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Energy and Exergy Evaluation of an Integrated Dark Fermentation and Microbial Electrolysis System for Sustainable Hydrogen Production

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This study evaluates hydrogen production from crude glycerol and vinasse using integrated dark fermentation and microbial electrolysis. Aspen Plus simulations showed high efficiency, with 95% COD reduction and hydrogen yields of 6.43 kg/h (fermentation) and 95.80 kg/h (electrolysis). Exergy efficiencies exceeded 81%, highlighting the system's potential for converting waste into renewable energy and supporting green hydrogen development.

1. Introduction

Global energy demand is rising rapidly, while hydrocarbon reserves are depleting and causing severe environmental issues like global warming and biodiversity loss. This urgency has driven the search for sustainable energy alternatives to meet demands while reducing environmental harm (Alcaraz-Gonzalez *et al.*, 2020). Hydrogen (H_2) is increasingly recognized as a key solution due to its versatility and potential as a renewable energy source. Advancements in production methods, including thermochemical, electrolytic, photochemical, and biological processes, have highlighted its potential. However, hydrogen production still predominantly relies on fossil fuels, which account for 96% of commercially available hydrogen and emit up to 13.6 kg of CO_2 per kg H_2 (Asrul *et al.*, 2021). Transitioning to green hydrogen through renewable-powered electrolysis and using waste-based substrates are crucial steps toward sustainability (Noori *et al.*, 2024).
Dark fermentation is a promising method for sustainable hydrogen production, using microbial catalysts to convert biomass into hydrogen under anaerobic conditions (García & Cammarota, 2018). Operating without sunlight, it enables continuous operation and simplifies bioreactor design while producing value-added by-products like volatile fatty acids and alcohols. This environmentally friendly approach offers low energy demand, mild operational conditions, and no inhibitory by-products, making it a practical alternative to traditional, energy-intensive methods.
Microbial electrolysis, another bioelectrochemical system (BES) technology, enables hydrogen production from organic wastes and wastewater. Using electroactive bacteria, microbial electrolysis cells (MECs) operate at significantly lower energy demands (33.2–117 kWh/kg H_2) compared to abiotic methods (170–995 kWh/kg H_2), making them cost-effective and efficient (Noori *et al.*, 2024). This process supports clean hydrogen production and addresses waste management challenges, though microbial system complexity introduces performance variability due to microbial dynamics, reactor configuration, and operational conditions (Muddasar *et al.*, 2021).
Crude glycerol and vinasse, byproducts of biodiesel and ethanol production, are rich in organic content and suitable for biofuel production. Crude glycerol, generated at 1 kg per 10 kg of biodiesel, reached 5.87 billion pounds by 2020 (Kumar *et al.*, 2019), while vinasse, produced at 8–15 liters per liter of ethanol, accounted for over 370 billion liters in Brazil's 2022–2023 sugarcane ethanol harvest (Menezes *et al.*, 2023). Co-fermentation processes improve hydrogen yields by balancing nutrients and diluting inhibitory compounds (Yang & Wang, 2017). Using these byproducts supports sustainable biofuel production and mitigates waste issues like soil salinization and groundwater contamination (Ribeiro *et al.*, 2021).

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This study simulates and analyzes hydrogen production via dark fermentation and microbial electrolysis using crude glycerol and vinasse as substrates. It evaluates process efficiency and sustainability, aiming to maximize hydrogen yield while minimizing energy use and environmental impact. Detailed modeling and exergy analysis provide insights into transforming waste streams into renewable energy, advancing sustainable biorefinery systems.

2. Methodology

2.1 Exergy Analysis

Exergy analysis is a fundamental and straightforward method for evaluating the usable energy within a process, providing insights into its efficiency and sustainability. This approach is rooted in the Second Law of Thermodynamics, enabling the estimation of not only external energy losses but also internal inefficiencies caused by the degradation of materials and energy due to entropy production (Heijden and Ptasinsky, 2012). By quantifying these losses, exergy analysis offers a comprehensive understanding of where and how energy dissipation occurs within a system. Figure 1 illustrates an exergy balance applied to a process, showcasing the distribution of energy and entropy across different units. Using this concept, it was possible to calculate the exergy losses for each process unit, highlighting specific areas where performance improvements can be targeted.

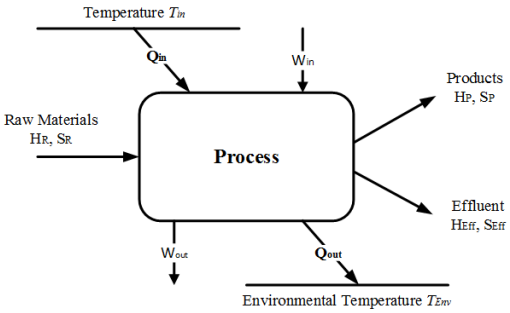

Figure 1: Exergy Analysis Schematics

Where: H is enthalpy, S is entropy, Q is heat, W is work, T is temperature; and the subscripts denote R (raw materials), P (products), Eff (effluents), and Env (environment). Figure 1 illustrates the balance, represented by Equations 1–9 below, incorporating the term Irr, which accounts for process irreversibilities (exergy losses).

$$\sum_{in}\dot{E}_i+\sum_{in}\dot{E}_j^{ch}+\sum_{in}\dot{E}_k^{Q}+\sum_{in}\dot{E}_l^{W}=\sum_{out}\dot{E}_m+\sum_{out}\dot{E}_n^{ch}+\sum_{out}\dot{E}_p^{Q}+\sum_{out}\dot{E}_q^{W}+Irr \quad (1)$$

$$\dot{E}_i=H_{R,i}-H_{R,i}^0-T_0(S_{R,i}-S_{R,i}^0) \quad (2)$$

$$\dot{E}_j^{ch}=\Psi_{ch}^0.n_j^c \quad (3)$$

$$\dot{E}_k^{Q}=Q_{in}\left(1-\frac{T_{Env}}{T_{in}}\right) \quad (4)$$

$$\dot{E}_l^{W}=W_{in} \quad (5)$$

$$\dot{E}_m=H_{P,m}-H_{P,m}^0-T_{Env}\left(S_{P,m}-S_{P,m}^0\right)+H_{Eff,m}-H_{Eff,m}^0-T_{Env}(S_{Eff,m}-S_{Eff,m}^0) \quad (6)$$

$$\dot{E}_n^{ch}=\Psi_{ch}^0.n_n^c \quad (7)$$

$$\dot{E}_p^{Q}=Q_{out}\left(1-\frac{T_{Env}}{T_{out}}\right) \quad (8)$$

$$\dot{E}_q^{W}=W_{out} \quad (9)$$

Exergy efficiency is defined in two ways: one based on the product exergy, specifically hydrogen (Equations 9 and 10) and carbon dioxide (Equation 10), and the other incorporating heat-derived exergy (Equations 11 and 12). In the latter, the right side of Equation 1 is adjusted to represent the total input exergy of the process.

$$\eta_P = \frac{\dot{E}_{Hydrogen}}{E_+} \quad (9) \qquad \eta_P = \frac{\dot{E}_{Hydrogen} + \dot{E}_{CO_2}}{E_+} \quad (11)$$

$$\eta_O = \frac{\dot{E}_{Hydrogen} + \sum_{out} \dot{E}_n^Q}{E_+} \quad (10) \qquad \eta_O = \frac{\dot{E}_{Hydrogen} + \dot{E}_{CO_2} + \sum_{out} \dot{E}_n^Q}{E_+} \quad (12)$$

In Equations 9–12, the term E_+ replaces the right side of Equation 1, representing the total exergy input to the process.

2.2 Process Simulation

The simulation software used was ASPEN Plus v14.1. To model electrolyte systems, the thermodynamic packages ELECNRTL and ENRTL-RK were applied. ELECNRTL, suited for aqueous systems with detailed ionic interactions, was primarily used, while ENRTL-RK handled mixed electrolyte and non-electrolyte systems, modeling microbial electrolysis cells.

As shown in Figure 2, vinasse (VINASSE) (Kumar *et al.*, 2019) and crude glycerol (CR-GLY), with variability in crude glycerol composition simulated using Monte Carlo methods (14-87% glycerol, 0.014-0.078% nitrogen, 0.2-5.47% NaCl, 0.93-6.34% ash, and 8.16-43.42% water) (Carrilho *et al.* 2016), are mixed (M-101) and pumped (P-101) to the fermentation area. The fermentation reactions were modeled based on the studies by Lo *et al.* (2007, 2013). The reactor feed was fixed to 50 $g_{glycerol}$/L, with the vinasse input adjusted to align with the glycerol concentration. Eight parallel fermentation reactors (Figure 3a, modeled as R-CSTR) operated with *Clostridium pasteurianum* CH4, producing biogas (H_2 and CO_2) along with organic products, including 1,3-propanediol, butanol, ethanol, acetic acid, and butyric acid, under conditions of 35°C and atmospheric pressure.

Fermentation gases are combined and purified, while liquid products and some microorganisms move to the separation and recycling system (MO-REC) and then to microbial electrolysis. In the flash vessel (F-101), water is separated, and biogas enters a membrane system (S-101), recovering 99% hydrogen (Hawkes *et al.* 2007) and generating purified H_2 and CO_2 streams.

In microbial electrolysis, four reactors (Figure 3b) arranged in series process liquid fermentation products. Two conversion reactors (R-YIELD) simulate anode reactions (organic decomposition to CO_2 and H^+) and cathode reactions (H_2 formation). A separation block (SEP) represents the Proton Exchange Membrane (PEM), enabling H^+ ion passage. The resulting gases (CO_2 and H_2) are combined with purified fermentation streams, compressed (145 atm for H_2, 57 atm for CO_2), and cooled to ambient temperature, completing production and storage.

3. Results

3.1 Process

Table 1 presents the yields from dark fermentation and microbial electrolysis processes. In the fermentation stage, glycerol conversion achieved a remarkable average of 99.41% with a minimal standard deviation (0.06%), while glucose conversion reached 72.64% with a slightly higher variability (1.29%). The process generated 6.43 kg/h of H_2 and 160.83 kg/h of CO_2. In contrast, microbial electrolysis demonstrated a significant reduction in COD from 925.49 kg/h (initial) to 46.66 kg/h (final), reflecting substantial organic matter removal. Additionally, the microbial electrolysis process produced 95.80 kg/h of H_2, far surpassing the fermentation yield, along with 966.04 kg/h of CO_2.

Table 1: Dark Fermentation and Microbial Electrolysis Yield

Fermentation	avg.	s.d	Microbial electrolysis	avg.	s.d.
Glycerol Conversion	99.41%	0.06%	Initial COD (kg/h)	925.49	154.29
Glucose Conversion	72.64%	1.29%	Final COD (kg/h)	46.66	7.78
H_2 generated (kg/h)	6.43	0.93	H_2 generated (kg/h)	95.80	15.63
CO_2 generated(kg/h)	160.83	23.34	CO_2 generated(kg/h)	966.04	163.15

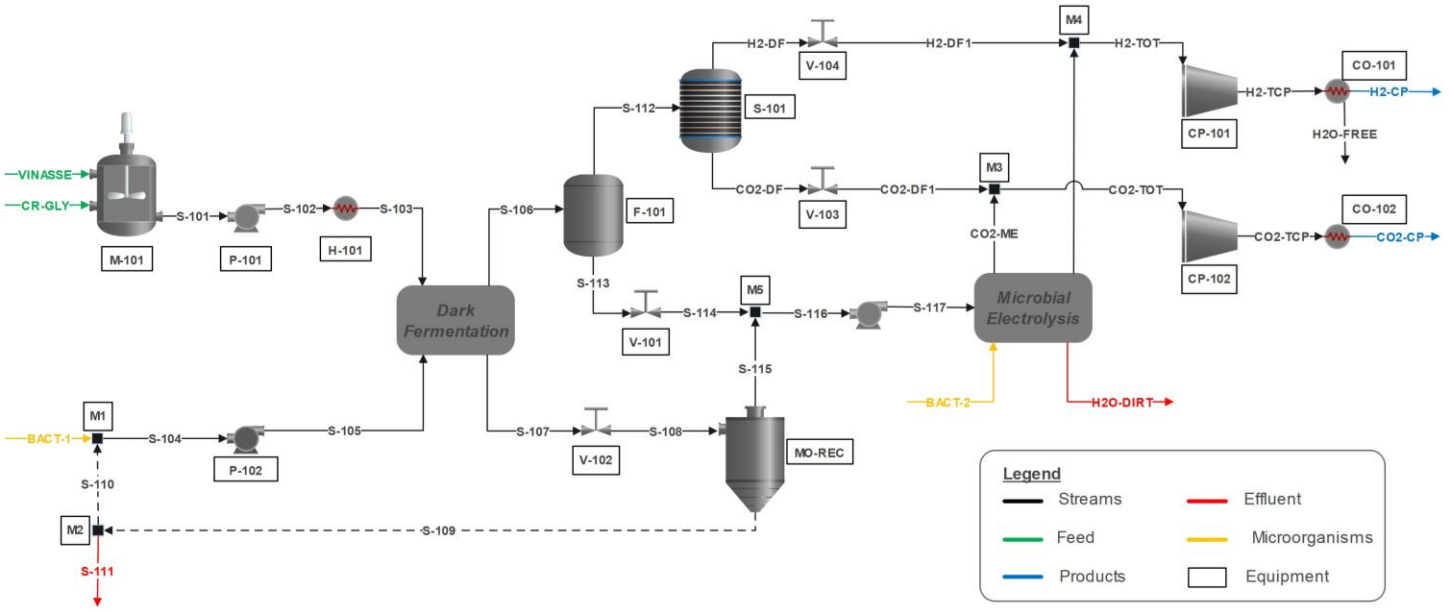

Figure 2: Main Process Flowchart

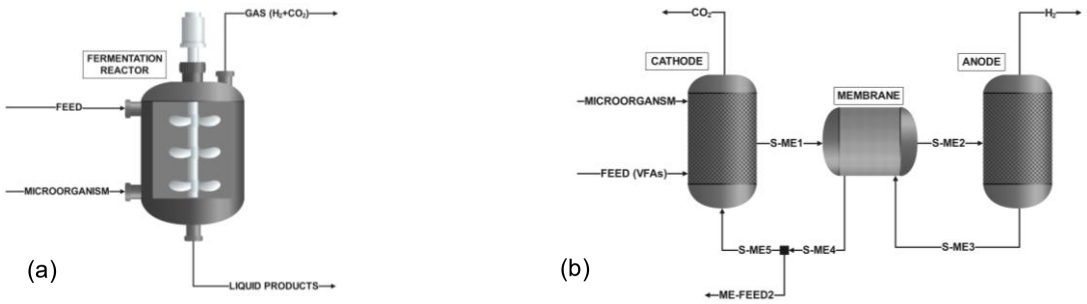

Figure 3: (a) Fermentation Reactor; (b) Microbial Electrolysis Cell Simulation Scheme.

3.2 Energy Analysis

Table 2 summarizes the energy balance across the main system, dark fermentation, and microbial electrolysis stages, presenting average energy flows and their variability. In the main system, significant energy demand is observed in CP-101 and CP-102 (4.39E+05 and 1.22E+05 kcal/h), while pumps (P-101 to P-103) and heat exchangers exhibit low consumption with minimal variability. The dark fermentation reactors (R-DF1 to R-DF8) exhibit consistent cooling requirements (~-3.18E+03 kcal/h) with negligible deviations, The dark fermentation reactors (R-DF1 to R-DF8) exhibit consistent cooling requirements (~-3.18E+03 kcal/h) with negligible deviations, reflecting robust operation and effectively dampening variability in the process. In microbial electrolysis, energy usage varies significantly across the reactors and membrane due to their configuration. It is essential to analyze the system as a single integrated cell when assessing energy performance. This analysis does not account for thermal effects or overpotential, which are common in practice. Instead, it focuses solely on the chemical energy required to decompose the molecules.

Table 2: Energy consumption per equipment

		Equipment	Energy(kcal/h)		Equipment	Energy(kcal/h)	
			avg.	s.d.		avg.	s.d.
Main	W	P-101	9.78E+01	8.33E+00	P-102	1.46E-01	2.21E-02
		P-103	9.71E+01	6.36E+04	CP-101	4.39E+05	6.36E+04
		CP-102	1.22E+05	1.03E+03			
	Q	H-101	6.73E+04	1.21E+04	SEP-101	-4.16E+02	5.99E+01
		F-101	-5.70E+03	8.24E+02	CO-101	-4.50E+05	2.22E+04
		CO-102	-1.44E+05	2.22E+04	MO-REC	3.19E-01	3.85E-02
Dark Fermentation	Q	R-DF1	-3.18E+03	4.71E+02	R-DF2	-3.18E+03	4.71E+02
		R-DF3	-3.18E+03	4.71E+02	R-DF4	-3.18E+03	4.71E+02
		R-DF5	-3.18E+03	4.71E+02	R-DF6	-3.18E+03	4.71E+02
		R-DF7	-3.18E+03	4.71E+02	R-DF8	-3.18E+03	4.71E+02
Microbial Electrolysis	Q	ME-AN01	3.00E+05	4.82E+04	ME-AN02	1.92E+05	3.18E+04
		ME-MB01	2.30E+04	3.94E+03	ME-MB02	6.78E+03	1.17E+03
		ME-CA01	6.80E+03	1.51E+03	ME-CA02	3.89E+02	1.63E+02
		ME-AN03	5.10E+01	2.93E+01	ME-AN04	4.18E+04	6.89E+03
		ME-MB03	2.41E+03	4.30E+02	ME-MB04	9.57E+02	1.65E+02
		MB-CA03	1.21E+02	3.61E+01	ME-CA04	1.93E+02	4.08E+01

3.3 Exergy Analysis

Table 3 presents the exergy analysis and process efficiencies, highlighting the distribution and performance of input and output exergy. Despite considerable variability in crude glycerol composition at the inlet the final exergy does not exhibit wide fluctuations. Table 3 presents the exergy analysis and process efficiencies, highlighting the distribution and performance of input and output exergy. The total input exergy (E^+) is 3.56E+09 kcal/h, with chemical exergy (E^ch) as the largest contributor (3.53E+09 kcal/h). The total output exergy (E^-) is 3.42E+09 kcal/h, resulting in a net exergy loss (ΔE) of 1.38E+08 kcal/h. Efficiencies for hydrogen production and combined hydrogen-CO_2 production reach 81.92% and 82.25%, respectively, with minimal variability (~1.85–1.86%)..

Table 3: Exergy Analysis

Exergy (kcal/h)				Efficiency			
	avg.	*s.d.*		*avg.*	*s.d.*		*avg.*	*s.d.*
E^+	3.56E+09	5.29E+08	E	5.85E+04	1.07E+05			
			E^Q	2.18E+03	3.91E+02			
			E^W	5.61E+05	9.19E+04	$\eta_{E_{Hydrogen}/E^+}$	81.92%	1.85%
			E^{ch}	3.53E+09	5.92E+08	$\eta_{(E_{Hydrogen}+E^Q)/E^+}$	81.92%	1.85%
E^-	3.42E+09	5.15E+08	E	-6.81E+04	1.03E+05	$\eta_{(E_{Hydrogen}+E_{CO_2})/E^+}$	82.25%	1.86%
			E^Q	-3.80E+03	6.28E+02	$\eta_{(E_{Hydrogen}+E_{CO_2}+E^Q)/E^+}$	82.25%	1.86%
			E^W	0.00E+00	0.00E+00			
			E^{ch}	3.42E+09	5.77E+08			
ΔE	1.38E+08	1.44E+07						

4. Conclusions

The analysis of dark fermentation and microbial electrolysis processes underscores the system's exceptional robustness and efficiency in hydrogen production from waste substrates such as glycerol and vinasse. Energy and exergy assessments confirm high performance, showcasing the system's capability to maximize resource utilization. Monte Carlo simulations applied to raw materials reveal minimal variability in key parameters, affirming system stability, while a net exergy loss of 1.38E+08 kcal/h highlights clear opportunities for further optimization. This integrated approach highlights the potential to transform waste streams into clean energy and contributes to the advancement of more sustainable and efficient biorefinery systems.

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