Júlia Santos Schramm
Licenciada em Engenharia Sanitária e Ambiental

Life Cycle Assessment of bioH_2 and biogas produced from the OFMSW in a two-stage configuration

Dissertação para obtenção do Grau de Mestre em Engenharia de Energias Renováveis

Orientador: Doutor Nuno Carlos Lapa dos Santos Nunes, Professor Auxiliar, FCT-UNL

Júri:

Presidente: Doutora Anabela Monteiro Gonçalves Pronto (FCT-UNL)

Vogais: Doutora Carla Alexandre Monteiro da Silva (Arguente) (FC-UL)

Doutor Nuno Carlos Lapa dos Santos Nunes (Orientador) (FCT-UNL)

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Aos meus pais, que mais uma vez tornaram um sonho meu possível.

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ABSTRACT

A few authors have stated that for a process to be energetically sustainable, it needs to produce more usable energy than the one required for its operation. Furthermore, its potential environmental impacts need to be evaluated to allow for a thorough picture of its sustainability. In this study, a Life Cycle Assessment (LCA) was performed to investigate the potential environmental impacts and energy balance of a pre-defined configuration. The studied system consisted of a bioH_2 and biogas production process from the organic fraction of municipal solid waste in a two-stage bioreactor, of 2.1 and 2.75 liters respectively. The analysis enabled a comparison of both stages' energy and environmental performance, as well as the identification of the major energy consumption inputs of each stage. The scenarios investigated for both processes were based on results from (i) a hydraulic retention time for the dark fermentation process of 4 days and (ii) a hydraulic retention time of 5 days. The LCA was carried out with the openLCA v. 1.8.0 program, with the functional unit of 1 kJ of produced gas, and both CML 2 baseline 2000 and ReCiPe Midpoint (H) were applied as Life Cycle Impact Assessment (LCIA) methods. The results indicated that the dark fermentation process of OFMSW for bioH_2 production in the first stage had the best net energy balance of all the systems. In contrast, the methanogenesis of volatile fatty acids (VFA) in the second stage for biogas production had the lowest environmental impacts per kJ produced. The energy balance of the conventional anaerobic digestion of the OFMSW was performed for comparison, with the conclusion that the proposed configuration presented higher net energy production than the conventional anaerobic digestion process.

Keywords: Life cycle assessment; bioH_2; biogas; two-stage configuration; energy balance.

RESUMO

Alguns autores afirmam que para que um processo seja energeticamente sustentável, ele precisa produzir mais energia útil do que a necessária para sua operação. Além disso, seus potenciais impactos ambientais precisam ser avaliados de maneira a permitir uma análise completa de sua sustentabilidade. Neste estudo, foi realizada uma Análise de Ciclo de Vida (ACV) para investigar os potenciais impactos ambientais e o balanço de energia da configuração selecionada. O sistema estudado tratou-se de um processo de produção de bioH_2 e biogás a partir da fração orgânica dos resíduos sólidos urbanos (FORSU) em um biorreator em duas etapas, de 2,1 e 2,75 litros respectivamente. A análise permitiu a comparação do desempenho energético e ambiental das duas etapas, assim como a identificação dos principais insumos de consumo de energia de cada etapa. Os cenários investigados para ambos os processos foram baseados em resultados de (i) tempo de retenção hidráulica de 4 dias para o processo de fermentação no escuro e (ii) tempo de retenção hidráulica de 5 dias. A ACV foi realizada com o programa *openLCA* v. 1.8.0, com unidade funcional de 1 kJ de gás produzido, e ambas metodologias CML 2 baseline 2000 e ReCiPe Midpoint (H) foram aplicadas na Avaliação de Impacto do Ciclo de Vida. Os resultados indicaram que o processo de fermentação no escuro da FORSU para produção de bioH_2 na primeira etapa apresentou o melhor balanço energético líquido de todos os sistemas. Em contraste, a metanogênese dos ácidos orgânicos voláteis (AOV) no segundo estágio para produção de biogás teve os menores impactos ambientais por kJ produzido. O balanço energético da digestão anaeróbia convencional da FORSU foi realizado para fins de comparação, com a conclusão de que a configuração proposta apresentou maior produção de energia líquida do que o processo de digestão anaeróbia convencional.

Palavras-chave: Análise de Ciclo de Vida; bioH_2; biogás; configuração em duas etapas; balanço energético.

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ACRONYMS

AD – Anaerobic Digestion
APOS – Allocation at the Point of Substitution
CML – Centrum voor Milieukunde Leiden
DALY – Disability-adjusted Life Years
DCTB – Department of Sciences and Technology of Biomass
DF – Dark fermentation
E – Egalitarian
EDIP – Environmental Design of Industrial Products
GC-TDC – Gas chromatography - Thermal Conductivity Detector
GHG – Greenhouse Gases
GWP – Global Warming Potential
H – Hierarchist
HCL – Hydrochloric Acid
HHV – Higher Heating Value
HRT – Hydraulic Retention Time
I – Individualist
ILCD – International Reference Life Cycle Data System
IPCC – Intergovernmental Panel on Climate Change
ISO – International Standards Organization
IT – Italy
LCA – Life Cycle Assessment
LCI - Life Cycle Inventory
LCIA - Life Cycle Impact Assessment
LHV – Lower Heating Value
MSW – Municipal Solid Waste
NG – Natural Gas
NER – Net Energy Ratio
OFMSW – Organic Fraction of Municipal Solid Waste
PH – Potential of Hydrogen
RPM – Revolutions Per Minute
SS – Sewage Sludge
TSAD – Two-stage Anaerobic Digestion
UNEP/SETAC – United Nations Environment Programme/Society of Environmental Toxicology and Chemistry
V – Volume
VFA – Volatile Fatty Acids
VS – Volatile Solids

1. INTRODUCTION

In today's social and economic dynamics, energy is an essential feature in daily life. There is a direct and proportional relation, for instance, between the living standard of a country and the energy consumed by its population (Demirbas, 2016). Henceforth, the global energy demand, mostly dependent on fossil fuels, is increasing at an exponential rate, following the also exponential growth of the world population (Demirbas, 2016; Dong et al., 2020; Reaño, 2020). In the meanwhile, the fossil fuels deplete at ever-increasing rates (Demirbas, 2016).

It has become a common knowledge that CO_2 emissions can contribute to environmental damages and adverse toxic effects on many species. In light of that, Gómez et al. (2011) state that recent research activities have focused extensively on finding alternative fuels for energy production, aiming to reduce the high consumption of fossil fuels to reduce Greenhouse Gas (GHG) global emissions. The authors also point out the increasing concern of society regarding climate change, directly associated with the rise of CO_2 emissions that are, among other things, deriving from the use of fossil fuels. All of this makes the use of new renewable fuels capable of zero CO_2 emissions an urgent need to mitigate the impacts of global warming.

In the context of alternative sources of energy, the attention towards renewable sources has been escalating due to their environmental benefits and the fact that these sources can be restored in a short while by nature, overcoming the problem of resource depletion that fossil fuels face (Demirbas, 2016). Hence, different ways to harness the energy from clean, renewable sources, such as the sun, wind, hydro, hydrogen, and biomass, have already been developed, but the search for reliable energy sources continues (Demirbas, 2016; Ghimire et al., 2015).

Several biomass resources can be used to produce renewable energy, notably agricultural and forest residues, algae and grasses, animal manure, and organic wastes (Demirbas, 2016). When talking about waste, it is well known that municipal solid waste (MSW) generation worldwide has been increasing significantly as a result of the same population growth and economic development that affects the already mentioned boost of energy demand. MSW handling and treatment is a growing area of environmental and health concern, and an adequately treated waste can lead to the production of bioenergy, biofuels, and compost, all in essence, valuable end products deriving from waste (Arancon et al., 2013; Dabe et al., 2019).

With that in mind, energy production from biomass, and more specifically, from waste, can not only result in far fewer air emissions than the use of fossil fuels but also reduce the amount of waste that ends up in landfills (Demirbas, 2016). Among the different existing methods for waste treatment and consequent energy production, this study focuses mainly on the anaerobic digestion (AD) of organic waste. On that matter, Khan et al. (2018) have found that AD has been primarily used to produce biogas over the past few years, but that most recent studies have proven the technical feasibility also to produce biohydrogen.

Biogas is considered a clean and renewable intermediate form of energy that could substitute conventional energy sources, such as natural gas (Demirbas, 2016). Likewise, hydrogen is seen by many authors as a worthy alternative to these sources due to its high energy yield (143 $MJ.kg^{-1}$ at ambient pressure) (Mazloomi and Gomes, 2012) and clean combustion product (mainly water vapor), which means that its combustion poses little danger to the environment and does not contribute to CO_2 emissions (Gómez et al., 2011; Khan et al., 2018).

To produce both gases (biogas and biohydrogen) within an anaerobic digestion configuration and enhance the gas production, two-stage systems have been proposed by distinct authors (Gómez et al., 2011; Han and Shin, 2004; Ruggeri et al., 2015), in which biohydrogen and biogas productions are separated in two bioreactors, operating under different conditions to optimize both processes.

1.1. Description of the problem

In the laboratory of biological assays of the Dept. of Sciences and Technology of Biomass (DCTB), LAQV-REQUIMTE, FCT-NOVA, a pilot project was performed in 2018/2019, in which both biohydrogen ($bioH_2$) and biogas (CH_4 + CO_2 + minor gases) were produced from the organic fraction of municipal solid waste (OFMSW) in a two-stage bioreactor. The first bioreactor was operated with a working volume of 2.1 liters, and the second, with 2.75 liters.

The project operated in a way that the OFMSW was fed into the first bioreactor, which produced $bioH_2$ through dark fermentation; this bioreactor was run under such conditions that favored the acidogenesis stage and inhibited methanogenesis, therefore enhancing the production of $bioH_2$. The outflow from the first bioreactor, rich in volatile fatty acids (VFA), was used as feedstock to feed the second bioreactor, which produced biogas through methanogenesis.

This study's main goal was to perform the environmental analysis and energy balance of these $bioH_2$ and biogas production processes from the two-stage bioreactor's results. For this, the Life Cycle Assessment (LCA) methodology was used, which was supported by the software *openLCA* v. 1.8.0 (GreenDelta, Berlin, Germany). As a result of this study, answers to the following questions were expected to be achieved: *What are the most significant environmental impacts of the two-stage bioreactor to produce $bioH_2$ and biogas (CH_4 + CO_2)? Is the two-stage bioreactor self-sustainable in terms of energy?*

1.2. Structure of the document

The building blocks that structure this thesis are sequenced as follows:

Chapter 1 – Introduction. The main problem is presented in this chapter.

Chapter 2 – Theoretical Framework. This chapter is when this research's theoretical background is defined, including the main definitions of processes described in this work and the fundamentals of the Life Cycle Assessment (LCA) methodology. Furthermore, a state of the art of LCA of two-stage fermentative systems is presented as the foundation for the studied system.

Chapter 3 – Methodology. The LCA methodology and its application to this study are presented in this chapter, with its Goal and Scope definition, the data collection process, the Life Cycle Inventory (LCI) approach, and the methods applied for the Impact Assessment phase. Finally, the study results regarding the chosen methods are explained in this chapter, along with the sensitivity analysis.

Chapter 4 – Results. This chapter aims to present and explain the achieved results, compare and unravel the different scenarios, and the sensitivity analysis results.

Chapter 5 – Conclusion and Future Work. Finally, this study's contributions are discussed in this chapter, together with the meaning of the obtained results within this study's framework and their comparison with similar studies available in the literature. Along with this research's limitations, some identified suggestions for future research are also included in this section.

Chapter 6 – References. All the referenced material used for this research is presented in this final chapter.

1.3. Innovative character

This study's innovative character lies in the following:

a. Although the two-stage configuration for anaerobic digestion of OFMSW has been previously studied by other students of the same MSc Programme (FCT – MEER), in which they assessed the bioH_2 and biogas production separately, the current study corresponds to the first time an energy balance and Life Cycle Assessment of this configuration was performed in this program;
b. The energy balance for bioH_2 and biogas production processes has been studied by different authors. Nevertheless, it was not found in the literature an energy balance for the two-stage configuration that took into account the necessary energy consumption to produce both gases;
c. No LCA of a similar system has been found in the literature to allow for result comparison.

2. THEORETICAL FRAMEWORK

This chapter's structure is founded as follows: Firstly, the principles and global overview of the anaerobic digestion (AD) process are presented (section 2.1), including the main reactions involved and some characteristics of the produced biogas. As one of the outcomes of AD processes can be the production of biohydrogen, the production of this gas through dark fermentation is discussed in the sequence (section 2.2). Further, since this study aims to evaluate bioH_2 and biogas' production in a two-stage system, this concept is introduced in the next topic (section 2.3), presenting a few authors' opinions and findings when studying these systems and their main characteristics. Finally, as an important part of this study, the LCA methodology is presented (section 2.4) with its fundamentals, primary structure, strengths, and limitations as a tool to perform environmental analysis. Having established the LCA ground, some literature regarding the LCA of two-stage systems is summarized (section 2.5), pointing the authors' opinions towards this type of configuration for bioH_2 and biogas production.

2.1. Anaerobic Digestion

Considered as an efficient and sustainable way to treat organic waste (Khan et al., 2016), anaerobic digestion (AD) is a biological decomposition process in which, in the absence of oxygen, anaerobic microorganisms convert organic matter into an energetic gas (biogas) and a nutrient-rich residue (digestate) (Khan et al., 2018).

As described by many authors (Ahammad and Sreekrishnan, 2016; Khan et al., 2018; Lapa et al., 2018; Ruggeri et al., 2013), anaerobic digestion involves four major stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In the initial stage of the organic matter decomposition, the hydrolysis, bigger organic polymeric chains get broken down into smaller molecules (Ahammad and Sreekrishnan, 2016). The hydrolysis process involves converting insoluble organic compounds, such as carbohydrates, proteins, and fats, into their soluble derivatives, amino acids, sugars, and fatty acids (Khan et al., 2018; Ruggeri et al., 2013).

In the sequence, acidogenic bacteria exploit the products of hydrolysis during the acidogenesis stage, converting the produced molecules into volatile fatty acids (VFAs), alcohols, acetates, and gases (CO_2, H_2, and NH_3) (Lapa et al., 2018; Ruggeri et al., 2013). Acidogenesis is referred to as the hydrogen production stage of anaerobic digestion (Khan et al., 2018).

The main products of acidogenesis (VFAs and alcohols) cannot be directly fermented by methanogenic bacteria to produce methane. Therefore, acetogenesis is the third stage of anaerobic digestion, in which some VFAs (acetic, propionic, and butyric acid) and alcohols are converted into acetate, hydrogen gas, and carbon dioxide (Lapa et al., 2018; Ruggeri et al., 2013).

Finally, methanogenesis is the final stage of anaerobic digestion, in which methanogenic bacteria transform either acetate, H_2, or CO_2 into methane gas (Ahammad and Sreekrishnan, 2016), a principal component of the produced biogas in the AD process. Figure 2.1 shows a global overview of the main biological pathway of the anaerobic digestion process.

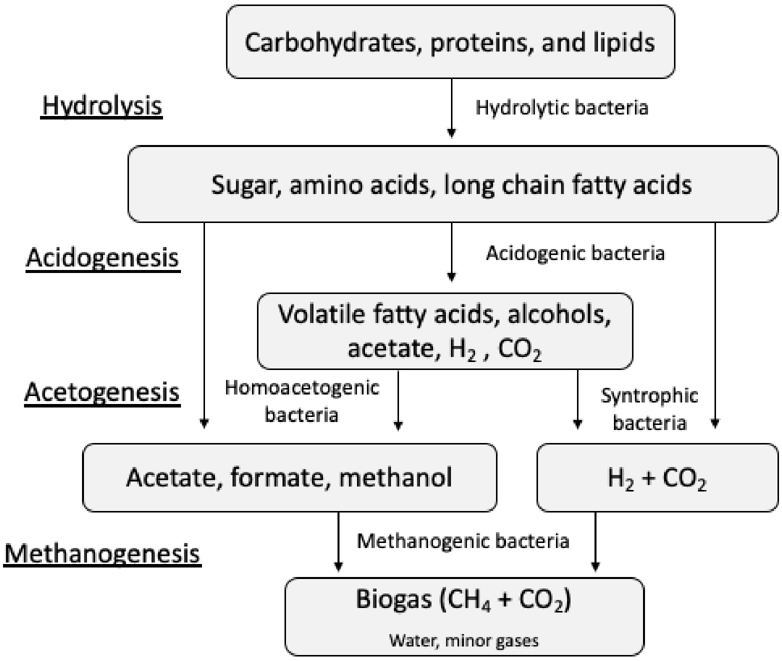

Figure 2.1 – Schematic representation of anaerobic digestion (adapted from Ahammad and Sreekrishnan, 2016; Lapa et al., 2018)

The biogas resulting from the process, typically composed of 60%-70% methane, 30%-40% carbon dioxide, hydrogen, and hydrogen sulfide, can be used to produce electricity and heat (Ruggeri et al., 2013; Xu et al., 2018), as well as a biomethane for the transportation sector (Lapa et al., 2018). With its Lower Heating Value (LHV) typically ranging from 17-25 MJ/m^3, the biogas can be combusted or oxidized, releasing energy and allowing it to be used as a fuel (Ardolino et al., 2018; Bhatia, 2014).

When it comes to the ways it can be used, Lapa et al. (2018) explain that biogas can be applied in a similar way as Natural Gas (NG), after a prior upgrading process, being used for injection in NG grids, fuel for vehicles, and fuel cells.

The biogas produced through anaerobic digestion can offer different environmental and social benefits, such as (1) organic waste reduction and valorization, (2) reduction of greenhouse gases (GHG) emission from fossil fuels, and (3) reduction of dependency on fossil fuels (Lapa et al., 2018).

2.2. Biohydrogen production through dark fermentation

Hydrogen production from renewable and non-renewable energy sources has previously been studied in the literature by different authors (Dincer and Acar, 2015; Khan et al., 2018; Lapa et al., 2018; Manish and Banerjee, 2008; Suleman et al., 2015; Valente et al., 2017; Xiao et al., 2013). Among distinct methods to produce H_2 from renewable sources (such as water and biomass), the ones most mentioned in these studies are water electrolysis, water photolysis, thermal processes, and biological processes. For Ghimire et al. (2015), biological processes for hydrogen production are less energy-intensive and more environmentally positive in CO_2 reduction. When the route chosen for H_2 production uses either biological feedstocks or comes from biological processes such as anaerobic digestion of renewable matter, the resulting fuel is called biohydrogen (bioH_2) (Lapa et al., 2018).

In their research, Ruggeri et al. (2013) indicate that dark and photo-fermentation are the two main processes for biohydrogen production through the anaerobic route, additionally describing dark fermentation (DF) as the production of bioH_2 and VFA in the absence of light, which occurs during the acidogenesis phase of anaerobic digestion. During DF, carbohydrate-rich substrates are broken down by anaerobic microorganisms, producing molecular hydrogen (H_2) (Ghimire et al., 2015). Figure 2.2 shows a simplified and schematic representation of the main steps involved in the DF process.

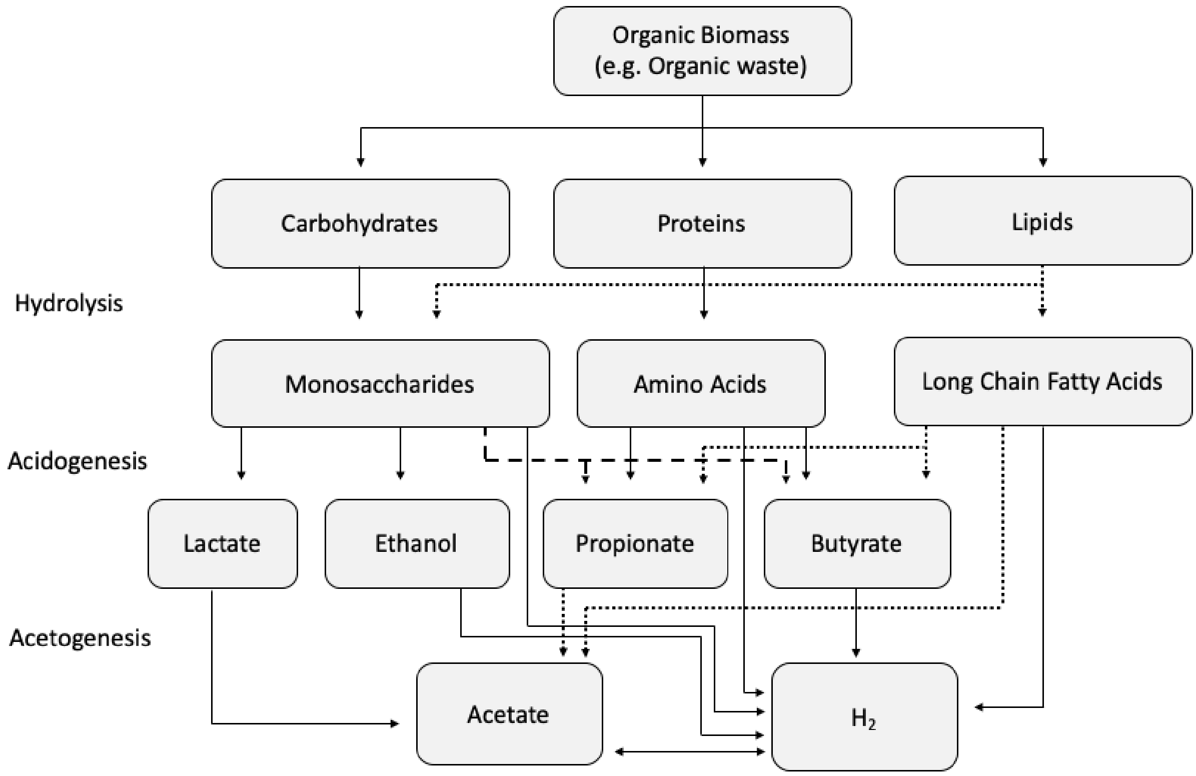

Figure 2.2 – Main steps in dark fermentation of waste biomass (adapted from Ghimire et al., 2015)

Due to its high production rates, dark fermentation is the most studied and promising technology for combined organic waste treatment and biohydrogen production (Ghimire et al., 2015). Dark fermentation of organic waste has several advantages, serving as a significant route to produce hydrogen and representing a possibility of treating and stabilizing the biological waste, which has a potential danger of environmental contamination. Coupled with that, producing hydrogen from organic waste can reduce hydrogen production costs since the material is cheap and readily available (Dincer and Acar, 2015).

As Ghimire et al. (2015) pointed out, the system's energy balance is essential for the process's sustainability. Correspondingly, a few of the studies compiled by the authors suggest joining DF processes with AD to obtain a more positive net energy balance from the processes' energy recovery. On top of that, these authors mention that anaerobic digestion is required to stabilize further the residues generated during dark fermentation, which makes the combination of these two processes a compelling approach.

2.2.1. Biohydrogen as an energy carrier

The gas of biological origin produced during dark fermentation is a mixture composed mainly of H_2 and CO_2 (Gómez et al., 2011). Among other things, the fact that hydrogen has near-zero emissions makes it an ideal sustainable energy carrier (Dincer and Acar, 2015; Suleman et al., 2015). As an energy carrier, hydrogen can be used for transportation, heating, power generation, and as a replacement for current fuels, which is why Suleman et al. (2015) state that renewable-based hydrogen can lead to notably lower environmental impacts when compared to different sources of energy applied for the same purposes.

Hydrogen has the highest energy content of all known fuels, with values in the literature ranging from 142 $kJ.g^{-1}$ to 143 $kJ.g^{-1}$ at ambient pressure (Lapa et al., 2018; Mazloomi and Gomes, 2012). Compared to natural gas, for example, the fossil fuel with the highest energy content (50 $kJ.g^{-1}$), H_2 has about 184% more energy per mass unit. Also, hydrogen is considered one of the cleanest energy sources, and it does not contribute to climate change (Lapa et al., 2018; Ruggeri et al., 2013). In like manner, Dincer and Acar (2015) highlight some advantages of hydrogen, such as (1) higher energy conversion efficiencies than other fuels, (2) different forms of storage, (3) long-distance transportation, (4) higher HHV and LHV than most the conventional fossil fuels. However, the authors also have drawn attention to the fact that most H_2 production methods are not yet mature for an up-scaling step to an industrial scale.

2.3. Two-stage systems

In conventional AD, acidogenesis and methanogenesis typically occur in the same bioreactor. Considering that the microorganisms involved in the two stages differ profoundly from each other in terms of some environmental required conditions, such as pH and temperature, a delicate balance needs to be attained in the bioreactor to obtain the desired biogas production in the process (Ahammad and Sreekrishnan, 2016).

According to Xu et al. (2018), anaerobic digestion of food waste faces many technical challenges. Among different instabilities, the authors mention the rapid conversion of easily digestible material to volatile fatty acids (VFAs) occurring too early in the process, which can result in a drastic pH drop. This sudden pH drop can inhibit the methanogenesis archae bacteria (Lyberatos and Skiadas, 1999).

On the other hand, when analyzing the dark fermentation process itself, Ruggeri et al. (2010) point out that even after the stabilization of the process, the outlet of the bioreactor still has energetic chemical content that could be used for further energy production, suggesting the anaerobic digestion process as an option for methane production from this energetic content.

To solve these issues and enhance the gas production of both these processes, two-stage systems have been proposed (Gómez et al., 2011; Han and Shin, 2004; Ruggeri et al., 2015), in which biohydrogen and biogas productions are separated into two different bioreactors. In this system, the first bioreactor operates at an acidic pH and shorter hydraulic retention time (HRT) than the second bioreactor. These conditions promote acid fermentation and the production of bioH_2. The second bioreactor's goal is to facilitate the methanogenesis stage through the fermentation of the organic acids coming from the first bioreactor and to enhance methane production (Xu et al., 2018).

Ahammad and Sreekrishnan (2016) mention that separating these processes into two bioreactors makes it possible to provide the microorganisms involved with optimum growth conditions, enhancing overall productivity, process stability, and facilitating process monitoring and control.

Furthermore, Ruggeri et al. (2013) suggest that the production of these two high-value gases (hydrogen and methane) within this configuration is a solution that results in several energetic and environmental advantages. Splitting acetogenesis from methanogenesis optimizes the fermentation of organic matter and enhances the overall energy production of the process when compared to standard AD (Ruggeri et al., 2013). Likewise, Kraemer and Bagley (2005) demonstrated that the addition of a methanogenic phase after a hydrogen-producing bioreactor could increase the renewable energy recovery of the process in the form of H_2 and CH_4.

All things considered, the two-step anaerobic digestion (TSAD) system is seen as a process with great potential to enhance energy production from organic wastes. Favorable aspects of TSAD are already known, yet more in-depth knowledge and further research are necessary to overcome obstacles to reach the process's industrial-scale application (Ruggeri et al., 2015).

A key point that Ruggeri et al. (2013) set forth concerning H_2 and CH_4 production by anaerobic digestion is regarding the sustainability of energy production technology. To be sustainable, the authors illustrate that an energy production technology must produce at least the amount of energy needed to sustain itself, namely, operational necessities and reproduction, and a surplus to feed the economy in an appropriate form. In other words, the relation between the amount of energy produced and the energy needed to produce it, meaning its energy balance, can indicate whether such technology is justifiable from a sustainability perspective.

Within this context, the authors further suggest that life cycle assessment (LCA) can be a useful tool to support this analysis, as it takes into consideration all the aspects of such technology (e.g., environmental impact and energy use). Thus, through the analysis of the inputs and outputs of a system throughout its life cycle, LCA can be used as support for the evaluation of the energy conversion and potential environmental impacts of a given technology.

2.4. LCA: Fundamentals

The International Standard Organization (ISO) provides a series of standards (14040) for definitions, framework, and principles of a life cycle assessment, defining LCA as the “compilation and evaluation of the inputs, outputs, and potential environmental impacts of a product system throughout its life cycle” (ISO International Standard 14040, 2006). Hence, LCA is a tool used to analyze the environmental consequences of products or processes in every stage of their life cycle – comprising the extraction of resources, production of materials, use and maintenance of the product, and disposal or treatment of all final waste when it reaches its end-of-life, therefore, on a ‘cradle to grave’ perspective (Guinée et al., 2002). The same authors mention that in the ISO definition, the term ‘product’ is taken in a broader sense, involving not only physical goods but services as well.

The environmental consequences analyzed in an LCA cover different impacts upon the environment, including the extraction of resources, land use, and emission of hazardous substances (Guinée et al., 2002). When talking about environmental impacts, Bjørn et al. (2017c) highlight that considering an LCA's uncertainty, it is more accurate to say that it assesses the potential for these impacts to happen.

LCA has become more expressive in research, industry, and policymaking in the last decade, becoming the leading tool applied to study the entire life cycle of a product in terms of sustainability (Mehmeti et al., 2018). Because of its quantitative nature, LCA can be used to compare the environmental impacts of different processes and product systems, quantifying their potential to impact the environment (Bjørn et al., 2017c). Coupled with that, Guinée et al. (2002) consider LCA to be, as far as possible, quantitative in character; and when this is not possible, qualitative aspects should be taken into account to give a possible complete picture of the environmental impacts involved in the study.

The purpose of an LCA study is to assemble and assess the environmental impacts of the scenario under study, excluding financial, political, social, and any other factors. In their work, Guinée et al. (2002) point out that this approach does not imply that these other aspects are of less importance but that this only delimits the study's scope since the LCA's goal is to focus the analysis purely on the environment. Nevertheless, costs can be considered in a Life Cycle Cost (LCC) analysis, and social aspects can be taken into account in a social Life Cycle Analysis (sLCA).

For the assessment of these environmental impacts, LCA has comprehensive coverage of environmental issues, not focusing exclusively on only one impact, like climate change, but also including issues such as freshwater use, land occupation, aquatic eutrophication, toxic impacts on human health, and depletion of non-renewable resources (Bjørn et al., 2017c). According to these authors, the main reason for considering multiple environmental issues, which are typically around fifteen, is to avoid burden shifting, i.e., when efforts to lower one impact increase other types of environmental impacts.

Different applications of LCA include the analysis of the origins of problems related to a particular product; the comparison of improvement variants of a given product; and the choice between several comparable products or systems, for instance, the comparison between different types of waste management approaches in a given municipality (Guinée et al., 2002).

2.4.1.LCA Structure

As established by ISO 14040, the methodological framework on LCAis defined in four phases (Figure 2.3): (i) goal and scope definition, (ii) inventory analysis, (iii) impact assessment quantification, and (iv) interpretation. This fixed protocol was established to allow performing such a complex study as LCA under strict standard guidelines (Guinée et al., 2002).

In short, as defined by Agostini et al. (2020), in the first phase, the intended application and reasons for performing the study are defined. Following these definitions, the second phase is carried to compile the data inventory for every input and output related to the system under study, followed by the third phase, when the results from this inventory are assessed to understand their environmental implications. Finally, the fourth phase is considered by the authors as the critical step, in which the whole study and its results are analyzed for their quality and capability to achieve the goals previously defined.

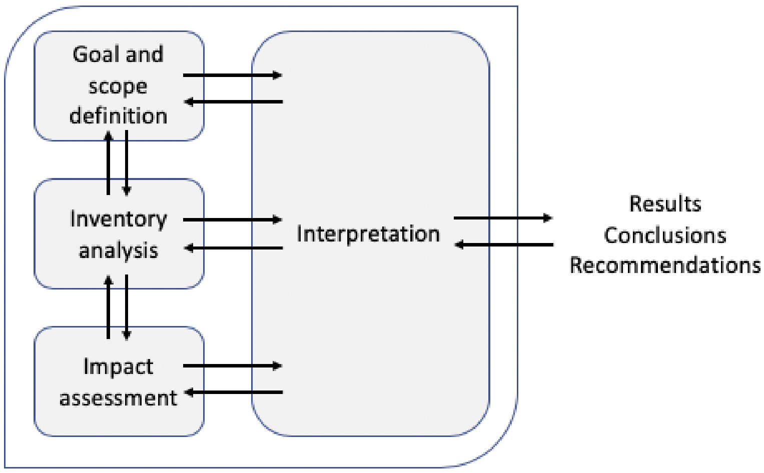

Figure 2.3 - General methodological framework of LCA, as established in ISO 14040

These four phases of an LCA are further defined in the subsequent subchapters.

2.4.1.1. Goal and scope definition

The goal definition sets the LCA context and defines the purpose of the analysis, serving as the basis for the scope definition, which outlines and frames the study (Hauschild, 2017; Mehmeti et al., 2018). Going further into detail, the LCA should start with a well-described definition of the goal of the study, contemplating the reason why the study is being performed, the questions it intends to answer, for whom it is being performed, and the intended use of the results (Guinée et al., n.d.; Hauschild, 2017). It is a mandatory step for every LCA study and is the phase where all assumptions and value judgment that had been taken should be detailed and justified (Guinée et al., 2002).

By saying that the scope definition outlines the study, Hauschild (2017) and Mehmeti et al. (2018) explain that this is the phase where the LCA practitioner defines the functional unit to be analyzed, chooses the boundaries to study the system, selects the assessment parameters for the impact evaluation, and defines the methods used for the impact assessment.

Included in the goal and scope definition, the functional unit expresses, in quantitative terms, the measurement unit of the product or system assessed by the LCA, describing the primary function fulfilled by this product and how much of this function will be considered in the analysis (Guinée et al., 2002; Hauschild, 2017). Furthermore, these authors agree that because of its quantitative nature, the functional unit allows for different systems to be treated and analyzed as functionally equivalent, also serving as a basis for the determination of a reference flow of the product that will be used in the next LCA phase, the inventory analysis.

2.4.1.1. Life cycle inventory

Once the study's goal and scope are defined, the following phase of an LCA is known as a Life Cycle Inventory (LCI) analysis. It is the phase where the relevant data regarding resources, energy, and material inputs, as well as emissions, wastes, and other outputs for a given flow, are collected and quantified (Mehmeti et al., 2018). The result of this process, according to Bjørn et al. (2017a), is a list of quantified flows that cross the system boundary, further to serve as input to the subsequent Life Cycle Impact Assessment (LCIA) phase.

One primary feature of the LCI phase, as elucidated by Hauschild et al. (2017), is the fact that it often relies on generic data from databases, presenting every input and output flow for one unit process, such as the production of a specific material or the generation of electricity. It is one reason why the LCI analysis is the phase that requires most efforts and resources within an LCA, resulting in the need for several iterations between the LCI and LCIA phase to achieve the goal of the study (Bjørn et al., 2017a). As a matter of fact, these authors also add that as a result, each iteration ends up providing useful information on which inventory data are most relevant and representative in the LCA results.

Modeling approach

The choice of the inventory modelling approach needs to be defined as to fulfill the goals set for the study, since it has a strong influence on its results. The approach can be consequential, attributional, or a combination of them both (hybrid approaches), for example an attributional approach with elements of consequential (Agostini et al., 2020).

To start differentiating them, Ekvall et al. (2016) illustrate that while an Attributional LCI considers the flows in the environment within a specific temporal window, a Consequential LCI takes into consideration how these flows change as consequences of decisions.

Going a bit further into the definition, in UNEP/SETAC Life Cycle initiative guidelines (Sonnemann and Vigon, 2011), an attributional approach is defined as the share of global burdens that can be associated with a product, meaning which inputs and outputs are attributed to the functional unit of this product system. Furthermore, Agostini et al. (2020) state that the attributional approach defines the impacts of a specific product without considering its impacts on other sectors of the economy. It is, therefore, appropriate to be applied when the study aims to support a microscale decision, for example.

By contrast, a consequential approach defines information on the environmental burdens that occur as a response to a decision, in which activities in a product system are linked in a way that they are expected to change the demand for the functional unit, for instance (Sonnemann and Vigon, 2011). In a nutshell, the consequential approach also considers the scale effects, making it suitable for capturing the impact of macroscale choices, such as policy changes (Agostini et al., 2020).

The *ecoinvent* database offers three system models for the LCI: cut-off by classification, allocation at the point of substitution (APOS), and consequential system model, where the first two are defined as allocation approaches, and the latter, as a consequential approach. This database does not offer a hybrid approach (Ecoinvent, 2014).

As per the definitions offered by the database, the cut-off by classification approach allocates the production of materials to their primary user, meaning the positive and negative impacts of a specific process are not considered for another process part of its chain. On the other hand, the allocation at the point of substitution approach (APOS) allocates a burden proportionally to the processes. Finally, the consequential approach assesses the consequences of changes to an existing system (Ecoinvent, 2014).

Multifunctionality

Bioenergy production systems can often be multifunctional in the sense that they provide more than just one product along the entire process. Agostini et al. (2020) provide an excellent example to illustrate this point when pointing out that both vegetable oil for biodiesel and protein meal for animal feed can be obtained from soybean crops. According to ISO standards (ISO 14040), there are two main ways to solve these multifunctionalities: by allocation or by system expansion.

While allocation basically consists in dividing shares of the impacts to different products or services, considering, for example, the economic value or some physical properties of the products, system expansion involves the enlargement of the system boundaries to include additional functions, so it becomes possible to compare it with other systems that provide the same products or services (Agostini et al., 2020).

2.4.1.2. Life cycle impact assessment

The third phase of an LCA, entitled Life Cycle Impact Assessment (LCIA), takes place when the LCA practitioner takes the inputs and outputs defined in the inventory, i.e., the physical flows and interventions, and translates them into impacts on the environment through specific models, aiming at a better understanding of their environmental magnitude (Hauschild, 2017; Mehmeti et al., 2018).

According to the ISO 14040 standards, the impact assessment consists of five elements, of which only the first three are mandatory: the selection of impact categories, classification, characterization, normalization, and weighting (the latter two being optional). Briefly defining these elements, Hauschild (2017) illustrates: (i) impact categories are selected based on their representativeness in the assessment parameters chosen in the scope definition; (ii) the classification of elementary flows is done by assigning them to impact categories; and (iii) characterization is performed using environmental models for the impact category, quantifying the magnitude of each flow to impact an indicator of the category (Figure 2.4). Moreover, the author describes: (iv) normalization expresses the characterized scores of the impact categories relatively to a standard set of reference impact, a general reference being the background impact from society; and (v) weighting supports comparison across the impact categories, allowing the practitioner to use weighting factors for each category and giving a quantitative figure of its severity compared to other categories.

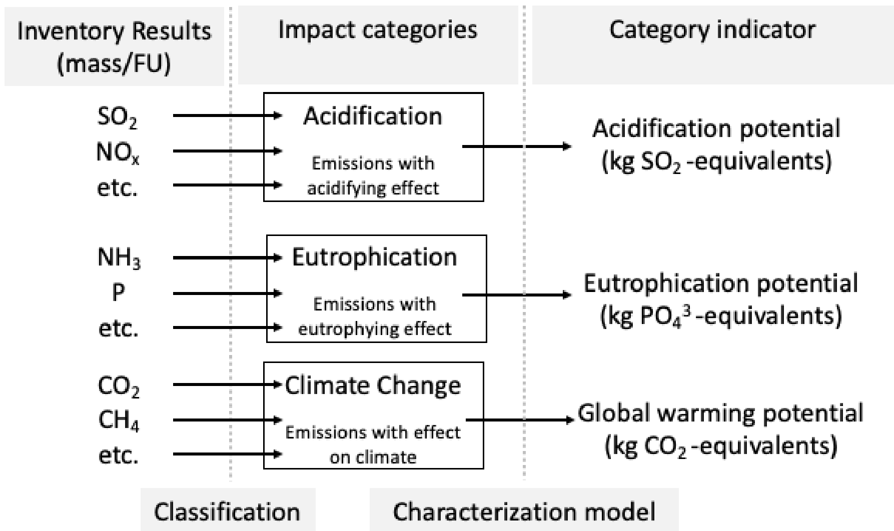

Figure 2.4 – Impact categories, classification and characterization in the impact assessment phase (adapted from Klöpffer and Grahl, 2014)

Alongside the definition of impact assessment elements, ISO 14042 states that the selection of impact categories must take the defined goal and scope into consideration, reflecting the environmental issues related to the production system under study (ISO International Standard 14042, 2000E). Within this context, Laurent et al. (2017) recommend that to avoid burden-shifting from one impact category to another, all impact categories should be taken as relevant when assessing electricity generation systems. On that note, the authors point out that an exclusive focus on the impact on climate change could be deceiving if the goal of a study is to consider the total environmental burden.

Different LCIA methods have been developed, aiming to connect the LCI results to the associated environmental impacts. As stated previously, according to ISO 14042, the results from the LCI phase are classified into impact categories, each with a category indicator. This indicator can be located in different points between the LCI result and the chain's endpoint, where the environmental impact actually occurs (Jolliet et al., 2003). Within this framework, two main characterization approaches have been developed: a midpoint approach and an endpoint approach, and the LCIA methods available can vary according to not just the selected impact categories but also to which approach they apply.

Considering the possibility of having different outcomes in an impact assessment, Bjørn et al. (2017b) raise an important point by recommending to apply more than one LCIA method to test the sensitivity of the results to the choice of the assessment method.

Characterization Approaches

When choosing which model to apply to an LCIA, one must keep in mind the objectives of the study stated in the goal and scope definition, aiming to define the most suitable approach. Characterization at the midpoint level (e.g., CML and EDIP methodologies) limits the modeling to early stages in the cause-effect chain, somewhere between the emissions/resource consumption and the endpoint level, grouping the results into the so-called midpoint categories. On the other hand, characterization at the endpoint level (e.g., Eco-indicator 99 and ReCiPe endpoint) models the cause-effect chain all the way up to the endpoint categories (Agostini et al., 2020; Jolliet et al., 2003).

Explaining it further, Agostini et al. (2020) elucidate that a midpoint approach, also known as a problem-oriented method, aggregates the relevant emissions for a given environmental area without considering the damage they may cause, for instance, when providing the total GHG emissions measured in kilograms of CO_2 equivalent without analyzing their impact to the environment (global warming potential).

However, in the cause-effect chain, these biological changes, such as increased GHG emissions, may represent damages to the Areas of Protection (natural environment's ecosystems, human health, and resource availability) (Jolliet et al., 2003). Therefore, an endpoint approach (or damage-oriented method) can be applied to provide indicators of the actual damage resulting from the impact, such as skin cancer resulting from stratospheric ozone depletion.

To Agostini et al. (2020), endpoint indicators provide more aggregated results, which simplifies the interpretation and means that a lot of the information can be lost in the process. As an example to this statement, the authors explain that endpoint methods may aggregate all the impacts to human health into one single indicator, such as disability-adjusted life years (DALY), which means that the information on whether those impacts come from emissions to air or water gets lost in the process. Jolliet et al. (2003) add up to this idea, stating that, in practice, a damage indicator result is a simplified model of a complex reality; one should stage, of a very complex reality.

In short, both methodologies are valid and accepted as far as they can allow one to achieve the study's goals. In order to decide which approach to apply, it helps to understand that endpoints may be more helpful to compare alternative products, while midpoints can be more useful to identify where the impacts are generated along the production chain (Agostini et al., 2020; Jolliet et al., 2003).

Within the framework explained above, the definition study of the UNEP/SETAC Life Cycle Initiative (Sonnemann and Vigon, 2011) has suggested combining both approaches (midpoint and endpoint) into one new methodology, which was later applied into more recent LCIA Methodologies such as ReCiPe and Impact 2002+.

2.4.1.3. Interpretation

Once the impact assessment phase is finished, the following step of an LCA is to conduct the interpretation phase, which is the phase where the results found in the LCI and LCIA phase are considered together and analyzed, taking into consideration the uncertainties of the data and the assumptions made in the study (Hauschild et al., 2017). Since the results of an LCA study aim to answer the question(s) asked in the goal and scope definition, the interpretation must be performed within the boundaries determined in the scope definition, respecting the intentions of the goal definition, and taking into account the purpose of the functional unit determined (Hauschild, 2017; Hauschild et al., 2017). In short, Klöpffer and Grahl (2014) state that the interpretation phase presents the reasons for performing the study, and Agostini et al. (2020) consider it the key step to guarantee quality and consistency, giving meaning to the study.

Adding an important point, Mehmeti et al. (2018) highlight that even though the outcome of the interpretation phase are the conclusions of the study and recommendations, the results presented should be interpreted as an indicative simulation of pros and cons of different pathways, rather than considering them as a precise prediction.

The interpretation phase also includes the sensitivity and uncertainty analysis, an iterative process used to outline and identify the key parameters that need to be varied in the assessment to understand the impacts they have on the study's conclusions (Laurent et al., 2017). Accordingly, Hauschild (2017) distinguishes how to perform a sensitivity analysis: either as a contribution analysis, where the practitioner quantifies the contribution from each process to the total results, or as a dominance analysis, where the practitioner ranks the processes according to their relative share in the results.

This phase is used to assess the reliability and robustness of the final results, together with the conclusions and recommendations taken from them, also allowing one to identify the main points that need further work in order to strengthen the conclusions of the study (Hauschild, 2017; Hauschild et al., 2017).

To Agostini et al. (2020), the most challenging part of the interpretation phase is the relation between the results and conclusions presented and the questions previously set in the goal and scope definition. For the study to be consistent, the authors emphasize that the conclusions and recommendations cannot go beyond the study's limitations.

2.4.2. LCA strengths and limitations

To Bjørn et al. (2017c), a notable strength of the LCA is its comprehensiveness when applying a life cycle perspective to cover different environmental issues, which allows the comparison of production systems with multiple processes, different resources use, and emissions that take place in various places and time. However, this 'holistic' nature can be both its major strength and its limitation, as it requires simplifications and generalizations of some aspects in order to achieve the broad scope of a product's complete life cycle (Bjørn et al., 2017c; Guinée et al., 2002)

This simplification is what prevents LCA from calculating actual environmental impacts, and since the impacts studied are usually not specified in time and space, and are commonly related to a functional until, they are often described as potential impacts rather than actual consequences (Bjørn et al., 2017c; Guinée et al., 2002).

Equally important, as stated by Bjørn et al. (2017c), is to keep in mind that when performing an LCA, one can only conclude which product (or process) is better for the environment, never knowing with this "if better" is "good enough". For that reason, the authors point out that it would be wrong to conclude that a product is absolutely sustainable with reference only to an LCA that shows this product has a lower environmental impact than another one. In like manner, Guinée et al. (2002) highlight LCA's nature as an analytical tool since it provides information for decision support, and it is not suitable to replace the decision-making process itself.

Even though the LCA is a scientific tool, it involves multiple technical assumptions that must be made by the practitioner. These are standardized by ISO in order to avoid arbitrariness. However, they can still invalidate the analysis results, which is why Guinée et al. (2002) mention that an essential aim when performing and communicating an LCA is to make these assumptions as transparent as possible.

Finally, some further limitations of the LCA are the time aspect, since it is a steady-state rather than a dynamic approach, and the availability of data, seeing that data are frequently obsolete, incomparable, or of unknown quality (Guinée et al., 2002).

2.5. LCA of two-stage systems in AD processes

As seen in previous sections (2.2 and 2.3), two-stage systems can improve the AD process by having separate bioreactors for the process's different reactions. For Ruggeri et al. (2015), a multi-stage

AD with separate bioreactors can provide flexibility for optimizing the reactions, increasing the process overall performance, particularly its energy production. However, the authors do not find the two-stage system an optimal configuration since it does not consider the optimization of all the stages within an anaerobic digestion process. Still, they acknowledge that a two-stage anaerobic digestion process enables more flexibility to the operation and a higher energy yield than a regular one-step AD.

Although this may be true, it is not easy to find in the literature extensive explanations to support TSAD. Most of the studies recurrently are directed to specific cases, with particular substrates and operational conditions (Ruggeri et al., 2015). As an illustration, Albini et al. (2018) applied the LCA tool to investigate bioenergy recovery from waste in a specific study case in Tuscany (IT). A DF process coupled with AD for the co-treatment of sewage sludge (SS) and OFMSW was analyzed, producing both bioH_2 and biogas in a two-step system. The results found that this scenario does not appear very advantageous compared to regular AD, mostly because the energy recovered resulted in being lower and the production of hydrogen-rich gas, not very high. However, when concluding their study, they highlight that a prior DF process could increase the gas production of the subsequent AD phase, which would change their results and improve DF scenarios.

Sun et al. (2019), in a like manner, performed an LCA to evaluate the so-called industrial-scaled *biohythane* (i.e., biohydrogen and biomethane) production through the digestion of microalgae and food waste. The fermentation process under study consisted of acidification followed by methanogenesis in a two-stage anaerobic configuration system. Even though the net GHG emissions resulting from this configuration were lower than those arising from conventional food waste-based biogas production, the authors found that biomethane production via direct AD seemed to be overall more suitable than *biohythane* production via two-stage fermentation. In light of these findings, they point that two-stage anaerobic processes still have many technical challenges to overcome.

Correspondingly, Ruggeri et al. (2015) evaluated the energy efficiency of a TSAD system, considering both the energy produced as H_2 and as CH_4, and found that the production of energy, in this case, was higher than that resulting from a one-step AD. Even though the contribution of the H_2 energy content resulting from the first stage was relatively low when compared with the total energy harvested from the process, to the authors' opinion, the hydrogen phase represents a pretreatment step in the process, allowing the second stage to produce a more substantial amount of methane.

Finally, the same authors highlight that most TSAD studies in the literature focus on enhancing energy recovery resulting from the metabolic phase separation. Simultaneously, few of them actually compare the potential energy recovery of TSAD with that of one-stage AD (Ruggeri et al., 2015).

3. METHODOLOGY

This section aims at explaining in detail how the LCA methodology was applied in this study. It starts by defining the considerations and outlines made in the goal and scope definition, followed by the inventory phase's data collection process. Finally, the chosen modeling approach is presented, along with the main impact categories analyzed for the impact assessment and how the results were interpreted.

3.1. Analyzed scenario

In the laboratory of biological assays of the Dept. of Sciences and Technology of Biomass (DCTB), LAQV-REQUIMTE, FCT-NOVA, a two-step anaerobic digestion (TSAD) pilot system was studied between December 2018 and July 2019. The system was designed so that the organic fraction of municipal solid waste (OFMSW) was fed into the first bioreactor, which produced bioH_2 via dark fermentation. The outflow of this bioreactor, rich in VFAs, was used as the feedstock to feed a second bioreactor, which produced biogas through methanogenesis. The OFMSW used for both scenarios came from Valorsul, which is the company responsible for the recovery and treatment of urban waste in the Northern region of Lisbon Metropolitan Area. The OFMSW was collected in the inflow of the hydrolysis tank, after the mechanical treatment of the food wastes to remove metals, glass, plastics, and other inert materials.

3.1.1. First stage – Dark Fermentation (DF)

The first bioreactor (working volume of 2.1 L) (New Brunswick Scientific, BIOFLO 1000) was operated under such conditions to favor the acidogenesis stage and inhibited methanogenesis, therefore promoting the production of bioH_2. The analysis performed for this stage intended to evaluate the impact that different hydraulic retention times (HRTs) had in the bioH_2 production during the dark fermentation (DF) of OFMSW, under mesophilic conditions (37 ºC) and continuous flow. The inoculum used for the DF process consisted of a mixed culture of bacteria. The HRT of 4, 5, and 6 days was analyzed in different trials. The trial with a HRT of 5 days was the one with the best results in terms of bioH_2 production, followed by the HRT of 4 days (Martins, 2019).

Throughout each trial, the bioreactor was fed once a day through the aid of a pumping system (Watson Marlow model 313S) (Figure 3.1), after the prior heating of the sample to 37ºC, to avoid thermal shocks in the bacteria pool. To heat up the sample, a stirring mechanism was applied until it achieved the desired temperature of 37ºC. The sample’s pH, temperature, redox potential, and conductivity were analyzed daily, except during weekends. Small volumes of HCl (1N) were fed into the bioreactor through a peristaltic pumping system (Heidolph Pumpdrive 5001 - Figure 3.1) each time the pH went above a pre-defined threshold (5.5) in order to maintain the process' pH within the established limits. The bioH_2 measurements were performed every time the process was on steady-state conditions (constant production of bioH_2 for a period time of 2 x HRT). By the end of all trials, the daily average bioH_2 produced was measured, and the content of CO_2/H_2 was analyzed and quantified by GC-TDC. The hydrogen percentage (% v/v) was then calculated for each trial.

Figure 3.1 - Pumping system and peristaltic pump for acidification

Figure 3.2 – pH electrode

The bioreactor's continuous stirring was applied by a mechanical stirring system, permanently connected at a significantly reduced speed (around 10 rpm). The bioreactor's operating conditions were mesophilic (37 ± 1ºC) with the use of a heating band and a thermocouple system. Digital control modules performed the pH, temperature, and redox potential monitoring through a pH electrode (Hanna edge, model HI 2002-02) (Figure 3.2), a thermocouple, and a redox potential electrode (Thermo Scientific, Orion 97-78), respectively.

In the outflow of the bioreactor, conductivity test was performed using a conductivity meter (Thermo Scientific, Orion Star A215) (Figure 3.4 – 1). Finally, the produced gas was collected in two acrylic columns. Figure 3.3 and Figure 3.4 show the configuration and main components of this first stage.

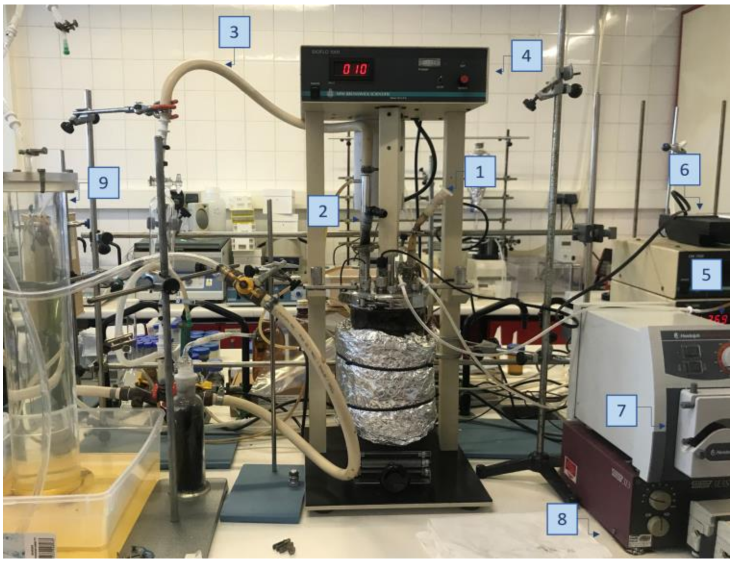

Figure 3.3 - Bioreactor 1 | Dark Fermentation system

Legend:
1: Bioreactor inlet
2: Bioreactor outlet
3: Biogas outflow
4: Continuous stirring system
5: Temperature control: thermocouple system
6: Redox potential electrode
7: HCl pumping system
8: Bioreactor pumping system
9: Glass columns for bioH_2 storage

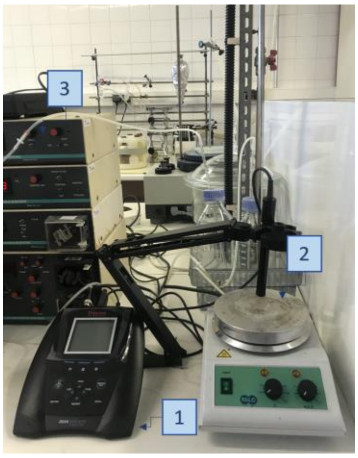

Figure 3.4 – Bioreactor 1 | Other components

<u>Legend</u>:
1: Conductivity meter
2: Stirring mechanism
3: Temperature control

Martins (2019) reported to have estimated the energetic content of bioH_2 based on the typical lower heating value (LHV) of the gas (120.7 $MJ.kg^{-1}$ H_2) available in the literature, and on the daily H_2 production per kg of Volatile Solids (VS) present in the organic substrate that was fed to the bioreactor.

The scenario of HRT 5 days (the one with the best results), ran for thirty-two (32) days and showed a percentage of hydrogen of 32% v/v, which corresponds to an H_2 production rate of 0.33 $L_{H2}.L^{-1}_{bioreactor}.d^{-1}$. The energy content of the produced bioH_2 was 175 $kJ.kg^{-1}_{VS,in}$, which was considered by the author as being equivalent to an electric energetic potential of 48.6 $kWh.t^{-1}_{VS,in}$ (Martins, 2019).

The scenario of HRT 4 days operated during thirty-nine (39) days, resulting in a percentage of hydrogen of 25% v/v, which corresponds to an H_2 production rate of 0.20 $L_{H2}.L^{-1}_{bioreactor}.d^{-1}$. The energy content of the produced H_2 was 123 $kJ.kg^{-2}_{VS,in}$, being equivalent to an energetic potential of 34.2 $kWh.t^{-1}_{VS,in}$ (Martins, 2019).

3.1.2. Second stage – Methanogenesis and anaerobic digestion (AD)

The second stage of the system aimed to study the methanogenesis of VFAs produced in the DF bioreactor (first stage). The trials of this second stage analyzed three different scenarios: the first one using as inlet for methanogenesis the VFA from DF process with an HRT of four (4) days (VFA4); the second trial using VFA from DF process with an HRT of five (5) days (VFA5); and the third one performing a conventional anaerobic digestion of the raw OFMSW, for comparison. The scenarios that showed the most significant potential for electric energy production were those using substrates rich in VFAs for methanogenesis (VFA4 and VFA5 trials). The trial that used VFA from DF with an HRT of 4 days showed the most promising results (VFA4).

The anaerobic bioreactor was fed daily with a peristaltic pump (Watson Marlow, model 302S). Simultaneously, through the outlet tube, an equal volume of the inlet was collected as effluent from the anaerobic bioreactor. Prior to each time the bioreactor was fed, the sample was heated up in a heating plate (Agimatic-N) until it reached the temperature of 37 ºC.

The system was operated under mesophilic conditions (37 ± 1ºC) and being monitored daily, with a temperature meter (Hanna Instruments, model HI 9053) (Figure 3.5). The heating system applied consisted of a coil placed around the bioreactor, which was covered with fiberglass insulation to prevent heat loss to the surrounding environment. Furthermore, a heating bath (Nüve bath, model NB 20) (Figure 3.6) was used to heat water, that was then pumped to circulate through the coil, heating the entire bioreactor. The total energy and water consumed by this system were measured within the life cycle inventory of this study to evaluate the energy and mass balance of the system.

Figure 3.5 - Temperature meter

Figure 3.6 - Water bath for heating system

The bioreactor's constant stirring was done by a magnetic stirring plate (Agimatic-N) placed on its bottom. The foam recirculation system operated twice a day, for 15 minutes in each operation period and through the same peristaltic pump previously mentioned, through which the foam that got accumulated in the upper part of the bioreactor would be pumped to its bottom.

On a daily basis, after feeding the bioreactor, the pH of the effluent was measured with a pH meter (Hanna edge, model HI 2002-02), as well as its conductivity, using a conductivity electrode (Thermo Scientific, model Orion Star A215). The feedstock's conductivity was also measured daily, while its pH was measured three (3) times throughout the entire trial, only to confirm the data collected from the continuous monitoring system.

Finally, the biogas produced by the anaerobic bioreactor was quantified by measuring the biogas' volume accumulated in the water columns. Figure 3.7 shows the configuration and main components of the second stage system.

Figure 3.7 - Bioreactor 2 | Anaerobic digestion and methanogenesis system

Legend:

1: Bioreactor inlet	6: Magnetic stirring plate
2: Bioreactor outlet	7: Temperature meter
3: Foam recirculation system	8: Water inlet to the coil for heating
4: Biogas outflow	9: Fiberglass insulation
5: Bioreactor pumping system	10: Glass columns for biogas storage

The biogas' energetic content directly relates to the CH_4 content in the gas and its typical LHV (8.5 kcal/m^3 at 0º and 1 atm) (Salvaterra 2019). Based on the CH_4 content of the produced gas, its LHV, and the achieved production yield, Salvaterra (2019) defined its electric energy potential for each scenario.

The scenario VFA4, the one with the most favorable results, resulted in biogas with 73.1% v/v of CH_4, showing the highest electric energy potential (7.2 kWh.kg$^{-1}_{VSapplied}$) and a production rate of 721 L_{CH4}.kg$^{-1}_{VSapplied}$ (Salvaterra, 2019). The electric energy potential of the different scenarios was estimated by Salvaterra (2019) based on the typical LHV of the gas, and on the biogas production yield (m^3/kg$_{VS}$).

The scenario VFA5 presented 69.5% v/v CH_4, an electric energy potential of 6.7 kWh.kg$^{-1}_{VSapplied}$, and a production rate of 660 L_{CH4}. kg$^{-1}_{VSapplied}$ (Salvaterra, 2019).

The third scenario, that used the raw OFMSW for comparison, presented 50.4% v/v CH_4, an electric energy potential of 3.2 kWh.kg$^{-1}_{VSapplied}$, and a production rate of 321 L_{CH4}. kg$^{-1}_{VSapplied}$ (Salvaterra, 2019).

3.2. LCA Methodology

The details and descriptions of the applied LCA methodology are further presented in this subchapter, covering every step from goal and scope definition, data collection process, life cycle inventory, all the way to the life cycle impact assessment, and the interpretation phase.

3.2.1. Goal and scope definition

The LCA of bioH_2 and biogas production from the organic fraction of the municipal solid waste via a two-stage anaerobic digestion process was carried out with the support of the software *openLCA* v1.8.0 (GreenDelta, Berlin, Germany), aligned with ISO guidelines (ISO 14040) and the framework it defines: goal and scope definition, inventory analysis, impact assessment, and interpretation. This study aimed to evaluate the energy balance and life cycle impacts of bioH_2 and biogas production from the OFMSW in a two-stage fermentation process, including material flow, energy consumption, and environmental impacts. The functional unit used in this assessment was 1 kJ of energy produced. Important to notice that, because of the two-stage configuration, the energy was measured in terms of kJ of produced bioH_2 in the first stage and kJ of produced biogas in the second stage. All unitary operations in the inventory phase were considered based on the amount of gas produced in each stage during the duration of the trials.

The system's spatial and temporal boundaries were the activities and processes carried out within the scope of the experiment. The referred trial took place in the laboratory of biological assays of the Dept. of Sciences and Technology of Biomass (DCTB), LAQV-REQUIMTE, FCT-NOVA, between December 2018 and July 2019. It is imperative to highlight that the life cycle impacts of other processes beyond the defined system boundaries were not considered in this study, e.g., the waste production, waste collection, or disposal of the final effluent. The overall flow diagram of the product system is shown in Figure 3.8. Since this study's goal was to assess the system working in a two-stage configuration, rather than each process individually, this LCA was performed for the pre-defined conditions that presented the best results in terms of energy production. These conditions are as follows:

<u>Scenario 1:</u> Dark Fermentation of OFMSW with a Hydraulic Retention Time of 4 days (HRT4) + Methanogenesis of Volatile Fatty Acids from that DF process (VFA4). This scenario presented the best results in the methanogenesis stage and biogas production;

<u>Scenario 2:</u> Dark Fermentation of OFMSW with a Hydraulic Retention Time of 5 days (HRT5) + Methanogenesis of Volatile Fatty Acids from that DF process (VFA5). This scenario presented the best results in the Dark Fermentation stage and bioH_2 production.

The conventional Anaerobic Digestion of OFMSW (scenario S3) did not present favorable results in the energy balance when compared to the two-stage configuration, as it will be further seen in this study. Therefore, the environmental impacts of this scenario were not analyzed as part of the scope of this LCA.

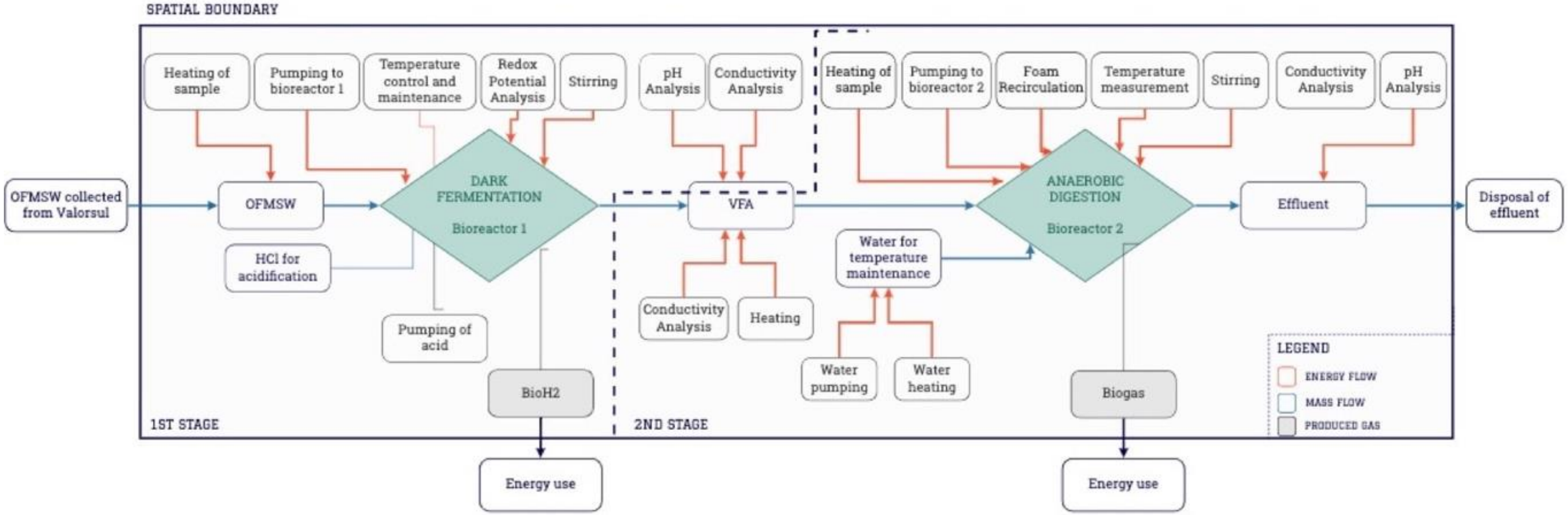

Figure 3.8 – System boundaries for the scenarios under analysis

Each energy input and output flow considered for this scenario was used to estimate the system's energy requirements and the resulting energy balance. This balance includes the energy inputs for the system's operation (such as electricity used for pumping, heating, and mixing), as well as the inputs for assessing and controlling the operation conditions (such as pH and conductivity analysis). As energy output, the energy content of the final produced gas (bioH_2 and biogas) was considered. Furthermore, for the system's mass balance, both bioreactors' inlet and outlet were considered, alongside the acid consumption for acidification of the first bioreactor and the water consumption for temperature control of the second bioreactor.

The *ecoinvent* v3.4 database was used in this assessment, with allocation, cut-off by classification as a system model. Since this approach allocates the impacts of a specific process to the product's primary user and does not consider them for another process part of its chain, it was perceived as the most appropriate one for this study, aligning with the goal of this LCA (Ecoinvent, 2014). A consequential approach was not considered suitable since this study's objective was not to assess the consequences of changes to an existing system but rather to evaluate the performance and environmental impacts of two proposed systems within the defined boundaries.

The life cycle environmental impacts were assessed by means of the methodologies CML and ReCiPe. As defined in the theoretical framework, the ReCiPe method combines both midpoint and endpoint approaches. In this study, the main midpoint categories addressed by the ReCiPe Midpoint (H) methodology were: Stratospheric Ozone Depletion, Human non-Carcinogenic Toxicity, Human Carcinogenic Toxicity, Terrestrial Acidification, Global Warming (GW100), Freshwater Eutrophication, Marine Eutrophication, Freshwater Ecotoxicity, Terrestrial Ecotoxicity, Marine Ecotoxicity, Ozone Formation (Human Health and Terrestrial Ecosystems), Fine Particulate Matter Formation, and Water Consumption. The endpoint categories were not assessed as this study's goal was to identify the major impacts throughout the production chain, instead of comparing alternative products and their overall impact at the end of the chain.

To test the sensitivity of the results in the interpretation phase to the method used, the CML method was also applied for the impact assessment phase, as recommended by Bjørn et al. (2017b). CML methodology (CML 2 Baseline 2000) was applied as a midpoint method assessing the following impact categories: Abiotic Depletion, Acidification, Eutrophication, Freshwater Aquatic Ecotoxicity, Global Warming Potential (GWP100), Human Toxicity, Marine Aquatic Ecotoxicity, Ozone Layer Depletion, Photochemical Oxidation, and Terrestrial Ecotoxicity.

The purpose of this analysis was to understand, within a life cycle approach, whether the proposed system is advantageous from an environmental and energy production perspective. Therefore, the aim was to quantify and compare the energy balance, enabling the assessment of the environmental impacts of these bioH_2 and biogas production pathways in the two different conditions described.

The two studies analyzed (Martins, 2019; Salvaterra, 2019) had considerably favorable results: while the study of the Dark Fermentation process pointed it as a promising technology for bioH_2 production, the study of the Methanogenesis process indicated that an inlet flow rich in VFA can present higher electric energy potential and higher biogas production yields when compared to regular routes (OFMSW as inlet). Nevertheless, the need to understand if these results made sense from a life cycle perspective arose from both analyzed studies. There is no specific intended use for this study's results, but the hope is that it serves as a basis for future research in the scope here defined. The upscaling of this scenario to an industrial scale could allow the analysis of the system's environmental impacts when considered on a larger scale.

3.2.1.1. Assumptions

As previously defined in this study, a Life Cycle Assessment may involve the need to take multiple technical assumptions, which need to be reported in the most transparent possible way (Guinée et al. 2002). Very few assumptions were taken in this study, as most of the data collection took place while the experimental lab-scale assays were held. Nevertheless, some information and measurements were not possible to be collected due to different constraints, which is why the following assumptions needed to be taken:

1. The energy consumption of the conductivity meter (Thermo Scientific, Orion Star A215) was considered to be similar to the one of the pH meter (Hanna Edge HI 2002-02), considering the time of use of both equipment and their technical characteristics;
2. The amount of HCl used for the acidification of the bioreactor for Dark Fermentation process (bioreactor 1), as well as its energy consumption, were estimated based on assumptions taken from interviews with the personnel responsible for operating the system;
3. The amount of water consumed in the heating bath, used for the temperature control of the bioreactor for the Methanogenesis process (bioreactor 2), was estimated based on an average taken during 16 days of use and applied to the entire process.

3.2.2. Life Cycle Inventory

The inventory data consisted of the system's energy and material flows collected between April and June of 2019, when the pilot project was held. These flows are defined by the energy and material inputs and outputs considered for the system, such as the energy consumption from the pumps, the energy used for heating the feedstock material, or the water used for the bioreactor's temperature maintenance. For the system output, the produced gases' energy content determines the total energy produced by the system, which comes from the results of the studies on this pilot project (Martins, 2019; Salvaterra, 2019).

All the necessary physicochemical characteristics of the samples used in both scenarios, such as total volatile solids (VS) in the effluent, were also taken from the two MSc students' data (Martins, 2019; Salvaterra, 2019). Additional necessary data were obtained from *ecoinvent* 3.4 database, such as the electricity mix (market for electricity, medium voltage, label-certified, Portugal), the HCl composition (hydrochloric acid production, from the reaction of hydrogen with chlorine), the water (market for tap water) and the organic waste composition (market for biowaste), for the purpose of the life cycle assessment.

3.2.2.1. Data collection

As previously stated, the primary data for this study were collected between April and June of 2019, when the two-phase pilot system was operating. The collected data comprised all operational inputs and outputs associated with the bioH_2 and biogas production chain. When it was not possible to measure or quantify the specific information, secondary data were taken from the *ecoinvent* database, as well as from the results of the studies of Martins (2019) and Salvaterra (2019). To minimize uncertainty and enhance the data quality, the primary data measured in the laboratory was collected at different times and for different durations, allowing average values to be used in the LCA model.

Following the definitions presented in the Theoretical Framework of this study, one of the first steps when performing an LCA is determining a reference flow for the LCI analysis. The reference flow analyzed in this study consisted of the flow applied in the pilot project, as previously described in the goal and scope definition of this study. To evaluate both processes' energy flow independently, they were separated into Process 1 and 2. The outcome of Process 1 was the bioH_2 produced in the first bioreactor and the VFAs used as income in Process 2, while the outcome of Process 2 was the biogas produced in the second bioreactor and the effluent of the system.

Taking this into account, the energy and mass flow of both processes (Figure 3.10 and Figure 3.11) were distinguished and measured at different times during the execution of the experiment, with the aid of the energy measuring device PM 231 E (Brennenstuhl) (Figure 3.9). In Annex 1 and Annex 2 the results of this data collection are summarized as the detailed Life Cycle Inventory of this study.

Figure 3.9 - Energy measuring device PM 231

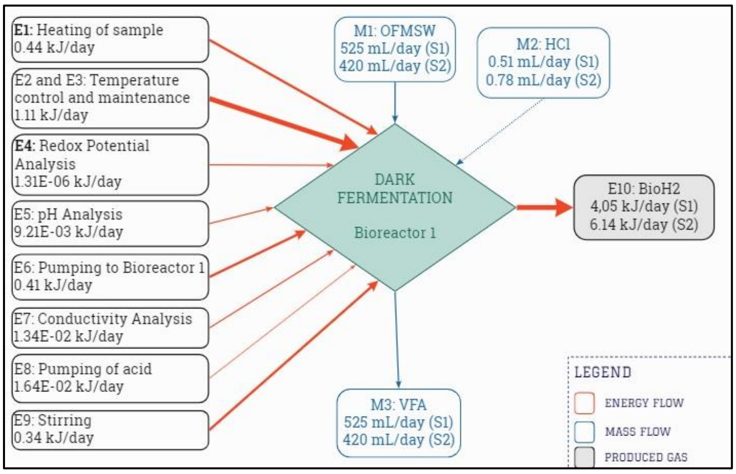

Figure 3.10 - Energy and mass flow of Process 1 (bioH_2 production via dark fermentation)

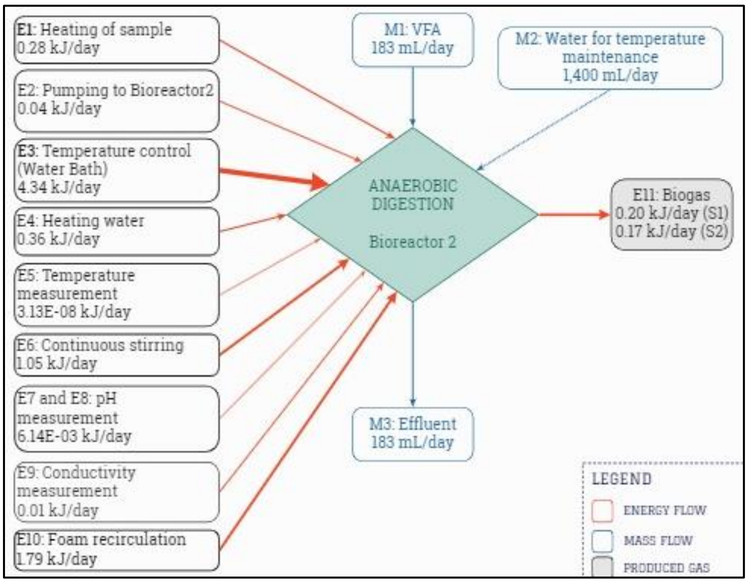

Figure 3.11 - Energy and mass flow of Process 2 (biogas production via methanogenesis)

3.2.2.2. Multifunctionality and system modelling approach

To keep the analysis into the pre-defined boundaries of this study, i.e., since it consisted of a gate-to-gate analysis of an organic waste sample after it had arrived at the laboratory, and of the outcome of the processes in the bioreactors, without considering their course of treatment or destination, the multifunctionality of the system was not entirely considered for this LCA.

Considering that this study's purpose was to evaluate the impacts of a specific pilot project, an expansion of the system was not perceived as an adequate modeling approach. Instead, the Allocation, Cut-off by classification system model of the *ecoinvent* database was applied. By its general foundation, all impacts of a product system are allocated to this product's primary user. Therefore, if a material gets recycled, the primary producer does not receive credit for recycled materials that end up in the market. This means that recyclable materials, or biowastes for this specific study, are available burden-free to the subsequent processes. The treatment of waste is entirely allocated to the waste producer. All valuable by-products of waste treatment are cut off in the waste treatment and become available burden-free (Ecoinvent, 2014).

For this reason, the cut-off approach was perceived as most suitable for this case. Nevertheless, for future studies and when scaling up this scenario to an industrial scale, the proposed system's multifunctional aspect should be better examined to consider its multifunctionality beyond its boundaries, namely in what concerns the production of bioH_2, biogas, and digestate.

3.2.3.LCIA

As previously stated in this study, the Life Cycle Impact Assessment (LCIA) is the phase when the LCA practitioner applies impact assessment models to the data from the inventory to better understand their impact on the environment.

After reviewing 47 studies on life cycle assessment of electricity generation, Barros et al. (2020) demonstrated that, while climate change was the most commonly used impact category among all studies, the most applied impact assessment methods were ReCiPe, CML, and IPCC. Since IPCC (Intergovernmental Panel on Climate Change) methodology specifically addresses the climate change impact, expressing results in terms of Global Warming Potential (GWP), but does not cover other impact categories, its application was not considered as a good fit for this assessment.

That being so, this LCIA was performed employing ReCiPe Midpoint (H) and CML baseline 2002 methodologies, present in the *ecoinvent* 3.4 database, and applied through *openLCA* v.1.8.0 software. The decision to apply two different methodologies was to allow the sensitivity analysis of the results with regards to the applied methodology.

By definition, the ReCiPe methodology combines both midpoint and endpoint approaches, therefore not only covering impact categories in the early stages in the cause-effect chain but also addressing the final damage that can result from these impacts. The regional validity for this methodology is Europe, which was considered appropriate for this study regarding the location where the lab assays were held. ReCiPe has three different versions for both midpoints and endpoints approaches - Hierarchist (H), Individualist (I), and Egalitarian (E) -, that take into account three different cultural perspectives. Considering the timeframe analyzed by the applied CML methodology for the Global Warming impact category (100 years for GWP100), the Hierarchist (H) version was the one applied for ReCipe, which also uses the medium time frame of 100 years for global warming potential. Considered the most appropriate and to allow for comparison with the CML methodology, the ReCiPe midpoint approach was the one applied to this study.

On the other hand, CML is a midpoint-oriented method, which groups the impact categories into two groups: baseline (obligatory) impact categories and optional impact categories. Even though it was developed for the European region, this method's regional validity is global, except for acidification and photo-oxidation formation impact categories (ILCD handbook, 2010). Table 3.1 summarizes the impacts analyzed in each of the applied methodologies and their respective areas of protection.

Table 3.1 – LCIA methods and the analyzed Impact Categories

Methodology	Approach	Impact categories (Midpoint categories)	Areas of protection
ReCiPe (H)	Midpoint	Stratospheric ozone depletion, Human non-carcinogenic toxicity, Human carcinogenic toxicity, Terrestrial Acidification, Global Warming (GW100), Freshwater Eutrophication, Marine Eutrophication, Freshwater ecotoxicity, Terrestrial Ecotoxicity, Marine Ecotoxicity, Ozone Formation, Fine particulate matter formation, Water Consumption	Human Health Ecosystem and Resources
CML 2000	Midpoint (baseline)	Abiotic Depletion, Acidification, Eutrophication, Freshwater Aquatic Ecotoxicity, Global Warming Potential (GWP100), Human Toxicity, Marine Aquatic Ecotoxicity, Ozone Layer Depletion, Photochemical Oxidation, Terrestrial Ecotoxicity.	Human Health, Natural Environmental, Man-made Environment, Human Resources

3.2.4. Results and interpretation

As has been previously seen in this study, in the inventory phase, the data for energy and mass flows from the system was collected (Annex 1 and Annex 2). To use this data for the LCIA phase, in terms of the defined functional unit, it was necessary to perform an energy and mass balance for both processes and their correspondent scenarios. These energy and mass balance results were the data used for the LCIA calculations in terms of the total energy produced in the systems (expressed in kJ of produced bioH_2 and biogas).

The CML and ReCiPe methodologies were applied in parallel to both processes. To allow for comparison across the impact categories, the first analyzed results were the normalized results, expressed for each category regarding the system's total impact. This approach enabled identifying the highest impact categories in each methodology's results and for both processes (bioH_2 and biogas production).

Once the normalized results were analyzed for both methodologies and the different scenarios, the most relevant categories were selected across the methodologies. Further in the process, the results were analyzed in more detail for these selected categories. Simulations were run multiple times to obtain the detailed results for each process's scenarios, also applying the two studied methodologies.

Finally, the contribution of each flow of the process (e.g., energy consumption, water consumption) was analyzed for these selected categories, allowing for the identification of the highest contributions to a given impact category.

3.2.4.1. Energy and mass balance

The energy and mass balances were calculated in terms of the total energy produced in the systems (expressed in kJ of produced bioH_2 and biogas). The balances were done based on the previously calculated daily consumption (Annex 1 and Annex 2) and then applied to each system's total period (39 days and 32 days for bioH_2 production scenarios, respectively, and 23 days for both biogas production scenarios). Furthermore, the resulting value was then expressed in terms of the average kJ produced for each scenario.

Once the energy balance of the production system for each process was obtained, a Net Energy Ratio (NER) was calculated for both processes independently, as well as for the proposed two-stage configuration. Equation (1) shows the calculation for NER (Manish and Banerjee, 2008). Different authors have applied the NER as a significant parameter for comparing different production pathways, which can also be used to determine the industrial feasibility of a process (Manish and Banerjee, 2008; Reaño, 2020; Sun et al., 2019).

$$NER = \frac{Energy\ Output\ (kJ\ of\ bioH_2\ and/or\ biogas)}{Energy\ Input\ (kJ)} \qquad (1)$$

The net energy ratios for both processes and the proposed two-stage configuration are presented in this study's results.

3.2.4.2. Impact Categories

Based on the normalized results obtained with the applied methodologies, a few categories were selected to be studied in more detail, allowing for a more detailed comparison not only between methodologies but also across the processes and scenarios under study.

This selection was based, at first, on the identification of the categories which presented the highest normalized results for the impact assessment. However, since this study's interpretation phase's goal was to also allow for the comparison between the applied methodologies, a criterion of common categories between both methodologies was applied to this selection. Finally, the categories were defined based on their representativeness and added value to the results. To illustrate this last point, it was found that the impact category names as "human toxicity" showed a different trend than the others, allowing for comparison, as shown in the results of this study. This approach means that the categories selected, in the end, were not only the ones that showed the highest results, but also those that were somehow distinctive and common to both methodologies, measured with the same units. The categories resulting from this selection criteria are presented in Table 3.2.

Table 3.2 – Impact categories for interpretation

Impact Category (unit)	CML Label	ReCiPe Label
Global Warming Potential (kg CO_2 eq)	GWP100	Climate Change
Acidification (kg SO_2 eq)	Acidification	Terrestrial Acidification
Marine Ecotoxicity (kg 1,4-DB eq)	Marine Aquatic Ecotoxicity	Marine Ecotoxicity
Human Toxicity (kg 1,4-DB eq)	Human Toxicity	Human Toxicity

1,4-DB: 1,4-dichlorobenzene

To these impact categories, the results were studied to compare methodologies and their results for the different scenarios of each process, as well as compare the scenarios in each method and both processes. Furthermore, an analysis of each flow's contribution to the results obtained for these selected categories was performed for the two processes.

The final stage of the interpretation phase of these results was a sensitivity analysis to the applied methodology and some pre-selected parameters, showing the different results obtained for each scenario and the differences between processes in the light of the different methods.

3.2.4.3. Sensitivity and Uncertainty

The sensitivity analysis took place after the interpretation phase of the LCIA in regard to the uncertainty of the data, and the identified significant contribution points to the results. As previously seen in this study's theoretical framework, this analysis shows the impact of the selected methodologies and the influence of the analyzed flows and assumptions made on the results.

The original data and results were defined as reference values to the sensitivity analysis, further analyzing the new LCIA results obtained with the proposed changes compared to the reference, as indicated by ISO 14040 (ISO International Standard 14040, 2006).

As stated by Reaño (2020), changes in parameters of the process can direct to the identification of required changes in technology, which is why a sensitivity analysis is critical in identifying which flows and parameters would require improvement in the process. To perform the sensitivity analysis of this study within the proposed approach, there was first the need to identify the energy and mass flow representing the highest contribution to the LCIA results, considering the energy balance and the previously selected impact categories. The resulting identified flows are the ones that follow:

1. In the bioH_2 production process via dark fermentation: Heating of the OFMSW sample (E1 – daily energy consumption of 0.44 $kJ.day^{-1}$).
2. In the biogas production via methanogenesis: Temperature control of the bioreactor (E3 – daily energy consumption of 4.34 $kJ.day^{-1}$) and Foam Recirculation (E10 – daily energy consumption of 0.89 $kJ.day^{-1}$).

Furthermore, in the bioH_2 production process, the HCl consumption for the bioreactor's acidification was investigated for the sensitivity analysis, given the uncertainty of the data in the LCI phase and its dependency on the substrate's characteristics used as input to the process.

Once these flows were identified, modifications to the data collected in the LCI phase were suggested (Table 3.3).

Table 3.3 – Parameters studied for sensitivity analysis

Process		Energy Consumption for Base Scenario	Sensitivity Analysis
BioH_2	HCl use for acidification	4x in Scenario 1 (S1) 5x in Scenario 2 (S2)	5x in Scenario 1 (S1) 4x in Scenario 1 (S2)
	Heating of OFMSW sample (E1)	0.44 $kJ.day^{-1}$	Energy consumption reduced by 20% considering the use of a more energy efficient equipment
Biogas	Bioreactor temperature control (E3)	4.34 $kJ.day^{-1}$	Energy consumption considered to be 25% of the measured one by the use of a more energy efficient system
	Foam recirculation (E10)	0.89 $kJ.day^{-1}$	Energy consumption reduced by 30% considering the use of a more energy efficient equipment

The proposed changes to the acidification recurrence of the bioreactor come from the variability of the substrate and its direct impact on the sample's pH, as stated by Martins (2019), and as it will be further discussed in this study. On the other hand, the proposed changes to energy flows come, at first, from the identified high energy consumption of these flows, that in comparison to other processes, seem to be higher than necessary.

To clarify the stated above, through the data collected for E1 (Heating of OFMSW) of the bioH_2 production process, it was possible to identify that according to the equipment used to heat the sample, the energy consumption could be 20% lower when using one equipment than when using the other. Therefore, the suggestion to use more energy-efficient equipment for the process, proposing a reduction of 20% in its overall energy consumption.

To the biogas production process, a similar approach to the one stated above was applied, mostly based on the fact that the equipment used to control the bioreactor's temperature was known as not to be very energy efficient. Compared to the bioH_2 production process and its temperature control system, for example, the energy consumption from the E3 flow of the biogas production process was approximately four times higher. Hence, the simulation of a 75% more energy efficient system for this flow seemed to be necessary.

The last energy flow studied in the sensitivity analysis was the E10 (foam recirculation) of the biogas production process, since the equipment used for this process was the same pump used to feed the input to the bioreactor. When feeding the bioreactor, the pump was used for an average of 1 minute. In contrast, for the foam recirculation, the average time of use was 15 minutes per use, being used twice a day. For that reason, a reduction of 30% of this energy consumption was proposed, considering the use of more energy-efficient equipment that could be applied only for this flow.

Finally, as part of the sensitivity analysis and in a similar manner to the one applied in the LCIA of this study, the resulting values from the proposed variations were analyzed for both methodologies (CML and ReCiPe), applied to the different scenarios of both processes under study.

4. RESULTS AND DISCUSSION

In this chapter, the global and detailed results from this assessment are presented and discussed, including the energy balance outcomes and interpretation of the results. Furthermore, the detailed results from the LCIA phase are explored, both for normalized results and the detailed analyzed categories.

Finally, the analysis of the flow contribution of both processes (e.g., energy consumption, water consumption) is presented for the selected categories, making it possible to identify the highest contributions to a given impact category. The chapter concludes by presenting the sensitivity analysis results to the applied methodologies and to the proposed changes.

4.1. Energy and mass balance

As described in the methodology section of this study, the energy and mass balance were calculated in terms of the total energy produced in the different systems for the total period of each system (39 days and 32 days for bioH_2 production scenarios, respectively, and 23 days for both biogas production scenarios). All results were expressed in total kJ of bioH_2 and total kJ of produced biogas in each scenario.

The detailed results and interpretation of this balance are described in the subsequent subchapters, individually for each process as the results were calculated in terms of bioH_2 production and biogas production separately.

4.1.1. bioH_2 production via dark fermentation

For the energy and mass balance of the bioH_2 production process via dark fermentation, each energy and mass flow necessary as input and output for the process was considered separately, as previously described in section 3.2.2.1. All these flows were quantified and calculated in relation to the total energy produced in kJ of bioH_2 for each scenario (Table 4.1).

As previously presented, for the bioH_2 production process, scenario S1 refers to the dark fermentation of OFMSW with an HRT of 4 days. Scenario S2 represents the dark fermentation of OFMSW with an HRT of 5 days. The acronyms E1-E9 and M1-M3 are references made to the previously identified energy and mass flows (Figure 3.10 and Figure 3.11, and Annex 1 and Annex 2).

Table 4.1 – Energy and mass balance of bioH_2 production process via dark fermentation

BioH$_2$ Production via Dark Fermentation | Energy and mass balances						
	Energy flow	**Daily energy consumption (kJ)**	**Total consumption for S1(kJ)**	**Total consumption for S2 (kJ)**	**Total consumption for S1 per kJ of produced bioH$_2$ (kJ/kJ bioH$_2$)**	**Total consumption for S2 per kJ of produced bioH$_2$ (kJ/kJ bioH$_2$)**
E1	OFMSW Heating	0.44	17.26	14.16	0.11	0.07
E2 E3	Temperature control and bioreactor heating	1.11	43.46	35.66	0.27	0.18
E4	Redox potential measurement	1.31E-06	5.12E-05	4.20E-05	3.24E-07	2.14E-07
E5	pH Measurement	9.21E-03	0.36	0.29	2.27E-03	1.50E-03
E6	Bioreactor feeding	0.41	15.80	12.96	0.10	0.07
E7	Conductivity measurement of inflow and outflow	1.34E-02	0.52	0.43	3.30E-03	2.18E-03
E8	Acid addition	1.64E-02	6.54E-02	8.18E-02	4.14E-04	4.16E-04
E9	Continuous stirring of the bioreactor content	0.34	13.42	11.01	0.08	0.06
	Mass flow	**Daily consumption**	**Total consumption for S1**	**Total consumption for S2**	**Total consumption for S1 per kJ of produced bioH$_2$**	**Total consumption for S2 per kJ of produced bioH$_2$**
M1	Inlet	525 mL for S1 420 mL for S2	20,475 mL	13,440 mL	129.48 mL/kJ bioH$_2$	68.38 mL/kJ bioH$_2$
	Content of SV in inlet	49.5 g_{SV} for S1 37.7 g_{SV} for S2	1,932 g	1,207 g	12.22 g/kJ bioH$_2$	6.14 g/kJ bioH$_2$
M2	Acidification (HCl)	-	20 mL	25 mL	0.126 mL/kJ bioH$_2$	0.127 mL/kJ bioH$_2$
M3	Outlet	525 mL for S1 420 mL for S2	20,475 mL	13,440 mL	129.48 mL/kJ bioH$_2$	68.38 mL/kJ bioH$_2$
	Content of SV in outlet	22.1 g_{SV} for S1 16.5 g_{SV} for S2	864 g	529 g	5.46 g/kJ bioH$_2$	2.69 g/kJ bioH$_2$

The interpretation of these results and further identification of the process's global energy consumption distribution are depicted in Figure 4.1.

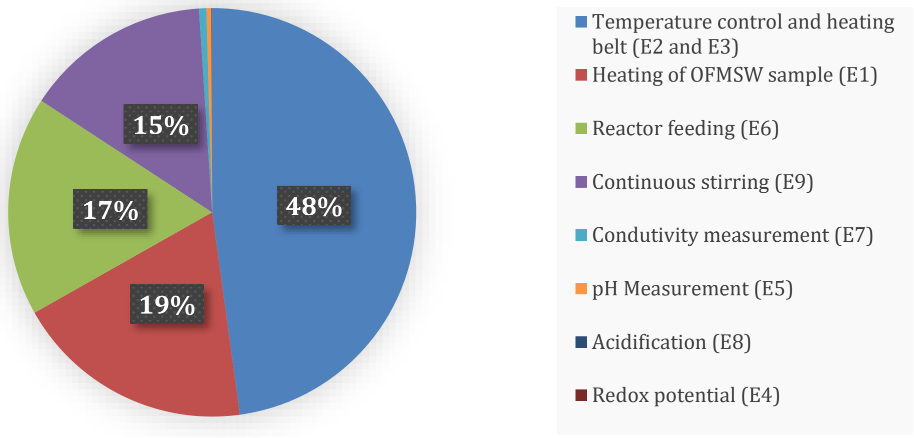

Figure 4.1 – Global energy consumption distribution in the bioH_2 production process via dark fermentation

As shown above, the highest energy consumption of the bioH_2 production process via dark fermentation comes from the temperature control system of the bioreactor, composed of a heating belt and thermocouple system (E2 and E3), representing nearly half (48%) of the total energy consumption of the process.

Following this energy input, the second highest energy consumption comes from the heating (E1) of the OFMSW collected at Valorsul-ETVO. OFMSW had to be heated up until 37 ºC each time prior to the feeding of the bioreactor to avoid thermal stresses in the bacterial populations. This energy input represents an average of 19% of the total energy consumption of the process.

As for the comparative analysis of the different scenarios (S1 and S2), it can be seen that Scenario 1, which represented the dark fermentation process with an HRT of 4 days, had a higher specific energy consumption (in terms of kJ consumed/kJ produced bioH_2) than Scenario 2, with an HRT of 5 days. From this analysis, it can be assumed that Scenario 2, with an HRT of 5 days, was more energy-efficient than Scenario 1. This conclusion can be further supported by both scenarios' final energy ratio, later presented in this chapter.

4.1.2. Biogas production via methanogenesis and conventional anaerobic digestion

In a similar manner to what was presented to the bioH_2 production process, the energy and mass balance of biogas production via methanogenesis and anaerobic digestion was performed considering each energy and mass flow necessary as input and output for the process. Flows were quantified and calculated based on the total energy produced in terms of kJ of biogas for each scenario (Table 4.2).

For the biogas production process, scenario S1 refers to the methanogenesis of VFA from the DF process with an HRT of 4 days. Scenario S2 represents the methanogenesis of VFA from the DF process with an HRT of 5 days. For the biogas production process's energy balance, a third scenario was also analyzed. Scenario S3 refers to the conventional anaerobic digestion of the raw OFMSW, performed by Salvaterra (2019) to allow for comparison with the two-stage configuration.

The acronyms E1-E10 and M1-M3 are references made to the previously identified energy and mass flows (Figure 3.10 and Figure 3.11, Annex 1 and Annex 2).

Table 4.2 – Energy and mass balance of biogas production process via methanogenesis and anaerobic digestion

Biogas Production via Methanogenesis and Anaerobic Digestion | Energy and mass balances						
	Energy flow	**Daily energy consumption (kJ)**	**Total consumption for S1, S2 and S3 (kJ)**	**Total consumption for S1 per kJ of produced biogas (kJ/kJ biogas)**	**Total consumption for S2 per kJ of produced biogas (kJ/kJ biogas)**	**Total consumption for S3 per kJ of produced biogas (kJ/kJ biogas)**
E1	Feed heating	0.28	6.43	1.37	1.65	2.08
E2	Bioreactor feeding	0.04	0.92	0.20	0.24	0.30
E3	Temperature control (water bath)	4.34	99.74	21.32	25.52	32.19
E4	Bioreactor heating	0.36	8.23	1.76	2.11	2.66
E5	Temperature measurement inside the bioreactor	3.13E-08	7.20E-07	1.54E-07	1.84E-07	2.32E-07
E6	Continuous stirring of bioreactor content	1.05	24.08	5.15	6.16	7.77
E7	pH measurement of samples	6.14E-03	0.14	3.02E-02	3.61E-02	4.55E-02
E8	pH measurement of feedstock	-	1.84E-02	3.93E-03	4.71E-03	5.94E-03
E9	Conductivity measurement of inlet and outlet	5.63E-03	0.26	0.06	0.07	0.08
E10	Foam recirculation	0.89	41.07	8.78	10.51	13.26
	Mass flow	**Daily consumption**	**Total consumption for S1, S2 and S3**	**Total consumption for S1 per kJ of produced biogas**	**Total consumption for S2 per kJ of produced biogas**	**Total consumption for S3 per kJ of produced biogas**
M1	Inlet	183 mL	4,209 mL	899.6 mL/kJ biogas	1,076.9 mL/kJ biogas	1,258.5 mL/kJ biogas
	Content of SV in inlet	7.74 g_{SV} for S1 7.04 g_{SV} for S2 11.7 g_{SV} for S3	178.04 g for S1 162.05 g for S2 268.96 g for S3	38.05 g/kJ biogas	41.46 g/kJ biogas	86.81 g/kJ biogas
M2	Water	1,400 mL	32,200 mL	6,881.9 mL/kJ biogas	8,238.3 mL/kJ biogas	10,392.6 mL/kJ biogas
M3	Outlet	183 mL	4,209 mL	899.6 mL/kJ biogas	1,076.9 mL/kJ biogas	1,258.5 mL/kJ biogas
	Content of SV in outlet	2.16 g_{SV} for S1 1.85 g_{SV} for S2	49.67 g for S1 42.51 g for S2	10.61 g/kJ biogas	10.88 g/kJ biogas	22.41 g/kJ biogas

The results presented in Table 4.2 were analyzed based on the process's global energy consumption distribution (Figure 4.2).

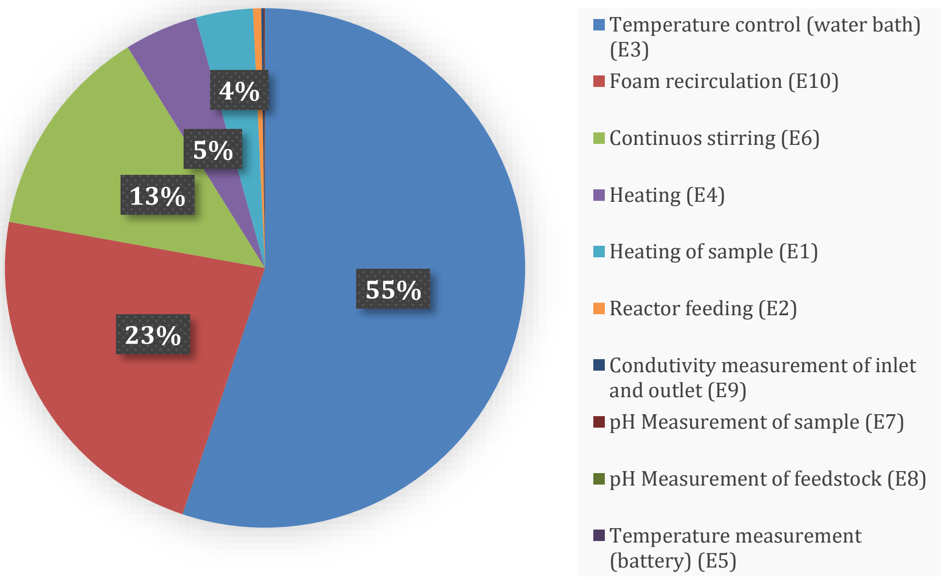

Figure 4.2 – Global energy consumption distribution in the biogas production process via methanogenesis

It can be read from the chart presented above that the highest energy consumption of the biogas production process via methanogenesis comes from the temperature control of the bioreactor (water bath) (E3), representing over half (55%) of the total energy consumption of this biological process.

Correspondingly, the second highest energy consumption comes from the foam recirculation system (E10), operated twice a day for 15 minutes through the same peristaltic pump used to feed the VFA sample to the bioreactor, so the foam that got accumulated in the upper part of the bioreactor could be pumped to its bottom.

When comparing the results for the different scenarios (S1 and S2), it can be seen that in an opposite way to what was observed for the bioH_2 production, scenario S1 was more energy-efficient than scenario S2 when it comes to specific energy consumption per kJ of produced biogas. Different reasons can explain this result, one of them being the concentration of VFAs in the process's input, as stated by Salvaterra (2019). Substrates rich in VFAs can result in higher yields of biogas production through methanogenesis in anaerobic digestion (Braguglia et al., 2018). To illustrate, scenario S1 showed a higher production of biogas when using as input for the process the samples from the dark fermentation process with an HRT of 4 days (referred to as VFA4), which from Martins' data had higher VFA content than the samples of scenario S2 (Martins, 2019). On the other hand, for scenario S2, the input was the sample from the dark fermentation process with a hydraulic retention time (HRT) of 5 days (referred to as VFA5), resulting in lower specific energy consumption than for scenario S1.

Despite the performance differences obtained for scenario S1 and scenario S2, the energy balance shows that the methanogenesis process of VFA for biogas production showed better results for specific energy consumption per kJ of produced biogas than the conventional anaerobic digestion of OFMSW in scenario S3. This outcome is a good indicator that the proposed two-stage configuration can be a better alternative for bioenergy production than conventional anaerobic digestion.

These results can be further supported by the different scenarios' final energy ratio, presented in the following subchapter.

4.1.3.Energy ratio

The Net Energy Ratio (NER) was calculated for both processes to identify their feasibility for energy production purposes. From Table 4.3 it can be seen that both bioH_2 production scenarios had higher energy ratios than the biogas production scenarios. Furthermore, the NER of bioH_2 production scenarios being greater than 1 means this system produces more energy than it consumes. In contrast, the NER of biogas production scenarios being lower than 1 indicates that the system is actually consuming more energy than producing.

These results are also validated by the global energy net of both production systems, that for both bioH_2 production scenarios resulted in a positive value, while for biogas production scenarios, negative results were obtained. This means that the biogas production scenarios were consuming more energy than the system was producing.

As previously seen in the energy balance analysis, the results from scenario S2 for the bioH_2 production process, meaning the dark fermentation process with an HRT of 5 days, had a higher energy net than scenario S1, with an HRT of 4 days, and therefore also higher net energy ratio. Scenario S2 resulted in a NER of 2.64, and scenario S1, in a NER of 1.74. The results obtained for the dark fermentation process are aligned with those found in the literature. While Reaño (2020) has found an energy ratio of 1.25 for this process, Manish and Banerjee (2008) have found an energy ratio of 1.9 for dark fermentation of biomass for bioH_2 production.

On the other hand, opposite results were found for the biogas production process scenarios, meaning that scenario S2 presented a lower Energy Net and lower Energy Ratio than scenario S1. The scenario S3 analyzed for the biogas production through conventional anaerobic digestion of OFMSW presented the lowest energy net of all the analyzed scenarios, as the total energy produced in this system was the lowest one.

Table 4.3 – Energy Balance for the different scenarios

	Total Energy Input (kJ)	Total Produced Energy (kJ)	Energy Net (kJ)	Energy Ratio (ER)
bioH_2 S1	90.9	158	67.1	1.74
bioH_2 S2	74.6	197	122	2.64
Biogas S1	181	4.68	-176	0.03
Biogas S2	181	3.91	-177	0.02
Biogas S3	181	3.10	-178	0.02
Two-stage[1] S1	272	163	-109	0.60
Two-stage S2	255	200	-55.0	0.78

[1] The two-stage configuration refers to the configuration of both processes combined, as previously explained in Chapter 1.1.

When analyzing the overall picture, meaning the two-stage configuration of the two processes combined, both scenarios (S1 and S2) presented better results for Energy Ratio and Energy Net than the conventional anaerobic digestion of raw OFMSW (Biogas S3). Scenario S2 (HRT = 5 days) for the two-stage configuration presented the best results for Energy Ratio. Still, its final result was lower than 1, which means that even though the results were promising and showed better outcomes than the conventional anaerobic digestion, the analyzed system is not yet energetically sustainable, as it consumes more energy than it produces.

4.2. LCIA results for bioH_2 production process

The results from the LCIA of the bioH_2 production process via dark fermentation are presented first as normalized results for both of the applied methodologies, followed by detailed results of the analysis of the categories selected to be studied in more detail. In this analysis, a negative result means a positive impact on the environment, where a positive one represents a burden to the environment. Since almost all impact categories presented negative results in the LCIA, except for the Water Depletion category in the ReCiPe methodology, the overall result represents a positive impact on the environment instead of a burden.

4.2.1. Normalized Results

The normalized results for the LCIA of the bioH_2 production process are depicted in Figure 4.3 and Figure 4.4. All results were obtained as negative values, which implies an overall positive impact of the bioH_2 production on the analyzed categories.

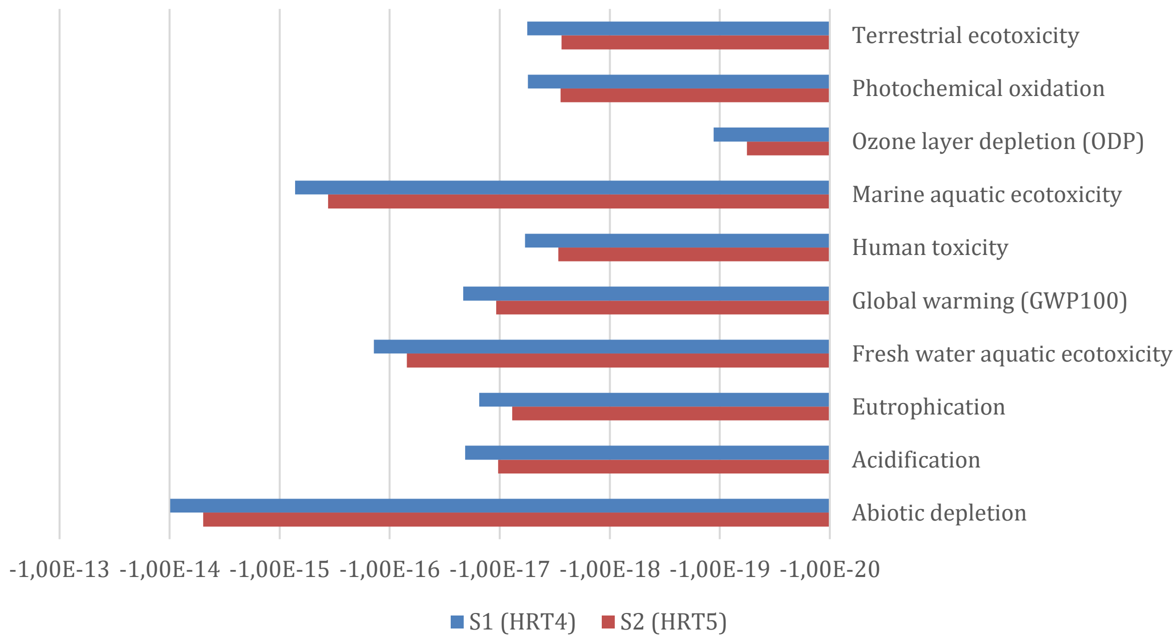

Figure 4.3 – Normalized results (world baseline) for bioH_2 production via dark fermentation, according to CML 2 baseline 2000 methodology

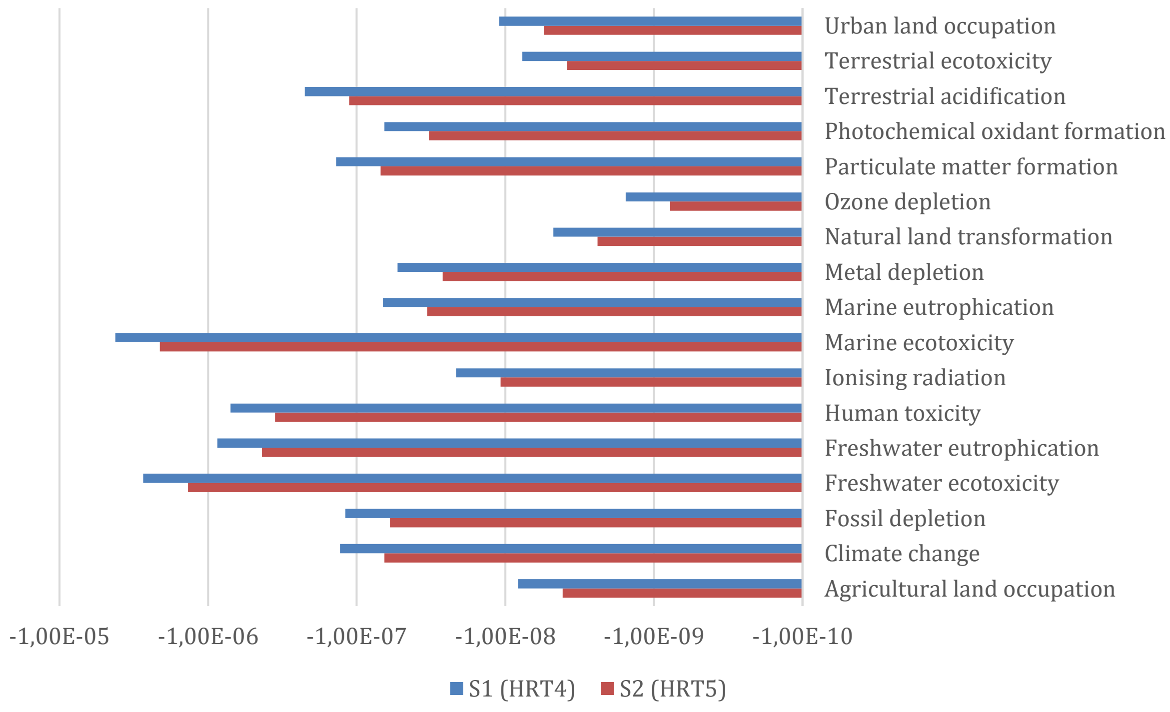

Figure 4.4 – Normalized results (world baseline) for bioH_2 production via dark fermentation, according to ReCiPe Midpoint (H) methodology

Despite the visible magnitude difference of the results obtained with the two applied methodologies (CML and ReCiPe), both methods resulted in higher positive impacts for scenario S1 in all impact categories. Although this scenario presented higher energy consumption and lower bioH_2 production than scenario S2, this outcome can be explained by a combination of two main factors.

Firstly, it has been seen that the *ecoinvent* cut-off by classification approach applied to this assessment means that biowaste is available burden-free to the system. The approach results in this mass input representing a positive contribution to the final impact: the fact that the resource used for energy production is the OFMSW can create a positive impact on the environment.

Correspondingly, in scenario S1 not only a higher volume of biowaste was used (525 mL, instead of 420 mL for scenario S2), but also the sample had a higher content of solids (94.36 g VS.L^{-1}, instead of 89.79 g VS.L^{-1} for scenario S2) (Martins, 2019). These facts make the positive impact of this mass input much higher than the energy consumption of each scenario, which results in the better outcomes of scenario S1 regardless if its higher energy consumption.

As a result of a global analysis of both methodologies combined, the impact categories that had the highest positive results and are presented in common to both methodologies for bioH_2 production via dark fermentation are the ones that follow:

1. Marine ecotoxicity;
2. Freshwater ecotoxicity;
3. Acidification.

4.2.2. Interpretation

To the detailed interpretation of the results, a few categories were selected (Table 3.2) to be studied within a higher depth. Their selection was based on the lowest environmental impacts obtained for the LCIA, as well as on their presence in both methodologies applied.

The results obtained for these impact categories were analyzed at the first stage to compare the applied methodologies and the different results obtained for the bioH_2 production process via dark fermentation, both for scenario S1 (Figure 4.5) and scenario S2 (Figure 4.6).

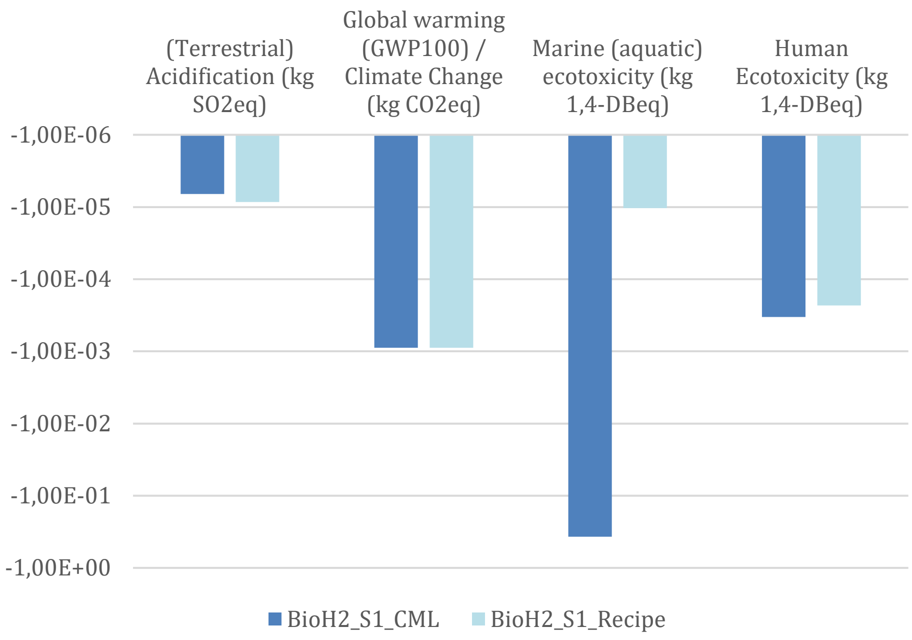

Figure 4.5 – LCIA Results for bioH_2 production process in S1, according to CML 2 baseline 2000 and ReCiPe Midpoint (H) methodologies

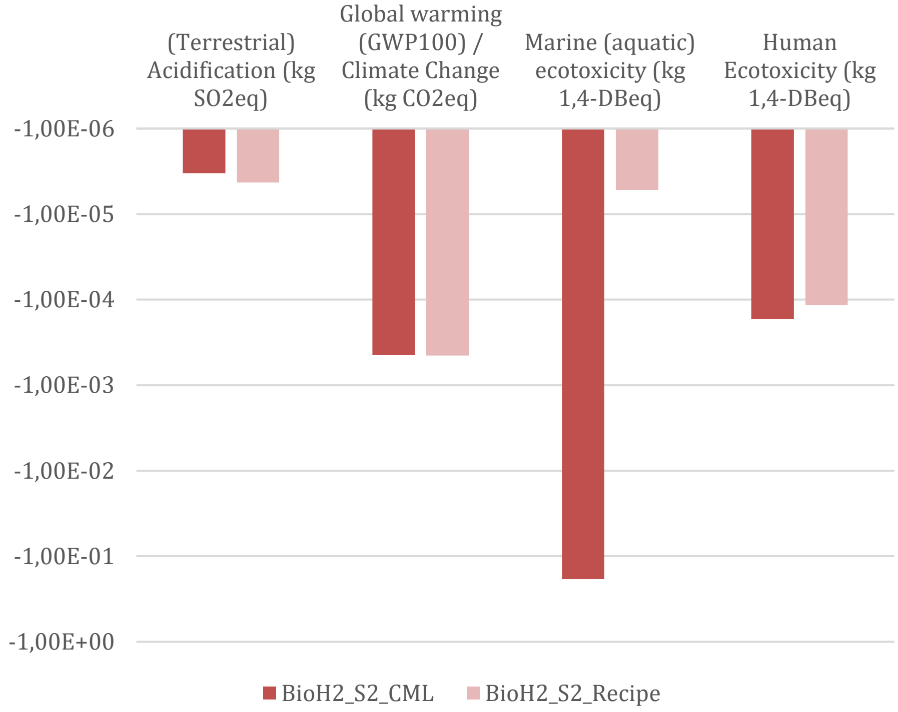

Figure 4.6 - LCIA Results for bioH_2 production process in S2, according to CML 2 baseline 2000 and ReCiPe Midpoint (H) methodologies

From Figure 4.5 and Figure 4.6, it can be seen that the resulting impact for categories "Terrestrial Acidification", "Global Warming Potential", and "Human Toxicity" are similar in both scenarios for the two different methods. However, while for the first two categories the results with the ReCiPe methodology were slightly higher, for the latter cattegory, the results were higher in the CML methodology. Additionally, for “Marine Ecotoxicity”, the results presented much higher sensitivity to the applied methodology, being more significant for the CML methodology for both analyzed scenarios.

A more detailed analysis was performed on each of the selected categories, and the results can be depicted in Figure 4.7 to Figure 4.10.

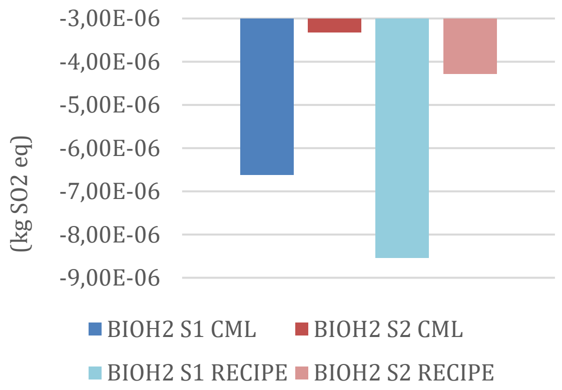

Figure 4.7 – Terrestrial Acidification impact category results for bioH_2 production

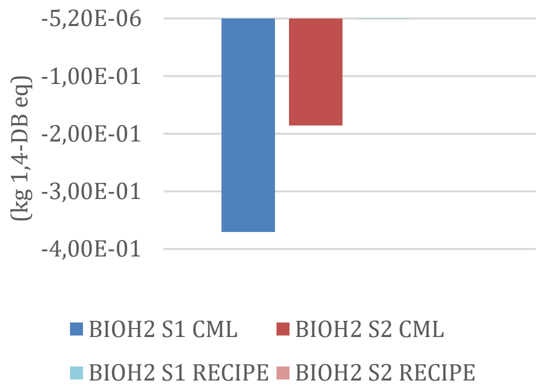

Figure 4.9 – Marine Ecotoxicity impact category results for bioH_2 production

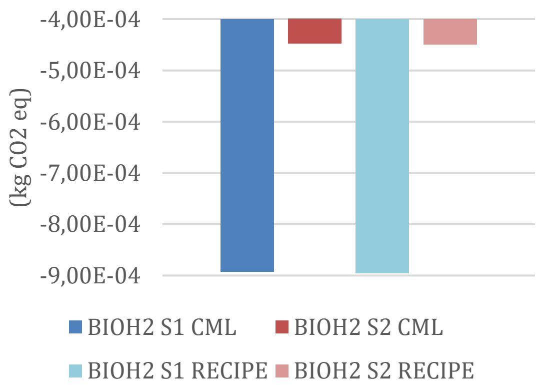

Figure 4.8 – GWP impact category results for bioH_2 production

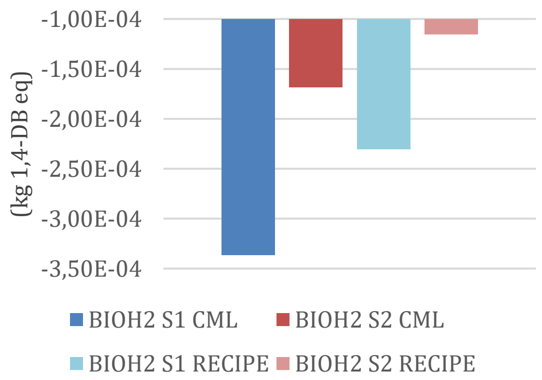

Figure 4.10 – Human Toxicity impact category results for bioH_2 production

Figure 4.7 to Figure 4.10 allow to conclude that the bioH_2 production process presents higher positive impacts for scenario S1 than for scenario S2, for both LCIA methods analyzed (CML and ReCiPe) and for all four impact categories. Nevertheless, for “Terrestrial Acidification” (Figure 4.7), the results obtained with the ReCiPe method are higher than the ones obtained with CML methodology, while for “Marine Ecotoxicity” (Figure 4.9) and “Human Toxicity” (Figure 4.10), the results for the CML methodology are higher. When it comes to “Global Warming Potential” (Figure 4.8), both methods present very similar results.

Further investigation on how the two methodologies are established and how they calculate the impacts is needed to understand the disparities in the different methodologies' results. Each methodology is built differently to calculate the results, based on specific characterization factors and individual approaches to quantify the impacts derived from the database flows. Nonetheless, investigating the calculations within the methodologies was not on the scope of this study.

4.3. LCIA results for biogas production process

During the LCIA of biogas production via methanogenesis, normalization was performed first, and the results were obtained for both applied LCIA methods (CML and ReCiPe). Following this stage, a detailed analysis of the selected categories was performed, and the results are presented in the sequence. Once again, as the impact categories presented negative results in the LCIA, the overall result represents a positive impact on the environment instead of a burden.

4.3.1.Normalized Results

The normalized results for both LCIA methods concerning the inventory data of the biogas production process are shown in Figure 4.11 and Figure 4.12. All results were obtained as negative values, which means an overall positive impact on the analyzed categories.

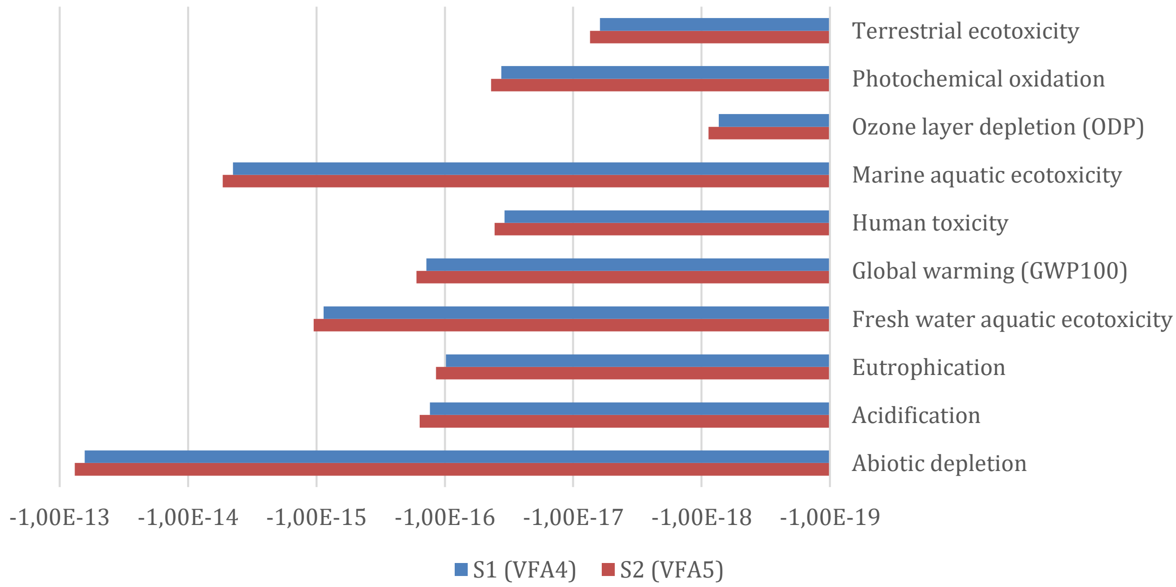

Figure 4.11 – Normalized results (world baseline) for biogas production via methanogenesis, according to CML 2 baseline 2000 methodology

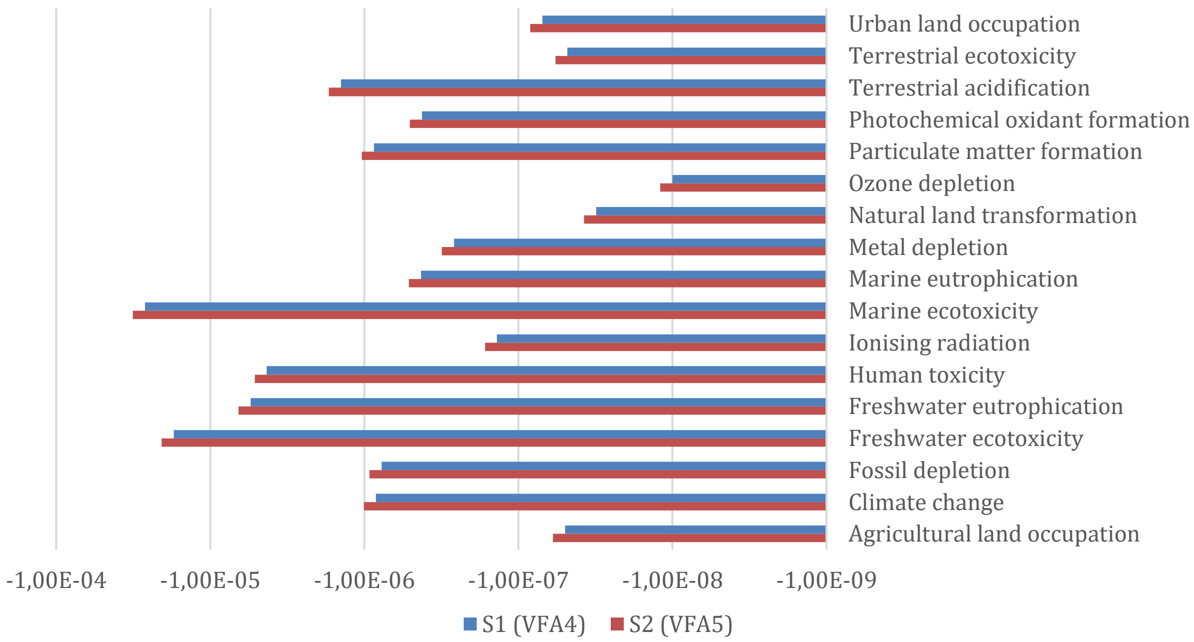

Figure 4.12 – Normalized results (world baseline) for biogas production via methanogenesis, according to ReCiPe Midpoint (H) methodology

Despite the difference in magnitude between both LCIA methods (CML and ReCiPe), the scenario S2 (VFA from Dark Fermentation with HRT = 5 days) resulted in higher positive impacts for all the impact categories. Similar to what was observed in the bioH_2 production process, even though scenario S2 was consuming more energy per kJ of produced biogas, its total environmental impacts were lower. This outcome reflects the influence of the positive impacts of using biowaste for energy production, which, as per the *ecoinvent* cut-off by classification approach, showed a higher magnitude than the system's energy consumption.

The explanation for this result is substantiated by the perception that for scenario S2, the sample's specific input (biowaste in terms of $g_{SV}.kJ^{-1}$ of produced biogas) was higher than the one observed in scenario S1 (Table 4.2). Hence the positive impacts showing higher figures as well regardless of the energy consumption of both scenarios.

As a result of a global analysis of both LCIA methods, the impact categories that had the highest positive results and are presented in common to both methodologies for biogas production via methanogenesis are the ones that follow:

1. Marine ecotoxicity;
2. Freshwater ecotoxicity;
3. Acidification.

4.3.2.Interpretation

Equally to the interpretation of the bioH_2 production process scenarios, to undertake a more detailed analysis of the results, a few categories were selected (Table 3.2) to be studied within a higher depth. Their selection followed the same criteria previously applied, meaning that it was based on the lowest environmental impacts obtained in the LCIA, combined with these impact categories in both LCIA methods and their representativeness.

Once again, the results obtained for these impact categories were analyzed to compare the applied methodologies for both scenario S1 (Figure 4.13) and scenario S2 (Figure 4.14), and the different results obtained.

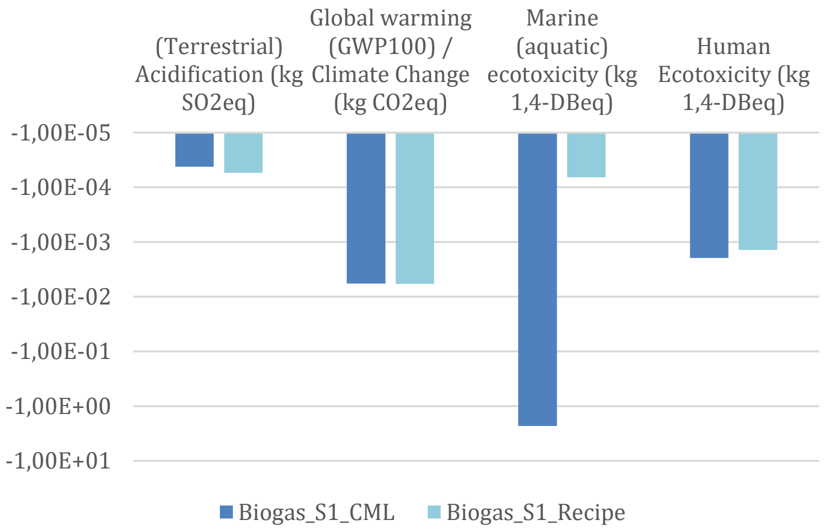

Figure 4.13 – LCIA Results for biogas production process in S1, according to CML 2 baseline 2000 and ReCiPe Midpoint (H) methodologies

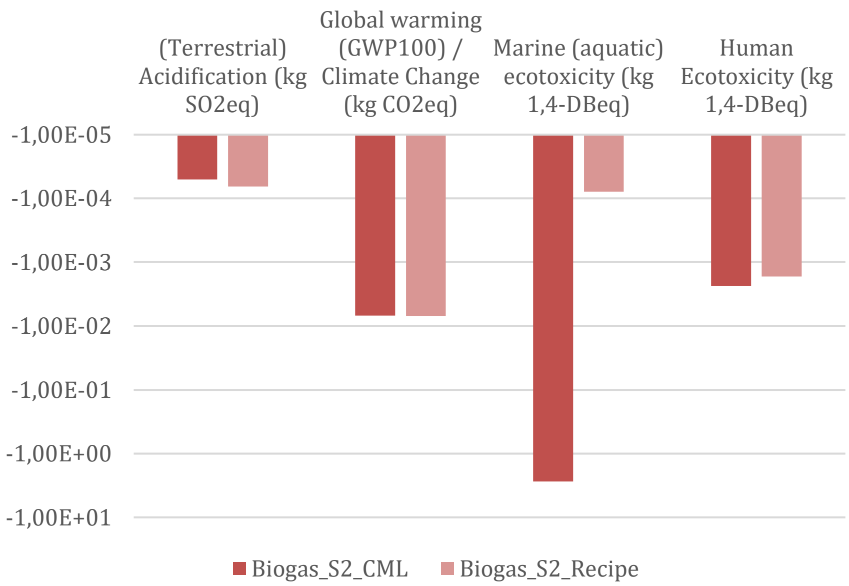

Figure 4.14 - LCIA Results for biogas production process in S2, according to CML 2 baseline 2000 and ReCiPe Midpoint (H) methodologies

Regardless of the differences between both processes, similar results were obtained for this first analysis between the methodologies applied: in a like manner to what was observed for the bioH_2 production process, it can be seen (Figure 4.13 and Figure 4.14) that the resulting impact for the categories "Terrestrial Acidification", "Global Warming Potential", and "Human Toxicity" were similar for the two different methods, for both scenarios, while for "Marine Ecotoxicity", the results presented higher sensitivity to the applied methodology, being greater in CML methodology for both analyzed scenarios. As it was observed for the bioH_2 production process, the results with the ReCiPe methodology were slightly higher for the first two categories. In comparison, for "Human Toxicity", the results were greater in the CML methodology.

Following the same procedure as the one applied to the bioH_2 production process, a more detailed analysis was performed of each of the selected categories (Figure 4.15 to Figure 4.18).

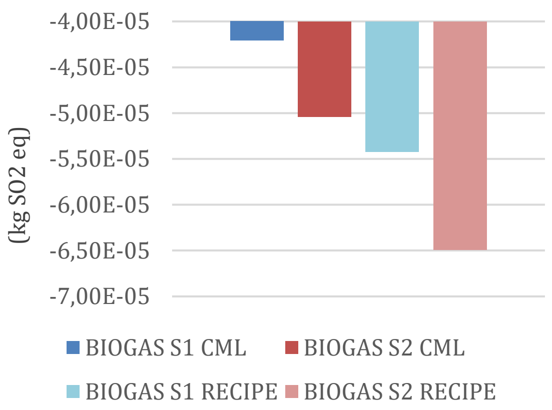

Figure 4.15 – Terrestrial Acidification impact category results for biogas production

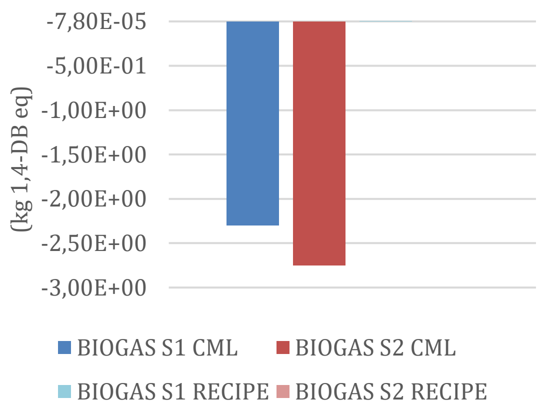

Figure 4.17 – Marine Ecotoxicity impact category results for biogas production

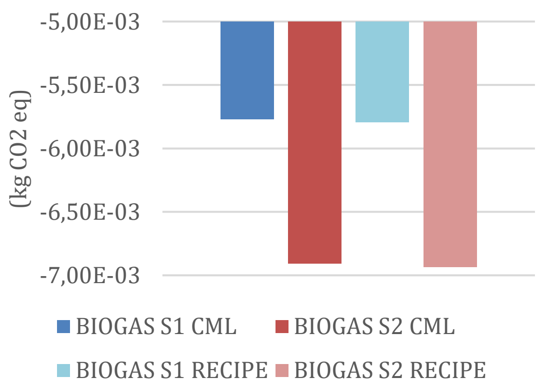

Figure 4.16 – GWP impact category results for biogas production

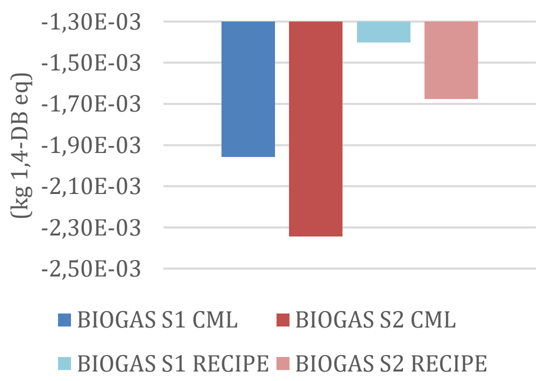

Figure 4.18 – Human Toxicity impact category results for biogas production

For scenarios S1 and S2, it can be observed that in an opposite way to what happened to the bioH_2 production, scenario S1 presented lower positive impacts on the environment than scenario S2, for both

LCIA methods analyzed (CML and ReCiPe) and for all impact categories considered in this phase of the study.

Nonetheless, similarly to what was previously observed for bioH_2 production, for the "Terrestrial Acidification" impact category (Figure 4.15), the results obtained with the ReCiPe method are higher than the ones obtained with CML methodology. In contrast, for "Marine Ecotoxicity" (Figure 4.17) and "Human Toxicity" (Figure 4.18), the results obtained with the CML method were higher. When it comes to "Global Warming Potential" (Figure 4.16), similar results were obtained for both methodologies.

In a similar manner to what was stated for the bioH2 scenarios, to understand where the difference in the calculations originate, there is the need to investigate more in-depth how the methodologies are built, and which flows and characterization factors they take into consideration when calculating the resulting impacts. Investigating the calculations within the methodologies was not on the scope of this study.

4.4. Sensitivity Analysis

As previously seen, some uncertainties were identified in the data collection and inventory phase, such as the amount of HCl used for acidification and the number of times this process occurred. A sensitivity analysis was performed for both processes to analyze these uncertainties, alongside the results' sensitivity to the selected methodology.

The sensitivity analysis results are presented in this chapter, first showing the results' sensitivity to the methods used in LCIA phase, then to the proposed changes in the selected inputs. The selection of flows and parameters was based not only on data uncertainties but also on their contribution to the environmental categories under study.

4.4.1. Impact contribution of inputs

To the previously selected impact categories (Acidification, Marine Ecotoxicity, Global Warming Potential, and Human Toxicity) (Table 3.2), the relative contribution of each of the energy and mass inputs identified in the production of bioH_2 and biogas was further studied, namely:

- bioH_2 production process: Energy consumption, OFMWS mass input, and HCl consumption for bioreactor acidification.
- Biogas production process: Energy consumption, VFA mass input, and water consumption for the bioreactor's temperature maintenance.

The results of this analysis can be seen in Figure 4.19 to Figure 4.22.

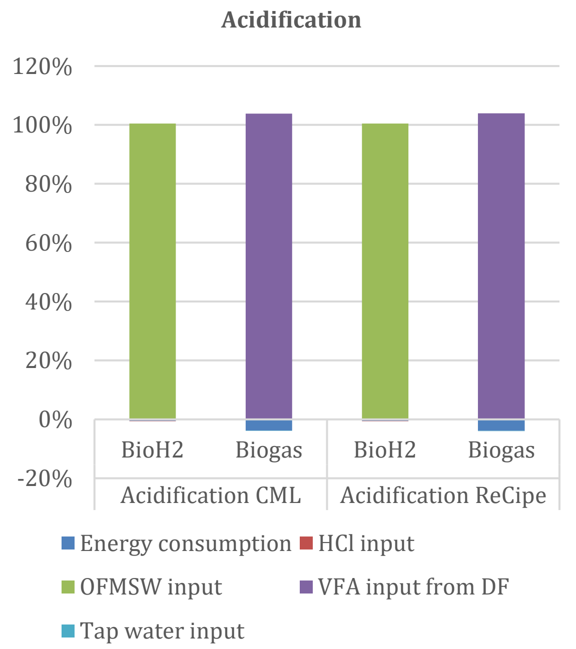

Figure 4.19 – Energy and mass inputs contribution to the Acidification impact category

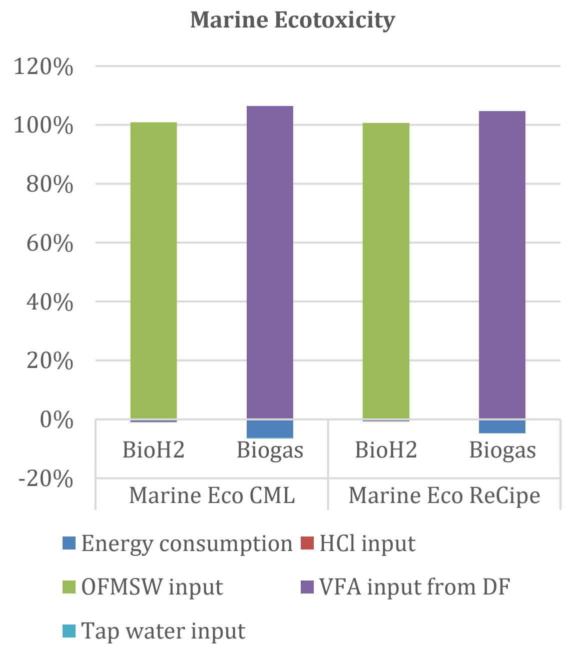

Figure 4.21 – Energy and mass inputs contribution to the Marine Ecotoxicity impact category

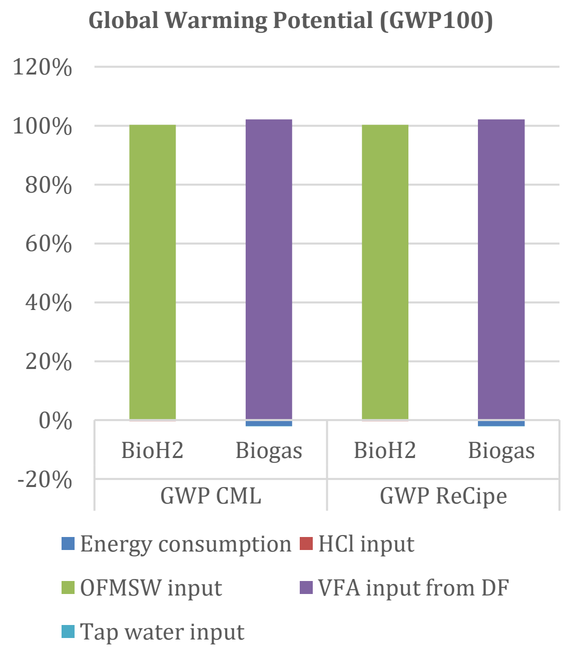

Figure 4.20 – Energy and mass inputs contribution to the GWP impact category

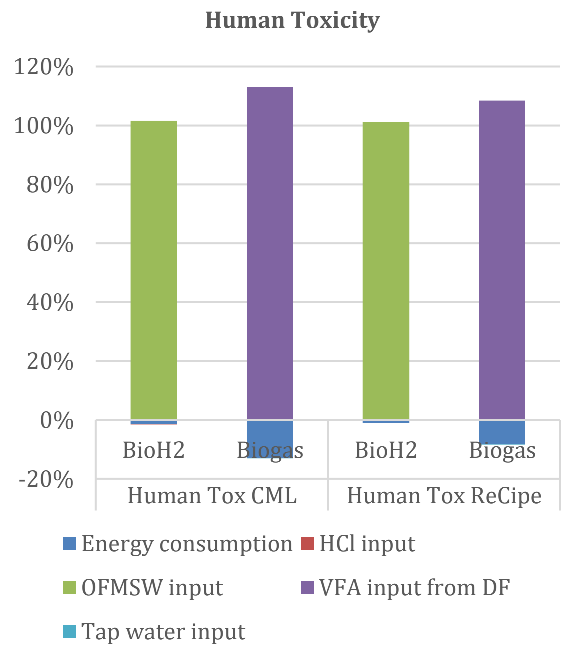

Figure 4.22 – Energy and mass inputs contribution to the Human Toxicity impact category

With this analysis, it can be perceived that in both production processes and for both LCIA methods, the mass flow represented by the organic fraction of the municipal solid waste (identified as OFMSW input in the bioH$_2$ production process and as VFA input from DF in the biogas production process) is the flow that contributes the most to the results of the LCIA. This flow represents a positive impact, at least in the categories studied in more in-depth detail.

Because of the cut-off by classification approach applied in the LCI phase, the biowaste input from the *ecoinvent* database does not carry the negative impacts of waste production, being available burden-free to this process. This means that this input represents a positive impact on the system since the biowaste as a source of energy production can reduce the amount of waste that would be sent to a landfill.

Although the other analyzed inputs, such as energy consumption and tap water consumption, represent different contributions to the impact categories, they all represent a negative contribution to the overall impact result, implying a burden to the environment. Nevertheless, these negative impacts represent a small contribution considering the magnitude of the positive impact caused by the biowaste as input to the system, which means that the resulting impact for all these four categories is still a positive impact on the environment.

Furthermore, from Figure 4.19 to Figure 4.22, it can also be visualized how the biogas production process's energy consumption has a higher impact on the "Human Toxicity" category than for the other categories.

The results and interpretation from this impact contribution analysis enabled the sensitivity analysis' planning to the proposed changes in some of the parameters and identified flows.

4.4.2. Sensitivity analysis of the methodology

The sensitivity analysis of the applied methodology was carried out to show the selected methodologies' impact on the results based on each LCIA method's outcomes. Figure 4.23 to Figure 4.30 present the results from this analysis for both studied scenarios of the two processes, bioH_2, and biogas production, to the four selected impact categories.

Within this configuration, the first two charts (Figure 4.23 and Figure 4.24) present for comparison the positive impacts obtained for the impact category "Acidification" with the CML method, compared to "Terrestrial Acidification" in the ReCiPe method, both measured in kg SO_{2eq}.

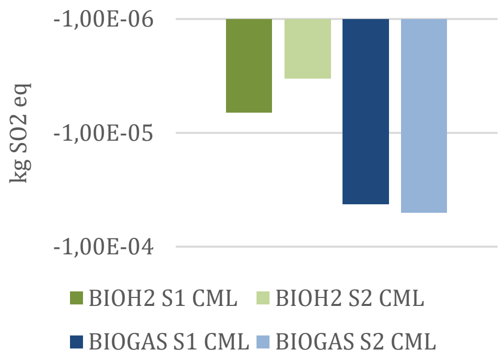

Figure 4.23 –Acidification impact category, according to CML 2 baseline 2000 methodology

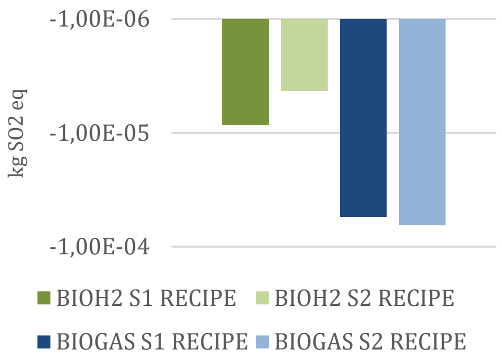

Figure 4.24 – Terrestrial Acidification impact category, according to ReCiPe Midpoint (H) methodology

As can be seen, the results are very similar to each other for both methods; having the biogas production process resulted in higher positive impacts for this category than the bioH_2 production process.

Figure 4.25 and Figure 4.26 compare the impact category GWP from the CML method to the “Climate Change” category of the ReCiPe method, considering that both categories take into consideration the global warming potential in a 100-year time horizon. For “Global Warming Potential” (GWP100), both methods presented very similar results, having the biogas production process once again resulted in higher positive impacts for this category than the bioH_2 production process.

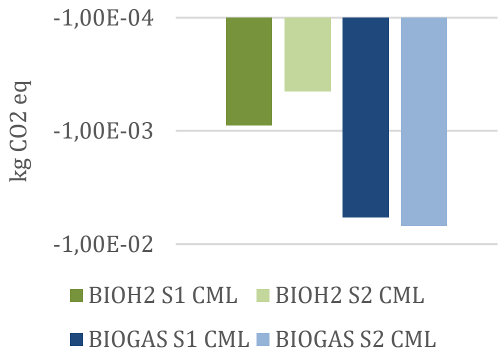

Figure 4.25 – Global Warming impact category, according to CML 2 baseline 2000 methodology

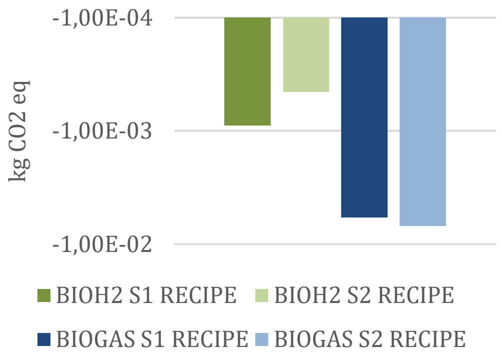

Figure 4.26 – Climate Change impact category, according to ReCiPe Midpoint (H) methodology

A similar result can be observed for the “Human Toxicity” impact category. As Figure 4.27 and Figure 4.28 show, both methodologies presented similar results for this category. Nevertheless, the biogas production process still presented higher positive impacts than the production of bioH_2.

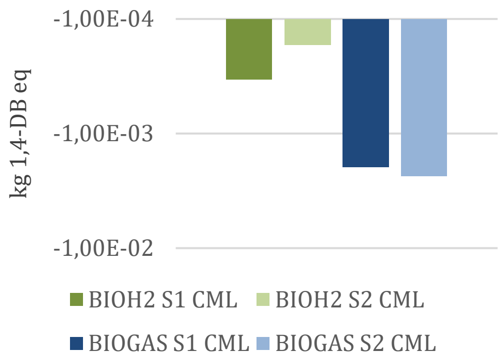

Figure 4.27 – Human Toxicity impact category, according to CML 2 baseline 2000 methodology

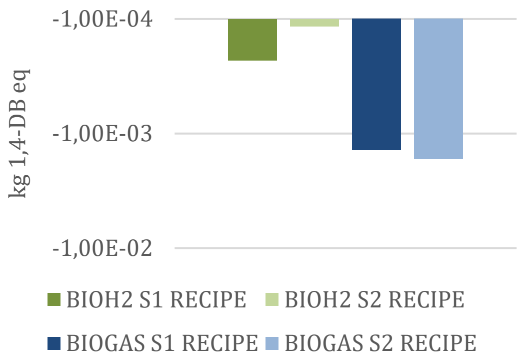

Figure 4.28 – Human Toxicity impact category, according to ReCiPe Midpoint (H) methodology

On the other hand, once the same analysis was performed for the "Marine Aquatic Ecotoxicity" impact category from the CML method when compared to the "Marine Ecotoxicity" category from the ReCiPe method, the results are not so similar as previously seen. As shown in Figure 4.29 and Figure 4.30, the CML method presented higher positive results for this category than those obtained from the ReCiPe method. Regardless of this alteration, the biogas production process still resulted in higher positive impacts for this category than the bioH_2 production process.

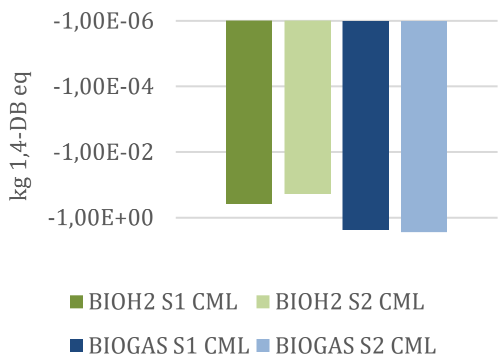

Figure 4.29 –Marine Aquatic Ecotoxicity impact category, according to CML 2 baseline 2000 methodology

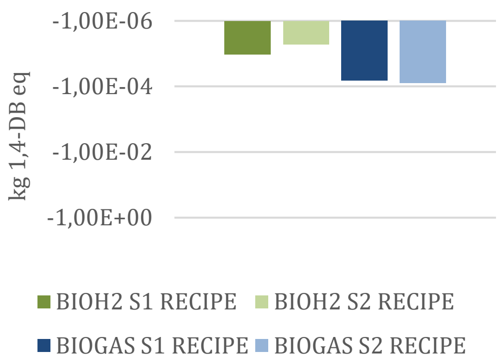

Figure 4.30 – Marine Ecotoxicity impact category, according to ReCiPe Midpoint (H) methodology

All things considered, to all four impact categories analyzed, and for both methods applied, the biogas production process resulted in higher positive impacts to the environment than the bioH_2 production process. These results were not expected at first since the biogas production process showed to be less energy efficient than the production process of bioH_2. However, this can be explained by the defined functional unit for the system, i.e., 1 kJ of produced gas, and how the LCIA results are calculated based on it.

First of all, in the two-stage configuration the inlet to the biogas production process is the outlet of the bioH_2 production process, which implies that the material carries the resulting impacts of the dark fermentation process. It has been seen that by the cut-off by classification approach applied to this assessment, the biowaste carries positive impacts as it comes burden-free to the system, which means that to both systems, this mass input represents a positive contribution to the final impact result. However, the bioH_2 production system produced more energy in terms of kJ of produced gas than the biogas production system. This indicates that to produce 1 kJ of gas, the biogas production system had to consume more biowaste content (VFA from the DF process) than the bioH_2 production system.

Consequently, the specific biowaste content input per kJ was higher in the biogas production system than in the bioH_2 production system, which resulted in a much higher positive impact deriving from this flow for the biogas system. Even though this system's energy consumption was higher and represented a higher negative contribution, its overall positive impact was still higher than the bioH_2 production system.

All points explained above are substantiated in Table 4.4.

Table 4.4 – Specific biowaste content input per kJ of produced gas for both bioH_2 and biogas production processes

	bioH_2 production process		**Biogas production process**		
	Scenario S1	**Scenario S2**	**Scenario S1**	**Scenario S2**	**Scenario S3**
Total energy produced (kJ)	158	196	5	4	3
Total biowaste consumed (g)	1,932	1,207	178.04	162.05	268.96
Specific biowaste content (g/kJ)	12.23	6.16	35.61	40.51	89.65

4.4.3.Sensitivity to parameters

The sensitivity analysis was performed to evaluate the effects that key parameters and assumptions had on the results of LCIA. Taking the original data and results as reference values, a few changes and improvements in some of the inputs, such as energy consumption, were proposed, therefore obtaining new LCIA results.

The inputs investigated in the sensitivity analysis have been presented in detail in Table 3.3; two of them applied specifically to the bioH_2 production process, and the other two to the biogas production process. The results from this analysis are presented in the following subchapters, for each of the biological processes separately.

4.4.3.1. bioH_2 production scenarios

For the bioH_2 production process and its different scenarios, the energy and mass flow selected for the sensitivity analysis were previously presented in this study (Table 3.3). The results of the 20% reduction in the energy consumption of flow E1 (heating of the OFMSW sample) and the changes of recurrences of HCl consumption for acidification in both scenarios are presented in Figure 4.31 to Figure 4.34. The same sensitivity analysis, meaning the variation of these two flows, was run for both bioH_2 production scenarios and applied with the two LCIA methodologies (CML and ReCiPe).

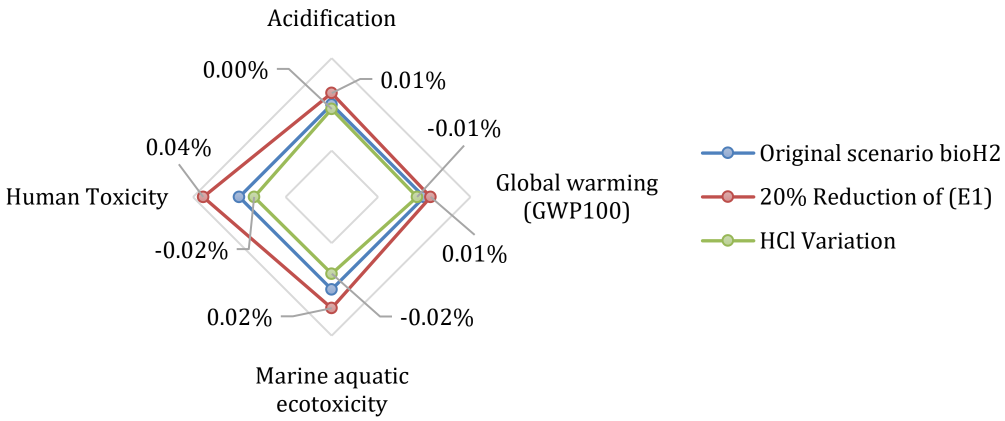

Figure 4.31 –Sensitivity Analysis for bioH_2 S1 with CML Methodology: reduction of energy consumption (E1) and variation of HCl consumption

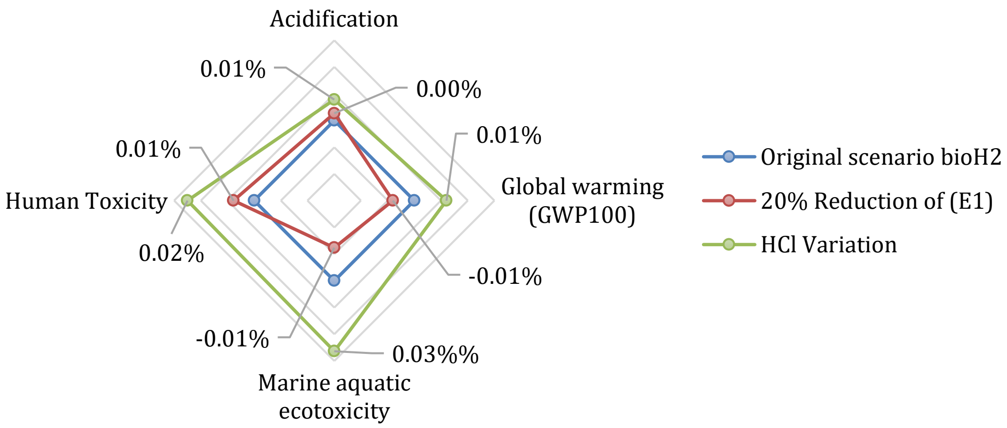

Figure 4.32 – Sensitivity Analysis for bioH_2 S2 with CML Methodology: reduction of energy consumption (E1) and variation of HCl consumption

The 20% reduction in the energy consumption of input E1 (heating of the OFMSW) had very little influence on the results of the LCIA for all the analyzed categories and both of the studied scenarios. This change represented in both methodologies a slightly positive result across the different categories for scenario S1 and a slightly negative (-0.01%) result for some categories in scenario S2, such as “Global Warming Potential” and “Marine Aquatic Ecotoxicity”. The low variations in the sensitivity analysis results show that even though a reduction of an input energy flow results in a better energy net for the overall process, it does not significantly affect the total environmental impact resulting from the production process. Nevertheless, if the process is scaled-up to an industrial scale, this input energy flow could come from the excess heat of the process produced in cogeneration engines. This improvement would eliminate the energy flow E1, therefore reducing the total environmental impact of the system.

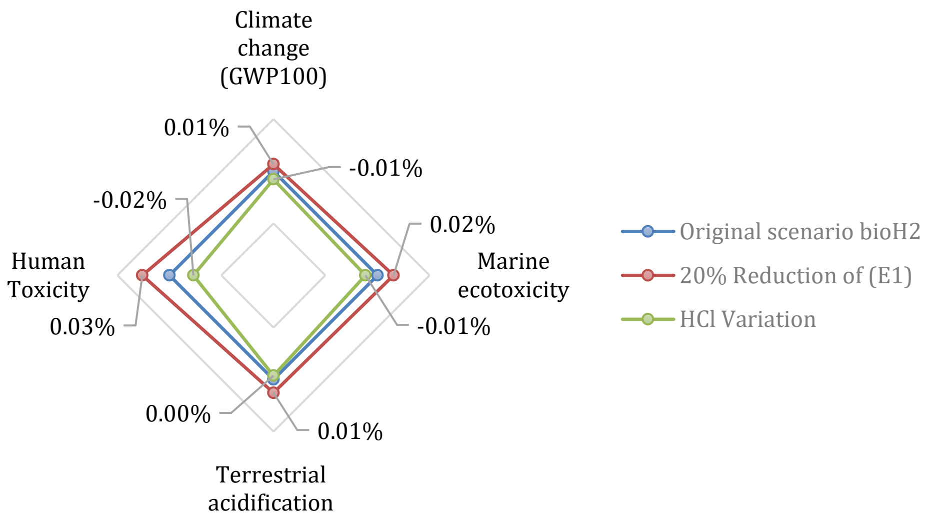

Figure 4.33 – Sensitivity Analysis for bioH_2 S1 with ReCiPe Methodology: reduction of energy consumption (E1) and variation of HCl consumption

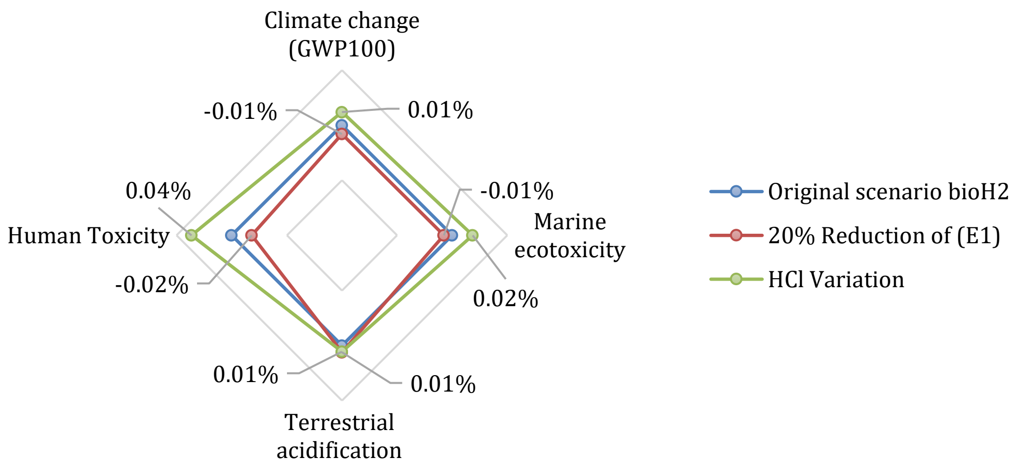

Figure 4.34 – Sensitivity Analysis for bioH_2 S2 with ReCiPe Methodology: reduction of energy consumption (E1) and variation of HCl consumption

The changes in the acidification recurrences for both scenarios and the resulting changes in total HCl consumption for each scenario harmed scenario S1 for both of the LCIA methods used. This outcome can be substantiated by the fact that an increase of acidification from 4 to 5 times results not only in increased energy consumption for this intake but also represents negative increases in the impact categories that take these flows as negative impacts on the environment, which was the case for all the analyzed categories. However, the sensitivity analysis's negative increases for this proposed change were minor for all categories, ranging from -0.01% to -0.02%.

When it comes to scenario S2, reducing the acidification recurrence from 5 to 4 times represented a positive impact in all analyzed categories. In both methodologies applied and in a similar magnitude, it represented a small change (0.01% to 0.04%) across the environmental categories.

4.4.3.2. Biogas production Scenarios

Correspondingly to the approach taken for the bioH_2 production process, for the biogas production process and its different scenarios, the energy and mass flows selected for the sensitivity analysis were previously presented in this study (Table 3.3). The results of the 75% reduction in the energy consumption of flow E3 (temperature control of the methanogenic bioreactor) and the 30% reduction in the energy consumption of flow E10 (foam recirculation pump) in both scenarios are presented Figure 4.35 to Figure 4.38. Once again, the same sensitivity analysis and correspondingly variation of these two inputs were run for both scenarios of biogas production, with the two studied LCIA methodologies (CML and ReCiPe).

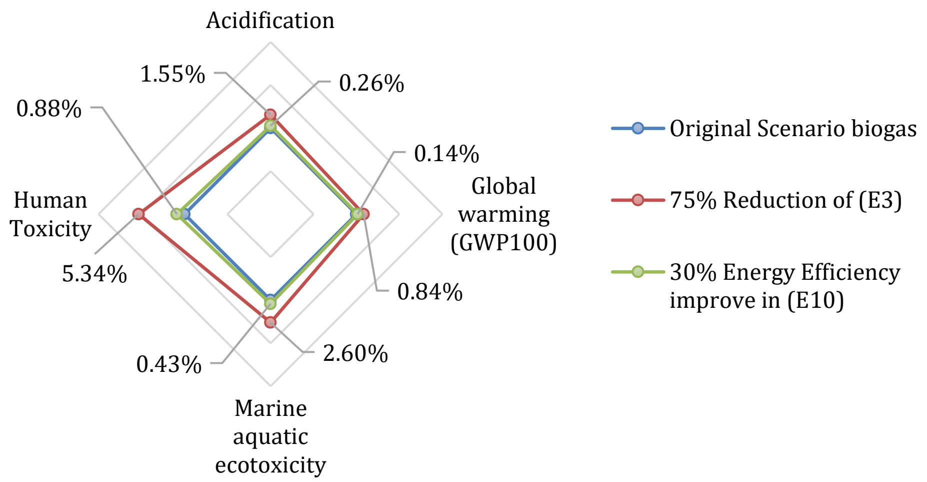

Figure 4.35 –Sensitivity Analysis for biogas S1 with CML Methodology: reduction of energy consumption (E3 and E10)

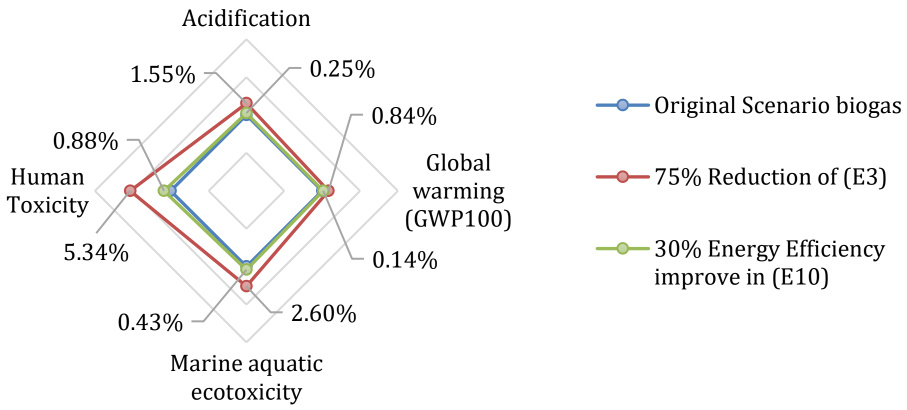

Figure 4.36 – Sensitivity Analysis for biogas S2 with CML Methodology: reduction of energy consumption (E3 and E10)

Generally, the 75% reduction in the energy consumption of flow E3 (bioreactor temperature control system) had a positive influence on the results of the LCIA for all analyzed categories for both scenarios and similarly in the methodologies applied. This influence slightly changes magnitude across the different categories, ranging from 0.8% to 5.3% in the CML methodology and from 0.8% to 3.4% in the ReCiPe methodology.

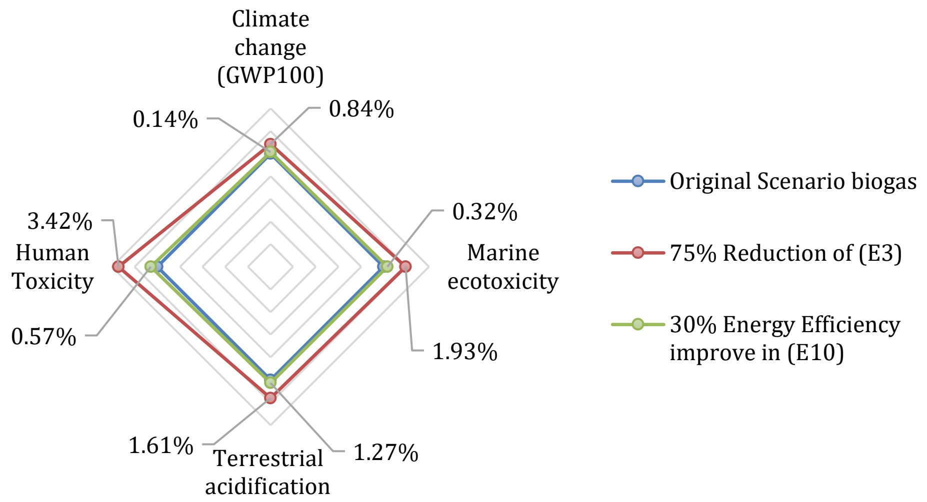

Figure 4.37 – Sensitivity Analysis for biogas S1 with ReCiPe Methodology: reduction of energy consumption (E3 and E10)

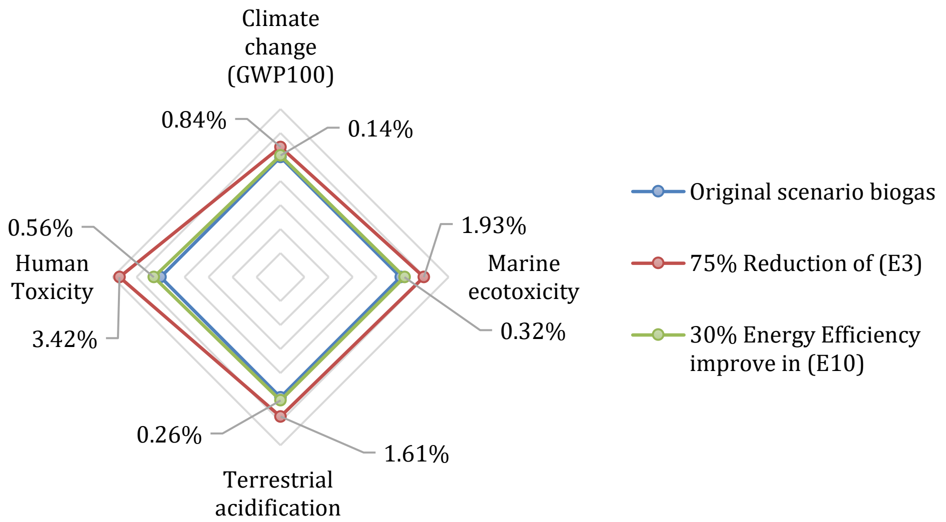

Figure 4.38 – Sensitivity Analysis for biogas S2 with ReCiPe Methodology: reduction of energy consumption (E3 and E10)

The second proposed change, i.e., the proposed 30% energy efficiency improvement of flow E10 (foam recirculation pump), had the same positive outcome across all categories of both methodologies and scenarios, representing a slightly lower positive result, of less than 1% of change for all categories and different methodologies in relation to the original scenario.

4.5. Points of improvement in the system

The energy balance and sensitivity analysis allowed identifying the highest energy consumption points and the highest inputs contributing to the analyzed environmental impact categories. Based on the findings, it was possible to identify a few points of improvement in the system in order for it to be more energy efficient.

Based on the identified energy inputs that represented the highest contribution to the overall energy consumption, the following improvements are suggested:

1. The employment of the most energy-efficient equipment to heat the OFMSW prior to feeding the bioreactor, as it was identified a variation of 20% in the energy consumption between the different equipment available in the laboratory;
2. For the second bioreactor's temperature control system, it was found that the equipment applied for this purpose was consuming four times more energy than the equipment used in the first bioreactor. The improvement of this component could significantly reduce the overall energy consumption of the system, therefore enhancing the net energy recovery;
3. The equipment applied for the foam recirculation in the second bioreactor resulted in higher energy consumption than the other analyzed inputs, which is why is suggested the use of a more energy-efficient pump for this input;
4. In the analyzed configuration, the outcome of bioreactor 1 had to be heated up before being fed to bioreactor 2. However, in an optimal configuration, or on an industrial scale, this consumption would not be necessary, and the process could be performed directly in sequence. This improvement would eliminate the need for this energy flow, reducing the overall energy consumption of the system;
5. If the process is scaled-up to an industrial scale, the energy necessary to preheat the OFMSW could come from the excess heat of the process that could be produced in cogeneration engines. This addition would reduce the overall energy consumption of the system, therefore enhancing the net energy ratio.

5. CONCLUSIONS AND FUTURE WORK

It has been seen that two-stage configuration systems for anaerobic digestion have been studied by different authors in the literature, whether the focus of these studies had been in the total hydrogen production, in the overall performance of the system, or in the energy sustainability of the configuration. Within this framework, the present study aimed to evaluate the proposed two-stage system's overall energy performance to identify, by means of Life Cycle Assessment, what environmental impacts were associated to this system and if the proposed configuration was energetically balanced.

It has been found that the proposed configuration of the studied technology, with the current lab-scale, was not energetically balanced. The results obtained for the energy balance and energy ratio of the system showed that the proposed two-stage configuration was consuming more energy than it was producing, for both scenarios analyzed. Still, scenario S2, which was operated with a hydraulic retention time in the dark fermentation process of 5 days, showed a better energy net (-55.0 kJ) than scenario S1 (HRT of 4 days and a final energy net of -109 kJ).

Aligned with their overall energy net, the energy ratio for both two-stage configuration scenarios showed a value lower than 1, meaning their energy input was higher than the energy output. While scenario S1 presented an energy ratio of 0.60 kJ, scenario S2 presented a slightly better value, of 0.78 kJ. When it comes to the system's energy efficiency, a significant factor to note is that the laboratory conditions of both bioreactors were not optimized, which can directly affect the energy consumption and overall performance of the system.

Despite the performance differences obtained for scenario S1 and scenario S2 and their overall energy ratio being lower than 1, the energy balance showed that this system presented better results than the conventional anaerobic digestion of OFMSW in scenario S3. This outcome is a good indicator that the proposed two-stage configuration can be a better alternative for bioenergy production than conventional anaerobic digestion, at least when it comes to total energy net (kJ).

When analyzing the two different processes individually, the bioH_2 production process via dark fermentation showed a positive energy net and an energy ratio higher than 1, which means this process, when operated individually, could produce more energy than it consumes. For the bioH_2 production process, scenario S2 was the one that showed better results, with an energy net of 122 kJ and an energy ratio of 2.64. In contrast, scenario S1 presented an energy net of 67.1 kJ and an energy ratio of 1.74. Aligned with the results obtained in this study, the literature has shown that the biohydrogen production via dark fermentation pathway can result in positive energy ratios.

On the other hand, the biogas production process via methanogenesis, when analyzed individually, showed the opposite situation. Not only the process did not present sustainable outcomes by resulting in a negative energy net, but scenario S1 was the most favorable one, with an energy net of -176 kJ and an energy ratio of 0.03, while scenario S2 showed an energy net of -177 kJ and an energy ratio of 0.02.

Still, scenario S3, representing the biogas production through conventional anaerobic digestion of OFMSW, presented the lowest energy net of all the analyzed scenarios.

Regarding the LCIA and the results obtained, in an opposite way to what was observed on the energy balance, the biogas production process presented higher positive impacts to the environment across all analyzed categories, for both scenarios and LCIA methods applied (CML and ReCiPe). This outcome can be explained by the difference between the total energy produced in both systems and how the impacts are calculated based on the system's functional unit, i.e., 1 kJ of produced gas.

As it has been described, the cut-off by classification approach indicates that the biowaste input comes burden-free to the system, representing a positive contribution to the final impact result of both systems. In addition, the bioH_2 production system produced more energy than the biogas production system, which resulted in a specific biowaste content input ($g.kJ^{-1}$) higher in the biogas production system than in the bioH_2 production system. This presented a higher positive impact deriving from this flow in the biogas system. Even though this system's energy consumption was higher and represented a higher negative contribution, its overall positive impact was still higher than the bioH_2 production system.

As seen in the life cycle inventory and the sensitivity analysis, a few of the identified energy flows represented a very high energy consumption, such as the biogas bioreactor's foam recirculation system or its temperature control system. In case this equipment was configurated in a more energy-efficient way, the energy balance of the biogas production process and all related analyzed impacts could be obtained with better results.

Based on all the points stated above, it can be concluded that the proposed two-stage configuration for anaerobic digestion was not optimal in terms of energy sustainability, as the system was consuming more energy than it was producing, for both scenarios analyzed. Nevertheless, it showed to be a better alternative for bioenergy production than conventional anaerobic digestion. Furthermore, when analyzed separately, the bioH_2 production process proved sustainable from an energy perspective, as it produced more energy than it consumed to operate within the defined boundaries. On the other hand, the biogas production process also showed as an unsustainable process energetically speaking, consuming more energy to operate than the energy it produced.

Still, both production processes presented positive impacts on the environment across all environmental categories analyzed for both applied LCIA methodologies. These outcomes could indicate that the proposed system could represent promising results from an energy production perspective and an environmental impact perspective when designed in a more optimal and energy-efficient way.

Furthermore, it is worth considering that the liquid outflow of the dark fermentation process in the first bioreactor still carries relevant organic content that should not be wasted. This point could be another means to justify the existence of the methanogenesis process in the second bioreactor within the proposed configuration. To make the global process more energy-efficient, the proposal is to enhance the system's highly energy-consuming processes, such as the foam recirculation system and the temperature control of the methanogenic bioreactor.

Finally, it is imperative to refer that this study had several limitations. Firstly, it was performed over a technology or specific configuration that does not exist yet on a full scale. At the laboratory scale, these biological reactors are not as efficient as they could be at a pilot or full scale. Promising results were obtained; however, it is important to scale-up the process to an industrial-scale application to fully evaluate its energy sustainability and consequent impacts on the environment.

The leading suggestions for future work on the LCA of the bioH_2 and biogas production from the OFMSW in a two-stage configuration, which may be complementary to this study, include:

- Further data collection on the pilot project, to over right a few assumptions taken such as HCl consumption in the bioH_2 bioreactor;
- Further research and data collection of similar configurations to simulate the industrial-scale application of the process;
- Perform an LCA of an industrial-scale configuration to optimize the system and analyze its energy and environmental sustainability;
- When comparing scenarios and production processes, the same volume and sample of the biowaste as input should be used for the LCI of the processes. This could allow the analysis to reflect the energy consumption difference between scenarios, as it has been seen in this study that the biowaste used as input can have a high contribution to the results.

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ANNEXES

Annex 1 – Detailed Life Cycle Inventory | bioH_2 production process via dark fermentation

Data collected for Process 1 – BioH_2 Production via Dark Fermentation | Energy and mass flows					
	Energy flow	**Equipment**	**Frequency of use**	**Average duration of use (h)**	**Daily energy consumption (kJ)**
E1	OFMSW Heating	Stirrer	1x/day and 5x/week	0.23	0.44
E2 E3	Temperature control and bioreactor heating	Meter	Constant	24.00	1.11
E4	Redox potential	Meter - Battery	2x/day and 10x/week	0.003	1.31E-06
E5	pH Measurement	Stirrer Meter	2x/day and 10x/week	0.02	9.21E-03
E6	Bioreactor feeding	Pump	5x/week	0.07	0.41
E7	Conductivity measurement	Stirrer Meter	2x/day and 10x/week	0.02	1.34E-02
E8	Acid addition	Pump (HCl)	4x for S1 5x for S2	0.003[1]	1.64E-02
E9	Continuous stirring	Stirrer	Constant	24.00	0.34
	Mass flow	**Description**		**Frequency of use**	**Daily consumption (mL)**
M1	Inlet	OFMSW		1x/day	525 for S1 420 for S2
M2	Acidification	HCl 1N		4x for S1 5x for S2	0.51[1] for S1 0.78[2] for S2
M3	Outlet	Outcome of bioreactor, VFA used for Process 2		1x/day	525 for S1 420 for S2
M4	BioH_2	Produced biogas		-	420 mL_{bioH2} for S1 660 mL_{bioH2} for S2

[1,2] Estimated value based on qualitative research, measurement was not possible

Annex 2 – Detailed Life Cycle Inventory | biogas production process via methanogenesis

Data collected for Process 2 – Biogas Production via Methanogenesis | Energy and mass flows					
	Energy flow	**Equipment**	**Frequency of use**	**Average duration of use (h)**	**Daily energy consumption (kJ)**
E1	Heating	Stirring	5x/day	0.11	0.28
E2	Bioreactor feeding	Pump	5x/day	0.02	0.04
E3	Temperature control (water bath)	Controller	Constant	24.00	4.34
E4	Heating	Water pump	Constant	24.00	0.36
E5	Temperature measurement (battery)	Meter	1x/day and 5x/week	0.003	3.13E-08
E6	Continuous stirring	Stirring	Constant	24.00	1.05
E7	pH Measurement of sample	Stirring Meter	5x/week	0.02	6.14E-03
E8	pH Measurement of feedstock	Stirring Meter	3x in total	0.02	
E9	Conductivity measurement of inlet and outlet	Stirring Meter	2x/day and 10x/week	0.02	0.01
E10	Foam recirculation	Pump	2x/day and 10x/week	0.25	1.79
	Mass flow	**Description**		**Frequency of use**	**Daily consumption**
M1	Inlet	VFA from Process 1		1x/day	183 mL
M2	Water	Water for temperature control		As needed	Average 1400 mL
M3	Outlet	Outcome of bioreactor		1x/day	183 mL
M4	Biogas	Produced biogas		-	7.6 L_{BIOGAS} for S1 6.7 L_{BIOGAS} for S2