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Evaluation of the Dark Fermentation Process as an Alternative for the Energy Valorization of the Organic Fraction of Municipal Solid Waste (OFMSW) for Bogotá, Colombia

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Abstract: In the context of valorizing the organic fraction of urban solid waste (OFMSW) in megacities, dark fermentation emerges as a central strategy alongside composting and anaerobic digestion. This article focuses on assessing the environmental, technical, and energy viability of dark fermentation using life cycle assessment (LCA) and circular economy principles. Dark fermentation for biohydrogen production is an active and promising research field in the quest for sustainable biofuels. In this context, defining operational parameters such as organic loading and the substrate-inoculum ratio is relevant for achieving better production yields. Laboratory tests were conducted using organic loading values of 5, 10, and 15 g of volatile solids per liter (gVS/L) and with substrate-inoculum ratios (s/x) of 1, 0.75, and 0.5 g of volatile solids of substrate per gram of volatile solids of inoculum (gVSs/gVSi). The combination with the best performance turned out to be an initial organic loading of 10 gVS/L and an s/x of 1 gVSs/gVSi. From this result, it was determined that the s/x had a greater impact on production. Finally, a valorization plant was dimensioned with the scaled-up process, starting from the municipal solid waste generated by Bogotá projected for 2042. The scaling was demonstrated to be energetically sustainable, producing a power of 2,368,358.72 kWh per day.

Keywords: OFMSW; dark fermentation; biohydrogen production; sustainable biofuels; biorefineries

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1. Introduction

Sustained demographic growth and increased economic activities in cities have contributed to the escalating rise in municipal solid waste (MSW). In Bogotá, by the year 2020, the disposal at the Doña Juana landfill reached 6237.655 tons/day, leading to pressure on facilities and adverse effects on the area's inhabitants [1,2]. In this regard, the national policy for integrated solid waste management introduces the concept of a circular economy, emphasizing the importance of utilization and valorization for reintegrating waste into the local production network [3]. In a megacity, organic waste accounts for 45 to 50% of the total MSW and represents the fraction with the highest potential for recovery [4]. Hence, all actions related to the utilization and valorization of the organic fraction of municipal solid waste (OFMSW) are pertinent. The failure to do so would lead to the decomposition of these waste materials, contributing to greenhouse gas (GHG) emissions, leachate production, landfill cell saturation, soil degradation, and other environmental impacts [5].

Among the primary strategies for valorizing the organic fraction of urban solid waste (OFUSW) in a megacity, composting (non-energy valorization), single-stage anaerobic digestion (aiming to produce biogas), and dark fermentation followed by anaerobic digestion (a developing scheme to produce biohydrogen and biogas) stand out. Evaluating these pathways through the lens of life cycle assessment will help to define their environmental, technical, and energy viability within the circular economy framework. This article assesses the dark fermentation process for a megacity, with Bogotá serving as a case study.

Anaerobic digestion (AD) is considered the most effective method for valorizing OFMSW and converting waste into energy, provided that the biodegradability exceeds 40% [6]. The benefits of AD include the ability to apply high loading rates due to reduced space requirements and the potential for recovering by-products, such as ammonia, through post-treatment methods [7]. Additionally, biogas valorization technology is currently being applied at the Doña Juana landfill, where an average flow of 7938 Nm^3/h of biogas was captured in 2019, resulting in an estimated 1,192,729.40 kWh of electricity generation and an average reduction of approximately 541 t CO_2 eq in GHG emissions [5].

While AD and biogas capture are relatively low-complexity alternatives for OFMSW utilization, analyzing each stage reveals that when the biochemical process is complete, the composition of the resulting biogas consists mainly of methane. However, a closer examination of each stage of AD shows that hydrogen can be biologically recovered from the hydrolysis stage (prior to methanogenesis), a product with higher energy value than methane. This hydrolysis stage is also known as dark fermentation, which produces volatile fatty acids (VFAs), carbon dioxide (CO_2), and biohydrogen. The latter is a biofuel with energy yields ranging from 120 MJ/kg to 140 MJ/kg, in comparison to other sources such as natural gas with 50–55 MJ/kg, crude oil 42–47 MJ/kg, or coal 10–23 MJ/kg [8].

In contrast to conventional hydrogen, which requires high-energy-demanding methods for recovery, such as the non-catalytic partial oxidation of fuels, steam methane reforming, membrane processes, selective methane oxidation, oxidative dehydrogenation, and electrochemical processes [9], biohydrogen recovered through dark fermentation is one of the metabolic by-products of microorganisms degrading sugars and carbohydrates found within organic matter; therefore, its energy demand is not significantly high.

In the dark fermentation process, anaerobic bacteria degrade carbohydrates under anaerobic conditions and absence of light to produce biohydrogen [10]. Starting from glucose, the maximum theoretical moles of H_2 can be obtained, corresponding to a value of 4 moles of H_2 when acetic acid and CO_2 are among the products, as shown in Equation (1). However, if butyric acid is among the products, the reaction's yield in hydrogen production will be equal to 2 moles of H_2, as shown in the development of Equation (2) [7].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2\ \Delta Go = -206\ kJ\ mol^{-1} \tag{1}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COO\text{-} + 2HCOO\text{-} + 4H^+ + 2H_2\ \Delta Go = -209.1\ kJ\ mol^{-1} \tag{2}$$

$$2HCOOH \rightarrow 2CO_2 + 2H_2\ \Delta Go = -6\ kJ\ mol^{-1} \tag{3}$$

In real conditions, the yield will be less than 4 moles because besides the mixed production of butyric and acetic acid, it is likely that hydrogen-consuming bacteria such as methanogenic organisms, sulfate-reducing bacteria (SRB), nitrate-reducing bacteria (NRB), propionate producers, iron-reducing bacteria, and lactic acid bacteria are present within the microbial consortium [10].

The recovery of biohydrogen through dark fermentation using biomass as a substrate has gained significance in recent years. Specifically in the field of biofuels, there is a variety of research focused on biohydrogen production from a wide range of substrates, from microalgae cultivation to agro-industrial waste.

In addition to substrates, microbial consortia and process variables such as temperature, pH, organic loading, and the substrate–inoculum ratio have also been studied to ensure the best possible biohydrogen production [11].

Regarding microorganisms participating as inocula in the dark fermentation process, both pure and mixed cultures have been used. With pure cultures, bioaugmentation tests have been conducted with strains of bacteria like *Clostridium pasteurianum*, *Clostridium acetobutylicum*, and *Lactobacillus bulgaris*. It was found that in bioaugmented cultures, the metabolic process was more stable than in mixed cultures, but hydrogen production was limited due to trophic competition between the strains and the original consortium [12]. On the other hand, when a mixed culture is subjected to a mixed micro-oxidative environment, the hydrogen yield remains similar to pure culture conditions, but after 9 days, the process becomes unstable, possibly due to prolonged stress on the culture [13].

pH has been considered an important parameter for achieving higher biohydrogen production, with the process's by-products depending on it and its variation during the process. For a pH lower than 5, production is primarily of lactic acid. If the pH value falls within the range of 5 to 5.5, the main products are biohydrogen and butyric acid. Finally, if the pH value exceeds 6, the main products are biohydrogen and sulfate [14]. The optimal pH for production is 5.5 since it results in the lowest production of volatile fatty acids. Low pH values inhibit enzymatic and hydrogenase activities, which consume hydrogen [15,16].

Waste materials as substrates for biohydrogen production have been utilized in different studies. Food waste has shown performance results in hydrogen production of 49.9 mL H_2F/g-VS [17], whereas OFMSW at a temperature of 37 °C yielded a production of 41.7 (±2.3) ml H_2/g-VS, attributed to the presence of organic compounds such as carbohydrates. These carbohydrates, with short chains, are easily assimilated by fermentative bacteria. The biogas obtained consists of H_2 and CH_4, representing 28% and 72% of the total energy recovery from the OFMSW [18].

Organic loading is considered a relevant variable since the overall efficiency of the fermentation process depends on it. If the organic loading is too low, there will be poor biohydrogen production, while if it is too high, the process will be inhibited [19]. Organic loading plays an essential role in defining the metabolic pathways the fermentation process will take. It has been observed that at high organic loadings, the metabolic pathway starts shifting from acetogenesis to solventogenesis, leading to a phase of inhibition due to the concentration of VFAs [20]. It has also been concluded that hydrogen productivity increases before reaching the point of inhibition due to saturation with increased organic loading, but the hydrogen yield rate decreases at high organic loadings [21].

The substrate–inoculum ratio (s/x) affects substrate biodegradability and, consequently, biogas generation and process by-products. If s/x is less than 0.5 gVSs/gVSi with an acidic substrate, biogas production may be inhibited due to acidification. If s/x exceeds 6 gVSs/gVSi, there may be low biogas production yields due to low substrate biodegradability [22,23].

Furthermore, s/x directly influences cell growth patterns (metabolism) since growth can be closely linked to the initial substrate concentration. The variable gains importance when using complex substrates that, due to their molecular composition, have an impact on process inhibition, resulting in reduced microbial activity and, consequently, reduced production of metabolites such as hydrogen [24].

In Colombia, research on waste valorization has been conducted using substrates like pig manure, organic waste from marketplaces, and various fruit crop residues [23,25–29]. It has been found that substrates like coffee mucilage have a high potential for hydrogen production compared to other raw materials such as wheat starch and cassava [30]. Coffee mucilage has also been combined with organic waste from marketplaces to obtain optimal conditions for dark fermentation [31]. Given the above, developing a technology for valorizing the organic fraction of municipal solid waste, including dark fermentation, is feasible for a megacity like Bogotá.

Therefore, defining the process conditions to achieve the highest efficiency in OFMSW conversion is relevant. This research evaluates the dark fermentation process as an alternative for the energy valorization of OFMSW produced by Bogotá, obtaining biohydrogen and energy as value-added products. Different combinations of initial organic loading and the substrate–inoculum ratio were used to analyze biogas production yields. The process was scaled with the results, and the energy valorization plant for OFMSW was dimensioned. From an energy perspective, the scaled process was found to be sustainable, but further studies are recommended, including subsequently anaerobic digestion and digestate composting, which address a broader dimension within waste management.

The results obtained in this research will serve as a fundamental basis for formulating a methodological proposal to integrate life cycle assessment into the comprehensive management of the organic fraction of urban solid waste in megacities. This proposal addresses the inclusion of the dark fermentation process before anaerobic digestion as an alternative to improve energy yields and reduce greenhouse gas generation.

2. Materials and Methods

2.1. Substrate

To ensure optimal operational conditions, the experimental development began with the collection and preparation of the substrate, obtained by segregating organic waste generated in a residence inhabited by a family of 4 people. Consequently, the substrate consists of fruit peels, vegetable residues, and leftovers from cooked food. The collection took place over a period of 3 days. The collected waste underwent cutting and particle size reduction operations, and then it was stored in sealed packages and placed in a refrigerator maintaining a temperature of −4 °C. Refrigeration delayed their decomposition, thus preserving their physicochemical characteristics until the start of the experiments during the experimental phase. It is noteworthy that the particle size reduction procedure was carried out to ensure a homogeneous mixture between the substrate and the inoculum [32].

2.2. Inoculum

A sample of inoculum was taken from the bioreactor of the wastewater treatment plant at Alpina Productos Alimenticios S.A, located in the municipality of Sopó, Cundinamarca [33]. In the laboratory, the sludge sample underwent a thermal shock at a temperature ranging between 80 °C and 90 °C for a duration of 30 min. This operation ensured the inactivation of methanogenic bacteria within the sludge, thereby reducing the potential hydrogen consumption by these microorganisms [34].

2.3. Experimental Design

In order to determine hydrogen recovery using OFMSW as a substrate under conditions favoring the dark fermentation process, experiments were designed to evaluate organic loads of 5, 10, and 15 g of volatile solids per liter (gVS/L). The influence of the substrate–inoculum ratio (s/x) was also assessed, expressed in units of grams of volatile solids of substrate per gram of volatile solids of inoculum (gVSs/gVSi), with values of 1, 0.75, and 0.5 gVSs/gVSi. A total of 9 experiments were conducted, each in triplicate. Additionally, for each experiment, a blank was set up in which only the inoculum was applied. This was performed to identify the hydrogen recovery resulting from its biological activity, which was subtracted from the total hydrogen recovery. Thus, the hydrogen production contributed by OFMSW was obtained.

Table 1 schematically illustrates the experimental design.

Table 1. Experimental design.

Combination	Organic Load (gVS/L)	s/x Ratio (gVSs/gVSi)
C1	5	0.5
C2	5	0.75
C3	5	1
C4	10	0.5
C5	10	0.75
C6	10	1
C7	15	0.5
C8	15	0.75
C9	15	1

Experiment C7 was discarded due to the negative outcome in the water volume obtained after calculating the quantities of substrate, inoculum, and water necessary to meet the conditions. This is attributed to substrate characteristics such as the percentage of total solids and its density.

The variables under control were pH and temperature. Considering the optimal pH range for maximum hydrogen yield falls between 5.2 and 6.0, a pH of 5.5 was utilized [35]. The assumed temperature for all experiments was 45 °C.

The experimental setups employed amber glass bottles of 250 mL, containing a 200 mL volume composed of substrate, inoculum, distilled water, and 10 mL of a buffer solution constituted by 37% HCl for pH adjustment. The reactors were sealed and placed in a thermostat bath to initiate the test [28].

For the measurement of hydrogen recovered during the FO phase, the volumetric displacement method was applied, where a liquid's volume is displaced by the generated volume of biogas [36]. Therefore, during the experiments, the biogas stream produced in the reactors was bubbled through a NaOH solution to capture the CO_2 present in the stream [28]. The bottle was connected to a third bottle through a micro-drip hose to collect and measure the volume of the displaced NaOH solution, which served as an indicator of the biogas volume produced during each trial [33].

Given that the present study aimed to determine hydrogen production from OFMSW using the FO process, each trial concluded upon detecting traces of CH_4 in the chemical composition of the biogas. This signified the end of the FO phase, transitioning into the methanogenesis phase. To verify the traces of substances in the biogas stream, the biogas composition was characterized every 24 h using the Biogas 5000 Landtec equipment, capable of detecting the presence of CH_4 [28].

The experimental results were statistically processed (average, standard deviation, and Pareto analysis), and the conditions yielding the highest performance were employed in developing the conceptual design of the dark fermentation plant.

2.4. Analytical Method

For the characterization of both the substrate and the digestate resulting from the FO conducted on the samples, the organic matter, total solids, and volatile solids were determined using an approximate analysis based on the procedures described by APHA 2540B for the determination of VS and TS.

Kjeldahl nitrogen, volatile fatty acids, and chemical oxygen demand were quantified following the methodology proposed by ASTM D3590-02 [37], ASTM D1076 [38], and ASTM D1252 [39], respectively. The elemental composition of the collected OFMSW was also assessed [28,33].

2.5. Scaling and Environmental Analysis Process

After selecting the best result in terms of biohydrogen production, the process was scaled up, considering the quantities of waste from OFMSW obtained from the literature review. Block diagrams and material balances were constructed to define the mass flows related to the process inputs, by-products, residual flows, energy flow, and the quantities of biohydrogen resulting from the scaled-up process. Once the quantities were defined, each process and unit operation with their respective input and output flows were entered into Excel v.16.78.3 software, where the dimensions of the valorization plant equipment were determined. Finally, with the scaled-up installation, an analysis was carried out focusing on the benefits and challenges of this valorization strategy within the context of waste management, biorefineries, and circular economy.

3. Results

In this section, an analysis of the data obtained from substrate characterization, hydrogen production, and volatile fatty acids (VFAs) generated from different proposed combinations is conducted. The block diagram of the scaling-up process for the city of Bogotá is presented, along with the sizing of the equipment in the plant.

3.1. Substrate and Inoculum Characterization

Table 2 presents the chemical characterization of the substrate. Notably, the highest mass percentage, as per the elemental analysis results, is distributed among carbon, oxygen, and hydrogen. When comparing these values with other studies, there is a similarity in the distribution and hierarchy of the results [40,41]. Concerning carbon, previous research indicates a percentage ranging from 40.6% to 48.6% for cities in Latin America [42]. The result of 48 in the current investigation may be attributed to the urban environment of Bogotá, where food waste comprises a higher proportion of lipids, proteins, and carbohydrates, making them directly susceptible to anaerobic digestion processes.

Table 2. Chemical characterization of the substrate.

Parameters	Value	Unit
TS	20.80	%
VT	15.07	%
VS on a dry basis	72.47	% dry basis
DQO	0.18	g/L
NTK	1.56	% dry basis
C	48	% dry basis
H_2	6.4	% dry basis
O_2	37.6	% dry basis
N_2	2.6	% dry basis
S_2	0.4	% dry basis
Ashes	5	%

On the other hand, the values obtained for N_2 may reflect difficulties in the growth and replacement of microbial cells responsible for substrate digestion. Additionally, in the event of an acidogenic phase, it is expected that the organic acids produced will be primarily of short-chain nature [43].

Regarding the resulting values in total solids and volatiles, it was found that they are below those reported in other studies, where the percentage of TS is around 30% and the percentage of VS is over 80% on a dry basis [44]. However, other studies report VS percentages of 66%, lower than the value obtained in this study [45]. In this sense, it is important to consider this heterogeneity in results, stemming from regional differences in variables such as economic context and dietary habits.

The result of VS determines how susceptible the substrate is to degradation by biological methods such as anaerobic digestion, with a higher fraction of VS indicating better affinity for these processes [44]. For the present case, biological treatment of the substrate is feasible, but due to the specific characteristics of OFMSW, biogas production yields might be lower compared to other research.

Regarding the inoculum, it shows values of 5.12% TS and 4.21% VS, results that also bear similarity to some studies (5.6 TS and 4.94 VS) [28], but differ more significantly from others (1.96% TS and 1.48% VS) [46]. This discrepancy may be because the inoculum used for biomethanization potential tests is often in liquid form, leading to variations due to the different densities in which the inoculum is presented for each research. It is crucial to consider these variations as the results contribute to defining the quantities of inoculum and substrate to use, ensuring the process operates under the most efficient initial organic load and s/x ratio values.

3.2. Hydrogen Production Potential and Selection of the Best-Performing Combination

Regarding the hydrogen production obtained for the different combinations of organic load and s/x tested in the experimental phase of the project, it was determined that, in general terms, the analyzed combinations had a hydrogen production period of around

9 to 10 days before the methane concentration in the biogas increased to levels greater than or equal to 20%, a definitive indicator of the onset of the methanogenic phase, and consequently, the conclusion of the experiment.

From the experimental phase, it was found that the combination with the best yields in terms of production was C6, with an operating time of 9 days, producing a total of 89,420 mL/gSV. The next combination was C3, which reported a production of 71,773 mL H_2/gSV. On the other hand, the combinations with lower productions were C4 and C7, which presented a production of 11,547 mL H_2/gSV and 24,173 mL H_2/gSV, respectively.

From Figure 1, it is identified that combinations C1, C2, C3, and C6 show the highest performance in biogas production. Excluding C6, the aforementioned combinations share the same value in organic load, 5 gVS/L. Taking this into account, it could be stated that low organic loads combined with low s/x ratios favor H_2 production. This situation has been evidenced in other studies that have concluded that an increase in organic load causes a decrease in hydrogen production and aspects such as COD and protein removal [46–48].

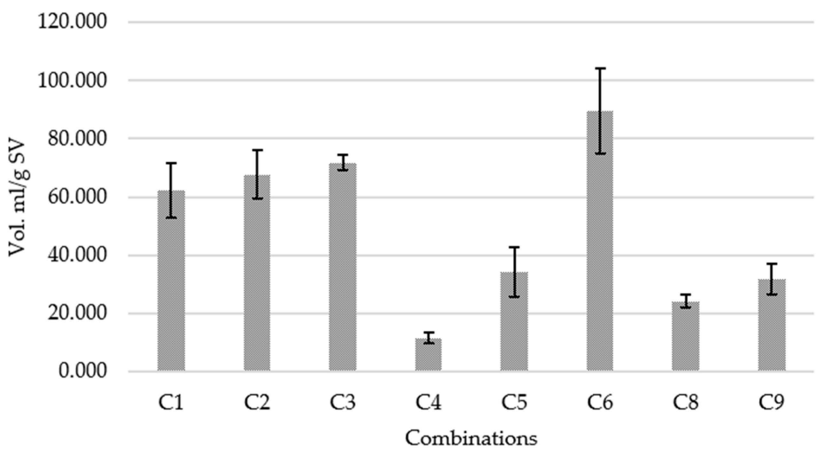

Figure 1. Biogas production obtained for each evaluated combination.

It is essential to consider the influence of s/x, as considerably low values may result in fermentative inhibition due to a lack of organic matter at low organic loads. Therefore, comparing the production obtained for each of the different combinations presented in Figure 1 reveals an influence of s/x on biogas production, where the highest volumes produced for each load were observed in combinations with s/x equal to 1. This result aligns with findings in other studies that demonstrated an increase in production with an increase in the s/x value [49,50]. On the other hand, other research suggests possible acidogenic pathways taken by the process with high levels of propionic acid and VFAs during the tests, but with very low yields in H_2 production, emphasizing the importance of controlling the s/x variable [46,51].

It is worth noting that studies conducted on FO using specific substrates have better hydrogen production yields than the present research. For example, those that have used substrates such as pig manure, cocoa mucilage, and coffee mucilage have organic matter determined by the percentage of volatile solids 20% higher than the current study [28,52]. The low process efficiency could be a result of metabolic deficiency affecting the microorganisms present in the inoculum. This assertion gains strength when reviewing the Pareto diagram obtained, where the highest H_2 productions for each evaluated initial organic load concentrate in combinations with s/x equal to 1, meaning those with a higher substrate-to-inoculum ratio. Therefore, it is expected to have a lesser influence of metabolic deficiency on the process in such combinations.

In Figure 2, it is evident that the percentages of biogas volume produced are distributed following a predetermined order that corresponds to the value of s/x. The higher the s/x, the greater the percentage of hydrogen produced by the combination. The same does not happen with the initial organic loads, for which it is not possible to define an order with respect to their production percentage. Therefore, it is analyzed that, under the evaluated values, the s/x variable has a greater impact on biogas production.

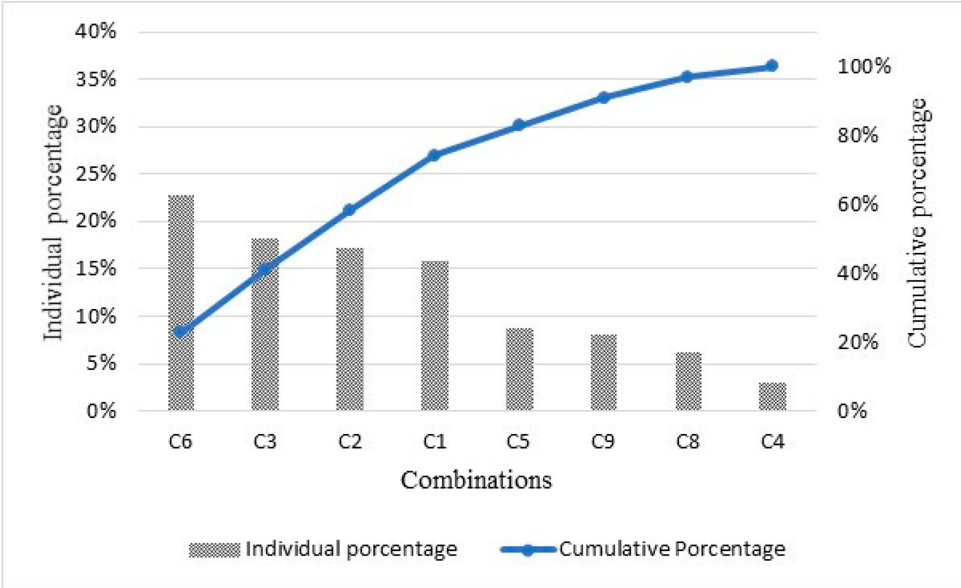

Figure 2. Pareto chart on biohydrogen production.

3.3. Quantification of VFAs in the Effluent

Regarding the effluent resulting from the biogas production in the experimental phase, the overall quantification of VFAs production was conducted to define the potential metabolic pathway followed by the reactors under the evaluated conditions of temperature, initial organic load, and s/x ratio. Figure 3 contrasts the levels of biogas production with the associated production of VFAs without detailing the specific substance.

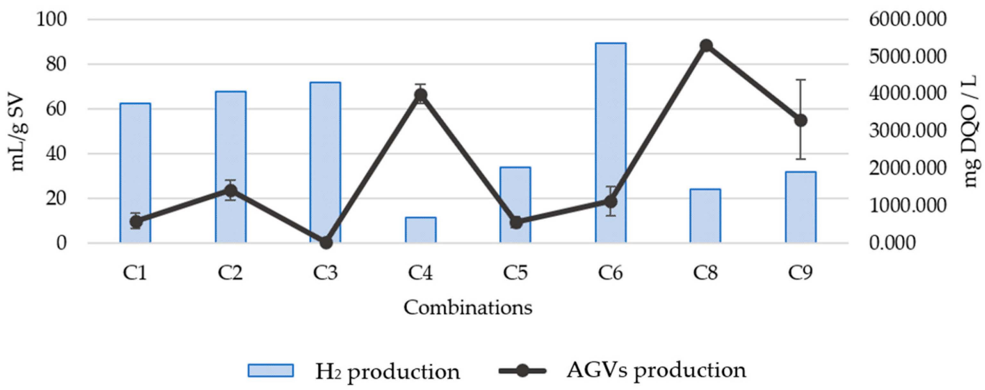

Figure 3. Biogas and volatile fatty acids production.

Reviewing the behavior of the combinations in Figure 3, for combinations with an s/x of 1, the increase in initial organic load meant an increase in the production of VFAs, which is in line with the results obtained by other studies [52]. This situation repeats for combinations with an s/x of 0.5, where the variation in produced VFAs is more evident with an increase in organic load. Therefore, it is evident that low organic loads are considered a limiting factor in VFAs production due to the small amount of substrate [20]. On the other hand, combinations with an s/x of 0.75 showed a different behavior. Specifically, C2, with a load of 5 gVS/L, had a higher production than C5, with a load of 10 gSV/L. Regarding the biogas produced, the conditions in C2 were more favorable for fermentation than in C5, as both biogas and VFAs production were higher, indicating better substrate digestion and therefore a better process performance.

The cases of C4 and C8 are noteworthy, as both show the lowest biogas production and, at the same time, the highest levels of VFAs. This indicates that fermentation under the values of the analyzed combinations leaned almost entirely towards acidogenic pathways. Considering that undissociated VFAs can penetrate the cell membrane of the microorganisms composing the inoculum, causing a pH reduction and leading to unfavorable physiological conditions, this can result in process inhibition [53]. While this could explain the behavior in both combinations, it is necessary to consider that in both cases and despite the low yields, total inhibition did not occur. This may be because, during the laboratory tests, the digestive process was completed to the methanization point for all combinations tested. In the case of mixed-culture inoculum (WWTP sludge), there could have been the presence of microorganisms that competed with H_2-producing bacteria, such as those associated with propionic acid production [54]. This is reflected in the high concentrations of VFAs recorded by the combinations in general and particularly by C4, C8, and C9, which coincidentally were the combinations with the lowest biogas production.

While all experimental phase tests generated high concentrations of VFAs, the biogas yield associated with the combinations C1 to C3 is mainly determined by the limited availability of substrate, considering significantly low initial organic loads and s/x. In other words, the substrate is the limiting factor of the process, a situation that extends to the combinations C5 and C6. On the other hand, fermentation in C4, C8, and C9 took acidogenesis as the main route, favoring the production of VFAs at the expense of consuming and/or inhibiting H_2 production. It was observed that this situation occurred when increasing the initial organic load while maintaining a low s/x, aligning with the results obtained in other studies [52].

3.4. Sizing and Scaling of the Utilization Plant

To develop the sizing of the utilization plant for OFMSW produced by the city of Bogotá, the best result in terms of biohydrogen production obtained in the tests with the previously defined loads and s/x ratio was scaled up. The results of this process and a general technical analysis will be presented below, with the central axes being solid waste management and alternative energy sources.

3.4.1. Population Projection and Substrate Availability

To estimate the population served by the valorization plant, we followed the guidelines outlined in the technical regulation of the water and sanitation sector to design municipal waste management systems [55]. A project lifespan of 20 years starting from 2022 was considered, and it was dimensioned to cater to the urban population of Bogotá projected for 2042. Considering the economic and demographic significance of the city, which accounts for approximately 25.6% of the national production [56], it was characterized as a system of high complexity, as shown in Table 3 [55].

Table 3. Projection methods according to complexity level.

	System Complexity Level			
Method to be Used	**Low**	**Medium**	**Medium-High**	**High**
Arithmetic	X	X	X	
Geometric	X	X	X	X
Wappaus	X	X	X	X
Graphical	X	X	X	
Exponential	X	X	X	
Detailed by Zones			X	X
Detailed by Densities			X	X

Considering that the complexity level for Bogotá is high, the detailed method by zones or demographic components was chosen. This method analyzes factors such as the birth rate, death rate, and net migration balance. For the year 2042, a projected urban population of 8,970,675 inhabitants was obtained [57]. With the population defined for the 20-year period, the annual production of solid waste expected for the projected year was calculated. For this calculation, it was multiplied by the projected population by a per capita solid waste production factor [55].

$$p_e = P_f \times F_p \tag{4}$$

where p_e is the expected solid waste production, P_f is the projected population, and F_p is the production factor whose values depend on the complexity level of the system/population that the project is intended to serve. The different values to be used for each complexity level are presented in Table 4.

Table 4. Per capita production factors.

Complexity Level	Minimum Value kg/Capita-Day	Maximum Value kg/Capita-Day	Average Value Kg/Capita-Day
Low	0.3	0.75	0.45
Medium	0.3	0.95	0.45
Medium-High	0.3	1	0.53
High	0.44	1.1	0.79

For the proposed valorization plant, a value of 0.79 kg/capital-day, the high average, was chosen to reduce the risk of over-sizing or under-sizing the plant. After applying the equation to calculate waste generated over 20 years, the projected value obtained was 7,086,833.25 kg/day.

With the results obtained for projected MSW in the urban area of Bogotá, an organic fraction percentage of MSW for the city was assumed, as stipulated in Decree 495 of 2016, which is 51.32%. With this percentage, Table 5 was constructed, indicating the quantities of waste belonging to the OFMSW for the projected year.

Table 5. Waste generation projection in the urban area of Bogotá.

Year	Daily Projected MSW Production (kg/Day)	Daily Projected OFMSW Production (kg/Day)
2042	7,086,833.25	3,636,962.82

With the retention time obtained in the laboratory results, a waste input flow to the valorization line of 32,732,665.38 kg was assumed. With this quantity, the hydrogen production process was scaled, and the input and energy requirements were defined to carry out the process. The size and quantity of the equipment involved in each of the intrinsic unit operations and processes for the valorization of urban organic waste through dark fermentation were determined.

3.4.2. Formulation of the Scaled Process Block Diagram

To define the operations and unit processes integrated into the valorization plant, theoretical designs of biomass valorization facilities through anaerobic digestion were taken as a starting point [58,59]. With the experimental results from the combination C6, the main material and energy flows theoretically involved in the valorization process were identified and constructed.

Figures 4–6 present the material and energy diagrams for three main stages, covering the substrate preparation, the fermentative process in a continuous stirred tank reactor (CSTR), and electricity generation from the scaled hydrogen combustion. To ensure homogeneous mixing in the reactors and maximize the surface contact area to increase biohydrogen production efficiency, it is proposed that before the fermentative process, the substrate in the mass flow input, in this case, the OFMSW, undergoes a preparation stage as shown in Figure 4.

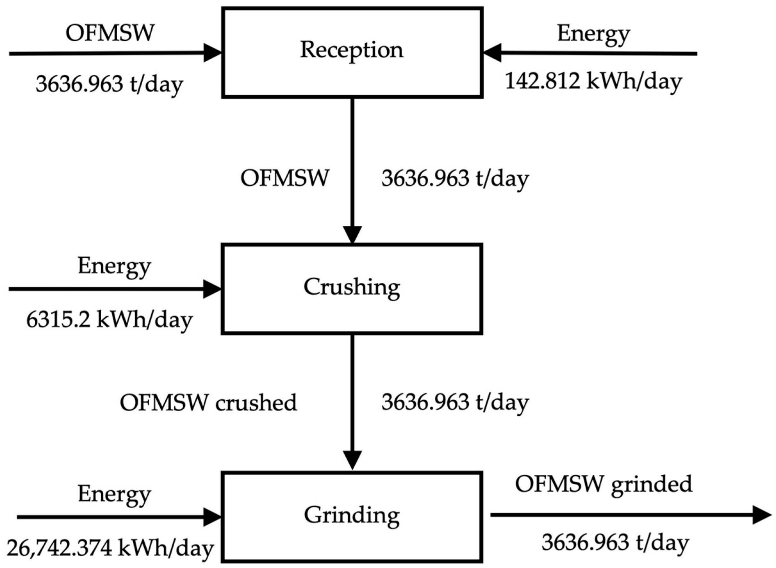

Figure 4. Substrate preparation stage.

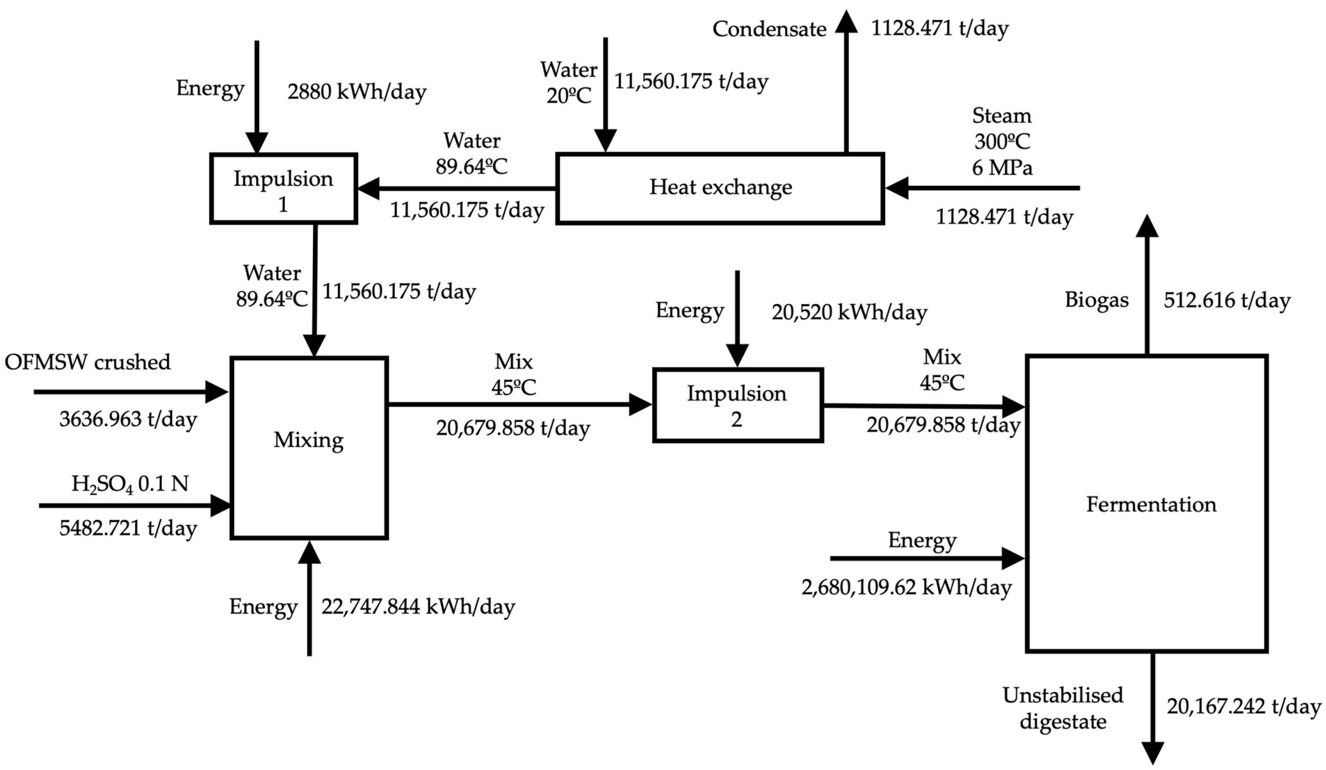

Figure 5. Mixing and fermentation stage.

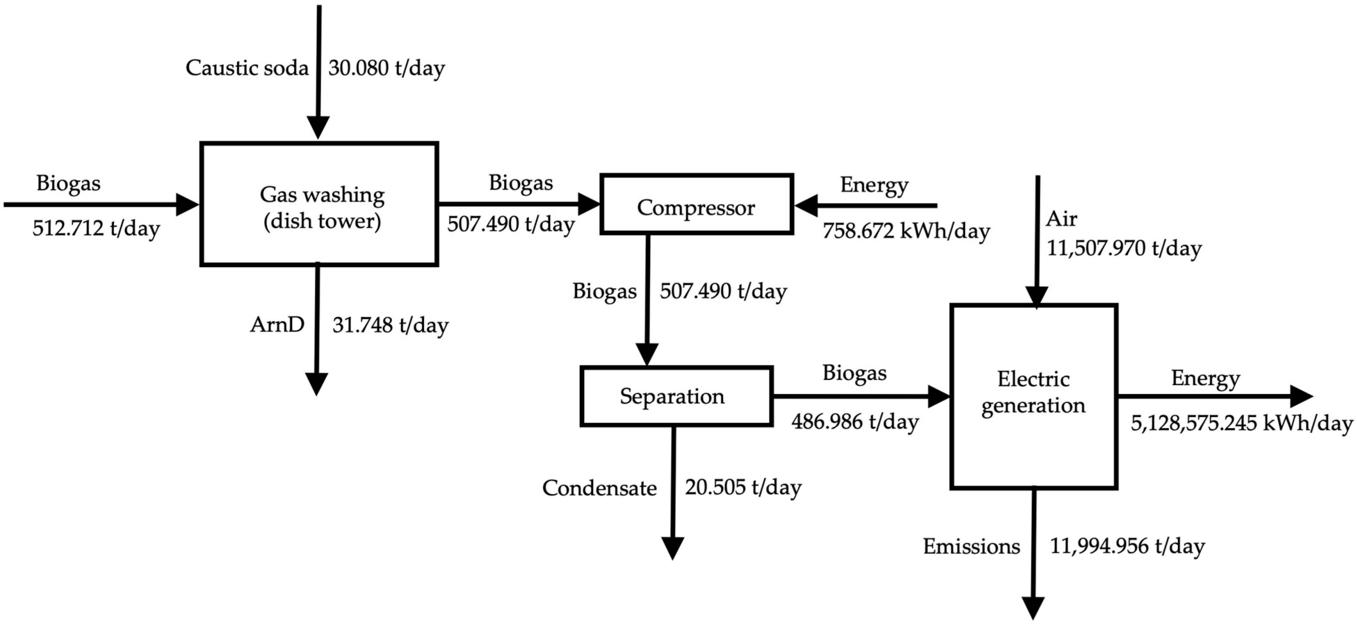

Figure 6. Biogas purification and power generation stage.

This stage is proposed in two particle size reduction operations. The first operation involves cutting or shredding the substrate, aiming to achieve a particle size suitable for feeding the mill. The second operation involves grinding the substrate to a particle size smaller than 5 mm. Considering that the feeding is conducted on a wet basis, a ball mill is proposed for this purpose [60]. Since this equipment can process wet organic matter and bring it to the desired particle size, it is not considered necessary to apply a drying operation to the substrate during the preparation stage.

Once the grinding stage is completed, it moves on to the mixing and fermentation stage as shown in Figure 5.

The OFMSW will be transferred to a mixing tank, where it will form a mixture consisting of 5482.72 t/day of H_2SO_4, which functions to maintain the pH at 5.5, and 11,560.175 t/day of water at a temperature of 89.64 °C. When combined with the other mass streams that make up the mixture, it will ensure an organic loading rate in the mixture of 10 gSV/L and a constant temperature of 45 °C.

To raise the temperature of the water stream to 45 °C, a heat exchange operation is proposed, where a high-pressure steam stream at 6 MPa and a temperature of 300 °C are used. Upon contact with the water stream at 20 °C, the temperature is raised to 89.64 °C. The water stream is driven by a centrifugal pump to the mixing tank.

Once homogenized, the mixture is transported to the CSTR reactors, preferred for continuous and large-scale hydrogen production [61]. In the reactors, a homogeneous mixture must be ensured so that microorganisms can fully utilize the substrate. It is important to monitor the substrate fermentation process in the reactor to ensure a sequential evolution of digestion during the residence time, which, in this case, is 9 days [62]. As a result of fermenting OFMSW inside the CSTRs, two mass flows emerge. The first is a stream of 512,612 t/day of biogas composed mainly of H_2, CO_2, H_2S, and H_2O that needs to be purified. The second flow is 20,167,242 t/day, consisting of digestate that is susceptible to biomethanization. A fraction of this could be incorporated into a new valorization line, while the rest must be used for the recovery, cultivation, and rehabilitation of the inoculum. This is a strategy to maintain the s/x ratio of 1 defined for the process.

To determine the mass flow and composition of the generated biogas, the process observed in the laboratory was scaled. Optimistic percentages were taken, fixing the H_2 percentage at 60%, CO_2 at 35%, 4% for water vapor, and 1% for the trace of H_2S [63]. Based on this mass composition, it was possible to define the mass flows of inputs and outputs for biogas washing, a unit process that is part of the biogas purification stage as shown in Figure 6.

It is proposed to use a plate tower fed with a 50% caustic soda flow as a strategy to eliminate the trace of H_2S through an oxidation reaction, thus producing a residual effluent composed of sodium sulfide and water. NaOH was chosen as the capture solution due to its high efficiency and low design and operating costs at low H_2S percentages, along with a simple technology [63].

After removing traces of H_2S, it is necessary to purify the water vapor within the biogas stream to ensure a better stoichiometry of combustion during power generation. For vapor removal, the pressure of the biogas stream is reduced to atmospheric pressure, causing the condensation of the H_2O present in the stream, which, for the scaling case, corresponds to 20,505 t/day.

Finally, the biogas mass flow reaches a combustion stack, where the combustion of H_2 takes place. In this reaction, atmospheric oxygen, representing 20.95% of the air, is used as the oxidizing agent, and the main product is water vapor. It is important to note that, along with the vapor produced from the combustion/oxidation of H_2, nitrogen at high temperatures from the captured air and CO_2 from the fermentation process are also released into the atmosphere. Depuration was not performed in the sizing as it does not pose a high risk of corrosion to the equipment responsible for gas propulsion, H_2O separation, and electricity generation.

Regarding power generation, the combustion of biogas will produce a total of 5,128,575.25 kWh/day of energy. Subtracting the electrical consumption of the equipment used in the process, which is 2,760,216.53 kWh/day, the net production of useful energy is equal to 2,368,358.72 kWh/day, which will be delivered to the city's energy system.

3.4.3. Equipment Sizing

For equipment sizing, in addition to considering the mass flows that make up the scaled process, references and technical data sheets of real equipment were consulted on international websites. From these references, the equipment with the highest capacities or at least the ones closest to the required capacities were selected. As a result, Table 5 was obtained, which includes details such as the operation or unit process to be developed, the equipment where it takes place, the capacities required according to scaling, the capacities offered by the equipment, and the number of required equipment units.

In Table 6, the determination of size and quantity of units required for each process is elucidated. For instance, in defining the quality and quantity of CSTR reactors, considerations encompassed the magnitude of inflow to the unit process and the hydraulic retention time specified in the experimental phase for the combination C6. This facilitated the determination of necessary useful volume, and subsequent exploration of market references yielded selections based on optimal performance. Notably, reactor volume served as the primary selection criterion. Similarly, for the centrifugal pumps, outcomes were informed by the maximum nominal flow rate of the chosen reference. This line of reasoning extends to the determination of the number of crushers and mixing tanks. Nonetheless, while results are grounded in market-available equipment, consideration of alternatives, such as bespoke designs, warrants attention. Such an approach could potentially streamline unit numbers but may also necessitate specialized logistics, potentially impacting spare-part availability and equipment maintenance practices.

Table 6. Capacities and number of proposed equipment for the valorization plant.

Operation/Unit Process	Equipment	Required Capacity	Offered Capacity	Operational Unit	Number of Equipment
Storage	Hopper	151.54	191	t/h	1
Dark Fermentation	CSTR Reactor	186,118.72	10,000	m^3	19
Impulsion 1	Centrifugal Pump	481.67	500.00	m^3/h	1
Impulsion 2	Sludge Pump	861.66	45.35	m^3/h	19
Biogas Impulsion	Compressor	307.57	360.00	m^3/h	1
Heat Exchange	Heat Exchanger	1700.23	1700.23	m^3/h	1
Gas Washing	Plate Tower	380.00	380.00	m^3/h	1
Mixing	Mixing Tank	861.66	50.00	t/h	17
Grinding	Ball Mill	151.54	170.00	t/h	1
Separation	Flash Separator	307.57	307.57	m^3/h	1
Crushing	Crusher	151,540.12	20,000.00	kg/h	8
Combustion Cell	Power Generation	5,128,575.25	264,000.00	kwh/dia	19

Additionally, it is pertinent to mention that for the flash separator, the plate tower, and the heat exchanger, references were found where the construction of these equipment items will depend on the flows and volumetric flows provided by the client. In other words, these industrial equipment items are built according to the mass streams with which they are intended to operate.

Regarding the hydrogen combustion cell, a phosphoric acid fuel cell (PAFC) model was selected due to the characteristics defined by the National Hydrogen Center (2018). These characteristics include the ability to accept impure hydrogen streams as a power source, such as the stream delivered by the flash separator, and a maximum generation capacity equivalent to 11,000 kWh, resulting in a total of 19 units.

3.5. Technical Analysis of the Process as an Alternative for the Energy Recovery of OFMSW

Regarding the environmental aspects related to the operation of the valorization plant, all operations and unit processes comprising the valorization process are linked to one or more environmental aspects. These include energy consumption, water usage, generation of effluents, atmospheric emissions, and potential production of special solid waste.

Concerning electrical energy consumption, it is noteworthy that the mixing and fermentation stage, depicted in Figure 5, has the most significant impact on this environmental aspect overall, representing 98.77% of the total energy expenditure throughout the scaling. This is primarily due to the fermentation of the mixture, where energy consumption amounts to 2,680,109.62 kWh/day. This high consumption is explained by considering the magnitude of the volume into the reactors units, which is 20,679,858 t/day, being the largest stream in the entire scaling process. Additionally, the density of the residues in the mixture and the RTH needs to be considered, implying more work and thus greater energy consumption by the reactor's mixer's engines. Strategies such as regular maintenance of the mixers and their engines to ensure their efficiency and the application of eco-design concepts in the plant's architectural design could help to minimize these energy expenses.

As for water consumption, it is concentrated in the mixing and fermentation stage, where the primary water stream is used to integrate the mixture to be fermented. This is crucial in defining the organic load of the mixing liquor fermented in the CSTR reactors. Another significant water flow is that of steam, which acts as a working fluid to transfer the necessary energy to raise the temperature of the mixture water to 89.64 °C. This steam becomes condensate that ends up being considered a discharge into the sewage system. Given that the process consumes a total of 12,688,645 t/day of water, proposing a recirculation and recycling system for these streams is necessary for efficient water use. Furthermore, to recycle the water stream feeding the mixing tanks, a wastewater treatment system focused on removing suspended solids and organic matter needs to be considered, as these could affect the operation of equipment such as the heat exchanger and the centrifugal pump.

The presence of effluents considered industrial or non-domestic wastewater discharges is notable, including condensate from steam used to heat water during the heat exchange operation, effluent from the plate washing tower composed of acidic waters, and condensate resulting from the flash separation. These discharges constitute a mass flow, as shown in Table 6, equal to 1,180,724 t/day. Therefore, it is necessary to consider strategies for managing, treating, and reducing the effluent from generated industrial wastewater. These strategies could range from recirculation, in the case of residual condensate from heat exchange to the application of coagulation and/or chemical oxidation treatments for acidic wastewater from gas washing. The main environmental aspects are summarized in Table 7.

Table 7. Main environmental aspects.

Environmental Aspect	Quantity	Unit of Measure
Water Consumption	12,688.65	t/day
Effluent from Industrial Wastewater	1180.72	t/day
Direct CO_2 Emissions	64,831.89	t CO_2 per year
Carbon Footprint from Indirect Emissions	126,942.36	t CO_2 eq per year
Total Carbon Footprint	191,774.24	t CO_2 eq per year

When discussing atmospheric emissions, they are categorized into direct and indirect emissions. Direct emissions result from the development of a process or unit operation within the production process, while indirect emissions are a consequence of activities carried out by the organization but occur in sources owned or controlled by another organization [64]. In terms of dimensioning, direct atmospheric emissions result from the electricity generation carried out in the combustion cell, emitting 2748.654 t/day of water vapor and 177.622 t/day of CO_2. The latter is classified as a process emission, not combustion-related, because the CO_2 is produced during the dark fermentation in the CSTR reactors of the plant. When annualizing this emission, the direct CO_2 emission is equal to 64,831.89 t CO_2 per year. The emitted N_2 corresponds to the nitrogen present in the air captured for the combustion of H_2. As for indirect emissions, these can be calculated by considering the total electrical energy used during the valorization process, which is 2,760,216.53 kWh/day, and multiplying it by the emission factor defined for the Colombian electrical grid, which, according to the Mining Energy Planning Unit, is 0.126 tons CO_2 eq/MW [65]. Following this calculation, the carbon footprint due to indirect emissions is 126,942.36 t CO_2 eq per year, resulting in a total carbon footprint of 82,686.768 t CO_2 eq per year.

Regarding unstabilized biodigestate, if it were to be discarded and sent to final disposal after completing the dark fermentation phase, it would become a residual flow requiring special management due to its physicochemical and biological characteristics. Additionally, halting anaerobic digestion would prevent the controlled development of the methanogenic phase, resulting in a loss of the methane potential present in the organic matter constituting the biodigestate.

Furthermore, final disposal of the biodigestate would hinder the possibility of obtaining by-products such as VFAs present in the fermentative effluent. Therefore, once evacuated from the biodigester, the biodigestate should be transferred to a new production line to exploit the fermentation by-products. For the current project, considering Figure 3, there is an attractive possibility of using the effluent/digestate as a source for extracting these chemical compounds. These compounds could be used, for example, in the synthesis of esters, ketones, aldehydes, alcohols, and alkanes—substances utilized in the pharmaceutical chemical industry and in the production of biopolymers as PHA precursors [54,66]. The presence of VFAs in the effluent and the potential methanization of the biodigestate open the door to incorporating the scaled process as part of a productive scheme under the concept of a biorefinery.

3.6. Análisis de Ciclo de Vida del Proceso

After defining the main material and energy flows involved in the biohydrogen production process using MSW as a raw material, it was decided to conduct a life cycle assessment using the SIMAPRO version 9.5 software [67]. The aim was to identify the environmental impacts associated with the inputs required to carry out the process. Additionally, the projected environmental performance of the proposed process in this article was compared with the performance of other alternatives for biohydrogen recovery from biomass using the dark fermentation process. To facilitate this comparison, Table 8 was constructed, displaying the data obtained in SIMAPRO.

Table 8. Life cycle assessment results for environmental impact.

Impact Category	Measure Unit	Total	Steam, in Chemical Industry	Sulfuric Acid	Sodium Hydroxide	Tap Water	Electricity, Low Voltage
Acidification (fate not incl.)	kg SO_2 eq	0.215	0.004	0.193	0.001	0.000	0.017
Eutrophication	kg $PO_4{}^{3-}$ eq	0.008	0.001	0.004	0.000	0.000	0.003
Global warming (GWP100a)	kg CO_2 eq	5.853	1.287	2.027	0.127	0.020	2.393
Photochemical oxidation	kg NMVOC	0.033	0.003	0.022	0.000	0.000	0.007
Abiotic depletion, elements	kg Sb eq	0.000	0.000	0.000	0.000	0.000	0.000
Abiotic depletion, fossil fuels	MJ	61.905	15.436	22.998	1.351	0.200	21.921
Water scarcity	m^3 eq	16.330	0.039	16.000	0.119	−0.129	0.309
Ozone layer depletion (ODP) (optional)	kg CFC-11 eq	0.000	0.000	0.000	0.000	0.000	0.000

Regarding these results, it can be mentioned that, when comparing the performance of the process with the results found by [68], the contribution of the process to global warming, at 5.85 kg CO_2 eq/kg H_2, is lower compared to alternatives such as methane steam reforming, which has a contribution of 12.9 kg CO_2 eq/kg H_2, or also compared to the alternative of biohydrogen production from microalgae, which resulted in 7.56 kg CO_2 eq/kg H_2 in that study. On the other hand, there is the contribution associated with processes using lignocellulosic biomass as raw material, where values of 5.60 kg CO_2 eq/kg H_2, 5.32 kg CO_2 eq/kg H_2, and 5.18 kg CO_2 eq/kg H_2 were reported for wheat straw, sweet sorghum stalk, and steam-exploded potato peels, respectively, presenting better performances than that obtained by the present study for recovered biohydrogen from MSW. In this line, it is also necessary to mention the results obtained by [68], in which processes such as urban solid waste gasification showed negative contributions, which should be interpreted as reductions in global warming with values ranging between −5.94 kg CO_2 eq/kg H_2 and −8.46 kg CO_2 eq/kg H_2.

When contrasting these recent results with those obtained by the present investigation, a considerable difference between both values of contribution to global warming becomes evident, with the value obtained by the process described in [69] being considerably lower. Hence, there arises the need to verify the contributions of each raw material and input used in the process sizing and scaling. In this regard, it is determined that the two major contributions are related to the consumption of electrical energy and sulfuric acid. This situation reveals the necessity to consider optimization alternatives to ensure an improvement in the energy consumption of the equipment, thereby reducing the major contribution to climate change generated by the process. Additionally, it is also appealing to analyze the sulfuric acid supply chain and identify which process stages contribute the most to global warming, opening the door to a process analysis framed within green engineering principles.

On the other hand, when comparing the contribution to climate change of the alternative explored in this study with the contribution to this environmental impact produced by OFMSW valorization technologies such as biogas production through anaerobic digestion, it is found that this technology is associated with a contribution of 62.9 kg CO_2 eq/kg CH_4 when the digestate is used as soil amendment or input for fertilizers [70]. Therefore, this alternative has a greater impact on climate change than valorization through DF under the conditions addressed in this study. Furthermore, considering that the incineration process as a treatment for OFMSW presents a contribution to climate change ranging from 58 kg CO_2 eq to a load of 408 kg CO_2 eq [71], the valorization alternative explored during this research for managing this fraction of municipal waste is much more attractive from the perspective of carbon emissions associated with the process.

4. Discussion

The study presents significant results in the energy valorization of organic municipal solid waste through a scaled-up process involving anaerobic fermentation. The findings, contextualized against previous research and our working hypotheses, reveal the effectiveness of the proposed technology in generating biogas and valuable by-products. The mixing and fermentation stage emerge as crucial in terms of energy consumption, emphasizing the importance of maintenance strategies to optimize the efficiency of impulsion pumps and the implementation of eco-design practices in equipment disposition to minimize energy losses.

In the environmental context, challenges such as effluent and atmospheric emissions management are identified. Strategies such as recycling condensate from heat exchange and chemical treatments for acidic wastewater are proposed to address these issues. Additionally, direct and indirect emissions are discussed, highlighting the importance of considering the entire life cycle of the process.

For future research, exploring specific equipment designs to reduce the number of required units and evaluating alternatives for treating biodigestate to harness its potential in chemical product synthesis is suggested. This comprehensive approach and consideration of environmental and energy aspects position this process as a promising alternative in sustainable urban waste management.

5. Conclusions

Concerning the laboratory results, the optimal combination, with an initial organic load of 10 gSV/L and s/x of 1, demonstrated a biogas yield of 89,420 mL/gSVi and AGVs production equivalent to 1128 mg COD/L. Comparing this combination to the other eight evaluated, it is evident that, for all loads, s/x values directly influenced biogas production. As the values increased, so did the yield, indicating that higher substrate-to-inoculum ratios improved biogas performance. This behavior can be explained by considering the composition percentages of the used substrate, OFMSW waste, which, compared to other organic wastes, exhibited a lower volatile solids content and, consequently, lower organic matter content. This directly impacted the inoculum's metabolism, especially under s/x conditions where the inoculum proportion was greater than that of the substrate, limiting the fermentation process.

Regarding the scaling of the energy valorization process, a positive energy balance was maintained, delivering a net electrical energy flow of 2,368,358.72 kWh/day, suggesting the process's sustainability from an energy perspective. However, it is advisable to explore and scale the process using higher s/x ratios, as the ones studied limited hydrogen production. Additionally, operating at low s/x ratios presents challenges in terms of the required inoculum quantities. Water consumption was identified as the main environmental aspect to address, emphasizing the need for strategies to save and responsibly use this resource.

From the perspective of integrated solid waste management (ISWM), the proposed valorization strategy aligns with waste utilization, offering an alternative to landfill disposal and promoting the lifespan of these facilities. Hydrogen production and the potential integration of byproducts, such as unstabilized digestate, into value chains like AGV production, bring the strategy closer to a biorefinery approach, meeting the guidelines set by CONPES 3874 in 2016.

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