

Article

# Microbial Electrolysis Cell Exergy Evaluation

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**Abstract:** Bio-electrochemical systems have increasingly become the focus of research due to their potential in environmental biotechnology, particularly in the domains of waste utilization and energy recovery. A prominent method within this domain is the transformation of organic matter into hydrogen via microbial electrolysis cells (MECs). This study offers a thorough analysis of MEC performance, employing exergy analysis and incorporating relevant data from the existing literature. The findings of this research indicate a relationship between process efficiency and effective electron transfer originating from biological oxidation to the cathode reaction, facilitating hydrogen generation. The assessment performed revealed that the exergy efficiency of the process varies by a wide range, depending on conditions such as substrate type and concentration, applied external voltage, and the presence of specific inhibitors. This interplay between substrate concentration, overall efficiency, and energy requirement underlines the complex dynamics of optimizing MEC performance. Our insights provide understanding of the challenges in bio-electrochemical systems, offering implications for their sustainable and efficient use in environmental biotechnology. The theoretical analysis involved assessing the utilization of glucose and glycerol, along with the evaluation of electrical energy consumption and hydrogen yield. Our results demonstrate that a higher applied voltage is associated with greater exergy efficiency. Furthermore, after comparing the use of glucose and glycerol as substrates, our study supports the preferential application of glucose for enhanced efficiency.

**Keywords:** microbial electrolysis cell; exergy balance; hydrogen



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## 1. Introduction

The ever-increasing global population and industrial development have led to a substantial surge in energy demands. This trend is evidenced by a 55% rise in energy consumption from 1990 to 2018, with an additional 42% increase anticipated by 2050 [1]. Concurrently, rapid urbanization and reliance on fossil fuels for energy production have significantly elevated greenhouse gas (GHG) emissions, which are now noticeably impacting the climate. The past decade marked a crucial period in the development of diverse policy initiatives aimed at reducing GHG and CO<sub>2</sub> emissions through the adoption of clean, green energy sources with a lower carbon footprint. While hydrogen (H<sub>2</sub>) is acknowledged as one of the most energy-dense and clean fuels, a mere 2% of the hydrogen produced is utilized for energy and heating purposes [1,2]. Predominantly, hydrogen gas is employed in chemical synthesis, such as in the production of methane and ammonia [1,3], and its role as an alternative energy source for the transportation sector is only beginning to be recognized in some developed countries [1].

Despite hydrogen's high energy content and the fact that its combustion only yields water vapor, thus not contributing to GHG emissions, acid rain, or ozone depletion [4], fossil fuels remain the primary raw material for commercial hydrogen production, accounting for 96% of the market [2,4]. Given the non-renewable nature and high cost of this production method, there is a growing need for alternatives that can reduce the environmental footprint. One such promising avenue is the utilization of various waste streams—including food, agricultural, and water waste—as substrates for hydrogen production [1].

The recognition of hydrogen ( $H_2$ ) as a key element in achieving energy sustainability has led to a significant increase in its production, underscoring its potential as a renewable energy source. Various methodologies are employed for hydrogen production, including thermochemical, electrolytic, photochemical, and biological processes. However, a major concern arises from the fact that hydrogen production from fossil fuels results in carbon dioxide emissions, adversely affecting the ecosystem [5]. Presently, fossil fuels remain the predominant raw material for hydrogen production, constituting 96% of commercially available hydrogen [2,6]. Given that this source is not renewable, and that the associated production process is economically demanding, there is an imperative need for alternative methods that can lower the environmental footprint.

Hydrogen stands out as an exceptionally favorable fuel due to its unparalleled energy content per unit weight, which surpasses all other known fuels. Consequently, it is widely recognized as a critical energy source across various industries. Notably, hydrogen possesses an energy content approximately three times greater than that of conventional fuels such as gasoline and natural gas. Specifically, the energy content of hydrogen is 120 MJ/kg, in contrast to gasoline's 44 MJ/kg [7]. In addition to its superior energy density, another significant advantage of hydrogen is its role as an energy carrier. This capability allows hydrogen to effectively store, transport, and deliver energy derived from other sources, enhancing its utility in a diverse range of applications.

In the pursuit of greater sustainability within the energy sector, and addressing the challenges posed by climate change, recent efforts towards developing alternative energy sources have significantly intensified. The European Union's Hydrogen Strategy exemplifies this shift, positioning hydrogen ( $H_2$ ) production as a cornerstone in the fight against climate change and heralding it as a future key energy source. The sustainability of hydrogen production is critically dependent on the energy sources used for its generation. Conventionally, 'grey' hydrogen is produced using energy from fossil fuels, while 'green' hydrogen is derived mainly through water electrolysis, utilizing electricity from renewable sources. However, the production of green hydrogen currently faces challenges due to the high costs associated with generating  $H_2$  in large quantities. To address this, exploring the use of waste materials—such as food, agricultural, and water waste—as substrates for hydrogen production presents a viable alternative, potentially enhancing both sustainability and cost effectiveness [1].

Current literature data [8] reveal a comprehensive overview of the global hydrogen production landscape. Approximately 50% of the world's hydrogen is produced through the steam reforming of natural gas, a process also commonly known simply as steam reforming. Additionally, 30% of hydrogen production is attributed to the steam reforming of petroleum products, and 18% originates from coal gasification. A smaller portion, amounting to 4%, is generated via water electrolysis, while the remaining 0.1% comes from various other methods and sources [9].

The steam reforming method for hydrogen production is a well-established and highly productive technology, renowned for its energy efficiency. The hydrogen produced through this method is predominantly used in the synthesis of ammonia and methanol. However, a notable drawback of steam reforming is its reliance on fossil fuels, resulting in substantial carbon dioxide emissions. In contrast, water electrolysis is a recognized method for producing 'green' hydrogen, free from harmful emissions. Yet, this approach is hampered by its high electricity consumption, posing a challenge for its widespread application.

In an effort to diminish reliance on non-renewable energy sources, biomass has been explored as an alternative raw material for hydrogen production. However, processes based on biomass present difficulties in control and optimization. Moreover, the incomplete combustion of biomass can lead to the release of harmful carbon emissions, further complicating its use.

Exergy analyses of these various hydrogen production methods have been conducted to assess their efficiencies [10]. The results revealed the following exergy efficiencies: 78.87% for steam reforming of natural gas, 87.92% for electrolysis using renewable energy, and

50.92% for coal gasification. These findings, corroborating the high energy and exergy efficiency of gas reforming, are also supported by the research of Suleman et al. [10].

A novel alternative for hydrogen production has been proposed by a group of researchers, focusing on biological processes [11]. This method encompasses techniques such as the bio-photolysis of water by algae, dark fermentation, and the photo-fermentation of organic materials, as well as sequential processes combining dark and photo-fermentation. While this approach presents an innovative direction in hydrogen production, it is currently marked by significant raw material costs and a comparatively low yield of hydrogen.

In light of the growing demand for eco-friendly energy solutions and the diminishing reserves of non-renewable energy sources, renewable energy resources have become increasingly vital. Among these, microbial fuel cells (MFCs) present a promising avenue. MFCs generate electricity through the degradation of substrates by microorganisms, releasing electrons in the process. Notably, MFCs are distinguished as one of the most environmentally friendly renewable energy resources, offering the dual benefits of energy production and wastewater purification [12]. Due to this unique attribute, MFCs have garnered significant interest within the global academic community. However, the relatively low energy output of MFCs has led to their prevalent use in more specialized applications, such as biosensors.

Bio-electrochemical systems (BES) have been intensively researched as a technology capable of simultaneously treating various types of wastewater and recovering resources and energy [13]. Among the diverse BES reactors, the microbial electrolysis cell (MEC) stands out for its ability to produce hydrogen as a byproduct [2,3,14,15]. Besides energy generation, MECs have shown potential in removing organic matter pollutants from wastewater and waste sludge. Despite the promising outcomes from MEC applications, it is acknowledged that MEC technology is still in the nascent stages of development, particularly in terms of hydrogen production rates per reactor volume and the challenges involved in scaling up the process.

The concept of using MECs for hydrogen production is not new, with the first reports dating back nearly two decades [2,16,17]. These systems require an external energy supply for operation and hydrogen production [2]. A notable advantage of MECs is their lower energy requirement compared to conventional electrolysis [2,18], as some electric current is generated by the bio-anode in the MEC reactor. Moreover, MECs can potentially achieve high-purity hydrogen production more efficiently than other biological processes like dark fermentation of organic matter, which typically yields only 17% of the theoretical maximum [2].

For sustainable hydrogen production and maximal efficiency, the performance of microbial electrolysis cells needs to be optimized. This optimization involves considering various factors such as biochemical, electrochemical, material, and design aspects, or identifying a characteristic that adequately represents them. One effective method for objective assessment is the implementation of thermodynamic analysis using the exergy method [19–22].

Exergy analysis evaluates the thermodynamic efficiencies of energy conversion processes. Beyond assessing overall efficiency, it also sheds light on the economic value of specific chemical transformations. A particular application of exergy analysis is in examining wastewater treatment facilities, focusing on exergy utilization. This involves comparing the physical and chemical exergy of treatment plant streams, assessing the exergy inputs to the treatment units against the inlet wastewater exergy, and offers valuable insights into the process's efficiency.

Thermodynamic analysis encompasses various methods that have evolved over time, each crucial for evaluating the energy efficiency of diverse systems. Among these are the Carnot method, the entropy method, and the exergy method. The first two, while fundamental, have limited applications, particularly when it comes to assessing complex systems. Such systems, characterized by intricate processes like chemical and electrochemical reactions, microbiological processes, and heat exchange, involve material and energy flows

of differing qualities, usefulness, and performance. For these complex systems, which include chemical–technological, electrochemical, and bio-electrochemical systems, the exergy approach has become the preferred modern method for thermodynamic analysis.

In complex systems, the processes are often related to the conversion of energy and matter, involving various types of energy. Despite the common features shared by these different energy types, as defined by the first law of thermodynamics, the second law imposes limitations on the conversion of one energy form to another. To effectively compare energies of different types and qualities, a universal measure is essential. Exergy serves as this measure, enabling a quantitative assessment of the quality of various energy and material flows, thereby facilitating comparison [19–22]. Essentially, exergy is a property of a given thermodynamic system or energy flow, defined as the maximum work possible in a reversible process that brings the flow's parameters (temperature, pressure, composition) into equilibrium with those of the environment (ambient temperature, pressure, environment composition).

In several studies [2,23,24], exergy analysis has been used to evaluate the processes in microbial electrolysis cells (MECs) for hydrogen production using different substrates. The energy efficiency in these studies is measured using indicators such as total energy efficiency, hydrogen yield, the energy yield relative to electrical energy consumed for the electrolysis process or substrate, Coulomb efficiency, and hydrogen yield compared to the theoretical maximum. These indicators involve energies of varying quality in both the numerator and denominator of the equations. Consequently, exergy efficiency is also calculated to serve as an objective indicator of the performance of the microbial electrolysis cell.

There is a substantial body of research focusing on the energy and exergy efficiency assessment of conventional fuel cells [25]. These cells are adept at converting the chemical energy of fuels, typically hydrogen, into electricity, alongside generating waste heat and water. Exergy analysis, a fundamental thermodynamic concept, is instrumental in quantifying the maximum useful work attainable from a system as it achieves equilibrium with its environment. The efficiency of exergy, defined as the ratio of actual work obtained to the maximum possible work, serves as a critical measure of a system's ability to effectively utilize its available energy resources. This analysis is particularly applicable in evaluating the performance of microbial electrolysis cells (MECs).

The process of exergy analysis initiates with the determination of the chemical composition and energy balance of a system, adhering to the law of mass conservation and the first law of thermodynamics for energy conservation. The subsequent phase involves computing the exergy balance, taking into account the quality of energy and material flows. This balance is rooted in the second law of thermodynamics. These principles are equally applicable to bio-electrochemical systems (BES), specifically microbial fuel cells (MFCs) and MECs, where their performance efficiency is gauged using energy and exergy coefficients.

For instance, an insightful exergy analysis conducted by Arshad et al., 2019, on solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) demonstrates this principle's application [25]. The study examined two system types: closed systems, where the cell exchanges energy but not mass with the environment, and open systems, where both energy and mass are exchanged in the form of heat and work. This analysis, grounded in the second law of thermodynamics, acknowledges the irreversibility of real-system processes due to entropy increase. Arshad et al.'s work provides theoretical and practical insights into the application of exergy in fuel cells, laying a foundation for the future development of fuel cells integrated with thermal systems.

Similarly, microbial metabolism in microbial electrolysis cells is another crucial area where exergy analysis is applicable. It helps evaluate microbial reactions in the anode chamber, considering factors like substrate utilization efficiency and the irreversibility of microbial processes. A notable study by Zhang et al., 2013 [26], on a membraneless MFC reactor exemplifies this. They defined energy efficiency as the ratio of the energy gained in the cell (electricity) to the input substrate energy (in their case, formic acid). Alongside this, they also computed exergy efficiency, defined as the ratio of the beneficial product

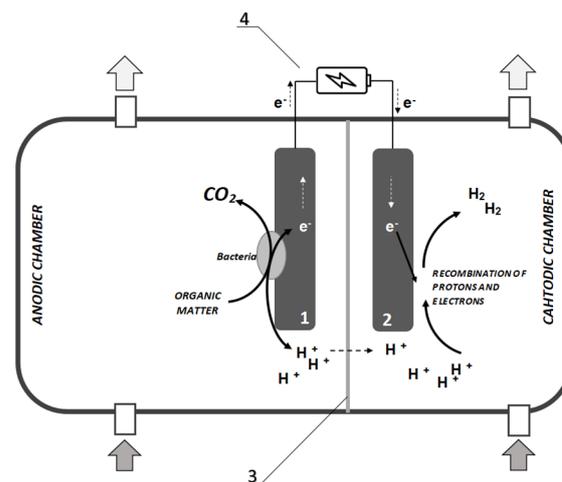
generated (electric current in this instance) to the exergy of the input substrate (formic acid). This approach provides insights into how efficiently the MEC system converts the chemical energy of the substrate into electrical or other forms of useful work.

The principles of energy and exergy analysis are not limited to MECs but are also applied to other electrochemical systems like fuel and electrolysis cells [2,27–31]. Recognizing a gap in the literature regarding the energy balance and its relation to exergy in MEC processes, our study aims to conduct a comprehensive thermodynamic assessment, particularly focusing on the use of glucose and glycerol as substrates. This endeavor is expected to fill the existing gap and enhance the understanding of energy utilization in these systems.

## 2. Materials and Methods

### 2.1. Working Principle of the Bio-Electrochemical Process

The operational model of a typical microbial electrolysis cell (MEC) is illustrated in Figure 1. The reactor under investigation comprises two distinct chambers: the anodic and the cathodic, each equipped with their respective electrodes (anode and cathode). A microbial biofilm, composed of electrochemically active bacteria, is established on the anode [32]. Here, an organic substrate is introduced and subsequently undergoes oxidation. This process results in the mineralization of the substrate, along with the generation of hydrogen ions ( $H^+$ ) and electrons. These electrons and hydrogen ions are then reduced to hydrogen gas ( $H_2$ ) at the cathode.



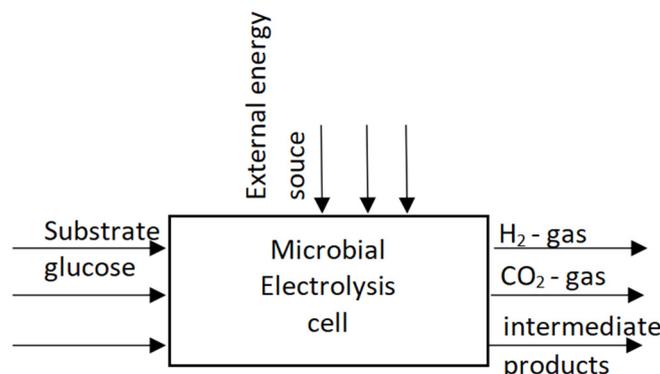
**Figure 1.** Schematic representation of the working principles of a microbial electrolysis cell. 1—anode; 2—cathode; 3—proton exchange membrane; 4—external electric power source.

In addition to the schematic representation illustrating the MEC's working principles, for the purposes of energy and exergy analysis the reactor can also be conceptualized as a 'black box' model, incorporating material and energy flows (Figure 2).

The energy assessment of the microbial electrolysis cell in this study relies on the literature data concerning process dynamics and kinetics [23,24]. Selembo et al., 2009, investigated the use of two different substrates—glucose and glycerol—at a concentration of 1 g/L, applying two external voltages (0.5 V and 0.9 V) for the electrolysis process. They reported that the utilization of each mole of glucose as a substrate results in the cathodic production of 6.4 to 7.2 moles of  $H_2$ , depending on the voltage applied. When using glycerol, the yield was 3.1 to 3.9 moles of  $H_2$  per mole of glycerol under the same electrochemical conditions.

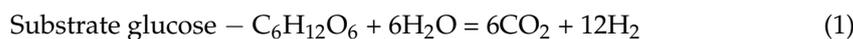
Zhang et al., 2016, found that the addition of 5% chloroform to the glucose medium inhibits methanogenesis, thereby increasing the Coulombic efficiency of the MEC. The maximum hydrogen yield observed in this experiment was 8.4 moles of  $H_2$  per mole of glucose at an external voltage of 0.8 V. It was also noted that, in the anaerobic conditions

of the anode chamber, 66% of the electrons do not contribute to hydrogen production but lead to the formation of intermediate products, primarily acetic acid and ethyl alcohol [24]. Under their experimental conditions, the MEC was operating with high energy efficiency in relation to the electrical input.



**Figure 2.** Energy and material flows in MEC.

The reactions taking place in the MEC with both types of substrates can be generalized as follows:



## 2.2. Methodology of Calculation

In the referenced experiments, the initial concentration of each substrate (glucose and glycerol) was set at 1 g/L. By taking into account the molecular masses of glucose and glycerol, the calculated molar concentrations of the introduced substrates are  $5.5 \times 10^{-3}$  mol/L for glucose and  $10.9 \times 10^{-3}$  mol/L for glycerol. Utilizing the stoichiometry of the reactions outlined in Equations (1) and (2), alongside the specified quantities of the substrates in moles, we can determine both the theoretical and actual amounts of hydrogen produced. These calculations are presented in Table 1. For this purpose, we have employed the experimental data and findings from Zhang et al. (2016) and Selembo et al. (2009).

**Table 1.** Theoretical (calculated) and experimentally reported H<sub>2</sub> produced in a microbial electrolysis cell depending on substrate and the external voltage applied.

Substrate	Concentration, g/L	Applied Voltage	Concentration, mol/L	Theoretical Yield of H <sub>2</sub> , mol/L	Actual Yield of H <sub>2</sub> , mol/L	Efficiency%
Glucose [23]	1	0.5	$5.5 \times 10^{-3}$	0.066	0.0352	53.3
Glucose [23]	1	0.9	$5.5 \times 10^{-3}$	0.066	0.0396	60.0
Glycerol [23]	1	0.5	$10.9 \times 10^{-3}$	0.0763	0.0340	44.6
Glycerol [23]	1	0.9	$10.9 \times 10^{-3}$	0.0763	0.0425	55.7
Glucose and inhibitor [24]	1	0.8	$5.5 \times 10^{-3}$	0.066	0.0462	70.0
Glucose and inhibitor [24]	2	0.8	$11.11 \times 10^{-3}$	0.133	0.0866	65.1
Glucose and inhibitor [24]	3	0.8	$16.67 \times 10^{-3}$	0.200	0.1150	57.5
Glucose and inhibitor [24]	4	0.8	$22.22 \times 10^{-3}$	0.267	0.1360	50.8

## 3. Results and Discussion

Exergy analysis, when applied to microbial electrolysis cells (MECs), demands an in-depth comprehension of the electrochemical and microbial processes involved, as well as the thermodynamic principles that govern substrate transformation. This form of analysis is crucial for gaining insights into the system's efficiency and sustainability. It does so by identifying areas prone to energy losses and suggesting potential improvement strategies.

The extent and focus of the analysis are dependent on the specific design and operational parameters of the MEC system being studied.

Furthermore, the energy effectiveness of an MEC can be calculated by examining the correlation between the quantity of imported substrate and the hydrogen produced through the electrochemical process. For these calculations, the criteria defined by Logan et al., 2008, are employed [27]. This approach allows for a quantifiable assessment of the system's energy dynamics, thereby aiding in the determination of its operational efficiency.

The energy balance of hydrogen production in a microbial electrolysis cell contains the amount of hydrogen recovered, the energy used for the process, and the energy of hydrogen combustion:

$$W_{H_2} = n_{H_2} \times \Delta H_{H_2} \quad (3)$$

where  $n_{H_2}$  mol is the actual yield of  $H_2$  (Table 1), and  $\Delta H_{H_2}$  is the energy content of  $H_2$  based on the heat released during the  $H_2$  combustion, 285.83 KJ/mol  $H_2$  [27].

The energy yield is calculated using the ratio of the recovered  $H_2$  to the input electrical energy:

$$\eta_E = \frac{W_{H_2}}{W_E} \times 100\% \quad (4)$$

Zhang et al. and Selembo et al. did calculate this parameter in their research [23,24]. The energy of the substrate is defined as:

$$W_S = n_S \times \Delta H_S \quad (5)$$

where  $\Delta H_S$  is the heat of substrate combustion (glucose or glycerol), while  $n_S$  is moles of substrate presented in the anodic compartment of the MEC. The relative yield of energy to the input substrate is calculated using Equation (6):

$$\eta_S = \frac{W_{H_2}}{W_S} \times 100\% \quad (6)$$

where  $W_S = 2802.7$  KJ/mol—the value of the energy of glucose combustion—while the corresponding value for glycerol is 1655.4 KJ/mol.

In reviewing the studies pertinent to microbial electrolysis cells (MECs), an important aspect warrants attention: the calculation of relative energy yield in the processes under observation. It is noteworthy that the majority of these studies overlook this critical calculation, thereby highlighting a significant gap in existing research. However, an exception is found in the work of Selembo et al., which stands out due to its thorough analysis of energy dynamics. Distinct from other studies, Selembo et al. extend their analysis beyond just the substrate used; they also take into account the energy consumed during the process when assessing overall energy utilization. This comprehensive approach not only fills a notable void in the literature but also significantly contributes to a deeper understanding of the energy yield in the processes being examined.

$$\eta_{E+S} = \frac{W_{H_2}}{W_E + W_S} \times 100\% \quad (7)$$

Given that energy conversion efficiency involves two distinct forms of energy—heat and work—with varying qualities or work abilities, a more objective evaluation of the microbial electrolysis cell energy efficiency introduces the concept of an exergy coefficient. This coefficient is being considered for a comprehensive assessment. The calculation involves a numerator representing the exergy of the product obtained and a denominator representing the exergy of the energy and material flows entering the considered system. Notably, the exergy at the input to the system encompasses both the exergy of the utilized substrate and the exergy of the input electrical energy. This methodological approach ensures a nuanced and thorough examination of the MEC's energy efficiency by considering the specific qualities of the involved energy forms:

$$\eta_e = \frac{E_{H_2}}{E_S + E_W} \times 100\% \quad (8)$$

where  $E_{H_2}$  is the exergy of hydrogen in KJ/mol,  $n_{H_2}$  are the moles of the obtained  $H_2$ ,  $E_S$  is the exergy of the substrate in KJ/mol,  $n_S$  are the moles of input substrate, and  $E_W$  is the energy of input electricity during the process of electrolysis in KJ.

In this paper, the method of Szargut et al. [19,20], is used for hydrogen and substrate (glucose and glycerol) exergy calculations.

In the calculations applied, it was accepted that electrolysis is carried out under ambient conditions ( $T_0 = 298.15$  K and  $P_0 = 101,325$  Pa) and, therefore, that the physical exergy of the hydrogen and the substrate is neglected. Only their chemical exergies are considered. The exergy of the electric current spent on the process equals the energy that it carries. For the calculation of the exergies of hydrogen and substrate, the environmental conditions described by Szargut et al., 1998, are accepted ( $T_0 = 298.15$  K and  $P_0 = 101,325$  Pa).  $T_0$  and  $P_0$  are the ambient temperature and the ambient pressure, respectively.

The chemical exergy defines the maximum work of a chemical reaction carried out reversibly at  $P_0$  and  $T_0$ , in which the substance under consideration is converted into a so-called 'reference' substance that is present in the environment. This reaction is called a 'devaluation reaction'. The chemical exergy consists of two parts—the exergy of devaluation and the exergy of the dissipation of the resulting reference substances into the environment [19–22].

$$E_{\text{chem}} = E_{\text{dev}} + E_{\text{dissip}} \quad (9)$$

$$E_{\text{dev}} = \Delta H_{\text{dev}} - T_0 \times \Delta S_{\text{dev}}, \quad (10)$$

$\Delta H_{\text{dev}}$ —change of the enthalpy of the devaluation reaction, KJ/mol.

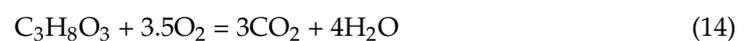
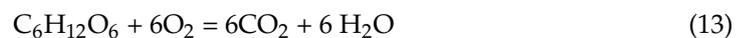
$$\Delta H_{\text{dev}} = \sum (x_i \times \Delta_f H_i^0)_{\text{reagents}} - \sum (x_i \times \Delta_f H_i^0)_{\text{products}} \quad (11)$$

$\Delta S_{\text{dev}}$ —change of the entropy of the devaluation reaction.

$$\Delta S_{\text{dev}} = \sum (x_i \times S_i^0)_{\text{reagents}} - \sum x_i \times (S_i^0)_{\text{products}} \quad (12)$$

$\Delta_f H_i^0$ —the standard molar enthalpy (heat) of formation at 298.15 K of the "i"—component participating in the reaction of devaluation, KJ/mol;  $x_i$ —stoichiometric coefficient for each component of the devaluation reaction;  $S_i^0$ —standard molar entropy at 298.15 K of the "i"—component participating in the devaluation reaction, J/mol.

The reactions of devaluation for both substrates are as follows:



The standard molar enthalpy (heat) of formation at 298.15 K ( $\Delta_f H^0$ ) in KJ/mol and the standard molar entropy at 298.15 K in J/mol.K ( $S^0$ ) for each component of the devaluation reaction are presented in Table 2 [33].

**Table 2.** Standard thermodynamic properties of chemical substances.

Component	$\Delta_f H^0$ , KJ/mol	$S^0$ , J/mol.K
$C_6H_{12}O_6$	−1273.3	212.1
$O_2$	0.0	205.2
$CO_2$	−393.5	213.8
$H_2O$	−241.8	188.8
$C_3H_8O_3$	−668.5	206.3

For the elements C, H, O, N, and the noble gases, the atmospheric air components serve as ‘reference’ compounds [19,20].

The execution of the devaluation reaction is only the first stage. Another has to be performed, namely, the ‘reference’ compounds (in this particular case, CO<sub>2</sub> and water vapor) are brought from state P<sub>0</sub>, T<sub>0</sub> to the partial pressure of the ‘reference’ compounds in the environment (P<sub>0</sub>, i, T<sub>0</sub>). The same process (with the opposite sign) brings the additional ‘reference’ substances (in this case, oxygen) from the state of the partial pressure of oxygen in the environment (P<sub>O<sub>2</sub></sub>, i) into the state P<sub>0</sub>, T<sub>0</sub>. This stage of chemical exergy is called dissipation exergy:

$$E_{\text{dissipation}} = -RT_0 \times \sum x_i \times \ln(P_{i,0}/P_0) \quad (15)$$

P<sub>i,0</sub>—partial pressure of the reference compounds in the environment, Pa.

In these calculations, the exergy of H<sub>2</sub> is taken from Szargut [19,20].

Table 3 shows the calculated enthalpies and entropies of devaluation reactions (12) and (13), the exergies of devaluation, the exergies of dissipating, and the chemical energies for both substrates (glucose and glycerol).

**Table 3.** Calculated enthalpy and entropy of devaluation reactions for glucose and glycerol.

Substrate	$\Delta H_{\text{dev.}}$ , KJ/mol	$\Delta S_{\text{dev.}}$ , J/mol.K	$E_{\text{dev.}}$ , KJ/mol	$E_{\text{dissip.}}$ , KJ/mol	$E_{\text{chem.}}$ , KJ/mol
Glucose	2538.50	−972.30	2828.39	166.67	2995.06
Glycerol	1478.10	−307.95	1569.92	92.93	1662.85

To determine the energy and exergy coefficient, the amount of utilization of the substrates, the electrical energy consumed, and the quantity of actual hydrogen obtained were used. The results obtained are shown in Table 4.

**Table 4.** Energy and exergy coefficients calculated for glucose and glycerol as substrates in a microbial electrolysis cell during production of hydrogen.

Substrate	$E_{\text{ap}}$ , V	$\eta_{\text{s}}$ , %	$\eta_{\text{E}}$ , %from the Literature *	$\eta_{\text{E+S}}$ , %	$\eta_{\text{e}}$ , %	Actual/Theoretical, %
Glucose	0.5	65.28	159	46.27	36.75	53.30
Glucose	0.9	73.46	152	49.52	39.42	60.00
Glycerol	0.5	53.88	198	42.35	35.13	44.56
Glycerol	0.9	67.34	139	45.37	37.67	55.70

\* Calculations based on article [23] in the reference list.

Examining Table 4 reveals a notable trend: higher voltages correspond to improved results. Furthermore, it becomes evident that glucose outperforms glycerol as a substrate for hydrogen production. This is evidenced by achieving comparable results at lower concentrations and voltages. The observed correlation between voltage levels and outcomes, as well as the substrate efficiency comparison, underscores the significance of these factors in the experimental outcomes.

Assessment of the concentration of glucose shows that 1 g of substrate is optimal for hydrogen gas production (Table 5). Moreover, increasing the glucose concentration actually results in a decrease in the process efficiency. An increase of four times the glucose concentration lowers the actual to theoretical ratio by around 20%.

The energy yield values exceeding 100% presented in these tables reflect the intricate nature of bio-electrochemical processes. These processes often exhibit behavior that deviates from both theoretical expectations and mathematical models [34]. The complexity of these factors contributes to unexpected outcomes, resulting in energy recovery values that surpass conventional limits. Understanding and addressing these nuances is crucial for refining

theoretical frameworks and enhancing the accuracy of mathematical models in the realm of bio-electrochemical research.

**Table 5.** Different concentrations of glucose as a substrate and voltage of 0.8 V \*.

Substrate, g	$\eta_s$ , %	$\eta_E$ , %	$\eta_{E+S}$ , %	$\eta_e$ , %	Act/Theor, %
1	85.33	173	57.15	45.49	70.00
2	79.48	172	54.35	43.24	65.11
3	70.35	166	49.41	39.27	57.51
4	62.41	158	44.74	35.52	50.76

\* Calculations based on data from article [24] in the reference list.

#### 4. Conclusions

Bio-electrochemical systems (BESs) excel in transforming the chemical energy of organic matter, including wastes found in wastewater and biomass, into electricity or hydrogen/chemical products, as seen in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), respectively. A prominent advantage of BESs is their ability to operate under mild conditions, utilizing a wide array of biodegradable organic substrates and relatively inexpensive metals as catalysts. While BESs have not yet achieved substantial commercial success, they show considerable promise by enabling the use of the chemical energy of diverse waste materials. In the realm of MECs, the application of exergy analysis emerges as a practical and invaluable tool for assessing and enhancing energy yield. Exergy, which represents the maximum useful work that a thermodynamic system can produce when achieving equilibrium with a reference environment through a reversible process, also serves as a means to quantify energy loss [35]. The nature and concentration of the substrate can be optimized to improve exergy efficiency, thus positively influencing hydrogen production in a microbial electrolysis cell.

A pertinent question arises regarding how exergy analysis can aid in optimizing the design and operation of a microbial electrolysis cell, and how exergy is specifically defined in the context of MECs, contrasting with its traditional definition. Fundamentally, the exergy method of thermodynamic analysis is utilized to examine the processes occurring within a given system, independent of the system's design. The system is treated as a 'black box', into which material and energy flows are introduced, yielding target products as well as waste material and energy flows that are discharged into the environment and remain unused. Exergy losses, both internal and external, are calculated in this context. External losses pertain to the exergies of material and energy flows released into the environment without utilization. Internal losses stem from the irreversible nature of various processes in the system, including contraction, expansion, and the irreversibility of electrochemical and chemical reactions, heat exchanges, and more. In this scenario, the design of the MEC indirectly impacts exergy efficiency; different designs can enhance electrochemical and microbiological processes, thereby increasing hydrogen yield and reducing electricity consumption, which in turn boosts exergy efficiency.

Traditionally, exergy efficiency is calculated by determining the ratio of the exergy of the target product or energy obtained to the exergy expended in material and energy flows at the system's input. This approach is similarly employed when calculating the exergy efficiency of MECs. The exergy of hydrogen, as the target product, is related to the exergy of the input substrate and the electrical energy consumed during electrolysis.

Focusing on MECs, it is crucial to note that the substrate serves as the sole electron donor for the electrogenic bacteria, which oxidizes the substrate and transfers electrons to the cathode via the anode, thus producing hydrogen gas. Consequently, selecting an appropriate substrate is vital for determining the ultimate hydrogen yields from MECs. A wide range of organic substrates can be used in MECs, from simple carbohydrates to more complex fermentable substances like biomass and wastewater [36]. Theoretically, up to 12 moles of H<sub>2</sub> can be produced per mole of glucose in microbial electrolysis, although practical yields are typically lower.

In this study, based on theoretical data regarding the utilization of glucose and glycerol, the electrical energy consumed, and the actual quantity of hydrogen produced, both the energy and exergy parameters were calculated. Two primary conclusions were drawn: (1) a higher applied voltage correlates with increased exergy efficiency, and (2) a comparison between the use of glucose and glycerol as substrates reveals a preference for glucose. Regarding the relationship between applied voltage and exergy efficiency, the results indicate that, at a higher voltage of 0.9 V compared to 0.5 V, the hydrogen yield is greater and the electrical power consumption is comparable, thus resulting in higher exergy efficiency at 0.9 V. Evidently, this effect is largely influenced by the exergy of the substrate. As the analysis is based on pre-existing experimental data without additional experimental insights, it is not possible to conclusively determine the optimal voltage value. Generally, a higher voltage leads to a more efficient electrochemical process, with more electrons reaching the cathode.

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