Technical and environmental assessment of the temperature influence in a real-scale dark fermentation process for bio-hydrogen production from residual biomass

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Abstract

This study aimed to evaluate the technical and environmental impacts resulting from the temperature influence for a dark fermentation (DF) process as an alternative in the treatment of residual biomass derived from Colombian agroindustry. Therefore, two different scenarios were established from previous research, environments of 35°C and 45°C, from optimum mixtures of coffee mucilage (CFM), cocoa mucilage (CCM) and pig manure (PM). The environmental performance was estimated through life cycle assessment (LCA) according to ISO 14040, by using the SimaPro software, where the behaviour of each scenario was evidenced by evaluating the impacts at each stage of the process. A comparison between the technical and environmental aspects for both temperatures, allowed to determine that at 35 °C a higher energy production is obtained. Likewise, global warming (GW), water scarcity (WS) and abiotic degradation by the use of fossil fuels (FF) have a larger contribution regarding adverse environmental effects.

Keywords: dark fermentation, bio-hydrogen, real-scale process, life cycle assessment

1. Introduction

The intensive use of fossil fuels to support the increasing energy demand is main responsible for the environmental pollution and the acceleration of climate change [1]; therefore, current research is driven to generate technologies for energy production that cause low or no net negative environmental impacts. In this context, hydrogen production from residual biomass is an alternative for electric energy supply due to its energy density (122 kJ/g) [2], its net-zero emissions and its contribution to waste management [3].

Hydrogen from residual biomass can be produced through anaerobic digestion (AD), this is a biological process in which organic matter is transformed into simpler components without the presence of oxygen [4]. AD includes four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis [6,7], in which complex carbohydrates and other organic matter are reduced into biogas, a mixture consisting mainly of methane, carbon dioxide and an organic residue rich in nitrogen [5]. Although is during acidogenesis and acetogenesis that DF occurs, this process is responsible for the conversion of simple sugars or disaccharides into hydrogen, carbon dioxide and organic acids using different microbial groups [7, 8].

The DF promotes the conversion of a wide range of residual biomass to bio-hydrogen and other compounds that can be used as by-products under a biorefinery approach. Certainly, DF is considered the most feasible route for bio-hydrogen synthesis, where the organic matter can be degraded under different metabolic pathways [9, 10]. Hence, the operative variables evaluation at lab-scale process has great importance to guarantee the feasibility of the DF process; since, bio-hydrogen yields can be improved by setting suitable conditions depending on the biomass [11]. Coupled with this, the physicochemical characterization of the substrates are decisive when evaluating the potential of the residual biomass, parameters such as: Chemical Oxygen Demand (COD), Total Solids (TS), Volatile Solids (VS), Carbon to Nitrogen ratio (C:N), Total Nitrogen (TN), among others [12, 13].

Regarding the environmental aspect, Life Cycle Assessment (LCA) is a tool that that enables the identification and evaluation of the environmental impacts associated with a process or product by quantifying the input streams (energy and materials) and the output streams (waste and discharges) to define possible improvements within the environmental management of the process [14]. Following this, the present paper evaluated a DF process for the valorization of three substrates: coffee mucilage (CFM), cocoa mucilage (CCM) and pig manure (PM); according to its availability, carbohydrate content and previous studies that assessed the same substrates for bio-hydrogen production [12, 13, 15]. Therefore, the LCA is included as a decision-making tool to determine the environmental impacts of temperature for bio-hydrogen production toward a biorefinery scheme.

2. Methodology

The methodology proposed followed two stages: the assessment of the technical framework, and the estimation of the environmental performance in a real-scale DF process for bio-hydrogen production.

Technical framework

Previous studies were used as a starting point for the definition of the treatment capacity of the plant by using the optimum conditions for hydrogen production at mesophilic and thermophilic conditions using CFM, CCM and PM as substrates. Amado et al. estimated in and out flows through the simulation of the chemical reactions in AspenPlus for the DF process for the temperatures of 35 °C and 45 °C. Additionally, [16-18] delivered different information over the availability of the substrates in Santander, Colombia, from 2007 to 2018 for the mucilages and from 2016 to 2019 for the PM. This allowed the sizing of the unit operations, the construction of mass and energy balances for each scenario and the industrial equipment definition.

Environmental performance by Life Cycle Assessment

The quantification of the potential environmental impacts was based in the standard method for LCA defined in the ISO 14040 by using the SimaPro software, this allowed the estimation of the environmental behavior of each scenario. According with the method, the LCA comprises the following stages:

1. Goal and scope definition: defined as a “gate to gate” analysis of the DF process for the valorization of CFM, CCM and PM, as a function of the temperature, 35 °C and 45 °C.

2. Life cycle inventory: in and out flows estimated by the previous simulation of the process scenarios.

3. Impact assessment using SimaPro software: The Environmental Product Declaration (EPD) methodology allowed the impact categories definition, each environmental factor was associated with the correspondent category, this allowed the quantification and representativeness of the environmental impacts (see table 1) [19].

Table 1. Potential environmental impacts categories evaluated according to the EPD methodology.

Impact categorie	*Equivalent unit*
Acidification (AC)	Kg SO_2 eq
Eutrophication (ET)	Kg PO_4 eq
Climate change (GW)	Kg CO_2 eq
Ozone depletion (OLP)	Kg CFC-11 eq
Photochemical oxidants (OP)	Kg C_2H_4 eq
Abiotic depletion (AD)	Kg Sb eq
Abiotic depletion potential of fossil fuel (ADFF)	MJ
Water scarcity (WS)	m^3 eq

3. Interpretation of the assessment and improvements suggestions: the interpretation of the results was accomplished by the generation of two environmental profiles, one for each temperature or scenario; the profile along with the results from previous stages allowed the quantification of the influence of each unit operation proposed over each impact category. On the other hand, the best scenario was defined by a comparative analysis.

3. Results and discussion

Technical framework

AspenPlus simulation

The simulation used the thermodynamic models NRTL and SRK, which allowed to evaluate the thermodynamic behaviour of the mixture of substrates and took into account the phases of hydrolysis, acidogenesis and acetogenesis for the quantification of the liquid and gaseous outlet streams from the fermentation reactor. Table 2 summarizes the values of these outputs, as well as the industrial capacity of the equipment, and the volumes of the reactors as a function of the temperatures. Furthermore, the simulation provided the concentrations of the composites found in the outlet streams, which were used to carry out the environmental impact assessment.

Table 2. AspenPlus simulation results [20].

Variable	**Temperature**	
	35 °C	**45 °C**
Installed capacity (ton)	4760.8	5669.9
Reactor volume (m^3)	5132.9	11482.4
Biogas production (ton/d)	0.113	0.541
Digestate (ton/d)	441.539	1240.86
Heat duty (kJ/d)	2,556,820.76	89,044,938.36

Mass and energy balances

In and Outflows were calculated for each scenario was based on information from ICA (Instituto Colombiano Agropecuario) and Agriculture Ministry [16-18] for Santander department projected to 20 years of operation. Also, the limiting substrate was settled, CFM for both scenarios. Table 3 shows the projection in terms of the residual biomass physicochemical characteristics.

Table 3. Substrate mixture percentage (% p).

Substrates / **Temperature**	**35 °C**	**45 °C**
EC	23.196	42.062
MCF	46.01	38.633
MCC	30.794	19.305

The general process encompasses a) mixer, to guarantee the homogenization of the substrate; b) CSTR reactor, where the DF take place; c) biogas purification processes, which includes all the stages to pretreat the biogas for combustion; d) digestate treatment processes, which allows the solid-liquid separation for the further valuation of the digestate. The simulation of the process resulted in the definition of the net energy and heat generated for each scenario (see Table 4). Including, the environmental aspects and emissions generated during each stage of the process.

Table 3. Heat and energy simulation results.

Temperature (°C)	**Energy (kWh/d)**	**Heat (kJ)**
35	453,13	3.311.990,20
45	439,88	3.215.102,29

DF bio-hydrogen production has been widely reported to increase with temperature [10, 15, 21, 22]. However, according to the quantification obtained from the balances, the energy production is less for the 45 °C process compared to the energy produced at 35 °C. This behavior is associated with the organic load, as the simulation in AspenPlus conducted by Rangel et al. considered an initial load of 8 g/L of COD for 35 °C and to 2 g/L of COD for 45 °C conditions [20]. Therefore, the effect of temperature can be associated with the amount of initial organic load and the physicochemical characteristics of the substrates, establishing a proportional relationship in the production of bio-hydrogen.

Life Cycle Assessment

For both scenarios, the graphical representation of the potential environmental impacts simulated in SimaPro includes the two most important mass flows of the bio-hydrogen production process: the digestate and the biogas generated. The EcoInvent3 database was used for the environmental impact assessment, as it consolidates the inputs of mass and energy needed. The inventory analysis made it possible to establish that the water consumption for the process, the energy consumption, the generation of wastewater resulting from the digestate separation processes, and the emissions associated with the use of conventional fuels in the boiler are environmental aspects of relevance in the production of biohydrogen. In addition, it should be noted that the emissions from the boiler were not taken into account in mass and energy balances, since the software considers natural gas emissions in the quantification of the impacts.

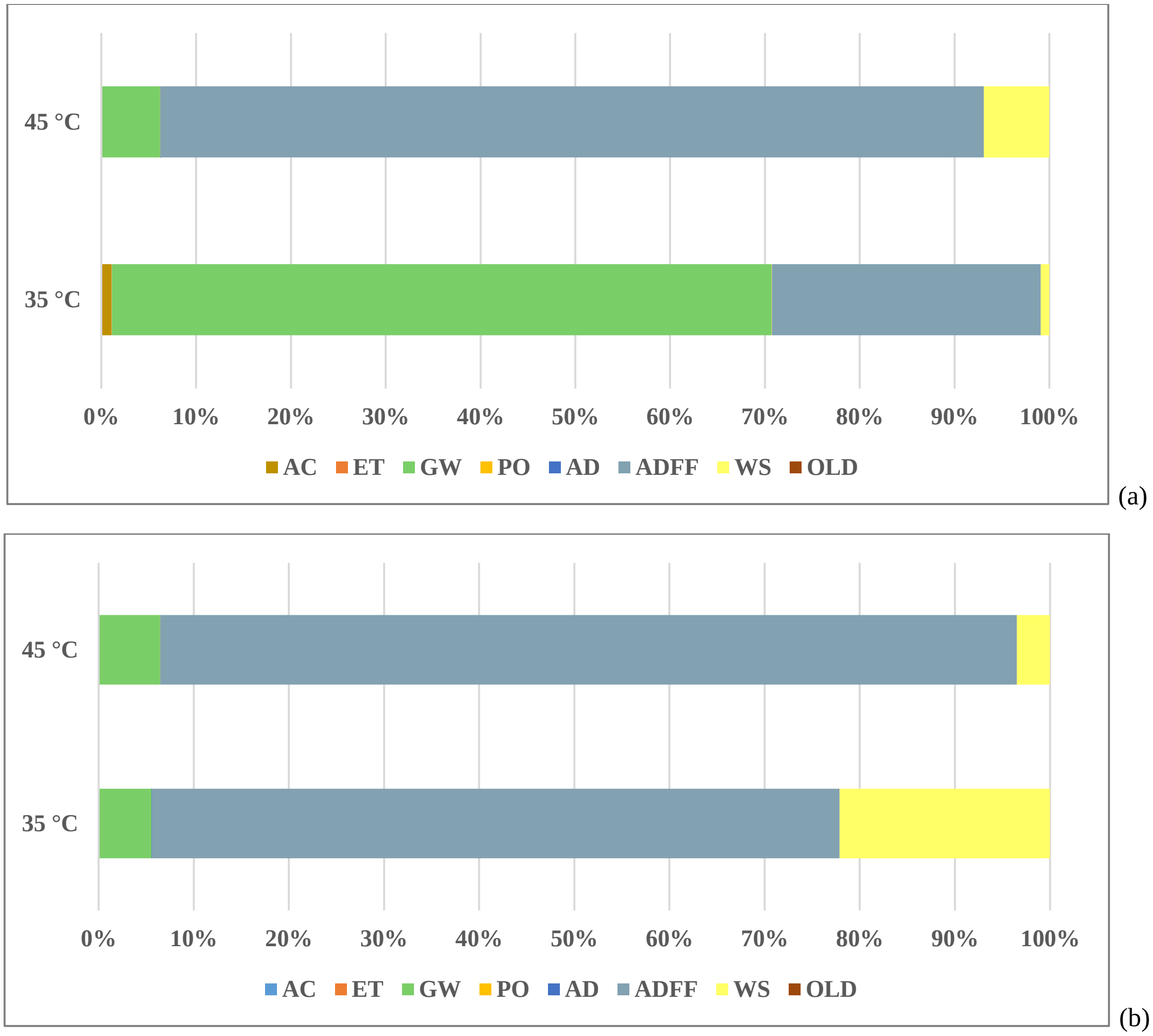

Figure 1. Comparative environmental profile for biogas (a) and digestate production (b).

Figure 1 presents the environmental impact profile diagram for the bio-hydrogen production process; a SimaPro contrast option was used to compare both scenarios. The impact categories with the higher contributions for 35 °C correspond to GW with more than 69.6% and AD close to 28.3% due to the use of fossil fuels. In contrast, for the 45 °C process, 86.9% of the potential environmental impacts are associated with ADFF, about 6.9% with WS, and 6.2% with GW. These impacts can be associated with the transport of biomass to the process, and the combustion reactions in the boiler and electric generator, as well as the electric energy duty of the industrial equipment. The WS is related to the high consumption of water in the process, both for the boiler feed, as well as for the operation of the reactor and the solutions used for the previous preparation of the substrates. On the other hand, treatment of the liquid streams, from the digestate solid-liquid separation systems, is necessary given the emissions of carbon dioxide (CO_2), nitrogen dioxide (NO_2) and methane (CH_4), gases that contribute to the GW category. Likewise, wastewater treatment in its storage and disposal phases generates direct and indirect greenhouse gas (GHG) emissions [23].

The application of a biorefinery approach, which is based on taking advantage of the outputs of industrial processes, as well as increasing energy efficiency and the use of less polluting raw materials, is closely related to LCA. Since environmental impact potential derived from biorefinery schemes, can be managed, and even eliminated, which is a postulate of circular economy [24]. Within this approach, different technologies have been proposed, including the pretreatment of raw materials and substrates, chemical and biological conversion, for the outputs of real-scale processes, as well as high value-added product-driven biorefinery schemes [24, 25].

Therefore, for a real-scale bio-hydrogen production, it is important to consider that during the separation of the solid phase of the digestate, composed mainly of organic matter that becomes sludge, the liquid phase may have a significant concentration of valued chemicals such as volatile fatty acids (VFAs). The VFAs are valued for the generation of biopolymers, alcohols, additives, agricultural products, and agents in energy production [26].

4. Conclusions

A real-scale production of bio-hydrogen from the use of CCM, CFM and PM for the generation of electrical energy, has limitations that must be addressed when considering its scale-up, such as the high consumption of water in the DF reactor, the transport of the substrates, the pretreatments, and the heat losses regarding the industrial equipment. The influence of temperature is linked to the initial organic load of the substrates since for the 35 °C scenario, 453.13 kWh/d were generated from an organic load of 8 g/L of COD. in contrast to the same process at 45 °C which managed ab initial organic load of 2 g / L of COD, reaching a production of 439.88 kWh/d.

The environmental impact categories with higher contributions were GW, ADFF and WS. However, the environmental impacts can be reduced by increasing the energy efficiency of the industrial process, minimizing losses and consumption, as well as guaranteeing the use of output currents. Therefore, under a biorefinery scheme, it is possible to reduce the limitations of real-scale bio-hydrogen production through the implementation of technologies that integrate the process and allow the generation of high value-added products.

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