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Life Cycle Assessment of Biogas Upgradation Using Microbial Electrosynthesis

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Summary:

This thesis evaluates a life cycle assessment (LCA) framework for biogas upgradation. A study and evaluation were conducted by comparing high-pressure water scrubbing (HPWS) for biogas upgrading and integration of Microbial electrosynthesis (MES) system. MES system is attached as a second reactor with anaerobic digestion (AD), from this integrated system biogas with higher methane content is pushed towards the biogas upgrading system. The goal and scope, and inventory analysis are addressed with the framework for both MES and HPWS cases. Global warming potential (GWP) and Eutrophication potential (EP) are mainly focused on environmental analysis in this system because the emission from the upgrading system primarily accounts for the GWP and eutrophication potential. Data are collected from different literature reviews and databases provided for LCA where the emissions from different parts of the process are compared. The study reveals that AD attached to the MES can reduce environmental emission comparing to AD without MES. A basis for assessing potential improvements in the environmental performance of the biogas upgrading system is investigated, and the reasons behind the lack of data have been discussed. Sufficient and appropriate data is valid for future studies in this area to perform better LCA for the upgrading system.

Preface

This report was written on the topic of "Life Cycle Assessment of Biogas Upgrading System Using Microbial Electrosynthesis" to fulfill the partial requirement for the Master's study program in Energy and Environmental Technology at the University of South-Eastern Norway, Faculty of Technology, Natural Science and Maritime Sciences.

The goal of the work was to compare the framework and the environmental impact of the biogas upgrading system with MES. Data were collected from databases and literature reviews and the comparison was made on the basis of the effects of the process on the environment.

I would like to express my sincere gratitude to my supervisor Assoc. Prof. Gamunu L. Samarakoon Arachchige, Prof. Carlos Dinamarca, and PhD Research Fellow Vasan Sivalingam for their guidance, support, technical advice, and feedback throughout the thesis.

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Porsgrunn, 18.05.2022 Ashim Aryal

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List of Abbreviations

AD	_	Anaerobic Digestion
EF	_	Environmental footprints
ELCD	_	European Reference Life Cycle Database
eq	_	Equivalent
g	_	Gram
GHG	_	Greenhouse Gas Protocol
h	_	Hour
HPWS	_	High Pressure Water Scrubbing
HRT	_	Hydraulic Retention Time
IHT	_	Interspecies Hydrogen Transfer
ISO	_	International Organization for Standardization
kg	_	Kilogram
kWh	_	Kilowatt Hour
LCA	_	Life Cycle Assessment
LCI	_	Life Cycle Inventories
LCIA	_	Life Cycle Impact Assessment
MEC	_	Microbial electrolysis cells
MES	_	Microbial Electrosynthesis
NAL	_	National Agricultural Lab
NHE	_	Normal Hydrogen Electrode
Nm ³	_	Normal meter cube
NREL	_	National Renewable Energy Laboratory
N eq	_	Kilogram Nitrogen Equivalent
PEF	_	Product Environmental Footprints
PSA	_	Pressure Swing Adsorption
SETAC	_	Society of Environmental Toxicology and Chemistry
SHE	_	Standard Hydrogen Electrode
UNEP	_	United Nations Environment Programme
USDA	_	United States Department of Agriculture

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1 Life cycle assessment

1.1 Introduction

Environmental concerns and energy and material constraints have prompted the development of life-cycle-oriented methods for product environmental profiling. As a result, life Cycle Assessment (LCA) has seen much growth in recent years. Since the first life-cycle-oriented methodologies were introduced in the 1960s, there has been significant progress in both methodology and applications [1]. LCA is a systematic technique of measuring and reporting a product's or process's environmental consequences throughout its entire life cycle [2].

The purpose of LCA is to compare the environmental performance of products so that the least onerous option may be chosen. The word "life cycle" terms to the idea that raw material creation, manufacture, distribution, use, and disposal (with transportation steps) must all be included for a fair, comprehensive evaluation. The product's 'life cycle' is so defined. The notion may also improve a particular product's (eco-design) or a company's environmental performance [3].

ISO 14040:2006, Environmental management - Life cycle assessment - Principles and framework, gives a broad variety of prospective users and stakeholders, including those with minimal understanding of LCA, a comprehensive overview of the practice, applications, and limits of LCA [3].

Environmental management - Life cycle assessment - Requirements and guidelines, ISO 14044:2006, is a standard for preparing, executing, and critically reviewing life cycle inventory analyses. It also offers advice on the impact assessment phase of LCA, the nature and quality of the data collected, and the interpretation of LCA results [3].

The major purpose of this thesis is to explore a framework for LCA in biogas upgrading methods. First, the typical environmental consequences of the biogas upgrading system theory and LCA history are studied. It is critical to use LCA in the biogas upgrading system to understand the total environmental impact when new methodologies are introduced. As a result, the next phase of this research will focus on how the biogas upgrading system may adopt an LCA. The research also analyses and compares the most appropriate LCA approaches for the biogas upgrading systems.

1.2 Theory

During the late '60s and,'70s the aspect of the life cycle was introduced to study the products and materials and focused on the issues like energy efficiency, the consumption of raw materials, and, to some points, waste disposal. LCA regained prominence in development and application at the end of the 1990s. Finally, in 1993, the International Organization of Standardization (ISO) began to build a global standard for LCA after holding several significant international conferences, collaboration, and coordination at universities. During this period, LCA was introduced to the world but was of limited interest, however, the scientist from Europe and North America was the small community to implement LCA at the first stage, and slowly it went into the real world [4].

Resources are being exploited and products are being manufactured, putting a strain on the natural environment that could be disastrous. Also, the ever-increasing demand for goods places further strain on the environment. The new standard will make it easier to assess a product's environmental impact over its entire life cycle, promoting resource efficiency and lowering liabilities, hence LCA is essential for the impact of certain goods or products throughout their lifespan [3].

LCA has been used to make decisions in both the private and public sectors. Energy and transportation sectors, chemical, nuclear, metal-polymer, paper and forest, water, electronics, and other industries are some of the more recent instances of LCA uses in business decision making. These applications have primarily included, but are not limited to, the following [5]:

- Environmental strategy formulation or strategic planning.
- Optimization of products and processes, design and innovation.
- Identifying potential for environmental improvement.
- reporting and marketing on the environment.
- establishing an environmental auditing framework.

1.3 LCA Database and Software Tools

The complexity of the LCA process has convinced the companies to rely on existing commercial software and database. By enlisting an appropriate software and database, the companies will be able to calculate the score of all impact categories and decide how to start or develop a much greener technology [6]. Moreover, apart from saving time and money, commercial databases and tools give companies the chance to test the results' sensitivity. In other words, competition has encouraged the database providers and software developers to cover more LCIA methodologies, so that, companies can calculate different impact classifications [7].

The Inventory Program of the UNEP/SETAC Life Cycle Initiative, on the other hand, assesses valuable resources, data gaps, and current datasets. Governments, scientific institutions, and corporations support the majority of the databases available. Sometimes organizations provide datasets for economic reasons, and other times organizations provide datasets for other reasons dedicated to long-term development through creating databases [8]. Below are some of the databases that are discussed for different purposes.

1.3.1 Ecoinvent

The Swiss Centre for Life Cycle Inventories created Ecoinvent. SimaPro 8 includes it because of its consistency and transparency, and it may also be used with GaBi 5, Umberto 5, and OpenLCA. Most LCA studies, are based on downloadable reports and use a cradle-to-gate model [9].

SimaPro's demo edition gives us access to 100 of SimaPro's 4000 processes. Ecoinvent is ideally suited for construction (materials) purposes when the full license is purchased, as

every category of construction materials is included and developed with a wide range of products [9]. There are many other databases, like ELCD (European Reference Life Cycle Database) [9], GaBi database [9], and Athena database [9], however, the data in this report were extracted from Ecoinvent and primarily focused.

1.3.2 LCA Commons

The LCA Commons is a database that contains representative LCA data for the United States. The 9200 datasets were created by various US government agencies, including the United States Department of Agriculture (USDA), the National Renewable Energy Laboratory (NREL), the National Agricultural Library (NAL), and the US Forest Service, and have diverse modeling views and terminology systems[10].

1.3.3 Carbon Minds

Carbon Minds known as cm.chemicals database is currently in its most recent (and first published) version. The life cycle data for chemicals and polymers in cm.chemicals is a large-scale dataset for environmental evaluation. cm.chemicals is a one-stop data source for ISO 14040/14044 compliant life-cycle assessment studies for chemicals and plastics, backed by a consistent, 3rd party certified methodology and annual updates. It covers 1000 chemicals in geographical regions [10].

1.3.4 Environmental Footprints

The European Commission's Single Market for Green Products project was inspired by Product Environmental Footprints (PEF). PEF's goal was to create a consistent technique for quantitatively assessing products' environmental consequences to enable their assessment and labeling. PEF category rules and organization environmental footprint sector guidelines are supported by the Environmental Footprint (EF) database. It includes supplementary life cycle inventory datasets and an EF impact assessment method meant to be compliant with the EF approach [10].

1.3.5 LCA software

Currently available European LCA software packages used for producing Life Cycle Inventories (LCI) as part of an overall life cycle analysis (LCA) are listed below. However, there are many other software houses that are not being listed because of lack of response, the leading European software's are [11]:

- The Boustead Model
- EcoPro 1.3
- GaBi 2.0
- KCL-ECO (with ECODATA database)
- LMS Eco-Inventory Tool
- PEMS 3.0
- PIA

- SimaPro 3.1
- SimaTool
- OpenLCA [10]

GaBi and SimaPro are the highly used LCA softwares.

2 Biogas upgrading technology

2.1 Theory

Methane (50-75%) and carbon dioxide (25-50%) are the most common gases in biogas, with tiny quantities of other gases and water vapour. In the anaerobic digestion (AD) process, microbes degrade complex organic material to create biogas [12]. Energy cost and security, and emissions of greenhouse gases (GHG) and other pollutants from current energy production methods are two significant issues that have prompted several technological advancements in alternative energy sources [13]. In the anaerobic digestion (AD) process, microbes degrade complex organic material to produce biogas. For millennia, this ability has been used in artificial systems (bioreactors) for energy generation [12]. In addition, the anaerobic digestion method has been widely utilized to treat a variety of organic wastes because it may provide value-added products such as an energy-rich gas and bio-fertilizer [14].

Biogas can be used as fuel once it has been converted to biomethane using gas purification processes, similar to compressed natural gas, which is also used in some internal combustion engines. For example, in Zurich, Switzerland, waste collection vehicles with diesel engines were run using purified and compressed sewage gas in 1942-44 [15]; hence biogas was upgraded to get pure methane (95-99% methane). Biogas is mainly upgraded by removing CO₂, which increases the energy value of the gas, allowing for greater driving distances with a constant gas storage capacity. CO₂ removal also ensures a consistent gas quality in terms of energy value. Carmakers view the latter as extremely important to achieve low nitrogen oxide emissions [16]. Currently, there are a different number of methods to upgrade biogas, the main biogas up-gradation processes are often employed to remove CO₂ from biogas, either to meet vehicle fuel specifications or to achieve natural gas quality for injection into the natural gas system [16].

In this section, the major gas upgrading methods are discussed (with the reason behind the selection of the method).

2.2 High-pressure water scrubbing

A high-pressure water scrubber (HPWS) is a physical scrubber that uses the fact that CO_2 is far more soluble in water than methane [17]. Scrubbing with water is the most extensively utilized, easiest, ecologically friendly, cost-effective, and generally applied method for cleaning and upgrading biogas [20, 21]. HPWS is a method that can absorb CO_2 and H_2S simultaneously, producing a CH₄-rich gas as a result. Because CO_2 and H_2S are more soluble than CH₄, N₂, or O₂, they are crucial to the process [20]. Using high pressure, usually 6-10 bar [19, 23], CO₂ is extracted from raw biogas and dissolved into the water in the absorption column in a water scrubber. By adding air at atmospheric pressure to the water in the desorption column, the CO₂ is liberated from the water once more [17]. Figure 2.1 shows the block flow diagram of the HPWS process.

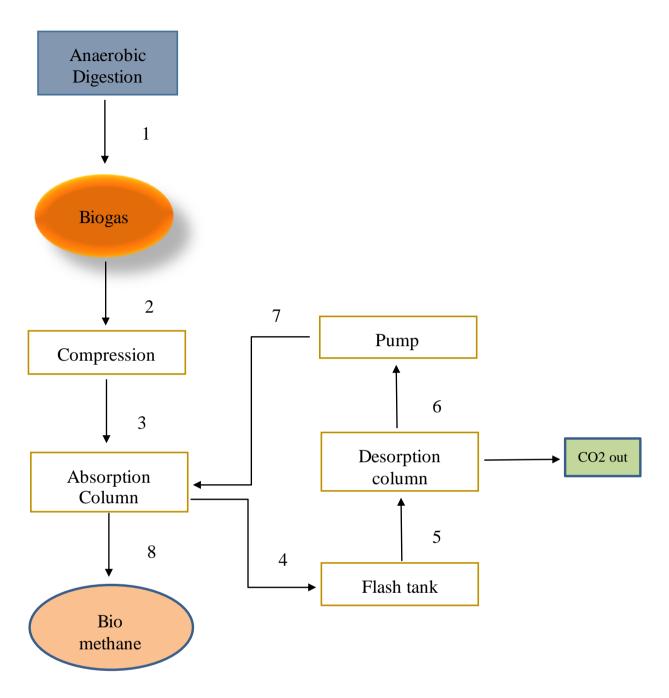


Figure 2.1 Block flow diagram of High Pressure Water Scrubbing with the respective steps for biogas upgradation

The numbers indicate the flow steps of biogas. The absorption column is usually filled with packing material for improved gas-liquid mass transfer. Compared to other technologies, this one has more significant water usage. Biomethane is in 6-10 bar pressure in absorption columns. The absorption solution is regenerated in the desorption column at atmospheric pressure by CO_2 stripping, injecting air, and releasing CO_2 rich off-gas from the top [21, p.].

The reason behind the selection of HPWC is that many countries widely use this process and some of them are mentioned below in table 2.1:

Country	City	Biogas Production	CH4	CO2	In	
		(landfill gas/sew	Requirements	Removal	operation	
		sludge/waste/manu	(%)	technique	since	
		re)				
France	Lille	Sewage sludge	97	HPWS	1993	
	Lille	Biowaste, manure	97	HPWS	2007	
Iceland	Reykjavik	Landfill gas	-	HPWS	2005	
Japan	Kobe	Sewage sludge	97		2004	
	Kobe	Sewage sludge	97	HPWS	2007	
Netherlan ds	Tilburg	Landfill gas	88	HPWS	1987	
Spain	Madrid		96.5	HPWS	2007	
Sweden	Stockholm	Sewage sludge	97	HPWS	2003	
	Uppsala	Waste from food industry, manure, sewage sludge	97	HPWS	1997	
	Trollhatta n	Sewage sludge, organic household waste	97	HPWS	1996	
	Norrkopin g	Sewage sludge	97	HPWS	2004	
	Norrkopin g	Residue from ethanol production, energy crops	97	HPWS	2006	

Table 2.1 List of countries using HPWS as biogas upgradation [22]

	Eskilstuna	Sewage Sludge	97	HPWS	2003
	Jonkoping	Sewage sludge, biowaste industry	97	HPWS	2000
	Vasteras	Biowaste household and pasture, Sewage sludge	97	HPWS	2004
	Kristiansta d	Biowaste household and pasture, Sewage sludge	97	HPWS	1999
	Linkoping	Biowaste household and pasture, Sewage sludge	97	HPWS	1997
USA	Renton	Sewage sludge	98	HPWS	1984

Compressor: When raw biogas arrives to the upgrading facility, it is usually permitted to reach temperatures of up to 40° C. Before entering the absorption column, the pressure of the raw biogas is raised to roughly 6-10 bars (depending on the manufacturer and application), this is done by the compressor [17].

Absorption column: The compressed biogas is fed into the absorption column's bottom, while water is injected into the top. The water and gas must move in opposite directions to reduce energy use and methane loss. The absorption column is filled with random packing to maximize the contact surface between the water and the biogas and ensure that the CO_2 and H_2S is absorbed as efficiently as possible in the water. A typical design of this packing is depicted in figure 2.2 [19, 25].



Figure 2.2 A typical design of random packing which is used in a water scrubber absorption column [17]

Flash column: The water is removed into a flash column to avoid releasing the methane collected by the water in the absorption column. The pressure in the flash column is reduced to roughly 2.5-3.5 bar. The water contains mainly CO_2 and some methane. Because CO_2 dissolves considerably more readily in water than methane, the released gas in the flash column will typically be 80-90% CO_2 and 10-20% methane. As a result, the partial pressure of methane in the flash column will be just 10-20% of the pressure in the flash column, resulting in limited methane solubility [17].

Desorption column: The water delivered from flash column to the desorption column will include most of the CO_2 in the raw biogas, but less than 1% of the methane. The CO_2 is released from the water in the desorption column after the flash column has removed the methane. Water enters the desorption column from the top, whereas air enters from the bottom. Random packing is also used to improve the constant surface between the air and the water in this column. The water that exits the desorption column is almost CO_2 free and is pumped into the absorption column's top [17].

2.3 Pressure swing adsorption

Pressure Swing Adsorption (PSA) is a cyclic dynamic process carried out cyclically. Figure 2.3 shows the flow diagram of PSA.

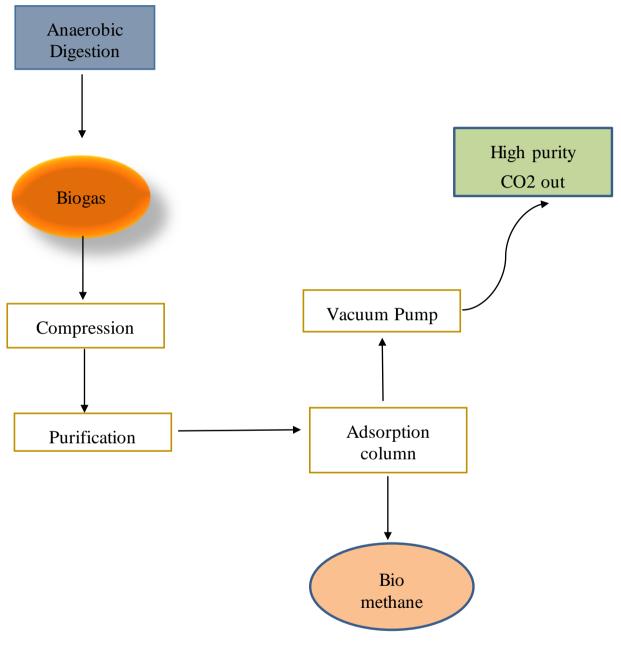


Figure 2.3 Block flow diagram of Pressure Swing Adsorption for biogas upgradation

Pressurization with feed or pure product, high-pressure adsorption, pressure equalization (s), blowdown, and purge are the key operational processes of a PSA process. PSA technique has

a minimal energy need and has previously been employed in small or intermediate-scale biogas, landfill gas, and natural gas production to produce high purity methane [24]. The effectiveness of this process is determined by various parameters, including adsorbent material pore size, adsorbate partial pressure, system temperature, and adsorbate and adsorbent material interaction forces. Furthermore, the adsorbent material's ability to regenerate under specified conditions impacts the process' efficiency [19].

The raw biogas stream is taken from an anaerobic digestion tank that has been processed to remove pollutants such as H_2O , H_2S , C_2H_6 , and other contaminants. As a result, it is safe to infer that the raw biogas comprises solely CH_4 and CO_2 [24]. Adsorbents such as zeolite and carbon-based adsorbents are often utilized in the biogas upgradation process [19, 21]. To preferentially retain CO_2 , N_2 , O_2 , and other gases inside the pores of the adsorbent, PSA columns are frequently operated at 4-10 pressure. CH_4 runs unrestricted through the column and may be collected at the top by lowering the pressure. The aforementioned processes are repeated in a cyclic pattern. Within this sequence, commercial upgrading facilities run four, six, or nine adsorber columns in sequence. The regeneration of densely loaded adsorbent with CO_2 gas is a step-by-step procedure. The Skarstrom cycle is a cyclic series of adsorption and regeneration that lasts 2-10 minutes [19]. A PSA column cycle is divided into four phases: pressurization, feed, blowdown, and purge respectively, which are depicted in the figure along with a pressure profile for each step [17].

The column is fed with raw biogas during the feed phase. While the methane runs through the column, the CO_2 is deposited on the bed material. The feed is closed when the bed is saturated with CO_2 , and the blowdown phase begins. The pressure is reduced significantly to desorb the CO_2 from the adsorbent, and the CO_2 rich gas is pumped out of the column. Because the column was filled with raw biogas at the start of this phase, some methane is lost along with the desorbed CO_2 . The purge is started at the lowest column pressure. The column is blown with upgraded gas to remove all of the CO_2 from the column bed. The column has been regenerated and can be repressurized with either raw biogas or upgraded gas, completing the cycle [17]. Figure 2.4 shows the four cycle phase pressure profile of PSA.

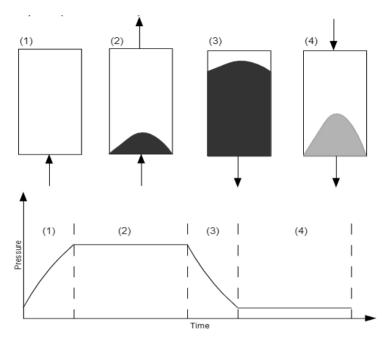


Figure 2.4 Four phase cycle and a pressure profile [17]

Feed: The CH₄-CO₂ combination is supplied to the fixed bed, which contains the adsorbent. At the column product end, at high pressure, selective CO₂ adsorption occurs, yielding pure CH₄ [25].

Blowdown: The column should be refreshed right before CO_2 bursts through. This is accomplished by stopping the feed step and lowering the pressure applied to the feed step by the column counter. This step should ideally be repeated until a new equilibrium condition is reached. When the flow rate of CO_2 rich stream departing the column is low, however, the blowdown process is stopped. CO_2 is partially desorbed from the adsorbent as pressure is reduced. The system's lowest pressure is obtained in this step [25].

Purge: When the low pressure is reached, the column will include CO_2 molecules in both the adsorbed and gas phases. A purge step is done counter-current to the feed step to lower the amount of CO_2 in both phases. Some of the purified methane is recycled (mild recycle) to replace CO_2 from the CH₄ product end during the purge [25].

Pressurization: The pressure should be increased to start a new cycle because the purge is also done at low pressure. The pressurization can be done in parallel with the feed stream of purified CH_4 or counter-currently. The choice of pressurization approach is not easy and can result in quite varied outcomes [25].

Table 2.1 shows the list of countries that uses PSA as biogas upgradation.

Country	City	Biogas Production (landfill gas/sew sludge/waste/manu re	CH4 Requiremen ts (%)	CO2 Removal Technique	In Operatio n Since
Austria	Pucking	Manure	97	PSA	2005
Germany	Kerpen	Energy crops		PSA	2006
	Pliening	Energy crops		PSA	2006
	Straelen	Energy crops, manure		PSA	2006
	Rathenow	Energy crops, manure		PSA	2006/200 7
Netherlan	Nuenen	Landfill gas	88	PSA	1990
ds	Wijster	Landfill gas	88	PSA	1989
Norway	Fredrikstad	Sew sludge/ waste	95 ± 2	PSA	2001
Sweden	Helsingborg	Biowaste household and industry manure	97	PSA	2002
	Stockholm	Sewage sludge	97	PSA	2000
	Skovde	Sewage sludge, slaughter waste	97	PSA	2003
Switzerlan d	Bachenbulac h	Biowaste	96	PSA	1996
	Lucerne	Sewage sludge	96	PSA	2004
	Otelfingen	Biowaste	96	PSA	1998
	Rumlang	Biowaste	96	PSA	1995

Table 2.2 List of countries using PSA as biogas upgradation [22]

	Samstagern	Biowaste	96	PSA	1998
USA	Cincinnatti	Landfill gas		PSA	1986
	Dallas	Landfill gas		PSA	2000

2.4 MES technology

Microbial electrosynthesis (MES) primarily uses microorganisms as catalysts to transform biomass energy into chemical energy in organic wastewater via applied voltage. Studies have shown that only a small amount of energy is required to drive the electrochemical process of microorganisms allowing H+ and electrons to breakthrough energy barriers, combine to form hydrogen, or further from methane, which is significantly less than the energy input required for traditional electrolysis processes [26].

Microbial electrosynthesis is an artificial type of photosynthesis with numerous advantages over bioenergy strategies that rely on biological photosynthesis when the electricity for microbial electrosynthesis is derived from various renewable electricity sources. Initial proof of concept investigations showed that acetogenic bacteria like Sporomusa and Clostridium species could take electrons from negatively charged graphite electrodes as the electron donor for reducing CO_2 to acetate released extracellularly. Clostridium ljungdahlii, one of the strains capable of electrosynthesis can be genetically modified, promising to produce compounds with more value than acetate [27].

Microbial electrosynthesis will require optimization before it can be commercialized. Enhancing electron interaction at the cathode surface while keeping costs down is one of the essential features. Understanding how microorganisms transport electrons to electrodes has improved significantly [27].

In recent years, there have been many studies on adding electro methanogenesis into the anaerobic digestion process. These investigations have shown that accelerating electro methanogenesis has various advantages over traditional digesters, including improved methane productivity, kinetics, and process stability [28].

Two ways are considered to achieve electrochemical CO₂ reduction [29]:

Indirect electron transfer (MEC Cathode)

 $2H^+ + 2e^- \rightarrow H_2E = -0.414 \text{ V vs NHE}$ (2.1) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (2.2)

Direct electron transfer (MES Cathode)

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2OE = -0.244 \text{ V vs NHE}$$
 (2.3)

Direct electron transfer is defined as the electron transport that does not need the diffusion of a mobile component to and from the cell. While, the development or utilization of so called

electron shuttles, which transfer electrons from the cell to the electrode, is the indirect technique for the indirect electron transfer [30].

The theoretical potential for reaction (2.3), which converts CO_2 to CH_4 with an 8 electron transfer, is lower than the theoretical potential for H_2 electrolysis (2.1). Direct electron transfer microorganisms would gain more energy than organisms that use indirect electron transfer, in which the hydrogen molecule functions as a shuttle for electron transfer. Interspecies hydrogen transfer (IHT) allows methane-producing MECs (Microbial electrolysis cells) to carry out microbial processes in which hydrogen is not the ultimate product but rather an electron mediator. According to the electrochemical principle, a lower potential for the transfer of a certain quantity of electrons is more effective than a higher potential for the same quantity of electrons [29].

As a result, the MES direct electron transfer process (2.3), which employs a lower voltage, is superior to the MEC cathode reactions. Figure 2.5 shows the schematic representation of membrane-less MES and MEC for the treatment of wastewater and CO_2 .

MEC Anode

 $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-E = -0.280 V \text{ vs SHE}$ (2.4)

MES Anode

 $2H_2O \rightarrow O_2 + 4H^+ + 4e^-E = 0.820 \text{ V vs SHE}$ (2.5)

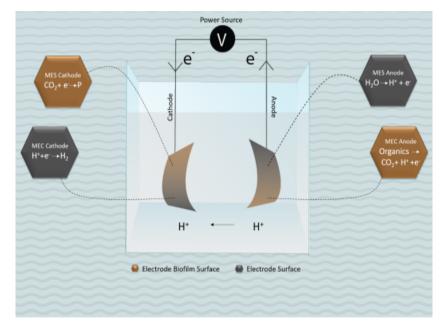


Figure 2.5 A schematic representation of membrane-less MES and MEC for the treatment of wastewater and CO_2 [29]

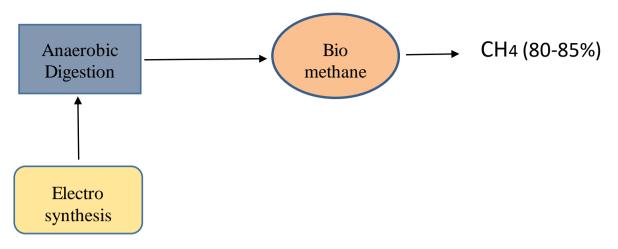


Figure 2.6 Block diagram representing Microbial Electro synthesis integrated with anaerobic digestion process

One of the key reasons for choosing MES is to eliminate the separation of the hydrogen generation stage, which has proven to be an economic hurdle to electrolysis coupled methanation based biogas upgradation solutions effectiveness. Second, to look at the possibility for electrochemical destruction of residual organic matter found in an AD effluent. Furthermore, it provides a cost-effective solution for upgrading existing wastewater treatment plants without incurring significant capital or operating cost [31].

3 Life Cycle Assessment Framework

The design/development phase is frequently left out of LCAs since it is thought not to contribute much. However, there is a grown interest/demand for LCA at design phase, since decisions made during the design/development phase significantly impact the environmental impacts of subsequent life cycle stages [32].

ISO 14040 provides a framework to conduct the LCA process. Four main steps can be identified in ISO 14040 recommendations, figure 3.1 is provided with the steps [33].

- Definition of goal and scope
- Inventory analysis
- Impact assessment
- Interpretation of results

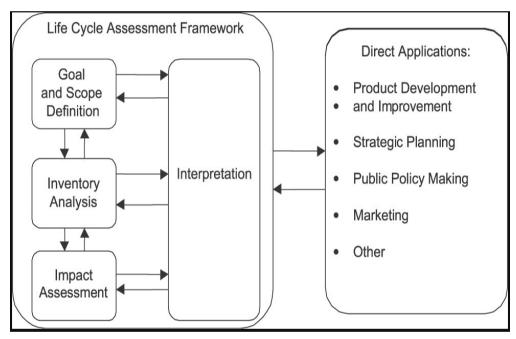


Figure 3.1 Phases and applications of a LCA [33]

3.1 Goal and Scope

The purpose of the goal and scope is to establish the outset, describing the breadth and depth of the product system under consideration [34]. The main objective of this research is to develop a framework for the determination of the environmental impact of biogas upgrading systems (an existing system) when microbial electrosynthesis is applied in biogas process. The research is carried out using life cycle assessment (LCA) principles, taking into account the effect categories of primary energy and some secondary resources (materials) and greenhouse gas balance, and eutrophication balance.

3.1.1 System boundaries

The total amount of water and energy used in the biogas upgrading process is included in LCA. The full-scale study of HPWS and MES are included with the flow diagram, and figure 3.1 shows the system boundary of the LCA. The system boundary is considered after anaerobic digestion after the production of biogas. The produced biogas contains CH_4 (by volume, 50-75%) and CO_2 (by volume, 25-50%) [21]. Here we are considering 60% of methane by volume and 40% of CO_2 by volume during biogas production. 85% of methane and 15% of CO_2 [35] is considered after microbial electrosynthesis.

The biogas generation process (landfilling, anaerobic digesters, wastewater treatment facilities), biogas pretreatment, the housing unit for the entire system, the material used to create the smaller parts of the system, and biomethane transportation to the natural gas grid were all excluded from the evaluation because they share common characteristics [36].

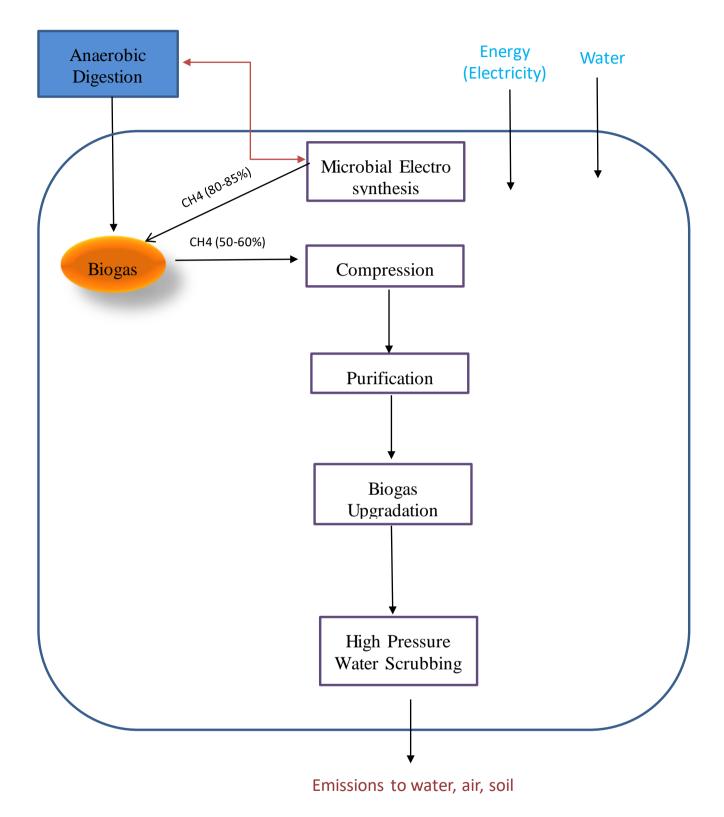


Figure 3.2 The outline (dark blue) is considered as the system boundary for LCA

3.1.2 Functional unit

The LCA's functional unit is meant to serve as a point of reference for different systems. The results of all LCAs are provided in terms of the functional unit. This unit should be chosen so that options can be compared directly [37]. In this case, the functional unit (FU) is 100m³ of upgraded biogas per hour.

Impurities such as H_2S are ignored because they are usually eliminated previously by filters [36].

3.2 Inventory analysis

In this report, upgrading technology HPWS is compared with MES technology. The relevant data were collected from different sources and referenced accordingly. Table 3.1 shows the emission from each step of the process inflow in HPWS, while table 3.2 shows the emission from each step of the process outflow in HPWS.

Process Steps	Inflow	Inflow (quantity) ^a	Emissio n (direct)	Impact Categories	
				GWP	EP
Compressio n	Electricity (kWh)	117.32	GWP	49.41 kgCO ₂ eq/100 Nm ³	
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂) kg/h	604.55	GWP	-	
Absorption	Electricity (kWh)	0	GWP	-	
Column	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	853.45	GWP	-	
	Tap water (kg/h)	2000	EP	-	4.17E-06 kgN

Table 3.1 Process inflows of HPWS with	impact category
Tuble 5.11100003 millows of The WB with	impact category

					eq/100 Nm ³
Flash Tank	Electricity (kWh)	8.538	GWP	3.60 kgCO ₂ eq/100 Nm ³	
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	0	GWP	-	
	Tap water (kg/h)	84365 (H ₂ O)	EP	-	1.76E-04 kgN eq/100 Nm ³
Desorption column	Electricity (kWh)	7.76	GWP	3.27 kgCO ₂ eq/100 Nm ³	
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	0	GWP	-	
	Tap water (kg/h)	84702	EP	-	1.77E-04 kgN eq/100 Nm ³
Pump	Electricity (kWh)	30	GWP	12.63 kgCO ₂ eq/100 Nm ³	-

Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	-	GWP	-	-
Tap water (kg/h)	-	EP	-	-

 a, all the data from the column were taken from [38].

Process Flow Diagram	Outflow	Outflow (quantity) ^a	Emission (direct)	Impact Categories	
				GWP	EP
Compressio n	Electricity (kWh)	0	GWP	-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂) kg/h	853.45	GWP	-	-
Absortion Column	Electricity (kWh)	0	GWP	-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	223.92	GWP	-	-
	Tap water (kg/h)	84365 (H ₂ O)	EP	-	1.76E-04 kgN eq/100 Nm ³
Flash Tank	Electricity (kWh)	7.839	GWP	3.30 kgCO ₂ eq/100 Nm ³	-

Table 3.2 Process outflows of HPWS with impact category

	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	237.76	GWP	-	-
	Tap water (kg/h)	84365 (H ₂ O)	EP	-	1.76E-04 kgN eq/100 Nm ³
Desorption column	Electricity (kWh)	0	GWP	-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	1684.54	GWP	-	-
	Tap water (kg/h)	82370	EP	-	1.72E-04 kgN eq/100 Nm ³
Pump	Electricity (kWh)	-	GWP	-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	-	GWP	-	-
	Tap water (kg/h)	82370	EP	-	1.72E-04 kgN eq/100 Nm ³

^{a,} all the data from the column were taken from [38].

While in the next step, when the biogas is sent to a reactor with MES, the outcome of the biogas is 85% methane and 15% CO₂, which means 25% more pure methane before sending it into the biogas upgrading system (HPWS), while MES uses 2 kWh of energy for every 100 m³/h of upgraded biogas. Table 3.3 shows the emission during inflow after the biogas come out from MES, while table 3.4 shows the emission during outflow after the biogas come out from MES.

Process Flow Diagram	Inflow	Inflow (quantity)	25% more purity after MES	Impact Cate	gories
				GWP	EP
Compressio n	Electricity (kWh)	117.32	117.32	49.41 kgCO ₂ eq/100 Nm ³	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂) kg/h	604.55	604.55	-	_
Absortion Column	Electricity (kWh)	0		-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	853.45	853.45	-	-
	Tap water (kg/h)	2000	500	-	1.04E-06 kgN eq/100 Nm ³
Flash Tank	Electricity (kWh)	8.538	2.1345	0.90 kgCO ₂ eq/100 Nm ³	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	0		-	-
	Tap water (kg/h)	84365 (H ₂ O)	21091.25	-	4.39E-05 kgN

Table 3.3 Impacts after higher methane content from MES, pushed towards the HPWS

					eq/100 Nm ³
Desorption column	Electricity (kWh)	7.76	1.94	0.82 kgCO ₂ eq/10 0 Nm ³	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	0	-	-	-
	Tap water (kg/h)	84702	21175.5	-	4.41E-05 kgN eq/100 Nm ³
Pump	Electricity (kWh)	30	30	12.63 kgCO ₂ eq/10 0 Nm ³	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	-	-	-	-
	Tap water (kg/h)	-	-	-	-

Table 3.4 Impacts after higher methane content from MES, pushed towards the HPWS

Process Flow Diagram	Outflow	Outflow (quantity)	25% more purity after MES	Impact Cat	egories
				GWP	EP

Compressio n	Electricity (kWh)	0	-	-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂) kg/h	853.45	853.45	-	-
Absortion Column	Electricity (kWh)	0	-	-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	223.92	223.92	-	-
	Tap water (kg/h)	84365 (H ₂ O)	21091.25	-	4.39E-05 kgN eq/100Nm 3
Flash Tank	Electricity (kWh)	7.839	1.95975	0.825 kgCO ₂ eq/100Nm 3	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	237.76	237.76	-	-
	Tap water (kg/h)	84365 (H ₂ O)	21091.25	-	4.39E-05 kgN eq/100Nm ³
Desorption column	Electricity (kWh)	0	-	-	-

	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	1684.54	1684.54	-	-
	Tap water (kg/h)	82370	20592.5	-	4.29E-05 kgN eq/100 Nm ³
Pump	Electricity (kWh)	-	-	-	-
	Biogas (CO ₂ /CH ₄ /H ₂ S/N ₂ /H ₂ O) kg/h	-	-	-	-
	Tap water (kg/h)	82370	20592.5	-	4.29E-05 kgN eq/100 Nm ³

Furthermore, apart from the energy, water, and leakage of biogas, other factors affect the environment, such as the major materials used in operating the plants. Tables 3.5 and 3.6 show the materials used in the HPWS and MES plants respectively. However, for MES, some assumptions were made based on the reference due to a lack of data.

Material	Quantity (kg) ^b	CO2 emission	Total emission	Unit (functional unit)
Fiberglass composite material (moulded FRP)	1500	2.04 kg CO2eq/kg [39]	17.46575342	gCO2eq/h
Electric installation (copper wiring and jointing)	108	0.0000011 kgCO2eq/kg [40]	6.74943E-10	gCO2eq/h

Table 3.5 Emission by the materials used in HPWS

HDPE piping	600	2.5 kgCO2eq/kg [41]	8.561643836	gCO2eq/h
PVC piping	850	5.9 kgCO2eq/kg [42]	28.60934075	gCO2eq/h
Stainless steel piping	1088	7.1 kgCO2eq/kg [43]	44.07106164	gCO2eq/h
Steel (mild galvanized steel)	2825	1.113kgCO2eq/kg [10]	17.94648973	gCO2eq/h

^{b,} all the data from the column were taken from [34].

Since the data regarding full scale design of MES was barely available, some of the assumptions were made according to the pilot-scale reference [44]. Table 3.6 shows some of the assumed values (with the calculation) and expected values for MES.

Quantities	Result	Remarks	Reference
HRT	3 h	Expected	
Flow rate (inlet and outlet)	200 m ³ /h	Expected	
Reactor orientation	Vertical with the concrete foundation	Selected	[44]
Material of reactor	SS 316	Selected	[44]
MPR (Methane production rate)	100 m³/h	Calculated	
Surface area of each electrode	450 m ²	Theoretical value	[44]

 Table 3.6 Results of the designed reactor with remarks

Table 3.7 shows the materials being used in MES.

Materials	Quantity	Unit
Mass of one electrode with spacers and rod	245.7	kg
Mass of only one electrode	209.75	kg
Mass of spacer and rod (plastic)	35.95	kg
Total number of electrode	105	
Total wt. of electrode	22023.75	kg
Total wt. of spacer and rod (plastic)	3774.75	kg

Table 3.7 Materials used in MES (plant)

Table 3.8 shows the emission created by the materials

 Table 3.8 Emission created by the materials

Material with specification	Quantity (kg)	CO2 emission	Total emission	Unit
Pipe electrode reactor vessel (SS 316)	22023.75	7.1 kgCO2eq/kg	892.515	gCO2eq/ h
The spacer electrode rod (rigid PVC)	3774.75	5.9 kgCO2eq/kg	127.05	gCO2eq/ h

3.3 Impact assessment phase

The result of the impact assessment analysis for the HPWS technology is presented in Tables 3.1 and 3.2. In both the tables, the results are divided into two self-appointed categories (global warming potential, eutrophication potential) to compare all the methodologies applied in this study. It's worth noting that LCA approaches are classified into two groups: problem-oriented (as belonging to the environmental impact categories to which they contribute) and damage-oriented (as belonging to the environmental impact categories to which they contribute) [38].

Greenhouse gases global warming potential is measured in carbon dioxide equivalents (CO_2 eq.) [38]. The GWP of 100 years is calculated. CO_2 and CH_4 have been recognized as

greenhouse gases because of their contribution to global warming. Also, indirect emissions released during energy usage contribute to global warming potential [38].

The eutrophication potential is associated with the water used during the process and is calculated in nitrogen equivalent (N eq.). The two upgrading technologies were compared by performing a more detailed and framework for full-scale LCA. In this report, it was only possible to perform a simplified LCA due to data limitations.

4 Discussion

The energy consumption (power) in the biogas upgrading system (HPWS) was summarized in Tables 3.1, and 3.2. It is considered that producing 309.36 Nm³/h upgraded biogas requires 171.5 kWh of total energy [38], which means producing 100 Nm³/h of upgraded biogas requires 55.4 kWh of energy. Although this study is taken as the initial stage for improving MES and its impact on the environment, the data had some limitations. Some of the limitations are discussed. Since there is no more information about the large-scale construction of MES, many of the data regarding MES were assumed and some of them were calculated. Hence, the framework for the biogas upgrading system is mainly focused on this thesis. GaBi software is commercially used for full-scale LCA, and the use of the database varies according to the process flows. For this thesis, if there is much more study on the large scale of MES, the complete emission work will be done, and full-scale LCA can be done precisely.

MES is expected to be 680 m³ of reactor vessel volume with 600 m³ of wastewater volume flow, HRT 3 hours, and flow rate of 200 m³/h. The lab ratio, is the amount of wastewater tasted in the lab per volume of reactor vessel i.e.; 8/9 is considered for the reference ratio in design [44]. While the power consumed by MES to generate 100 Nm³/h of methane is expected to be 2 kWh [45]. The calculations are shown in Appendix C. In this thesis, CO₂ emission is mostly targeted, which contribute to global warming potential. Figure 4.1 and 4.2 shows the graphical representation of the emission from the inflow and outflow of the HPWS process respectively.

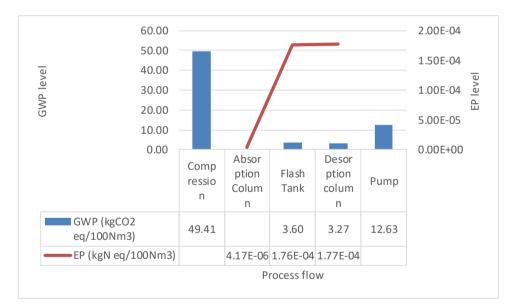


Figure 4.1 GWP and EP emission from inflow HPWS process

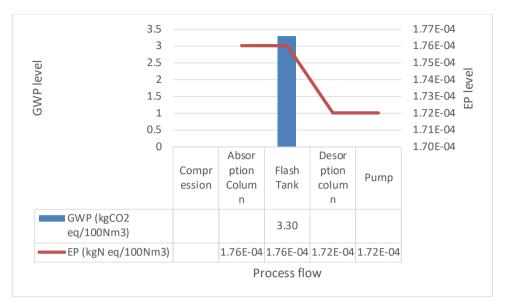


Figure 4.2 GWP and EP emission from outflow HPWS process

In figure 4.1, it can be seen that the energy used in the compression process has a higher impact on GWP, giving us the value of e 49410.49 gCO₂ eq/Nm³. The Eutrophication potential shown in all the stages is almost the same at all stages with the range of 1.7E-04 in outflow and inflow, apart from the absorption column, where the value is 4.17E-06. It can be concluded that if the pressure is lowered, the impact will also reduce. However, to compensate for the loss of efficiency, more water would be necessary, resulting in a larger vessel and equipment, which might have a greater rather than a lesser impact. Because this is unlikely to be an easy or practical undertaking, another method to decrease the impact would be to use renewable energy, but this would not necessarily be possible for all installations [36].

The following remedies are proposed to mitigate the disadvantage of HPWS technology [38].

- CO₂ can be isolated, stored, or used for industrial reasons (only if sufficient quality is provided)
- Decreasing electricity consumption by increasing renewable energy supplies
- Because H_2S is poisonous and corrosive, a pre-removal step before the washing procedure is recommended as a more environmentally friendly technique
- Methane loss can be reduced by treating the off-gas leaving the system with thermal or catalytic oxidation. A biofilter is a less expensive and environmentally beneficial option.

The uses of MES, are discussed in chapter 2.3. It is attached as a sub reactor and an anaerobic digestion reactor (main reactor) as a biogas upgrading plant. Figures 4.3 and 4.4 show the emission after the biogas passes from MES to HPWS, that is 25% more pure methane after MES.

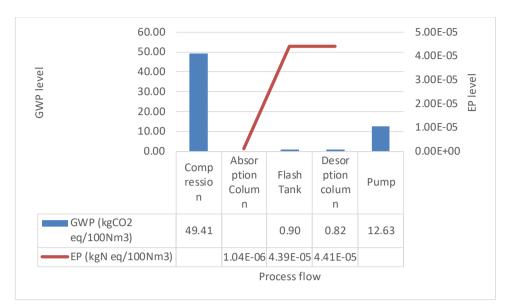


Figure 4.3 HPWS inflow emission with 25% more pure methane

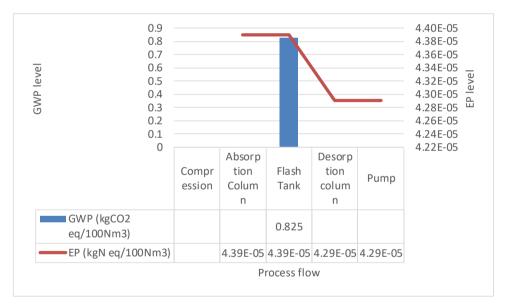


Figure 4.4 HPWS outflow emission with 25% more pure methane

Even though the methane is 25% purer, the amount will be the same in the compressor to be compressed during inflow. Hence there is no actual change in the emission during the period. Since the methane is purer, the used water can be less in the absorption column, so the EP emission has decreased from 4.17E-06 to 1.04E-06 kgNeq/100Nm³. Likewise, in a flash tank, EP emission has dropped from 1.76E-04 to 4.39E-05 kgNeq/100Nm³ and GWP emission has also decreased from 3595.864 to 898.97 gCO₂ eq/100Nm³. Similarly, the pump needs the same energy to send the same amount of gas back to the absorption column, there is no change in the energy, while in the desorption column, in EP amount has decreased from 1.77E-04 to

 $4.41E-05 \text{ kgNeq}/100 \text{Nm}^3$ and GWP emission has decreased from $3268.202 \text{ to } 817.05 \text{ gCO}_2 \text{ eq}/100 \text{Nm}^3$.

Furthermore, during the outflow, eutrophication potential has the same range around 4.2-4.3E-05 where the value is lower than the EP in HPWS outflow. Therefore, apart from EP, the value of GWP has also decreased in the flash tank from 3301.47 gCO₂ eq/100Nm³ to 825.36 gCO₂ eq/100Nm³. However, a decrease in energy consumption is one part however there is extra energy used in operating the MES, where 2 kWh of energy is used per 100 Nm³/h of methane production and HPWS needs 55.43 kWh of energy per 100 Nm³/h. This shows that the total energy for both MES and HPWS will be 57.43 kWh, where the emission for GWP will be 24271.45 gCO₂ eq/100Nm³.

Materials used for both the systems are shown in Tables 3.7 and 3.8. Considering only two types of materials in MES, many materials are highly used in HPWS. The life scale of materials was taken as 20 years. Therefore, the emission made from the production of the materials is also shown in the same tables. The emission of materials is calculated from their production impact on the environment. Fiberglass composite material is highly used in HPWS, however, the most environmental impact was shown by stainless steel piping (44.07 gCO₂eq/h), followed by PVC piping (28.6 gCO₂eq/h) in the HPWS process. A total of 108 kg of electric installation was set on the HPWS system which has less impact on the environment, i: e; 6.75E-10 gCO₂eq/h. MES has two main materials, which are Stainless steel 316 and rigid PVC. Stainless steel has more quantity which is 22023.75 kg and the rigid PVC has 3774.75 kg and the emission was 892.5 gCO₂eq/h and 127.05 gCO₂eq/h respectively.

5 Recommendations

Here present some recommendations based on the thesis work. The owner or operator of the activity has little or no prior experience compiling environmental data, where environmental data is generally recorded on an organizational level rather than a function level, if at all. Similarly, the LCA practitioner may have minimal prior experience with the data collection procedure. Therefore, it is necessary to engage in mutual learning and awareness-raising. This is also pointed out in previously published studies [32]. Several methodological decisions are required for the compilation. First, in any process that provides more than one unit of service or function, decisions must be made on dividing the total inputs and outputs among the many functions. Measurement points relevant to the query (i.e.; input/output per unit function, for example, the electricity consumption for a specific operation) may be absent from a technical standpoint. The generated list and statistics for a unit process can appear to be an "environmental parallel" to a cost statement (product-related activity-based costing) or reveal personal technology details. As a result, companies often consider such data sensitive when conducting external LCA assessments, however, such hurdles can be bypassed by adopting default approximations or industry averages without more detailed data.

6 Conclusion

In this study, a comparison of the biogas upgrading system (HPWS) was done with MES and assessed with the LCA. This particular LCA study considered that global warming and human toxicity are the main impact categories associated with the upgrading system for biogas. Overall the upgradation with MES was found to have the potential to reduce the environmental impact. However, some of the areas in the process that should be considered for optimization are discussed, for example, exhaust gas from the desorption column and energy consumption. Hence, the more solutions for the energy reduction in the HPWS process, the more it would be considered best. Furthermore, studies on the data and use of different LCA methodologies and comparison of their results could improve the reliability of the assessment of the HPWS process.

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Appendices

Appendix A <Assignment Task>

SV University of South-Eastern Norway

Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Life cycle assessment of biogas upgradation using MES technology.

USN supervisor: Gamunu Samarakoon, Vasan Sivalingam, Carlos Dinamarca

External partner:

Task background:

Anaerobic digestion (AD) process is a highly economical and efficient method to produce methane (CH₄) from organic matter. It produces biogas containing 50 -70 % CH₄ and 50-30 % CO₂, meaning that the typical biogas has a low calorific value, which limits its use, e.g., as a transport fuel. Therefore, biogas is upgraded by removing CO₂ to increase the calorific value. Recently, Microbial Electrosynthesis (MES) for biogas upgrading by converting CO₂ to CH₄ has received attention. MES refers to the chemical synthesis of desired products through chemical reactions catalysed by microorganisms and powered by electrical energy. Even though, it is experimentally proved that MES integrated with the biogas process can increase the quality and quantity of the biogas production, yet no full-scale applications are implemented. An environmental impact assessment of this new application will be beneficial to commercialize the technology.

Life cycle assessment (LCA) is described as a comprehensive approach to identifying the environmental consequences of a product, process, or activity through its entire life cycle and to identifying opportunities for achieving environmental improvements. More and more industries are *trend* to conduct LCA since it assists sustainable development in many ways.

Task description:

- Literature review on LCA studies on commonly used biogas upgrading processes
- Prepare a framework for a LCA of biogas upgradation processes (preferably, to run a LCA as such on an available open-source software tool).
- A review on suitable methods, databases and software tools used in LCA of biogas upgrading processes.
- Compare the environmental impact of the MES technology to the currently used upgrading processes with MES technology to identify its' environmental benefits.

The outcome of this thesis work is important for the USN's strategic project on MES integrated biogas process.

Student category: EET or PT students

Is the task suitable for online students (not present at the campus)? Yes

<u>Practical arrangements</u>: openLCA (<u>https://www.openlca.org</u>) is open-source software for LCA study. However, the candidate can use any convenient tool(s).

Supervision:

As a general rule, the student is entitled to 15-20 hours of supervision. This includes necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc).

Signatures:

Supervisor (date and signature): Gamunu Samarakeen. 26-01-2022 Student (write clearly in all capitalized letters): ASIPIM ARYAL Student (date and signature): Hind - 26-01-2022

S.N	Energy	Unit		Emission	Unit	Functional Unit
1	1	kwh	emits	421.16 [46]	gCO2 eq	
	117.32	kwh	emits	49410.49	gCO2 eq	
2	100	Nm3/h	uses	55.43 [38]	kwh	
3	55.43	kwh	emits	23344.9	gCO2 eq	per 100Nm3
	1	kwh	emits	421.16	gCO2 eq	per 100Nm3
	117.32	kwh	emits	49410.49	gCO2 eq	per 100Nm3

Appendix B <calculation of GWP with functional unit>

Likewise, all the energy emissions were calculated accordingly

Appendix C <calculations for MES reactor dimensions>

Hydraulic retention time (HRT) = 3 hours
 Flow rate (Q) = 200 m³/h
 Hence,
 the waste water volume (V_w) = HRT * Q = 600 m³

And:

- Reactor vessel volume (V) = $\frac{V_w}{R} = 600 * \frac{9}{8} \approx 680 \text{ m}^3$ where, R = lab ratio = amount of wastewater tested in lab / vol. of reactor vessel [44]
- $V = \pi h r^2$ $h = \frac{680}{\pi r^2}$
- 2. Total inside surface area:

 $A = 2\pi r^2 + \pi r h$

where: r = inside radius

h = height of vessel

Also from;

objective function, $f(r)_{min} = 2\pi r^2 + \frac{680}{r}$

or,
$$\frac{\partial f}{\partial r} = 4\pi r - \frac{680}{r^2}$$

or, $4\pi r^2 - 680 = 0$
or, $r = \sqrt[3]{\frac{680}{4\pi}}$
 $\therefore r = 3.78 \text{ m}$

Hence, from equation (A)

$$h = \frac{680}{\pi * (3.78)^2}$$
$$h = 15 m$$

Reference were taken from a pilot scale calculation, since the results were 2.5 times the calculation of reference, all the other assumptions were made accordingly.

(A)