% Ar, 15% H2, and 70% CO. Furthermore, the syngas C was pure CO. To simulate the industrial bioethanol production plants equipped with gasification units, three types of
syngas with different chemical compositions were used and their effects on the exergetic performance of the bioreactor were assessed. Generally speaking, gasification is a process through which organic matters are converted mainly into CO, CO₂, H₂, and CH₄. Argon was used as the internal standard for the gas analysis in syngas A and B. The composition of the syngases used was close to that of different syngases obtained through the gasification process of biowastes (see also Table 1) (Couto et al., 2013). Such syngas could be achieved at an economical rate. The sampling and subsequent analyses of the liquid and syngas were performed in the same manner as comprehensively explained elsewhere (Younesi et al., 2005).

2.2. Theoretical considerations

Fig. 3 schematically represents the bioreactor as a control volume applied for exergy analysis including both input and output terms.

The mass and exergy balance equations (Eqs. (1) and (2), respectively) for the continuous bioreactor as a control volume can be given considering the details presented in Fig. 3 as follows:

\[
\frac{(m_{\text{MOL}} + \Delta t - m_{\text{MOL},i})}{\Delta t} + \frac{(m_{\text{CM}}, \Delta t - m_{\text{CM},i})}{\Delta t} = \left( \frac{m_{\text{LIM}, \text{in}} - m_{\text{LIM}, \text{out}}}{} \right)
\]

\[
+ \left( \frac{m_{\text{SG}, \text{in}} - m_{\text{SG}, \text{out}}}{} \right) + \left( \frac{m_{\text{CW}, \text{in}} - m_{\text{CW}, \text{out}}}{} \right) - m_{\text{MOL}, \text{in}}
\]

where \(m_{\text{MOL}}\) and \(m_{\text{CM}}\) represent the masses related to microorganisms and fresh liquid media, accumulated in the bioreactor, respectively, at times \(t\) and \(t + \Delta t\), while \(m_{\text{LIM}}\), \(m_{\text{SG}}\), and \(m_{\text{CW}}\) denote the mass flow rates of inflow and outflow liquid media, syngas, and cooling water, respectively. \(m_{\text{MOL}, \text{in}}\) shows the mass flow rate of living organisms leaving the bioreactor.

\[
\frac{(B_{\text{MOL}} + \Delta t - B_{\text{MOL},i})}{\Delta t} + \frac{(B_{\text{CM}}, \Delta t - B_{\text{CM},i})}{\Delta t} = \left( \frac{B_{\text{LIM}, \text{in}} - B_{\text{LIM}, \text{out}}}{} \right)
\]
where \( b_{OM} \) and \( B_{CM} \) stand for the exergetic quantities of culture media and microorganisms accumulated in the bioreactor, respectively, at times \( t \) and \( t + \Delta t \). Moreover, \( B_{IM} \), \( B_{SC} \), and \( B_{CW} \) denote the exergy flow rate of liquid media, syngas, and cooling water into/from the bioreactor, respectively. \( B_{W} \) and \( B_{MIOut} \) denote the exergetic flow rate of mechanical work transferred from the agitator to the liquid media and exergetic flow rate of microorganisms leaving the bioreactor, respectively. Finally, \( B_{des} \) presents the rate of the exergy destruction in the bioreactor during the experiment.

The exergy quantity of the culture media accumulated inside the continuous bioreactor at distinct times was found using the following formula:

\[
B_{CM} = n_{CM} \left( \sum_{i} y_{i} \beta_{i} + R_{T} \sum_{i} y_{i} \ln \left( \frac{T_{CM}}{T_{0}} \right) \right)
+ m_{CM} C_{CM} \left( T_{CM} - T_{0} - T_{0} \ln \left( \frac{T_{CM}}{T_{0}} \right) \right)
\]

(3)

where \( n_{CM} \) and \( m_{CM} \) denote the mole number and mass of material accumulated inside the bioreactor, respectively, and \( y_{i} \) and \( \beta_{i} \) represent the molar fraction and standard chemical exergy of the \( i \)th constituent accumulated inside the bioreactor, respectively. \( C_{CM} \) and \( T_{CM} \) are the specific heat capacity and temperature of the culture media, respectively. \( R \) denotes the gas constant (8.314 J/mol K). Finally, \( T_{0} \) represents the dead state temperature which was considered to be 25 \(^\circ\)C. It is worth mentioning that the specific heat capacity of the liquid media was postulated to be equal to the pure water, since at least 98% of the liquid media composed of the pure water.

Furthermore, the exergetical quantities of the inflow and outflow liquid media were computed using the following equation:

\[
B_{IM} = n_{IM} \left( \sum_{i} y_{i} \beta_{i} + R_{T} \sum_{i} y_{i} \ln \left( \frac{T_{IM}}{T_{0}} \right) \right)
+ m_{IM} C_{IM} \left( T_{IM} - T_{0} - T_{0} \ln \left( \frac{T_{IM}}{T_{0}} \right) \right)
\]

(4)

where \( n_{IM} \) and \( m_{IM} \) present the mole and mass rates of inflow and outflow liquid media, respectively, while \( y_{i} \) and \( \beta_{i} \) represent the molar fraction and standard chemical exergy of the \( i \)th constituent in the inflow and outflow liquid media, respectively. \( C_{IM} \) and \( T_{IM} \) stand for the specific heat capacity and temperature of the inflow and outflow liquid media, respectively.

The following linear mathematical formula reported by Song et al. (2012) was applied in order to compute the specific chemical exergy of organic materials used for preparation of the culture media or produced during fermentation:

\[
b_{OM} = 363.439C + 1075.633H - 86.308O + 4.14N + 190.798S - 21.1A
\]

(5)

\[
\beta_{OM} = M_{OM} b_{OM}
\]

(6)

where \( b_{OM} \) and \( M_{OM} \) represent the specific chemical exergy and molecular mass of an organic material (kg/mol), respectively, while C, H, O, N, S and A are the percentages of carbon, hydrogen, oxygen, nitrogen, sulphur, and ash in an organic material, respectively.

Additionally, the standard chemical exergy of the inorganic materials applied in this study were found using the report published by Wall (2009). Table 2 summarizes the standard chemical exergy of the inorganic materials used for culture media preparation according to Wall (2009). The following formula in addition to the data tabulated in Table 2 was applied to compute the standard chemical exergy of the remained inorganic materials which was not attainable in the literature.

\[
\beta = -\Delta G + \sum_{j} n_{j} \beta_{j} - \sum_{k} n_{k} \beta_{k}
\]

(7)

where \( \beta \) denotes the standard chemical exergy of inorganic material which was not accessible in the literature, \( \Delta G \) stands for the variation in Gibbs function for the reaction, \( n_{j} \) and \( n_{k} \) represent the mole of the products and reactants, respectively. Finally, \( \beta_{j} \) and \( \beta_{k} \) show the standard chemical exergy of the products and reactants, respectively.

The exergetic flow rates of the inflow and outflow syngas were found using the following equation:

\[
B_{SC} = n_{SC} \left( \sum_{m} y_{m} \beta_{m} + R_{T} \sum_{m} y_{m} \ln \left( \frac{T_{SC}}{T_{0}} \right) \right)
+ m_{SC} C_{SC} \left( T_{SC} - T_{0} - T_{0} \ln \left( \frac{T_{SC}}{T_{0}} \right) \right)
\]

(8)

where \( n_{SC} \) and \( m_{SC} \) show the mole and mass rates of the inflow and outflow syngas, respectively, \( y_{m} \) is the molar fraction related to each constituent, \( \beta_{m} \) represents the standard chemical exergy of the \( m \)th constituent, \( P \) and \( P_{0} \) depict the pressure of syngas and dead state (kPa), respectively, and \( C_{SC} \) and \( T_{SC} \) denote the specific heat capacity and temperature of the inflow and outflow syngas, respectively. Finally, it is worth quoting that the dead state pressure was supposed to be 100 kPa.

The specific heat capacity of the inflow and outflow gases was determined as follows:

\[
C_{SC} = \sum_{n} x_{n} C_{n}
\]

(9)

where \( x_{n} \) and \( C_{n} \) represent the mass fraction and specific heat capacity of each component, respectively.

The mathematical equations used in the calculation of the specific heat capacity of syngas components together with their standard chemical exergies are given in Table 3.

The exergy loss rate to the cooling water around the bioreactor was determined using the following formula:

\[
B_{CW} = m_{CW} C_{CW} \left( T_{CW} - T_{0} - T_{0} \ln \left( \frac{T_{CW}}{T_{0}} \right) \right)
\]

(10)

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

In addition, the following equation was utilized for computing the chemical exergy of the microorganisms accumulated in the bioreactor:

\[
B_{MO} = 18.7 m_{MO}
\]

(11)
where the chemical exergy of the constituent (Draganovic et al., 2013). Therefore, the following equations presented by Jørgensen et al. (2005) were used to calculate the eco-exergy (Φ) content of the living microorganisms.

\[
\Phi = \frac{7.34 \times 10^5 B_{MO} + B_{MO} \ln 20}{n_{\text{number of nucleotides}} - n_{\text{number of repeating genes}}} \quad (13)
\]

\[
0 = 1 + \ln(20) (n_{\text{number of repeating genes}} - n_{\text{number of nucleotides}}) - 7.34 \times 10^5 \quad (14)
\]

\[
W = \frac{n_{\text{number of nucleotides}}}{n_{\text{number of repeating genes}}} \quad (15)
\]

where \(\varrho\) represents the weighting factor reported by Jørgensen et al. (2005). This value was found to be 8.5 for bacteria referring to the genetic information carried by their genomes leading to have more energy work compared to the non-living constituents whose only possess chemical exergy.

The Reynolds number \((Re)\) which is needed for calculating the magnitude of the mechanical work transferred to the culture media for agitating the liquid in the bioreactor could be found using the equation given below:

\[
Re = \frac{nD^2}{\mu} \quad (16)
\]

where \(\rho\) denotes the fluid density, \(N\) is the speed of impeller. While, \(D\) and \(\mu\) are the impeller diameter and fluid viscosity, respectively.

Therefore, the magnitude of the mechanical work transferred to the liquid media is proportional to the Reynolds number was found according to the formula equation (Ismail et al., 2008):

\[
W = \frac{\varrho nD^2}{\mu} \quad (17)
\]

where \(W\) and \(\varrho\) represent the agitation work and power number of the agitation rate, respectively.

It should be highlighted that the agitator power was equivalent to the exergy rate of the mechanical work transferred to the liquid media in the bioreactor.

\[
B_W = W \quad (18)
\]

Moreover, the rational exergy efficiency of the bioreactor was achieved according to the following formula:

\[
\eta = \frac{B_{MO,t} + \Delta t + B_{IM,t} + \Delta t + (B_{IL,out} + B_{SG,out} + B_{MO,out} + B_{CW,out})}{B_{MO,t} + B_{IM,t} + (B_{IL,in} + B_{SG,in} + B_{CW,in} + B_W)} \Delta t \quad (19)
\]

Furthermore, the exergetic productivity index given below was used to calculate the optimum mass flow rate of the syngas based on the exergy of the products and the magnitude of the exergy.

Table 2

<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>0.92</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>NH4Cl</td>
<td>331.3</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KC1</td>
<td>19.62</td>
</tr>
<tr>
<td>Magnesium sulfate</td>
<td>MgSO4.H2O</td>
<td>87.44</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>14.32</td>
</tr>
<tr>
<td>Monopotassium phosphate</td>
<td>KH2PO4</td>
<td>50.07</td>
</tr>
<tr>
<td>Calcium chloride dodecahydrate</td>
<td>CaCl2.2H2O</td>
<td>89.72</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>C6H12O2</td>
<td>9305.46</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>NaHCO3</td>
<td>216.2</td>
</tr>
<tr>
<td>Fructose</td>
<td>C6H12O6</td>
<td>1091.57</td>
</tr>
<tr>
<td>Nitroacetic acid</td>
<td>C7H6O4N</td>
<td>2772.12</td>
</tr>
<tr>
<td>Manganese(II) sulfite hydrate</td>
<td>MnSO4.H2O</td>
<td>143.31</td>
</tr>
<tr>
<td>Zinc sulphate heptahydrate</td>
<td>ZnSO4.7H2O</td>
<td>88.64</td>
</tr>
<tr>
<td>Ammonium iron(II) sulfite hexahydrate</td>
<td>(NH4)2Fe(SO4)2.6H2O</td>
<td>885.39</td>
</tr>
<tr>
<td>Cobalt(II) chloride hexahydrate</td>
<td>CoCl3.6H2O</td>
<td>124.24</td>
</tr>
<tr>
<td>Copper(II) chloride dehydrate</td>
<td>CuCl2.2H2O</td>
<td>83.94</td>
</tr>
<tr>
<td>Nickel(II) chloride hexahydrate</td>
<td>NiCl2.6H2O</td>
<td>102.64</td>
</tr>
<tr>
<td>Copper(II) sulfate</td>
<td>CuSO4.5H2O</td>
<td>913.94</td>
</tr>
<tr>
<td>Sodium molybdate dehydrate</td>
<td>Na2MoO4.2H2O</td>
<td>22.44</td>
</tr>
<tr>
<td>Sodium tungstate dehydrate</td>
<td>Na2MoO4.2H2O</td>
<td>812.25</td>
</tr>
<tr>
<td>Sodium selenate</td>
<td>Na2SeO4</td>
<td>55.28</td>
</tr>
<tr>
<td>Biotin</td>
<td>C6H12N2O5S</td>
<td>6308.96</td>
</tr>
<tr>
<td>Folic acid</td>
<td>C6H8N4O4</td>
<td>9565.79</td>
</tr>
<tr>
<td>Pyridoxine HCl</td>
<td>C6H7NO3.HCl</td>
<td>4300.73</td>
</tr>
<tr>
<td>Thiamine HCl</td>
<td>C12H16N4O5.HCl</td>
<td>7587.87</td>
</tr>
<tr>
<td>Riboflavin</td>
<td>C11H14N4O6</td>
<td>8738.78</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>C10H14N2O6</td>
<td>2890.80</td>
</tr>
<tr>
<td>Calcium (++) pantothenate</td>
<td>CaH2(CO2)</td>
<td>9827.79</td>
</tr>
<tr>
<td>Cyanocobalamin</td>
<td>C42H70FeNiO14P</td>
<td>35107.88</td>
</tr>
<tr>
<td>p-aminobenzoic acid</td>
<td>C7H7NO2</td>
<td>3544.15</td>
</tr>
<tr>
<td>Thioctic acid</td>
<td>C18H19N3O5S2</td>
<td>5957.38</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>NaCH3CO2</td>
<td>873.59</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C2H5OH</td>
<td>1363.9</td>
</tr>
<tr>
<td>Sodium sulfite monohydrate</td>
<td>Na2S.2H2O</td>
<td>9295.18</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>74.94</td>
</tr>
</tbody>
</table>
| Cystine HCl       | C11H22N2O6.HCl  | 2494.38                          

Table 3

<table>
<thead>
<tr>
<th>Component</th>
<th>Mathematical equation for specific heat calculation ((\beta = \theta (\text{kelvin})/1000))</th>
<th>Standard chemical exergy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H2)</td>
<td>(C_h = 13.46 + 4.600 \times 10^{-5} + 3.790 \beta^3)</td>
<td>236.1</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>(C_CO = 1.10 - 0.46 \beta + 1.00 \beta^2 - 0.45 \beta^3)</td>
<td>275.30</td>
</tr>
<tr>
<td>Carbon dioxide (CO2)</td>
<td>(C_{CO2} = 0.45 + 1.67 \beta - 1.27 \beta^2 + 0.39 \beta^3)</td>
<td>19.87</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>(C_A = 0.52)</td>
<td>11.69</td>
</tr>
</tbody>
</table>

\(^a\) Obtained from Wall (2009).

\(^b\) Calculated based on Eqs. (5) and (6).

\(^c\) Calculated based on Eq. (7).

\(^d\) Obtained from http://www.expergeology.com/.
Table 4
Physical and chemical exergies parameters used to compute the photobioreactor’s exergetic performance indexes.

| Time (h) | Liquid media flow rate (mL/min) | Syngas type | Syngas flow rate (mL/min) | Agitation speed (rpm) | Exergy rate of inflow syngas (kJ/s) | Exergy rate of outflow syngas (kJ/s) | Exergy rate of inflow liquid (kJ/s) | Exergy rate of outflow liquid (kJ/s) | Exergy of culture media (kJ) | Exergy of micro-organism within culture media (kJ) | Eco-exergy of micro-organism within culture media (kJ) | Exergy of agitation (kJ/s) | Exergy of inflow cooling water (kJ/s) | Exergy of outflow cooling water (kJ/s) |
|---------|--------------------------------|-------------|---------------------------|----------------------|-------------------------------------|-------------------------------------|------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 120     | 0.65                           | A           | 14                        | 400                  | 1.9016                              | 0.4068                              | 0.0039                             | 0.0046                          | 852.2233                        | 73.0596                         | 621.0067                        | 0.3300                          | 0.0231                          | 0.0432                          |
| 240     | 0.55                           | A           | 12                        | 400                  | 1.6299                              | 0.8516                              | 0.0033                             | 0.0041                          | 915.0906                        | 81.5738                         | 693.3780                        | 0.3300                          | 0.0201                          | 0.0421                          |
| 360     | 0.55                           | A           | 8                         | 450                  | 1.0866                              | 0.3912                              | 0.0013                             | 0.0041                          | 904.5582                        | 93.6315                         | 795.8679                        | 0.4698                          | 0.0197                          | 0.0672                          |
| 480     | 0.55                           | A           | 12                        | 450                  | 1.6299                              | 0.7116                              | 0.0033                             | 0.0043                          | 943.0256                        | 95.0505                         | 807.9298                        | 0.4698                          | 0.0241                          | 0.0608                          |
| 600     | 0.55                           | B           | 14                        | 450                  | 2.1718                              | 0.3447                              | 0.0033                             | 0.0044                          | 980.1604                        | 24.1152                         | 204.9798                        | 0.4698                          | 0.0236                          | 0.0612                          |
| 720     | 0.55                           | B           | 14                        | 450                  | 2.1718                              | 0.9435                              | 0.0033                             | 0.0046                          | 1023.7706                       | 113.4981                        | 964.7344                        | 0.4698                          | 0.0241                          | 0.0609                          |
| 840     | 0.55                           | B           | 12                        | 500                  | 1.8615                              | 0.4886                              | 0.0033                             | 0.0048                          | 1064.2803                       | 131.9372                        | 1121.4667                       | 0.6445                          | 0.0208                          | 0.0809                          |
| 840     | 0.55                           | B           | 12                        | 500                  | 1.8615                              | 0.2782                              | 0.0033                             | 0.0044                          | 967.5359                        | 111.3653                        | 946.6054                        | 0.6445                          | 0.0216                          | 0.0813                          |
| 960     | 0.55                           | B           | 12                        | 550                  | 1.7064                              | 0.3740                              | 0.0033                             | 0.0042                          | 935.0311                        | 120.5933                        | 1025.0438                       | 0.8578                          | 0.0257                          | 0.0992                          |
| 1080    | 0.55                           | B           | 12                        | 550                  | 1.7064                              | 0.3740                              | 0.0033                             | 0.0042                          | 935.0311                        | 120.5933                        | 1025.0438                       | 0.8578                          | 0.0257                          | 0.0992                          |
| 1200    | 0.55                           | C           | 14                        | 550                  | 2.6238                              | 0.5892                              | 0.0033                             | 0.0048                          | 1061.6224                       | 152.5091                        | 1296.3280                       | 0.8578                          | 0.0189                          | 0.1003                          |
| 1320    | 0.55                           | C           | 10                        | 550                  | 1.8741                              | 0.3006                              | 0.0033                             | 0.0049                          | 1077.9182                       | 107.1082                        | 910.4198                        | 0.8578                          | 0.0204                          | 0.0987                          |
| 1440    | 0.55                           | C           | 8                         | 550                  | 1.4993                              | 0.3303                              | 0.0033                             | 0.0043                          | 939.4970                        | 46.1062                         | 391.9030                        | 0.8578                          | 0.0223                          | 0.1106                          |
| 1560    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.8681                              | 0.0033                             | 0.0049                          | 1070.2035                       | 137.6134                        | 1169.7143                       | 0.6445                          | 0.0256                          | 0.0817                          |
| 1680    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.5367                              | 0.0033                             | 0.0051                          | 1113.2470                       | 186.5577                        | 1585.7411                       | 0.6445                          | 0.0240                          | 0.0823                          |
| 1800    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.4875                              | 0.0033                             | 0.0052                          | 1148.0987                       | 170.2430                        | 1447.0655                       | 0.6445                          | 0.0232                          | 0.0900                          |
| 1920    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.5244                              | 0.0033                             | 0.0047                          | 1045.9601                       | 168.1186                        | 1429.0838                       | 0.6445                          | 0.0239                          | 0.0873                          |
| 2040    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.4673                              | 0.0033                             | 0.0048                          | 1066.2245                       | 169.5377                        | 1441.0707                       | 0.6445                          | 0.0232                          | 0.0809                          |
| 2160    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.3033                              | 0.0033                             | 0.0044                          | 971.1340                        | 126.2610                        | 1073.2192                       | 0.6445                          | 0.0234                          | 0.0804                          |
| 2280    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.2981                              | 0.0033                             | 0.0048                          | 1055.1325                       | 126.2610                        | 1073.2192                       | 0.6445                          | 0.0231                          | 0.0817                          |
| 2400    | 0.55                           | C           | 14                        | 500                  | 2.6238                              | 0.2530                              | 0.0033                             | 0.0051                          | 1130.6372                       | 124.1367                        | 1055.3624                       | 0.6445                          | 0.0240                          | 0.0846                          |
destruction during the fermentation time.

\[
\psi = \frac{B_{\text{EthOH}} + B_{\text{AC}}}{B_{\text{des}}}
\]  

(20)

where \(B_{\text{EthOH}}\) and \(B_{\text{AC}}\) represent the chemical exergy rate of the produced ethanol and sodium acetate, respectively.

Also, the sustainability index defined as a function of the rational exergy efficiency was computed as follows:

\[
SI = \frac{1}{1 - \psi}
\]  

(21)

Finally, the exergetic improvement potential rate was found using the formula given below:

\[
\psi = \frac{(1 - \psi)(B_{\text{in}} - B_{\text{out}})}{\Delta t}
\]  

(22)

### 3. Results and discussions

By way of example, Table 4 tabulates some of the physical and chemical exergies parameters used to compute the photobioreactor’s exergetic performance indexes. Obviously, the exergy rate of the inflow and outflow syngas followed by the exergy rate of agitation were the main components affecting the exergy balance of the photobioreactor. Moreover, the exergy of the culture media accumulated in the photobioreactor was remarkably higher than the exergy and eco-exergy of the living microorganisms. As presented in Table 4, the eco-exergy of microorganisms at a given time was drastically higher than its corresponding exergy value. This could be attributed to the fact that unlike the exergy approach, the eco-exergy approach takes into account the work of the genetic information carried by the microorganisms as considered in the eco-exergetic calculations.

Fig. 4A and B exhibits the effect of process variables on pH and cell dry weight as well as exergy and eco-exergy of the microorganisms accumulated in the bioreactor as a function of fermentation time. Obviously, the exergy and eco-exergy of microorganisms constantly augmented till 240 h of the fermentation process due to the remarkable growth of microorganisms during this period. However, the exergy and eco-exergy of the microorganisms reached their lower values at 588 and 1440 h of the process. This occurred due to the harsh acidic conditions developed in the bioreactor which must have led to cell damage or death by lowering carbon and electron flow from the substrate to the cells. Nevertheless, the exergy and eco-exergy of microorganisms recovered to their initial values by addition of 10 ml of Na2S·H2O solution (10% w/v) at those times. Younesi et al. (2006) reported similar findings for the cell dry weight of C. ljungdahlii during fermentation process (Fig. 4B). In better words, both exergy and eco-exergy of the microorganisms were exactly related to cell dry weight based on Eqs. (11) and (13). Furthermore, both exergy and eco-exergy values of the microorganisms at a given time had a similar trend. But the eco-exergy of the microorganisms was drastically higher than its chemical exergy content because of the incorporation of the work of the genetic information carried by microorganisms as considered in the eco-exergetic calculations.

Fig. 5 manifests the exergy and eco-exergy rates of the outflow microorganisms from the bioreactor as a function of the fermentation time. Similar trends were observed between both exergetic and eco-exergetic quantities of the microorganisms exhausting from the bioreactor and the exergy and eco-exergy of the microorganisms cumulated in the bioreactor. Interestingly, increasing the inflow rate of the liquid media could augment both exergy and eco-exergy values of the microorganisms leaving the bioreactor because of the unfavorable wash-out phenomenon at higher liquid media flow rates. This could extremely reduce the cell density and retention time in the bioreactor and consequently decrease ethanol and acetate formation.

Fig. 6 shows the effect of process variables on exergy flow rate of syngas entering into and exiting from the bioreactor during the fermentation process. The exergy flow rate of inlet syngas followed a trend similar to that of its volume flow rate (compare Figs. 2B and 6). This could be attributed to the fact the exergy of the inflow syngas was directly proportional to its molar rate. Moreover, the exergy rate of inflow syngas increased with increasing the CO percentage because of higher standard chemical exergy of CO compared with CO2, H2, and Ar (Table 3). It is interesting to note that the exergy flow rate of the outlet syngas decreased drastically due to the consumption of the carbon monoxide and hydrogen through the Wood–Ljungdahls pathway to
generate acetyl coenzyme A for supporting cell growth, fermenting ethanol and acetate, and producing carbon dioxide. The Wood-Ljungdahl pathway can be illustrated by the following reactions:

\[
6\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 4\text{CO}_2
\]  
(23)

\[
4\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{CO}_2
\]  
(24)

\[
6\text{CO} + 6\text{H}_2 \rightarrow 2\text{CH}_3\text{CH}_2\text{OH} + 2\text{CO}_2
\]  
(25)

In addition to the above mentioned reactions, carbon dioxide available in the inlet syngas as well as that generated through the Wood-Ljungdahl pathway may also participate in reactions involving hydrogen as an electron donor to generate acetate and ethanol as follows:

\[
2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O}
\]  
(26)

\[
2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}
\]  
(27)

It is worth mentioning that the fermented acetic acid was converted to sodium acetate in the presence of sodium bicarbonate in liquid media to support bacterial growth and as an organic end-product. The process can be represented using the following equations:

\[
\text{CH}_3\text{COOH} + \text{NaHCO}_3 \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{CO}_3
\]  
(28)

\[
\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2
\]  
(29)

The exergy of the outlet syngas remarkably decreased up to 120 h of the fermentation process owing to the rapid bioconversion of carbon monoxide and hydrogen to ethanol and acetate in the presence of adequate bacterial cell density in the bioreactor. Interestingly, the exergy of the outflow syngas approached the exergy of the inflow syngas at 294, 348, and 498 h of the fermentation process due to the poorer bio-upgrading of syngas into the fermentative products. It can be generally concluded that the exergy of the outflow syngas was profoundly influenced by the density of microbial cells or the exergy of the microorganisms.

Fig. 7 illustrates the effect of process variables on the exergy flow rate of the liquid media inflowing into and withdrawing from the bioreactor during 2472 h of the fermentation process. The effect of process parameters on the exergy of the culture media amassed in the bioreactor is also given in Fig. 7. Evidently, the exergy of the inflow liquid directly varied with the volume flow rate of liquid media based on Eq. (4) (also see Fig. 2A). Moreover, the exergy of the outflow liquid was remarkably higher than that of the inflow liquid at a given time due to the production of the ethanol and acetate by \textit{C. ljungdahlii} by uptaking carbon monoxide, hydrogen, and carbon dioxide present in the inflow syngas. However, the exergy of the inflow liquid was similar to the accumulated exergy in the bioreactor since the outlet liquid overflowed from the top of bioreactor. Also, the stored exergy in the bioreactor had a similar trend to that of the exergy of the microorganisms (compare Figs. 4A and 7), signifying that the cell population was the most important factor in the production of ethanol and acetate. It must be noted that a portion of the generated acetate was consumed by \textit{C. ljungdahlii} to propagate and accomplish Wood-Ljungdahl reactions.

Fig. 8A and B represents the effect of process variables on exergy destruction rate and exergetic productivity index of the fermentation process using both conventional exergy and eco-exergy concepts.
3.02 kJ/s using both concepts at the conditions surveyed. However, the highest exergetic productivity index was found to be 6.82 and 6.90 based on the conventional and eco-exergy concepts, respectively, at 450 rpm agitation speed, 0.55 ml/min liquid media flow rate, 8 ml/min syngas A volume flow rate containing 10% CO₂, 15% Ar, 20% H₂, and 55% CO. Intensive chemical and biochemical reactions, severe mixing processes, heat transfer to the coolant, utilization of substrate by microorganism, and reproduction and death of microorganisms could be mentioned as sources of exergy destruction during continuous ethanol and acetate fermentation. It is worth quoting that single exergy destruction or process yield cannot be a reliable performance metric for appraising such complicated process. Hence, a combination of the exergy destruction and process yield into a unified indicator, i.e., exergetic productivity index could be fruitfully applied as a decision-making tool to optimize the operational conditions of industrial bioreactors aiming at both improved system sustainability and biofuel production rate.

Although it was initially envisioned that the results of the conventional exergy and eco-exergy concepts would differ as the latter considers the work of the genetic information carried by the living fraction of the system, the eco-exergetic computations led to approximately similar results to those of the conventional exergy concept. This could be ascribed to the small size of the employed bioreactor or low population density of the microorganisms. In spite of that, it is still strongly recommended to use the eco-exergy principle for thermodynamic analysis of energy conversion systems involving living microorganisms as natural catalysts.

The effects of process variables on exergy efficiency and sustainability index of the ethanol and acetate fermentation over 2472 h of the fermentation process are displayed in Fig. 9A and B, respectively. The exergy efficiency of the fermentation process was found to be in the range of 8.14–89.51% and 8.86–89.52% using the conventional exergy and eco-exergy concepts, respectively. However, the sustainability index varied from a minimum value of 1.09 to a maximum value of 9.54 using both concepts. A comparison between the Figs. 8A and 9A reveals that the exergy efficiency of the process increased with decreasing the rate of exergy destruction, since the exergy efficiency was conversely related to the exergy destruction rate. It is worth mentioning that single exergy efficiency could not be employed as a decision-making to identify the most eco-friendly and cost-effective fermentation conditions. As a result, conceptual indicators like exergetic productivity index should be computed by taking into account the rate of products formation. This means that the thermodynamic investigation of biological fuel production must be supported by process considerations to improve not only the production rate but also the environmental savings. Obviously, both exergy efficiency and sustainability index of the fermentation process had a similar trend over the processing time because of the direct relation between them according to Eq. (20).

Table 5 tabulates the maximum rational exergy efficiency of various bioethanol production pathways previously reported in the literature. The exergy efficiency of syngas bioconversion into ethanol using microbial catalysts was well above the average bioethanol production by other methods. Thus, this environmental-benign route of bioethanol production can be a promising alternative to the other available routes for sustainable, cost-effective, and eco-friendly production of bioethanol.

Fig. 10 exhibits the effect of process variables on exergetic improvement potential rate of fermentation process during 2472 h
using both conventional exergy and eco-exergy concepts. The exergetic improvement potential rate was found to be in the range of 0.02–2.77 kJ/s using both concepts. The exergetic improvement potential rate of the fermentation process was found directly related to the exergy destruction rate and was inversely related to the exergy efficiency according to Eq. (21). Overall, the maximum improvement in the exergy efficiency of the fermentation process could be achieved when the exergy destruction was minimized. Moreover, the findings of the present study showed that exergy analysis could offer a more holistic substitute to many available techniques for environmentally-conscious decision making. Therefore, exergy analysis should be employed to design and optimize biological energy conversion systems to achieve the highest feasible thermodynamic efficiencies.

4. Conclusions

The exergetic performance assessment of a continuous ethanol and acetate fermentation from syngas using C. ljungdahlii in a 2 L bioreactor under controlled pH condition was carried out by the use of conventional exergy and eco-exergy concepts. These approaches were used to establish a conceptual framework for decision making on liquid media flow rate, syngas volume flow rate, and agitation speed for identifying the most sustainable and productive operational conditions. The highest exergetic productivity index was found to be 6.82 and 6.90 using the conventional exergy and eco-exergy theorems, respectively. This occurred when the liquid media flow rate, syngas A volume flow rate, and agitation speed were adjusted to 0.55 ml/min, 8 ml/min, and 450 rpm, respectively. Even though the exergetic performance parameters of the bioreactor showed similar trends using both concepts, the eco-exergy approach could be strongly suggested for sustainability appraisal of energy conversion systems embedding living organisms. Moreover, comprehensive optimization studies must be carried out using advanced optimization techniques like evolutionary paradigms in order to increase the sustainably and productivity of such bioreactors. Generally, the exergetic results reported herein not only will be beneficial for the determination of optimum design of industrial-scale bioreactors, but also could provide invaluable insights into the resource destruction in bioethanol fermentation systems. Finally, integrated approaches like exergoeconomic and exergoenvironmental analyses are suggested for improving exergetic parameters as they could provide additional information on the real cost and environmental impacts of biofuel production systems.

Nomenclatures

- \( A \) ash percentage (%)
- \( b \) specific exergy (kJ/kg)
- \( B \) exergy (kJ)
- \( B' \) exergy rate (kJ/s)
- \( C \) specific heat capacity (kJ/kg K)
- \( C' \) carbon percentage (%)
- \( D \) impeller diameter (m)
- \( G \) Gibbs function (kJ)
- \( H \) hydrogen percentage (%)
- \( IP \) exergetic improvement potential rate (kJ/s)
- \( m \) mass (kg)
- \( M \) molecular mass (kg/mol)
- \( m' \) mass flow rate (kg/s)
- \( n \) mole number (dimensionless)
- \( n' \) mole flow rate (mol/s)
- \( N \) impeller speed (rpm)
- \( \eta \) power number (dimensionless)
- \( O \) oxygen percentage (%)
- \( P \) pressure (kPa)
- \( R \) universal gas constant (8.314 J/mol K)
- \( Re \) Reynolds number (dimensionless)
- \( S \) sulphur percentage (%)
- \( SI \) sustainability index (dimensionless)
- \( T \) temperature (K)
- \( W \) agitation work (kW)
- \( x \) mass fraction (dimensionless)
- \( y \) molar fraction (dimensionless)

Subscripts

- \( 0 \) dead state
- \( AC \) acetate
- \( Ar \) argon
- \( CM \) culture media
- \( CO \) carbon monoxide
- \( CO_2 \) carbon dioxide
- \( CW \) cooling water
- \( des \) destruction
- \( EthOH \) ethanol
- \( H_2 \) hydrogen
- \( i,j,k,l,m,n \) numerator
- \( in \) inlet
- \( LM \) liquid media
- \( MO \) microorganism
- \( out \) outlet
- \( SG \) syngas
- \( t \) time (h)
- \( W \) work
- \( \Delta t \) time interval (h)

Greeks

- \( \beta \) standard chemical exergy (kJ/mol)
- \( \Phi \) eco-exergy content of the living microorganisms
- \( \Phi' \) weighting factor
- \( \rho \) fluid density (kg/m³)
References


