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Thesis For The Degree Of Doctor Of Philosophy In Environmental and Hydraulics Engineering

Application of Life Cycle Assessment of Integrated Processes for Organic Waste Valorization

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"There are two powers in the world; one is the sword and the other is the pen. There is a great competition and rivalry between the two. There is a third power stronger than both, that of the women."

Muhammad Ali Jinnah

Abstract

Energy demand is one of the major significant contributors to environmental problems. This research aims to evaluate the environmental performance of a sustainable energy production pathway using the Life Cycle Assessment (LCA) methodology. The focus is on the integrated bio and electrochemical System (IBES), an innovative configuration of electrochemical cell combines with a dark fermentation process. The system was developed and experimentally tested in the environmental engineering laboratory at Sapienza University of Rome, Italy. IBES provided a self-sustained operational configuration produces enough electric current to derive a redox reaction for syngas (H_2 +CO_2) production. The research focuses mainly on addressing the complexity of IBES by evaluating the environmental impacts in relation to its key performance parameters such as hydrogen yield and maximum resource recovery benchmark with the conventional process, Anaerobic Digestion(AD). The LCA is conducted according to ISO14040:2006 and ISO14044:2006. The environment foot print 3.0(EF3.0) method is applied for impact calculations. The results showed that IBES outperformed in reduced impact of 2.94E+01kg CO_2 eq/t.CW in climate change and 8.57E-03kg. NMVOC eq/t.CW in photochemical ozone formation,as compared to baseline conventional AD process that is 2.02E+04kg CO_2 eq/t.CW and 6.03E+00kg NMVOC eq/t.CW respectively. The IBES shows high freshwater ecotoxicity due to inorganic and metals pollutions, and resource demand in terms of energy use 7.00E+01MJ/t.CW and water use 3.51E+01 m^3/t.CW. An insight into the handling of downstream degraded biomass feedstock and upgrading of produced syngas is applied while keepig the focus on Carbon Capture and Storage (CCS) to achieve potential benefits in terms of reduced impacts. The IBES is thus incorporated into an integrated biorefinery (IBR) approach converting biodegradable wastes into H_2, carbonated residues, biochar, and many other by-products through an appropriate combination of bio, electrochemical and thermochemical processes. The environmental impact result showed reduced values over energy and water consumption, 2.80E+01MJ/t.CW and 3.28E+00 m^3 depriv./t.CW, respectively. This concluded that the environmental implications do not reflect the operational and functional advantages that IBES offers over conventional AD such as improved waste treatment efficiency or increased energy recovery, unless IBES combined with downstream Integrated processes in an IBR and offers reduced impact effectively. This research identifies optimal solutions to reduced environmental impacts of various integrated process to provide a sustainable approach in IBR research practices.

Keywords: energy demand, hydrogen, bio electrochemical, life cycle assessment, sustainability

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This work is dedicated to all those who believe in the transformative power of research, innovation, and sustainability.

Maryam Khaliq
Rome, September, 2025

Nomenclature

AC Acidification

AD Anaerobic Digestion

APC Air Pollution Control

CBR Conventional Biorefinery

CC Climate Change

CC-Biogenic Climate Change - Biogenic

CC-Fossil Climate Change - Fossil

CFBC Circulating Fluidized Bed Combustion

CW Cheese whey

DF Dark Fermentation

Ef Ecotoxicity, Freshwater

Ef-Inorganics Ecotoxicity, Freshwater - Inorganics

Ef-Metals Ecotoxicity, FreshwaterMetals

Ef-Organics Ecotoxicity, Freshwater Organics

Et-Freshwater Eutrophication, Freshwater

Et-Marine Eutrophication, Marine

Et-Terrestrial Eutrophication, Terrestrial

HC Hydrochar

HTc Human Toxicity, Cancer

HTc-Inorganics Human Toxicity, Cancer Inorganics

HTc-Metals Human Toxicity, Cancer Metals

HTc-Organics Human Toxicity, Cancer Organics

HTnc Human Toxicity, Non-Cancer

HTnc-Inorganics Human Toxicity, Non-Cancer - Inorganics

HTnc-Metals Human Toxicity, Non-Cancer - Metals

HTnc-Organics Human Toxicity, Non-Cancer - Organics

IBES Integrated Bio Electrochemical System

IBR Integrated Biorefinery

IR Ionising Radiation

LCA Life Cycle Assessment

LCI Life Cycle Inventory

LCIA Life Cycle Impact Assessment

LCT Life Cycle Thinking

LF Liquid Fraction

LU Land Use and Land Use Change

MA Mineral Aggregate

OD Ozone Depletion

OpenLCA Open Source of Life Cycle Assessment

PFD Process Flow Diagram

PFDs Process Flow Diagrams

PM Particulate Matter

POF Photochemical Ozone Formation

Ruf Resource Use, Fossils

Rumm Resource Use, Minerals and Metals

WU Water Use

Chapter 1

Introduction

1.1 Background and Problem Statement

With the global population surpassing 8billion in 2022 and continue to rise [1], accelerating industrialization and increase pressure on natural resources and ecosystems are generated, leading to complex environmental challenges such as climate change, resource depletion, pollution and energy demand [2]. These trends intensified the unsustainable use of natural resources and increase in global warming. To address these concerns and support sustainable development, decision-makers, in both public and private sectors, required a comprehensive approach that can quantify the entire life cycle of the earth's finite resources, ensuring long term sustainability and ecological balance. The policymakers require a significant tool particularly for detailed quantification of environmental impacts and trade-offs between environmental pressures and benefits [2, 3]. Environmental policies and legislation in European union (EU) highly emphasize the importance of "Life Cycle Thinking (LCT)" as a basic framework to guide policy makers [3]. On the other hand, energy demand is predicted to increase by 40% by 2035 due to the world's rapid urbanization [4], energy is essential to the socioeconomic advancement of a country, it must be met in a way that is both sustainable and promotes economic growth [5]. Fossil fuels also experience unpredictable price fluctuations along with not negligible impact on the environment. Additionally, approximately half of the fossil fuel reserves are in the world's most unstable geopolitical areas with low accessibility.

Given the drawbacks of using conventional fossil fuels, biofuels are now a feasible alternative and their commercial production has already begun. Biofuel production from organic waste has emerged as a key environmental solution, highlighting the role of biotechnological advances in transforming organic wastes into valuable biofuels, like hydrogen. This approach presents a promising strategy to improve energy security while promoting the use of sustainable and circular resources [6]. Traditional waste treatment methods for biomass conversion are not sustainable and significantly contribute

to greenhouse gas (GHG) emissions. As an example, by 2025, traditional wastewater treatment plants are responsible for 12.1 Ktd^{-1} of global GHG emissions. Thus, innovative waste treatment technologies with synergistic renewable energy production and resource recovery are currently being developed [7]. Integrated waste management practices that utilize bio processing to handle large volume of biowaste and simultaneously generate biofuels and other bio-based products are the latest trend in the development of sustainable waste biorefinery [8]. In principle, a biorefinery cannot be sufficiently sustainable if it only produces one type of biofuel or value-added product; therefore, to develop sustainable waste management practices, varieties of bioproducts must be produced [9]. Significant research began in advancement of sustainable waste biorefineries after the first paper published in the 1980. Foley et al. compares the environmental performance of three wastewater treatment technologies. The results revealed that microbial electrolysis cells (MECs) offer the greatest environmental benefits due to their potential to displace energy-intensive chemical production, while microbial fuel cells (MFCs) provided limited improvements over conventional anaerobic digestion[10]. A review by Jozsef, et al. focused on the environmental and economic impacts of the production of biofuels from diversified feedstocks [11]. In 2014, a study reveals the cost of turning biomass feedstocks into valuable biofuels as a subject of one of these studies [12]. In 2015, research began to integrate conventional methods with more efficient feedstock conversion technologies to make full resource use and reduce environmental impacts.

Incorporation of bioprocess integration with two or more units of operations simultaneously in a single process, 'the so-called integrated biorefinery (IBR)' can be a paramount approach to efficient energy production and resource recovery. The goal of an integrated biorefinery (IBR) is to utilize all organic fractions to maximize the resource recovery per waste input [13]. Alternative technologies, such as direct anaerobic degradation (AD) of organic fractions in combination with the application of Bio Electrochemical Systems (BES) offers integrated solution of efficient biofuel production and maximum resource recovery from waste. BESs are advanced electrochemical devices capable of producing electricity, and conversion of biomass into various biochemical compounds through bio-electrochemical redox reaction. These systems support the catalytic activity of pure microbial cultures, bacterial communities, or isolated enzymes to drive redox reaction, making them a promising approach for sustainable energy production [14]. Microbial Electrolysis Cells (MECs), a type of BESs represent an emerging technology which could play a vital role in future integrated biorefineries for converting organic waste into bio-based products such as hydrogen. The MECs employ exo electrogenic microbes at the anode to break down biodegradable substrates release protons (H^+). These electrons are transferred to the cathode, where they reduce protons helps in additional H^+ ions conversion into H_2 molecules, hence additional electrochemical hydrogen (H_2) production. Since microbial electrolysis is an endothermic process with positive Gibbs free energy,

it does not occur spontaneously unless the hydrogen partial pressure is extremely low. To enable H_2 gas production at the cathode, a small voltage must be applied between the electrodes to drive the redox reaction. This applied voltage typically between 0.2–0.8V is significantly lower than the voltage required for traditional water electrolysis (1.8–3.5 V). The energy needed can be supplied by sustainable sources such as small solar panels, low-grade heat, or microbial fuel cells (MFCs), making MECs a more energy-efficient and environmentally friendly alternative. The gap of energy input between microbial and pure electrochemical electrolysis is provided by chemical energy stored in the organic material. In addition to H_2 gas production other inorganic and organic chemicals, such as CH_4, H_2O_2 and formic acid also produced using a similar process[15]

Moreover, although biofuel produced from waste sources is considered carbon-neutral, its overall environmental impact can remain significant due to emissions generated from resource consumption and energy use throughout the production process, upgrading, and distribution stages to the end user. Minimizing the environmental impact of biofuel production from waste requires reduction of emissions from entire production chain. Life cycle thinking has also been suggested in the waste framework directive (Directive 2008/98/EC as amended by directive 2018/251) as a useful method for the environmental impact calculation in waste management and for the identification of the resource efficiency pathways. Life Cycle Assessment (LCA) is an internationally standardized framework of methodology for the quantification of the magnitude of the environmental impacts of any product/process/services. LCA is thus a valuable tool for decision-making process to provide a comprehensive picture of the environmental impacts of a system.

The LCA applied to the BES-based IBR considers energy and mass flows and the whole set of environmental emissions throughout the process chain. There is a lack of data in quantitative assessment of environmental performance of BES technology. To the best author's knowledge, the only evaluation at commercial scale is by Aleksander et al. who calculated the MEC technology's target price of 1220€/m^3 Anode-Chamber (at 5A/cm^3, 0.9 kWh/kg COD removed) at which H_2 -MECs for wastewater treatment break even financially after seven years [9, 10]. BESs can simultaneously treat waste and generate electricity or other valuable products. To match the energy recovery efficiency of conventional anaerobic digestion with biogas production, Rabaey and Verstraete suggested that another bio electrochemical system, the so called microbial fuel cells (MFCs) would need to achieve a power density of 1000 Wm^{-3} of reactor volume, operating at an organic loading rate of 10 $kgm^{-3}day^{-1}$ [12].

Despite growing interest, previous LCA studies on the use of BESs in IBR face several challenges complex cultivation of feedstocks, diverse technological pathways, and variations in LCA methodologies and system boundaries. Furthermore, there is a significant data gap in the techno-economic evaluation of this emerging technology that limits a comprehensive assessment of its feasibility and

scalability for large-scale implementation [11].

Given the limited literature on LCA studies of BES based IBR, this research aims to conduct an LCA of a BES system that is innovative in its configuration [15]. This system has an integrated configuration of BES and self-sustained in its operation for producing biofuel (green H_2+biogenic CO_2) as the primary product from an initial biomass stream (Figure 1.1). The research focused on evaluating the environmental performance and complexity of the system performance of an integrated bio electrochemical system (IBES) proposed by DE GIOANNIS, Giorgia, et al. with its key performance parameters such as the efficiency of hydrogen production on a large scale [15]. In addition, the research was extended to investigate the potential benefits (in terms of reduced impacts) of a proposed IBR scheme by converting biodegradable waste into syngas production followed by bio H_2 separation from the sygas, hydrochar production, through an appropriate combination of bio electrochemical and thermochemical processes. In addition, CO_2 emission from the proposed process scheme was limited thanks to the implementation of an accelerated carbonation process for CO_2 capture and its storage. By doing so, the study practiced enough to achieve optimal solutions for achieving minimum carbon emissions and zero waste generation at the end user, hence contributes to climate change mitigation and advancing sustainability of emerging BES technologies in IBR practices.

1.2 Research Objectives

The doctoral research was conducted with three principal objectives:

I. The research first analyzed the environmental sustainability of an innovative organic waste treatment method, Integrated Bioelectrochemical System (IBES), aimed at producing syngas mainly composed of hydrogen and carbon dioxide. This analysis was conducted using the Life Cycle Assessment (LCA) framework.

II. Subsequently, the research extended the LCA framework to evaluate the environmental sustainability of upgrading process of the produced syngas, with particular focus onCarbon Capture and Storage (CCS) using industrial alkaline residual waste's stream,Hydrogen separation using polysulfone membranes, and the use of separated hydrogen in a Proton Exchange Membrane Fuel Cell (PEMFC) for energy provision in an Integrated Waste Biorefinery (IBR), which included various emerging and integrated technologies in waste valorization.

III. Finally, LCA was applied to Hydrothermal Carbonization (HTC) of the degraded biomass from the IBES cell, with the primary goal of producing hydrochar (HC). The study further assessed the use of HC in a Combined Heat and Power (CHP) plant for district heating.

This stage focused on the environmental sustainability of emerging technologies and aimed to achieve maximum resource recovery while generating zero waste.

1.3 Research Project Overview

Three-year doctoral research activities are in line with the project"Biomaterials, Biofuels, CO_2 Sequestration, and Circularity **(BBCircle)**", focusing on the implementation of a waste biorefinery in the Lazio region. The research aimed to develop a theoretical framework for interpreting the environmental impacts of an innovative Integrated Bio-Electrochemical System (IBES) to produce hydrogen as primary bio product from dairy industry biomass. The research introduced IBES in broader goals of the Integrated waste Biorefinery (IBR) and proposed a schematic of various integrated waste valorization methods that facilitates waste-to-energy routes efficiently.

1.3.1 Stage 1: Innovative and integrated bio electrochemical system (IBES) combined with dark fermentation for hydrogen(H_2)

In the first stage of IBR, an Innovative Bio Electrochemical System (IBES) is employed. This system integrates a dark fermentation (DF) process with a bio-electrochemical system (BES) having a dual-reactor setup. First reactor is a Continuous Stirred Tank Reactor (CSTR); it acts as the cathode compartment containing organic waste as substrate. The second reactor serves as the anodic compartment and contains an anolyte solution ($ZnSO_4$). This dual-compartment system, equipped with a zinc anode and titanium cathode form a galvanic cell configuration. An Anion Exchange Membrane (AEM) ensures electro neutrality between the catholyte and anolyte. The electrons released due to oxidation of metallic element in the anode chamber, while titanium cathode though not involved in chemical reactions, supports electron transfer. These electrons enhance the H^+ ions, released during the fermentation process, conversion into H_2 gas. The primary functions of this stage are the generation of electricity and bio and electrochemical H_2 gas in combination with CO_2.

1.3.2 Stage 2: Biogas upgrading through mineral carbonation process and permanent carbon capture and storage (CCS) using industrial alkaline residual waste

The second stage involves biogas upgrading with the inclusion of Carbon Capture and Storage (CCS). Industrial alkaline residual waste utilized to capture carbon from CO_2 gas stream and stored in a form of carbonated mineral aggregates. While the purified H_2 gas is used in polyelectrolyte membrane fuel cell (PEMFC) for electrical power generation in fuel cell.

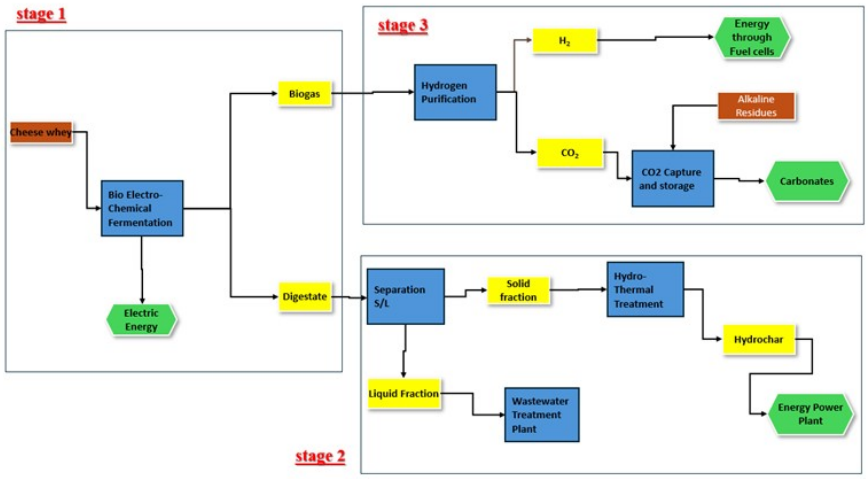

Figure 1.1: Proposed Process Scheme of Integrated Bio Refinery

1.3.3 Stage 3: Hydrothermal carbonization of IBES digestate to produce hydrochar

This stage focuses on management of the effluent from the cathode compartment of IBES (digestate). Hydrothermal Carbonization (HTC) process is applied to the digestate with the primary objective of producing hydrochar which is another value-added bio product.

1.4 Applied Framework of LCA in this research

The LCA study conducted is represented in this thesis in two parts:

- Life Cycle Assessment (LCA) of producing syngas through an integrated BES process in comparison to conventional biogas production through Anaerobic Digestion (AD) process. At this stage, LCA aimed to identify the environmental sustainability of IBES unit process and potential areas for improvements **(Chapter 3)**
- Secondly, system boundaries were extended to an Integrated Biorefinery (IBR) process scheme to account the environmental performance of producing various biofuels where the IBES serves as primary process in combination with multiple integrated post treatment technologies **(Chapter 4)**.

1.5 Goal and Scope Definition of LCA in this Research

The primary goal of the applied LCA framework is to evaluate the environmental performance of IBES in following stages: Producing syngas (H_2+CO_2) through IBES.

- Purification of produced H_2 gas from gas mixture by membrane separation process, with a particular focus on carbon capture and storage (CCS) by mineral carbonation of industrial alkaline residual waste in form of carbonated mineral aggregates.
- Use of purified hydrogen in polymer electrolyte membrane fuel cell (PEMFC) for electric power generation.
- Hydrothermal treatment of fermented Cheese Whey (IBES's effluent) to produce hydrochar and the application of hydrochar in Combined heat and power (CHP) plant.

Benchmark with conventional biorefinery (CBR) in which compare with

- Conventional Anaerobic Digestion (AD) process for CH_4 rich biogas production.
- Utilisation of CH_4 rich biogas in CHP plant for energy provision.
- Centrifugation of digestate and use of the solid fraction of digestate on land in soil application.

1.6 System Boundary

The system boundaries include all stages associated with IBR and CBR. The primary processes within the system boundaries of IBR include; IBES process for H_2 rich gas production from cheese whey (CW) with additional advantage of current production through electrochemical redox reaction; 2) H_2 gas separation process using membrane; 3) mineral carbonation process for carbon capture and storage from CO_2 gas; 4) use of purified H_2 gas in PEMFC; 5) hydrothermal treatment of digestate and hyrochar production; 5) use of produced hyrochar in a CHP plant for energy provision. To facilitate comparative assessment, the system boundary also includes benchmark CBR as; 1) AD process; 2) CH_4 rich biogas production; 3) energy provisions from CH_4 rich biogas in CHP plant; 4) centrifugation of the AD outflow; 5) use of dry matter as soil fertilizer.

For both scenarios, the inputs cover raw material synthesis, energy utilities, chemicals used in processes. The output covers syngas and biogas production from both scenarios and energy recovery from them, waste generation, and emissions. The primary experimental data for IBES process is adopted from lab experiments performed in the environmental engineering laboratory of Sapienza University of Rome, Italy, while the experimental data for AD process is collected from the literature (details are given in Table 3.3). The background data related to the production processes of utilities, fuels, chemicals, and manufactured materials entering the processes, generated wastes, and emissions are adopted from the eco invent database version 3.11 included within the system boundaries. Carbon emissions from biogenic CO_2 is considered carbon neutral. The system

boundaries do not incorporate the impact from the construction of the plant's unit. The multi-functional issues of the compared scenarios are addressed by the method of allocation referring the average data in system model. This boundary framework enables a comprehensive evaluation of the environmental impacts of introducing a novel IBES into IBR in comparison to conventional technologies.

1.7 Functional Unit

The functional unit adopted in this LCA is one ton (1t) of effluent from cheese making process (collected at an Italian dairy industry producing mozzarella cheese from a mixture of cow and buffalo's milk) so-called Cheese Whey (CW).

1.8 Structure of Thesis

Chapter 2: Literature Review

This chapter provides a comprehensive overview of biological hydrogen production and bio electrochemical systems, highlighting their principles, technologies, and potential for sustainable energy generation. It discusses how microorganisms can be used to produce hydrogen through biological processes, offering a renewable alternative to fossil-fuel-based hydrogen. The chapter also explores bio electrochemical systems technologies that combine biological and electrochemical processes to produce energy or treat wastewater, highlighting their innovative role in the bioenergy sector. In addition to technological aspects, the chapter introduces the Life Cycle Assessment (LCA) methodology. LCA is a critical tool that is used to evaluate the environmental impacts of bioenergy systems throughout their life cycle, from raw material extraction to end-of-life disposal. By incorporating LCA, the chapter emphasizes the importance of assessing not just the energy output, but also the sustainability and environmental footprint of these systems.

Chapter 3: LCA of IBES Compared with Anaerobic Digestion

This chapter compares the environmental impacts of Integrated Bioelectrochemical Systems (IBES) with conventional anaerobic digestion (AD), focusing on sustainability. It presents detailed system modeling and inventory data to assess the performance of both technologies. Through these models, the chapter analyzes key environmental factors like energy use, emissions, and resource consumption. The results highlight the sustainability benefits of IBES, such as potentially higher energy efficiency or lower greenhouse gas emissions, while also identifying trade-offs, such as higher technological complexity or material demands. Overall, the comparison provides insights into the relative strengths and weaknesses of each system, offering a clearer understanding of their potential

for sustainable waste-to-energy applications.

Chapter 4: LCA of Integrated Waste Biorefinery Compared With Conventional waste Biorefinery

This chapter evaluates an integrated waste biorefinery concept, which combines various advanced processes for sustainable waste management and energy production. Specifically, it looks at the integration of syngas upgrading with Carbon Capture and Storage (CCS), hydrothermal carbonization (HTC), and hydrogen utilization. The chapter develops process models and compiles inventory data to simulate how these processes work together. It also includes impact assessments to evaluate the environmental, economic, and operational performance of the entire system. By integrating these technologies, the chapter aims to assess how well they can convert waste into valuable products, reduce carbon emissions, and improve overall sustainability. The goal is to determine the viability and benefits of this integrated approach for waste-to-energy applications and carbon management.

Chapter 2

Literature Review

2.1 Introduction

The demand for sustainable and low-carbon energy carriers has increased substantially in recent years as global efforts intensify to mitigate climate change, reduce greenhouse gas (GHG) emissions, and transition away from fossil fuel dependence [16]. Among the emerging solutions, hydrogen has gained attention as a versatile and clean energy vector capable of supporting decarbonization in energy-intensive industries, transport, and power generation. Its high energy density, compatibility with fuel cell systems, and potential for large-scale integration with renewable energy make hydrogen a cornerstone in the vision of a climate-neutral future. However, the sustainability of hydrogen depends fundamentally on the production pathway employed. Conventional routes such as steam methane reforming (SMR) and coal gasification remain carbon-intensive and environmentally unsustainable, thus necessitating the development of alternative low-emission technologies that align with the integration of renewable energy and principles of circular economy [17].

Parallel to biological routes, bio-electrochemical systems (BES) particularly microbial electrolysis cells (MECs) have emerged as an innovative class of technologies combining microbial catalysis with electrochemical processes [18] . In MECs, electroactive bacteria oxidize organic matter at the anode, while protons are reduced at the cathode to form hydrogen, with assistance from an externally applied voltage [19]. This approach is attractive because it couples hydrogen production with wastewater treatment, offering a dual function of waste valorization and clean energy generation. Advances in high-surface-area electrode materials, biofilm engineering, and the replacement of costly catalysts with sustainable alternatives (e.g., nickel iron alloys) have significantly improved the efficiency and cost-effectiveness of MECs [20] . Recent demonstrations of wastewater-fed MECs highlight their potential to reduce treatment costs while simultaneously producing hydrogen, reinforcing their role within circular economy frameworks [21].

To ensure that such technologies genuinely contribute to sustainability, it is critical to adopt a comprehensive environmental evaluation framework [22]. For this reason, this chapter also introduces the Life Cycle Assessment (LCA) as a key methodological tool to analyze the environmental implications of hydrogen production technologies throughout their entire life cycle [23]. Unlike conventional assessments that focus narrowly on operational efficiency, LCA provides a cradle-to-grave perspective, accounting for impacts from raw material extraction and system construction to operation, waste management, and decommissioning. By quantifying metrics such as GHG emissions, resource depletion, water consumption, and toxicity, LCA facilitates objective comparisons between conventional and emerging hydrogen production pathways [24]. It also identifies environmental 'hot spots' and trade-offs, guiding both researchers and policymakers toward more sustainable system designs.

The integration of biological hydrogen production, bioelectrochemical hydrogen production via MECs, industrial integration opportunities and challenges, and LCA methodologies within this chapter ensures a holistic analysis [25]. Rather than considering each technology in isolation, the chapter emphasizes their role within broader energy and industrial ecosystems, highlighting both their potential and limitations. In doing so, it underscores the importance of aligning technological innovation with environmental responsibility, resource efficiency, and circular economy objectives. This chapter provide a framework for understanding how hydrogen production pathways can evolve beyond laboratory concepts to practical, large-scale solutions that genuinely support global climate and sustainability goals.

2.1.1 Biological Hydrogen Production: *Fermentation Process*

Biological hydrogen production from organic substrates represents a sustainable alternative to fossil fuel based hydrogen generation, leveraging microbial metabolism to valorize low-cost, renewable feedstocks such as agricultural residues, food waste, and dairy effluents [26]. Two primary biological routes: dark fermentation (DF) and photo-fermentation (PF) are widely explored. In DF, anaerobic bacteria metabolize carbohydrates under oxygen-deprived conditions to produce hydrogen. Recent advancements include metabolic engineering approaches aimed at enhancing hydrogenase enzyme activity to improve yield [27]. Conversely, PF employs photosynthetic bacteria like Rhizobacteria to convert short chain organic acids into hydrogen in the presence of light. The development of bio hybrid systems integrating photosynthetic microbes with nano structured light absorbing materials has significantly improved photon utilization efficiency, reportedly increasing hydrogen production by 30% to 50% [28]. Both biological approaches have drawbacks such as low conversion efficiency and substrate restrictions but improvements in reactor design and metabolic engineering provide a route

to commercial success [26–28]. Despite these innovations challenges persist, including substrate specificity, low conversion rates, and scalability limitations.

2.1.2 Bio-Electrochemical Hydrogen Production:*Microbial Electrolysis Cells (MECs)*

A new and promising technique that combines electrical energy and microbial activity to improve hydrogen creation is bio-electrochemical hydrogen production. Microbial electrolysis cells (MEC) are the most well-known technology in this field [29]. MECs use electro active bacteria to oxidize organic compounds at the anode and reduce protons at the cathode to produce hydrogen using external electrical energy [30]. Key technological advancements include the development of high-surface-area electrode materials (e;g graphene-based composites) and biofilm engineering to enhance electron transfer kinetics and microbial adherence. The substitution of platinum group catalysts with more sustainable and cost effective alternatives such as nickel-iron alloys has emerged as a crucial step in reducing environmental burdens and operational costs [31]. Recent studies indicate that optimized MECs can achieve up to 40% increased hydrogen output when operated with complex organic waste stream, such as food processing effluents. Innovations in dual-chamber reactor design have further enhanced hydrogen purity and reduced external energy input by 10% relative to conventional configurations . These advancements demonstrate MECs potential as dual function systems for waste valorization and renewable hydrogen production, reinforcing their relevance in circular economy frameworks[32].

2.2 Integration with existing Industrial system:*challenges and opportunities*

The transition from fossil fuel-based hydrogen production methods; such as Steam Methane Reforming (SMR), coal gasification, and hydrocarbon oxidation, to biological and bio-electrochemical pathways remains constrained by both techno economic and systemic limitations [33]. Industrial sectors with high hydrogen demands (e.g. steel, cement, petrochemicals) often face a scalability mismatch with current biological systems [34] . Many companies have shown interest in switching to clean fuel, especially those in energy intensive and heavy manufacturing sectors. Their primary feedstocks (natural gas, coal, oil) are carbon-intensive, leading to significant CO_2 emissions [35]. There are possibilities as well as problems in integrating biological and bio-electrochemical hydrogen production into current existing industrial system [36]. Biological processes typically produce smaller volumes of hydrogen than traditional steam methane reforming (SMR), the scale mismatch between the existing industrial hydrogen demand and the production capability of biological sys-

tems continues to be a significant hurdle[33–35]. However, the logistics of integrating sustainable hydrogen generation into current operations are challenging [36]. The biological pathways in integration with electrochemical cells can bring a holistic innovation into the existing industrial systems. Retrofitting current industrial infrastructure to support integrated hydrogen production and storage is another obstacle in this way. Gas storage, distribution, and safety procedures must be significantly altered to integrate bioelectrochemical hydrogen production into existing industrial systems that are frequently built around fossil fuels [37] . Not with standing these difficulties, bio-electrochemical systems and more particularly, MECs offer remarkable chances for integration with sectors that produce a lot of organic waste [38]. For example, MECs that treat wastewater and produce hydrogen as a byproduct can help the food and beverage sector, which generates a lot of wastewater, and support circular economy models. Wastewater-fed MECs have the potential to produce hydrogen while lowering treatment costs by up to 20%, according to recent test trials [39]. Additionally, to further reduce their carbon footprint, businesses with high levels of renewable energy integration, including the production of steel and cement, can use off-grid renewable energy sources to fuel the synthesis of bio-electrochemical hydrogen. Since renewable power can supply the necessary low voltage input, integration with renewable energy systems has demonstrated promising in improving the economic viability of MECs. This makes bioelectrochemical hydrogen production a feasible part of decentralized energy systems[40].

2.3 Introduction of Life Cycle Assessment

Environmental Life Cycle Assessment often abbreviated as LCA, is a comprehensive and systematic approach for evaluating the environmental impacts of a product, process, or technology at its developing stage and before introducing at commercial level. LCA has emerged as one of the most widely accepted and standardized tools for evaluating the environmental performance of products, processes, and services. Unlike traditional environmental assessments that focus on single phases of a system's life (e.g., production or disposal), LCA provides a holistic perspective by considering the entire life cycle from raw material extraction to final disposal or recycling [41]. The International Standardization of Organization (ISO), a global federation of international standard bodies (ISO member bodies) set a framework for LCA in ISO 14040:2006 and ISO 14044:2006 which include four phases[42]. Together, these phases form a consistent and iterative framework that ensures transparency, comparability, and scientific rigor. In practice, an LCA does not follow a purely linear path; instead, it often requires iterative adjustments as new data, assumptions, or methodological insights emerge[43] .

2.3.1 Goal and Scope Definition

Describe the goal of the LCA and set system boundaries of a process and product to establish the context in which the environmental assessment to be done. Also define the Functional Unit (FU) of the reference flow against which all inputs and outputs are normalized. For example, in energy systems, the FU might be defined as "1kWh of electricity generated," ensuring that different technologies are compared on a consistent basis . Equally important is the definition of system boundaries, which determine which processes are included or excluded in the analysis. Depending on the research question, system boundaries can range from "cradle-to-gate" (raw material extraction to factory output) to "cradle-to-grave" (raw material extraction to disposal). The choices made in this phase have a profound influence on the reliability and applicability of the LCA results, and thus must be carefully justified.

2.3.2 Life Cycle Inventory

Once the scope has been defined, the next step is the life cycle inventory phase. This involves collecting quantitative data on all relevant energy and material flows within the system, as well as emissions and wastes released into the environment. The inventory may include flows such as raw materials, fuels, water use, air emissions, wastewater discharges, and solid waste. Developing an accurate LCI requires access to primary data from industrial operations or, where unavailable, the use of secondary data from databases such as Ecoinvent.

The quality of the LCI is often a limiting factor in LCA, as data availability, representativeness, and accuracy vary significantly depending on the system under study. Emerging technologies, such as bio electrochemical systems or waste biorefineries, often rely on laboratory- or pilot-scale data, which introduces additional uncertainties. Nevertheless, the LCI phase provides the quantitative backbone of LCA and determines the robustness of the subsequent impact assessment.

2.3.3 Life Cycle Impact Assessment(LCIA)

LCIA quantifies the potential human and ecological consequences of flows coming from the inventory analysis and their release into environment. LCIA is the phase where quantitative data of various flows are collected and analyzed enabling a comprehensive understanding of how a flow has its impacts to the selected impact categories. Impact categories are predefined environmental issues, such as climate change, acidification, eutrophication, and eco toxicity, each representing a particular aspect of environmental impact that need to account. The LCIA methodology operates within the framework of internationally recognized standards, ISO 14044, and ISO 14040.

2.3.4 Life Cycle Interpretation

The final phase of LCA is interpretation, where the results of the inventory and impact assessment are analyzed in relation to the defined goal and scope. The main objectives of interpretation are to identify key issues, check the completeness and consistency of the study, evaluate the sensitivity of assumptions, and draw conclusions that can inform decision-making. Interpretation is not a stand-alone phase; rather, it interacts with all other phases of LCA in an iterative manner. For example, if data gaps or inconsistencies are identified during interpretation, analysts may return to the inventory phase to improve data quality or adjust system boundaries. Ultimately, interpretation ensures that the study is transparent, credible, and fit for purpose. LCA is increasingly applied in the early stages of technology development, where it serves as a powerful decision-support tool. For novel processes such as integrated bio electrochemical systems (IBES), hydrogen production, or waste bio refineries, LCA can highlight potential environmental advantages and identify design trade-offs long before large-scale implementation. This early application helps prevent "lock-in" of unsustainable technologies and supports the transition towards a circular economy. Moreover, LCA enables the assessment of multi-functional systems, where a process generates multiple outputs, such as energy, bio fuels with various by-products. In such cases, system expansion or allocation methods are applied to fairly distribute environmental burdens. This is particularly relevant for bio refineries, where residues and co-products often contribute significantly to environmental performance.

2.4 Summary

In sustainable energy production pathways, biological and bio electrochemical technologies are emerging as promising innovations for reducing reliance on fossil fuels and supporting a low-carbon future. Among them, bio-electrochemical techniques such as microbial electrolysis cells (MECs) have gained significant attention due to their ability to efficiently convert organic waste streams into hydrogen and other value-added products. These systems not only produce clean energy but also enable the recovery of valuable resources from industrial and municipal waste water, thereby promoting circular economy principles. On the other hand, biological processes such as dark fermentation and photo-fermentation provide environmentally friendly routes for hydrogen production, utilizing renewable biomass or waste as feedstock. Together, these technologies demonstrate great potential for integration into industrial waste management and energy recovery systems.

Despite these advantages, there are substantial challenges to scaling up and integrating these technologies into existing industrial infrastructures. Industrial systems are typically optimized for conventional energy pathways, and introducing new processes often requires significant modifications to infrastructure, logistics, and regulatory frameworks. Technical obstacles include optimizing

process efficiency, ensuring long-term stability of microbial consortia, and managing operational costs at a commercial scale. Furthermore, uncertainties regarding feedstock availability, system durability, and product quality remain barriers to widespread adoption. Overcoming these challenges demands not only technological innovation but also robust assessment tools that can evaluate potential environmental and economic trade-offs before large-scale implementation.

This is where Life Cycle Assessment (LCA) plays a central role. LCA enables a comprehensive understanding of the full spectrum of environmental consequences associated with emerging processes from the manufacturing of materials and construction of systems, through operational use, to the management of end-of-life waste streams. By systematically evaluating inputs and outputs across each stage, LCA provides a cradle-to-grave perspective that helps identify environmental "hot spots" and opportunities for improvement. Importantly, it allows comparison of new technologies with conventional energy systems under consistent functional units and boundaries, thereby supporting fair and evidence-based decision-making.

In the context of bio electrochemical and biological hydrogen production, LCA can quantify and analyze critical indicators such as energy consumption, greenhouse gas (GHG) emissions, resource depletion, water use, and toxic emissions. Beyond environmental impacts, LCA results can be linked with techno economic assessment (TEA) to provide insights into cost, market feasibility, and scalability. This holistic approach ensures that the promotion of new technologies does not inadvertently shift burdens from one environmental compartment to another for example, reducing greenhouse gas emissions while increasing toxic chemical use. Instead, it provides a balanced framework for guiding scientific research, industrial innovation, and policymaking.

Ultimately, LCA acts as a decision-support tool that bridges the gap between laboratory-scale innovation and real-world implementation. For businesses, it provides a framework for developing environmentally responsible products and complying with sustainability standards. For governments, it informs policy development, subsidy allocation, and regulatory approval of novel technologies. For researchers, it highlights the environmental trade-offs of different process designs, guiding optimization efforts. In this way, LCA contributes not only to advancing sustainable energy pathways but also to fostering a broader transition towards a circular and climate-neutral economy.

Chapter 3

Life Cycle Assessment of Integrated Bio Electrochemical System Compared with Baseline Anaerobic Digestion Process

3.1 Introduction

The potential for hydrogen production from organic matter is a viable prospect, which occures through a complex series of metabolic processes known as dark fermentation (DF) process. Theoretically, the maximum hydrogen yield stands at twelve moles of hydrogen per mole of glucose consumed[44, 45].

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 \tag{3.1}$$

In many instances, the actual hydrogen yield achieved is only four moles of hydrogen per mole of glucose consumed when acetate is the final metabolic product of the fermentation process. This yield remains economically challenging compared to the commercial level practices [46]. In response to this challenge, a recent and innovative strategy has emerged, focusing on enhancing bio and electrochemical hydrogen recovery by integrating biological process with electrochemical cells [47]. This integration not only offers the potential for enhanced hydrogen production but also presents a solution that bridges the gap between theoretical potential and practical applicability. The increased hydrogen yield obtained through this integration makes hydrogen production more economically viable as an alternative to conventional methods.

This chapter evaluate the environmental concerns, and the scalability options of an energetically self-sustained integrated electrochemical cell developed and tested in Environmental Engineering laboratory at the Department of Civil, Building and Environmental Engineering (DICEA) at

Sapienza University of Rome, Italy. The research reported by De Gioannis Giorgia, et al. provides an integrated electrochemical cell combine with DF process, so called IBES (Figure 3.3) based on the electrochemical reduction of protons released during the dissociation of volatile fatty acids (VFAs) produced in the DF process, resulting in additional hydrogen (H_2) production [15]. The redox reaction is driven by the electrons produced from the oxidation of a metallic element (Zn anode) in the anodic compartment of IBES, thereby generating an electric current. An inert electrode (Ti cathode) which serves as an electron carrier rather than participating directly in the reaction, is immersed in the fermentation medium in cathode compartment of IBES. Both electrodes are connected via an external electric circuit. The ion flow between the two compartments essential for maintaining electro neutrality achieved through an appropriate connection. The reactions occurring in bio electrochemical cell are given below along with their corresponding reduction potentials (E_0).

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^-, \quad E^\circ(\mathrm{Zn}^{2+}/\mathrm{Zn}) = -0.762 \text{ V} \tag{3.2}$$

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2, \quad E^\circ(2\mathrm{H}^+/\mathrm{H}_2) = 0.000 \text{ V} \tag{3.3}$$

Consequently, IBES benefits from conventional biochemical hydrogen production additionally the production of electrochemical hydrogen (H_2) using reduction of protons derived from metabolites through electrones released from oxidation of mattelic element at aode. Because of its galvanic cell design, the system uses energy to maintain itself. The integration of bio-electrochemical hydrogen recovery into conventional DF provides several distinct advantages. First, it significantly enhances hydrogen yield beyond the biochemical limits of DF alone, improving the overall energy recovery efficiency of the process. Second, it creates opportunities for waste valorization by coupling hydrogen production with the treatment of organic rich waste streams such as food processing wastewater or agricultural effluents. Third, the system's self sustaining galvanic design reduces dependence on external electricity, thereby lowering operating costs and improving scalability. Finally, by stabilizing pH through proton consumption, IBES alleviates one of the major bottle necks in DF operation, which is the inhibitory effect of excessive acidification on microbial metabolism. Despite these benefits, challenges remain with respect to scalability, long-term electrode stability, and integration into existing industrial infrastructure. Electrode material costs, fouling, and the durability of components under complex waste stream conditions represent critical technical barriers. Additionally, large-scale deployment would require careful assessment of system compatibility with existing hydrogen production and distribution infrastructure. Importantly, the conversion of protons to H_2 gas molecule also contributes to reducing the acidification of the solvent, thus reducing the need of external buffering to maintain optimal pH levels that might reduce microbial

activity. While the technological promise of IBES is evident, its environmental sustainability compared to established anaerobic digestion (AD) systems remains underexplored. Both IBES and AD are capable of valorizing organic waste streams while producing renewable energy carriers (hydrogen or methane). However, the relative impacts of these systems on climate change, resource use, acidification, eutrophication, and toxicity are not straightforward and depend heavily on process design, energy inputs, and waste management practices.

Life Cycle Assessment (LCA) provides a robust methodological framework to evaluate these aspects by quantifying environmental impacts across the full life cycle of each system from feedstock acquisition to energy conversion and by-product management. By applying LCA to compare IBES with baseline AD, this study aims to provide scientifically grounded insights into the environmental trade-offs associated with transitioning from conventional DF process to advanced bio electrochemical for hydrogen production systems. The results will be a preliminary support for researchers, decision makers, industrial stakeholders, and policy makers on the feasibility, benefits, and challenges of adopting IBES at larger scales.

3.2 The Framework

3.2.1 Goal of LCA

The goal of this LCA is:

1. To evaluate the environmental performance of the electrochemical cell, combined with dark fermentation (IBES), as a stand-alone unit process to quantify all the resource use (e.g; chemicals, water, energy) and outputs (hydrogen, electricity). This LCA specifically the environmental impacts associated with innovative IBES process only, excluding downstream impacts. The goal of this LCA is to identify the potential areas of improvement within IBES.

2. Secondly, the IBES process is compared with baseline conventional anaerobic digestion (AD) process aimed to understand the potential of scalability of this new and integrated approach in industrial scale application.

3.2.2 System Definition

The system boundaries include the IBES process for H_2 rich syngas production, conventional AD process for CH_4 rich biogas production. The functional unit adopted for comparison is one ton of cheese whey (1t CW). The process includes the boundaries of synthesis of materials, energy utilities, products, by-products. The avoided burdens are subtracted from the outputs in the system allowing

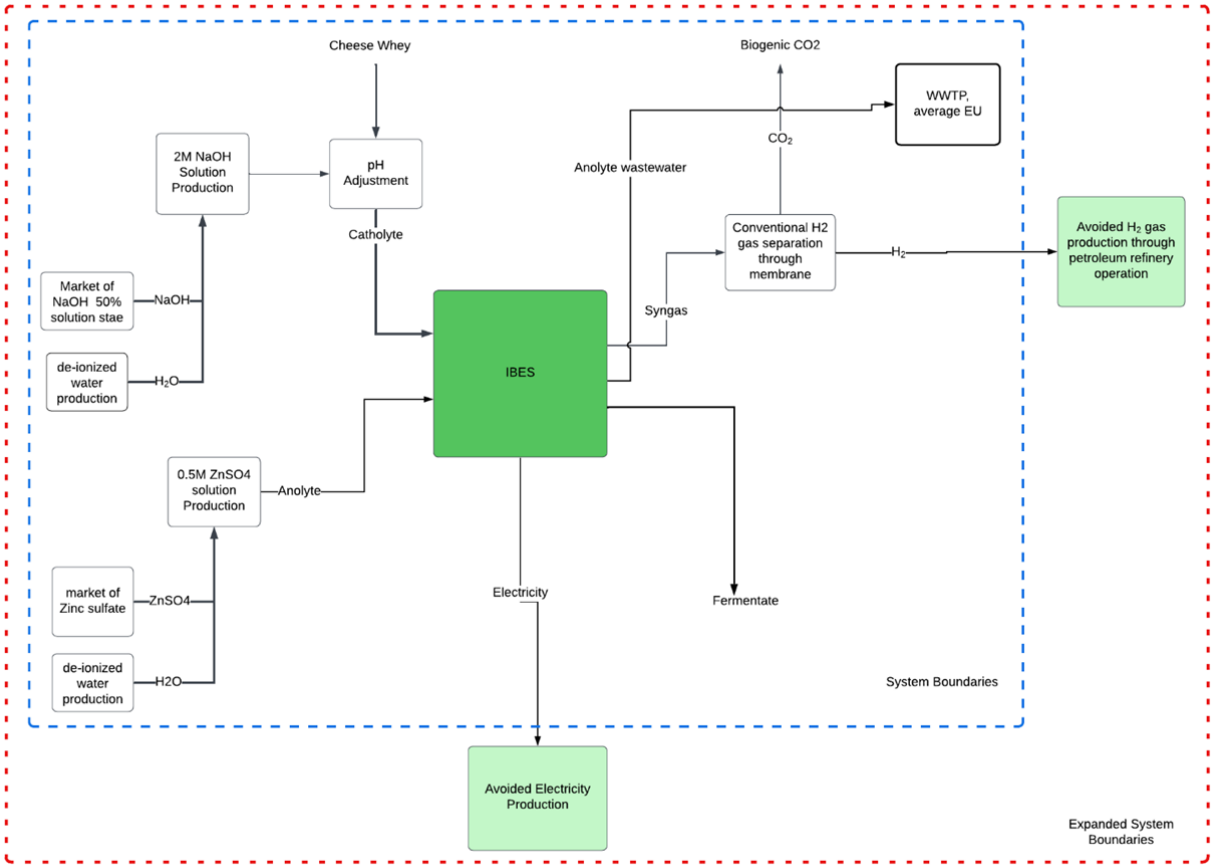

Figure 3.1: System boundaries of IBES process

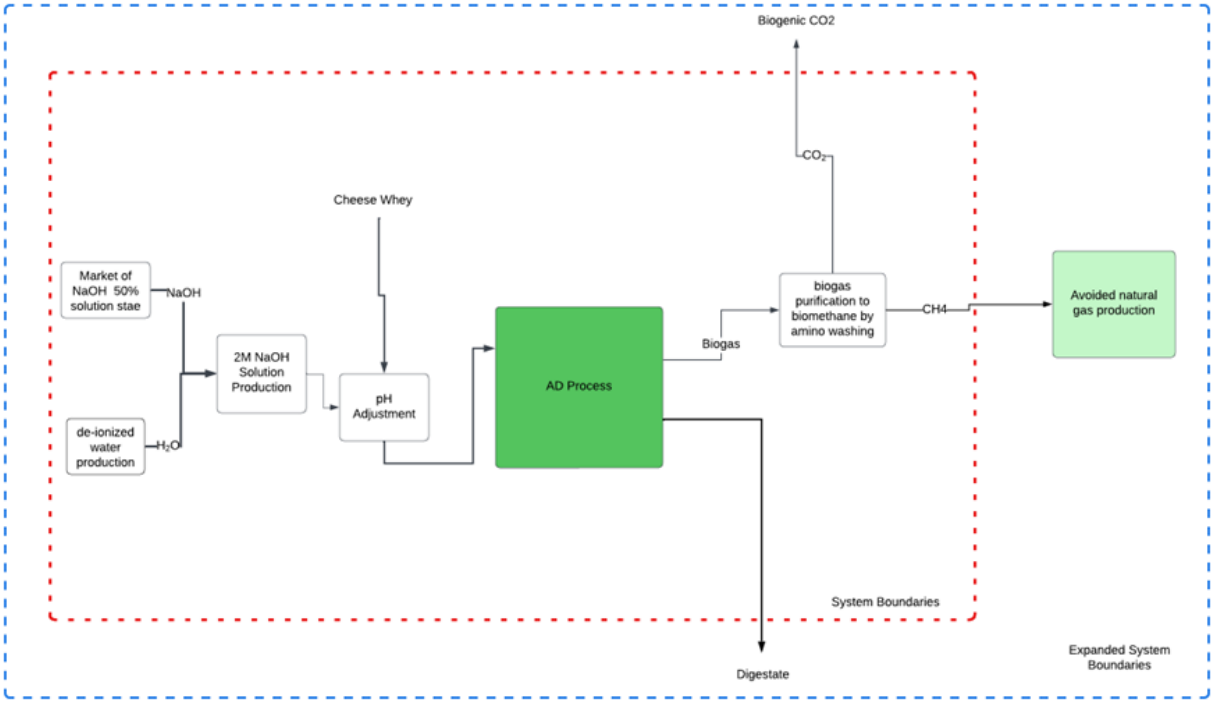

Figure 3.2: System boundaries of AD process

the model to capture the environmental credits associated with the displacement of conventional methods. The hydrogen gas is separated from biogenic CO_2 through a conventional membrane adsorption process and credited to petroleum refinery hydrogen production process available at commercial scale. A proper eco invent dataset in record "hydrogen production, gaseous, petroleum refinery operation | hydrogen, gaseous | APOS, U" is used for substitution. Methane rich biogas is upgraded through conventional amino washing process and credited by replacing with fossil-derived natural gas using the dataset "Natural gas, high pressure, at plant/GLO, U" in eco invent record. The provider process is used from an Eco invent record; heat and power co-generation, natural gas replaced by hydrogen, IBES, combined cycle power plant, 400MW electrical | electricity, high voltage | APOS, U. The CO_2 emissions from both processes is considered biogenic. The effluent streams from DF and AD reactors are by-product of the process are included in the system boundaries, but their further treatment is not evaluated at this stage of LCA. The sole purpose of this LCA is to investigate the impact caused by producing a biofuel using innovative IBES, and its comparison with the conventionally available process AD processes at industrial scale. The impact caused by the construction of the plant is not included in system boundaries.

3.3 Inventory Analysis

3.3.1 Inventory of IBES Process

Cheese whey (CW) is sourced from an Italian dairy plant producing mozzarella cheese from cow and buffalo milk. It exhibits varying pH levels based on the cheese production process, with pH values of 5.9-6.6 for semi-hard or soft cheese-derived whey and a more acidic pH range of 4.3-4.6 for whey generated during mineral acid-precipitated casein production [48]. The process begins by adjusting the pH of the CW to 7.5 using a 2M solution of Sodium Hydroxide (NaOH). Subsequently, one ton of CW with the characteristics described in Table 3.1 is introduced into a continuous stirred tank reactor (CSTR). This reactor functions as the cathodic compartment within the electrochemical cell setup. Another reactor of identical size and dimensions serves as the anodic compartment and contains an anolyte solution ($ZnSO_4$ solution, 0.5M). Both compartments work in conjunction with a Zinc (Zn) anode and a Titanium (Ti) cathode to constitute a complete galvanic cell. To maintain electroneutrality in the catholyte and anolyte, Anion Exchange Membrane (AEM) is positioned between both of compartments allowing the selective flow of anions from the cathodic to the anodic compartment. The electrons released because of the metallic element oxidation in the anodic chamber are traveled through a wire connected to the cathode generating an electric current. A voltmeter is installed to measure the intensity of this current. The Ti cathode that does not take part in any biological or chemical reactions but facilitate electron transfer from anode to cathode

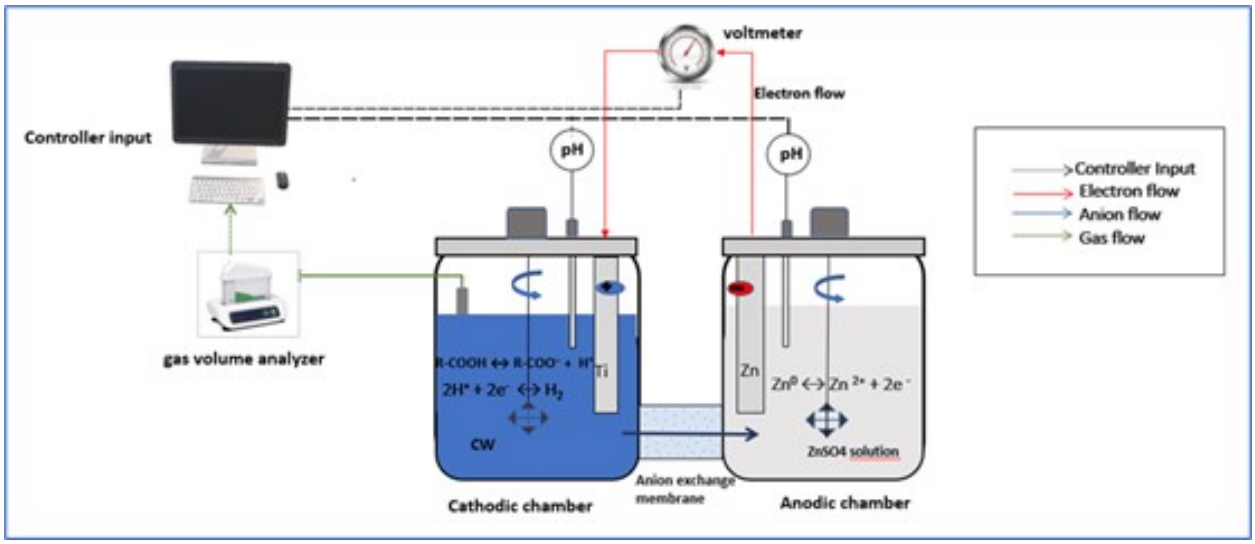

Figure 3.3: IBES process

compartment. The presence of H^+ions released during the dissociation of various volatile fatty acids (VFAs) in the fermentation process further promotes the electrochemical reduction (Redox reaction) leading to additional electrochemical H_2 molecule yield. The observed electrochemical and biochemical hydrogen yield falls within the range of 75.5-78.8 NLH_2/kgTOC at the laboratory scale with a volumetric composition of 60.8% H_2 and 39.2% CO_2 at 44 hours while the reactor operates in batch mode . All the operational conditions and materials and energy requirements are described in Table 3.3 and Table 3.4. It is hypothesized that a similar yield can be achieved under continuous flow conditions at an industrial scale when HRT of 44h is adopted. The critical aspect of the IBES is the scaling up of laboratory experiment to industrial scale, so that it was assumed that one ton of CW yield produced an equivalent of 3085NL of H_2 gas is assumed.

Table 3.1: Initial Characteristics of CW.

Parameters	**Unit**	**Values**
carbohydrates	g glucose/l CW	38.50
TOC	g C/l CW	39.30
TS	g/l CW	74
VS	g/l CW	64
pH	-	3.60
density	g/mL	1.00
acetic acid	mg HAc/l CW	364.00
butyric acid	mg HBu/l CW	<DL
ethanol	mg EtOH/l CW	3360.00

3.3.2 Scaling Up of IBES Process According to Functional Unit

A laboratory experiment is typically conducted in a batch reactor with stirring and if necessary, heating or cooling. It is a discontinuous process in which the reactor is filled with feed and then emptied after the reaction has occurred. In contrast, in a continuous process, the reactor is fed and emptied continuously after a specific HRT without any interruption. Continuous Flow Stirred Tank Reactors (CSTRs) are widely used to optimize continuous processes at industrial level. Dimensional analysis and experimental methods are required in the scaling of the reactor that involve some essential parameters, for example, the stirring power at a specific volume and the linear terminal velocity of the impeller [29, 49]. The problem in successful scaling is that the results obtained by such methods are not known until experiments are performed in a scaled-up reactor. However, the scaling up process in LCA allows a comparison of emerging technologies to improve their environmental sustainability at the commercial level [50, 51].

Piccino et al. proposed an engineering-based scale-up procedure to simulate processes and perform LCA studies on a commercial scale with laboratory protocol [52]. The amount of CW used in a laboratory reaction is 0.5l which is scaled up linearly using a functional unit for LCA that is 1000l. The actual volume of a reactor (Vreactor) typically exceeds the quantity to be processed in it (Vmix). After adjustment of the pH of 1000l of cheese whey, the volume of the reaction mixture is 1073l or $1.07m^3$. The increase in reactor volume 10% is assumed to be greater than the volume of the reaction mixture[52].

$$Vmix = Q \times \text{HRT}, (10\% increase) \tag{3.4}$$

Where: Vmix = Volume of mixture

Q = Volumetric Flow Rate

HRT = Hydraulic Retention Time

Volume of mixture, Vmix = $1.07m^3$ with Increase in space head for safety measures = 10%.

For all the calculations, the HRT at which the observed hydrogen yield is maximum, t = 44h, 44/24= 1.83day

$$\text{Flow rate} = \frac{V}{t} = \frac{1.07 \text{ m}^3}{1.83 \text{ day}} = 0.58 \text{ m}^3 \text{ day}^{-1} \tag{3.5}$$

The surface area(A) of a cylindrical reactor can be calculated using the diameter (D) and height (L). The suggested height and diameter for a 1000L reactor is 1.11m [52].

A = $2\ \pi r(r + L) = 2 \times 3.1415 \times 0.55 \times (0.55 + 1.11) = 5.72$ m^2 Where,

Diameter of reactor, D = 1.11m

Height of the reactor, L = 1.11m

Radius of the Reactor, r = 0.55m

Total volume of reactor = 1.05 + (1.07 ×10%) = 1.157m^3

Total organic carbon is 39.30 gram in a litter of cheese whey, calculated during lab experiment. TOC = 39.30gC/l CW = 39.30kg TOC/m^3.CW

$$\text{OLR} = \text{TOC}\ \left(\frac{\text{kg}}{\text{m}^3\ \text{CW}}\right) \times \text{Flow Rate}\ \left(\frac{\text{m}^3\ \text{CW}}{\text{day}}\right) \times \frac{1}{\text{HRT (day)}}$$

$\text{OLR} = 39.30 \times 0.58 \times \frac{1}{1.83} = 12.45\ \text{kg TOC} \cdot \text{m}^{-3} \cdot \text{day}^{-1}$(3.6)

3.3.3 Material/Energy Requirement for pH Adjustment of Catholyte

The pH of CW was adjusted to 7.5 at the beginning of the DF experiments using 2M NaOH solution in laboratory experiment [51]. The reported amount of sodium hydroxide and de-ionized water to prepare the 2M solution for one ton of CW is assumed the same and reported in Table 3.3.

3.3.4 Material/Energy Requirement for Anolyte

The anolyte used in the batch test of IBES process is 0.5M of zinc sulphate solution [15] Considering the same anolyte solution. The amount of anolyte required for one ton of CW is reported in Table 3.3.

3.3.5 Material/Energy Requirement for Transferring Catholyte and Anolyte into Reactors

The reaction mixture is to be transferred into the fermentation reactor before starting the process. This transfer normally occurs in pipes, and the energy comes from a pump. The reactors work in continuous flow condition and pump energy is required to feed the mixture. The energy requirements at the inlet for both reactors (Anode and Cathode) are calculated by the equation given below [52].

$$E_{\text{pump}} = \frac{m \times \Delta h}{\eta_{\text{pump}}} \tag{3.7}$$

Where "m" is the mass of reaction mixture and "g" is gravitational field strength 9.81m/sec^2, Δh is hydraulic head from the ground surface to the pipe. The hydraulic head and pump efficiency are unknown parameters in the equation in the scaling up procedure. For industrial use positive displacement pumps such as reciprocating pumps with low head are proposed to operate with high

flow. The change in hydraulic head (Δh) is the sum of gravitational head, dynamic head, static head and frictional head and indicates the energy consumption of a pump.

$$\Delta h = \Delta h_g + \Delta h_{\mathrm{dy}} + \Delta h_{\mathrm{fr}} + \Delta h_{\mathrm{st}} \tag{3.8}$$

Where Δh_g is the gravitational head; the height difference between starting and end point. Δh_{dy} is the dynamic head influenced by the average speed of the fluid (v). Δh_{st} is the static head; the pressure differences of starting to end point. Δh_{fr} is frictional head; the pressure loss through friction depending on the friction factor (λ), pipe length (l) and diameter (d) as well as the average speed (v). The friction factor "λ" in pipe varies between laminar and turbulent flow (Re $<$ 2300 laminar flow; Re $>$ 4000 turbulent flow) and depends on the pipe surface roughness "k" (k value depends on the pipe material used). The gravitational head is standardized at 4m ensuring that the height of the reactor should be overcome. The pipe parameters have been standardized for the industrial framework to a diameter of 0.2m and a length of 30m and steel is the suggested material with the surface roughness k= 0.1 mm. Using an average speed of 1m/s in turbulent flow, then the hydraulic head (Δh) results in 4.2m [53]. Assuming the efficiency of reciprocating pumps is 0.75, the pump energy requirements at inlet/outlet.

3.3.6 Stirring Energy Requirement:

A certain amount of stirring energy is consumed during reaction in both compartments of the IBES. The stirring power required for both cathode and anode compartment are calculated using the equation [52].

$$E_{\mathrm{stir}} = \frac{N_p\, \rho_{\mathrm{mix}}\, N^3\, d^5\, t}{\eta_{\mathrm{stir}}} \tag{3.9}$$

The power number of impeller (Np) and diameter (d) of the impeller, rotational velocity of stirring (N), density of the reaction mixture ($\rho_{\mathbf{mix}}$) and the reaction time, all influence on the stirring energy. An axial flow type impeller is preferable than a radial type of impeller for an average speed of mixing because the power number of impeller is very high in a radial type of impeller . The impeller diameter is assumed to be one-third of the reactor diameter. According to dimensional analysis theory, the power number N_p is a dimensionless number and is specific to a specific type of impeller but remains constant in turbulent flow. The turbulent flow is commonly used in mixing, so the power number 0.79 is fixed in the calculations of which an average speed of $1.41 s^{-1}$. Density of CW is assumed as 1000kg/m^3 and density of ZnSO_4 solution is 1050 kg/m^3, time of reaction taken as HRT (44h) and agitator efficiency for both compartments is constant as

90%.

Diameter of reactor, d = 1.11m

Diameter of impeller = 1.11×1/3=0.37m

3.3.7 Heat Energy Requirement For The Fermentation Process

The expected temperature of CW after dairy processing is 25C while the DF is carried out at 38C. Heating is required to achieve the desired temperature of the feed stock, calculated by the equation give below.

$$Q_{\text{react}} = \frac{Q_{\text{loss}}}{\eta_{\text{heating element}}} \tag{3.10}$$

Where "Qloss" is heat loss from the reactor surface, calculated as

$$Q_{\text{loss}} = \frac{A \cdot k_a}{s} (T_r - T_0)\, t \tag{3.11}$$

Where,

A = Area of the reactor, A = 2 $\pi r \times (rL)$

k_a = thermal conductivity of insulation material, W/m K

s = thickness of insulation, m

t = Time of reaction, h

T_r = Temperature of reaction, K

T_o = Initial temperature, K

The insulation material is typically selected based on the temperature required. The thickness is to be decided considering the economic values that compares the costs of the material to be used and the costs of heat losses and determines the appropriate size of the reactor as discussed in section 3.3.2. Fibber glass is a commonly available insulation material with a temperature range of 20 - 45 °C and a thermal conductivity of 0.032 to 0.052 W/m^2.K. Assuming the reactor is insulated by glass fibber with 75mm thickness, then the calculated thermal conductivity of insulation (ka) is 0.042 W/m.K, and the heat transfer coefficient of insulation (k_a/s) is 0.56 W/m^2K. The heating device's efficiency can be measured by the ratio of energy transferred to the reaction mixture to the energy consumed by the heating element. The efficiency of a heating element is determined by several factors including type of material, fluid, and temperature. The value is standardized at 75% for the 1000l reactor and scaled up with a scaling factor of 0.02 being the best approximation. Assuming heating source is natural gas, and a heating coil to heat the reactor that is made of stainless-steel, the heat energy required during the fermentation reaction is 2.48kJ.

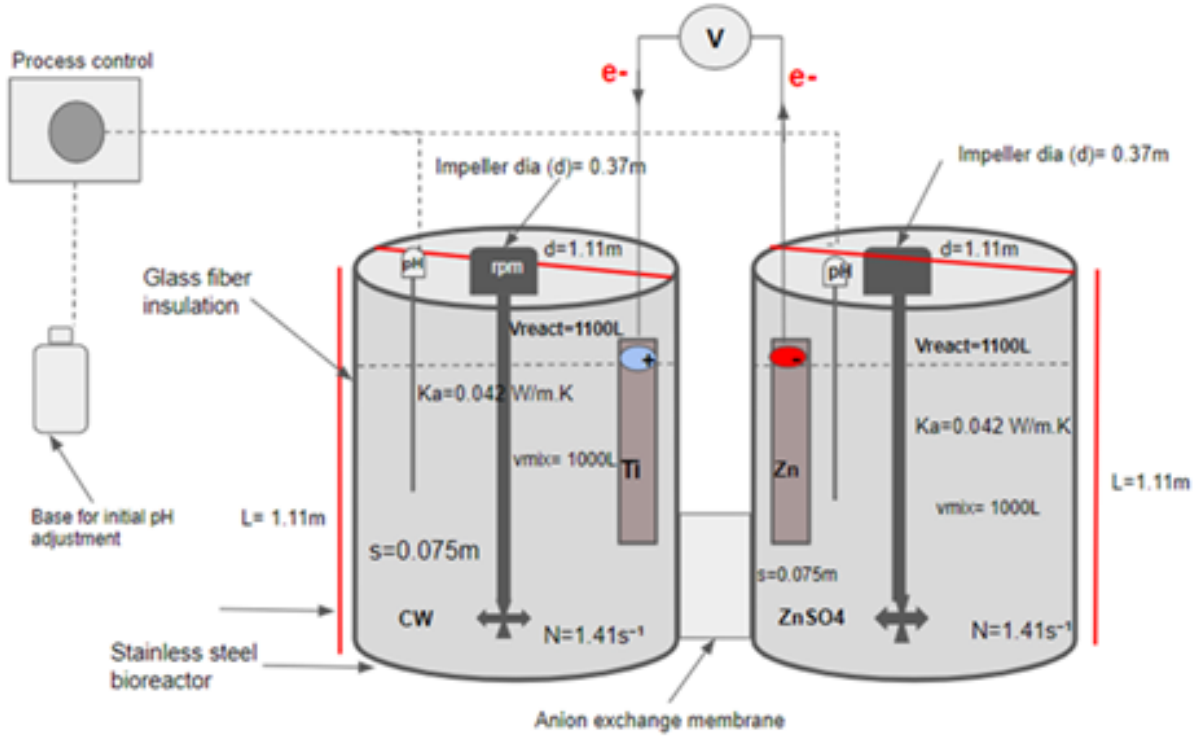

Figure 3.4: proposed scaled-up reactor design of IBES process

3.3.8 Anaerobic Digestion (AD) Process

For the anaerobic digestion (AD) process, average input data were sourced from previous literature and are presented in table 3.2. The operating conditions for the AD system are summarized in the second part of 3.3. Cheese whey (CW) is assumed to possess the same initial characteristics as those described in table 3.1 for the IBES process. The AD process is assumed in a single-stage, continuous stirred tank reactor (CSTR). The initial pH of CW is 3.6 while the optimal pH required for AD process is 7.33 (table 3.3). To achieve this, pH adjustment is assumed using a 2M NaOH solution. The material includes the use of NaOH (5.85 kg) and water (72.18l) to prepare 73.17l of the required 2M NaOH solution for 1t of CW. After neutralization, the resulting reaction mixture of CW and 2M NaOH (total volume: 1.07t) is fed into the CSTR at a flow rate of $3.28 m^3$/t.CW/day, with a hydraulic retention time (HRT) of 19.49 days, and maintained at a mesophilic temperature of 35 °C. The energy required for transferring the reaction mixture is 0.03 kWh/t.CW, continuous mixing into the reactor is 8.22 kWh/t.CW, heating is 1.91kJ/t.CW as mentioned in table 3.4, calculated using the equations mentioned in material and energy requirements section (in Chapter 3). This stage results in biogas composed of 60.69% methane (CH_4) and 39.31% carbon dioxide (CO_2). The system is considered as a unit process, and all the material and energy requirements are calculated at industrial scale accordingly functional unit.

Table 3.2: Summary of Anaerobic Digestion Studies on Various Reactor Types

Reactor Type	HRT (days)	TS (g/L)	VS (g/L)	Temperature (°C)	OLR (kgVS/L/day)	pH	CH_4 Production (L CH_4/kg VS)	CH_4 (%)	References
Single CSTR	25	73.62	61.82	38	2.54	7.5	241.80	60.43	[54]
Two-phase CSTR	23.03	62.10	52.00	37	0.003	7.5	320.00	53.00	[3]
Co-digestion in CSTR	16.60	67.70	31.20	35	0.002	7.6	625.00	35.40	[56]
Co-digestion in CSTR*	16.00	62.40	37.50	37.5	8.30	7.8	585.50	–	[58]
Two-stage CSTR	8.90	68.00	–	35	0.34	7.74	0.147	68.10	[58]
Two-stage CSTR**	6.20	–	–	38	–	–	–	–	[59]
Average	**19.68**	**64.11**	**43.18**	**36.5**	**1.70**	**7.53**	**241.80**	–	**60.68**

Table 3.3: Operational Conditions of IBES and Benchmark AD Process.

1. Operating Parameters for IBES and Benchmark AD Scenario			
CATHODE COMPARTMENT (Fermentation Reactor)			
Parameters	**Values**	**Unit**	**References**
Amount of diluted solution of CW (CW+NaOH)	1.07	t	Calculated
Operating temperature, T	38	°C	[48, 49, 54]
Hydraulic retention time, HRT	1.83	day	[48]
Flow rate of Solution (CW+2M NaOH), Q	0.58	t/day	Calculated
pH	7.5	–	[54]
Organic loading rate, OLR	12.45	kg TOC/m^3·day	[48, 49, 54]
Volume of reactor	1.15	m^3	Calculated
Ti Cathode surface area	0.6	m^2	Calculated
Produced Syngas	4.42	Nm^3 syngas/t CW	[54]
Volumetric ratio of H_2 gas	60.80	%	[54]
Volumetric ratio of CO_2 gas	39.20	%	[54]
ANODE Compartment			
Anolyte (0.5M Zinc Sulphate)	1.073	t	[54]
Anolyte flow rate	0.58	t/day	Calculated
Temperature	Room temp	°C	[54]
Anode Plate	1.32	m^2	calculated
S/V ratio of AEM	1.35	m^2/l	calculated
2. Operating parameters for Benchmark AD Scenario (average data from literature)			
Anaerobic Digestion Reactor			
Reaction mixture (CW+2M NaOH) volume	1.073	t	Calculated
Flow rate	0.053	t/day	Calculated
Organic loading rate, OLR	10.78	kgVS/m^3/day	[55–58]
pH	7.33	–	[55]
HRT	19.49	day	Calculated
Temperature	35.00	°C	[48, 49, 54]
Produced biogas	10.15	Nm^3/t CW	[54]
Volumetric ratio of CH_4 gas	60.69	%	[54]
Volumetric ratio of CO_2 gas	39.31	%	[54]

3.4 Material/Energy Requirements For Anaerobic Process

The process requires the addition of 5.85kg of sodium hydroxide (NaOH) per ton of CW to maintain optimal pH conditions for microbial activity, along with 73.18l of deionized water to support the reaction condition. In terms of energy consumption, electricity usage for transferring the reaction mixture is minimal (0.03 kWh/t.CW), while mixing inside the reactor demands a higher input of 8.22 kWh/t.CW highlighting the importance of proper agitation for uniform conditions to enhance digestion efficiency. The heat energy required for the AD process is also relatively low at 2.48 kJ/t CW, suggesting mesophilic operating temperature.

Table 3.4: Material/Energy Requirements for IBES and AD Process

IBES Process		
Material/Energy	**Values**	**Unit**
Amount of Cheese Whey (CW)	1	t
Amount of Sodium Hydroxide (NaOH)	5.85	kg / t CW
Amount of de-ionized water (H_2O)	1059	kg/t.CW
Anion exchange membrane (AEM)	1.35	m^2/t.CW
Zinc Sulphate ($ZnSO_4$)	86	kg / t CW
Weight of Anode, Zn plate	162.42	kg Zn / t CW
Weight of Cathode, Ti grid	32.13	kg Ti / t CW
Electricity for transferring reaction mixture	0.03	kWh/t.CW
Heat Energy requirement for DF process	2.48	kJ / t CW
Electricity for mixing (cathodic compartment)	0.75	kWh/t.CW
Electricity for mixing (anodic compartment)	0.79	kWh/t.CW
Produced Syngas (H_2 + CO_2)	4.42	Nm^3 syngas/t CW
Anaerobic Digestion Process		
Amount of Sodium Hydroxide (NaOH)	5.85	kg/t CW
Amount of de-ionized water (H_2O)	73.18	kg H_2O / t CW
Electricity for transferring reaction mixture	0.03	kWh / t CW
Heat Requirement for AD process	2.48	kJ/t CW
Electricity for mixing the reactor	8.22	kWh/t CW
Produced biogas (CH_4 + CO_2)	10.15	Nm^3 biogas / t CW

3.5 Model Development

3.5.1 IBES Model

The present inventory data sources for LCA are largely restricted to conventional technologies, and they do not directly incorporate integrated and innovative technological approaches that are emerging and not fully established at industrial scale. As a result, it becomes necessary to adopt a critical and adaptive approach in the development of life cycle models. This involves leveraging and modifying existing data flows from traditional processes to better reflect the novel technological processes that are being investigated. Data from conventional technologies is carefully adapted or supplemented to represent the functionality and outcomes of the innovative approach being modelled for IBES. By applying this critical and systematic approach to data flow modification, the model can simulate the performance of new technology in an accurate and scientifically credible manner, even though the original database does not directly support such innovations. This approach enables the testing of integrated waste treatment technologies in a way that is not reflected in the traditional datasets. They are used as categorized in primary (foreground) and secondary (background) dataset forms. In case where the traditional data flows are insufficient, additional data is sourced from laboratory results or scientific literature to accurately represent the new technology. The Ecoinvent

Table 3.5: Database of AD model in OpenLCA

Flow	Category	Amount	Unit	Provider	Description
Electricity, low voltage {FR} market for | Cut-off, S - Copied from Ecoinvent - IT	Others/Ecoinvent cut-off S copy	8.24	kWh	market for electricity, low voltage - IT	Calculated with a fixed factor per t of input treated
Heat, central or small-scale, other than natural gas {Europe without Switzerland} market for heat, central or small-scale, other than natural gas | Cut-off, S - Copied from Ecoinvent	Others/Ecoinvent cut-off S copy	0.0024	MJ	market for heat, central or small-scale, other than natural gas Europe without S - Europe without Switzerland	Calculated with a fixed factor per m^3 biogas produced
Sodium Hydroxide Solution_2M	1.BESproject/IBES Process Flows	73.18	kg	Sodium Hydroxide Solution 2M - IT	
Whey, at Plant - IT	1.BESproject/IBES Process Flows	1000	kg		
OUTPUT					
Biogas, from anaerobic digestion of biowaste	Anaerobic Digestion	16575	kg		
Carbon dioxide, biogenic	Elementary flows/Emission to air/low population density	1.67×16575	kg		1.67 kg CO_2 per kg CH_4
F. Digestate, from anaerobic digestion of biowaste	Chemicals/Fertiliser (organic)/Digestate	1031	kg		Adapted from "anaerobic digestion of manure CH" with data from Ardolino et al. (2018).
Methane, biogenic	Elementary flows/Emission to air/low population density	$0.1 * 0.609 * 16575 * 1.2$	kg		10% (1–18%) of the methane content of biogas (50.8%) is assumed to be lost to the environment. Density of biogas: 1.2 kg/m^3.

database is one of the most comprehensive and widely used life cycle inventory (LCI) available database, provides an extensive data on materials, energy, emissions, and waste for a wide range of industrial processes and sectors. This supplemental data is then integrated into the existing framework. To ensure that the model captured all relevant aspects of the novel approach, table 3.5, each process is characterized by its inflows, outflows, and the associated environmental emissions. For example, a unit process of producing 2M sodium hydroxide solution comprised with the inputs such as acquiring market for sodium hydroxide and production of de-ionized water datasets. It yields outputs along with their associated environmental impact. Developing a waste treatment process model, the quantity of waste that is going to be treated is set as "Reference flow" of whole model. In IBES model, waste flow of 1ton of CW is the reference flow. All other flows within the processes are interconnected by providing a provider process flows and adding the necessary amounts of materials and energy. This comprehensive approach ensures that every stage and aspects of the IBES process is thoroughly evaluated in terms of its environmental consequences. The OpeLCA software is used in this research for the model development.

3.5.2 AD Model

AD model is developed using the developed inventory during the inventory analysis. For the input and output flows of the AD model, the existing database flows in ecoinvent 3.11 version is modified according to the created scenario. The dataset used is a French dataset of an organic fertilizer's characteristics for a conventional AD plant reported in [56]. The data reported a study on screening LCA of a french organic amendments and fertilizers with an unspecified boundary in emissions in nature. This activity produces biogas and digestate from biowaste. The methane content of the biogas is calculated depending on the substrate input. A new flow is created as waste flow adding the properties of material's contents in CW such as total solids (TS), volatile solids (VS), total organic carbon (TOC), and other organic contents. The electricity demand calculated with a fixed factor per ton of treated waste, and the heat demand is calculated with a fixed factor per cubic meter biogas produced in the given mode. A specific CO_2 emission was assumed as 1.67kg CO_2/kg CH_4 produced. The fugitive emissions were assumed as 10% of the methane content in the total CH_4 produced (60.69% of biogas)[56].

3.5.3 System Expansion

To accurately attributing environmental impacts between multiple outputs of interest, ISO:14044 recommends allocation by distributing the environmental impacts among the different outputs based on their relevant factor. However, where multiple processes combine and represent a single product system ISO:14044 preferences are to avoid allocation by expanding system boundaries (system expansion). The system expansion is applied and the hydrogen produced through IBES is substituted by conventionally produced hydrogen through petroleum refinery and replaced by proper Ecoinvent record "hydrogen production, gaseous, petroleum refinery operation | hydrogen, gaseous | APOS, U". Similarly, the methane produced through AD system is substituted with fossil-derived natural gas, in eco invent dataset "Natural gas, high pressure, at plant/GLO, U". These avoided burdens are subtracted from the outputs in the system allowing the model to capture the environmental credits associated with the displacement of conventional methods.

3.6 Impact Assessment

The product environmental footprint (PEF) method is useful for undertaking environmental footprint studies for a product and is supported by the 2013 recommendation to the european commission (EC) Communication "Building the single market for green products and facilitating better information on the environmental performance of products and organisations [57]. EF version 3.0

method has been developed by the Directorate General Joint Research Centre (JRC) of the EC in close cooperation with the Directorate General for Environment (DG ENV) [58]. The structure of the EF3.0 method for accounting environmental foot printing of a product are five identified key principles; 1) Relevance 2) Completeness 3) Accuracy 4) Consistency 5) Transparency. Based on those principles EF3.0 is categorized into set of fourteen main impact catagories among them climate change (CC), acidification (AC), eutrophication (EU), land use (LU), ozone depletion (OD), particulate matter (PM), photochemical ozone formation (POF), resource usage (fossils, minerals, and metals), and water use (WU) are the associated with nontoxic impact categories. The three categories that addressed toxicity-related impacts are freshwater ecotoxicity (ETf), human toxicity cancer (HTc), and human toxicity non-cancer (HTnc)[59]. The number of inventory results parameters can range from a few dozens to hundreds, making the output of the study difficult to understand. Each flow's impact is classified into their relevant impact category (i;e climate change, eutrophication) in different environmental compartments (i;e soil, air, water) according to their environmental load. Each flow can also have multiple impacts in more than one impact category, for example, an emission of NOx can be assigned to acidification and eutrophication category and even to photochemical oxidation potential, given the nature of this pollutant. Then the amount of each flow is multiplied by their respective characterization factors (pre defined values set in impact assessment model) which are based on the possible environmental consequences of all inventory flows (inputs and outputs), such as carbon dioxide, nitrogen oxides, and sulphur dioxide emissions[60]. In accordance with FU. This results into changing the flow's quantity in a standardized unit that represents its impact potential. The associated CO_2 emissions/t.CW are multiplied by its characterization factor 1kg CO_2 equivalent/kg.CO_2 emissions, for instance, since 1kg CO_2 emission has characterization factor of 1kg CO_2 equivalent. This provides the emissions as per FU (kg $CO2$ eq./t CW). The implications of each material, energy, and waste flow measurement are specified by these indicators. A definition of "characterization" and "characterization factor" refers to the calculation of the magnitude of the contribution of each classified input and output to their respective impact categories" and "aggregation of the contributions within each category". This is carried out by multiplying the inventoried values by the relevant characterization factor for each impact category considered. The characterization factors are substance or resource-specific. They represent the impact intensity of a substance relative to a common reference substance for an impact category and used to calculate the relative impact category indicator.

3.7 Results and Discussion

This section presents the environmental impacts as assessed according to the adapted EF3.0 method. The results expressed per functional unit (1t of CW) are reported in table3.6, for the two main scenarios, IBES and benchmark AD unit processes. Results indicate that IBES exhibits higher freshwater ecotoxicity due to inorganic and metal pollutants, suggesting potential risks to aquatic ecosystems. It's resource demand is also notable with substantially higher fossil energy use (2.25E+02MJ) and water consumption (3.61E+01m^3) compared to AD indicating challenges in resource sustainability especially in water-scarce regions. This indicates based on the considered inventory of the use of material and energy, for example, the production process of zinc monosulphate, market of sodium hydroxide and de-ionized water production gains significant impacts. This underscores the need for careful management of resource use and pollutant mitigation to fully realize IBES potential as a sustainable hydrogen production method. Therefore, even though the suggested procedure is novel, it must be improved to compete with a more conventional management alternative in terms of environmental impacts 3.5 and 3.6.

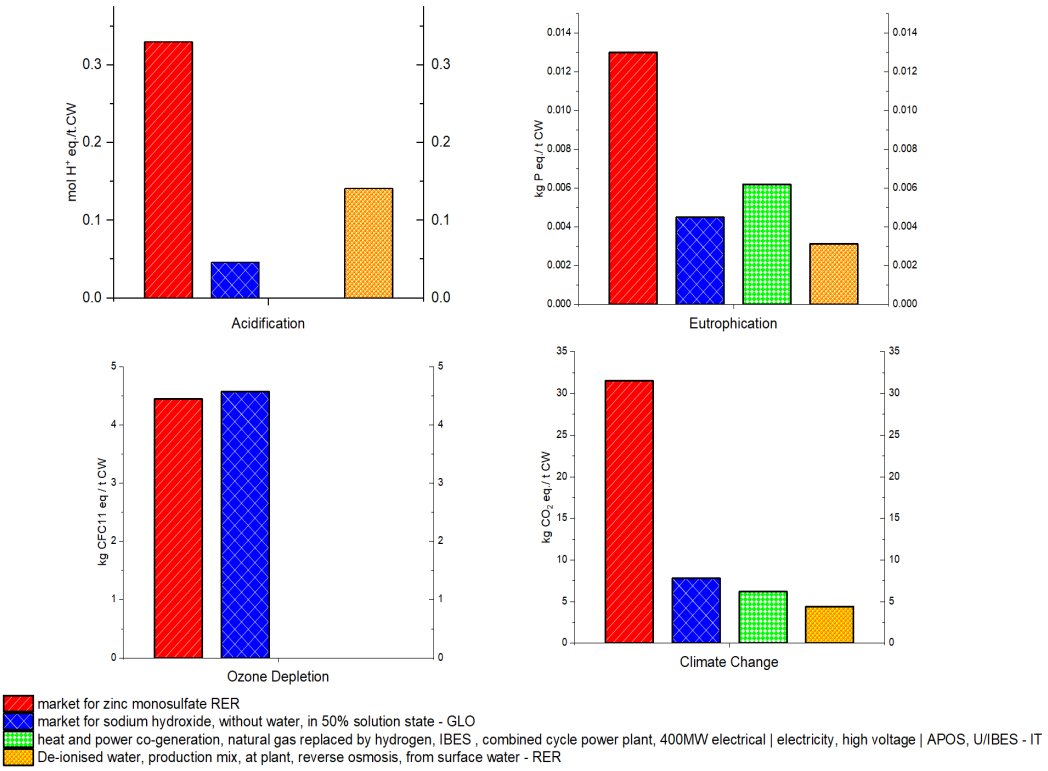

Figure 3.5: Contribution of main flows of IBES process in high impact categories; acidification, eutrophication, climate change and ozone depletion in their relevant environmental compartments.

In fact, IBES Scenario's higher environmental impact is caused by its higher energy and material

Table 3.6: Impact Assessment results of IBES and AD Process

Name	**Unit**	**Impact assessment result**	
		AD	*IBES*
Acidification	mol H^+ eq/t CW	4.98E-02	3.84E-01
Climate change	kg CO_2 eq/t CW	2.02E+04	2.94E+01
Climate change - Biogenic	kg CO_2 eq/t CW	2.02E+04	8.47E-02
Climate change - Fossil	kg CO_2 eq/t CW	8.43E+00	2.93E+01
Climate change - LU change	kg CO_2 eq/t CW	1.21E-02	2.35E-02
Ecotoxicity, freshwater	CTUe/t CW	3.81E+02	8.16E+02
Ecotoxicity, freshwater - inorganics	CTUe/t CW	2.83E+01	8.87E+01
Ecotoxicity, freshwater - metals	CTUe/t CW	1.66E+02	7.27E+02
Ecotoxicity, freshwater - organics	CTUe/t CW	1.91E+02	9.19E+00
Eutrophication, freshwater	kg P eq/t CW	4.75E-03	1.78E-02
Eutrophication, marine	kg N eq/t CW	9.78E-03	4.11E-02
Eutrophication, terrestrial	mol N eq/t CW	1.03E-01	4.56E-01
Human toxicity, cancer	CTUh/t CW	4.22E-09	2.48E-08
Human toxicity, cancer - inorganics	CTUh/t CW	0.00E+00	-2.53E-09
Human toxicity, cancer - metals	CTUh/t CW	2.92E-09	1.79E-08
Human toxicity, cancer - organics	CTUh/t CW	1.31E-09	3.85E-09
Human toxicity, non-cancer	CTUh/t CW	2.81E-05	1.28E-05
Human toxicity, non-cancer - inorganics	CTUh/t CW	2.28E-05	3.17E-05
Human toxicity, non-cancer - metals	CTUh/t CW	1.52E-07	1.27E-05
Human toxicity, non-cancer - organics	CTUh/t CW	2.79E-05	9.96E-09
Ionising radiation	kBq U-235 eq/t CW	3.63E+00	4.26E+00
Land use	Pt/t CW	2.70E+01	8.44E+00
Ozone depletion	kg CFC11 eq/t CW	4.87E-06	3.85E-07
Particulate matter	disease incid./t CW	3.73E-07	1.62E-07
Photochemical ozone formation	kg NMVOC eq/t CW	6.03E+00	8.57E-03
Resource use, fossils	MJ/t CW	1.55E+02	7.00E+01
Resource use, minerals/metals	kg Sb eq/t CW	3.93E-05	1.24E-05
Water use	m^3 depriv./t CW	8.08E+00	3.51E+01

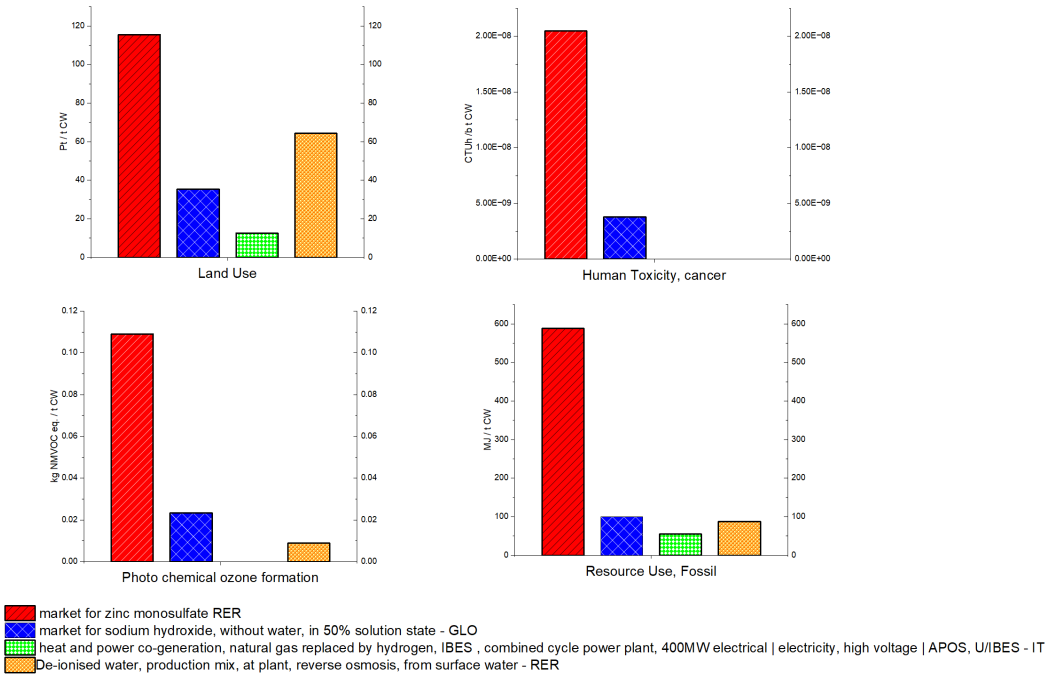

Figure 3.6: Contribution of main flows of IBES process in high impact categories; human toxicity cancer, photochemical ozone formation, resource use and land use in their relevant environmental compartments.

consumption in comparison to the benchmark AD Scenario. However, IBES performed significantly better than AD in terms of climate change impact and photochemical ozone formation offers clear benefits in air quality improvement. Thus, IBES process although offers operational and functional advantages over conventional AD (e.g., higher energy recovery or better waste treatment efficiency) but these benefits are not reflected in the impact assessment which focuses solely on environmental burdens. Including functional performance or process wise metrics provide a more balanced and meaningful comparison. The significantly higher contribution of IBES in categories; freshwater eco toxicity, and resource use raise questions about the reasons behind these impacts possibly caused by some specific material and energy flow, for example, in eco toxicity (freshwater), emissions of aluminum and zinc from zinc mono sulfate production are key contributor particularly through air and soil pathways. These emissions represent substantial toxicological burdens on aquatic ecosystems with chloride emissions to water further enhancing the impact. Similarly, the sodium hydroxide production and market process contributes to eco toxicity due to use of aluminum and chloride, although the associated emissions of aluminum and chloride are less impactful compared to those of zinc mono sulfate. Also, the zinc mono sulfate from production process of zinc sulfate solution exhibits heavy reliance on non-renewable resources, with natural gas, crude oil, and coal as primary contributors, reflecting its high fossil energy demand. The sodium hydroxide flow while less intensive still draws significantly on coal and natural gas resources and indicating a non-negligible

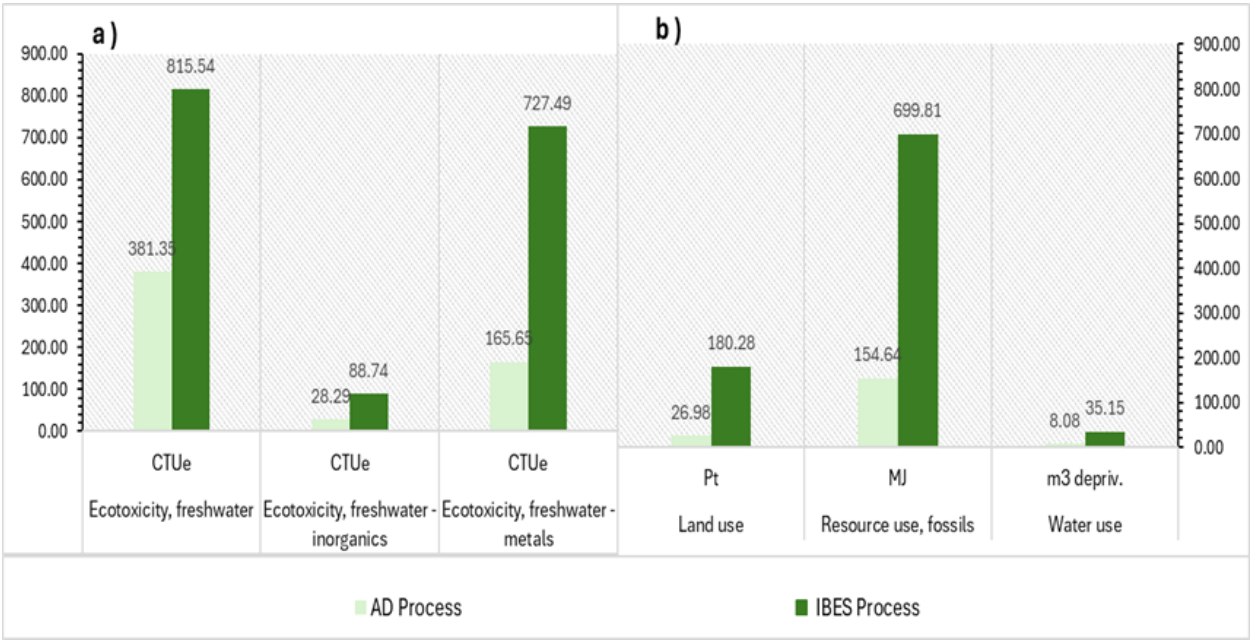

Figure 3.7: Comparative environmental impacts of the AD and IBES processes: (a) ecotoxicity indicators including freshwater ecotoxicity, ecotoxicity from inorganics, and ecotoxicity from metals (measured in CTUe); (b) land use (Pt), fossil resource use (MJ), and water use (m^3 deprivation). The IBES process shows significantly higher impacts across all categories compared to the AD process

depletion of fossil reserves. The de-ionized water production process demonstrates significant surface water consumption, a concerning aspect of its environmental footprint. However, this is partially mitigated by a net replenishment effect observed from river water use, which offsets some water deprivation impacts. Based on above results, there is crucial need for targeted interventions to address resource inefficiencies and emission hot spot, particularly for zinc monosulfate production, while also recognize the potential opportunities for improvement in water resource management.

3.8 Conclusion

The comparative Life Cycle Assessment (LCA) of the Integrated Bio-Electrochemical System (IBES) and the benchmark Anaerobic Digestion (AD) process highlights the dual nature of emerging hydrogen production technologies: while they offer important opportunities for innovation and climate mitigation, they also introduce new sustainability challenges. The analysis shows that IBES provides promising advantages in certain environmental categories, yet it also generates notable drawbacks that cannot be overlooked if the technology is to become a realistic alternative to conventional systems. A central finding of this study is the superior performance of IBES in terms of climate change mitigation and photochemical ozone formation. These benefits are primarily linked to the higher hydrogen yields achievable through the combined biological and electrochemical process. By capturing additional protons released during dark fermentation and converting them into hydrogen, IBES

produces more energy per unit of organic waste than traditional AD. As a result, greenhouse gas emissions per functional unit are reduced, and the potential for photochemical smog is minimized. These results suggest that IBES could play a significant role in future low-carbon energy systems, particularly where reducing greenhouse gas emissions is a priority. At the same time, the environmental profile of IBES is challenged by significantly higher burdens in other impact categories, most notably freshwater eco toxicity, fossil energy demand, and water use. These negative outcomes stem from upstream processes that supply critical materials and inputs to the IBES system. The potential emission of zinc monosulfate, sodium hydroxide, and de-ionized water introduces toxic emissions, high fossil resource consumption, and heavy water demand into the life cycle of IBES. For example, zinc and aluminum emissions from zinc monosulfate production contribute disproportionately to freshwater eco toxicity, threatening aquatic ecosystems. Similarly, reliance on fossil fuels for sodium hydroxide production places additional pressure on non-renewable energy sources, while the production of de-ionized water consumes large amounts of freshwater, which could become problematic in water-scarce regions. These trade-offs underline a key challenge in developing next-generation hydrogen technologies: the environmental gains from improved performance must not be offset by increased burdens elsewhere in the system. While IBES shows technological and functional promise, its sustainability performance remains uneven. Addressing these weaknesses requires targeted interventions. Substituting zinc-based materials with environmentally benign alternatives, optimizing processes to reduce chemical consumption, and integrating renewable energy into input production could significantly lower IBES's overall footprint. Similarly, improved water resource management strategies—such as closed-loop water systems or the use of lower-quality water for certain processes—would help mitigate the pressure on freshwater resources. From a broader perspective, IBES also provides functional and operational advantages that may justify continued research and investment. The system not only generates higher hydrogen yields but also facilitates the valorization of organic waste streams, offering synergies with waste management and circular economy strategies. Its galvanic cell design provides the potential for decentralized, self-sustaining energy recovery, which could be particularly valuable in regions without access to centralized infrastructure. These qualities extend the value of IBES beyond its immediate environmental impacts, pointing to its role in integrated resource recovery systems. Nevertheless, the findings of this study make it clear that IBES is not yet ready to replace AD at scale. Conventional AD remains more environmentally robust in several impact categories, reflecting its maturity, optimization, and lower reliance on specialized chemicals and materials. For IBES to achieve technology readiness as AD process, further innovation is required. Advancements in material science, the development of low-impact electrode and electrolyte alternatives, and improved integration with renewable energy sources will be central to reducing its environmental footprint.

In conclusion, IBES represents an innovative and promising pathway for sustainable hydrogen production, but it remains an emerging technology with significant areas for improvement. Its ability to enhance hydrogen yields and reduce greenhouse gas emissions is encouraging, yet the environmental burdens associated with its inputs highlight the need for careful system design and targeted interventions. Future research should focus on scaling up laboratory and pilot studies to industrial contexts, assessing long-term performance under real conditions, and exploring circular strategies to minimize toxic emissions and resource depletion. By systematically addressing the identified challenges, IBES has the potential to evolve into a viable contributor to the renewable hydrogen economy. With continued innovation, integration into circular resource management frameworks, and adoption of cleaner input pathways, IBES could complement or even surpass conventional AD in sustainability performance. Ultimately, this technology could support global efforts toward climate neutrality, resource efficiency, and the transition to a more resilient and sustainable energy system.

Chapter 4

Life Cycle Assessment of Integrated Waste Biorefinery

4.1 Introduction

Utilizing integrated bio electrochemical method with post treatment processes in a waste biorefinery (Figure 4.1) relies on the appropriate combination of several process chains (e;g fermented whey valorization, syngas upgrading) to improve the overall process performance. The aim is in fact to achieve the environmental benefits is a comprehensive approach towards maximum energy recovery and comprehensive waste management. In contrast to conventional biorefineries which frequently manage energy generation and waste treatment in conventional ways, the so called integrated biorefinery (IBR) approach combine a novel microbial fuel cell process and a post-treatment of the generated effluent, as well as the upgrading of produced syngas with primary focus on carbon capture and utilization. The syngas upgrading process separate energy-rich H_2 gas with Carbon capture and storage. The hydrothermal treatment convert byproduct into biochar while the IBES effectively transforms organic waste into valuable syngas with other byproducts. The IBES process plays a central role in the suggested scheme of IBR by converting organic-rich waste streams such as cheese whey (CW) into hydrogen through a combination of dark fermentation and electrochemical cell. Post-treatment processes further enhance system performance. Hydrothermal treatment of fermentes cheese whey provides recovery of nutrients after fermentation process while minimizing disposal related impacts. Similarly, syngas upgrading integrated with carbon capture and utilization (CCU) technology facilitates the recovery of high-purity hydrogen from gaseous product while simultaneously reducing greenhouse gas emissions through carbon capture process. Together, these processes enable the biorefinery to operate as a closed loop system that transform waste stream into valuable bioproducts while addressing climate and resource sustainability challenges.

The Life Cycle Assessment (LCA) of the proposed IBR process provides a comprehensive evaluation of the environmental consequences of integrating IBES with digestate treatment and syngas upgrading. By analyzing energy and material flows across the entire system, LCA identifies the trade-off and benefit of combining these processes into a unified scheme. The results are crucial for understanding how integrated designs can minimize environmental burdens, optimize resource use, and enhance the overall sustainability of hydrogen production pathways. This chapter therefore explains the application of LCA to the integrated biorefinery process (Figure 4.1), focusing on how the combined operations contribute to reducing emissions, improving energy recovery, and supporting the transition toward climate-neutral energy systems. The LCA application to the proposed process scheme of IBR, Figure 4.1, is explained in this chapter. This analysis resulted into the identification of moderate environmental burdens while optimizing energy and material recovery by combining multiple integrated operations.

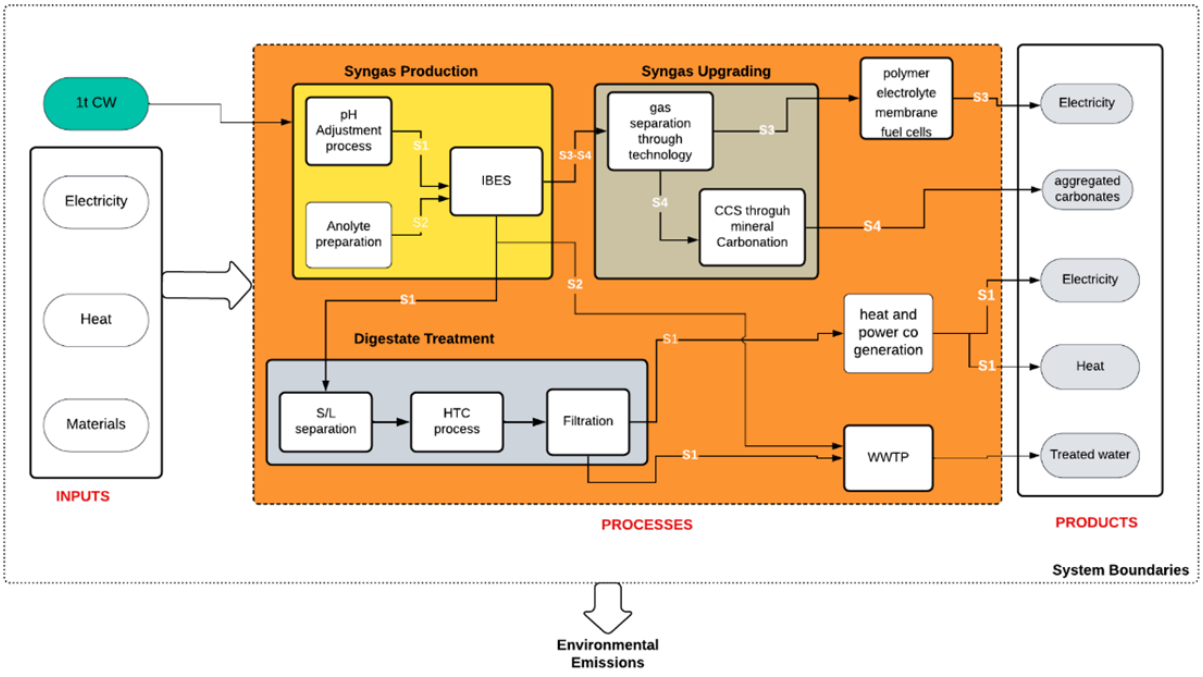

Figure 4.1: System boundaries of the proposed integrated waste bio refinery

4.1.1 Upgrading of produced syngas with special focus on Carbon Capture and Storage

Hydrogen produced through IBES contains non-combustible gases, e.g. biogenic CO_2. In a hydrogen-based economy, producing hydrogen with ultra-high purity (>99.95 %) is crucial, as outlined in the ISO 14687–2025 standard (ISO 14687). Therefore, hydrogen enrichment and upgrading are just as critical as its production. It is important to note that hydrogen can be utilized as an energy fuel

in specific applications, such as fuel cells, when its purity is around 99.99%. Although no studies have yet documented the upgrading of hydrogen gas produced from the DF process, but hydrogen produced through other conventional techniques has been subjected to various physical and chemical upgrading methods. Physical techniques involve pressure swing adsorption (PSA), temperature swing adsorption (TSA), Cryogenic and membrane separation techniques are generally considered established technologies in various chemical and Petro chemical refineries[61]. In membrane separation technology, hydrogen-selective membranes are engineered in which primary species in the permeate is hydrogen and the remaining components of the gas mixture remain in the retentate[62] . Hydrogen selective membranes are used in various applications where high-purity of hydrogen is required such as in fuel cells . Based on the material used, hydrogen selective membranes are broadly categorized into four types: (i) polymer (ii) metallic (iii) carbon (iv) ceramic (Table 4.1). The metallic, carbon, and ceramic are known as inorganic membranes while polymer membranes are organic. Inorganic membranes can be further classified into two groups based on raw material used: metal membranes and ceramic membranes. Additionally, they are divided into porous (mesoporous and microporous) and nonporous (dense) membranes[63] . Microporous inorganic membranes are prepared as thin films supported on a porous inorganic base. Dense inorganic membranes are typically made from polycrystalline ceramics or metals. Dense ceramic membranes, including perovskite, bismuth oxide, and solid-electrolytes are developed and commercialized now [64]. A self-supporting dense metallic membranes particularly those based on palladium (Pd) and with a thickness greater than 0.1mm have become unattractive for hydrogen separation due to their high cost, low permeance, and low chemical stability [65]. As a result, dense inorganic membranes are usually prepared as thin films on porous medium which provide mechanical support with minimal mass resistance. Due to this, gas separation using polymer membranes is a preferable technology with good ability to cope up with high pressure drops and low cost that makes key advantages of use of polymer membranes in hydrogen purification process. The performance of a membrane can be discussed in terms of flux (or permeance) and selectivity. The flux is the total transport of material through the membrane and can be expressed as mass or mole per unit time per unit area. Similarly, permeance is defined as the flux per unit pressure difference between upstream (retentate) and downstream (permeate) sides [66].

4.1.2 Hydrothermal Carbonization (HTC) of Fermented Cheese Whey

As mentioned in earlier in Chapter 3, a significant portion of the carbon associated with initial substrate (CW) during DF remains in the fermented cheese whey thus the potential energy content of the organic waste stays in the effluent of IBES at the end of the process in the form of metabolites

(e.g. VFAs and alcohols) which implies further treatment. The characteristics of the fermented cheese whey is mentioned in table 4.6. To maximize the net benefit of the entire multistage process a treatment of the DF effluent is focused for the maximum resource recovery and to reduce the pollutants in the final effluent. The hydrothermal carbonization process is an attractive option that effectively densify the nutrient in organic waste without the need for a prior drying process. In hydrothermal carbonization, process a series of hydrolysis, condensation, decarboxylation, and dehydration reactions correspond [67]. Three products are obtained at the end of HTC process: solid hydrochar, aqueous chemicals, and gases [68]. The gas product which mostly consists of CO_2 from 1-3% of the raw material [69]. After HTC process, the aqueous solutions are then filtered to remove the nutrients, thus nutrients rich liquid as second product of the HTC. Their main constituents include organic acids, sugar, and inorganic salts. Because of thermal treatment, the third product of HTC is hydrochar a homogenized, carbon-rich, and energy-dense solid fuel [70] .

4.2 The Framework

4.2.1 Goal and Scope Definition

The goal of life cycle assessment in this chapter is to determine how the waste biorefinery approach particularly IBES with multiple integrated post processing phases work together to achieve the following collective goals such as:

- Upgrading H_2 rich biogas with CCS using alkaline residual waste stream: stage 2 of the proposed scheme, **Chapter 3**.
- HTC treatment of digestate of cathode compartment of the IBES: Stage 3 of the proposed process scheme, **Chapter 3**.

4.2.2 System Boundary

System boundaries include:
Production of syngas with additional benefits of electricity generation in IBES process. Then upgrading of syngas; H_2 gas separation from gas mixture using membrane adsorption process and CCS using alkaline industrial residual waste via carbonation process. The hydrogen gas is used in polymer electrolyte membrane fuel cells (PEMFCs) for electric power generation in electric vehicles and carbon from CO_2 stream is permanently stored in form of carbonated mineral aggregates. Effluent of IBES is further treated to produce hydrochar through HTC process. Then hydrochar is used in a combined heat and power plant (CHP) for energy provision. The generated liquid wastes in each step are sent to the conventional wastewater treatment plant. All inputs raw materials,

chemicals, fuels, and energy as well as emissions and resource use, are considered within system boundaries.

Upstream impact of the IBES include materials and chemicals used as inputs and modelled using the ecoinvent flows such as "Sodium hydroxide, 2M, RER", "Zinc sulphate solution, 0.5M, RER", "Titanium grid, cathode production, RER", "Zinc plate, anode production, RER", "Anode production, for zinc, RER", "Sodium sulphate, RER", and "Ion exchange membrane, RER". These flows required to create IBES scenario for syngas and hydrogen generation. The syngas is upgraded through "Membrane separation for H_2 purification is modelled using the eco invent flow "Polymer membrane, Polysulfone of high H_2/CO_2 selectivity, gas purification at Industry" in dataset. The hydrogen is used in power converter process in polymer electrolyte membrane fuel cells (PEMFC) using ecoinvent record "polymer electrolyte membrane, 2kW electrical, future | fuel cell, polymer electrolyte membrane, 2kW electrical, future | APOS, U". This electricity generated from hydrogen as fuel is credited by substituting "Electricity, low voltage, IT".

The fermented CW undergoes solid liquid separation phase after HTC process. The recovered solid part (hydrochar) is first dried then used in a coal-based CHP system modelled using "heat and power co-generation, hard coal | heat, district or industrial, other than natural gas | APOS, U", for the generation of heat and electricity both. These energy outputs of CHP system are credited by substituting "Heat, district or industrial, natural gas, IT" and "Electricity, low voltage, IT", respectively.

All the flows are allocated by following the system expansion via substitution method (avoided burden approach) in existing dataset in allocation tab of OpenLCA software. The useful co-products such as electricity, heat, hydrogen, are credited and modified by replacing conventionally available italian datasets, that are effectively avoiding their environmental burdens. Additionally, the system includes CO_2 mineral carbonation representing a permanent carbon capture and storage (CCS) step which avoids the release of biogenic CO_2. Wastewater generated during each process is handled through wastewater treatment plant using eco invent database record: wastewater treatment, at wastewater treatment plant, industrial wastewater according to the Directive 91/271/EEC concerning urban wastewater treatment, slightly organic and inorganic contaminated. The impact associated with infrastructure (construction, machinery, buildings) are explicitly excluded.

4.3 Inventory Analysis

4.3.1 Inventory of Process of Separating H_2 gas from Syngas Using Membrane Technology

Following the syngas production phase within the IBES, produced hydrogen goes to the purification process with the process condition mentioned in table 4.2. The syngas is then fed into the gas separation unit that includes the polymer membrane module, typically consists of a feed gas inlet, permeate (hydrogen-rich) gas outlet, and retentate (CO_2 gas) outlet. The hydrogen-selective membrane, the goal is to exploit the high diffusivity of the hydrogen molecule and to limit the effect of the lower solubility. As hydrogen is one of the smallest gas molecules, but it also has a much lower critical temperature than most of the other gases. The small size of the hydrogen molecule gives hydrogen its high diffusivity. However, the significantly lower critical temperature suggests that the condensability and hence the solubility of the hydrogen is going to tend to be much lower. The membrane module involves (figure 4.2) two main stages: gas compression and separation. The inflow pressure required for the physical adsorption of hydrogen gas is 10bar [71] . The optimization of internal pressure in multistage compressor required intercooling, is described by Lugo et al. in which the authors note that "for design purpose and to approach the lowest energy consumption, the compression ratio is split in two or more stages, cooling the compressed gas in between. This approach minimize the work required for compression and is particularly beneficial when dealing with high pressure ratios [72]. When high compression ratio >2 is needed, the compression is typically performed in multiple stages with intercooling between stages [72]. This approach offers significant power savings and help to maintain the hydrogen gas temperature after each compression stage [73]. The required pressure of hydrogen gas is 10bar. The hydrogen gas is initially compressed from 1bar (atmospheric pressure) to 3.5bar in the first compressor, and then from 3.5bar to 10bar in the second compressor. After the first stage of compression, the hydrogen gas temperature rises from 311.15K to 448K. To ensure the gas temperature is within the permissible durability range of polymer membrane, the intercooling is required to prevent membrane breakage. For this purpose, the gas temperature is reduced back to 311.15K before it enters the second compression stage. The compressed gas at 3.5bar is then passed to the second compressor, achieved the required discharge pressure of 10bar required for the membrane adsorption process. The compression ratio is maintained at 1:3.5:10 to achieve the necessary pressure [73]. The compressed gas stream than passed through the H_2 gas selective polymer membrane allows hydrogen molecules to permeate across membrane walls. Gas transport through polymer membrane typically occurs via solution diffusion mechanisms. The gas molecules dissolve into the membrane material on the high-pressure side. The dissolved gas molecules then diffuse through the membrane material to the low-pressure side. The

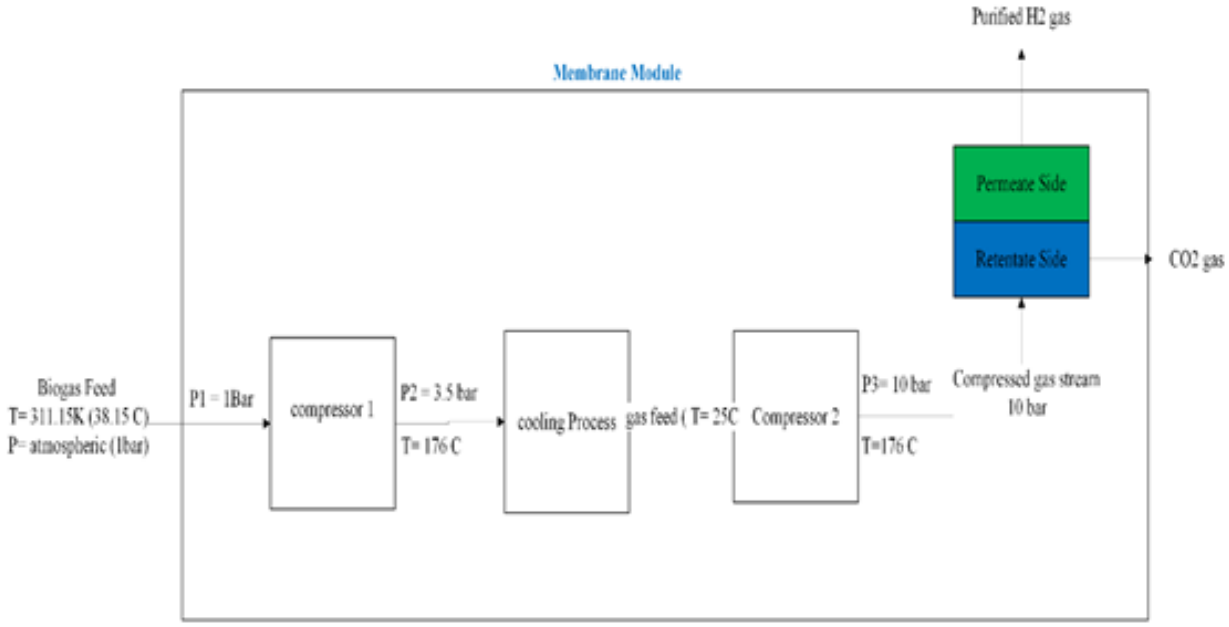

Figure 4.2: Membrane Module for Hydrogen Purification from Syngas produced in IBES

gas molecules desorb from the membrane material on the low-pressure side [74].

Table 4.1: H_2 permeability and selectivity for different polymers

Polymer	**H_2 Permeability** (Barrer)	**Selectivity** (H_2/N_2)	**Selectivity** (H_2/CH_4)	**Selectivity** (H_2/CO_2)
polysulfone	12.1	15.1	0.3	2.0
polystyrene	2.0	3.8	39.7	29.8
polymethyl methacrylate	2.4	2.0	4.0	4.0
polyvinylidene fluoride	2.4	3.4	1.8	2.0

Note:1 Barrer $= 10^{-10}$ ***cm^3 (STP)cm/(cm^2.s.cmHg), where STP=standard temperature and pressure***

The standard assumed process conditions (table 4.2) are applied. The demonstrated recovery rate is through the analysis of a conventional membrane-based and hybrid multi-configuration systems for purifying hydrogen from ammonia steam reforming and fuelling stations recovery rate and purity of 99.5%.

Energy Requirements Thermodynamic power calculations for multistage compressors with intercooling can be performed using the isentropic model based on several assumptions[75]. This model helps to determine the efficiency and power requirement for compression. The power required for a single stage compressor is calculated using a formula based on the gas constant, efficiency, and pressure ratios.

$$P_{\text{single stage}} = \left(\frac{k}{k-1}\right)\left(\frac{Z}{\eta_{\text{isen}}}\right) T_{\text{suc}}\, q_m\, R \left[\left(\frac{P_{\text{disc}}}{P_{\text{suc}}}\right)^{\frac{k-1}{k}} - 1\right] \tag{4.1}$$

where,

k = ratio of specific heat under constant pressure to the ratio of specific heat under constant volume, Cp /Cv 1.41 (Hydrogen)

Z= Average compressibility Factor typically in the range 1.0 - 1.4 For Hydrogen

$T_{suc} = Suction/InletTemperature, 311.15K$

$Tdis = Discharge/outletTemperature, 448K$

P_{suc} = Suction / Inlet Pressure, 1bar

P_{dis} = Discharge / outlet Pressure, 3.5Bar

R = Universal gas constant, 8.314 J/mol. K

q_m = Molar Flow Rate of gas, 3.24 moles/sec.

The isentropic efficiency of the compressor is set at 75%, and the gas-specific constant, k, is 1.41 (dimensionless). The gas compression begins at a suction pressure (Psuc) of 1bar and is compressed to a discharge pressure (Pdisc) of 3.5bar. The temperature at suction is 311.15K, and the discharge temperature (Tdis) is 448K. The compressibility factor (Z) is 1, and the gas flow rate (qm) is 3.24 moles/sec [76, 77]. With these parameters, the energy required for a single stage compressor is calculated to be 75.24 kJ. Given that the system includes two compressors, the total energy required for compression is 33.76kJ. This translates to an electricity consumption of 0.0093kWh. After compression, the gas undergoes to inter-cooling process to reduce its temperature before membrane (table 4.3). The energy required for this cooling is calculated using the specific heat capacity of the gas (14,300J/kg/K), the mass flow rate of 3.78 kg of biogas, and a temperature difference (ΔT) of 137K (the difference between the discharge temperature and the cooling temperature of 311.15K). The energy required for inter-cooling is 7400.76kJ, which corresponds to an electricity consumption of 2.06kWh.

$$Q = m \cdot C_p \cdot \Delta T \tag{4.2}$$

Table 4.2: Operating Parameters of Polymer Membrane

Operating Parameters	**Values**	**Unit**	**References**
Pressure ratio	10	bar	[78]
Temperature	311.15	K	[79]
Feed gas flow rate	3.24	mol/sec	[80]
Recovery percentage of polymer membrane	99	%	[81]
Hydrogen gas recovery	2.68	Nm^3	-

Additionally, vacuum energy is required at the permeate side of the system to maintain pressure. The energy required for this process is 27.46 kJ/mole/sec. which results in a power consumption of 0.0076 kWh. This data provides a comprehensive view of the energy demands for compressing and

cooling hydrogen in a multi-stage compressor system, ensuring efficient energy utilization throughout the process. The energy requirements for a membrane module are shown in table 4.6.

Table 4.3: Operating Parameters in syngas Compression and the energy Consumption

Parameters	**Values**	**Unit**	**References**
Number of compressors	2	-	[81]
Efficiency of compressor	75.00	%	[82]
Energy required for single compressor	75.24	kJ	[83]
Total Energy for both compressors	33.76	kJ	[82]
Electricity consumption	0.0093	kWh	calculated
Mass flow of material, m	3.24	mol syngas/sec	calculated
Specific heat capacity of material, Cp	14300	J/kg/K	calculated
Required cooling temperature, T_{cool}	311.15	K	[84]
Difference in Temperature discharge at compressor 1 and cooling temperature, $\Delta T = (T_{disc} - T_{cool})$	137	K	-
Reaction time, HRT	34.55	minutes	[85]
Energy requiremet for inter cooling	7400.76	kJ/Nm^3 syngas	calculated
Electricity consumption (kWh)	2.06	kWh/Nm^3 syngas	calculated
H_2 gas recoveralsy	98	%	calculated

Table 4.4: Parameteric conditions of Hydration process

Parameter	**Value**	**Units**
Amount of Binder	3.158	L/kg CO_2
Liquid-to-Solid (L/S) Ratio	0.24	l/kg
Particle Size (D50)	1.00	mm

4.3.2 Inventory of Mineral Carbonation process for Carbon Capture and Storage (CCS) Using Alkaline Industrial Residual Waste

The separated CO_2 gas is assumed to be utilized in a rotary drum type reactor during mineral carbonation process. The types of alkaline residues reported in previous literature for CO_2 storage includes steelmaking slags, residues from thermal treatment processes like biomass ash, ash from oil and lignite combustion, waste incineration byproducts such as bottom ash and air pollution control (APC) residues, as well as byproducts from cement and paper production contains a variety of metal oxides, including alumina (Al_2O_3), calcium oxide (CaO), and iron oxide (Fe_2O_3) and useful to store in form of carbonated aggregates [87, 90, 91].

Assuming the circulating fluidized bed combustion (CFBC) residual characteristics mentioned in table 4.7, with a particle size (D50) of 1.00mm and an optimal liquid-to-solid (L/S) ratio of 0.24 litter per kilogram of residues, a dense slurry prepared before starting carbonation reaction. To form a slurry in the reactor, deionized water is added together with the residues in a controlled conditions

Table 4.5: Parametric Conditions of CO_2 Capture and Storage through Mineral Carbonation Process

Parameter	Value	Units	References
Reactor Type	Rotary drum	-	[86]
HRT	30	min	-
Temperature	30	°C	-
Pressure	3	bar	[86]
CO_2 Concentration in Feed	100	%vol	[86, 87]
Gas Pressure	1	bar	[87, 88]
CO_2 Flow Rate	0.110	kg CO_2/min	calculated
Gas Feeding Time	30	min	[89]
Solid Feeding Time	30	min	-
Input Flow of Solids	1.45	kg/min	-
Steam Feeding Time	30	min	-
Input Flow of Liquid	0.35	l/min	-
CO_2 Uptake	0.076	gCO_2 uptake/g residue	calculated
Carbonated Residues Produced	43.47	kg residue	calculated

Table 4.6: Energy consumption in CO_2 Capture and Storage through Mineral Carbonation Process

Process Stage	Energy per Unit CO_2	Total Energy Required
Gas Compression	83.42 kJ/kg CO_2	275.62 kJ
Reactor Heating	1263.52 kJ/kg CO_2	4174.86 kJ
Reactor Rotation	31.14 kJ/kg CO_2	102.89 kJ

for 10 minutes at 30 °C and 3bar of pressure [89]. Then CO_2 is introduced with concentration of 100 by volume and a flow rate of 0.06 m^3 CO_2 /min. The total gas feeding time is assumed 30 minutes, but it can be varied with the gas composition when the process will carry out in real.

Table 4.7: Alkaline Industrial Residual waste Composition

Element	Amount in Residual waste (kg/kg Ash)	Oxides	Amount in residual waste (g/kg)
Al	0.035	Al_2O_3	0.1338
Ca	0.298	CaO	0.418
Fe	0.029	Fe_2O_3	0.0843
K	0.012	K_2O	0.0298
Mg	0.024	MgO	0.0402
Si	0.082	Na_2O	0.0075
Ba	0.003	SiO_2	0.1762

All the process parameters of hydration process are mentioned in table 4.4, and for carbonation process is mentioned in table 4.5. In much published research the reaction conditions are maintained at 60°C to maximum optimize CO_2 uptake. Following a curing period of 28 days, the carbonation final product is expected to exhibit an inorganic carbon concentration of 0.83% and a total carbon content of 2.7%. The carbonation efficiency, based on CO_2 uptake, is calculated at 0.076 kg of CO_2 per kilogram of residue with a total CO_2 uptake of 3.30 kg [89, 92, 93]. This process results in the production of 13.16kg carbonated residue per kg CO_2 uptake can be used in construction or other applications effectively saving the carbon in a stable form.

Energy Requirements

The energy requirements for carbonation process involves gas compression, reactor heating, and reactor rotation. Energy requirements are calculated based on a standard energy consumption available in previous literature (mentioned in table 4.6) .

4.3.3 Inventory of Utilizing Purified H_2 gas in Polymer Electrolyte Membrane Fuel Cell (PEMFC) for Energy Provision

The H_2 gas produced by IBES, $2.41m^3$ of H_2 purified gas/t.CW is fed into the Polymer Electrolyte membrane fuel cell PEMFC serve as the primary fuel for energy production. In the PEMFC, H_2 gas enters the anode side of the cell, where it is split into protons and electrons by a catalyst, protons pass through the polymer electrolyte membrane while the electrons are forced to travel through an external circuit generating electricity and water as final product. The reaction occurs in a PEMFC is given as:

$$2H_2 + O_2 -> 2H_2O + Energy(-572\ kJ) \tag{4.3}$$

For every two moles of hydrogen the amount of of heat released is then equal to -572kJ. Hydrogen has value of 143 kJ/g. The ecoinvent database reported an efficiency of PEMFC equal to 87% indicating that 87% of the hydrogen's inherent energy is converted into usable electrical energy. Under this conditions, the energy produced in the fuel cell is derived by multiplying the inherent energy content of hydrogen by the efficiency, this resulting in a total energy production of 29858.4 kJ/t CW when utilizing H_2 gas in PEMFC.

4.3.4 Inventory of Hydrothermal Treatment of Effluent of IBES

After the electrochemical and biochemical degradation of the cheese whey (CW) the fermented cheese whey (FCW) solution is assumed to be sent to the Hydrothermal Carbonization (HTC) process.

Table 4.8: Characteristics of FCW

Parameters	**Amount**	**Unit**
Total wet weight of FCW	993.32	kg/t CW
Liquid fraction	94.16	%
Total solid	5.84	%
Carbohydrates	18.00	kg glucose/t CW
TOC	26.70	kg C/t CW
VS	40.00	kg VS/t CW
pH	3.50	–
NaOH	5.85	kg NaOH/t CW

Table 4.9: Operational Conditions of Centrifugation Process

Parameters	Amount	Unit
Average energy consumption for industrial scale cetrifugation	0.55	kWh/100L
Solids content of FCW	23	%
Liquid content of FCW	77	%
Liquid waste produced after centrifugation	747.83	kg/t FCW

Table 4.10: Operational Conditions of HTC Process

Parameters	Amount	Unit	References
Temperature	180–250	°C	[98]
Pressure	10	MPa	-
Moisture	77	%	-
HRT	2–4	h	[99]
pH	<7	-	-

FCW still rich in organic matter (Table 4.8) received high moisture content (approximately equal to 94%) unsuitable for hydrothermal process, so centrifugation of FCW is required to separate the water from the solids to be sent to HTC. The centrifugation process intended to achieve a specific solid content >= 23%. The 993.32kg of FCW obtained with a composition of 5.8% solids and 94.2% liquid is sent for centrifugation. After centrifugation, the total wet weight is reduced to 252.17kg. The dry matter content reaches 23%, aligning with the process requirements, and the liquid fraction after centrifugation is 194.17kg in total wet weight. The centrifugation process generated 747.83kg of liquid waste, primarily water, which is removed during centrifugation. The key parameters of centrifugation process are described in table 4.9.

The life cycle inventory (LCI) of the hydrothermal carbonization (HTC) process begins with centrifuged feedstock, which is characterized by 195kg/t FCW liquid fraction and 58kg/t FCW of dry matter in FCW, a neutral $pH = 7$, and an initial energy content of approximately 145,260.87MJ based on an assumed higher heating value (HHV) of 10 MJ/kg. The HTC process is carried out under thermochemical conditions with applied temperature range of 180–250°C and pressure range from 10-40 bar with a hydraulic retention time (HRT) of around 4 hours (table 4.10). During the reaction, the organic matter present in feedstock converted into hydrochar (HC), while remaining is converted into gases (mainly CO_2) and nutrient rich liquid. Hydrochar yield on wet basis is around 52.7% of the feedstock mass, amounting to 132.9 kg of HC from the process with a total solid content of 17.4 kg, volatile solids (VS) of 21.08 kg, and total organic carbon (TOC) of 14.07kg, while the remaining 87 kg is water and 17.4kg is CO_2 contributing to a total output mass of 252.17kg/t.FCW [94]. Following this, a filtration step is applied to separate solid hydrochar from the liquid filtrate. Approximately 4% of the mass is retained as filtered cake (9.39kg) with the remaining 94% process water as a filtrate[95]. The filtered cake contains 5.63 kg of total solids, with VS and ash contents

Table 4.11: Energy Cosumption in HTC Process

Parameters	***Value***	***Unit***
Electricity required for stirring	0.07	kWh/t FCW
Heat energy required for hydrothermal Process	2.69	kJ/t FCW
Electrical energy required for centrifugation process	4.29	kWh/t FCW

Table 4.12: Product distribution of HTC Process

Parameter	**Value**	**Unit**
Hydrochar (dried) Yield		
Dried HC Yield	6.78	%
Dried HC Mass	3.02	kg/t FCW
TS (%)	35.8	%
VS (%)	66.02	%
Ash (%)	29.11	%
TOC (%)	-	%
Fix carbon ratio	0.0385	%
Gas Yield		
Gases produced (mainly CO_2)	7.57	%
CO_2 mass produced	17.40	kg/t FCW
Liquid Yield		
Process water produced	166.06	kg
Total water content in system	17.40	kg/t FCW
Initial energy in CW	145260.87	MJ/t FCW

respectively 6.83 kg and 3.07kg, respectively, while retaining 3.76kg of water. This hydrochar is then subjected to a thermal drying or air-drying process to reduce its moisture content further, achieving a final total solid content of 92% and leaving only 4% moisture in the final product. After drying, the hydrochar mass is reduced to 6.02kg, with TS at 5.64kg, VS at 5.95kg, and ash content at 2.08kg, indicating a significant improvement in energy density and material stability. The dried hydrochar yield is approximately 6.78% of the original feedstock mass [96].

From a compositional standpoint, the final hydrochar contains 35.83% total solids, 66.03% volatile solids, 29.11% ash, and a fixed carbon content of approximately 3.85%. During the HTC reaction, gas evolution occurs primarily in the form of CO_2, with a total yield of 17.4kg, equating to about 7.57% of the raw feedstock. A substantial portion of the mass is converted into liquid effluent, or process water, amounting to 166.06kg, representing most of the mass transfer in the system containing dissolved organic matter, nutrients, and volatile fatty acids, which may require post treatment (Table 4.15). In terms of energy transformation, although the hydrochar accounts for only a small fraction of the mass converted, it provides approximately 120.8MJ of energy with an HHV of 13.41MJ/kg that represent an energy yield of 60.6% of original feedstock energy content. This suggests a significant enhancement in energy density due to carbonization.

Table 4.13: Mass flow throughout HTC process chain

Parameters	Value	Unit
HTC Process		
Mass yield of hydrochar	52.7	% wet weight
Hydrochar yield	0.527	kg HC/kg FCW
Total wet weight HC	132.90	kg
Total solids	17.40	kg TS
Volatile Solids (VS)	21.08	kg
Ash	9.486	kg
TOC	14.07	kg C
Water	87.00	kg
CO_2	17.40	kg CO_2
Mass Balance (Total)	252.17	kg
Filtration Process		
% Mass of Filtered Cake	4.00	% wet weight
% Filtrate	94.00	% wet weight
% TS in Filtered Cake	60.00	% wet weight
Mass of Filtered Cake	9.39	kg
Total Solids	5.63	kg
VS	6.83	kg
Ash	3.07	kg
TOC	-	-
Water	3.76	kg
Thermal/Air Drying		
% TS after drying	92.00	%
% Moisture	4.00	%
Total Solids (TS)	5.64	kg
VS	5.95	kg
Ash	2.08	kg
TOC	-	-
Total Dried HC Mass	6.02	kg

The process thus shows clear partitioning of the feedstock into three major phases: solid (hydrochar), liquid (process water), and gas (mainly CO_2), each requiring dedicated handling or further processing depending on the targeted end-use or environmental considerations. The balance of mass and energy (table 4.13) in the HTC process represents itself as a sustainable waste to energy route, however, the optimization of water and gas handling remains key factors for its overall efficiency and environmental performance.

4.4 Inventory of Conventional Biorefinery

The inventory of conventional processes scenario is carried out taking into account a waste biorefinery approach based on a commercially available process. Conventional waste biorefinery that usesuses CW as primary feedstock has several stages,ages, starting with the anaerobic digestion

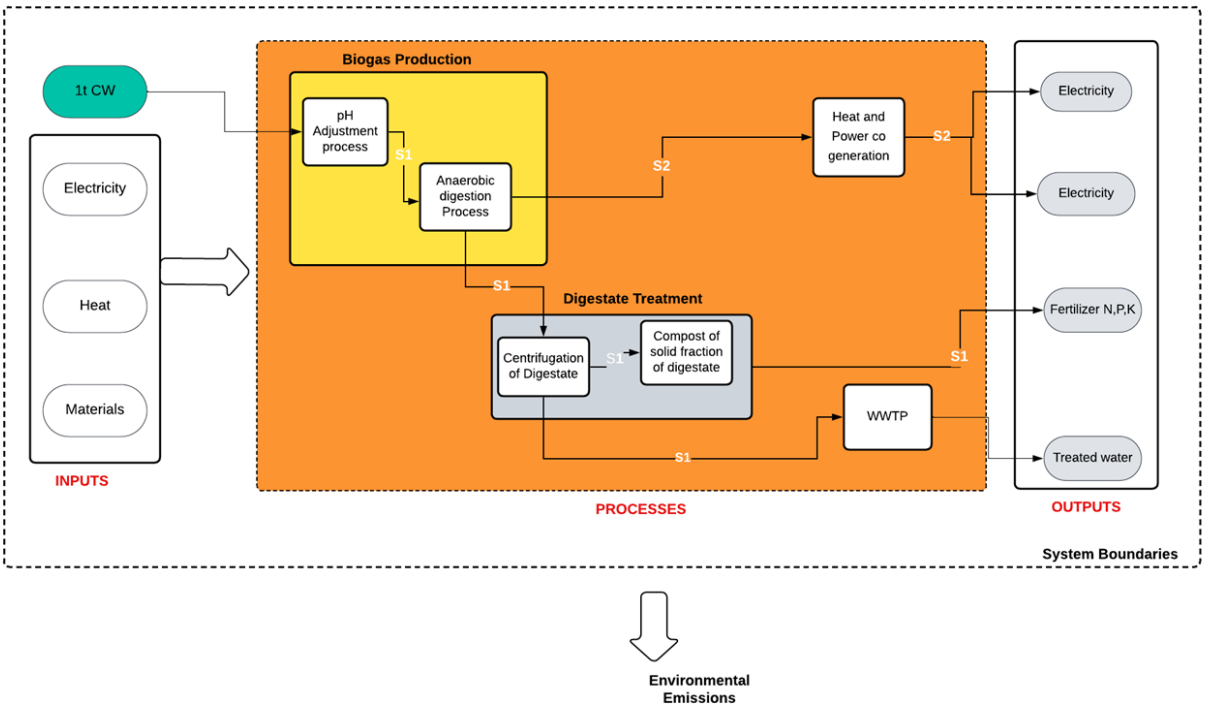

Figure 4.3: System boundaries of conventional biorefinery

process in a CSTR reactor with a flow rate of 3.28kg VS / t CW / day at the / day at the assumed HRT of 19.49 days and at a tempe° Cture of 35 ° C as reported in Chapter 3. The biogas produced in this case is 10.15 m^3 biogas/t Cw. The biogas composition is approximately 60.69% CH_4 (6.06 m^3 CH_4/t CW) and 39.31% CO_2 (3.94 m^3 CO_2/t CW). Produced biogas is used in a combine heat and power (CHP) plant. The digestate produced from anaerobic digestion is separated by centrifugation into 20-30% solid fraction. The centrifuged is thermally dried to 70-80% solid digestate is applied as organic fertilizer on agriculture soil in accordance with Italian legislation. The specific nutrient values for the digestate is obtained from literature from typical nutrient concentration in raw cheese whey (CW), with N, P, and K content equal to 2.63%, 0.125%, and 0.305% of TS contents and replaced with a substitution ratio of 3kg of solid digestate with 1kg average mineral fertilizer, as K_2O ratio3:1 [56]. The liquid fraction, a nutrient-rich liquid, possible treatment is applicable. The solid digestate, classified as green waste, provides additional value in compost application, the datasets available in ecoinvent version 3.0 [56].

4.5 Process Flow Diagrams(PFDs)

The Process Flow Diagram (PFD) is a line and symbol graphic representation of the major inputs and waste streams through the process stages in the proposed configuration. The PFD drawing shows arrows lines representing directional pipelines, tag numbers representing major treatment

units and equipment, as well as pumps and valves. However, the PFD for the proposed waste biorefinery scheme does not show complete plant and all features, it only shows the features that are researched in this thesis. This simplified PFD allows a quick development of easily recognizable characteristics and flows of the different waste streams that are then reflected in the mass balance. A total of 5 PFDs is presented (figure4.5 to 4.8).

4.5.1 Functions of PFDs

For the following media, the PFD shows how the material flows through the treatment plant goes:

1. Cheese Whey (CW)
2. Fermented Cheese Whey (FCW)
3. Main product: syngas (H_2+CO_2)
4. Other byproducts e; g mineral aggregates (MA), hydrochar (HC), Liquid fraction (LF)

4.5.2 PFD-1

The IBR-1, figure4.4, process stage, two key solutions are prepared: a 0.5M ZnSO_4 solution and a 2M NaOH solution. The ZnSO_4 solution is prepared in block 1B-1 by mixing 71.62 kg of ZnSO_4 with 958.67 kg of water. The NaOH solution is prepared in block 1B-2 using 79.70kg of NaOH and 42.79kg of water. These solutions, along with 1000kg of cooling water (CW), are introduced into the IBES (block 1B-3). Inside the reactor, microbial and electrochemical processes occur, leading to the generation of a gas mixture composed of hydrogen (H_2) and carbon dioxide (CO_2). Additionally, the process produces 211.26kg of wastewater (WW 1B-3), fermented whey (FCW), and 419.69 kWh of electrical energy (EE).

4.5.3 PFD-2

In the IBR-2 process, figure4.5 the gas mixture generated in PFD-1 undergoes upgrading H_2 and CO_2 at a volume of $4.23m^3$, is first passed through two stages of compression and cooling. The first compressor (2C-1) raises the pressure, followed by heat exchanger 1 (2E-1), which reduces the temperature to around 311.15 K. This is followed by a second compression (2C-2) and cooling stage (2E-2) to ensure the gas is at optimal conditions for separation. The compressed gas is then passed through an air pump (2P-1) and directed to a Pressure Swing Adsorption (PSA) unit containing an H_2-selective membrane. This unit effectively separates 2.68m^3 of pure hydrogen gas, which is later utilized for energy applications. The remaining gas, primarily CO_2, is sent to the Carbon Capture System (CCS), which converts 2.94 m^3 of CO_2 into a stable carbonated residues (CR)

weighing 25.11kg. The process also generates 10.43kg of wastewater (WW 2B-2) from gas handling and separation units. This phase is critical for isolating hydrogen as a clean energy source and capturing CO_2 and reuse.

4.5.4 PFD-3

PFD-3 describes the transformation of liquid waste from PFD-1 into solid fuel via hydrothermal carbonization, figure 4.6. The FCW stream of 1000kg is first pumped using liquid pump 1 (3P-1) and heated through heat exchanger 1 to reach a temperature of 493.15K. The pressurized liquid is further pumped by liquid pump 2 (3P-2) and sent into the HTC reactor (block 3B-2). This process converts the organic components in the liquid into a carbon-rich slurry. The slurry, with a mass of 224.57kg is separated in block 3B-3 using centrifugation. The solid portion is filtered and dried in block 3B-4, resulting in the production of 4.80kg of hydrochar (HC). The liquid portions from the HTC process are separated into two wastewater streams: 211.26kg from centrifugation (WW 3B-3) and 747.82 kg from the drying and filtration process (WW 3B-4). This phase enables the valorization of process water into usable solid fuels while generating wastewater that is treated in the next stage. PFD-4: Wastewater Treatment System

4.5.5 PFD-4

PFD-4 integrates all wastewater streams produced in the IBR process into a centralized treatment system, figure 4.7. The wastewater streams include: WW 1B-3 (211.26 kg) from the BES unit, WW 2B-2 (10.43 kg) from the gas separation phase, and two streams from the HTC section — WW 3B-3 (211.26 kg) and WW 3B-4 (747.82 kg). These are collectively sent to the industrial wastewater treatment unit (block 4B-1). The treatment facility is designed in accordance with EU Directive 91/271/EEC, which mandates the removal of both organic and inorganic contaminants. The plant ensures that effluents meet regulatory discharge limits before being released or reused.

4.5.6 PFD-5

The final stage of the IBR process, illustrated in figure 4.8, showcases the valorization of all major products into commercially viable outputs. The purified hydrogen gas is used in hydrogen fuel cell system for clean mobility applications. The carbonate residue (CR) repurposed in the manufacturing of building blocks, contributing to the construction industry as a sustainable material. The hydrochar (HC) produced during the HTC process is utilized in Combined Heat and Power (CHP) plants as a renewable solid fuel. Additionally, the electrical energy (419.69 kWh) generated during the bio-electrochemical fermentation stage is supplied for commercial use, potentially feeding into

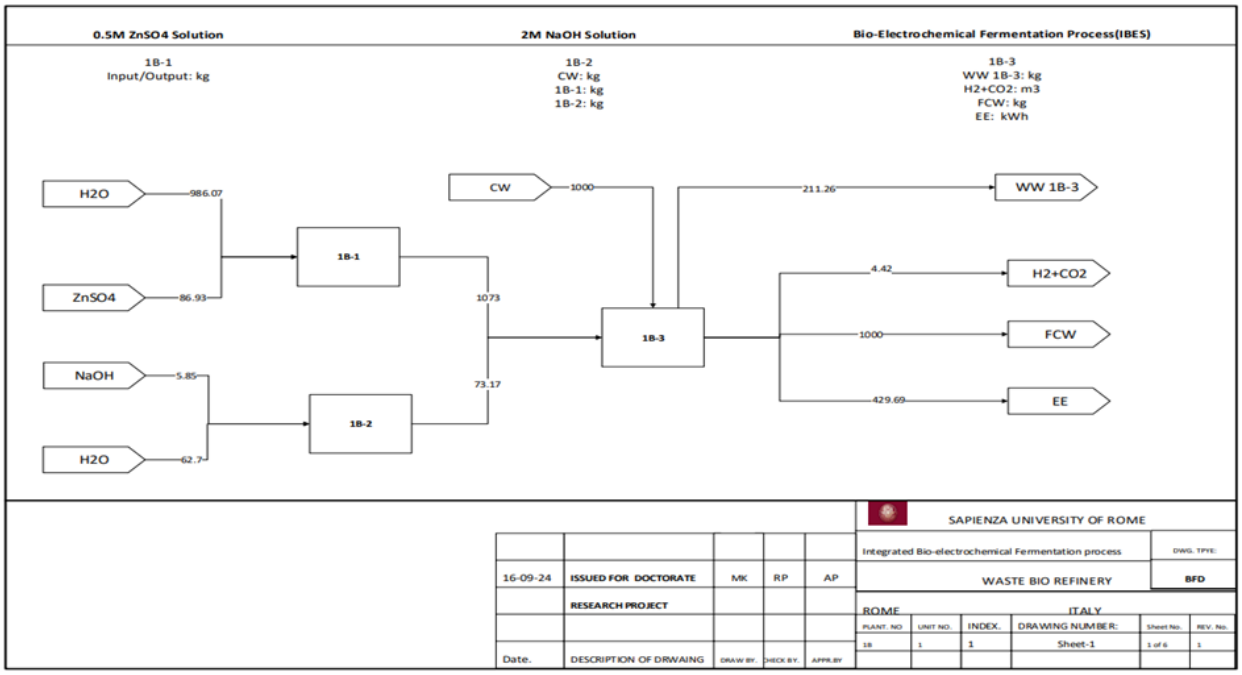

Figure 4.4: PFD-1 of IBR

the local grid or powering on-site operations. This phase exemplifies the circular economy approach by ensuring that every stream from the process finds a valuable application, minimizing waste and maximizing resource efficiency.

Figure 4.9 represents the legend of all the symbols and acronyms used in the 5 PFD.

4.6 Mass Balance

The mass balance reported is accounts for the material's mass flow through the treatment process. Flow rates are expressed in units of kilogram per day (kg/d). Variations in the mass balance are developed at each stage to represent different loading conditions. The mass balance, in Table **??**, is based on the same pathways followed explained in PFDs.

The mass balance represents the balance of materials through the treatment process, including the liquid flow rates:

1. Total Solids (TS)
2. Volatile Solids (VS)
3. Total Organic Carbon (TOC)
4. Water Content

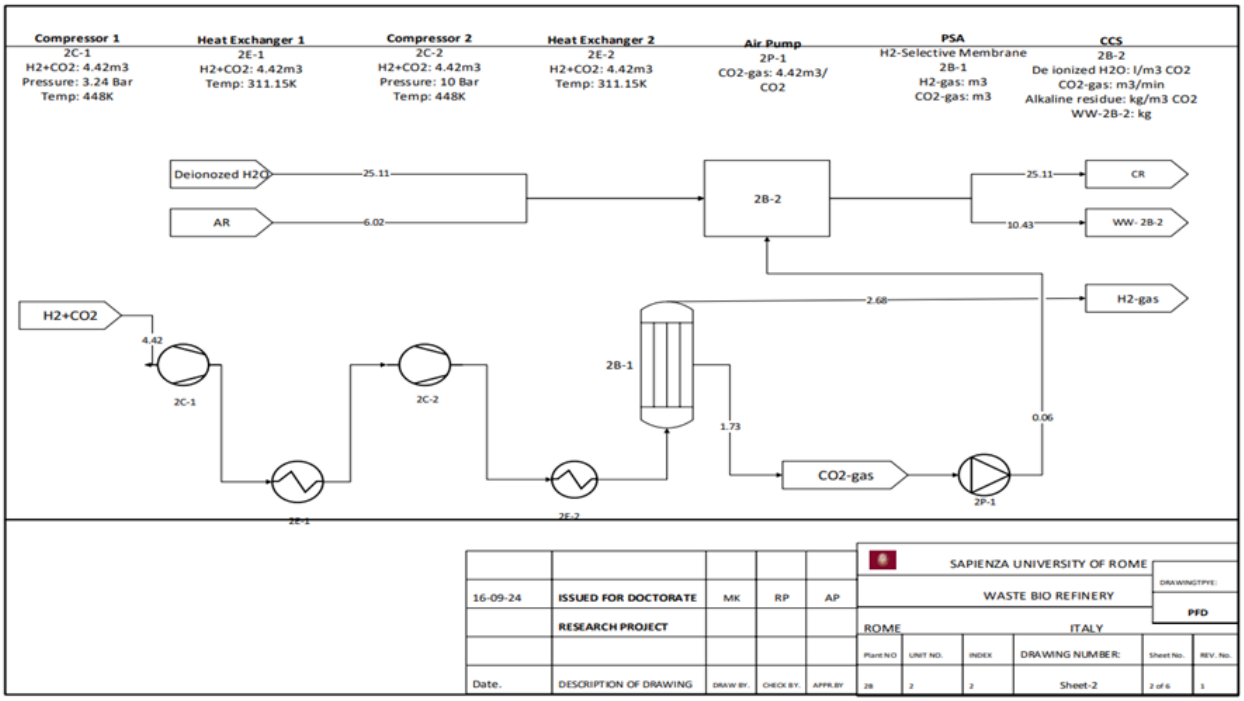

Figure 4.5: PFD-2 of IBR

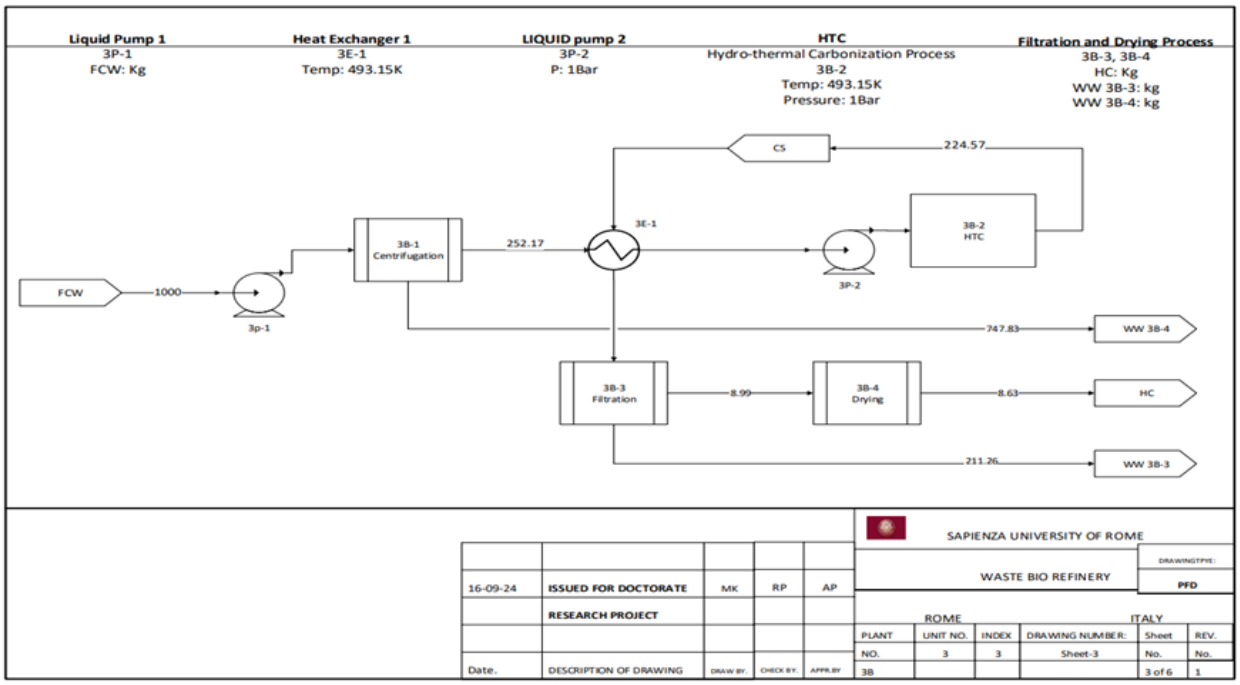

Figure 4.6: PFD-3 of IBR

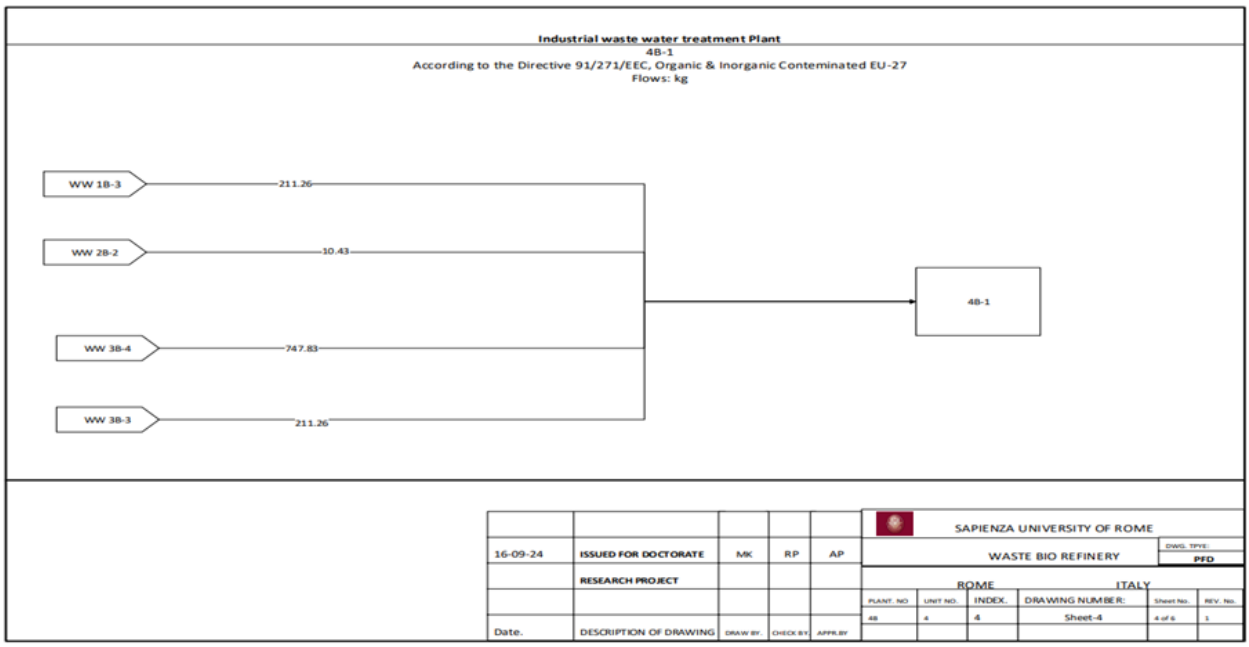

Figure 4.7: PFD-4 of IBR

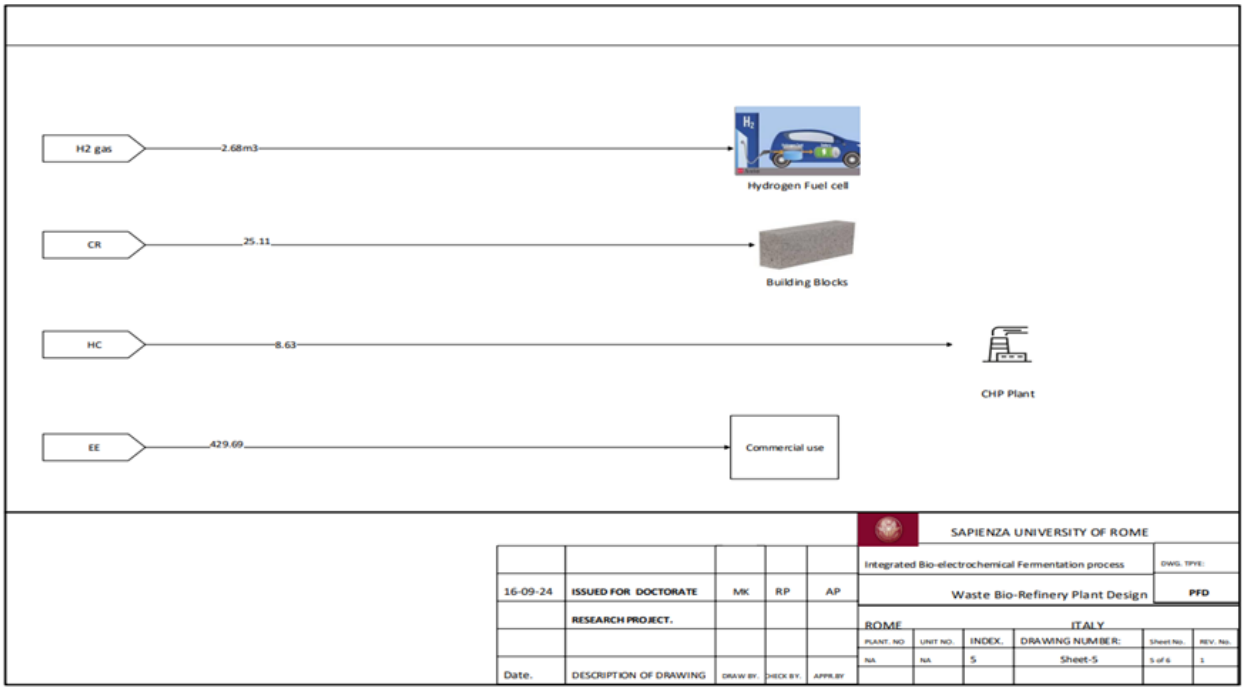

Figure 4.8: PFD-5 of IBR

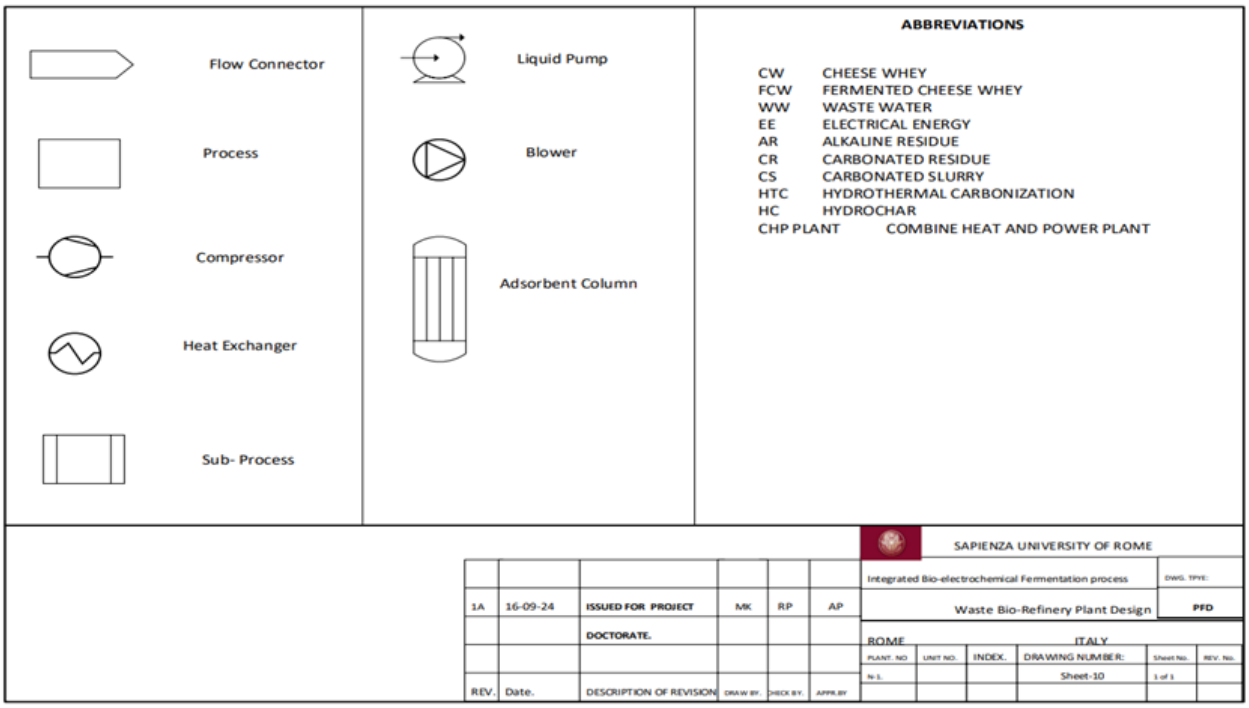

Figure 4.9: PFD-6 of IBR

4.7 Energy Balance

Energy balance is a critical aspect in evaluating the sustainability and efficiency of integrated waste treatment processes. In the context of modern waste management, the ability to recover energy from waste treatment technologies not only improves the overall energy efficiency but also contributes to environmental and economic benefits. The energy balance analysis focuses on the energy flows within a series of advanced and traditional waste treatment processes, as outlined in the Table.

4.8 Model Development

Following the inventories, schematic representations, and the conceptual design of the waste biorefinery, a rigorous model was developed using the openLCA software. Initially, individual process models were constructed for each unit operation in IBR with precise calculations of required material's quantity. These unit processes serve as the foundational activities within the product system, encompassing operations such as raw material extraction, manufacturing, and transportation and marketing. The processes are interconnected through flows which represent the exchange of materials, energy, or emissions between processes and the environment. Each flow is defined by its properties (mass, energy content) measured in specified unit groups and connected with actors which denote the stakeholders or entities involved, such as suppliers, manufacturers or end-users. The data collected in the inventories reported above, are utilized with ecoinvent version3.0 datasets,

Table 4.14: *Energy balance and net energy benefits analysis (in kJ/t.CW)*

Process	**EE request**	HE request	**Total energy request**	**Energy produced**	**Net**
Integrated bio-Electrochemical Process (IBES)	7757.26	2.48	7759.74	429697.19	-421937.45
Centrifugation Process	40642.1	0	40642.1	0	40642.11
Hydrothermal Carbonization (HTC) Process	2783.45	2.69	3841.16	0	-87752680.56
Filtration Process	11710.13	0	11710.13	0	11710.13
Co-generation Heat and Power (CHP)	0	0	0	120958	-120958
Membrane Separation Process	19564.65	0	19564.65	0	19564.65
Carbon Capture and Storage (CCS)	11982.60	4174.66	11982.60	0	11982.60
Polymer Electrolyte Membrane Fuel Cell (PEMFC)	0	0	0	29858.4	-29858.4

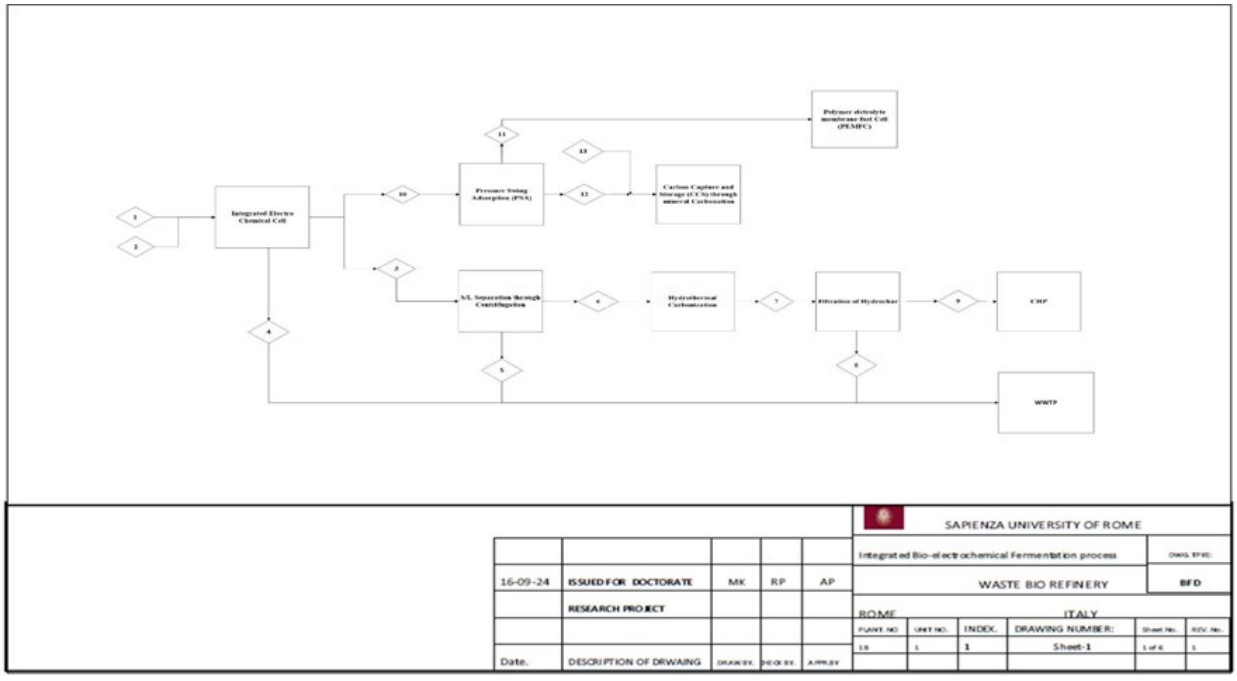

Figure 4.10: mass flow at each stage of IBR

Table 4.15: Mass flow at each stage of suggested IBR process scheme

Parameter	1	2	3	4	5	6	7	8	9	10	11	12	13
Total Solids (kg)	79.85	86.93	58	86.93	-	58	17.40	-	5.63	-	-	-	43.48
Water (kg)	999.18	986	942	986	747.83	194.17	217.37	220.63	3.76	-	-	-	10.43
Volatile Solids (kg)	64	-	40	-	-	40	21.06	-	6.83	-	-	-	-
Carbon Content (kg)	39.30	-	26.70	-	-	26.70	14.07	-	-	-	-	-	-
Temperature (°C)	38	-	38	-	-	180	1801	-	180	-	-	-	-
Pressure (bar)	-	-	-	-	-	10	10	-	-	-	-	-	-
Flow rate (t/day)	0.59	-	0.59	-	-	-	-	-	-	-	-	-	-
Gas content (kg)	-	-	-	-	-	17.40	-	-	3.54	0.24	0.24	3.3	-
H_2 content (kg)	-	-	-	-	-	-	-	-	0.24	0.24	-	-	-
CO_2 content (kg)	-	-	-	-	-	-	-	-	3.3	-	-	-	-

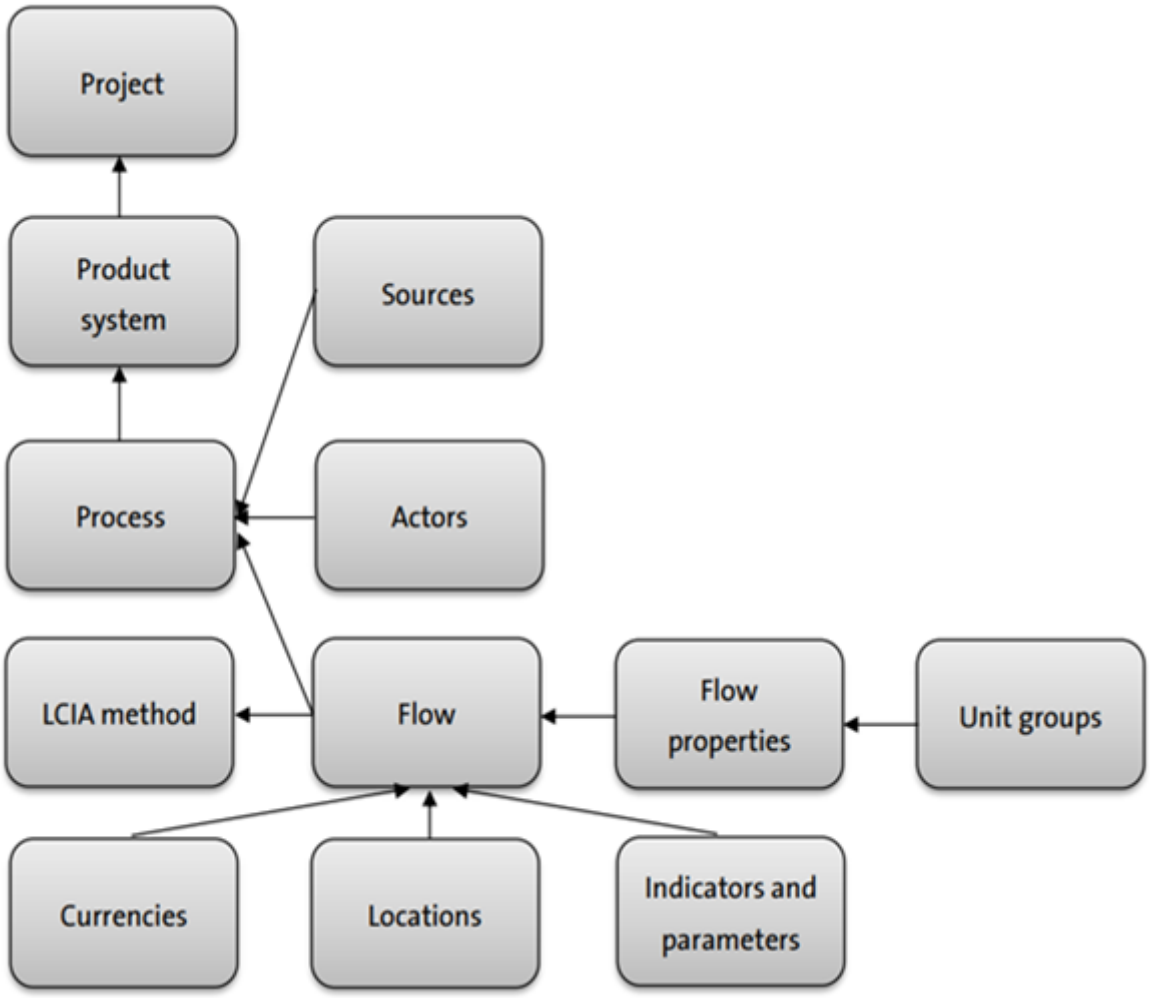

Figure 4.11: Model Framework of OpenLCA

modified for energies, emissions and waste flows where required. For each unit process data from conventional technologies is carefully adapted or supplemented to represent the functionality and outcomes of the innovative approach being modelled. By applying this critical and systematic approach to data flow modification, the model can simulate the performance of new technologies in an accurate and scientifically credible manner, even though the original database does not directly contain specific information for this innovative scheme/process.

Subsequently, an integrated product system developed to represent all unit processes included specifications of relevant flows, flow properties, units, and quantified values for each environmental indicator. This model setup systematically implemented to ensure accuracy and consistency across all components of all unit processes in the simulation.

4.8.1 Cut-off Crteria

The cut-off criteria are applied to the inventory data by choosing only the relevant processes and flows in the existing database that meet specified threshold. This can be done manually during the data selection process by using datasets that have already comprised cut-off criteria. Processes or flows that are below the cut-off threshold of less than 5% are excluded during the system boundary definition. Upstream or downstream activities that add very little mass or energy to the system or that have a small environmental impact is skipped during impact assessment.

4.9 Results & Discussion

4.9.1 Impact Assessment

The findings of the Life Cycle Impact Assessment (LCIA) demonstrate notable distinctions between conventional and integrated technologies in the context of waste biorefinery in suggested impacts catagories. In climate change, conventional biorefinery scenario increases greenhouse gas emission to 1.52E+03 kg CO_2 eq./t CW but integrated biorefinery scenario shows minimum emissions to 2.87E+00 kg CO_2 eq./t CW. When compared to impact on aquatic life, integrated one has a significantly lower impact in freshwater ecotoxicity, 3.17E+01CTUe/t CW. Eutrophication from nutrient runoff is almost non-existent in integrated approach (7.05E-04 kg P eq./t CW). With an acidification potential of 2.67E-02 mol H+ eq, integrated approach has substantially larger potential of 2.67E - 02 mol H^+ eq/t CW compared to conventional process. Overall, the IBR scenario shows substantial reductions in greenhouse gas emission with climate change impact including biogenic, fossil, and land use decreased by several order of magnitude compared to the CBR, provide more carbon management possibly through improved energy integration or the use of renewable sources.

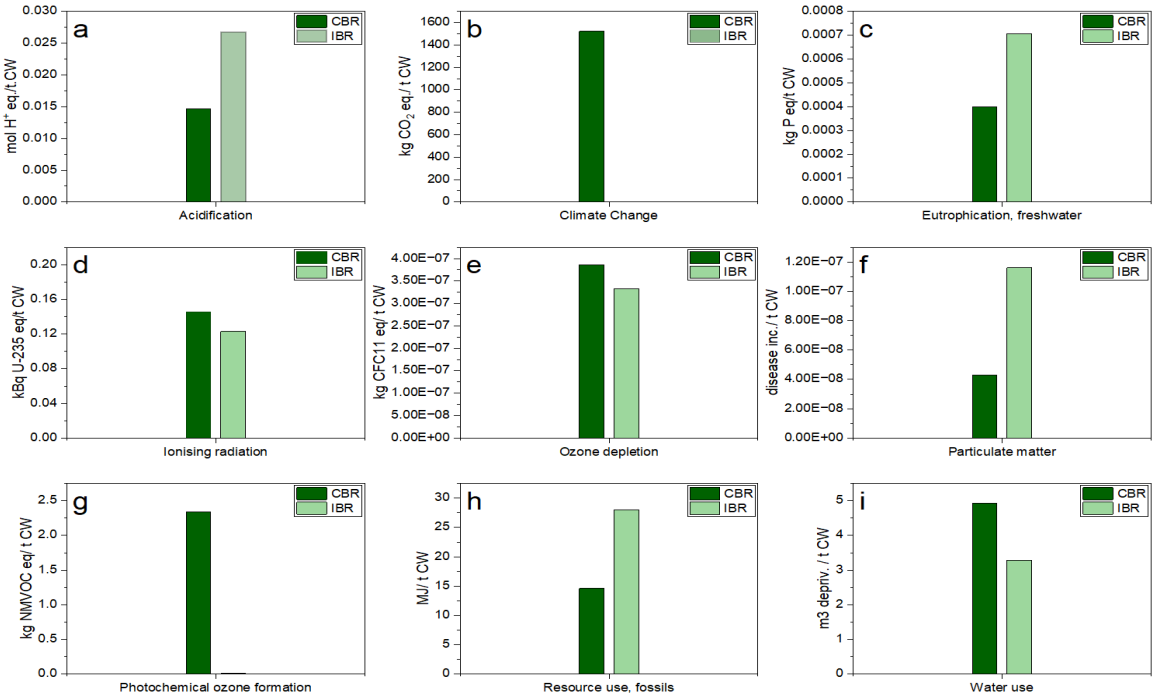

Figure 4.12: Environmental Impact of IBR compared with CBR in considered impact categories in their relevant environmental compartment

Significant reductions are also observed in ecotoxicity indicators, particularly in freshwater environments where impacts from inorganics, metals, and organics decline dramatically, suggesting that IBR incorporates more effective pollutant removal and containment systems. Eutrophication impact, both freshwater and marine are notably mitigated in the IBR scenario approach a negligible level, indicative of enhanced nutrient recovery or discharge control.

Human toxicity impacts both (cancer and non-cancer) are substantially lowered in the IBR system, particularly for inorganic substances where some impacts are eliminated entirely, reflecting more advanced waste processing or cleaner input streams. Resource use is another domain where the IBR excels, showing a drastic decrease in fossil and mineral resource consumption, as well as water use, which plummets from 6.98E+04 to just 3.28E+00 m^3 depriv. /t CW, underscoring the efficiency and conservation capabilities of the integrated system. While the IBR demonstrates impressive overall environmental benefits, some categories such as ionizing radiation and particulate matter show smaller, though still notable, improvements, potentially due to residual upstream energy dependencies or limitations in emission controls that require further optimization. Additionally, the moderate changes observed in ozone depletion and photochemical ozone formation suggest that while the IBR is generally cleaner, certain air pollutants may persist and merit additional attention.

Table 4.16: Life Cycle Impact Assessment Results of the integrated waste biorefinery (IBR) Approach Benchmark with Conventional Waste Biorefinery (CBR)

Name	Unit	Impact Assessment Results CBR	Impact Assessment Results IBR
Acidification	mol H^+ eq/t CW	1.46E-02	2.67E-02
Climate change	kg CO_2 eq/t CW	1.52E+03	2.87E+00
Climate change - Biogenic	kg CO_2 eq/t CW	1.52E+03	1.27E+02
Climate change - Fossil	kg CO_2 eq/t CW	1.82E+00	2.86E+00
Climate change - Land use and LU change	kg CO_2 eq/t CW	9.29E-04	9.91E-04
Ecotoxicity, freshwater	CTUe/t CW	3.06E+01	3.17E+01
Ecotoxicity, freshwater - inorganics	CTUe/t CW	2.54E+00	3.22E+00
Ecotoxicity, freshwater - metals	CTUe/t CW	1.41E+01	2.86E+01
Ecotoxicity, freshwater - organics	CTUe/t CW	1.43E+01	3.21E+01
Eutrophication, freshwater	kg P eq/t CW	3.98E-04	7.05E-04
Eutrophication, marine	kg N eq/t CW	1.95E-03	2.59E-03
Eutrophication, terrestrial	mol N eq/t CW	2.39E-02	4.53E-02
Human toxicity, cancer	CTUh/t CW	4.21E-10	1.09E-09
Human toxicity, cancer - inorganics	CTUh/t CW	0.00E+00	0.00E+00
Human toxicity, cancer - metals	CTUh/t CW	2.91E-10	7.69E-10
Human toxicity, cancer - organics	CTUh/t CW	1.30E-10	3.25E-10
Human toxicity, non-cancer	CTUh/t CW	2.11E-06	3.66E-07
Human toxicity, non-cancer - inorganics	CTUh/t CW	2.09E-09	3.01E-09
Human toxicity, non-cancer - metals	CTUh/t CW	1.52E-08	3.62E-07
Human toxicity, non-cancer - organics	CTUh/t CW	2.10E-06	9.40E-10
Ionising radiation	kBq U-235 eq/t CW	3.54E-01	2.23E-01
Land use	Pt/t CW	2.77E+00	8.44E+00
Ozone depletion	kg CFC11 eq/t CW	3.86E-07	3.35E-07
Particulate matter	disease inc./t CW	4.29E-05	1.16E-07
Photochemical ozone formation	kg NMVOC eq/t CW	2.40E+00	8.57E-03
Resource use, fossils	MJ/t CW	1.46E+01	2.80E+01
Resource use, minerals and metals	kg Sb eq/t CW	3.06E-10	1.24E-05
Water use	m^3 depriv./t CW	4.92E+00	3.28E+00

4.9.2 Contribution Analysis

Scenario's Contribution

Contribution analysis of both scenarios compares the environmental performance of IBR and CBR across different impact categories highlight the areas where IBR have a higher contribution than CBR or vice versa. To account the contribution of impacts coming from three main streams in IBR, the stream 1 (S1) follow the path of hydrothermal carbonization of digestate starting from the organic feed stock 1t CW. The process begins with pH adjustment of the waste, followed by treatment in a bio-electrochemical cell that generates electricity. The digestate is then centrifuged, with the liquid stream proceeding to hydrothermal treatment to produce carbonated slurry and process water. The slurry undergoes filtration, yielding carbonated residue for hydrochar production and additional process water. The hydrochar is utilized in a co-generation plant to produce electricity and heat, while process water is treated in a wastewater treatment plant, yielding treated water. Stream 2 (S2) focused on the flow of anolyte solution. It begins with the preparation of a 0.5M $ZnSO_4$ solution using zinc sulfate and deionized water. This anolyte solution is fed into an integrated bio-electrochemical cell, where heat and electricity are supplied to drive the process. The cell produces 1.07 ton of anolyte wastewater as an output, which is then treated in a wastewater treatment plant (WWTP). The WWTP processes the wastewater, generating treated water for potential reuse

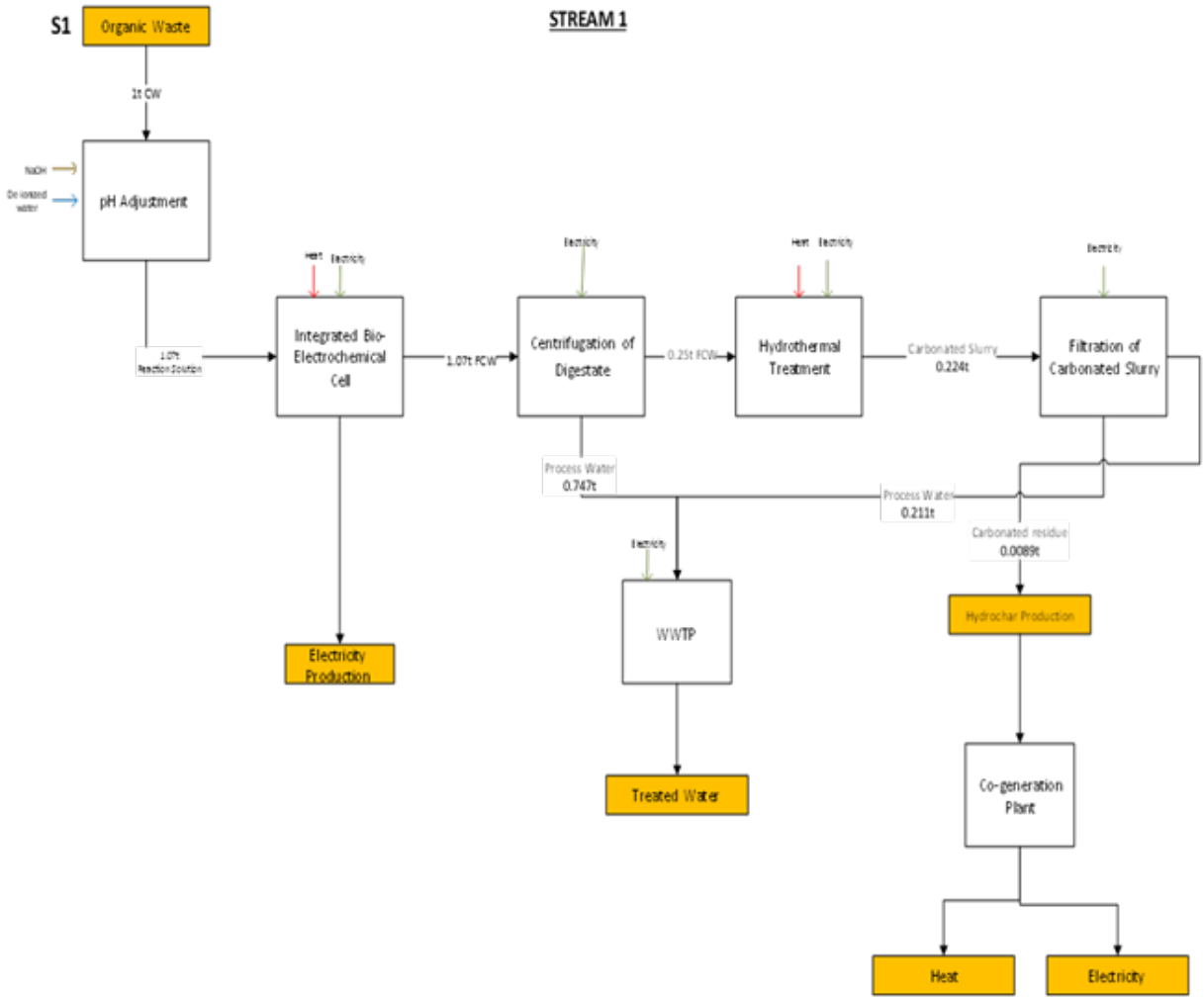

Figure 4.13: Stream 1 (S1) Flow in IBR process

or safe discharge. Streams 3-4 follow the hydrogen purification process through polymer membranes and the carbon capture and storage in form of mineral carbonates. The carbon dioxide equivalent (CO_2 eq.) emissions linked to different processes in S1, S2 and S3-4 are calculated. The CCS has a particularly significant effect in lowering CO_2 level. On the other hand, the carbon footprint is significantly increased by wastewater treatment plant (WWTP) and membrane process for hydrogen purification which shows notable positive emissions. While the use of de-ionized water has a modest decrease in emissions, other process such as IBES and electricity avoidance have negligible emissions. The graph illustrates how proposed technologies differs in carbon emissions; some aid in mitigation efforts, while others raise the total carbon footprint.

4.9.3 Energy Analysis

As illustrated in table 4.17 in the energy input and output of each processing unit the highest energy requiring process in the system is centrifugation which requires 15444KJ, followed by hydrothermal treatment of digestate and filtration at 4449.85KJ. Membrane process for hydrogen

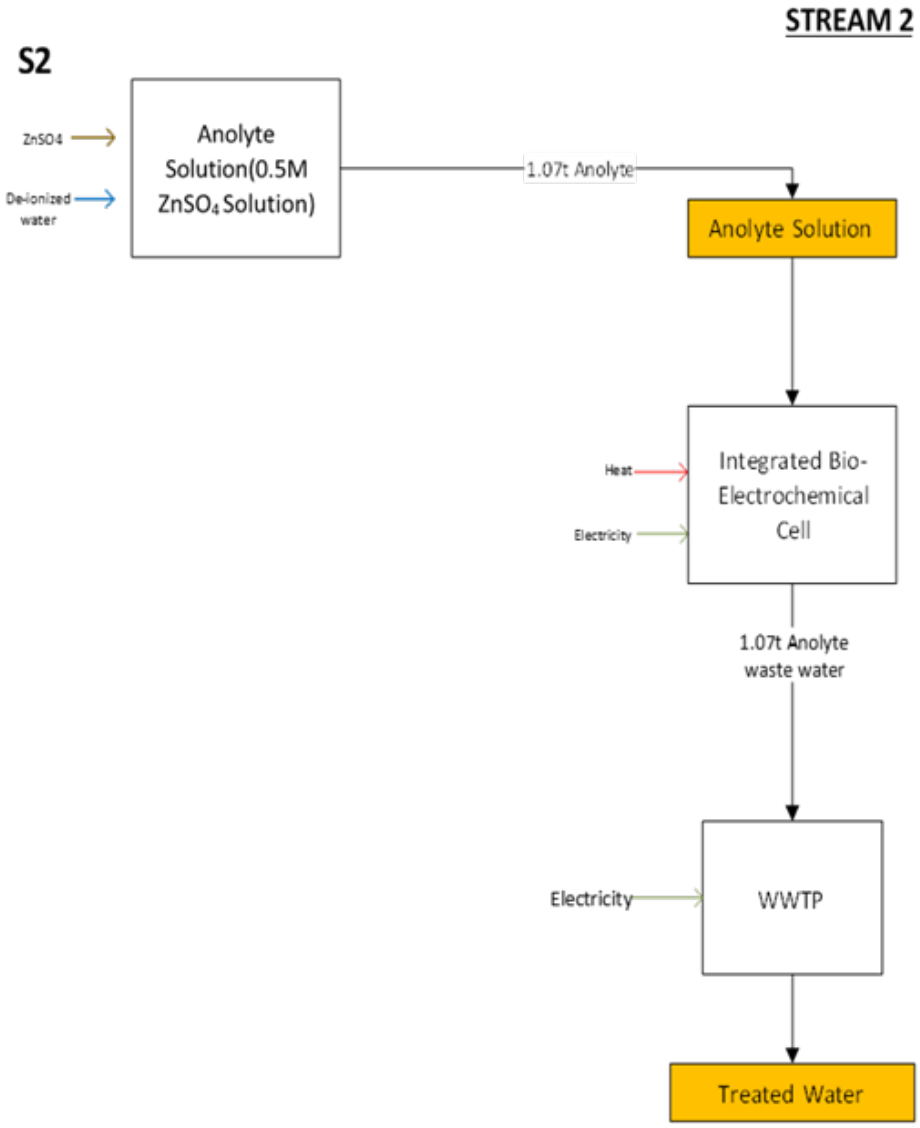

Figure 4.14: Stream 2 (S2) Flow in IBR process

Table 4.17: Energy balance and Net energy benefits analysis (kJ/t.CW)

PROCESS	EE REQUEST	HE REQUEST	TOTAL ENERGYREQUEST	ENERGY PRODUCED	NET
Integrated bio-Electrochemical Process (IBES)	7757.26	2.48	7759.74	429697.19	-421937.45
Centrifugation Process	40642.1	0	40642.1	0	40642.1
Hydrothermal Carbonization (HTC) Process	2783.45	2.69	3841.16	0	-87752860.56
Filtration Process	11710.13	0	11710.13	0	11710.13
Co-generation Heat and Power (CHP)	0	0	0	120958	-120958
Membrane Separation Process	19564.65	0	19564.65	0	19564.65
Carbon Capture and Storage (CCS)	11982.60	4174.66	11982.60	0	11982.60
Polymer Electrolyte membrane fuel cell (PEMFC)	0	0	0	29858.4	-29858.4

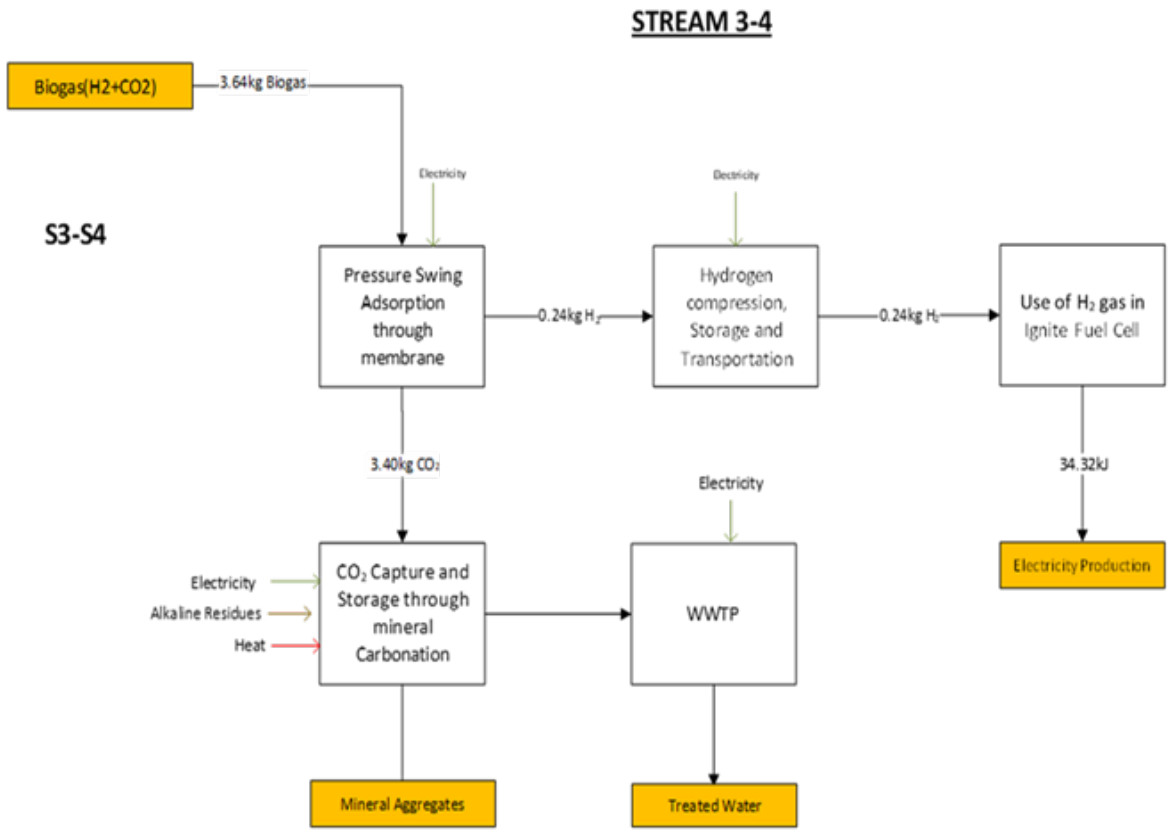

Figure 4.15: Stream 3-4 (S3-4) Flow in IBR process

separation requires 7462KJ. These processes, though critical for system operation, the issue has been raised regarding their overall contribution to the system's energy efficiency. Centrifugation and filtration are energy-intensive processes, which indicate that process optimization or coupling with less energy-intensive alternative can enhance system performance. For instance, waste heat recovery from energy-generating processes or coupling renewable energy sources can offset these losses. While CCS is crucial for the management of carbon its substantial energy requirement underscores the significance of advances in low-energy carbon capture technologies when combining with gas separation process using membranes. The greenhouse gas mitigation versus increased hydrogen production scenario is represented by the analysis of hydrogen production and avoided CO_2 equivalent (CO_2 eq.) emissions at different functional units (FU) of cheese whey (CW). The production of hydrogen grows significantly as the amount of CW increases from 1 ton to 100 tons, reaching over 275 cubic meters at 100 tons. Concurrently, as the scale grows, the CO_2 emissions showed a decrease in climate impact. Emissions are marginally positive at lower quantities, such 1 ton of CW, but they turn negative as the CW input rises. The largest reduction, around -110kg CO_2 eq, occurs at 100 tons of CW. This suggests that producing hydrogen on a greater scale from CW is an environmentally advantageous technique since it not only increases hydrogen output but also significantly reduces greenhouse gas emissions.

4.9.4 Uncertainty Analysis

The Monte Carlo simulations were performed within the developed model in openLCA, to assess uncertainty in each complex system's database by running multiple simulation trials. The simulation was executed 100 times, and the results varied within a wider range, with a mean value of approximately 0.105kg CO_2eq. /t. CW and a standard deviation of 0.092kg CO_2eq. /t. CW in histogram shown in Figure 4.17. This indicated moderate variability in the outcomes, suggesting that the simulated process involves more uncertainty compared to a fully deterministic or stable system. The results span is approximately -0.169 to 0.508 with a 90% confidence interval (between the 5th percentile at -0.033 and the 95th percentile at 0.231). The presence of both negative and positive values implies that the process being modeled can sometimes result in emissions (positive values) and at other times in avoided emissions or sequestration (negative values), depending on the variation in input data. This behavior is clearly associated with processes of Carbon Capture and Storage (CCS) or Hydrothermal Carbonization (HTC), which are under certain conditions may significantly reduce emissions. However the extent of the reduction can vary depending on parameters like energy input, feedstock, or background data. The histogram's distribution shows a slightly skewed pattern, with most results concentrated around the mean and median (0.105 and 0.102, respectively). However, the presence of outliers on both ends highlights that some simulation scenarios may yield significantly higher or lower impacts, reflecting the sensitivity of the model to input data uncertainty. Overall, this Monte Carlo analysis demonstrates reasonably consistent performance. There is some degree of variability which is important for understanding the potential range of climate change related impact (in kg CO_2 eq) in real world applications.

4.10 Conclusion

This study has demonstrated the environmental and energetic viability of Integrated Biorefinery (IBR) approach for organic waste valorization, particularly cheese whey (CW), using advanced configurations that include Integrated Bio-electrochemical Systems (IBES), Hydrothermal Carbonization (HTC), Carbon Capture and Storage (CCS) using an integrated approach by using industrial alkaline residual waste stream, and membrane-based hydrogen purification. Through the application of Life Cycle Assessment (LCA) in accordance with ISO 14040/44 and the Environmental Footprint (EF) 3.0 methodology, the environmental performance of IBR has been systematically benchmarked against a Conventional Biorefinery (CBR) scenario. The IBR system exhibited significant reductions across multiple environmental impact categories. Notably, climate change impact was drastically reduced from 1.52E+03 kg CO_2 eq/t.CW in the CBR to just 2.87E+00 kg CO_2 eq/t.CW in the IBR, indicating enhanced carbon management and sequestration. This reduction is attributed to effective

integration of CCS and process energy optimization. Similarly, freshwater ecotoxicity and eutrophication potentials were reduced due to improved pollutant containment, enhanced nutrient recovery, and reduced discharge. Acidification potential was also lowered, suggesting minimal acidifying emissions from the integrated system. In human toxicity categories, especially for inorganic pollutants, the IBR demonstrated substantial impact reduction, likely resulting from cleaner feedstocks and more advanced waste treatment methods. Resource consumption especially fossil energy and water use was significantly minimized, with water deprivation reduced from 6.98E+04 to 3.28E+00 m^3/t.CW, underscoring the conservation efficiency of the IBR configuration. Energy use was optimized through recovery systems and valorization of hydrochar and hydrogen co-products. However, energy-intensive processes like centrifugation (15.44 kJ/t) and membrane purification (7.462 kJ/t) represent hotspots in the system and should be targeted for further optimization. Potential solutions include integration of renewable energy sources, heat recovery systems, and low-energy alternatives for separation and purification. A contribution analysis of the three main IBR process streams revealed that Stream 1 (digestate valorization via HTC and hydrochar use) and Stream 2 (anolyte treatment) significantly contribute to environmental gains, while Stream 3–4 (hydrogen purification and CCS) delivers net carbon benefits. The CCS system in particular provides measurable CO_2 mitigation, although it introduces moderate energy demands. The environmental performance is highly dependent on efficient downstream integration and synergy among the sub-processes. Monte Carlo simulations, conducted using 100 iterations in openLCA, identified moderate variability in impact results, with a mean of 0.105 and a standard deviation of 0.092. The results indicate the system's sensitivity to input data uncertainty, particularly in CCS and HTC modules. The simulation outcomes ranged from negative to positive emission values, further validating the dual potential of the system for both emission generation and avoidance. This variability highlights the need for careful parameter control, accurate database selection, and further empirical data validation.

From a scale-up perspective, the analysis revealed that increasing CW input from 1 to 100 tons significantly enhances hydrogen production while decreasing net CO_2 emissions transitioning from positive to strongly negative values (–110 kg CO_2 eq at 100 tons). This suggests strong scalability potential for IBR, provided that the system's energy balance and material recovery processes remain optimized. In summary, the IBR system represents a scientifically robust, environmentally beneficial alternative to conventional organic waste treatment methods. It maximizes energy and material recovery while minimizing environmental burdens through a well-integrated combination of biological, electrochemical, and thermochemical technologies. While certain subsystems require further optimization to reduce energy inputs, the overall framework aligns with the principles of circular economy, resource efficiency, and climate neutrality. The study affirms that IBR can play a pivotal role in the transition toward sustainable waste-to-energy systems and future bioeconomy

development.

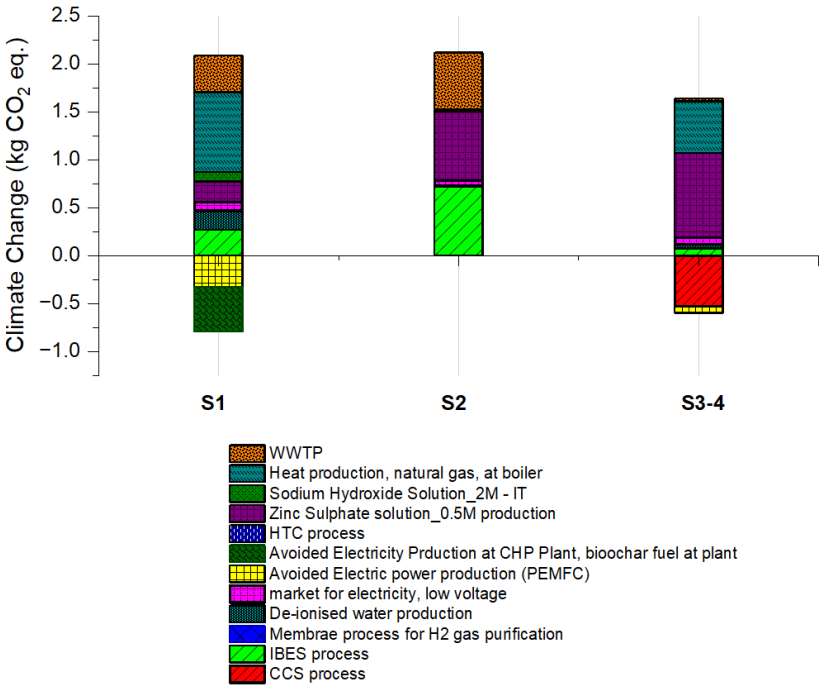

Figure 4.16: Impact's Contribution of S1, S2 and S3-4

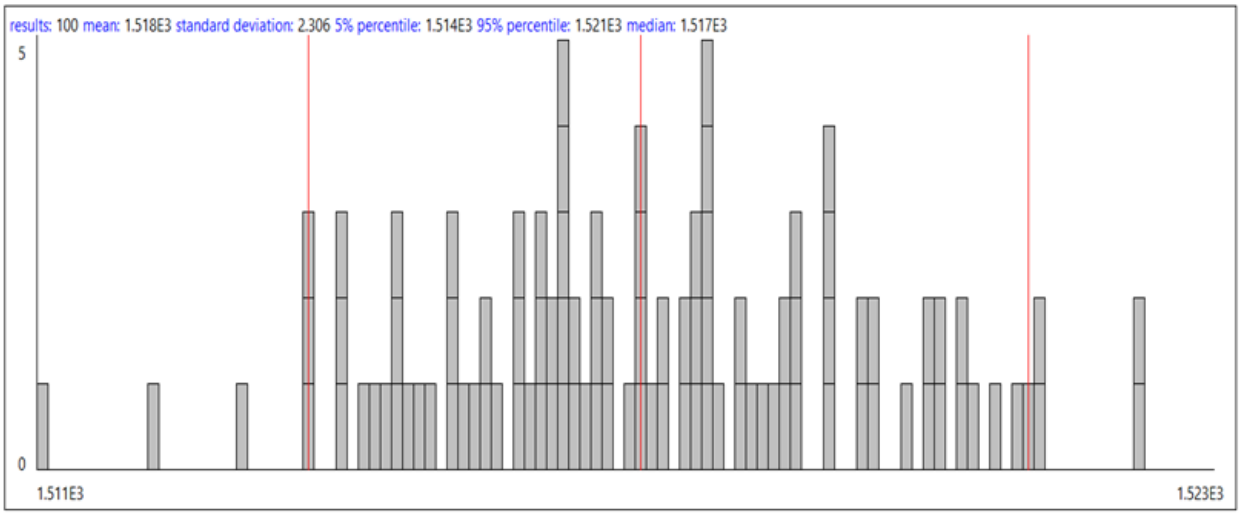

Figure 4.17: Uncertainty in results of climate change showing Monte Carlo simulation in OpenLCA runs 100times. The x-axis represents the resulting impact scores ranged between –0.169 and 0.508. The bars are grey and outline how often certain results appeared. The y-axis shows frequency for each run. Left red line -0.033 minimum percentile. Middle red line 0.102: Median. and right red line 0.231: maximum percentile.

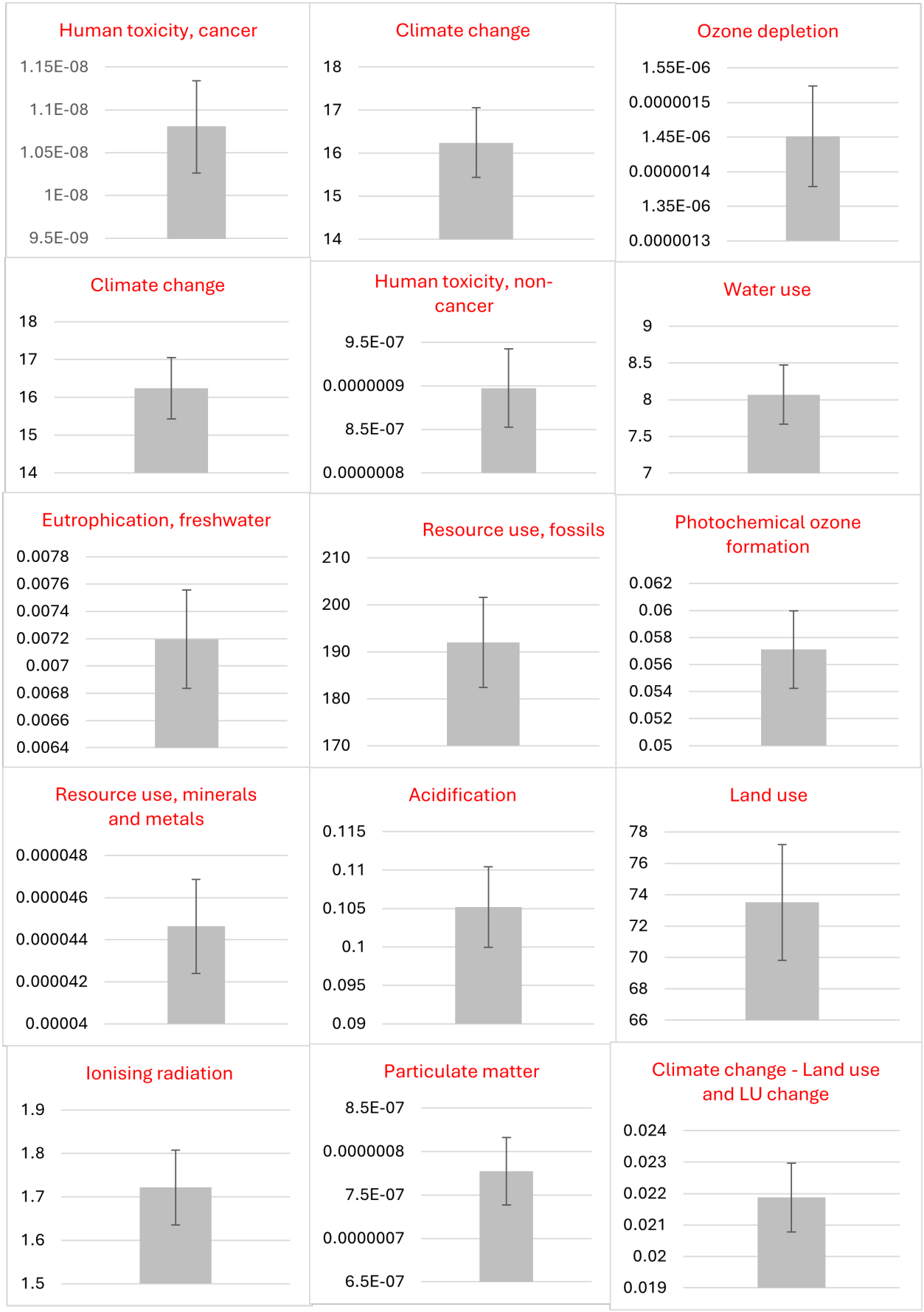

Figure 4.18: Sensitivity analysis of the environmental impacts of IBR Scenario in OpenLCA, expressed across midpoint impact categories in their relevant units. The bars represent the variation in impact scores due to changes in key input parameters.

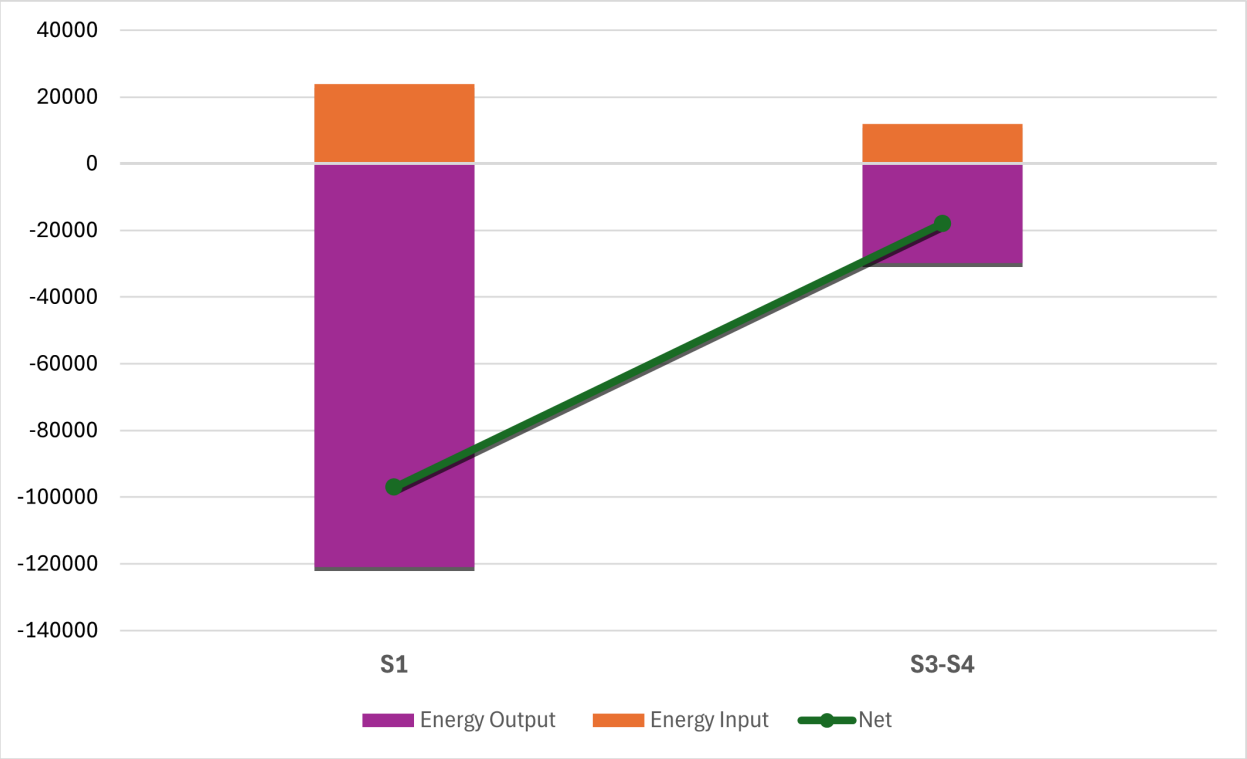

Figure 4.19: Net Energy request and benefits analysis of Integrated waste biorefinery process.

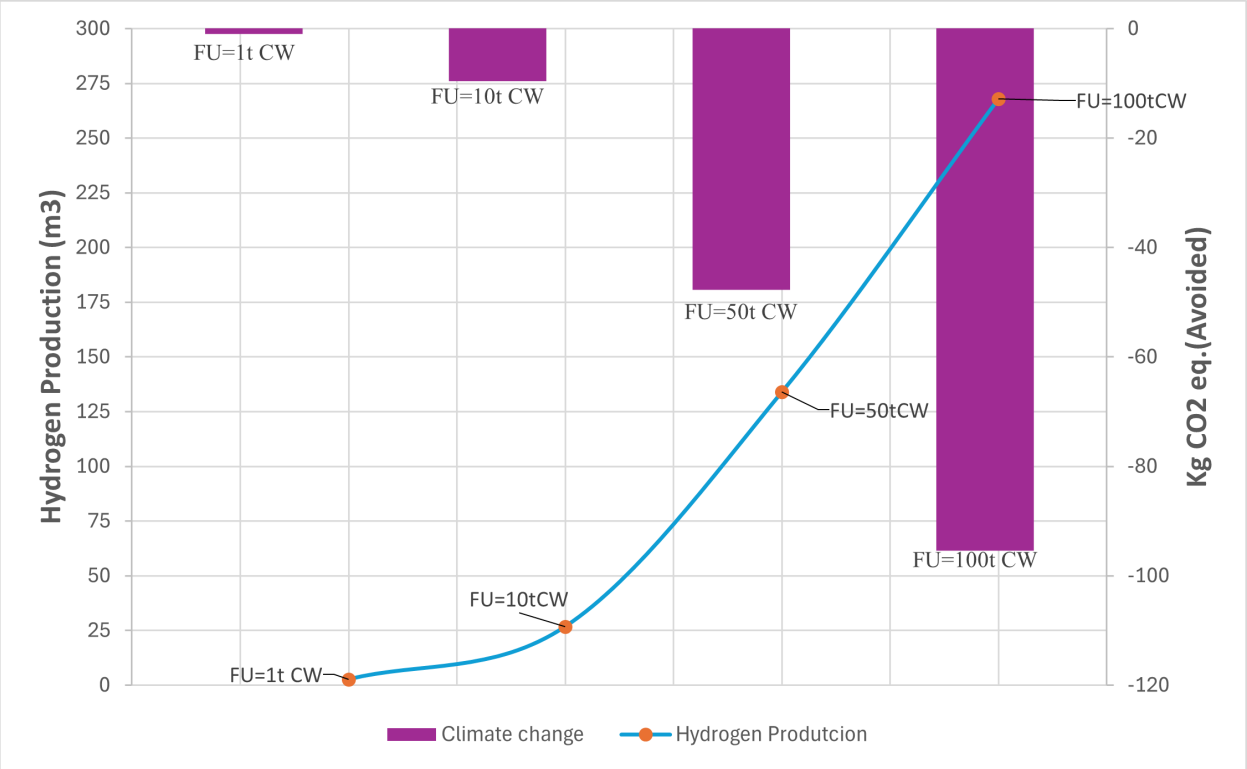

Figure 4.20: Hydrogen Production and kgCO_2 eq. emissions at different Functional Unit of cheese whey.

Chapter 5

Conclusion

5.1 Conclusion

The results from the comparative assessments of both the Integrated Bio-Electrochemical System (IBES) and the broader Integrated waste Bio-Refinery (IBR) system reveal significant potential for innovation in sustainable hydrogen production and organic waste valorization. While each system; IBES and IBR was evaluated in comparison to its respective conventional technologies;Anaerobic Digestion (AD) and Conventional Biorefinery (CBR). Both analyses covered insights into integrated, multi process approach to achieve meaningful environmental benefits but they also bring new challenges that require targeted interventions. From the IBES perspective, the system demonstrates superior performance in critical impact categories such as climate change mitigation and photochemical ozone formation, primarily due to its enhanced hydrogen yield through the synergistic combination of biological fermentation and electrochemical processes. By capturing and converting additional protons during dark fermentation, IBES generates significantly more energy per unit of organic waste compared to traditional AD. This positioned IBES as a promising pathway for reducing greenhouse gas emissions and contributing to future low-carbon energy systems. However, this potential is counterbalanced by elevated impacts in freshwater ecotoxicity, fossil energy demand, and water use, largely driven by the production and use of zinc sulfate, sodium hydroxide, and deionized water. These upstream inputs introduce toxicity, depletes non renewable resources and pose challenges in water scarce regions. Therefore, while IBES holds technological promise, its uneven sustainability profile underscores the need for material substitution, cleaner input sourcing, and water management improvements.

In the broader context, the IBR system, which integrates IBES with Hydrothermal Carbonization (HTC), Carbon Capture and Storage (CCS), and membrane-based gas separation, delivers even more compelling outcomes. Life Cycle Assessment (LCA) results show drastic reductions in

climate impact, with CO_2 emissions dropping from 1.52E+03 kg CO_2 eq/t.CW in the CBR scenario to just 2.87kg CO_2 eq/t.CW in IBR. Similarly, water deprivation is minimized by several orders of magnitude, highlighting the system's potential for water conservation. The environmental performance across categories such as acidification, eutrophication, and toxicity is also significantly improved, thanks to optimized feedstock processing, nutrient recovery, and advanced waste treatment. Moreover, energy efficiency is enhanced through the valorization of hydrochar and hydrogen, although energy intensive units like centrifugation and membrane purification remain hot spots. These findings are further explained by contribution and uncertainty analyses, which indicate that system level integration and input variability are critical drivers of environmental performance.

What emerges from both assessments is; IBES, while not yet ready to replace AD at scale, offers a foundation for future hydrogen technologies, especially if supported by advances in material science and renewable integration. Meanwhile, the IBR system, with its strong scalability potential and circular economy alignment, stands as a scientifically robust alternative to conventional waste treatment methods. In conclusion, the study affirms that integrated bio-refinery approaches, particularly those combining biological, electrochemical, and thermochemical technologies, can significantly advance the sustainability of organic waste-to-energy systems. While both IBES and IBR exhibit certain limitations, these are not insurmountable. With continued research, optimization of subsystems, and the adoption of cleaner, low-impact inputs, these technologies can play a pivotal role in supporting global transitions toward climate neutrality, resource efficiency, and resilient bioeconomy infrastructures. The integration of hydrogen production, CO_2 capture, and organic waste valorization in a closed-loop system represents not just a technological opportunity, but a strategic pathway for addressing some of the most pressing environmental challenges of our time.

5.2 Future Recommendation

While the Integrated Bio-Electrochemical System (IBES) and the broader Integrated Bio-Refinery (IBR) framework have demonstrated considerable promise in advancing sustainable hydrogen production and organic waste valorization, several areas require further exploration to enhance technical feasibility, environmental performance, and scalability.

First and foremost, material substitution and process optimization should be a primary focus of future research. The high environmental burdens associated with critical inputs such as zinc sulfate, sodium hydroxide, and deionized water highlight the need to identify and validate more sustainable alternatives. Investigating low-toxicity and bio-based electrolytes, recyclable electrode materials, or non-metallic catalysts could significantly reduce freshwater ecotoxicity and fossil energy demand. Additionally, optimizing the operational conditions of the bio electrochemical process

to reduce chemical consumption and energy intensity will be essential for improving overall system sustainability. Another important direction involves the integration of renewable energy sources within the IBR infrastructure. While the system already recovers energy through hydrochar combustion and hydrogen utilization, supplementing energy-intensive stages such as centrifugation, gas compression, and membrane separation with biological source of energy could further reduce the carbon footprint and enhance the system's resilience to fossil fuel price volatility.

Moreover, the development and testing of closed-loop water systems and alternative water sources (wastewater reuse) could mitigate the high water demand identified in the life cycle assessment. Research into advanced water recovery technologies, membrane distillation, may provide viable solutions to minimize water loss and maintain water balance within the system. At the systems level, real-world pilot-scale studies are critical to validate the scalability and operational robustness of both IBES and IBR under variable environmental and feedstock conditions. These studies should include long-term monitoring of system performance, process stability, product quality, and emissions under fluctuating load and waste input characteristics. Techno-economic assessments of (TEAs) integrated with sensitivity analyses and risk assessments will be necessary to determine commercial viability and identify key cost drivers. Further research is also needed to explore policy integration, regulatory frameworks, and market pathways for the widespread adoption of IBR technologies. This includes developing mechanisms for carbon capture, waste valorization, and decentralized renewable hydrogen production, as well as establishing standardized environmental performance benchmarks across regions and industries.

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