Environmental and Experimental Evaluation of Producing Chemicals from CO_2 using Bioelectrochemical Systems

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by

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Abstract

Microbial electrosynthesis (MES) which uses microbes and electricity to generate high grade chemicals could contribute to the reduction of greenhouse emissions as it uses CO_2 in the process. The implementation of this technology on an industrial scale could be on the horizon. Currently, little is known about the environmental loads associated with the successful scale up of the technology with regards to global warming potential and other environmental burdens. Such knowledge is needed in order for relatively new bioprocesses like MES to be sustainably scaled up and industrially applied.

This research conducted an empirical and environmental investigation of MES for the synthesis of chemicals from CO_2. Experimentally, MES for bio production of chemicals from CO_2 was investigated using mixed culture as biocatalyst. CO_2 introduced into H-shaped bioelectrochemical systems produced methane, formic, acetic and propionic acids more readily however under some conditions isobutyric acid and ethanol were synthesized. Different polarizations (-0.8V, -1.0V, -1.2V and -1.4V vs Ag/AgCl) and temperatures (27^{o}C and 40^{o}C) were used revealing that bioproduction was affected by changes to these parameters. Biofilm growth and gradual acclimation to CO_2 achieved a maximum production rate of 3677µM/day at -1.4V vs Ag/AgCl and 40^{o}C. However an average decline of 18 percent in the coulombic efficiency was observed when the potential was reduced by 0.2V.This showed that there may be energy and environmental risks associated with products synthesized at lower potentials needing confirmation by an environmental analysis.

The environmental impacts of products synthesized through MES were examined by modelling a simulated industrial plant (1000 tonnes/year). Environmental analyses were used to reveal the main products to target for MES. Different MES plants generating a range of biochemicals were modelled considering two sources of energy (natural gas and UK national grid), one at a time. This gave specific and detailed scenarios that allowed comparison of the environmental impacts. Results shows that the synthesis of acetic acid, propionic acid, ethanol and methanol released more carbon dioxide than it used for both natural gas and the UK national grid. However, formic acid (-3,421 tonnes CO_2 eqv) was found to be the only product having a negative global warming potential using natural gas and comparatively low environmental impacts in other environmental categories. It was concluded that formic acid synthesis through MES is a more suitable product than the other biochemicals analysed in terms of energy efficiency, global warming potential and other potentially harmful environmental impact categories.

Acknowledgement

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Table of Contents

List of Figures

List of Tables

List of Abbreviations

AC	Acidification
AER	Abiotic Electrochemical Reactor
Ag/AgCl	Standard Potential of the Silver Chloride Reference Electrode
BES	Bioelectrochemical System
CA	Chronoamperometry
CCU	Carbon Capture and Utilization
CE	Current Efficiency
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CTUe	Comparative Toxic Unit for ecosystem
CTUh	Comparative Toxic Unit for human
CV	Cyclic Voltammetry
DET	Direct Electron Transfer
EC	Ecotoxicity
EFC	Enzymatic Fuel Cell
EG	Energy Gain
FE	Freshwater Europhication
Fe	Iron
GC	Gas Chromatography
GHG	Green House Gas
GJ	Giga Joules
GJ/yr	Giga Joules per year
GWP	Global Warming Potential
GWR	Global Warming Ratio
H_2	Hydrogen
HCD	Hydrogenation of Carbon Dioxide
HMF	Hydrolysis of Methyl Formate
HT	Human Toxicity cancer effects
ILCD	International Reference Life Cycle Data System

IR	Ionising Radiation
LC	Liquid Chromatography
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LSV	Linear Sweep Voltammetry
MDC	Microbial Desalination Cell
MEC	Microbial Electrolysis Cell
MES	Microbial Electrosynthesis
MET	Mediated Electron Transfer
MFC	Microbial Fuel Cell
Mn	Manganese
MSC	Microbial Solar Cell
N	Nitrogen
NEC	Net Energy Consumption
NMVOC	Non Methane Volatile Organic Compounds
NRTL	Non Random Two Liquid
O_2	Oxygen
OD	Ozone Depletion
P	Phosphate
Pd	Palladium
PEM	Proton Exchange Membrane
PM	Particulate Matter
PM2.5 Eqv	Particulate Matter with a diameter of 2.5µm
POF	Photochemical Ozone Formation
ppmv	Parts per million in volume
PVC	Polyvinyl Chloride
R11	Trichlorofluoromethane
Re	Rhenium
Rpm	Revolutions per minutes
Sb	Antimony

T/yr	Tonnes per year
U235	Uranium 235
UK	United Kingdom
VFA	Volatile Fatty Acid

Chapter 1: Introduction

1.1 Background of study

Global warming has experienced comprehensive environment and energy recognition in recent times. It occurs as a result of greenhouse gases emissions into the atmosphere. Carbon dioxide (CO_2) one of such greenhouse gases contributes over half to global warming as over 30,000million tonnes of it is currently being released each year worldwide (IEA, 2018). This represents a more than 50 percent increase from the levels of 1990 (Huang and Tan, 2014). CO_2 is discharged predominantly from anthropogenic fossil fuel burning through small disseminated sources such as car engines and enormous combustion systems. Other greenhouse gases such as methane (CH_4), nitrous oxide, hydrofluorocarbons, sulphur hexafluoride and prefluorocarbons accumulating in the atmosphere are also mainly generated by human activities (Montzka *et al.*, 2011).

During pre-industrial times CO_2 levels were about 280 parts per million in volume (ppmv) but in the year 2018 concentration was measured to be 408ppmv (Huang and Tan, 2014; ESRL, 2017; ESRL, 2018). This represents a considerable increase something climate scientists have noticed over the past century and in the past ten years it was observed to see an increment of on average 2ppmv per year (IEA, 2015; IEA, 2018). This is indicative that CO_2 is being seen as a waste product instead of a possible raw material.

Figure 1A shows that the production of electricity and heat causes the most CO_2 to be emitted. It is estimated that this sector accounts for about 41% of all anthropogenic CO_2 releases, and alongside the transport sector (21%) close to two-third. Comparing countries (See Figure 1B), the world's most populous nation China (19.21% share of world's population) is leading the way with CO_2 emission rates (9.102 $GtCO_2$) that is a little over a quarter of all emissions (Burck *et al.*, 2016; IEA, 2018). A correlation exists between a country's gross domestic product and the amount of CO_2 it releases as countries such as United States and China with high gross domestic product tends to emit more CO_2 (Burck *et al.*, 2016). Figure 1C shows that for every region of the world except Europe CO_2 emissions have gone up in the past two decades. A target of 20% below 1990 levels was set by the European Union in 2007 and put into legislation in 2009, this may have contributed to the decrease in CO_2 emissions across Europe (Böhringer *et al.*, 2009). This positive trend should continue not only in Europe but other regions as previously unchecked CO_2 emissions has led to our generation experiencing some consequences which could turn disastrous if even greater strides are not achieved. One

of such consequences is an increase in the average surface temperature of the earth which has risen by about 0.7°C since the late 1800 (Bessou *et al.*, 2011; IPCC, 2014).The rise in sea levels, melting polar ice, extreme heat waves and excessive rainfall are also issues we all have to contend with as a result of anthropogenic CO_2 emissions (Bessou *et al.*, 2011).

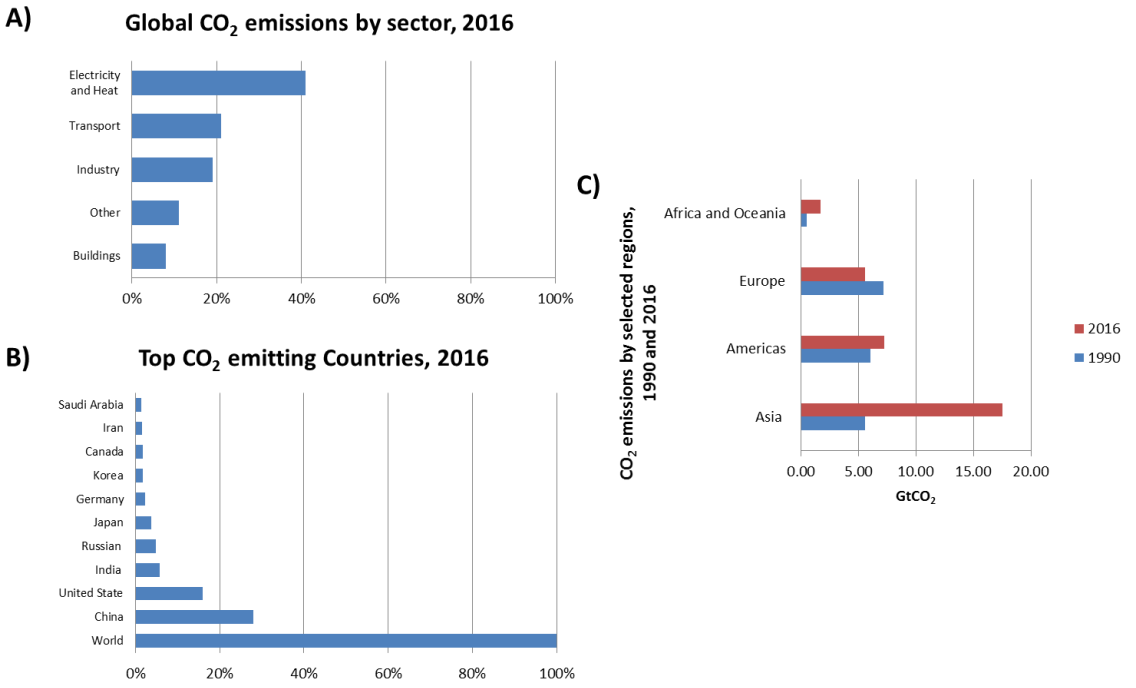


Figure 1: A) Global CO_2 emitted by sector in 2013 (Adapted from (IEA, 2018)) B) Top 10 CO_2 emitting countries(Adapted from (Burck *et al.*, 2016)) C) CO_2 emitted by region in the year 1991 and 2013(Adapted from (IEA, 2018))

Carbon capture and utilization (CCU) involves creating value from CO_2 by using it as a carbon source for the production of useful commodities (Markewitz *et al.*, 2012). This could serve as a solution to the world's anthropogenic CO_2 discharge problem and its resulting repercussions since the gas now becomes an important raw material. CO_2 is thermodynamically stable and highly oxidized therefore it usually requires the use of very reactive catalysts and compounds for chemical utilization. However biologically, it can directly be transformed to valuable products such as methane and acetic acid through the use of microbes (Omae, 2012).

A new emerging technology called Bioelectrochemical Systems (BESs) has the ability to biologically convert CO_2 to methane, acetic acid, formic acid and other higher fuels when appropriate microbes are used (Jiang and Jianxiong Zeng, 2018). This process is known as microbial electrosynthesis and was first coined in 2010 when (Nevin *et al.*, 2010) demonstrated that the bacteria *Sporomusa ovata* taking electrons from an electrode had the

ability to use CO_2 and produce acetate with trace amounts of 2-oxobutyrate. Bacteria cells or biomolecules which are used as biocatalysts in BESs can operate at either or both electrodes of the system (Liu *et al.*, 2014). They can apart from CO_2 reduction be used to produce electricity or hydrogen in BESs. BESs are subsequently classified as either microbial fuel cells (MFCs), microbial electrolysis cells (MECs), enzymatic fuel cells (EFCs), microbial solar cells (MSCs) or microbial desalination cells (MDCs) based on their operation. The ability to operate at moderate conditions makes BESs advantageous over some conventional fuel cells. The research community in recent times has shown great interest in BESs development as it considered a viable means of utilizing carbon.

Several studies have investigated MES on a lab scale basis since it was first coined (Nevin *et al.*, 2010). Pilot plant test could be the next stage on its path to industrial application. However little is known about the environmental effects of such a move. This study uses environmental assessment tools to help identify specific chemicals to target for maximum environmental benefit of using the technology on a large scale.

1.1 Aims and objectives

The overall aim of this PhD study is to environmentally evaluate and empirically investigate the synthesis of useable chemicals from CO_2 through MES. This was achieved by conducting four studies each having their own aims and objectives geared towards achieving the overall aim. Each of the studies objectives are outlined below;

Aim 1: To acquire knowledge on start-up and running of robust mixed culture biocathodes for the synthesis of chemicals or fuel.

Objectives:

- To develop a stable CO_2 reducing biocathode in BES from a mixed culture inoculum.
- To evaluate the performance of a stable cathodic biofilm in BES to synthesize products over a long period of time.
- To evaluate the effect of cathode potential on CO_2 reduction, metabolic pathway and bio production.

Aim 2: To evaluate the energy requirements and global warming potential of microbial electrosynthesis scaled up beyond the laboratory for the synthesis of chemicals.

Objectives:

- To evaluate the energy requirement of scaling up the MES process.
- To assess the global warming potential of producing chemicals using MES.
- To compare the global warming potential of using MES with conventional routes.

Aim 3: To assess the environmental impacts of using microbial electro synthesis for the production of chemicals

Objectives:

- To assess the environmental sustainability of producing chemicals using MES when the United Kingdom national grid is used as energy source.
- To assess the environmental sustainability of producing chemical using abiotic electrochemical reduction.
- To compare the environmental effects of producing chemicals using MES with that of abiotic electrochemical reduction.
- Identify the environmental trade-offs of MES implementation.

Aim 4: To evaluate and compare the environmental impacts of formic acid production routes

Objectives:

- To assess the environmental sustainability of producing formic acid using methyl formate hydrolysis.
- To assess the environmental sustainability of producing formic acid using homogenous abiotic catalysts.
- To compare the environmental effects of producing formic acid using MES with that of both abiotic electrochemical reduction and conventional routes.

1.2 Structure of the thesis

The thesis is divided into eight chapters. These chapters alongside a short description of the content of each chapter where applicable is outlined below;

1. Introduction
2. Literature review
3. Methodology
4. Investigation of bioproduction using mixed culture
    - Mixed culture bio cathodes are gown in reactors and operated with different poise potential and temperatures. Results explain the effects of these changes.
5. Energy and global warming assessment of using carbon dioxide in microbial electrosynthesis
    - Energy and global warming potential of microbial electrosynthesis for the production of acetic acid, propionic acid, formic acid, ethanol and methanol is analysed in this chapter.
6. Environmental assessment of microbial electrosynthesis
    - GaBi life cycle assessment software was used to analyse the environmental effects of using microbial electrosynthesis.
7. Environmental assessment of formic acid manufacturing routes
    - Four different formic acid production routes are compared in this chapter.
8. Conclusion
9. Appendix

Chapter 2: Literature review

2.1 Introduction to electro-catalytic carbon dioxide reduction

Electro-catalytic reduction involves using specific catalysts to drive reduction reactions. The electro-catalytic reduction of CO_2 provides a sustainable way to effectively utilize CO_2 as the technology can be used to produce chemical feedstocks (e.g CO) and valuable fuels (e.g ethanol) from the gas (Matsubara *et al.*, 2015). There are two principle ways in which CO_2 can be electro-catalytic reduced using electrolysis cells; biotically and abiotically. The principle and setup used in both systems are similar except instead of abiotic catalysts microorganisms such as *methanobacterium palustre* (Cheng *et al.*, 2009b) are used in biotic cells.

2.1.1 Abiotic Systems

Abiotic electro-catalytic reduction of CO_2 usually involves the use of metals as catalysts. These metal could be both rare metals (i.e Pd and Re) which were the focus of earlier research into the technology and readily available transition metals (i.e Fe and Mn)(Francke *et al.*, 2018). For CO_2 to be electrochemically reduced a pathway of one, two, four, six or eight electrons is typically followed. These pathways usually yields carbon monoxide, formic acid, formaldehyde, oxalic acid and methanol more readily (Qiao *et al.*, 2014). Methane, ethylene and ethanol can also be obtained but these have proved more challenging to standalone produce. Hence they are usually seen as by-products (Francke *et al.*, 2018).

Table 1: Relevant CO_2 reduction reactions and equivalent standard redox potential for aqueous solutions(Qiao *et al.*, 2014)

S/N	Reduction reactions	Electrode Potential (vs SHE, V)
1	$CO_2(g) + 2H^+ + 2e^- \rightarrow HCOOH(l)$	-0.25
2	$CO_2(g) + H_2O(l) + 2e^- \rightarrow HCOO^-(aq) + OH^-$	-1.08
3	$CO_2(g) + 4H^+ + 4e^- \rightarrow CH_2O(l) + H_2O(l)$	-0.07
4	$CO_2(g) + 3H_2O(l) + 4e^- \rightarrow CH_2O(l) + 4OH^-$	-0.90
5	$CO_2(g) + 6H^+ + 6e^- \rightarrow CH_3OH(l) + H_2O(l)$	+0.02
6	$CO_2(g) + 5H_2O(l) + 6e^- \rightarrow CH_3OH(l) + 6OH^-$	-0.81
7	$CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + 2H_2O(l)$	+0.17
8	$CO_2(g) + 6H_2O(l) + 8e^- \rightarrow CH_4(g) + 8OH^-$	-0.66
9	$2CO_2(g) + 12H^+ + 12e^- \rightarrow CH_2CH_2(g) + 4H_2O(l)$	+0.06
10	$2CO_2(g) + 12H^+ + 12e^- \rightarrow CH_3CH_2OH(g) + 3H_2O(l)$	+0.08

Table 1 shows the standard redox potential of some selected CO_2 reduction reactions in aqueous solution. The standard Gibbs energies of reactants are used to determine these values seen in Table 1. Therefore it just denotes the thermodynamics of the reactions, specifying that a certain reaction pathway is probable at a stated electrode potential. However in practice overpotentials causes more negative potential to be needed to drive the reaction for good reaction rates to be achieved. Another problem also seen in practice is the selectivity of the CO_2 reduction reactions. As there are different possible pathways it is usually observed that multiple products are generated. Optimization of the electro-catalyst employed is important in order to produce the desired products at high rate with reduced overpotentials(Francke *et al.*, 2018).

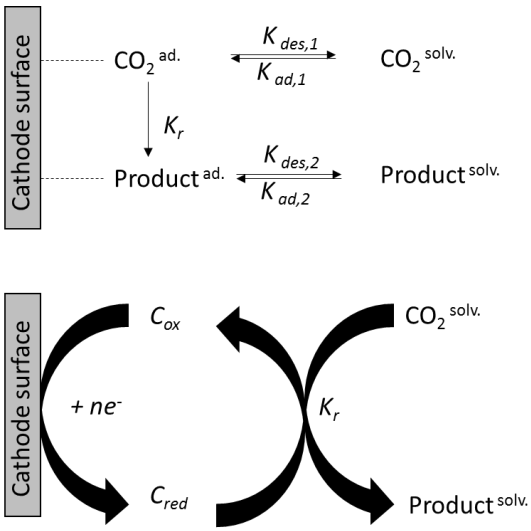


Figure 2: Electro-catalytic reduction of CO2 using heterogeneous (top) and homogeneous catalysts (bottom) Adapted (Francke *et al.*, 2018)

There are two types of electro-catalyst used for abiotic CO_2 reduction. These include heterogeneous and homogeneous catalysts (see Figure 2). Direct uncatalized electrochemical reduction of CO_2 on inert electrodes such as carbon have been reported in literature(Eggins *et al.*, 1988; Hara *et al.*, 1997). However to improve faradaic efficiency, selectivity of products and save cost the use of catalysts is preferred and has been extensively researched. When employing heterogenous catalysts reduction occurs at the electrode surface (Yang *et al.*, 2016b). CO_2 is absorbed on the electrode surface before electrons are introduced achieving the effect of reducing the activation energy and controlling reaction selectivity (Francke *et al.*, 2018). Heterogeneous catalysts are characterised into metals, metal alloys, transition metal oxides and metal organic frameworks(Francke *et al.*, 2018). They are usually associated with certain types of product generation. For example silver and gold as electro-catalysts are

known to reduce CO_2 to CO (Hori *et al.*, 1994) while copper typically generates hydrocarbons and methanol (Gattrell *et al.*, 2006; Le *et al.*, 2011). Homogeneous catalyst on the other hand reduces CO_2 in solution. This method is often referred to as indirect electrolysis where the catalyst serves as a vehicle for transportation of electrons between the electrode and CO_2. CO_2 in this method would be reduced at the potential of the electro-catalyst rather than that of the electrode. Therefore the potential of the catalyst must be more negative than that of the electrode (Francke *et al.*, 2018). The choice between heterogeneous and homogenous catalysts is still not clear as both have their advantages and disadvantages. Using heterogeneous catalysts makes separation of reduction products and effluent management easier as the catalyst is not mixed with the desired chemical. The advantage of homogenous catalysts is it tends to have improved selectivity as high faradaic efficiency (>95%) can be achieved. The challenge with using heterogeneous catalysts is that the performance of the catalytic electrode can be affected by intermediates and by-products. As for homogenous catalyst side reactions causes the degradation of the molecular catalyst(Francke *et al.*, 2018). Longevity of both catalyst types is still an issue as both usually have a working life of less than 100h and have to be improved for the technology to be implemented industrially.

2.1.2 Biotic Systems

Biotic electro-catalytic reduction of CO_2 takes places in so called bioelectrochemical systems (BESs). BESs use biocatalysts at either or both electrodes to catalyse electrochemical reactions (Liu *et al.*, 2014). Apart from CO_2 reduction to value adding compounds the systems are capable of producing electricity or hydrogen from electron transfer between electrodes and electrochemical active microbes or biomolecules (Kelly and He, 2014; Lu *et al.*, 2015). Protons alongside these electrons are also generated from microbes making use of accessible substrate. These protons aid the formation of energy loaded phosphate bonds required for metabolic activities and growth of microbes (Venkata Mohan *et al.*, 2014b). The adoption of BESs is advantageous over other conventional fuel cells because it can be operated at moderate conditions whist making use of a broad range of organic substrate alongside eliminating the use of rare and expensive metal catalysts such as palladium. Based on their mode of operation and/or the type of biocatalyst used BESs can be categorised into either microbial fuel cells (MFCs), microbial electrolysis cells (MECs), enzymatic fuel cells (EFCs), microbial solar cells (MSCs) or microbial desalination cells (MDCs)(See Figure 3 for

schematic diagram of the different types of BESs) (Pant *et al.*, 2012). The most popular of these are MFCs and MECs.

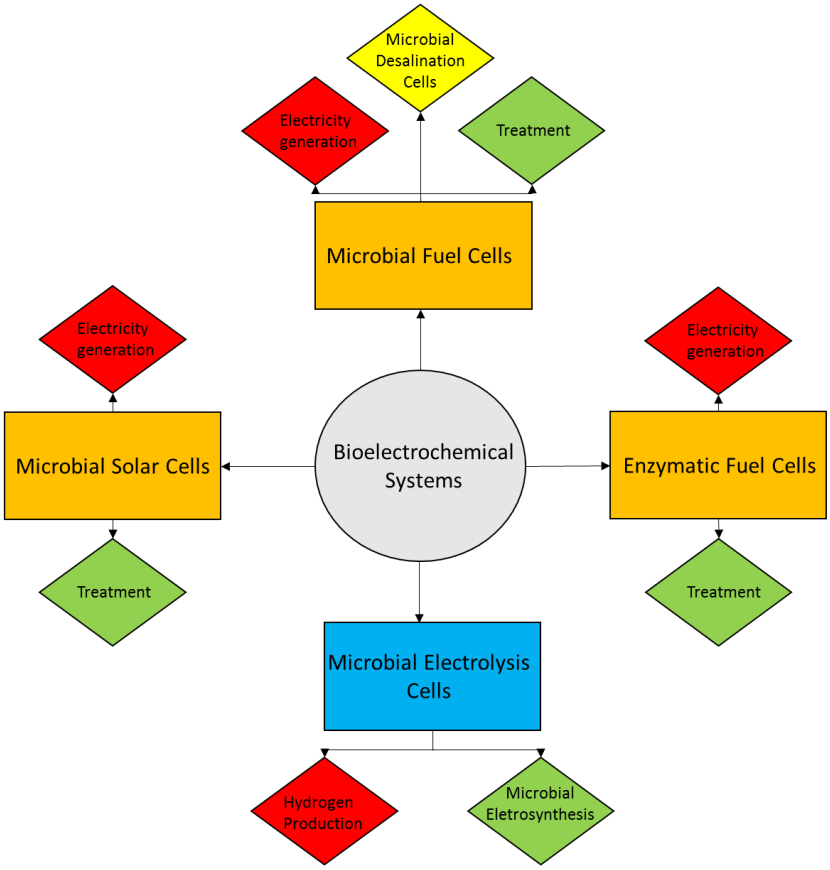


Figure 3: Schematic diagram of the different types of bioelectrochemical systems; Adapted from (Bajracharya *et al.*, 2016))

A BESs is termed MFCs if its operation results in the production of electricity and MECs if energy is added to the system in order to perform chemical reactions (Hamelers *et al.*, 2010). Figure 4 shows the operating principles of both a MFCs and MECs. A primary electron donor and terminal electron acceptor must be provided in order for these systems to function. They usually have two chambers, the anode and cathode which are separated by a proton exchange membrane. This is advantageous because it enables the isolation of products formed from reduction and oxidation reactions (Hamelers *et al.*, 2010; Zhou *et al.*, 2013).

During the initial stages of BESs research the focus was on electricity generation by MFCs. However scientist in this field realized that its standard power density of 0.1KW/m^3 is still too small when compared to that of a typical chemical fuel cell (140 KW/m^3) as well as other sources of energy. This led to the recent expansion of BESs research into other more rewarding areas such as hydrogen production in MECs and chemical synthesis (Arends and Verstraete, 2012; Zhang *et al.*, 2012; Kelly and He, 2014).

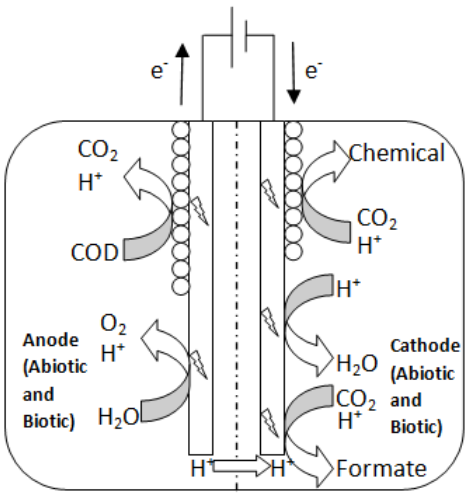


Figure 4: Operating principle of Bioelectrochemical Systems; Adapted from (Villano *et al.*, 2010; Pant *et al.*, 2012; Lovley and Nevin, 2013)

Biocatalysts used in BESs are usually electro active microorganisms or enzymes (Liu *et al.*, 2014). When microorganisms are used the ability to recover electrons from the cathode directly or utilize electrochemically generated hydrogen /organic carbon are required for electro-synthesis (see Figure 5). The kinetics of cathodic reactions would not only be reliant on mass and electron transport between electrode, biocatalyst and electrolyte but on substrate and electron movement within selected organisms (Liu *et al.*, 2014). Products formed also depends on the cathode potential and type of reduction reaction happening. If the cathode potential is higher than that at the anode electricity is generated and if the reverse is the case energy needs to be added to synthesize chemicals (Hamelers *et al.*, 2010).

The use of bio-cathode in BESs is obviously very beneficial. Apart from product synthesis it reduces BESs construction and operating cost by dealing with the issue of using metal catalysts or constantly replacing artificial electron mediators (He and Angenent, 2006). However it does have it challenges such as poor electron transfer between electrode and biocatalyst. Complexity in engineering biocatalysts when mixed culture are used and the slow growth rate of most electroactive microbes are also other issues (Rabaey *et al.*, 2008; Zhang *et al.*, 2012; Liu *et al.*, 2014).

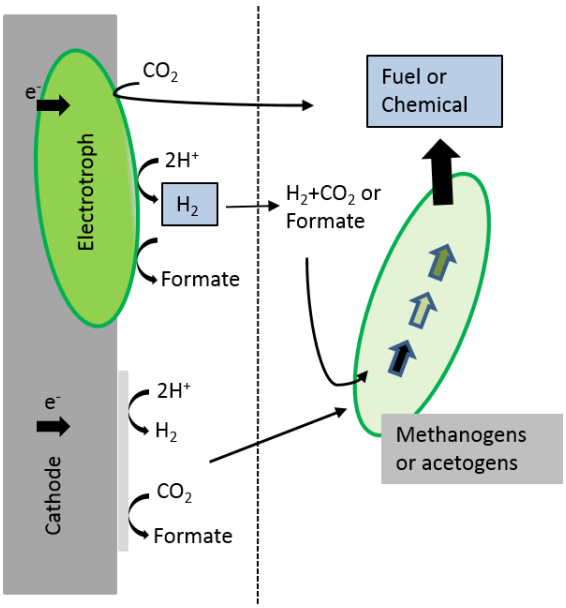


Figure 5: Schematic of Pathways for microbial electro-synthesis using cathode biocatalysts Adapted from (Liu *et al.*, 2014)

2.2 Microbial Electrosynthesis

Microbial electro-synthesis (MES) is usually described as the electricity driven reduction of CO_2 to useful chemicals or fuels when microorganisms are used in BESs. It involves electrons being provided by an electrode to these organisms (Hamelers *et al.*, 2010; Pant *et al.*, 2012; Hallenbeck *et al.*, 2014). MES redox reactions occurs in BESs consisting of an anode and cathode. At the anode, oxidation needing an electron donor is combined with the biotic reduction of CO_2 at the cathode. Water is often oxidized at the anode for protons and electrons generation (See Figure 6) requiring a standard electrode potential of 0.82V versus SHE at pH7 (Rabaey and Rozendal, 2010). This can be coupled for example with acetate (E^o=-0.28V vs SHE) production from CO_2 at the cathode giving a cell voltage (-1.1V) which is negative. This indicates the need for additional energy to be supplied as the voltage is negative. Figure 6 shows that other electron donors such as acetate and glucose can be employed for oxidation reaction in BESs undergoing MES. This usually requires substrate oxidizing anaerobic bacteria attaching themselves to the anode. The amount of energy that needs to be supplied for the redox reaction to occur can be reduced using this method. Gong and co-worker combined microbial oxidation of sulphide and acetate production from CO_2 in a proof of concept experiment (Gong *et al.*, 2013). Wastewater can also be used as substrate for an anodic biofilm (Xiang *et al.*, 2017). This excellently combines wastewater treatment with product generation using MES. However using substrate oxidizing bioanode may have its limitations as it has been shown to hinder the ability of biocathode to synthesize products at

high applied potential (Lim *et al.*, 2017). Hence in the majority of MES experiments water is split for the much needed protons and electrons.

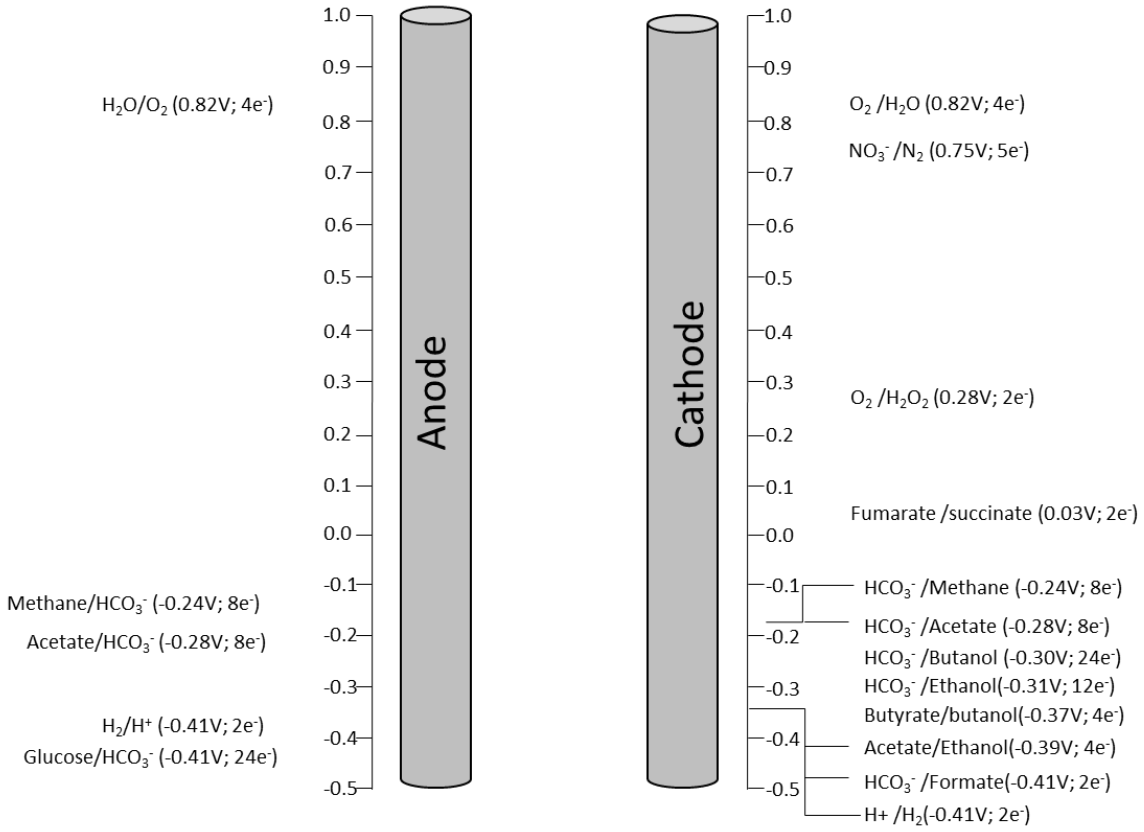


Figure 6: Electron donor and acceptor used in Bioelectrochemical Systems ; Adapted from (Rabaey and Rozendal, 2010)

MES was first coined in 2010 when (Nevin *et al.*, 2010) demonstrated that the bacteria *Sporomusa ovata* had the ability to utilize electrons from a graphite cathode electrode as well as reduce CO_2 to acetate and trace amounts of 2-oxobutyrate. In (Schroder *et al.*, 2015) review of microbial electrochemistry they argued that the term should not be limited to only CO_2 reduction but to any biocatalysed conversion of a substance into an intended commodity in BESs. This may be the new way we see and use this term in the future but for the purpose of this thesis we assume the former definition. Researchers have shown that methane (Cheng *et al.*, 2009b; Villano *et al.*, 2010; Jiang *et al.*, 2013; Batlle-Vilanova *et al.*, 2015; Siegert *et al.*, 2015; van Eerten-Jansen *et al.*, 2015; Feng and Song, 2016), acetate (Blanchet *et al.*, 2015; Tremblay *et al.*, 2015; Faraghiparapari and Zengler, 2017), Hydrogen (Villano *et al.*, 2010) and formic acid (Zhao *et al.*, 2012) can be produced in BESs when CO_2 is used as an electron acceptor. Further details are shown and described in the below subsections;

2.2.1 Methane

The generation of methane (CH_4) in BESs was once thought to be very problematic and is only recently being considered attractive. This was because hydrogen (H_2) was the sort after fuel then and any conversion of H_2 to CH_4 resulted in the loss of almost a quarter of its energy content (Pant *et al.*, 2012). However due to the pressing need to mitigate carbon emissions, bio-cathode production of methane using CO_2 as the electron acceptor is highly sort after. Researchers thus far have proved that both pure and mixed cultures can be used in BESs to generate methane from CO_2. In 2009, Cheng and his team presented the first evidence that methane could be produced through direct electron transfer when the microorganism *methanobacterium palustre* was used in BESs at cathode potential more negative of -800mV vs Ag/AgCl electrode with a maximum electron transfer efficiency of 96% at -1000mv vs Ag/AgCl and production rate of 9.6mL/d (Cheng *et al.*, 2009b). However at those potentials hydrogen could also be produced electrochemically and no data was provided to rule out synthesis of methane indirectly from hydrogen. Villano and co-worker on the hand showed that methane can be produced by direct electron transfer as well as through electrochemically synthesised hydrogen gas. They enriched a biocathode with mixed culture and poised the electrode at a potential equal to or more positive of -950mv vs Ag/AgCl to produce mostly methane through direct electron transfer and more negative of -950mV vs Ag/AgCl to produce methane via indirect abiotic hydrogen evolution (Villano *et al.*, 2010). However both researchers did not investigate the possibility of producing methane via acetate and formate as this was later shown to occur by van Eerten-Jansen and co-researchers as they used mixed culture to produce methane mostly from both electrochemically generated hydrogen and acetate at an electrode potential of -900mV vs Ag/AgCl. The average methane production recorded was 5.2 L/m^2 cathode per day with an electron transfer efficiency of around 75% (van Eerten-Jansen *et al.*, 2015).

Although using BESs is a relatively new way of generating methane it has some advantages over well-established methods such as anaerobic digester. Comparison of the two methods of generating methane reveals that BESs could lead to increases in methane concentration as organic oxidation and CO_2 reduction are split up processes. In anaerobic digester hydrolysis and methanogenesis occur in the same chamber which is not ideal as there would be mixture of the desired product (CH_4) and impurities which would require additional separation facility to obtain a more pure product. Another advantage is that it occurs at relatively low temperature of around 30^oC eliminating the need for heating and can deal with toxic compounds like ammonia which occurs at high pH and affects the growth and performance of

methanogenic bacteria. The challenge of using BES to generate methane is the energy that needs to be supplied (Hendriksen and Ahring, 1991; Rabaey and Rozendal, 2010; Zhang and Angelidaki, 2014).

2.2.2 Acetate

Researchers have proven that CO_2 can be converted to acetate and other higher carbon molecules in BESs using various lithoautotrophs. In nature and often BESs, synthesis is achieved via the wood-ljungdahl pathway where H_2 acts as the electron donor. This pathway is very energy efficient as most of the energy put in via H_2 and CO_2 redox reactions is recovered in the chemical synthesized (Lovley and Nevin, 2013; Bajracharya *et al.*, 2015). However, the electrochemical generation of H_2 at pH7 under biological conditions has a cathode potential upper limit of -600mV vs Ag/AgCl, reduced further by overpotential. This suggests that if acetate or indeed any other commodity is produced at a more positive potential only direct electron transfer might be occurring. To better understand the mechanism behind this Nevin and co-researchers used *sporomusa ovata* at -600mV vs Ag/AgCl to reduce CO_2 to acetate but as with others who attempted with various cultures at this potential the product yield was modest. Most achieved a volumetric flowrate of no more than 1.13 mM/d (Nevin *et al.*, 2010; Nie *et al.*, 2013; Zaybak *et al.*, 2013). Interestingly researchers that reduced their potential beyond this threshold achieved better results alongside generation of other sub-products (Marshall *et al.*, 2012; Jiang *et al.*, 2013; Xafenias and Mapelli, 2014; Bajracharya *et al.*, 2015). This could be because at more negative potential of -600mV H_2 and CO_2 redox reaction via the wood-ljungdahl pathway supplements direct electron transfer (Bajracharya *et al.*, 2015). Jourdin and co-workers achieved a high rate (22148mM) of acetate production at cathode potential -1300mV vs Ag/AgCl electrode (Jourdin *et al.*, 2016). This was achieved by optimizing electrode design and operating conditions (pH 6.7). The significant of producing acetate in BESs is that it can be used to make essential plastics, polymers, and solvents. It can also be used as a precursor in the production of higher carbon fuels (Marshall *et al.*, 2013).

2.2.3 Hydrogen

Hydrogen gas produced in the cathode chamber of a dual chamber BESs occurs in two ways namely water or proton reduction. The amount of gas produced is however limited if hydrogentrophic methanogenic bacteria is present in the cathode chamber as methanogenesis tends to oxidize hydrogen (Hamelers *et al.*, 2010; Zhou *et al.*, 2013). Hydrogen generation through proton reduction depends strongly on pH going from Nernst equation and since the

anode and cathode are connected ionically the reaction usually occurs at pH7 or higher with an equilibrium potential of -600mV vs Ag/AgCl or lower (Hamelers *et al.*, 2010). Hydrogen produced by researchers attempting to reduce CO_2 in BES is mostly as a result of the cathode potential being poised more negative of that for hydrolysis of water. This can be seen in the case of villano and co-worker as hydrogen was produced because their cathode was poised at a potential between -850mV to -1100mV vs Ag/AgCl. In this case hydrogen was then subsequently used by hydrogen methanogens to generate methane (Villano *et al.*, 2010) . Other researcher that produced hydrogen are seen to pose their cathode electrode at a potential more negative of -600mV vs Ag/AgCl (Marshall *et al.*, 2012; Jiang *et al.*, 2013; Bajracharya *et al.*, 2015).

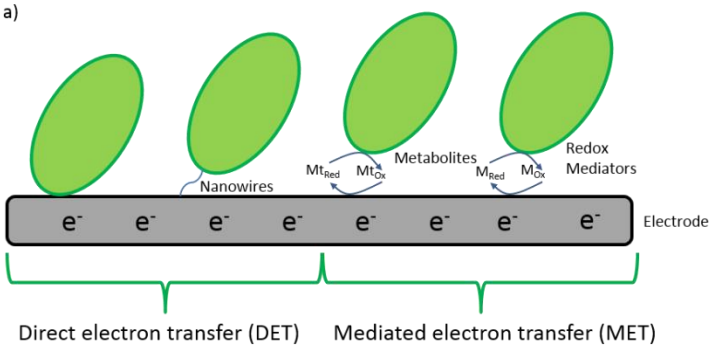
2.2.4 Formic acid

Formic acid is an important raw material in the pharmaceutical, paper and pulp manufacturing industries (Zhang and Angelidaki, 2014). Production of formic acid from CO_2 in BESs has been reported and as formic acid is a very valuable commodity it has attracted some attention within the research community (Zhou *et al.*, 2012). Zhou and co-researchers used lead plates as cathode electrodes in dual chamber BESs to produced formic acid at a rate of $4.27 mgL^{-1}h^{-1}$. The electron transfer efficiency was found to be 64.8% with the energy required for formic acid generation supplied by 5 MFCs connected in series having an open circuit voltage of 2.73V.Formic acid production in BESs is affected by CO_2 mass transfer to the cathode as at ambient conditions CO_2 absorption by water is low (Wang *et al.*, 2015).

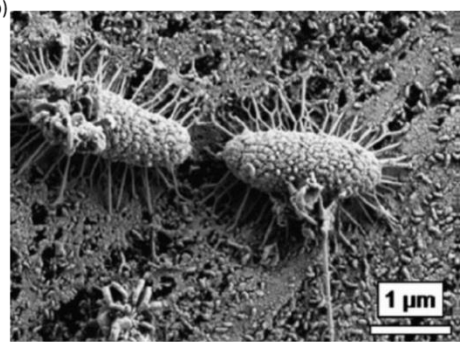
2.3 Electron transfer in electroactive microorganisms

Microorganisms that have the ability to receive or donate electrons from/to an electrode are said to be electrochemically active and are very critical for BESs operation (Zhou *et al.*, 2013). They include a wide range of microbes from gram-negative bacteria's like *Shewanella oneidensis* to diverse gram-positive archaea's (Sydow *et al.*, 2014). Understanding how they perform this feat is very important in order to be able to optimize MES (Zhi *et al.*, 2014). To date several studies have suggested that they do this in two possible ways, namely, direct electron transfer (DET) and mediated electron transfer (MET) (see Figure 7a) (Reguera *et al.*, 2005; Holmes *et al.*, 2006; Marsili *et al.*, 2008).

a)



b)



c)

S/N	Microorganism	Mechanism for Electron transfer	Researcher
1	*Geobacter Sulfurreducens*	DET	Holmes et al. (2006)
2	*Desulfovibrio Vulgaris*	DET	Kloeke et al. (1995)
5	*Aeromonas hydrophila*	DET	Pham et al. (2003)
4	*Shewanella Oneidensis*	MET	Marsili et al. (2008)
5	*Pseudomonas spp*	MET	Venkataraman et al. (2010)
6	*Enterococcus gallinarum*	MET	Rabaey et al. (2004)

Figure 7: a) Schematic representation of electron transfer mechanism; Adapted from (Venkata Mohan *et al.*, 2014a) b) Nanowires of sulphate reducing cells (Sherar *et al.*, 2011) c) Some microorganisms and their mechanism for electron transfer (Van Ommen Kloeke *et al.*, 1995; Pham *et al.*, 2003; Rabaey *et al.*, 2004; Holmes *et al.*, 2006; Marsili *et al.*, 2008; Venkataraman *et al.*, 2010)

2.3.1 Direct electron transfer

Direct electron transfer (DET) occurs when electron flows through direct physical contact between a microorganism cell membrane or membrane organelle and the outer layer of an electrode (Zhou *et al.*, 2013; Zhi *et al.*, 2014). It occurs without requiring any diffusional redox active mediators or species and usually means that the cells are constantly connected to the surface of the electrode as biofilm (Venkata Mohan *et al.*, 2014a; Schroder *et al.*, 2015). A number of researchers have found out some microorganism use this type of electron transfer mechanism adequately (see Figure 7c). C-type cytochromes on microorganism outer membrane or nanowires can be used for DET. Nanowires enables direct transfer over a long range and their properties differ with microorganisms (Venkata Mohan *et al.*, 2014b).

2.3.2 Mediated electron transfer

Mediated electron transfer (MET) involves the use of mediators functioning as electron carriers between microorganism and electrode (Zhi *et al.*, 2014). This enables electron transfer over longer distances than can be obtained from DET as contact between the microorganism and electrode surface is not required (Sydow *et al.*, 2014). Mediators could either be provided externally or supplied from within the microbes themselves (Zhou *et al.*, 2013). Marsili and co-workers proved this with *Shewanella Oneidensis* as they discovered it has the ability to produce riboflavin which in turn serves as a mediator for electron transfer.

When mixed cultures are used it is feasible that mediators could be provided by non-electrogenic microorganisms (Marsili *et al.*, 2008; Zhou *et al.*, 2013). Further research has to be undertaken to understand the complex anaerobic respiration and growth of mixed culture biofilms.

2.4 Electrochemical Principles and Characterization

2.4.1 Electrochemical Principles

BESs as mentioned earlier are electrochemical cells consisting of two electrodes an anode and a cathode inserted into an ionic conducting electrolyte. Therefore they follow well defined electrochemical principles. In BES current flows between the two electrodes when they are electronically connected. Oxidation reaction (Equation 1) where electrons are extracted from the cells occurs at the anode while reduction reaction (Equation 2) that supply electrons to the cell in the cathode.

Equation 1

$A \rightarrow A^{n+} + ne^{-}$ (Anode reaction)

Equation 2

$A^{n+} + ne^{-} \rightarrow A$ (Cathode reaction)

BESs redox reaction rates and current density can be related using faradays law of electrolysis shown below;

Equation 3

$$r_j = {}^{i}/_{nF}$$

Where, r_j is the rate of reaction, i is the current density, n is the number of moles of electrons and F is the faraday constant.

Gibbs free energy which is the maximum amount of work that can be removed from a closed system defines the highest potential that BESs can operate. Equation 4 defines the relationship between Gibbs free energy and cell potential.

Equation 4

$$\Delta G^{o} = -nF\Delta E^{o}$$

Where, $\Delta G^{o}$is the standard Gibbs free energy, ΔE^{o} is the standard potential difference, n is the number moles of electrons and F is the faraday constant.

From the Gibbs free energy equation the electrochemically important Nernst equation can be derived. Consider the redox reaction shown in Equation 5.

Equation 5

$$aA_{oxidation} + bB_{reduction} \rightarrow cA_{reduction} + dB_{oxidation}$$

The Gibbs free energy attributed to conditions that differs from standard conditions are shown using Equation 6 . This is for dilute solutions that concentration of reaction specie is assumed to determine activity. A negative gibbs free energy shows that the redox reaction would occur spontaneously while a positive value shows it is non-spontaneous.

Equation 6

$$\Delta G = \Delta G^o + \frac{RT}{nF} ln \frac{\lfloor A_{red} \rfloor^c \lfloor B_{ox} \rfloor^d}{\lfloor A_{ox} \rfloor^a \lfloor B_{red} \rfloor^b}$$

From Equation 4 and Equation 6 the Nernst can be derived and expressed in Equation 7

Equation 7

$$E = E^o - \frac{RT}{nF} ln \frac{\lfloor A_{red} \rfloor^c \lfloor B_{ox} \rfloor^d}{\lfloor A_{ox} \rfloor^a \lfloor B_{red} \rfloor^b}$$

Where, E^o is the standard potential, R is the rate constant, T is the temperature.

The equation is also often written in log base 10 and at standard temperature (25ºC) it is shown as;

Equation 8

$$E = E^o - \frac{0.059}{n} ln(Q)$$

Where, Q is the reaction quotient

This shows that for every 10 order magnitude change in concentration the half-cell potential moves by 59mV in a one electron redox reaction. Half-cell potential as the name implies is the potential of the anode or cathode and the standard potential of BES (E^o) is the difference between the potential of the cathode and anode. It is the maximum potential the whole cell can attain as no current is flowing between the two electrodes. A shift from the standard potential would occur when the electrodes become polarized as a result of current flow. Overpotential indicates the amount the cell potential differs from its standard potential due to current flow.

2.4.2 Electrochemical Loses in BESs

In BESs less or more energy is supplied than theoretically expected due to losses. Overpotential reduces the energy efficiency of the system and can be classified into either kinetic or thermodynamic losses (Liu *et al.*, 2014). When optimizing BESs processes it is important to take into account these losses as it affects the performance of the system. The figure below shows the different potentials at which losses occur;

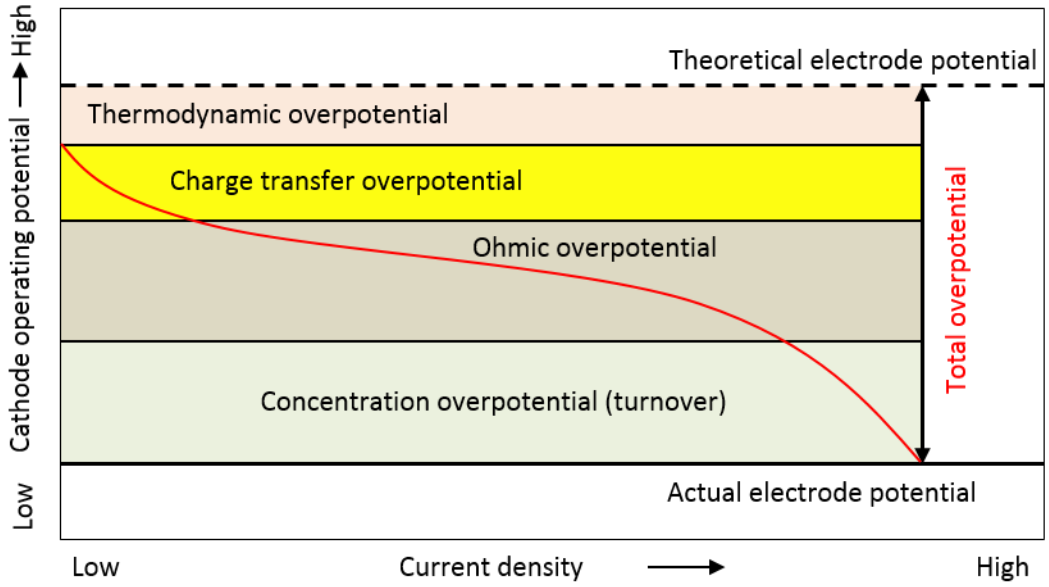


Figure 8: Polarization curve for a redox reaction in BESs; Adapted from (Liu *et al.*, 2014)

Electrode kinetic losses

Electrode kinetic describes the rate at which a reaction is taking place on an electrode. It determines the reaction rate limiting step and is routinely characterized by the tafel plot (Harnisch and Schroder, 2010). On BESs electrode kinetic losses occurs in three ways namely activation, ohmic and concentration losses (Liu *et al.*, 2014). Activation or charge transfer losses is the hindrance to the transmission of electrons from/ to an electrode by an electron acceptor or donor. It is usually observed pronouncedly at current density lower than $1mA/cm^3$. This type of loss can effectively be reduced by increasing both the electrode surface area and temperature of the system. It can also be minimized by utilizing an effective catalyst to reduce activation energy (Logan *et al.*, 2006; Venkata Mohan *et al.*, 2014a).

Ohmic losses develops at medium current densities by the resistance to ionic and electron flow in the electrolyte and electrode (Logan *et al.*, 2006). Concentration losses or turnover on the other hand occurs at high current densities when there is insufficient mass transfer near the electrode and can be minimized by using porous electrodes that aids diffusion (Liu *et al.*,

2014) The reduction of ohmic losses in BESs can be achieved by using PEMs with low resistivity as well as very conductive electrodes and electrolyte where practicable (Logan *et al.*, 2006; Venkata Mohan *et al.*, 2014a).

Thermodynamic losses

Thermodynamic losses occur when the maximum attainable energy from BESs decreases (see Figure 8). This would result in reduced cathode potential for MFCs leading to diminished voltage and the need for more energy input in the case of MECs. It is usually a product of redox cascades as a result of electrodes or substrate donating electrons to the active site of a biocatalyst for survival and growth such as cytochromes in microorganisms. If it is occurring at the anode this would result in electrons from oxidation of the substrate arriving the electrode at a more positive potential than originally intended. Also the cathode thermodynamic losses takes place in similar fashion as microbes use electrons from the cathode for redox cascading. This type of loss can be effectively minimized by engineering biocatalysts in such a way that reduces this phenomenon (Harnisch and Schroder, 2010; Liu *et al.*, 2014).

2.4.3 Mathematical Modelling of MES using Electrochemical principles

MES involves complex biological and electrochemical processes for achieving product formation. The amount and type of product generated depends on various parameters. The main parameters considered are quantity and/or species of microorganism, mixing and mass transfer phenomena, anodic and cathodic reactions, voltage or current supplied and performance of proton exchange (Oliveira *et al.*, 2013). Modelling of MES process, along with experimental data, could simplify experimental designs, help to identify the process limiting step and thus provide understanding for the scalability of this technology. Two detailed MES mathematical models have been reported: one developed by (Kazemi *et al.*, 2015) that describes acetate production in a pure culture biofilm taking into account kinetic rate and mass balance whereas the other shown in (Sadhukhan *et al.*, 2016) is more generic describing product formation by looking at the overall Gibbs free energy of the system.

Figure 9 shows a descriptive diagram of each reported MES model. Figure 9 (A) illustrates acetate synthesis from CO_2 using a *Sporomusa Ovata* biofilm coated cathode while water oxidation occurred in the anode (Kazemi *et al.*, 2015). Here, the amount of energy required for acetate formation was obtained using rate equations that explain bacterial growth and substrate consumption. This included the fraction and self-oxidation ability of active bacteria cells. Mass balances were used to describe the concentration of substrate present in the

biofilm and bulk electrolyte. The electric current demand to drive the reaction was estimated using ohms law and an electron balance (Figure 9 (A) − Equation(3)). In this model, electron active bacteria were considered to only be in a biofilm not presenting cell detachment. The transfer of electrons was based on electric conduction. Bacteria intracellular processes involved in electron transfer, were neglected. The diffusion coefficient of substrate in biofilm was taken as 79% of that in the bulk liquid catholyte. The rate of substrate consumption and subsequent bacteria growth was described using a modified double Monod equation (Figure 9 (A) – Equation (2)) to account for the limiting effect of both electron donors and acceptors. Mass balances were obtained assuming that CO_2 was supplied in a continuous fed mode with the rate limiting step being the diffusion of substrate in the biofilm. Fick's law was used to describe substrate diffusion into the matrix of the biofilm. The minimum substrate concentration and electric potential required to sustain a stable biofilm was calculated using equation 4 and 5, respectively (Figure 9 (A)). Performance of the system was calculated using columbic efficiency expressed as the ratio of energy converted to the desired product in relation to the energy supplied. The final model consists of a set of partial differential equations, which were solved in combination with boundary and initial value problems using MATLAB software packages based on the finite difference and shooting methods.
Upon parameter estimation it was observed that increasing substrate concentration affected coulombic efficiency negatively whilst the reverse occurred for an increased cathode potential.

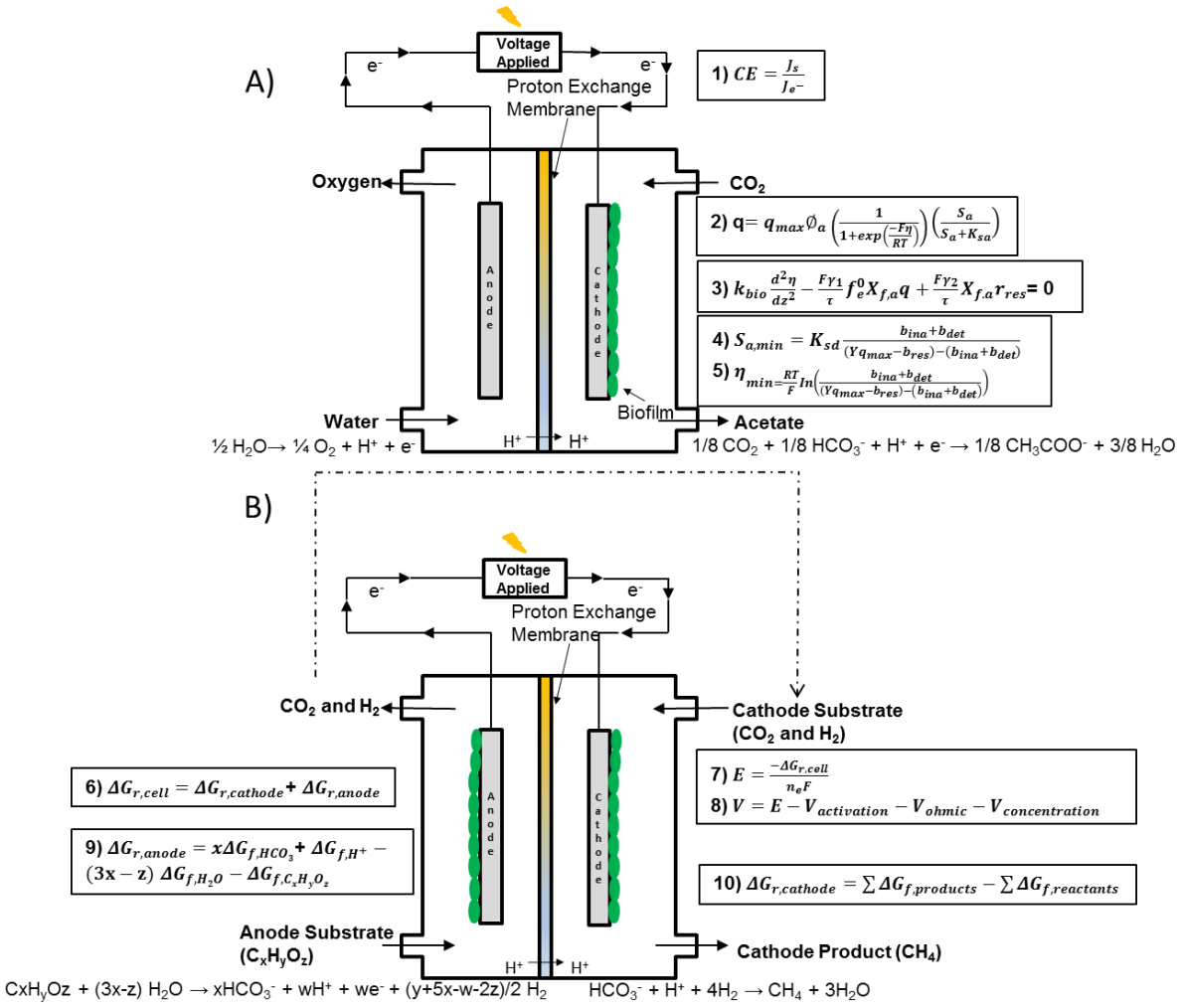


Figure 9: Diagrams obtained from mathematical model A) Kazemi model and B) Sadhukhan model; ΔG_r is the Gibbs free energy under standard conditions (25°C and 1 atm) and pH7

On the other hand, Figure 9 (B) shows (Sadhukhan *et al.*, 2016) model as a general model that can be applied to a wider range of BESs activities as it attempts to analyse overall energy performance. For MES investigations, methane production from CO_2 was used as the model reaction. This mathematical model uses the overall Gibbs free energy of the cell to obtain the theoretical maximum potential. To utilize this model the oxidation and reduction reactions of anode and cathode substrates alongside any products formed have to be initially obtained. This can be done experimentally by isolating and characterizing responsible bacteria with reactant and product concentrations measured at the end to predict the balanced stoichiometry equation of cathodic and anodic reactions (So and Young, 1999). Subsequently, the Gibbs free energy for both reactions can then be derived from the Gibbs free energy of formation of each species involved in the reactions (Figure 9 (B) − Equation (9) and (10)). In turn, the overall Gibbs free energy of the cell can be estimated by summing the Gibbs free energies between the cathode and anode reactions (Figure 9 (B) – Equation (6)).

The Nernst equation (Equation (7)) is used to obtain the theoretical maximum potential to drive the reaction. As the actual voltage supplied for MES is more than the theoretical voltage due to losses, the effects of activation, ohmic and concentration overpotentials are also taken into account (Equation (8)) using a linear approximation of the Butler-Volmer equation, Nernst equation and ohm's law, respectively. (Sadhukhan *et al.*, 2016) model is shown to be effective at assessing the energy efficiency of MES showing that the activation overpotential was the largest contributor to change in theoretical voltage. However, it is limited in its ability to estimate biofilm growth and calculate coulombic efficiencies of MES reactions.

2.4.4 Voltammetric Electrochemical Methods

Voltammetric methods are crucial tools used in electrochemistry to investigate reaction mechanisms involving both biotic and abiotic electrodes. The most commonly used method in electrochemical reactions involving bacteria as electro-catalysts are linear sweep voltammetry (LSV) and cyclic voltammetry (CV). They both involve the response current being measured when several voltages have been applied to the electrode. Linear sweep and cyclic voltammetry help identify electrochemical reactions occurring at certain potential in BES which helps characterise bacteria as electro-catalyst (Scott, 2016).

Linear sweep voltammetry

Linear sweep voltammetry (LSV) involves changing the poise potential of the working electrode linearly whilst measuring the current. This yields a wave form graph (Figure 10) and any specie on the electrode or in solution that can undergo oxidation or reduction reaction shows a distinct peak. Slow scan rates (<1000mV/s) are usually preferred when scanning biotic electrodes as those found in BES (Scott, 2016). As a voltammetry technique for biotic electrode analyses linear sweep is less popular than cyclic voltammetry.

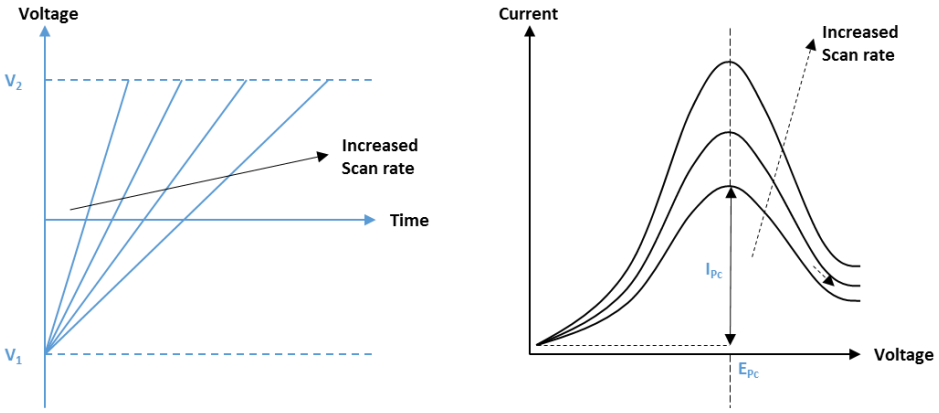


Figure 10: Potential change over time in linear sweep voltammetry (left) and current vs potential response from linear sweep voltammetry (right); Adapted from (Scott, 2016).

Cyclic voltammetry

Cyclic voltammetry (CV) uses the same procedure as linear sweep voltammetry where the poise potential of the working electrode is adjusted with time over a range of potentials. However, the difference between cyclic voltammetry and linear sweep voltammetry is that it involves both a forward and backward scan. Depending on initial scan direction the forward scan gives an oxidation curve whilst the backward scan gives a reduction curve (Heinze, 1981). Cyclic voltammetry shows current peaks for species that can both be reduced and oxidised making it more advantageous than linear sweep voltammetry (Figure 11). Cyclic voltammetry used on reversible reactions produce voltammograms with similar oxidation and reduction current peaks. This is due to the backward scan causing the product generated from the first oxidation reaction to be reduced. This gives crucial data about redox potential and can help identify reaction rates of electrochemical species present(Scott, 2016).

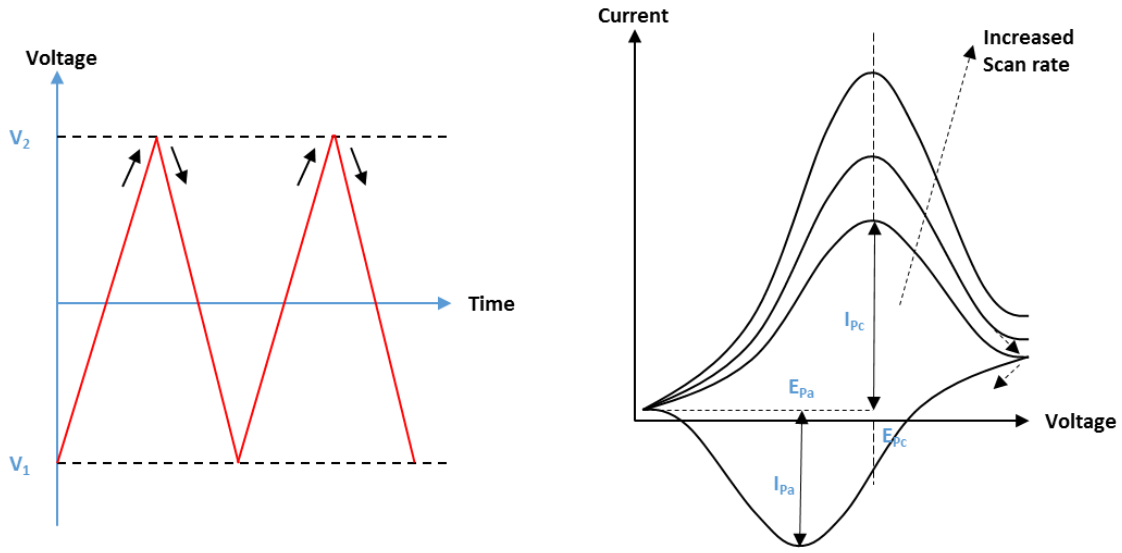


Figure 11: Potential change over time in cyclic voltammetry (left) and current vs potential response from cyclic voltammetry (right); Adapted from (Scott, 2016).

In electrochemistry diffusion to and from the electrode can considerably alter current response from CV therefore a steady environment needs to be employed. However when biotic electrodes are used where bacteria cells are constantly growing accurate data can be a challenge. During start-up bacterial cells propagate separately on the surface of the electrode with each cells acting as a microelectrode within its own diffusion boundary. As growth continues, bacteria cells start to interact with each other either directly or through nanowires causing diffusion to individual cells to become uneven. This makes internal diffusion become a key factor. At maturity a thick film of multi-layered bacteria cells would have formed resulting in the effect of internal diffusion becoming more significant. This makes the choice of scan rate in voltammetric methods important as slow scan rate may not show enough data about electron transfer and reaction species. This would have to be supplemented by data from faster scan rates or impedance spectroscopy. CV applied to bio electrodes without a donor substrate such as that used in MES can alongside indicating reduction and oxidation peaks reveal the potential where the current response in the form of a catalytic wave is at its maximum(Scott, 2016).

2.4.5 Amperometric Detection

Amperometric detection (CA) is a polarization technique where a potential is applied to the working electrode of an electrochemical cell and the current from the resulting electrochemical reaction recorded. Detection usually starts from open circuit to the desired poised potential (Heinze, 1981). CA is often used in MES to detect growth and performance of biofilm (Bajracharya *et al.*, 2015). Figure 12 shows an example of a scan obtained using CA

for a biocathode with potential starting close to zero indicating that biofilm electro-catalytic behaviour has not yet begun. As the biofilm develops using available substrate and electron current starts to become more negative. A steady state biofilm is formed when under the same conditions identical maximum currents are observed. This is however difficult in the case of bio-electrodes as bacteria cells and their interactions with themselves and the electrode surface constantly evolves. The poise potential used in CA can be varied to determine the biofilms real steady state as poise potential can affect current detection especially in the case of BES with long lag phase.

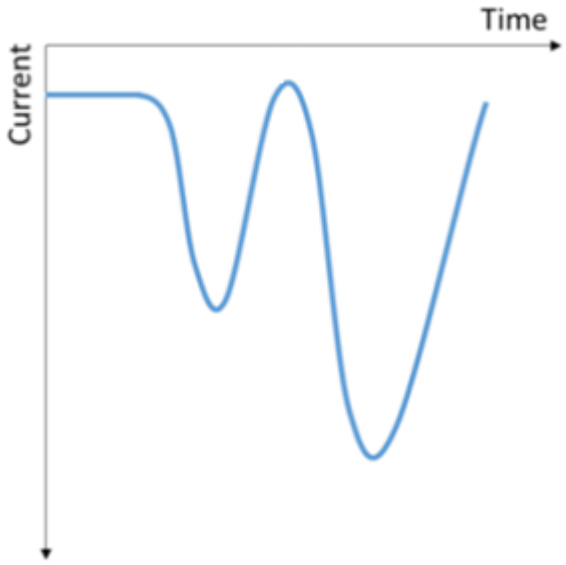


Figure 12: Amperometric detection scan

2.5 Sustainability Principles for Bioprocesses

2.5.1 Sustainability in bioprocesses

Bioprocesses have been in existence for the majority of modern human existence. It has become crucial for human survival and fulfils various essential needs. The 19th century was when the potential of modern biotechnology started to be realised as knowledge of bio-systems and biocatalysts improved. The important penicillin and other products started to be manufactured on a large scale in the 20th century (Fiechter, 2000). Today many bio-products are generated industrially leading to questions about sustainability. Figure 13 shows the ideal pathway for the industrial application of any bioprocess. It illustrations that sustainability assessment plays a vital role as non eco efficient processes should be discontinued. This would also be applicable in relatively new bioprocesses like BESs which are yet to be scaled up and industrially applied.

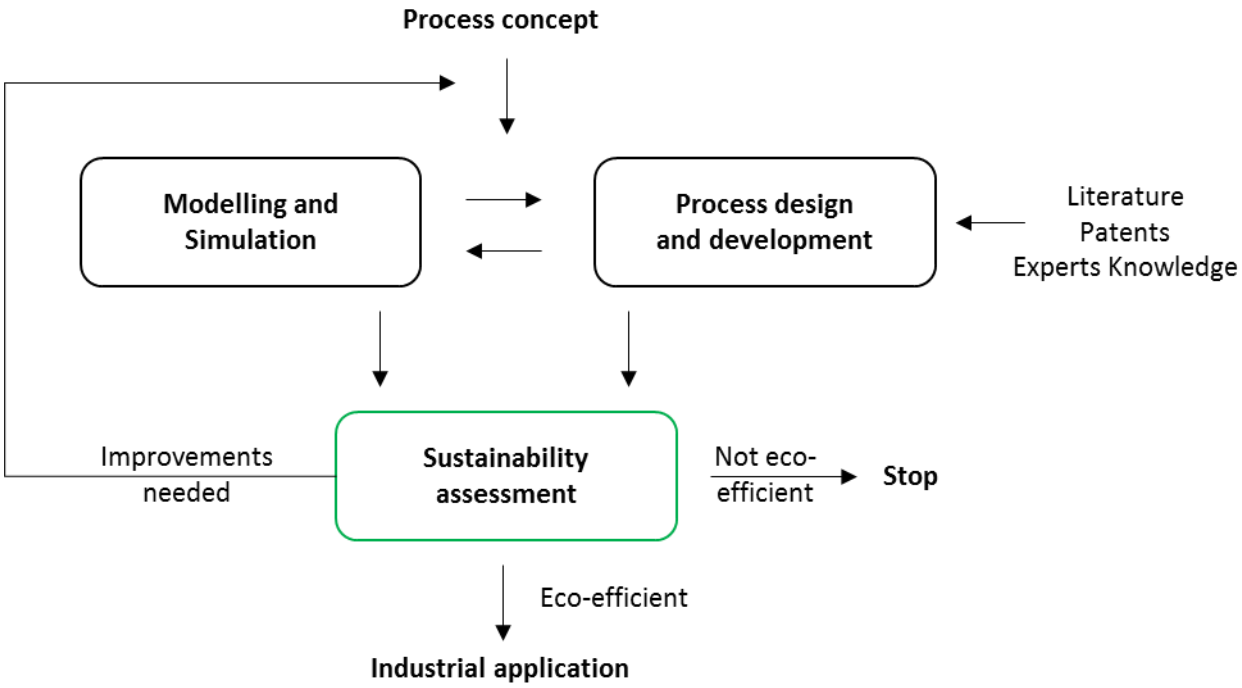


Figure 13: Industrial development of bioprocesses; Adapted from (Heinzle *et al.*, 2007)

A technology or process is said to be sustainability if it has the ability to fulfil the needs of today whilst protecting the interests of future generations (Heinzle *et al.*, 2007). The concept of sustainability management was started in 17th century Germany by the forestry industry. The industry wanted to prevent excess trees from being cut down for timber than that which can be replaced naturally (Klöpffer and Grahl, 2014). Sustainability however does not only imply conservation as responsible development can also be termed this. Technological advancement should strive to follow a growth part that safeguards the environment alongside improving social and economic conditions. Figure 14 shows the three pillars of sustainability which indicates that in sustainability assessment environmental, economic and social parts have to be considered. These aspects of sustainability interact with each other and are usually considered equally significant. This thesis focuses on the environmental sustainability of BESs and would be using life cycle analysis to evaluate it.

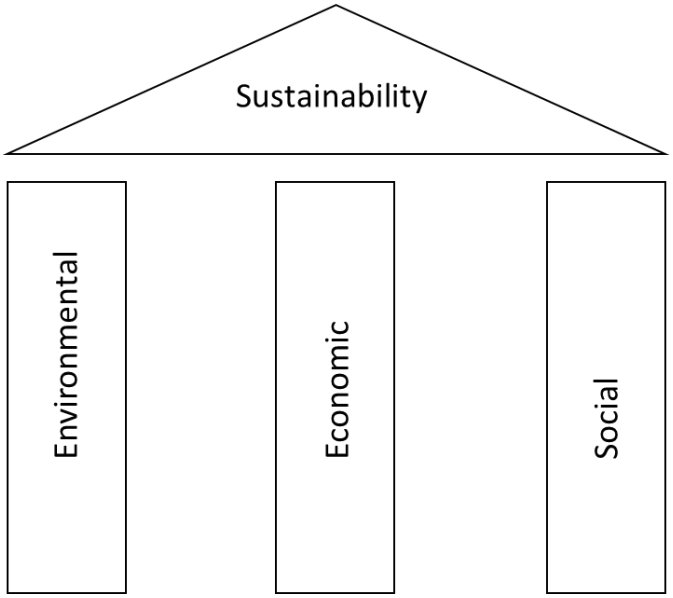


Figure 14: Three pillars of sustainability; Adapted from (Heinzle *et al.*, 2007)

2.5.2 Environmental Sustainability

Life Cycle Assessment

Life cycle assessment (LCA) is employed to analyse the environmental impact data of products from raw material extraction to the removal of waste (ISO, 2006a). Life cycle inventory which involves the collation of key data for the LCA is usually the most important activity. The impact assessment, compiling and interpretation of result are the next three steps to undertake after doing the life cycle inventory. This steps helps with comparison of the analysed system with others as well as structuring of recommendations. Figure 15 shows these four stages of a life cycle assessment described above.

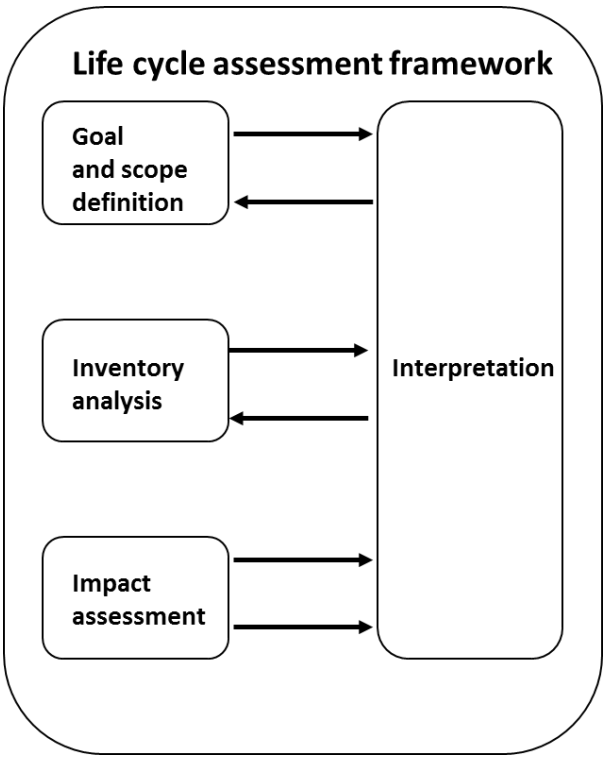


Figure 15: LCA framework and its four distinct phases as recommended by ISO 14040 (adapted from ISO 14040)

The four phases of a LCA are briefly described below;

Goal and scope definition – This is the initial stage of an LCA where the objectives for the study are outlined. It provides the definition, boundary and functional unit of the system or process being examined. The functional unit is the unit of investigation for the LCA and should be selected carefully as it would be used to compare and analyse alternative systems (Rebitzer *et al.*, 2004).

Inventory analysis – This phase of a LCA help identify and quantify inputs and outputs according to a selected functional unit. Material and energy flows are studied and used to identify the contribution of each sector of the process or system being investigated. Inventory analysis can be conducted using numerous LCI databases such as ecoinvent and the ILCD (International reference life cycle data system). The year of LCA study, data source and relevance countries should be shown in the inventory analysis as this may differ if changes to these parameters are made.

Impact Assessment – This phase is where system or process data collated in the inventory analysis are assessed for potential environmental impacts. This is achieved through the use of impact characterization factors. Looking specifically at climate change 1 Kg of CO2 is the widely accepted impact characterization factor with 1 Kg of methane having the same effect on climate change as 25 Kg of CO2 (Sadhukhan et al., 2014). This makes the gas 25 times

more lethal than CO_2 in this impact category. Apart from climate change, inventory data are allocated to other different impact categories. Table 2 shows important impact categories alongside their description.

Table 2: Different impact categories and their description (Sadhukhan *et al.*, 2014)

Impact Categories	**Description**
Climate Change	Alterations to the earth's climate due to greenhouse emissions from the actions of humans or other natural occurring events.
Ozone depletion	Reduction of stratospheric ozone that absorbs the ultraviolet rays of the sun. Unfiltered ultraviolet rays can cause skin cancer and negatively affect polar species.
Toxicity	Effect of a chemical or material on humans, animals and plants. Toxicity is normally characterised as human toxicity or ecotoxicity.
Particulate matter	Pollution as a result of particles less than or equal to 10 micrometres floating in the atmosphere. Inhalation of these small particles can cause health problems in humans and other animals.
Ionising radiation	Ionization of atoms or molecules by alpha, beta and gamma rays. This is particularly dangerous to living creatures as DNA structure can be altered.
Photochemical ozone formation	Formation of ozone at the lower atmosphere and troposphere. It is also referred to as urban smog and has a negative impact on human health and buildings.

Acidification	Chemical makeup (pH) of soil and water are made acidic as a result of sulphuric, carbonic and nitric acids being generated from chemical reactions and inefficient combustion processes.
Eutrophication	Excessive nutrient enrichment of a water body due to human and animal waste leading to an increase in biomass. This results in valuable resources such as oxygen being used up which can be dangerous to fish and other aquatic animals.

Interpretation – This is the final phase of the life cycle framework and it involves analysing and summarising life cycle inventory data and life cycle impact assessment in order to reach informed conclusions and recommend process or system improvement.

2.5.3 Review of past BESs Life Cycle Analysis Studies

As Bioelectrochemical systems (BESs) are relatively new technologies LCA needs to be used to verify if the environmental benefits of using these systems are offset by negative environmental burdens. In literature there are limited instances where LCA has been applied to BESs and this was found to be mostly for microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) rather than other types of BESs. Foley and co-workers published the first reported LCA analysis on BESs used for wastewater treatment in 2010 (Foley *et al.*, 2010). This was followed up in 2011 by a paper from Pant and researchers where a comprehensive methodology for conducting LCA on BESs were outlined(Pant *et al.*, 2011). Other recorded LCA conducted on BES can be found in the works of (Corbella *et al.*, 2017) on MFCs and (Francmanis *et al.*, 2016) on MECs. Table 3 presents a comparison of the different LCAs conducted on BESs.

Table 3: Comparison of LCAs done on BESs

S/N	Type of BESs	Functional unit	LCI	Impact Assessmet	Conclusion	References
1	MFC, MEC and conventional anaerobic digester	Waste water flowrate of 22000 m^3/d at a strength of 4000 mgCOD/L	SimaPro 7.1.8 LCA software (ecoinvent LCI database)	IMPACT 2002+ (v.2.03) from simaPro database	MEC showed more significant environmental benefits over both MFCs and conventional anaerobic system	(Foley *et al.*, 2010)
2	Conventional Horizontal subsurface flow constructed wetlands, and ones constructed with MFCs	1 m^3 of treated water	SimaPro 8	CML-IA baseline method	Graphite based anode MFC was the most environmentally friendly	(Corbella *et al.*, 2017)
3	Various MEC	1m^3 of hydrogen produced per 1m^3 of cell volume	No software (Ecoinvent 3.0 inventory data)	human health, ecosystem quality, climate change and resources	Various options	(Francmanis *et al.*, 2016)

In Foley's and co-researchers LCA a comparison of anaerobic wastewater treatment technology was undertaken. The goal was to evaluate the environmental impacts of treating wastewater with MFC, MEC and conventional anaerobic treatment (Foley *et al.*, 2010). Each of the systems produced by-products; electricity in MFC, hydrogen peroxide in MEC and biogas in anaerobic digester. Models simulated in SimaPro 7.1.8 LCA software were used for the LCA analysis with inventory data for the conventional anaerobic treatment obtained from design documents and vendor supplied information. Inventory data for MFC and MEC was

obtained from the material list of a pilot scale MFC plant built and operated by the University of Queensland. Background life inventory data such as 1 kWh electricity assumed to be from a united kingdom profile (approximately 32% coal and oil, 40% natural gas, 21% nuclear, 4% imported from france, 3% renewables) were obtained using the ecoinvent LCI database found in SimaPro. Lifecycle impact assessment used was IMPACT 2002+ (v.2.03) from the software database. Analysis showed that using MFCs does not provide significant environment benefit in terms of global warming and other environmental burdens to conventional means. However, MEC showed more significant environmental benefits over both MFCs and conventional anaerobic system due to its ability to produce hydrogen peroxide with little greenhouse emissions. The draw backs of this study was that conclusions were highly dependent on the assumed reactor material and reactor performance.

The environmental impacts of using MFCs in constructed wetlands for wastewater treatment was assessed by Corbella and coworkers (Corbella *et al.*, 2017). The goal of the study was to assess and compare the environmental benefits of using horizontal subsurface flow constructed wetlands for wastewater treatment coupled with MFC made of different materials. Three scenarios of constructed wetlands were analysed to achieve this goal, a conventional constructed wetlands system, one constructed using a gravel based anode MFC and another with a graphite based anode MFC. The functional unit of the study was $1m^3$ of treated water and the LCA software employed was SimaPro 8. Inventory data regarding construction processes, construction materials and electricity consumption were obtained during the construction of the three systems. Background data was obtained from Eco invent 3.1 database with the electricity profile being one from the spainish electricity grid (approximately 39% natural gas, 19% nuclear, 15.50% coal, 10.90% wind, hydro 8.8%, liquid fuels 5.80% and solid biomass 1%). The study used CML-IA baseline impact assessment method focusing primarily on abiotic depletion, abiotic depletion (fossil fuels), global warming potential, ozone layer depletion, acidification, eutrophication and photochemical oxidation. Results showed that the three scenarios were similar for each impact category except abiotic depletion potential. Abiotic resources are non-living natural resources such as iron ore and crude oil. They are usually strongly linked to electricity production (Pikoń, 2012). Results from this category showed that the graphite based anode MFC was the most environmentally friendly as it was 50 percent lower than conventional constructed wetlands systems and up to four times lower than the gravel based system.

A comprehensive analysis on the different types of MECs was done by Francmanis and coworkers (Francmanis *et al.*, 2016). The goal of their study was to do a comparative environmental assessment of MEC based on life cycle inventory data found in literature. These technical data were gathered from both laboratory experiments and modelling work published by other researchers. The functional unit chosen for the study was 1 m_3 of hydrogen per $1m^3$ of cell volume. The system boundary was however only limited to the MECs and reactions happening within the cells. The study made use of no specific LCA software and inventory data was solely obtained from the Ecoinvent 3.0 inventory data base. Four environmental impacts categories were selected for the assessment namely human health, ecosystem quality, climate change and resources. The study was mainly comparative therefore no definite conclusions can be drawn as there was fluctuation in the four categories selected. However the results show that platinium based cells with high hydrogen production have comparatively low impact to human health and climate change.

As LCA in literature is limited especially for production of chemicals using BESs it has become imperative that one has to be undertaken as the technology continues to mature. This study aims to achieve this and produced novel knowledge in this area.

Chapter 3: Methodology

3.1 Introduction

This chapter describes the methodology and procedures used to achieve all experimental and environmental objectives of this thesis. Section 3.2- 3.6 describes the methods used for experiments conducted while section 3.7 shows the procedures used for environmental sustainability analysis.

3.2 Cell Design and Experimental Setup

3.2.1 Dual Chamber Cells

Two types of H-type reactors (Reactor type A and B) were used for this study. Rectangular pieces of platinum-coated titanium mesh or plate was used as anode in each reactor with the cathode made of carbon felt (Product number 43200, Alfa Aesar, UK). Reactor type A had a total volume of 230ml (solution 215ml; headspace 15ml) per chamber with the cathode cut in a trapezium shape (3cm x 5cm x 8cm) having a working surface area of 64cm^2. The anode for these type of reactor were platinum-coated titanium mesh (working surface area 16cm^2). Reactor type B had an anode and a cathode chamber of 80 mL with a headspace of 30 mL. The electrodes in these reactors were platinum coated (1µm) titanium plate as the anode and 50cm^2 carbon felt as the cathode respectively (See

Figure 16 for schematic diagram of each reactor type). Pretreated nafion 117 proton exchange membrane (PEM) (Sigma Aldrich, UK) were used to separate the anode and cathode chambers of all reactor types. Membrane pre-treatment was achieved by boiling for 2 hours in H_2O_2 (3% v/v), 0.5M H_2SO_4 and deionized water. The PEM was stored in deionized water before use in the BESs. Anode and cathode chambers of each reactor were isolated and hermetically closed using parafilm and butyl rubber stoppers. For connection to the electrical power source, electrodes were attached with titanium wires extruding through butyl rubber cap on the top of each reactor chamber.

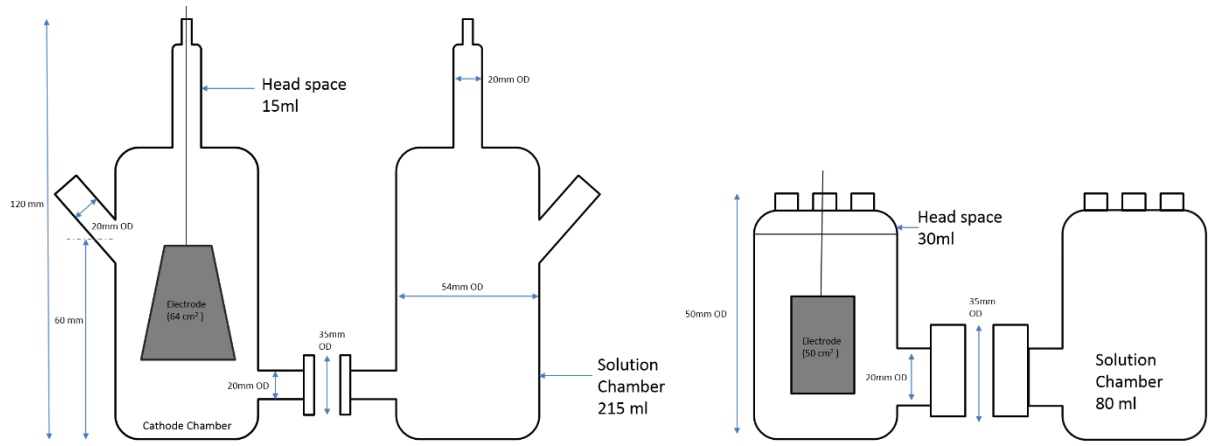


Figure 16: Schematic Diagram of reactor type A (Left) and reactor type B (Right)

Initially three of each reactor type were fabricated for experimental evaluation. The reactors were named BES-1, BES-2, BES-3, BES-4, C-1, and C-2 for convenience. Reactors BES-1, BES-2 and C-1 were reactor type A while BES-3, BES-4 and C-2 were reactor type B. For electrochemical potentiostatic measurements and monitoring BES-1, BES-2 and BES-3 were connected to palmsens multiEnStat multi channel potentiostat while BES-4 was connected to a single channel palmsens potentiostat. This was done using a three electrode configuration with the cathode as the working electrode and the anode as the counter electrode. Reference electrode used in all the cells were Ag/AgCl electrodes (+0.197 V vs. Standard Hydrogen electrode, Basi, UK) with the catholyte continuously stirred using magnetic stirrers revolving at between 100 -200 rpm (see Figure 17 for experimental setup). The potentiostats used in the experimental setup supplied the energy needed to achieve water oxidation (E^o= 0.82V vs SHE at pH7) for electrons and protons at the anode and poise the cathode at a set potential with respect to the reference electrode (Rabaey and Rozendal, 2010). As shown in the experimental setup seen in Figure 17 the reactors were placed in a Styrofoam chamber. This was done to control the temperature alongside a water bath (Grant T100 heated circulating bath, UK). Heated water from the bath was channelled round the Styrofoam chamber using PVC laboratory tubing (3mm ID x 6mm OD). This had the effect of heating the reactors to the required temperature for that period.

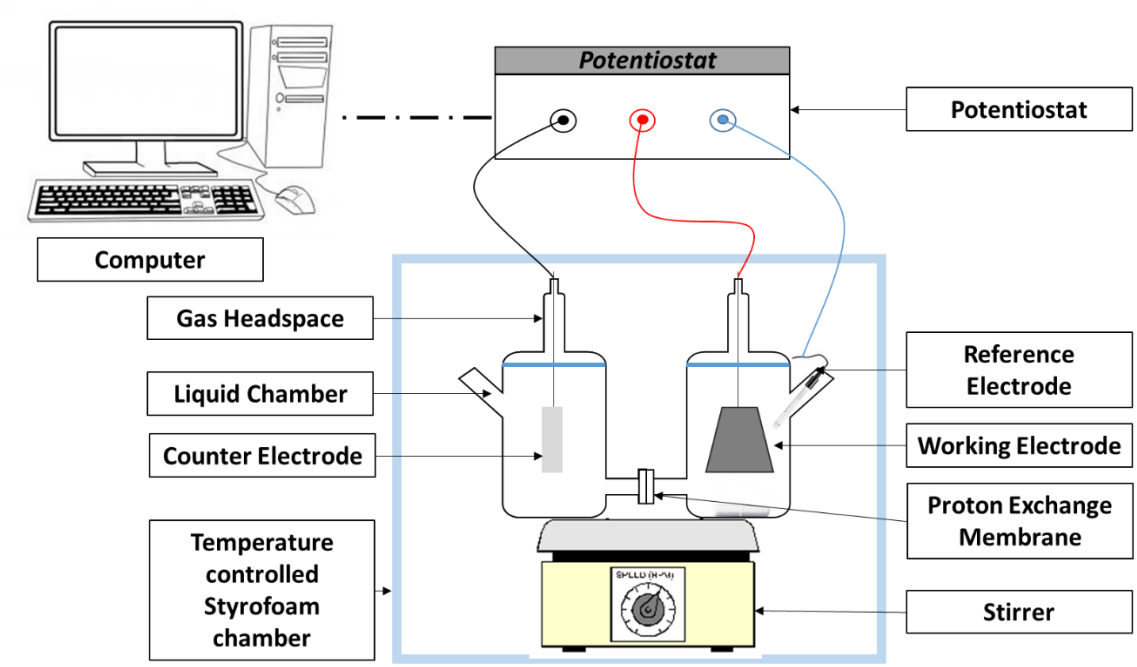


Figure 17: BESs Experimental Setup

3.2.2 Media preparation (inoculum and electrolytes)

BES-1, BES-2 and C-1 were inoculated with anaerobic sludge obtained from an existing anaerobic digester at cockle park farm, Newcastle. The sludge was first centrifuged at 3660 rpm for ten minutes to extract all the bulky particles (Eppendorf Centrifuge 5810, UK) with the supernatant (10ml) alongside 200ml of medium inoculated into the cathode chamber of the reactor. Bacteria Inoculation occurred until a stable biofilm was obtained, this was done as not to disturb the bacteria community attached to the electrode. BES-3, BES-4 and C-2 were all setup after the previously described reactors and were inoculated with effluence from BES-1 and BES-2 in order to develop a similar bacteria biofilm on its cathode. The medium used in both chambers of all reactors consisted of the following (per litre of distilled water); 0.2g NH_4CL; 0.04g $MgCl_2.6H_2O$; 0.015g $CaCl_2$; 3g $KH_2PO_4.2H_20$; 6g $Na_2HPO_4.2H_2O$ and 10ml of both Wolfe vitamin solution and modified Wolfe's mineral solution (Appendix A1). The pH of the medium was always set at pH 7.0 ± 0.1.

3.2.3 Start-up and cell operational conditions

All BESs were operated in a fed batch mode with each batch cycle lasting between 4 to 25 days. The batch was usually considered complete when the current starts to rise significantly signally substrate depletion (see Figure 18). After each cycle 80% of the catholyte was replaced with fresh medium. As BES-1, BES-2 and C-1 were started up initially the potential was first set at -860 mV vs Ag/AgCl (23 days for BES-1; 13 days for BES-2) and then -997

mV vs Ag/AgCl before BES-3, BES-4 and C-2 were inoculated at an initial polarization potential of -997 mV vs Ag/AgCl and commenced operation. This involved driving the working electrode to more negative potentials which increased the energy of electrons within it and facilitated electron flow from electrode to electrolyte (reduction current). On the other hand if poised at a positive potential the electron energy of the electrode would be lowered leading to the occurrence of oxidation current (Bard and Faulkner, 2001).The below subsections describe the subsequent conditions applied to all BESs (Table 4 for operational schemes).

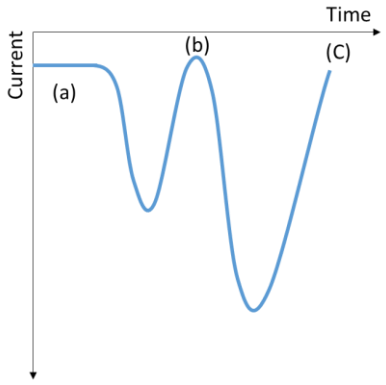


Figure 18: Amperometric detection scan showing batch beginning and end; a) detection begins b) batch 1 ends and batch 2 begins and c) batch 2 ends

3.2.3.1 Batch operation of BES with Bicarbonate

The biocathode for BES-1 and BES-2 was started using 2g of $NaHCO_3$ as a carbon source with the seed culture being anaerobic sludge bacteria. Anaerobic conditions in the reactors were maintained by sparging the medium and headspace with CO_2 gas. This was operated with the cathode potential initially set at -860mV vs Ag/AgCl and then -997mV vs Ag/AgCl till day 74 for BES-1 and day 66 for BES-2 after which the gas used for sparging was changed to pure nitrogen leaving $NaHCO_3$ as the sole carbon source for 5 days (Table 4 for operational scheme).

3.2.3.2 Hydrogen as additional electron source

Pure hydrogen gas was introduced into the reactors as an additional electron source to test the effect of the gas on biosynthesis. It was introduced into the reactors on day 79 for BES-1 and day 66 for BES-2 with the sole carbon source remaining $NaHCO_3$ (Table 4 for operational scheme). This was achieved by sparging the headspace and medium for 10minutes with H_2 instead of CO_2 or N_2. As with other batches reduction current was recorded every 300 seconds using a potentiostat.

3.2.3.3 Long term batch operation of BES with CO_2

After hydrogen was used as an additional electron source the BES-1 and BES-2 were operated in fed batch by continuously using CO_2 in the headspace as the sole carbon source without external supply of H_2. In the long term batch operation the cathode potential was always set between -797mV and -1397 mV vs Ag/AgCl to enable direct or H_2 mediated CO_2 reduction to chemicals. BES-1 and BES-2 were operated under these conditions for 288 days and 280 days respectively while BES-3 and BES-4 having been started up with pure CO_2 was operated for 166 days (Table 4 for operational scheme).

3.2.3.4 Polarization and temperature test

The theoretical reduction potential for hydrogen evolution at pH 7 is -614 mV vs Ag/AgCl but a lower potential usually have to be applied due to losses. Polarization test was done on all the reactors using CO_2 as the sole carbon source by applying four different poised potential -797 mV, -997 mV, -1197 mV and -1397 mV vs Ag/AgCl (Table 4). Additionally a temperature test was conducted on the lowest potential applied (-1397mV vs Ag/AgCl) to test the effect of change in temperature on biosynthesis. It was conducted at room temperature (approximately 26^{o}C) and 40^{o}C. Higher than normal temperature was selected based on the work done by Fu and co-workers where BESs operated at high temperature efficiently produce useful chemicals (Fu *et al.*, 2015). Each polarisation lasted from between 10 to 14 days with the reduction current recorded and products synthesized analysed.

Table 4: Operational Schemes and Phases of BESs experiments

Experimental Phases	**T °C**	**E_{cat} (mV)**	**BES-1 Day (Batch)**	**BES-2 Day (Batch)**	**BES-3 Day (Batch)**	**BES-4 Day (Batch)**
Microbes Inoculation	30	-860	2	2	0	0
2g $NaHCO_3$ as carbon source; CO_2 used to sparge medium and headspace	30	-860	0 (1)	0 (1)	-	-
2g $NaHCO_3$ as carbon source; CO_2 used to sparge medium and headspace	30	-997	23 (2-4)	13 (2-4)	-	-
2g $NaHCO_3$ as carbon source; N_2 used to sparge medium and headspace	30	-997	74 (5)	61 (5)	-	-
2g $NaHCO_3$ as carbon source; H_2 used to sparge medium and headspace	30	-997	79 (6)	66 (6)	-	-
CO_2 as carbon source; CO_2 used to sparge medium and headspace	30	-997	84 (7-14)	71 (7-14)	0 (1-7)	0 (1-7)
CO_2 as carbon source; CO_2 used to sparge medium and headspace	30	-1197	215 (15)	199 (15)	92 (8)	92 (8)
CO_2 as carbon source; CO_2 used to sparge medium and headspace	30	-797	237 (16)	222 (16)	114 (9)	114 (9)
CO_2 as carbon source; CO_2 used to sparge medium and headspace	27	-1197	247 (17)	232 (17)	124 (10)	124 (10)
CO_2 as carbon source; CO_2 used to sparge medium and headspace	27	-997	259 (18)	244 (18)	136 (11)	136 (11)
CO_2 as carbon source; CO_2 used to sparge medium and headspace	27	-1397	268 (19)	256 (19)	146 (12)	146 (12)
CO_2 as carbon source; CO_2 used to sparge medium and headspace	40	-1397	278-288 (20)	266-276 (20)	156-166 (13)	156-166 (13)

3.2.3.5 Gaseous carbon dioxide depletion and abiotic electrochemical comparative test

CO_2 reduction to bioproducts was performed in a double chamber H-shaped reactor B type cell as describe above. Five of these type of reactor was started up with three set up as BESs using anaerobic sludge from cockle farm, Newcastle. Alongside these reactors an abiotic electrochemical reactor (AER) and a control using the same reactor type were also initiated. The AER reactor used the same electrolyte as in previous setup without the addition of bacteria. Potential of the BESs and AER were initially set to -997mV vs Ag/AgCl as the same electrochemical techniques were applied to the reactors. Control had no poise potential applied but included inoculated bacteria. The cathode of all reactors were made of 50cm^2 carbon felt with the anode being platinum coated (1µm) titanium plate. As with the previous test cathode potential of the BES and AER were controlled using chronoamperometry from a potentiostat (palmsen multiEnstat multi channel potentiostat) with the reference electrode being Ag/AgCl electrode (+0.197 V vs. Standard Hydrogen electrode, Basi, UK). The catholyte was continuously stirred at 100-200 rpm using magnetic stirrers with liquid and gaseous samples taken.

3.3 Electrochemical analysis

The potentiostatically controlled experiments were conducted in H-shape cells using a 3 electrode configuration with carbon felt as the working electrode and the reference electrode being Ag/AgCl. Potentiostats which are devices used to fix the potential of the working electrode of an electrochemical cell with respect to a reference electrode were used for electrochemical analysis. Potentiostats accurately does this by controlling the potential of the counter electrode against the working electrode. In electrochemistry the working electrode is where the reaction that is being observed occurs while the counter electrode usually made of inert materials is used to complete the electric circuit (EC08, 2011). The system can be setup in three ways namely a two, three or four electrode setup (see Figure 19). In a two electrode setup an electrode is used as both the counter electrode and reference electrode while the other as the working electrode. This setup enables the potential across the whole cell including the electrolyte to be measured. A three electrode setup which is the most commonly used and as mentioned earlier is what is employed here makes use of separate counter, working, and reference electrodes to control the potential difference between the working and counter electrodes. The reference electrode is usually placed close to the working electrode in this setup. Four electrode setup is rare in electrochemistry experiment as there is a need for an additional sense electrode (EC08, 2011). All measurements and applied potential experiments

in this study were done using PSTrace potentiostats (palmsens single and multichannel potentiostats).

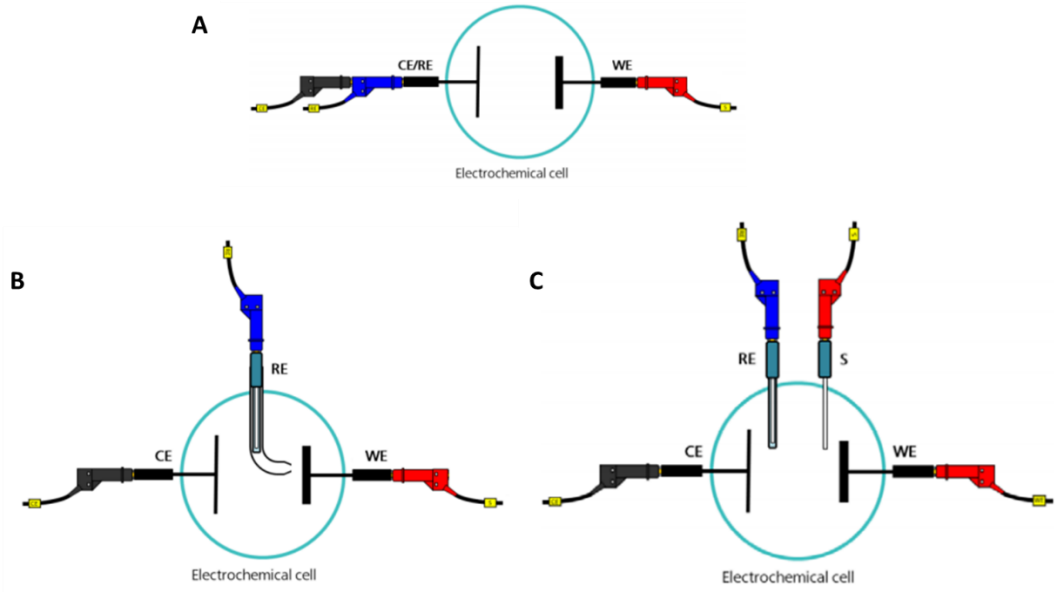


Figure 19: Schematic view of electrode setups A) 2 electrode setup B) 3 electrode setup C) 4 electrode setup (Adapted from (EC08, 2011)

3.3.1 Chronoamperometry method

Chronoamperometry technique involves fixing the potential of the working electrode (cathode in this study) and recording the resulting current from the reactions going on at the electrode. As this study involved the use of a 3 electrode setup the potential of the working electrode was set at a specific potential using reference and counter electrodes. The subsequent current from the reaction occurring at the working electrode was detected over time. Cottrell equation seen below shows the rate of decay of the faradaic current at the working electrode which is planar (Bard and Faulkner, 2001; Scott and Yu, 2016).

$$i = \frac{nFAD^{0.5}C_b}{(\pi t)^{0.5}}$$

Where, A is the electrode area, D is the diffusion coefficient and t is time

Figure 20 shows a regular potential step applied over time and the subsequent current response detected. The response applies for diffusion to planar electrodes under unstirred solution conditions with no other side reactions. Cottrel equation when rearranged can be used to obtain important diffusion coefficients when number of electrons and other variables in the equation are identified.

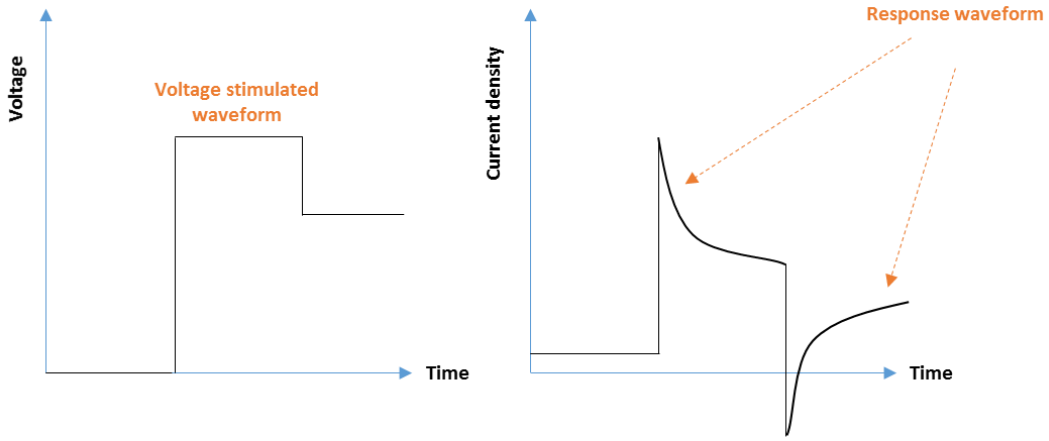


Figure 20: Potential step over time and current response in chronoamperometry. Adapted from (Scott and Yu, 2016)

Chronoamperometry is used frequently in experiments involving BESs to analyse biofilm growth and key performances (Scott and Yu, 2016). Chronoamperometry experiments in this study were performed using a PSTrace potentiostats consisting of four channels and a single channel potentiostat which together can run five parallel test simultaneously. To fix the potential of the cathode biofilm, cathode was connected as the working electrode while an Ag/AgCl electrode located in the same solution with cathode worked as the reference electrode. Anode worked as the counter electrode where the potentiostat adjusted its potential in order to fix the cathode potential (see Figure 17 for experimental setup). Biocathodes were subjected to a range of chronoamperometric test (see Table 4 for operational scheme).

3.3.2 Cyclic Voltammetry

Cyclic voltammetry is an electrochemical technique where the redox activity of a working electrode is analysed. Cyclic voltammetry can be used to know if the redox reaction involved in the electrochemical cell is reversible or irreversible. As bacteria is used as catalyst in bioelectrochemical systems the relationship between the biofilm and the working electrode can be studied using cyclic voltammetry. The potential of extracellur electron transfer reactions and performance of biofilm can be determined also using this electrochemical technique (Bard and Faulkner, 2001).

Cyclic voltammetry means basically changing the poise potential of the working electrode with time whist measuring the current generated. This is done in a forward and backward scan where the former gives an oxidation curve and the later a reduction curve depending on the initial scan direction (Figure 21). The forward or backward scan (dependent on initial scan direction) could yield a current peak for species that can be reduced over the range of potentials selected (Figure 21). The current will rise as potential gets close to the reduction potential of the species and then fall due to concentration of the specie diminishing close to

the working electrode. The redox reaction is deemed reversible if a similar peak is formed when the potential to reoxidize the product synthesized is reached. Cyclic voltammograms in this study were measured from -1.500 to 0 V (vs. Ag/AgCl) at a scan rate of 0.001 V/s. This slow scan rate was used so as not to damage the delicate biofilm growing on the electrode.

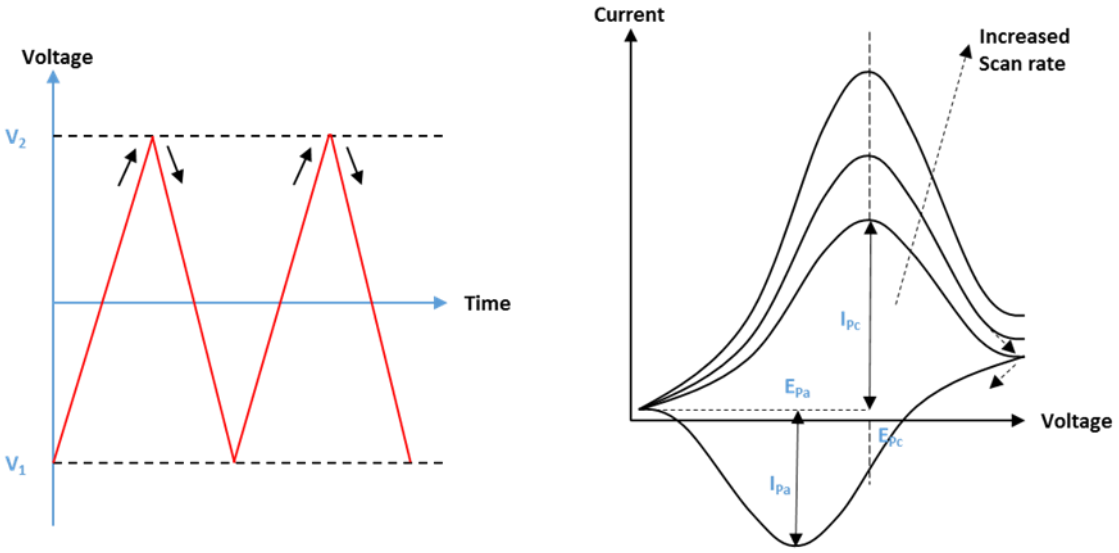


Figure 21: Potential change over time in cyclic voltammetry (left) and current vs potential response for reversible and irreversible reactions (right) (Scott and Yu, 2016)

3.4 Chemical analytical methods

3.4.1 Gas samples

Gas samples from the head space of the BESs were extracted using gas tight syringes. The constituent gases from the samples were detected using gas chromatography (Shimadzu Gas Chromatography GC-8A). Chromatography as an analytical tool is similar to distillation as it is meant to separate components from a mixture using different passage speeds through a column. In gas chromatography two phases are needed for application and separation. The phases are usually an inert gas, the mobile phase and a solid or non-volatile liquid in the column (Rose, 1959). To facilitate separation gas chromatographs apart from these phases must also have an injector port, a column where separation of gases occur, an oven used to control column temperature, a detector to identify different gases from column outlet and a recorder where chromatograms can be stored and displayed. Figure 22A shows the gas chromatography used which was equipped with all these having two steel columns (2m length x 5mm OD x 3mm ID) using different absorbent materials (Moleclar sieve 5A and Chromosorb 101). During sample analysis the oven temperature was set at 40^{o}C with the

carrier gas being 99.99% nitrogen continuously fed into the columns at 100Kpa. The thermal conductivity detector used retention time to distinguish the gases calibrated. Syringe dilution method was used to create gas standards with appropriate calibration curve plotted (Figure 22B for methane gas). These curves were generated by running the various dilutions of the gases to determine each gas response time and plot peak area against percentage (Appendix A2). Calibration curves were rerun regularly to check its validity alongside equipment accuracy.

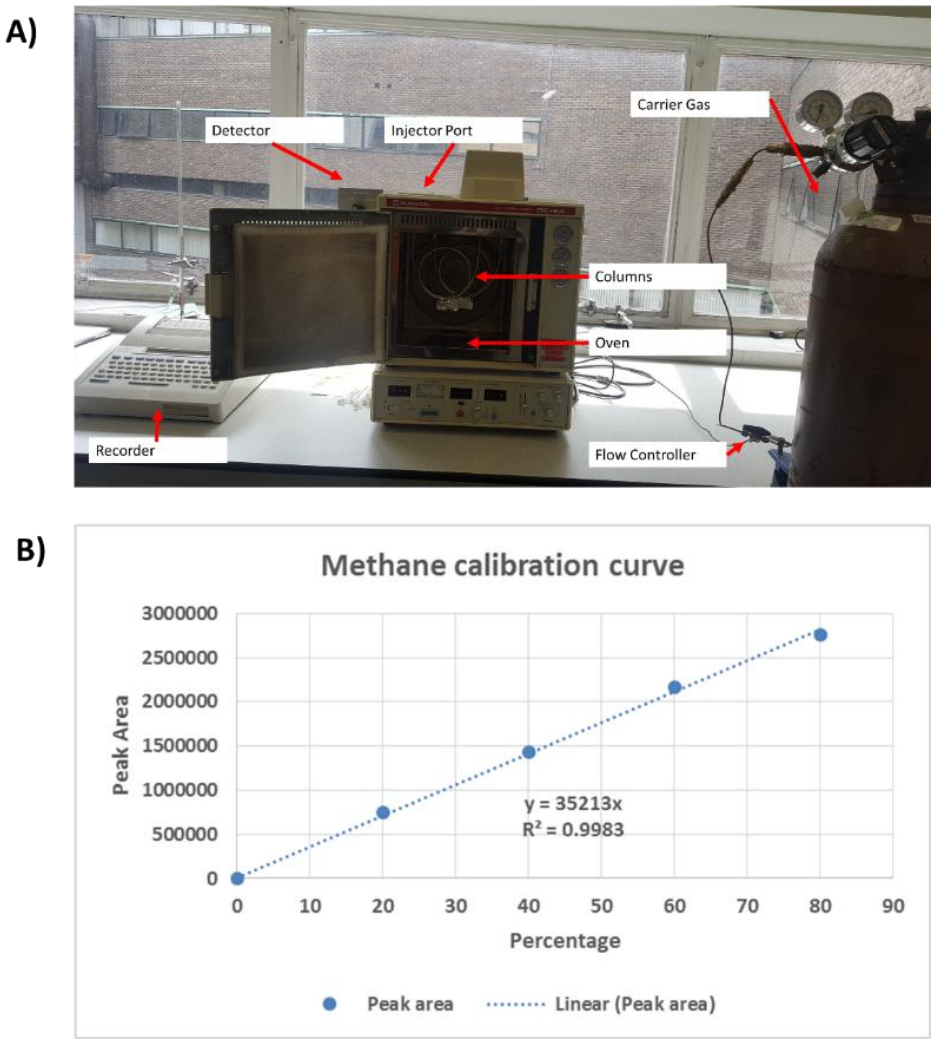


Figure 22: A) Gas Chromatography used for gas analysis (Shimadzu gas chromatography GC-8A) and B) Methane calibration curve

3.4.2 Liquid samples

Liquid samples were collected from the liquid chamber of the BESs and filtered using a 0.2µm syringe filter to remove bacteria cells. The samples were analysed for volatile fatty acid using gas chromatography (Shimadzu gas chromatography Tracera GC-2010) employing the same principle as described in section 3.4.1 (See Figure 23 for the gas chromatography

used). Samples were acidified using 0.1µL of 1M HCl for every 1µL of sample analysed. The carrier gas used by the gas chromatography was 99.99% helium flowing at 2 mL/min into the column (Zebron ZB-WAX-Plus capillary column 30m x 0.25mm x 0.25µm, Phenomenexl, UK). Column and injection port temperature was operated at 180°C with the barrier ionization discharge (BID) detector running at 280°C.

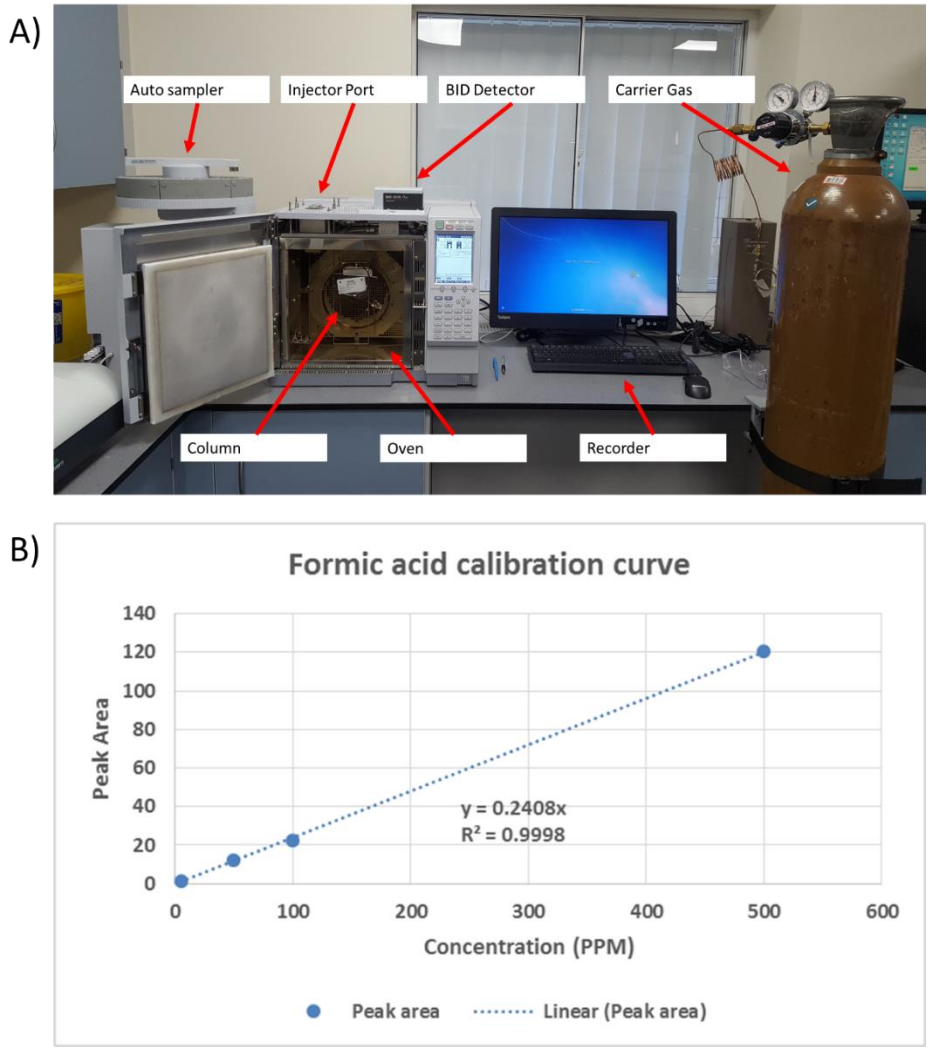


Figure 23: A) Gas chromatography used for liquid analysis (Shimadzu gas chromatography Tracera GC-2010) and B) Formic acid calibration curve

3.5 Calculations

The molarity of products synthesised at any time t from the batch operation of all BESs were calculated using equation 3.1 below;

$$n_{product,t} = \frac{V_{cat}\ x\ (C_{product,t} - C_{product,t_0})}{M_{product}}\ (\mu M) \qquad (3.1)$$

Where, V_{cat} is the total volume of electrolyte in the cathode, C is the concentration of product synthesized and $M_{product}$ is the molecular weight of the specific product. Subscripts t_0 and t denotes time between two consecutive samples.

Equation 3.2 shows how the rate of synthesis of each product was calculated;

$$S_{product,t} = \frac{(C_{product,t} - C_{product,t_0})}{t - t_0}\ (\mu M/d) \qquad (3.2)$$

Where, $t - t_0$ is the change in days between products synthesized at time t and those observed in the previous samples at time t_0.

Current efficiency (CE) is the efficiency of electron transformation from electric current to the products synthesized (Bajracharya *et al.*, 2015). This efficiency was calculated in this study for all products synthesized using equation 3.3 below;

$$CE = \frac{n_{product,t}\ x\ f_{e,product}\ x\ F)}{\int_{t_0}^{t} I\ dt}\ x\ 100\ (\%) \qquad (3.3)$$

Equation 3.4 was used to calculate the current efficiency for a batch;

$$CE = \frac{\Sigma(n_{product}\ x\ f_{e,product}\ )\ x\ F)}{\int_{t_0}^{t} I\ dt}\ x\ 100\ (\%) \qquad (3.4)$$

Where, $n_{product,t}$ is the moles of product evaluated at time t, $f_{e,product}$ is the molar conversion factor of the product synthesized, F is the faraday constant (96,485 C/mol) and I represent the current.

3.6 Reproducibility

Reproducibility is the ability of an investigator to obtain the same results from an experiment using the same equipment's, materials and conditions used by the original researchers (Goodman *et al.*, 2016). It is the minimum necessary condition for a result to be deemed valid. Experiments were conducted in two or four replicates assuring that reproducibility can be evaluated.

3.7 Environmental sustainability

3.7.1 The goal and purpose of the sustainability analysis

The purpose of this phase of the study was to gain an understanding of the environmental impacts of operating BESs for microbial electrosynthesis (MES). The study helped to illustrate possible opportunities to improve the environmental sustainability of different BESs operating scenarios. The different operating scenarios analysed focused on products synthesized from BESs and other alternative systems under specific operating conditions.

3.7.2 Definition and description of scenarios

Three scenarios were chosen to contrast five different products synthesized from BESs (Table 5). The system was analysed using electrical energy from two sources: pure natural gas and United Kingdom national grid for a ten year plant life. Analysis in the case of pure natural gas was done using excel for hand calculations of environmental impacts (energy consumption and global warming potential) and Aspen plus V82 taking into account only energy required for cathodic MES reaction. For the United Kingdom national grid analysis the life cycle assessment software GaBi was used to obtain midpoint impact categories according to the International Reference Life Cycle Data System (ILCD). The systems using natural gas as the electricity source was compared with most popular conventional means of synthesizing the products using sustainability indicators. On the other hand results from those using the United Kingdom national grid was compared with abiotic electrochemical methods. Finally scenario 3 analyses the best product in terms of environmental impacts and compare it with the three other methods the chemical can be industrially produced.

Table 5: Description of Scenarios

S/N	Scenarios	Functional Unit	Method Implemented	Electricity Source	Sustainability Indicators
1	Scenario 1 (Chapter 5)	1000 t/yr	Excel and Aspen plus V82	Pure natural gas	Net energy consumption, Global warming
2	Scenario 2 (Chapter 6)	1000 t/yr	Gabi LCA software	UK national grid	ILCD impact category
3	Scenario 3 (Chapter 7)	1000 t/yr	Gabi LCA software	UK national grid	ILCD impact category

3.7.3 Scope of study

The analysis in all scenarios were limited to a cradle-to-gate focus shown in the system boundary in Figure 24. All the steps shown in the system boundary were considered except the final product use. Life cycle methodology using the system boundary was based on that described in the standards ISO 14040 and 14044 and was done for a ten year timeframe (ISO, 2006a; ISO, 2006b).

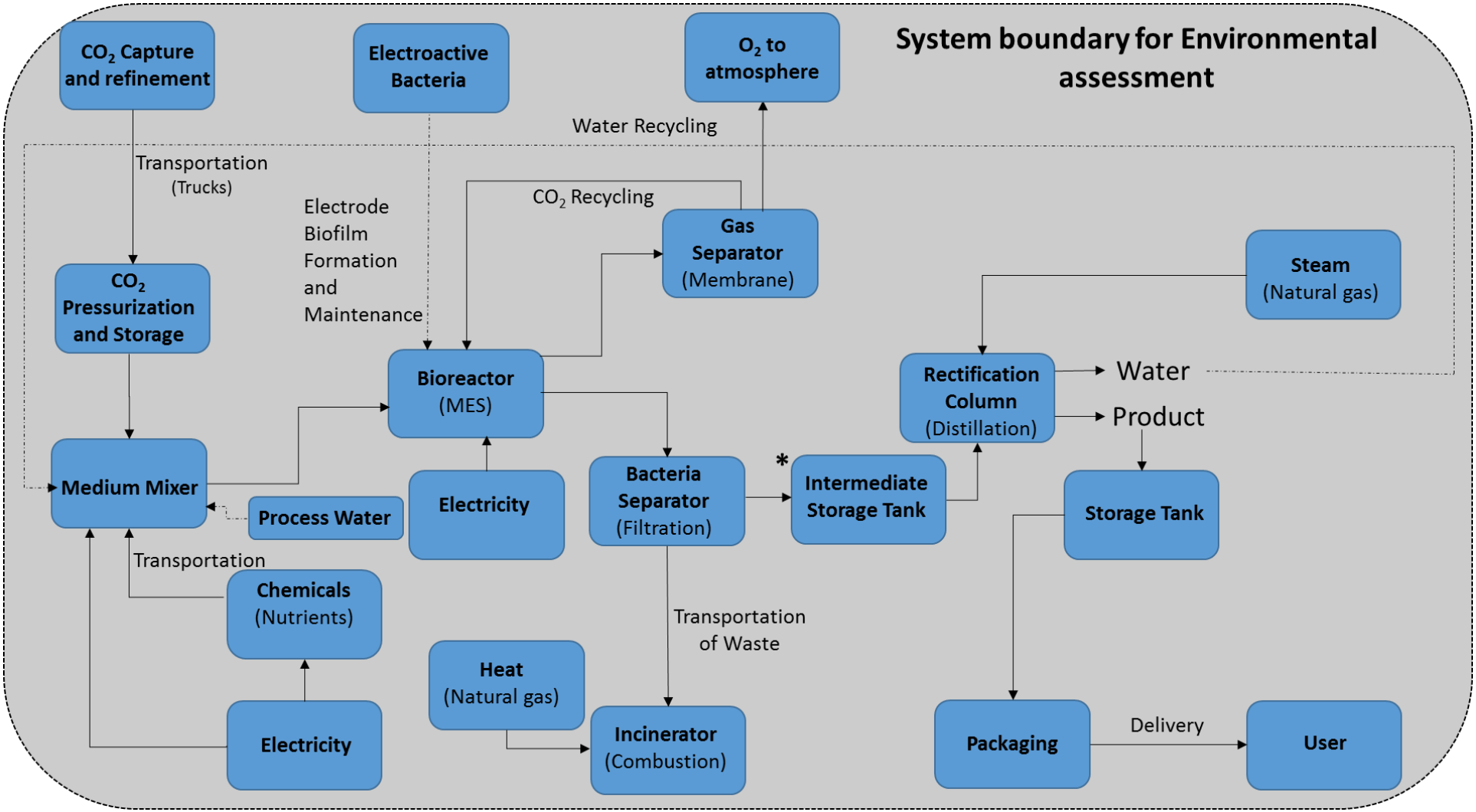


Figure 24: System boundary for a 1000 tonne per year MES plant. *Before this unit operation all processes are batch, the distillation process runs continuously.

3.7.4 Process description

Acetic, formic and propionic acids, methanol and ethanol were evaluated as products using a microbial electrosynthesis (MES) plant. The MES plant was assumed to be located at Newcastle Upon Tyne, UK. Large scale BESs in the form of fermentation batches were considered as reactors which also included electrodes, reaction medium and biofilm as a catalyst. The biofilm used in the reactor was assumed to be developed prior to the plant start-up. The plant was mainly operated in batch mode and ran for 8000 hours per year to produce 1000 tonnes per year (t/y) of product. A biocatalyst separator is used to remove any remaining bacterial in the effluent prior its entrance to the rectification column. Any excess CO_2 is recycled back to the MES reactor where the produced oxygen is released to atmosphere. The main unit operations are further described in the sub sections below with main assumption outlined in Table 6. Detailed description showing parameters used for unit operation analysis shown in Appendix A3 and A4.

Table 6: Main assumptions for MES plant unit operations

S/N	Unit operation	Assumptions
1	Mixer	A) CO_2 used in mixer captured from coal fired plant flue gas at 0.1758 GJ per tonne of CO_2 B) Chemicals used in mixer obtained using average energy in GJ/ tonnes to manufacture chemicals in Europe. C) 3 blade hydrofoil impellers used in the mixer. D) Mixing was approximated to last 20 minutes per batch.
2	MES reactor	A) Steady state biofilm developed prior to the MES plant start-up. B) Appropriate mixed culture or pure culture biofilm used for synthesis of products. C) Methanogenesis inhibited by using 2-bromomethanesulfonate D) Coulombic efficiency and CO_2 conversion rate estimated at 69% and 58.8%. E) Reactor required 3.66 days (88 h) per batch with temperature set to 25 ± 2 °C. F) Potential of anode for water oxidation assumed to be steady at 0.817 V vs SHE.
3	Gas separator	A) CO_2/O_2 separating membrane used as gas separator. B) CO_2/O_2 selectivity of membrane assumed to be 50.

		C) Capture efficiency assumed to be 99%.
4	Filtration system	A) Physical filtration by 0.2µm cartridge filters used to separate bacteria cells. B) Separated bacteria cells assumed to be incinerated 50km away from the MES plant.
5	Rectification unit	A) Energy required to manufacture entrainers used for rectification of acetic acid, propionic and formic acid not taken into account in the analysis

Mixer

An industrial mixer was used to prepare the reaction medium consisted of a number of minerals, salts (see Appendix A5) and CO_2. The mixing would last approximately for 20 minutes per batch. CO_2 used was captured and provided from a coal fired power plant placed 30 km away from the MES plant, transported, pressurized and stored onsite. It was assumed that CO_2 was captured from flue gas consisting of 13 mol% CO_2 at 0.1758 GJ per tonne of CO_2 (Bhown and Freeman, 2011). This reaction medium was subsequently pumped into reactors which consisted of steady state biofilms. The energy required to produce all chemicals used in medium preparation was obtained using the average energy in gigajoules per tonne (GJ/tonne) to manufacture chemicals in Europe (Cefic, 2014; Eurostat, 2014).

MES reactors

It was assumed that steady state biofilms were developed prior to the MES plant start-up. Some biofilm development procedures, parameters and assumptions were made based on data obtained experimentally (Marshall *et al.*, 2013). Biofilms were derived from wastewater obtained from the Clarence Town Waste Water treatment works (UK), 50 km away from the plant site. For the production of acetic acid, the biofilm consisted mainly of bacteria from Acetobacterium species (51–60%), Rhodobacteraceae family (15.9–18.7%) and Sulfurospirillum genus (18.9–26.9%). For the production of other evaluated products mixed cultures or pure cultures were used. The biofilm was developed in batches using 2-bromoethanesulfonate to inhibit methanogenic bacterial growth. Key properties of the wastewater source include nutrients composition, chemicals, vitamins and minerals can be found in Appendix A5. Optimal growth temperature was assumed between 25 ± 2 °C. Table 7 presents the reaction balances that take place in the MES reactor alongside their activation

energies. The energy values for acetic and formic acids were taken from experimental data which derived their activation energy to calculate energy balance (Nevin *et al.*, 2011; Marshall *et al.*, 2013). The work of marshal and co-workers was selected for acetic acid because it showed the long term viability of producing the chemical using MES (Marshall *et al.*, 2013). This indicated that MES can be deployed commercially on a large scale. However, formic acid unlike acetic acid is not widely reported as being synthesized by whole cell biocatalysts. This is because formic acid is a main intermediate in the wood-Ljungdahl pathway for the synthesis of other chemicals (Oswald *et al.*, 2018). Therefore, the chemical could be used as substrate by other formate consuming bacteria species attached to the biocathode after generation. However, using enzymatic electro-synthesis which uses CO_2 like MES high formic acid productivity has been achieved (Chiranjeevi *et al.*, 2019). Nevin and co-worker showed direct synthesis of good amounts of formic acid from CO_2 in MES at potentials similar to its theoretical value (-0.430 vs SHE) (Nevin *et al.*, 2011). This work was therefore chosen because good formic acid yield making use of whole cell biocatalysts instead of extracted enzymes was achieved. For propionic acid, methanol and ethanol values, the theoretical electrochemical data was used as at the time of assessment none of these products formation has yet been investigated directly using from CO_2.

Table 7: Reaction balances for CO_2 reduction into acetic, formic and propionic acids, methanol and ethanol MES Plants

Product	**Overall reaction**	**Targeted Flowrate (Moles per batch)**	**Cathode Theoretical potential (V vs. SHE)**	**Cathode Empirical potential (V vs. SHE)**	**MES reactor Potential (V vs SHE)**	**Bio-catalysts**	**References**
Acetic acid	$2CO_2 + 4H_2O \xrightarrow{Biocatalyst} CH_3COOH + 2H_2O + 2O_2$	166528	-0.290	-0.393	-1.210	Mixed culture (Mainly *acetogen*)	(Marshall *et al.*, 2013)
Formic acid	$CO_2 + H_2O \xrightarrow{Biocatalyst} HCOOH + 0.5O_2$	217273	-0.430	-0.400	-1.217	Mixed culture	(Nevin *et al.*, 2011; CEAE, 2014)
Propionic acid	$3CO_2 + 7H_2O \xrightarrow{Biocatalyst} CH_3CH_2COOH + 4H_2O + 3.5O_2$	134993	-0.290	N/A	-1.107	Mixed culture	(CEAE, 2014)
Methanol	$CO_2 + 3H_2O \xrightarrow{Biocatalyst} CH_3OH + H_2O + 1.5O_2$	312110	-0.390	N/A	-1.207	Mixed culture	(CEAE, 2014)
Ethanol	$2CO_2 + 6H_2O \xrightarrow{Biocatalyst} CH_3CH_2OH + 3H_2O + 3O_2$	217070	-0.335	N/A	-1.152	*Sporomus a ovata*	(Blanchet *et al.*, 2015)

A total number of four reactors were assumed to work in batches. The limiting unit operation was considered to be the MES reactor requiring 3.66 days (88 h) per batch with coulombic efficiency for product formation estimated at 69% (Marshall et al., 2013). The conversion rate of CO_2 was set at 58.8% with the remaining gas recycled back to the mixer. The targeted flowrate for all evaluated products considered are shown in Table 7.

Gas Separator (Membrane)

A vacuum pump was used to draw the output gas mixture from the reactor to a gas separating membrane. The gas consisted of mostly CO_2 and O_2 which differed based on product produced (i.e. 44.33 mol% CO_2 and 55.67 mol% O_2 for acetic acid). The CO_2/O_2 selectivity of the membrane was assumed to be 50 with a capture efficiency of 99%. The recycled CO_2 would enter the mixer to supplement CO_2 concentration requirements for the next batch. The

rest of the gas would be supplied by the CO_2 stored onsite. The produced O_2 would be released in the atmosphere.

Filtration System

The liquid effluent from the reactor, which contains the desired product alongside any other by-products, would be pumped through a cartridge filtration system to separate any remaining bacterial cells prior entrance to the rectification unit. Removed bacterial cells would be transported 50 km for incineration, whilst filtrate would be kept in a storage tank prior to it being pumped through the unit. The storage tank is used because thereafter all unit operations becomes continuous instead of batch.

Rectification Unit

Bacteria-free liquid product would be supplied to the rectification unit for purification. Equipment in the rectification unit would vary depending on properties of mixture from the MES reactor. The mixture gets separated by distillation in single or multiple columns to achieve the desired product in high concentrations and water. The separated water is recycled back to the process whilst pure products are stored and packaged onsite. Tight head steel drum containers (208 L) reused monthly would be used for packaging before transportation to the end user.

3.7.5 Functional unit

The basis for building the inventory for all scenarios was 1000 tonnes of products per year and this was the functional unit. Data used in this study contained the inputs and outputs by both the CO_2 capture and product synthesis plants to yield 1000 tonnes of products per year for a ten year plant life. This functional unit was selected to facilitate the environmental analysis of BES technology deployed on an industrial level scale. This also aided the comparison with other technologies for product synthesis already employed on a large scale.

3.7.6 Chosen sustainability indicators and impact categories

The system was analysed as previously stated for two electricity sources natural gas and United Kingdom national grid. For natural gas evaluations three sustainability indicators were selected; net energy consumption (NEC), energy gain (EG) and global warming ratio (GWR). NEC is the summation of the difference between the energy used and energy produced per unit operation expressed in gigajoules per year (GJ/year). EG is the ratio of the energy consumed to generate certain amounts of a product conventionally to the net energy consumption of that same product manufactured through MES. Conventionally, 5.28GJ is

required to produce one tonne of acetic acid through methanol carboxylation(Beaver, 2004), 12.60 GJ for formic acid through hydrolysis of methyl formate (Robledo-Diez, 2012), 19.00 GJ for propionic acid through carboxylation of ethylene (Ekman and Börjesson, 2011), 14.76 GJ for ethanol by fermentation of corn (Gallagher *et al.*, 2015) and 33.00 GJ for methanol through synthesis gas (UNIDO, 2010).

$$Net\ energy\ consumption\ (NEC) = \sum energy\ input\ per\ process\ unit - \sum energy\ output\ per\ process\ unit \quad (3.5)$$

$$Energy\ Gain\ (EG) = \frac{Net\ energy\ consumption\ of\ conventional\ process}{Net\ energy\ consumption\ of\ MES\ process} \quad (3.6)$$

GWR is the ratio of the contribution to global warming when a certain amount of product is generated using conventional methods to that when it is made through MES. In general, GWR measures the contribution of different greenhouse gases to global warming, expressed as equivalent CO_2 emission per unit energy (Tonne CO_2-eq/GJ). For natural gas evaluation only total CO_2 emissions were considered and derived from the calculated energy consumption. CO_2 captured in the MES reaction was subtracted from the overall CO_2 released. The CO_2 released was considered to be derived from the processing of natural gas used to generate electrical energy. According to this, it was considered that 0.05 t of CO_2-equivalent were emitted per GJ of electricity (EIA, 2016). GWR was used alongside EG to compare the efficiency of manufacturing a product using MES to methods widely used industrially.

$$Global\ warming\ ratio\ (GWR) = \frac{Contribution\ to\ global\ warming\ of\ conventional\ process}{Contribution\ to\ global\ warming\ of\ MES\ process} \quad (3.7)$$

The global warming contribution for each unit operation was calculated the equation below;

$$Contribution\ to\ global\ warming\ (GW) = \sum_i GWP_i \times E_i \quad (3.8)$$

Where E_i is the mass of compound i emitted to the air and GWP_i is the global warming potential of the compound i, calculated as the net GHG emissions through the life cycle.

For the UK national grid evaluation the International Reference Life Cycle Data System (ILCD) recommended impact category as implemented in GaBi was applied. GaBi software system is a commercially available life cycle assessment modelling application produced by thinkstep which is fully compliant with both ISO 14010 and 14044 standards. GaBi provides comprehensive life cycle inventory (LCI) and inventory assessment (LCIA) through its comprehensive database. Product life cycles in the software is modelled as plans comprising of process, material and energy flows creating a clear and transparent system (Thinkstep, 2017).

GaBi's ILCD method midpoint impact categories are used for the life impact assessment (See Figure 25). Midpoint impact categories measures all the significant emissions and resources from the life cycle inventory in terms of familiar reference items (e.g., Kg CO_2 Equivalent for global warming, Kg Phosphate Equivalent for eutrophication potential). These impact categories are created through rigorous environmental modelling up to some well-considered point on the cause and effect chain of complex environmental systems (Foley *et al.*, 2010). As the ILCD and background data was done based on the United Kingdom and European setting conclusions drawn in this study was only limited these situations.

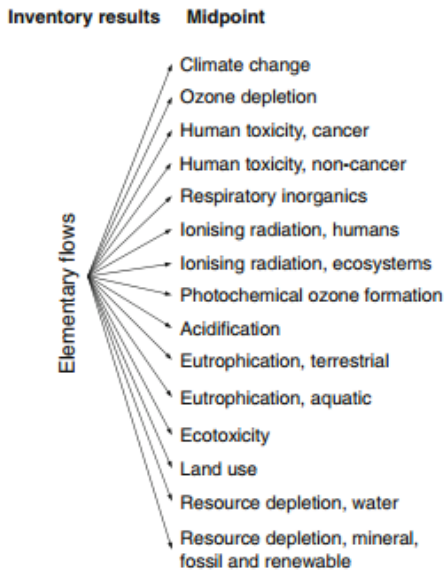


Figure 25: Framework of the ILCD method showing 15 midpoint impact categories (Hauschild *et al.*, 2013)

3.7.7 Data quality

The scenarios are projections of BESs used for MES applied on an industrial scale in the United Kingdom based on models constructed for this study. The data for energy consumption of each process in BESs modelling was calculated based on energy data and technical information available from contractors, open literature and the GaBI software (See Appendix A3). As rectification system differed with product, data for ethanol rectification was obtained from simulations done by Li and Bai (Li and Bai, 2012). For the remaining four product streams, the rectification unit was simulated using Aspen Plus V86 with non-random two-liquid (NRTL) activity and Hayden-O'Connell second viral coefficient models. Energy and material data for systems used to compare BESs technologies were obtained from literature and the database of GaBi.

Chapter 4: Investigation of bio production using mixed culture

4.1 Introduction

Anthropogenic actions and commencement of the industrial revolution has led to a steady rise in the concentration of carbon dioxide (CO_2) in the atmosphere and as at 2018 concentration was measured to be 408ppmv (IPCC, 2014; Bajracharya *et al.*, 2017; ESRL, 2018). This has compelled the need for other sources of energy to power the ever growing demand of today's world alongside discovering carbon reducing techniques (Srikanth *et al.*, 2018). This search has led researchers finding ways to link alternative sources of energy and CO_2 use to produce valuable chemicals or fuels. One of such techniques discovered is microbial electro synthesis (MES) where CO_2 and renewable energy can be utilized to produce industrial significant chemicals. MES involves the capacity of some types of electroactive microorganism to directly or indirectly take electrons from bio-electrodes and metabolically use them to synthesize chemicals and fuels such as acetate (Jourdin *et al.*, 2016) and methane (Cheng *et al.*, 2009a). This has been proven economically beneficial for some chemicals when compared with conventional means of manufacture (Christodoulou and Velasquez-Orta, 2016; Christodoulou *et al.*, 2017).

MES was first coined and demonstrated in 2010 when Nevin and co-workers used *Sporomusa ovata* to produce acetate by utilizing electrons from a graphite cathode electrode (Nevin *et al.*, 2010). Other researchers have shown that alongside pure cultures (Nevin *et al.*, 2011; Zhang *et al.*, 2013; Giddings *et al.*, 2015) mixed culture (Marshall *et al.*, 2013; Su *et al.*, 2013; Batlle-Vilanova *et al.*, 2016) can also be used for MES. Pure cultures such as *Sporomusa ovata* (Tremblay and Zhang, 2015) and *Clostridium Ljungdahlii* (Bajracharya *et al.*, 2015). have been shown to be up to 6 folds more efficient than mixed culture due to lack of competing bacteria strains. However even though lower efficiencies are usually obtained the use of mixed culture has numerous advantages. For one they have been shown to be more robust than pure culture as they have better adaptive qualities (Mateos *et al.*, 2018). Another plus is that different non-sterile substrate can be used showing good promise for practical applications (Mateos *et al.*, 2018). Apart from microbial community other factors affecting MES are electrode potential, culture medium, pH and substrate utilized (Jafary *et al.*, 2015). Interestingly as with the first case of MES, acetate has been the most consistently reported chemical. It is known to follow the reductive acetyl-CoA pathway as CO_2 is converted to acetate by acetogens (Ljungdhal, 1986). Mixed cultures contain these types of bacteria (*Sporomusa ovata* and *Clostridium Ljungdahlii*) and are known to be the main culprit for

acetate being observed in mixed culture biofilms (Liew *et al.*, 2013). Other organic chemicals can in part also be attributed to these acetogens although further pathways from the diverse bacteria types found in mixed culture are also involved (Mateos *et al.*, 2018).

Three electrode two chambers bioelectrochemical systems (BESs) with set potentials more negative of -600 mV vs Ag/AgCl are usually employed for laboratory experiments (Mohanakrishna *et al.*, 2016). This potential is applied as a threshold potential because hydrogen evolution at pH7 only occurs more negative of this value. However the potential can shift due to system overpotentials (Bajracharya *et al.*, 2015). Direct electron transfer could possibly be happening when MES is shown to occur at potentials lower than this threshold potential. This could be seen as more energy efficient but synthesis rates and yield are usually sacrificed (Lovley, 2011). Bio-cathodes in BESs tend to be difficult, unreliable and time consuming to start-up unlike bioanodes (Bajracharya *et al.*, 2015). This has led to bioanodes being started-up first in some cases and then switched to biocathode by changing to negative cathodic potentials (Hartline and Call, 2016; Yun *et al.*, 2017). However this is in the minority of cases as the required biofilm community may be lacking. Addition of electron shuttling hydrogen during start-up consequently can be deployed by researchers as it has been proven to be effective (Blanchet *et al.*, 2015)**.** This shows the important of abiotic generated hydrogen in MES for the propagation of hydrogen consuming acetogens and methanogens on biocathodes.

This study aims at acquiring knowledge on start-up and running of robust mixed culture biocathodes for the synthesis of chemicals or fuel. This was done by evaluating over a long period of time the performance of anaerobic digester inoculum biofilms. The impacts of poise potential and temperature on CO_2 reduction, metabolic pathway and bio production were also assessed. System performance are evaluated based on current efficiencies and production rates.

4.1.1 General Hypothesis

The hypotheses for this chapter is “Two chamber BESs using mixed culture bacteria to produce chemicals from CO_2 in the cathode can be optimized if key parameters affecting its performance are assessed”.

4.1.2 Objectives

The objectives associated with this hypothesis are;

- To develop a stable CO_2 reducing biocathode in BES from a mixed culture inoculum.
- To evaluate the performance of a stable cathodic biofilm in BES to synthesize products over a long period of time.
- To evaluate the effect of cathode potential on CO_2 reduction, metabolic pathway and bio production.

4.2 Experimental Procedure

All anaerobic biocathodes used for microbial electro synthesis discussed in this chapter were grown in poised potential half cells using two types of reactors. Details of setup, operation and medium used can be found in the methodology section (3.2-3.6). As described in the section BESs were operated in batch mode with medium changes at regular 1 to 2 weeks intervals to compensate for depletion of substrate and nutrients over time. Medium in the cells were also topped up to make up for losses due to evaporation or sampling. Batch operating conditions were selected over continuous flow due to its simplicity as the system saves time and resources.

BESs were classified BES-1 to BES-7 based on reactor type. BES-1 and BES-2 were reactor type 1 while BES-3 to BES-7 were reactor type 2 (see Figure 16 for schematic diagram). Each reactor type had cells not inoculated with bacteria which acted as control and in the second start-up an abiotic electrochemical reactor (AER-1). Anaerobic sludge used for initial start-ups were obtained from cockle park farm in Newcastle, England. Anaerobic digester sludge was used as it has been previously used to successfully generate anaerobic bio cathodes at the poised potential selected for start-up (Batlle-Vilanova *et al.*, 2016). The sludge has been proven to contain a wide variety of acidifiers, acetogens and methanogens giving the mixed biofilm a diverse range of microorganisms (Amaral *et al.*, 2002). Secondary inoculated cells

(BES-3 and BES-4) used 50% by volume of the effluent from existing half-cells with functioning anaerobic bio cathode (BES-1 and BES-2). It is worth nothing that secondary inoculated cells did not use new anaerobic sludge in order to reduce uncertainties associated with start-up as it is difficult to obtain the same bacteria composition if new anaerobic digester sludge was used (See Table 8).

In this study as mentioned previously three start-ups of BESs reactors using primary (anaerobic sludge) and secondary inoculum were operated. BES-1 and BES-2 were started up initially using primary inoculum while BES-3 and BES-4 using secondary inoculum. These 5 half cells allowed a comparison of bio production under different operational conditions and reactor configuration (see Table 1 methodology section for operational schemes). Additional primary inoculated BESs (BES-5, BES-6 and BES-7) with an abiotic electrochemical cell (no inoculum) were setup for 70 days in order to compare chemical production in biotic and abiotic electrodes, to investigate CO_2 depletion in reactor headspaces and to determine electrode coulombic efficiency through time. The effect of hydrogen on anaerobic bio cathode growth in BES-1 (day 74 to 84) and BES-2 (day 61 to 71) were also analysed.

Table 8: Experimental matrix of operational parameters and analysis for all BESs in the study. The BESs are labelled BES1-7, with an abiotic reactor (AER-1) and controls (C1-C3). The analyses are chronoamperometry (CA), cyclic voltammetry (CV), coulombic efficiency (CE), gas chromatography (GC) and liquid chromatography (LC)

Half cell	**Operational parameters**			**Analyses**						
	E_{cat} (mV)	**inoculum**	**Operational time (days)**	**CA**	**CV**	**CE**	**GC**			**LC**
							CH_4	**H_2**	**CO_2**	**VFA**
Experimental start-up 1										
BES-1	-797 to -1397	Primary	288	✓	✓	✓	✓	✓		✓
BES-2	-797 to -1397	Primary	276	✓	✓	✓	✓	✓		✓
BES-3	-797 to -1397	Secondary	166	✓	✓	✓	✓	✓		✓
BES-4	-797 to -1397	Secondary	166	✓	✓	✓	✓	✓		✓
C-1	none	primary	288	✓	✓	✓	✓	✓		✓
C-2	none	secondary	166	✓	✓	✓	✓	✓		✓
Experimental Start-up 2										
BES-5	-997	Primary	70	✓	✓	✓	✓	✓	✓	✓
BES-6	-997	Primary	70	✓	✓	✓	✓	✓	✓	✓
BES-7	-997	Primary	70	✓	✓	✓	✓	✓	✓	✓
AER-1	-997	none	70	✓	✓	✓	✓	✓	✓	✓
C-3	none	Primary	70	✓	✓	✓	✓	✓	✓	✓

A summary of all half cells with their operational parameters used in this study is shown in Table 8. The operational parameters shows the different ways in which all BESs, AER and controls were treated and run. As can be seen there is some difference between operational times in experimental start-up 1. The two primary inoculated cells, BES-1 and BES-2 were operated for different time while this also differed from the two secondary inoculated cells (BES-3 and BES-4) as they were operated for a shorter period. This presents issues with biofilm age as mixed cultures attached to electrode surfaces may change with time although the biofilms may reach steady state after certain time period. This may not be ideal way to

design an experiment and was partly the reason experimental start-up 2 was run simultaneously using the same inoculum. This should hopefully mitigate the effects associated with biofilm age and its unforeseen consequences in results obtained in this start-up.

Table 8 also shows the different analyses carried out on all half cells in this study. The methodology section describes in details individual analyses (section 3.3 to 3.4). Cyclic voltammetry were usually done at the beginning and end of each operational period for both biotic and abiotic cells at a scan rate of 1mV/s. Gas and liquid samples were taken at regular intervals using appropriate syringes and analysed using gas chromatography.

4.3 Results and Discussion

4.3.1 Start-up and operation of BES

Biotic experiments had comparable conditions for the same type of reactor, therefore start-up, acclimation and operation are discussed particularly for BES-1 and BES-3 using Figure 26 which shows applied poised potential and current response (See appendix B1 for BES-2 and BES-4).

BES-1 was initially polarized abiotically at -860mV vs Ag/AgCl for two days before bacteria inoculation. This was done to facilitate the accumulation of hydrogen gas in the reactors as it has been shown to improve start-up time due to the gas acting as an additional electron donor after bacteria addition (Blanchet et al., 2015a). Hydrogen evolution from proton reduction in aqueous electrolyte occurs at potential more negative of -600mV vs Ag/AgCl higher than the applied potential. After bacteria inoculation, the cathode electrodes were polarized for 23 days at -860mV vs Ag/AgCl using 2g of bicarbonate and gaseous CO_2 as carbon sources. It was observed that during the initial 23 days of polarization current response never exceeded -500µA. This could be because the selected poised potential was not sufficiently low enough to generate lower current values. After this start-up batch poise potential was subsequently reduced to -997mV vs Ag/AgCl leading to the current progressively reducing to -1000µA over the course of a batch. Potential applied to the cathode electrode was set at -997mV vs Ag/AgCl for 14 consecutive batches to test the long term viability of bio-production using mixed culture. During this time the current response never exceeded -2000µA with the average current usually around -800µA. A rise in current during these batches indicated substrate depletion and a need for medium change in the reactor. The system can be said to have reached steady state after batch 13 as no significant change in current response was observed for 6 consecutive batches. The poise potential after batch 15 was further reduced to -

1197mV vs Ag/AgCl leading to a sharp drop in current to -3000µA. The same effect was also observed in batch 18 when the same poise potential was applied to the system indicating response consistency. The highest poise potential (-797mV vs Ag/AgCl) was applied in batch 17 where the highest current response since inoculation 237 days ago was observed. In the last two batches the potential was reduced to its lowest level -1397mV vs Ag/AgCl with the lowest current response of -6000µA recorded more than 11 folds more than the maximum current (-500µA) observed when poise potential was set at -860mV.

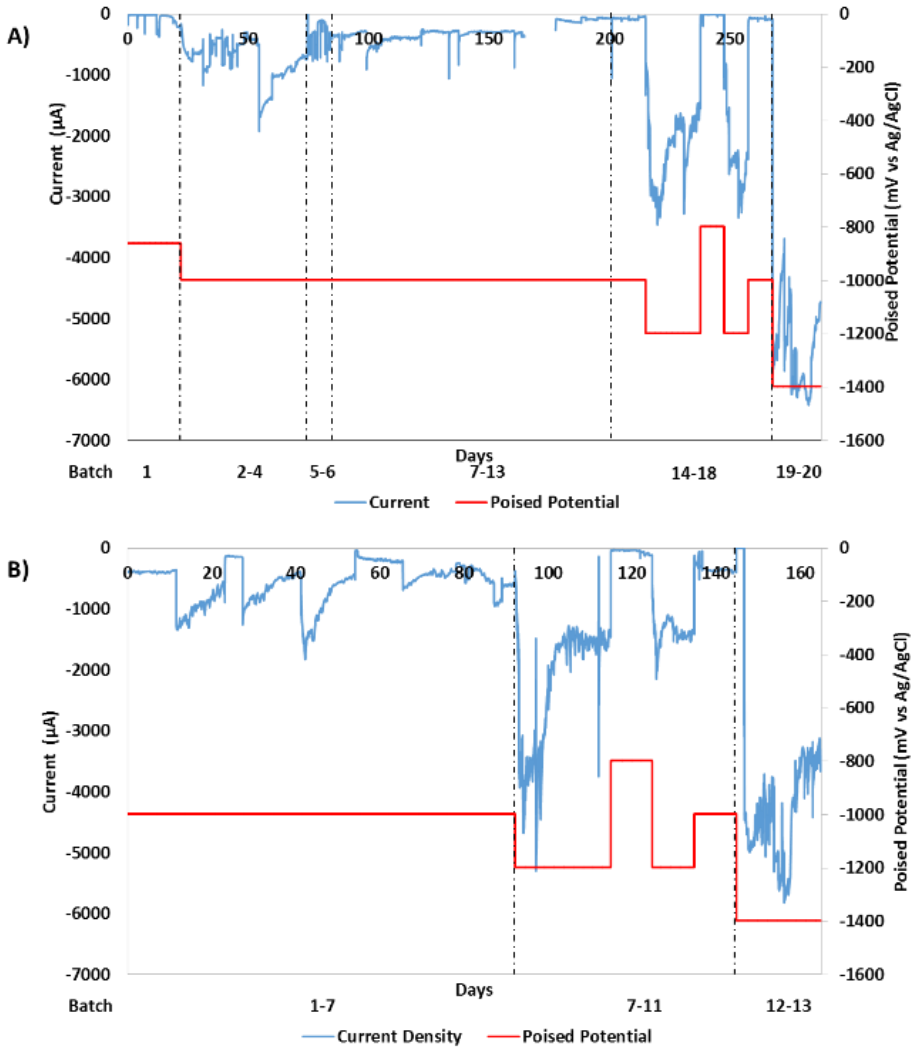


Figure 26: Current Density and Poised Potential for A) BES-1 (290 days) and B) BES-3 (166 days)

Start-up of BES-3 occurred using a poise potential of -997mV vs Ag/AgCl with effluence from BES-1 as bacteria source to recreate the same bacteria community on its bio-cathode. Pure CO_2 was used as the sole carbon source in BES-3 with the sole electron donor coming from the cathode. Figure 26b shows the poise potential applied to BES-3 and current response

over the course of 13 batches. The system after inoculation showed a lag phase of approximately 8 days as the current response remained constantly above -200µA during this conditioning period. BES-3 was operated at -997mV vs Ag/AgCl for 7 consecutive batches with the current response never exceeding -2000µA. This current response was similar to those observed in BES-1 discussed above as well as in BES-2 and BES-4 (see Appendix B1). As with other systems, poised potential was lowered to -1197mv vs Ag/AgCl after long term operation at -997mV vs Ag/AgCl. The current response (-3000µA) followed the same trend as other reactors as current reduction below the previously recorded levels were observed. Increasing poise potential to -797mV vs Ag/AgCl also yielded an increase in current to the highest level seen. The lowest current response observed as with BES-1 was when the potential was reduced to -1397mV vs Ag/AgCl peaking at -6000µA. Overall the observed current response with change in poise potential was found to be consistent with all systems operated. This shows that poise potential affect current response from stable electroactive biofilm and is consistent with what has been observed by the research community(Bosire and Rosenbaum, 2017).

4.3.2 Biosynthesis catalysed by mixed bacteria culture in BES

Figure 27a shows the methane produced in BES-1 and BES-2 during the course of 20 batches. Liquid products for BES-1 are shown in Figure 27b (see appendix B2 for liquid synthesis in BES-2). During the first 23 days of operation at -860mV vs Ag/AgCl no methane was detected in BES-1 but there was noticeable amount of acetic and propionic acid observed during this period. Methane syntheses in BES are usually detected at lower potential and this could explain the non-existence methane concentration. Methane gas with a concentration greater than 20µM was first detected in BES-1 and BES-2 when the potential was reduced to -997mV vs Ag/AgCl. This did not happen immediately however as a lag phase of 25 days was observed. It was observed that acetic acid was undetectable in batches at -997mV vs Ag/AgCl when methane was detected suggesting acetogenic methanogens may have propagated on the cathode electrode (See Figure 27b). Batch 6 saw the introduction of hydrogen as an additional electron donor in BES-1 and BES-2 leading to an increase in methane concentration in both systems. This was consistent with observations of Guo and co-researcher as oversaturation of hydrogen in their reactor led to an increase in synthesis rate (Guo *et al.*, 2018).This gives an indication that methanogenic bacteria could be making use of abiotically produced hydrogen gas alongside acetic acid (Jain *et al.*, 2015). The maximum methane concentration (370 µM) observed was in batch 15 when potential was reduced to -1197mV vs Ag/AgCl even though this was not the highest poise potential applied. At -1397mV vs Ag/AgCl the methane

concentration was around 200µM which is lower than those seen at peak methane concentration. The increased electron delivery did however show in the liquid products measured as at this potential they were noticeably higher than at -1197mV vs Ag/AgCl. Results presented here show that mixed culture biofilm can consistently produce methane through microbial electrosynthesis as the gas after the initial lag phase was consistently higher than the control which never exceeded 5µM. Consistency of results is however an issue with BES systems in general as methane concentration differed between BES-1 and BES-2.

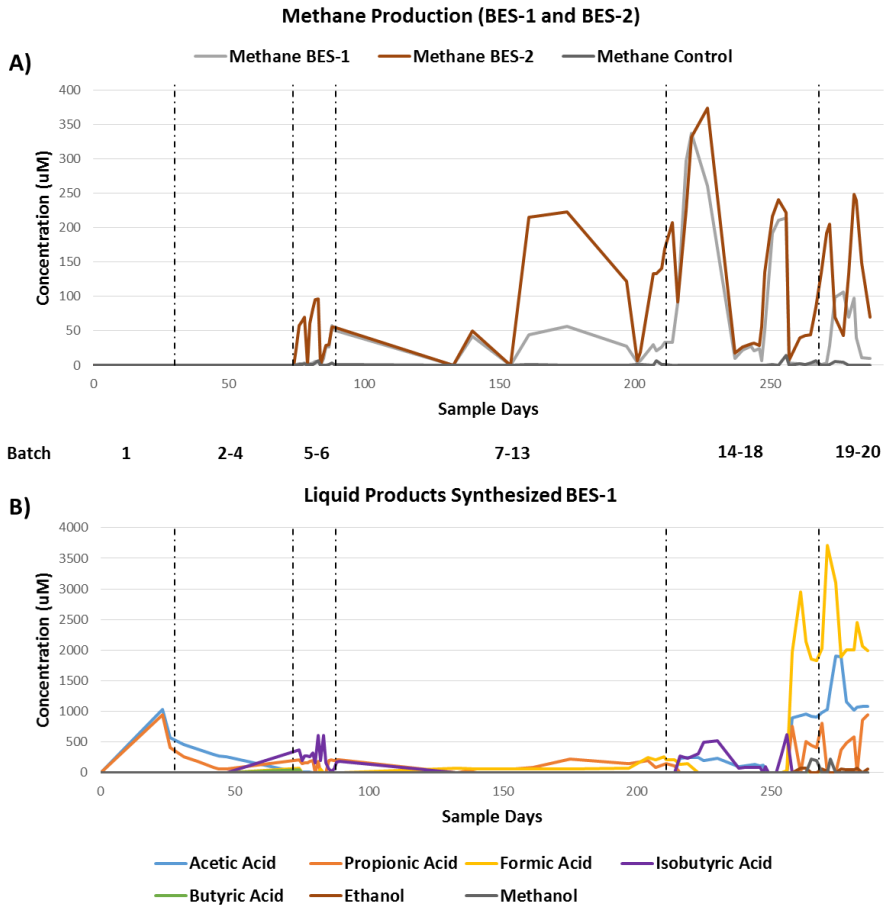


Figure 27: Products from BES-1 and BES-2 A) Gas products B) Liquid products BES-1. Dotted line signifies a change in condition

Figure 27b shows the volatile fatty acid produced over 20 batches in BES-1 (see appendix B2 for BES-2). In the first batch after start-up acetic acid and propionic acid was detected at poised potential of -860mV vs Ag/AgCl. The concentration of these acids increased over time in the batch with it peaking at a combined concentration of 1800µM. No methane as mentioned earlier was detected in this batch as CO_2 reducing acetogens may have prospered on the electrode surface. Isobutyric acid with a concentration above 100µM was first detected

in batch 2. This resulted in acetic acid being only detected in trace amounts. This may be due to acetate consuming bacteria becoming the dominate species in the system. Formic acid could also be used to synthesize isobutyric acid as it was not detected above 20µM when isobutyric acid was present over the course of 20 batches (Vassilev *et al.*, 2018). Results show that bioreactors can be run in a batch mode for a long period of time to produce volatile fatty acid (VFA). However product concentration is likely to change with time if mixed culture biofilm is grown as competition abound. Electroactive pure culture for this type of system should be employed if targeting specific product.

Figure 28a shows methane synthesized by mixed culture biofilm on electrode found in BES-3 and BES-4. Methane concentration observed in all 13 batches for both reactors were more than those seen in the control. Comparing the two reactors, it was observed that for 7 batches methane concentration in BES-4 was more than those seen in BES-3 at -997mV vs Ag/AgCl poise potential. Subsequent reduction in the poise potential (-1197mV vs Ag/AgCl) resulted in an increase in methane production with a maximum concentration of 750µM in BES-3 and 657µM for BES-4. A steep drop in methane was then observed as the poise potential was raised from -1197mV to -797mV vs Ag/AgCl. This follows trend observed in BES-1 and BES-2 (see Figure 27) as low potential caused a drop in methane production.

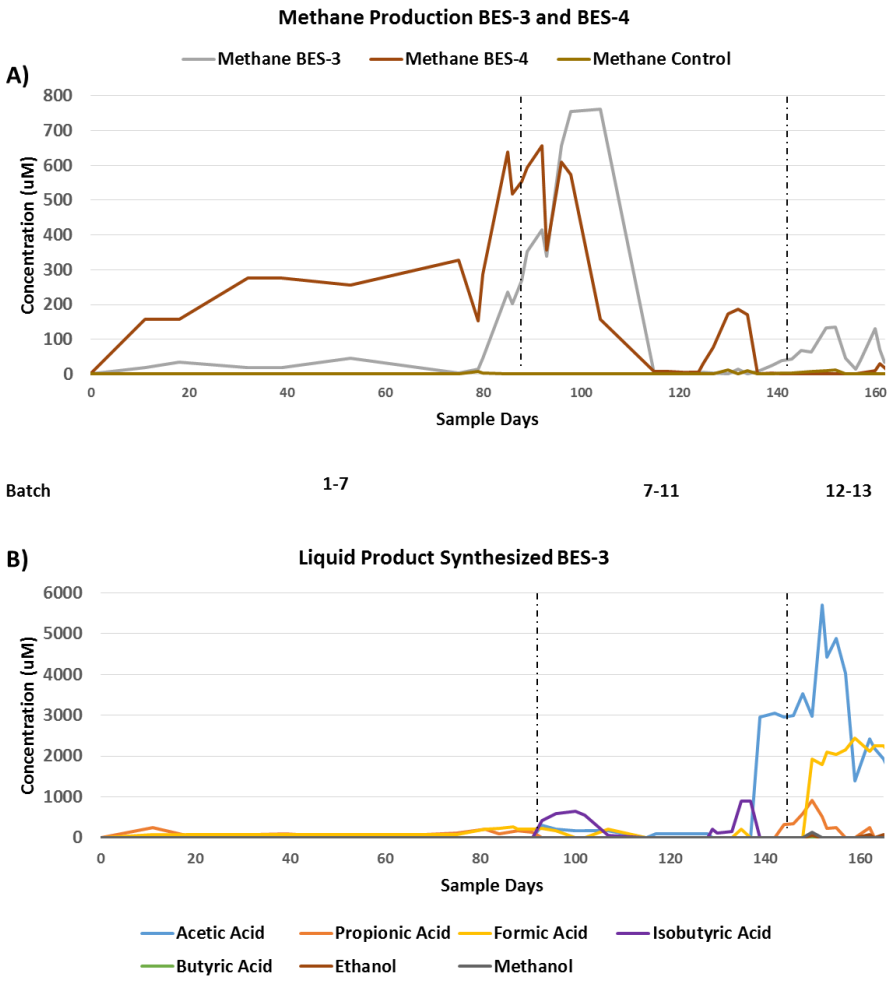


Figure 28: Products from BES-3 and BES-4 A) Gas products B) Liquid products BES-3 Dotted line signifies a change in condition

According to Figure 28b which shows the liquid detected in BES-3 over the course of 13 batches. Liquid observed during this period included both VFA (acetic acid, propionic acid, formic acid and isobutyric acid) and alcohols (ethanol and methanol). Batch 1 to 7 yield only formic and propionic acid as liquid products with a maximum concentration of 100 µM. Acetic acid was not seen as with BES-1 and BES-2. Isobutyric acid was only observed when the poise potential was reduced to -1197mV vs Ag/AgCl in batch 8 and 10. Concentration of acetic acid was again detectable in batch 11 and was for the first time detected with methane production at the lowest potential (-1397mV vs Ag/AgCl) applied. This could be due to enough electron being supplied by the electrode hence no need for methanogens to reduce acetic acid for energy (Thauer *et al.*, 2008). Formic acid was observed from start-up till 115 days when the potential was increased to -797mV vs Ag/AgCl suggesting that at low potentials formic acid was consumed by bacteria.

4.3.3 Hydrogen stimulates methanogenic bacteria growth

Hydrogen gas was introduced in batch 6 for BES-1 and BES-2 as an additional electron donor. This was achieved by sparging the medium and the headspace of the reactor with H_2 instead CO_2. The carbon source in this batch remained 2g of bicarbonate. Figure 29b shows the gas detected (methane and hydrogen) in the reactors during the batch. Figure 29a and c shows that observed in the previous and subsequent batches. As shown in Figure 29a methane detected in BES-2 (maximum concentration 70µM) was more than a hundred times that seen in BES-1. This remained relatively the same in batch 6 where hydrogen was introduced although the maximum concentration of methane observed in all reactor increased (98µM for BES-2). This could be attributed to the external hydrogen introduced into the reactor as trace methane was also detected in the control. Abiotic hydrogen synthesis from aqueous electrolyte occurs at -600mV vs Ag/AgCl so at batch 6 poise potential of -997mV vs Ag/AgCl abiotic hydrogen is expected. The subsequent batch where pure CO_2 was used to maintain anaerobic conditions and act as carbon source it was observed that methane production in BES-1 had increased to around 60µM which was similar to concentrations seen in BES-2. This indicates that hydrogen addition may have facilitated the growth of hydrogen consuming methanogens. Overpotential is known to shift the standard potential of abiotic hydrogen evolution and although the reactor are set-up to be alike different overpotentials due to cell assembly could be present. Further analysis needs to be undertaken to determine the overpotential of the different reactors to aid further understand.

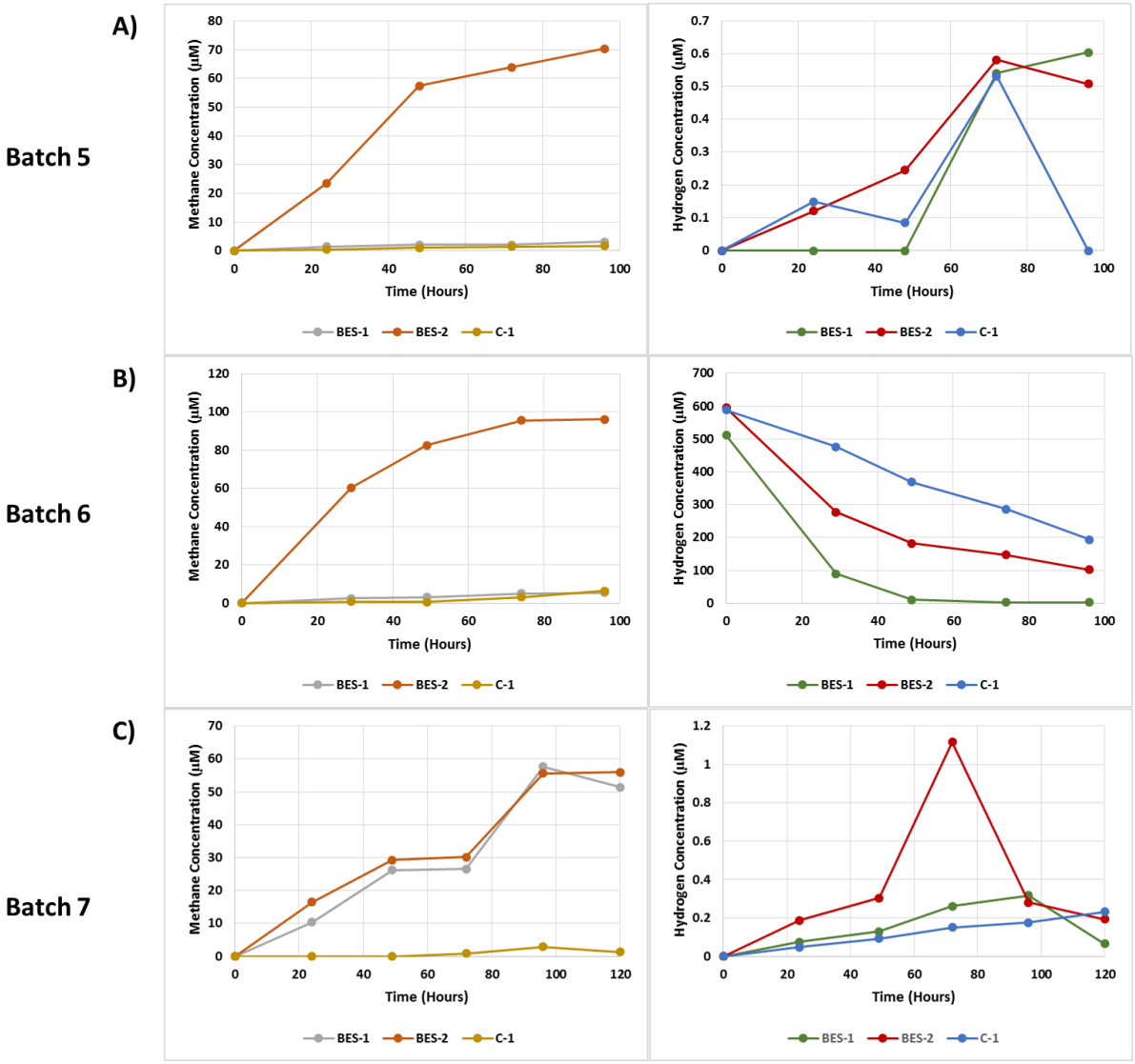


Figure 29: Gas detected in BES-1, BES-2 and C-1 for A) Batch 5 (Day 74-79 for BES-1: Day 61-66 for BES-2) B) Batch 6 (Day 79-84 for BES-1: Day 67-71 for BES-2) and C) Batch 7 (Day 84-88 for BES-1: Day 72-76 for BES-2)

4.3.4 Effect of poise potential on bio-production in BES

The effect of poise potential on products synthesized were analysed by conducting batch experiments under different potentiostatic conditions. The working electrodes of BES-1 to BES-4 were set in the range of -797mV to -1197mV vs Ag/AgCl (Batch 14-16 for BES-1 and BES-2; Batch 7-9 for BES-3 and BES-4). Figure 30 shows results of the test carried out and it was observed that setting the poise potential lower positively affected the product synthesis rate. A set potential of -1197mV (1275µM/day) produced over six times more product in BES-3/BES-4 than at -997mV (183µM/day). This subsequently was more than the products synthesized at -797mV (87µM/day). Another phenomenon noticed was that the type of products synthesized differed as poise potential was adjusted. Propionic acid (52µM/day in BES-1/BES-2; 40µM/day in BES-3/BES-4) was only found in significant quantity when the

poise potential was set at -997mV showing similar rates to formic acid (59 µM/day in BES-1/BES-2; 49µM/day in BES-3/BES-4) at the same potential. Isobutyric acid and hydrogen were also products not seen at all poise potentials. Isobutyric acid was only synthesized at -1197mV (237 µM/day in BES-1/BES-2; 555µM/day in BES-3/BES-4) and -797mV (34 µM/day in BES-1/BES-2; 30µM/day in BES-3/BES-4) accounting for the highest percentage in the former. Hydrogen on the other hand was only measured at higher potentials (-997mV and -1197mV). This indicates that abiotic hydrogen production is tied to poise potential. Higher product synthesis at these potentials (-997mV and -1197mV) suggests that only a fraction are produced through extracellular electron transfer. Metabolic pathways of some products especially methane and acetic acid can use abiotic hydrogen from water reduction. Therefore the contribution of these routes to overall products synthesized is strongly dependent on the poise potential set on the working electrode.

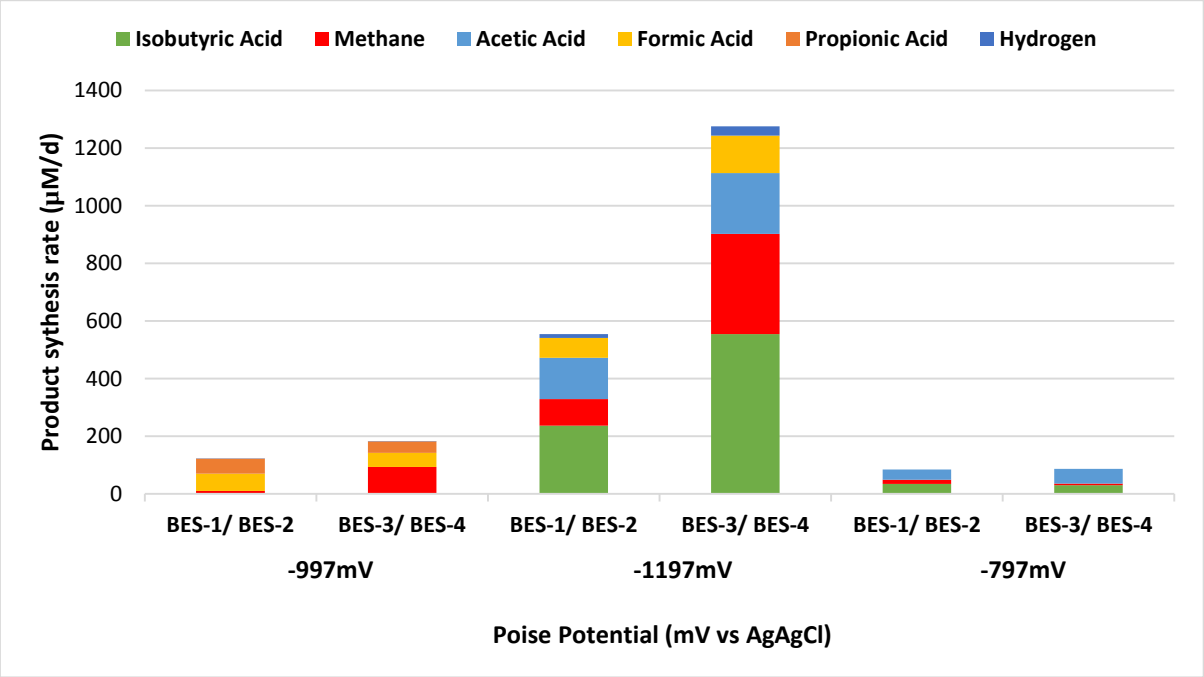


Figure 30: Effect of poise potential on product synthesis rate in BES. Values shown are means of similar BES reactors (BES-1/BES-2 and BES-3/BES-4).

These results suggest that poise potential has an effect on the rate of production as well as the type of products synthesized. Villano and co-researchers conducted similar test using methanogenic cultures for a range of potential between -850mV to -1100mV vs Ag/AgCl (Villano *et al.*, 2010). Results presented in this paper shows similar trend to ones obtained here as negligible hydrogen was found at potential higher than -900mV.

4.3.5 Effect of temperature on bio-production in BES

The effect of temperature change on products synthesized at a controlled potential of -1397mV vs Ag/AgCl in BES is shown in Figure 31. Temperature test measurements were done in the last two batches of BES-1 to BES-4 operation (Batch 19-20 for BES-1 and BES-2; Batch 12-13 for BES-3 and BES-4). It was observed that as the temperature increased from room temperature (27^{o}C) to 40 ^{o}C the total synthesis rate of detectable products increased form 1971 µM/day to 3589 µM/day for BES-1/BES-2 and 2479µM/day to 3677µM/day for BES-3/ BES-4. Formic acid was seen to have the highest rate of production with a maximum rate of 2436µM/day observed at 40^{o}C in BES-3/BES-4. This was more than two times what was seen at room temperature (1122µM/day). The same trend can be seen in other products as all except for propionic acid (226 µM/day at room temperature; 30 µM/day at 40^{o}C) and methane (32 µM/day at room temperature; 23 µM/day at 40^{o}C) in BES-3/BES-4 saw a decline with increased temperature.

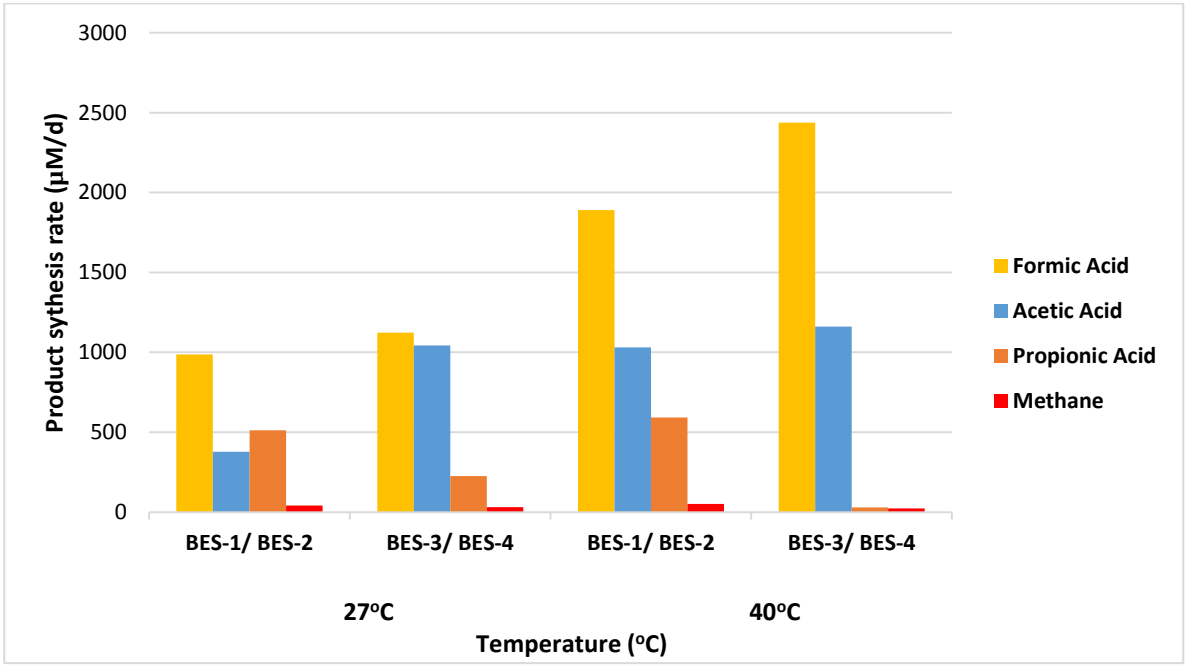


Figure 31: Effect of temperature on product synthesis rate in BES (cathode potential -1397mV vs Ag/AgCl). Values shown are means of similar BES reactors (BES-1/BES-2 and BES-3/BES-4).

These results suggest that temperature has an effect on rate of product synthesis in BESs with a mixed culture biofilm. Fu and co-workers demonstrated that thermophiles can be used as biocatalyst in BESs as an operating temperature of around 50^{o}C was used to produce high methane synthesis rate (Fu *et al.*, 2015). These findings was further collaborated by Yang and co-researchers as a temperature increase up to 50^{o}C showed a positive effect on synthesis rate from a mixed culture biofilm (Yang *et al.*, 2018). Temperature increase up to this value(50^{o}C)

was suggested to be preferable because it enhances microbial activity, reduces oxygen solubility and increases proton transfer rate in BES electrolyte (Yang *et al.*, 2018). Results presented here alongside literature suggest that temperature is a limiting factor in BES performance. This is significant especially if the technology is to be scaled up as maintaining thermophilic conditions would add more energy burden on an already energy intensive process. A balance between high production rate and energy efficiency taking into account temperature needs to be maintained if the system is to be implemented on an industrial scale.

4.3.6 Comparative overview of reactor performances

Operation of BES with mixed culture resulted in the synthesis of methane and organic compounds from CO_2 reduction in the different type of reactor named A (BES-1 and BES-2) and B (BES-3 and BES-4) for convenience. As both reactors can be said have been out of the lag phase and in steady state after batch 13 in reactor type A and batch 7 in reactor type B. A comparative overview of their performance can be carried out as the same conditions were applied to all reactor types. For the comparative analysis data obtained from batch 14 to 16 in reactor type A and batch 7 to 9 were used (see Figure 26 for current values).

Table 8 shows the average production rate for the two different types of reactor at the selected batches and poise potentials (-797mV, -997mV and -1197mV vs Ag/AgCl). It can be seen that the detectable products in the two reactors increased with lower poise potential. Reactor type B synthesized more products at lower poise potential (-997mV and -1197mv Ag/AgCl) than reactor type A. This could be due to solution chamber size especially in the case of liquid products. The solution chamber for reactor type A is 215mL while that of type B is less than 100mL. Therefore the electrode size in relation to catholyte presence favours higher concentration in reactor type B. Current response observed for the poise potential selected were also usually noticeably lower in reactor type A than B (see Figure 26). This could be attributed to the electrode size as the former had a larger surface area (64cm^2) than the later (50 cm^2). A larger surface area may result in more electroactive bacteria attaching to the surface of the electrode especially after steady state has been achieved. This results show that reactor configuration may affect current response as well as bio production in bio-electrochemical systems. Therefore care has to be taken in selecting reactor parameters such as electrode type, size and solution chamber.

Table 9: Average production rate at different potential for reactor type A and B

Batch	Potential (mV vs Ag/AgCl)	Reactor Type	Average rate of production (µM/day)					
			Methane	Formic acid	Acetic acid	Propionic acid	Isobutyric acid	Total detected product
16	0	A	0.000	0.000	10.387	0.000	0.000	10.387
16	-797	A	2.675	0.000	9.862	0.000	6.054	18.592
14	-997	A	8.580	14.975	0.000	7.630	0.000	31.206
15	-1197	A	26.445	0.000	13.460	0.000	25.603	65.592
9	0	B	0.365	0.000	10.011	0.000	0.000	10.376
9	-797	B	0.465	0.000	9.197	0.000	0.000	9.662
7	-997	B	38.318	14.922	0.000	6.988	0.000	60.240
8	-1197	B	38.214	12.302	50.026	0.000	7.522	148.938

4.3.7 Variations in cyclic voltammetry

Cyclic voltammetry (CV) is an electrochemical technique that can be used to identify electron mediators involved in microbial electrosynthesis. It can also reveal the way electrons are transferred from cathode to biofilm. CV was recorded intermediately during BESs operation at a scan rate of 1mV/s. This was done to obtain crucial information about the redox active component associated with the biofilm propagating on the BESs cathode. Figure 32A,B,C and D shows some key voltammogram recorded during the experimental period for BES-1 and BES-3. It was observed that in the control current response was lower than poised rectors with no redox peak present (Figure 32A). This may indicate that no electron shuttle was present in its medium at the time of the reading (batch 6).

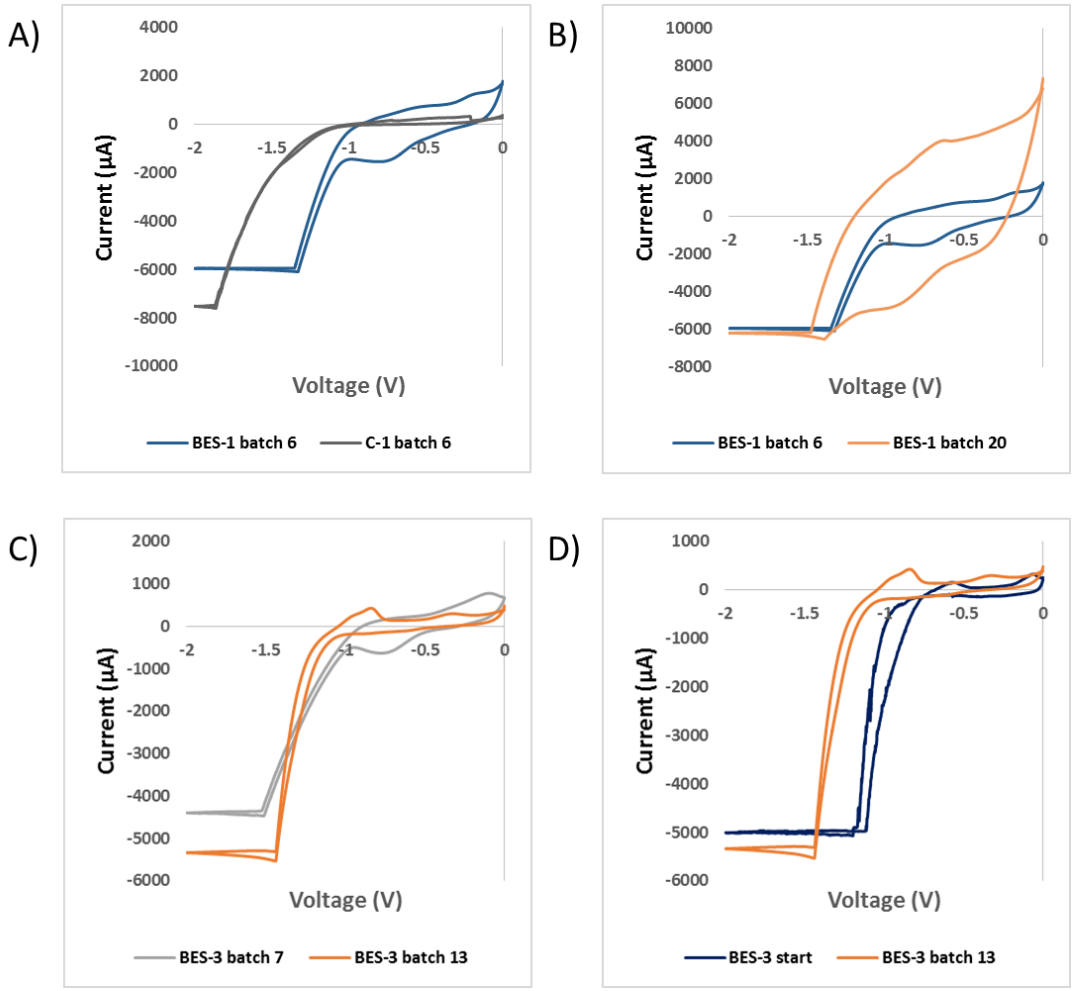


Figure 32: Cyclic voltammetries of A) BES-1 and C-1 during batch 6 B) BES-1 during batch 6 and 20 C) BES-3 during batch 7 and batch 13 and D) BES-3 at start-up and end (batch 13)

CV was performed intermediately on the BESs and it showed that for the different batches high current flow were detected. This indicated that synthesis of products from BES-1 and BES-3 at the different batches showed evidence of hydrogen gas as mediator. This was similar with other duplicate systems. According to Figure 32B there is a difference between the electrochemical behaviour of BES-1 in earlier (batch 6) and later batches (batch 20) as increased current response was detected. This however was not the case for batch 1, 7 and batch 13 in BES-3 (Figure 32C and D) as not much change in CV electrochemical performance was detected. This could be because of the use of secondary inoculum which may have already had the required bacteria community for anaerobic synthesis of products. Hydrogen production however increased in BES-3 between batch 7 and batch 13 (Figure 32C) as reduction current became more prominent. This could explain the increase rate of chemical production between the batches. In BES-1 as this phenomenon was also observed, specific bacteria species contributing to higher hydrogen production or other mediators such as

formate may be the reason. This requires further information to be confirmed, community analysis to identify specific bacteria species could be ideal. Figure 32D alongside other voltammograms showed that the abiotic hydrogen production can change due to pH change as medium becomes more acidic.

CV for the poised cells during the different batches usually indicated two distinct peaks. It is highly likely that this peaks are due to flavin and phenazines biological mediators. The midpoint potential of Flavin and phenazines are -415mV vs Ag/AgCl and -755mV vs Ag/AgCl respectively (Marsili *et al.*, 2008; del Pilar Anzola Rojas *et al.*, 2018). This could shift however due to pH and operational condition change which occurred severally during the course of experimental batches. Taking BES-3 batch 7 (Figure 32C and D) as an examples due to these peaks being more prominent, the midpoint potential can visually be said to be around -350mV vs Ag/AgCl. CO_2 synthesis to acetate, methane and ethanol all have theoretical potentials (-490mV, -450mV and 530mV vs Ag/AgCl) lower that this indicating that direct electron transfer is unlikely instead synthesis of these products is from hydrogen as a mediator. The volamograms shown are similar to those observered by researchers who also used mixed culture biofilm to synthesise products (Marshall *et al.*, 2013; Ganigué *et al.*, 2015; del Pilar Anzola Rojas *et al.*, 2018).

4.3.8 BESs Efficiency

Coulombic efficiency was used to evaluate the performance and efficiency of the bio-cathodes. Coulombic efficiency gives the percentage of current represented in product synthesized. During MES the electrons supplied can be used by the biofilm as hydrogen or directly from the cathode. Although data presented here does not confirm direct electron transfer, hydrogen gas was detected throughout the experiment signalling a more indirect route. Hydrogen gas acts as an electron carrier and aids the biofilm in the conversion of CO_2 to multi carbon chemicals.

Table 10 shows the maximum coulombic efficiency obtained from the different poised potential used. As expected the coulombic efficiency differs as poised potential was adjusted. Similar trends are seen in the different types of reactors used.

Table 10: Maximum Coulombic efficiency for bioproduction from mixed culture biofilm

S/N	Polarization Potentials (mV vs Ag/AgCl)	BES-1/BES-2 Maximum Coulombic Efficiency (%)	BES-3/BES-4 Maximum Coulombic Efficiency (%)
1	-797	99.00	31.13
3	-997	96.45	99.00
4	-1197	43.79	32.01
5	-1397	11.05	6.93

It was observed that at higher poise potential the coulombic efficiency tends to be high. This could be due to the fact that at high potential limited electrons supplied are not lost in unreacted abiotic hydrogen as lower potential would tend to produce more abiotic hydrogen. This may lead to pressure build up in the reactor headspace creating an avenue for the unreacted gas to escape. Even though this may be the case lower potentials tended to generated more multi carbon products. The difference in the coulombic efficiency between the poise potential could be also due to the constantly fluctuation of the types of products synthesized as well as their concentrations.

4.3.9 Gaseous carbon dioxide depletion and abiotic electrochemical test

Biocathode was started-up by inoculating anaerobic sludge to enrich mixed culture in BES-5, BES-6 and BES-7 which was maintained anaerobic by sparging with pure CO_2 gas and applying a cathode potential of -997mV vs Ag/AgCl. Abiotic cell was setup using the same setup and technique except the addition of mixed culture to the system. The cathode potential was maintained through a potentiostat using chronoamperometry with temperature adjusted to 30^{o}C using a water bath. Catholyte in this experiment was continuous stirred using magnetic stirrers.

Repetitive batch operation of CO_2 reduction in BES-5, BES-6, BES-7 and AER-1 was carried out for 60 days with each batch lasting between 10-14days. Figure 33 shows the current response for a batch after 60 days of running the system. The batch shown lasted for 11 days with the current response recorded by the potentiostat. It was observed that the current response in the biotic cell were much lower than those observed in the abiotic reactor. Current response for the three biotic cells were similar as they always exceeded -1000µA. The current

in the abiotic reactor never exceeded -6µA amount. This is indicative that electroactive bacteria propagated on the electrodes of the biotic reactors as current response is not associated with abiotic electrochemical reduction reaction.

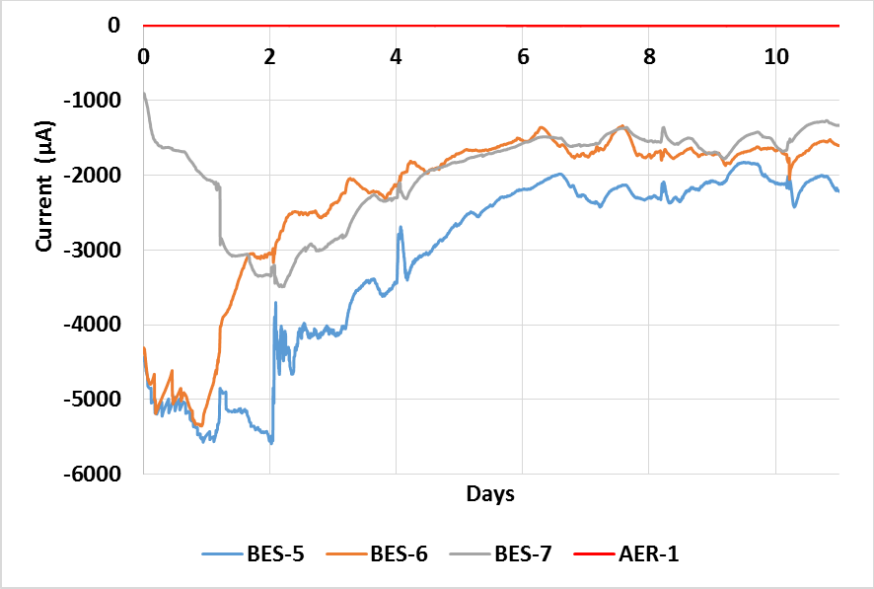


Figure 33: Current response in BES-5, BES-6, BES-7 and AER-1 at -997mV in a batch after 60 days

Figure 34 shows the gaseous product measured from the reactors after 60 days. It was observed that carbon dioxide depletion occurred faster in the biotic electrochemical reactors when compared to the abiotic and control reactors. This indicates that CO_2 diffusion into the aqueous medium occurred more readily as dissolved carbon in bicarbonate form is consumed in the bioelectrochemical reaction. Methane concentration in the biotic cells progressively increased on average to 155µM, this was more than a hundred times more than the abiotic and control. Results here show that gaseous carbon dioxide can be used to produce chemicals through microbial electro synthesis.

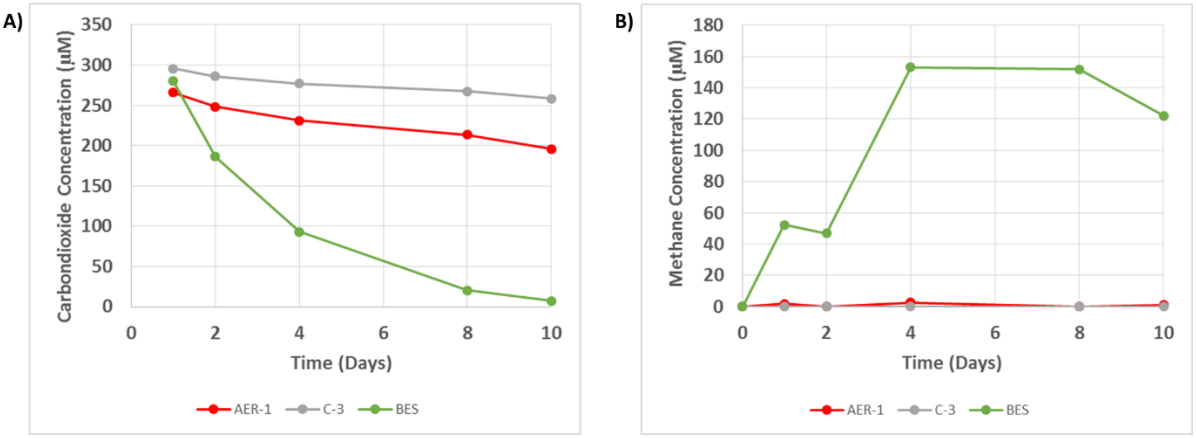


Figure 34: Gas observed in the reactor A) Carbon dioxide B) Methane

Additional analytical methods were used to evaluate the biofilm development on the cathode electrode. Cyclic Voltametric scans was performed before bacteria inoculation and 71 days after running the reactor at -997mV vs Ag/ AgCl. CV was measured at a slow scan rate of 1 mV/s so as to prevent damage to the bacteria cells attached to the electrode. As with previously seen voltammograms (see Figure 32) Figure 35a shows a clear change in slope for all the BES indicating the start of abiotic hydrogen evolution. Evolution occurred at a potential more negative of -900mV vs Ag/AgCl. This shows that the potential applied (-997mV vs Ag/AgCl) used in this test is sufficient for abiotic hydrogen evolution which could then act as an intermediary for other products synthesis. Figure 35a also shows an increase in current response of BES-5 than at the start of experiment. This is indicative of electroactive bacteria propagating on the electrode surface. Figure 35b show CV measured for BES-5, AER and control without application of poise potential (C-3) 71 days after start-up. Electroactivity can clearly be seen to be more in BES-5 than AER-1 and C-3 as current response was found to be higher.

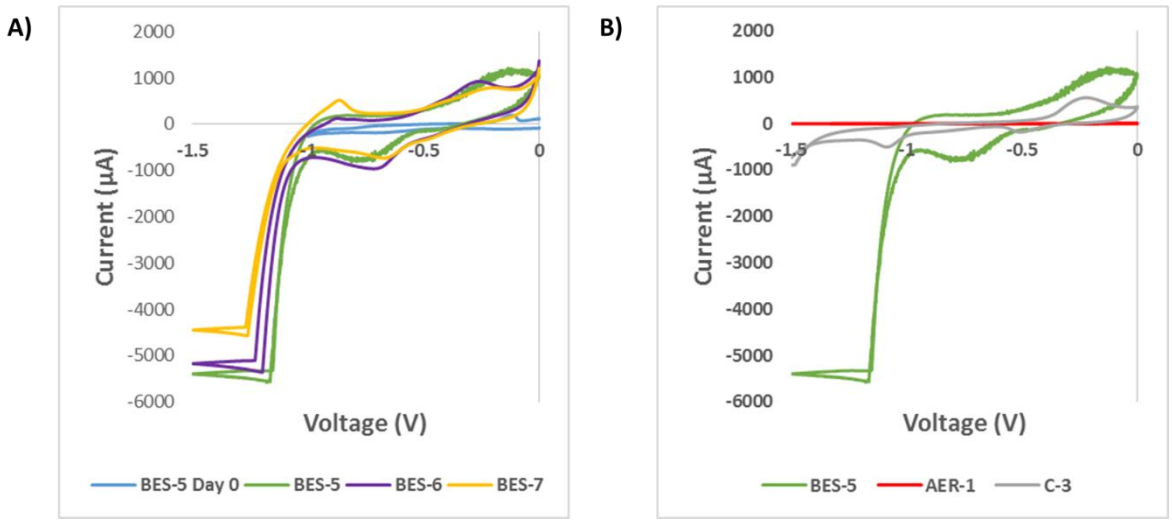


Figure 35: Cyclic voltammetry A) BES at day 0 for BES-5 and at 71 day for BES-5, BES-6 and BES-7 B) BES-5, AER-1 and C-3 at day 71

4.3.10 Hypothesized pathway of bioproduction

A hypothesized pathway is presented in Figure 36 to establish possible products synthesis pathways. The experiments conducted showed that mixed culture biofilm was able to produce various compounds using CO_2 as substrate. Various poise potential and temperature was used during the course of experimental batches which yielded different types of chemicals. Looking at the pathway it can be seen that the key intermediate in the synthesis of chemicals

is Acetyl-CoA. Considering products the wood-Ljundahl pathway is used to manufacture acetate using acetogenic bacteria (Rabaey *et al.*, 2011; Kracke *et al.*, 2018). Experimental observations suggests that acetate is a precursor to methane synthesis in a mixed culture biofilm agreeing with behaviours of some methanogens (Yang *et al.*, 2016a). Methane production caused negligible acetic acid concentration and was observed together only at high potentials (-1397mV vs Ag/AgCl). The chemical 2-bromoethanesulfonate could be used to inhibit methane production if needed. Vassilev and co-worker suggests that acetogens can change from acetogenesis to solventogenesis for the production of ethanol at high accumulation of undissociated acetic acid (Vassilev *et al.*, 2018). This reduces pH to levels that inhibit cellular metabolic activity forcing the bacteria to adjust. Experiments here tend to agree with this as trace ethanol were only observed in batches at high poise potential where this accumulation of acetic acid can occur.

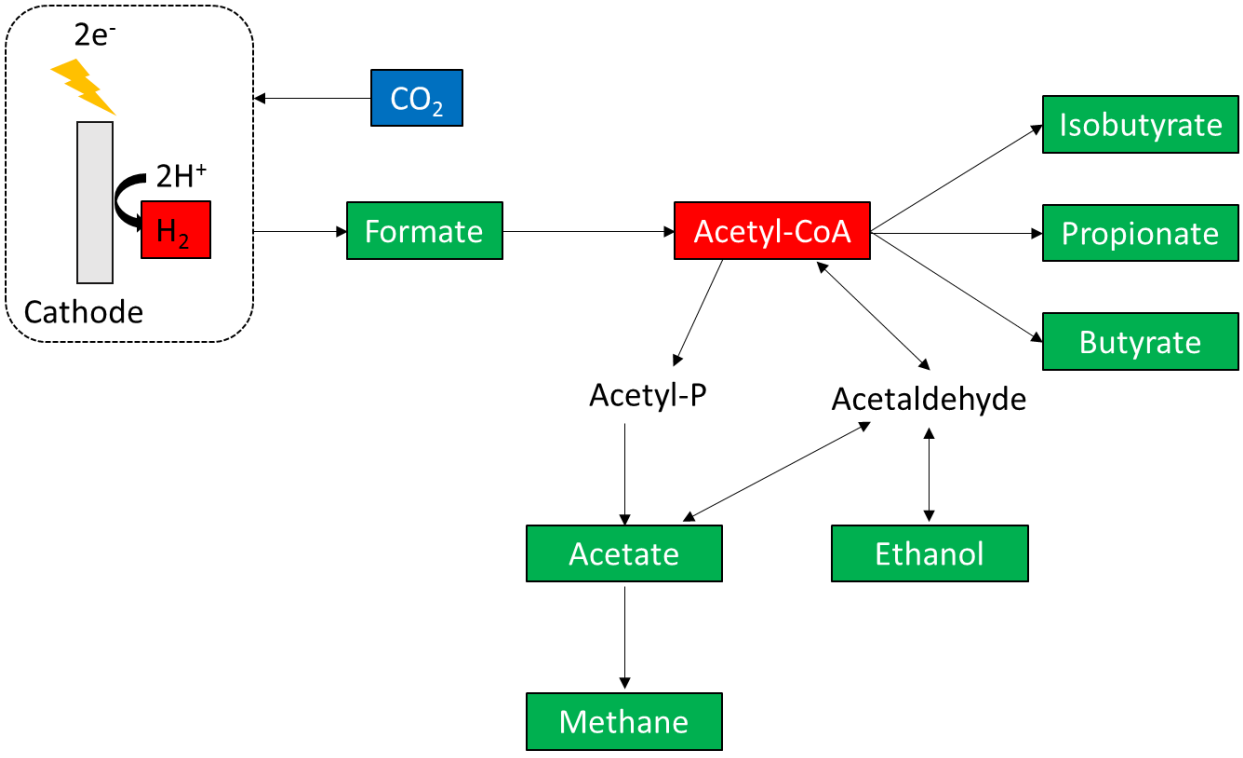


Figure 36: Hypothesized pathway of bioproduction using mixed culture biofilm

Although acetate and ethanol can be used as precursors to isobutyrate and butyrate production. A direct alternative is possible from CO_2 using the key intermediate acetyl-CoA. Batle-Vilanova and co-researchers suggested that high reducing potentials applied to BES may favour the more direct route (Batlle-Vilanova *et al.*, 2017). Results presented here shows that isobutyric and butyric acid was only observed at potential greater than -1197mV vs

Ag/AgCl with the exception of batch 6 when hydrogen was introduced externally to BES-1 and BES-2. As abiotic hydrogen is considered the mediator in chemical formation here adding more hydrogen should bring this outcome. A review by Gonzalez-Garcia on microbial propionic acid production stated that propionic acid can be manufactured using acetyl-CoA explaining the presence of the acid in our system (Gonzalez-Garcia *et al.*, 2017).

4.3.11 Conclusion

CO_2 reduction in BESs by mixed culture biofilms was repetitively proven using electrochemical techniques. CO_2 introduced into BESs produced methane, formic, acetic and propionic acids more readily however under some conditions isobutyric acid and ethanol were synthesized. Hydrogen was seen to function as an energy source for the generation of these products in the cathode chamber. This study confirms that BESs can consistently use CO_2 to synthesize high economic significance products than the usually detected acetic acid. Although these results are promising synthesis rates are still low and can hamper industrial adoption. Reducing poise potential was found to increase production rate however energy efficiency was sacrificed as low coulombic efficiencies was observed. Additional research needs to be undertaken to fulfil the potential of microbial electrosynthesis for carbon utilization and bring the technology closer to industrial implementation.

Chapter 5: Energy and global warming assessment of using carbon dioxide in microbial electrosynthesis

5.1 Introduction

Bioelectrochemistry involves the transfer of electrons between a solid electrode and immobilised bacteria. Immobilisation helps reduce the distance between the bacteria and the electrode in order to preserve activity (Gooding and Gonçales, 2017). Interest in this science has increased exponentially over the years as researchers become aware of its huge potential. Bioelectrochemical systems (BES) a technology that was originally developed for the conversion of waste water to energy is used for the process. The technology is manufactured with an anode and cathode electrode usually separated by a proton exchange membrane (Logan *et al.*, 2006). Oxidation and reduction occurs at the anode and cathode respectively. These redox reactions are driven by biocatalysts interacting with electrodes connected via an electrical circuit.

BESs has numerous application and depending on its application can be classified as microbial fuel cells (MFCs), microbial electrolysis cells (MECs), enzymatic fuel cells (EFCs), microbial solar cells (MSCs) or microbial desalination cells (MDCs). Focusing on microbial electrolysis cell which requires external energy to be supplied to the electrodes for the desired bioelectrochemical reaction to produce hydrogen to occur (Rabaey *et al.*, 2010). The electron transferred from the electrode to the microbes could be direct or indirect(Rabaey *et al.*, 2010). Microbial electrosynthesis works similar to MEC in its operation and has attracted recently a lot of research attention. MES can be used to produce methane, acetate, formic acid and other higher biofuels. Synthesis can be done using both bacteria and enzymes as biocatalyst. As MES uses carbon it can contribute to the CO_2 reduction target set for 2050.

Researchers have been able to improve productivity and resilience of biocatalysts used for MES. However after almost a decade commercial application of the technology has not be proven. This in a few years could be on the horizon as chemical yields have increased. Therefore it is necessary for an energy and global warming assessment be undertaken as the technology continues to mature. This chapter aims to evaluate the energy requirements and global warming potential of microbial electrosynthesis scaled up beyond the laboratory for the synthesis of chemicals.

5.1.1 General Hypothesis

The hypotheses for this chapter is that “Microbial electrosynthesis scaled up beyond the laboratory for the synthesis of chemicals would have less global warming potential than conventional means of production using natural gas as energy source”.

5.1.2 Objectives

The objectives associated with this hypothesis are;

- To evaluate the energy requirement of scaling up the MES process.
- To assess the global warming potential of producing chemicals using MES.
- To compare the global warming potential of using MES with conventional routes.

5.1.3 System boundary and Scope of Study

Process description, assumptions and associated plant unit operations are fully described in the methodology section (section 3.7). Figure 37 shows the system boundaries for microbial electro synthesis plants producing 1000 tonnes per year of acetic, formic and propionic acids, methanol and ethanol in terms of background and foreground systems (Clift *et al.*, 2000). Process data used for the foreground inventory were obtained from scientific literature (Marshall *et al.*, 2013) while electricity in the background system was considered to be from the processing of natural gas releasing 0.05t of CO_2 equivalent per GJ of electricity generated (EIA, 2016). Emissions from transportation and processing of raw materials were considered to be only total CO_2 emissions. Data for the whole process were processed by means of energy and mass balances using three sustainability indicators for a ten year timeframe. These indicators were net energy consumption (NEC), energy gain (EG) and global warming ratio (GWR) defined in the methodology section (Section 3.7).

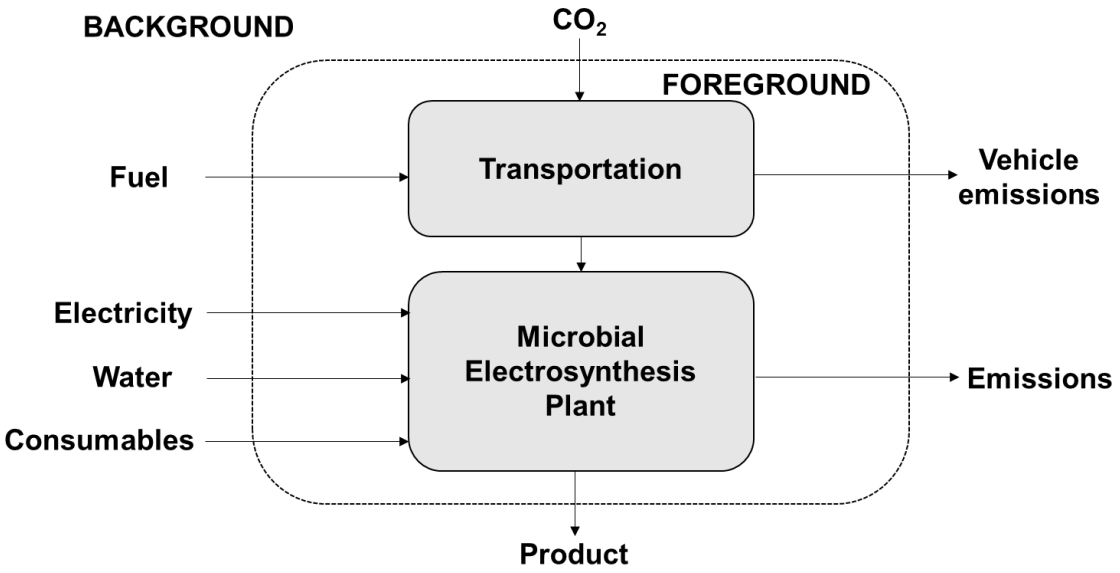


Figure 37: System boundaries for the microbial electrosynthesis production system under analysis

5.2 Results and Discussion

Table 11 shows a summary of the inputs (raw material) and outputs of the MES plants assuming that 1000 tonnes of products per year (t/yr) are synthesized. The values summarized in the table are grouped as raw materials, products and by products from the process. This study assumes that unreacted CO_2 and water are perfectly recycled back into the process.

Table 11: Raw materials and by-products of MES Plants producing 1000 tonnes per year of formic, acetic and propionic acids, methanol and ethanol.

	Unit	Acetic acid	Formic acid	Propionic acid	Methanol	Ethanol
Raw Material						
CO_2	t/yr	1677	1094	2039	1572	2186
Water	t/yr	740	435	930	1320	1448
Chemicals	t/yr	5.57	1.78	7.76	7.69	10.6
Outputs						
Oxygen	t/yr	1065	347	1512	1498	2083

It can be seen from Table 11 that the values for plants inputs and outputs varied with product. The CO_2 utilized by MES plants producing acetic, propionic, formic acids, ethanol and methanol ranged between 1092 and 2186 tonnes per year. The variances is mainly due to the differences in the reaction coefficients and molar mass of the specific products. MES plants producing ethanol used the most CO_2 and water while formic acid used the least. These values alongside energy consumption could help identify environmentally beneficial products. In terms of oxygen which could alternatively be seen as a by-product, ethanol (2083 t/yr) emitted the most around 20 percent more than propionic acid (1512 t/yr) and methanol (1498 t/yr). This is significant as it has an effect on the energy duty of the gas separator unit operation as recycled CO_2 has to be separated from the gas. The wide range of input and output values highlights the significance of conducting the environmental analysis as benefits will also vary. Focusing solely on results displayed in Table 11, ethanol should have the lowest global warming potential. However this may not be the case as other factors such as plant energy requirement may affect its value.

5.2.1 Energy consumption and global warming

Within the several factors that can decrease the sustainability of producing chemicals from bioprocesses, it has been shown that the most important ones are: production rates and energy use (Christodoulou and Velasquez-Orta, 2016). Figure 38 shows the energy and global warming values for different products derived from MES (Appendix C1 for energy and global warming value for each unit operation; Appendix C2 for formic acid sample calculations). Using a ten year timeframe, acetic acid production was observed to require the highest amount of energy (1,655,387 GJ) of all the products assessed (Figure 38). In contrast, formic acid production required the lowest energy; eleven times (150,214 GJ) lower than acetic acid production. These findings were partially based on energy balances and the amount of electrons needed for synthesizing the desired product. The electrochemical reaction for acetic acid production uses four times (8 e^-) more electrons than formic acid (2 e^-) and thus results to a higher energy demand. Thermodynamically, producing acetic acid (874.82 kJ/mol) would require higher energy than formic acid (269 kJ/mol). Another major factor affecting the energy consumption is the amount of water molecules produced, which tend to dilute the desired chemicals leading to energy intensive separation processes. Global warming contributions are highly linked to energy requirements when fossil fuels are used for energy generation. Formic acid (-3,421 tonnes CO_2 eqv) was shown to consume more greenhouse gas (CO_2) mass during production than the mass released to the atmosphere, resulting in a

negative global warming potential. Acetic, propionic acid, ethanol and methanol however released more CO_2 than it used.

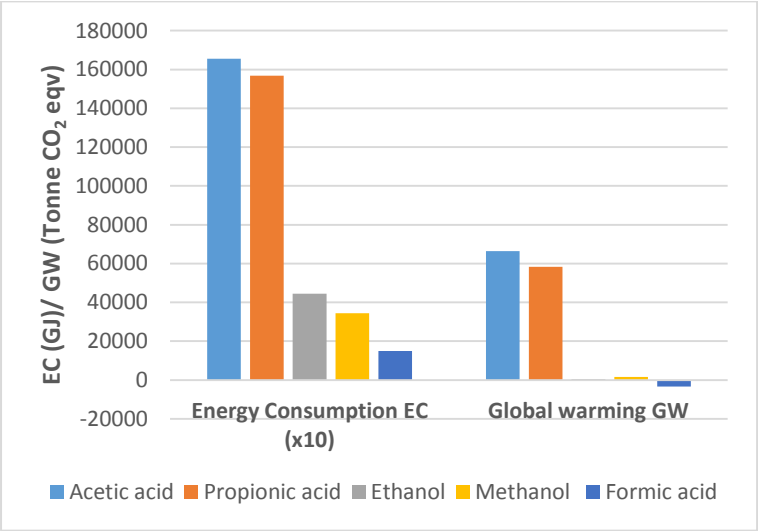


Figure 38: Energy used and Global warming yield of MES for the production of formic, acetic and propionic acids, methanol and ethanol.

This shows that using an MES system is dependent on the product synthesized ability to act as a carbon sink. Formic acid had the most positive effect on the environment in terms of global warming as it had the smallest global warming yield (-3,421 tonnes CO_2 eqv) around twenty times lower that acetic acid (66,406 tonne CO_2 equivalent). This suggests that formic acid should be favoured for synthesis over other evaluated products in order to maximise contributions to the environmental sustainable of the MES process.

5.2.2 Assessment of MES plant unit operations

It was observed that the overall energy requirements were mainly influenced by three unit operations; rectification, MES reactor and gas separator (see Appendix C1) presented in Figure 39. Rectification units and MES reactors were found more energy intensive than gas separators. These three unit operations are further described in the subsections below.

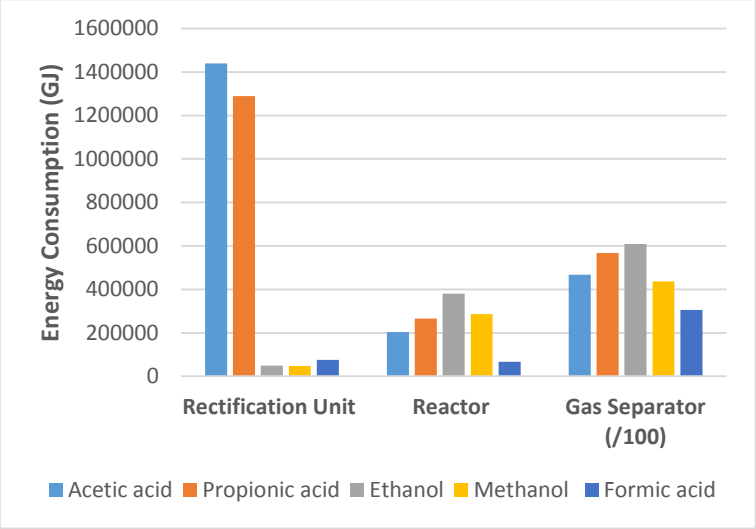


Figure 39: Energy requirement of MES plant different process units for 1000t per year production for a ten year timeframe

Rectification Unit

Industrially, product rectification is seen as one of the highest energy consuming unit operations (Jana, 2010). Rectification unit was simulated using Aspen Plus V86 with non-random two-liquid (NRTL) activity and Hayden-O'Connell second viral coefficient models (see Table 12 and Table 13 for parameters). Rectification of acetic acid (1,440,400 GJ) and propionic acid (1,289,320 GJ) required the most energy; significantly higher than for formic acid (75,980 GJ), ethanol (48,500 GJ) or methanol (47,930 GJ). This can be attributed to the amount of water mixed with the desired product and the use of an entrainer for most cases. Rectification of acetic and propionic acid required intensive energy due to a large comparative water content (1:2 and 1:4 ratio of acid to water molecules, respectively) and addition of an entrainer to overcome a water formed azeotrope (Tavan and Shahhosseini, 2016). Formic acid and ethanol also formed azeotropes with water (Banat *et al.*, 2003; Li and Bai, 2012; Wang and Huang, 2012; İnce *et al.*, 2014; Winarto *et al.*, 2015) methanol did not. For this reason, along with the fact that methanol synthesis produces low amounts of water (1:1 ratio of methanol to water molecules), methanol rectification was the least energy consumer.

Table 12: Material balance of rectification unit of MES plant capable of producing 1000 tonnes per year of formic, acetic and propionic acids, ethanol and methanol

Ethanol							
	Feed	**Distillate (Extractive Column)**	**Bottom (Extractive Column)**	**Distillate (Recovery Column)**	**Bottom (Recovery Column)**	**Distillate (Concentrate Column)**	**Bottom (Concentrate Column)**
Ethanol	0.8500	0.9950	0.0319	0.2021	6.8239e-10	0.8330	6.8501e-10
Water	0.1500	0.0004	0.1260	0.7978	6.1987e-05	0.1670	0.9999
Ethylene glycol	0.0000	6.5079e-05	4.8592e-05	4.8592e-05	0.9999	3.49e-31	6.4161e-05
Acetic Acid							
	Feed	**Distillate (Dehydration Column)**	**Bottom (Dehydration Column)**	**Bottom (Stripping Column)**			
Acetic Acid	0.1742	1.70e-15	0.99	5.00e-15			
Water	0.8258	0.2420	1.27e-11	0.99			
Vinyl Acetate	0.00	0.7580	2.94e-03	2.72e-12			
Propionic Acid							
	Feed	**Distillate (Dehydration Column)**	**Bottom (Dehydration Column)**	**Bottom (Stripping Column)**			
Propionic Acid	0.1083	0.0053	0.99	8.32e-04			
Water	0.8917	0.2602	1.19e-11	0.999			
Ethyl Acetate	0.0000	0.7344	1.16e-19	7.18e-10			
Formic Acid							
	Feed	**Distillate (Dehydration Column)**	**Bottom (Dehydration Column)**	**Decanter (Aqueous Phase)**			
Formic Acid	0.4451	0.0117	0.9795	0.0193			
Water	0.5549	0.3201	0.0096	0.9721			
Ethyl Acetate	0.0000	0.6680	0.0109	0.0086			
Methanol							
	Feed	**Distillate (Dehydration Column)**	**Bottom (Dehydration Column)**				
Methanol	0.4219	0.9914	0.0035				
Water	0.5781	0.0086	0.9965				

Table 13: Rectification unit operation process conditions

Ethanol			
Parameter	**Extractive Column**	**Recovery Column**	**Concentrate Column**
Number of Stages	25	12	25
Feed Stage	22	6	16
Entrainer Feed Stage	7	-	-
Reflux	0.1	0.5	3
Top Stage Pressure (atm)	1	1	1
Condenser Duty (kJ/h)	-10630	-3581.05	-2187.33
Reboiler Duty (kJ/h)	16464.612	6856.16	1109.59
Acetic Acid			
Parameter	**Dehydration Column**	**Stripping Column**	
Number of Stages	30	5	
Feed Stage	15	2	
Entrainer Feed Stage	1	-	
Reflux	0.9	0.9	
Top Stage Pressure (atm)	1	1	
Condenser Duty (kJ/h)	-2929210	-5011610	
Reboiler Duty (kJ/h)	3206770	5295320	
Propionic Acid			
Parameter	**Dehydration Column**	**Stripping Column**	
Number of Stages	30	10	
Feed Stage	14	5	
Entrainer Feed Stage	1	-	
Reflux	0.7	0.7	
Top Stage Pressure (atm)	1	1	
Condenser Duty (kJ/h)	-6654930	-14245.6	
Reboiler Duty (kJ/h)	7350470	69928.5	
Formic Acid			
Parameter	**Dehydration Column**		
Number of Stages	40		
Feed Stage	1		
Entrainer Feed Stage	10		
Reflux	0.9		
Top Stage Pressure (atm)	1		
Condenser Duty (kJ/h)	237300		
Reboiler Duty (kJ/h)	202200		
Methanol			
Parameter	**Dehydration Column**		
Number of Stages	30		
Feed Stage	15		
Reflux	0.99		
Top Stage Pressure (atm)	1		
Condenser Duty (kJ/h)	251600		
Reboiler Duty (kJ/h)	295600		

As stated previously material and energy balances for the synthesis of products from MES was simulated using Aspen Plus V86. The purpose was to determine the product flow composition and amount of energy used by the unit operation. Figure 40 shows the flowsheet for rectification units of acetic, propionic and formic, ethanol and methanol producing MES plants.

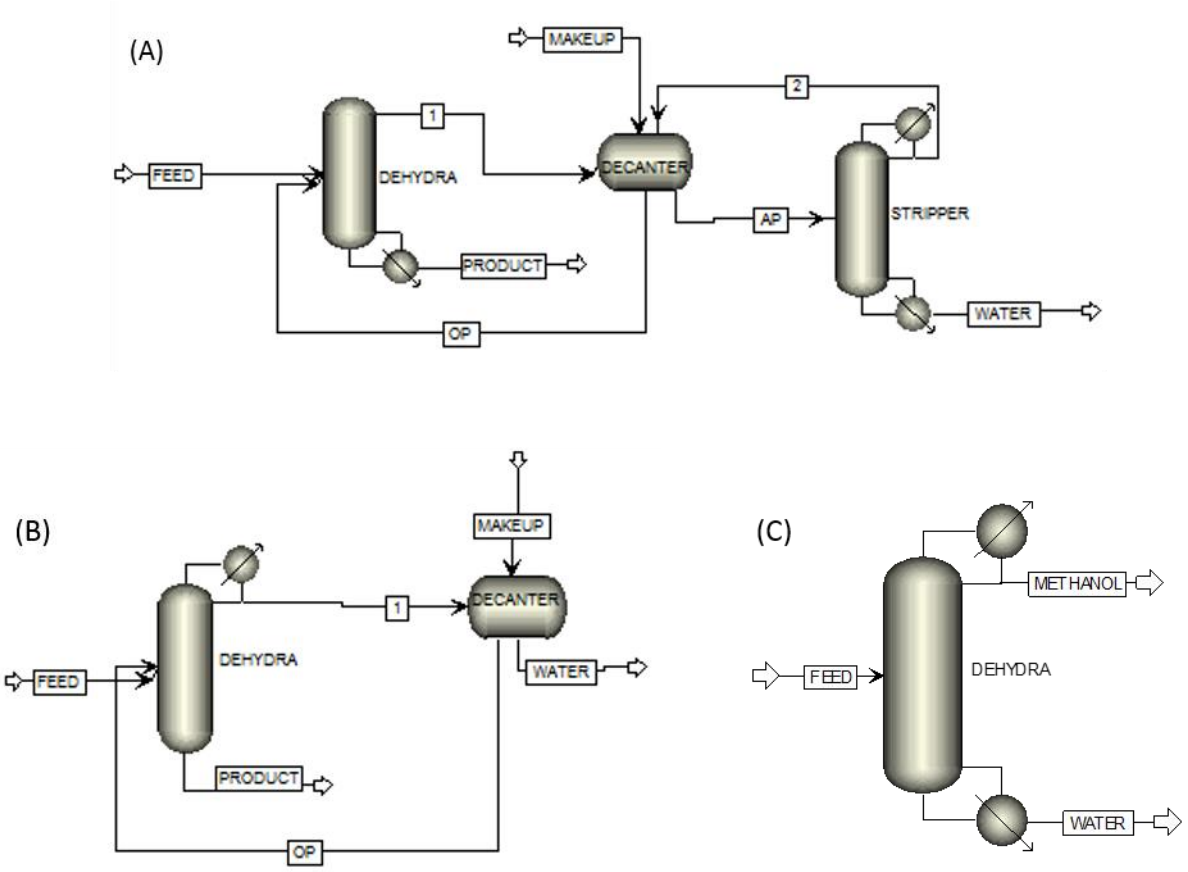


Figure 40: Rectification unit flowsheet from Aspen plus V86 A) Acetic acid and Propionic acid B) Formic acid C) Methanol

Figure 40a shows the flowsheet for rectification of acetic and propionic acid. The units consisted of two distillation columns alongside a decanter. The product (acetic and propionic acid) and water from the MES reactor are introduced into the first distillation column (dehydration unit). This column separates 99 percent of the products from water as the distillate would consist of majority water. The bottom product of this column would be made up of the desired chemical (acetic or propionic acid) and the required entrainer used. Vinyl acetate and ethyl acetate were the entrainer selected for acetic acid and propionic acid removal in this study as they have proven to be efficient in removing the chemicals from water (Chien *et al.*, 2004). The combination of product and entrainer in the bottom product of the dehydration unit is subsequently separated using a second distillation column (stripper). This gives the required 99 percent of pure product (acetic or propionic acid). The entrainer

used (vinyl acetate and ethyl acetate) is then recycled back to the decanter with a less than 1 percent makeup supplied.

The process of separating formic acid is shown in Figure 40b and it can be seen that the process consists of one distillation column and decanter. Here the feed from the MES reactor consisted of 55 and 45 percent water and formic acid respectively introduced into the distillation column. The distillate of the column was water and entrainer used ethyl acetate. This enters a decanter where water is separated from the entrainer. The desired product (formic acid) is seen as the bottom product of the distillation column. Methanol as stated previously does not require an entrainer and therefore was feed into a standalone distillation column. The distillation column had 30 stages with the feed supplied through stage 15 (see Table 13). The distillate in this distillation column was 99 percent methanol with the bottom product water.

MES Reactors

Comparing MES reactors, ethanol (380,371 GJ) and methanol (286,479 GJ) synthesis used the most energy. This can be attributed to the comparably large number of electrons needed (12 e^- for ethanol and 6 e^- for methanol) (CEAE, 2014; Blanchet *et al.*, 2015) .The MES reactor for propionic acid production was shown to be the third most energy intensive reactor (265,225 GJ) while that of formic and acetic acid were five (67,208 GJ) and two (204,301 GJ) times less energy intensive when compared to ethanol synthesis (380,371 GJ). This showed that MES reactors as a standalone unit operation could potentially be a contributor to carbon emissions if its high energy requirement is supplied through fossil fuels. However, this drawback could be offset by the amount of CO_2 consumed for synthesis.

Gas Separator

Regarding gas separation, the ethanol production process (6,080 GJ) had the highest energy demand followed by propionic acid (5,680 GJ), acetic acid (4,670 GJ) and methanol (4,370 GJ) processes. Based on reaction balances a higher flow of oxygen is produced during ethanol synthesis than for any other MES product. Ethanol production requires two moles of CO_2 which are not fully converted to products and hence releases three moles of oxygen, more than any other products synthesized. On the other hand, formic acid requires the least energy (3,040 GJ) for gas separation as it produces less oxygen (0.5 moles) compared to other products.

Additional energy may be needed for the separation of other unintended gaseous contaminants from the MES reaction. This could be in the form of unreacted hydrogen gas as the MES process usually proceeds through abiotically generated hydrogen gas (Blanchet *et al.*, 2015; del Pilar Anzola Rojas *et al.*, 2018). Other contaminants could be in the form of methane gas, however this is less likely as 2-bromoethanesulfonate is used to inhibit generation of the gas (Rago *et al.*, 2015). Further membrane separators would be required to remove these contaminants before CO_2 is recycled back into the MES reactor. Membrane separators have proven to be effective in separating CO_2 and H_2 and this would be deployed here (Myers *et al.*, 2008; Ahmad *et al.*, 2016). This is expected to add an extra 10 percent to the overall energy duty of the gas separator unit operation.

Other Unit Operations

Another indirect energy consumer is derived from the energy required to produce steel used in the process vessels, such as steel drums (208 litres; 16.6kg) employed for packaging. Studies have shown that production of stainless steel and standard steel drums requires considerable energy input (Fruehan *et al.*, 2000b; Rietveld and Hegger, 2014). Energy associated with steel accounted to around 1% of the total energy requirement for the total lifetime of the MES plant (10 years) in most cases.

5.2.3 Energy gained and Global warming ratio

To further assess the sustainability of using MES technology two indicators were used, namely EG and GWR. Figure 41 represents the EG and GWR from MES for the production of formic, acetic or propionic acids, methanol or ethanol compared to conventional routes. Industrially, acetic acid is produced by methanol carbonylation (Yoneda *et al.*, 2001), formic acid through hydrolysis of methyl formate (Reutemann and Kieczka, 2000), propionic acid by carbonylation of ethylene (Samel *et al.*, 2000), ethanol from fermentation of corn (Bothast and Schlicher, 2005) and methanol from synthesis gas (Bharadwaj and Schmidt, 1995). The EG obtained for all products synthesized using MES resulted in an EG lower than 1 indicating that already established routes would require less energy. However, EG values obtained for methanol (0.96) and formic acid (0.84) suggested that using MES to synthesize these products would require marginally higher energy than existing chemical processes. This has the potential to use less energy if MES reactor energy efficiencies (69 percent) are improved in the future. On the other hand, using MES for ethanol (0.33), propionic acid (0.12) and acetic acid (0.03) production indicates that already established routes offer far more benefits than MES (Beaver, 2004; Gallagher *et al.*, 2015). GWR values showed that using MES to

synthesize formic acid (-1.85) presented a reduction of CO_2 emissions suggesting that MES process used more carbon emissions than it produced. On the contrary, production of the acid using conventional method (hydrolysis of methyl formate) yielded positive carbon emissions. This was found to be almost twice the amount of carbon consumed when using the MES process. Ethanol (19.41) and methanol (10.45) synthesis using MES was found to emit nineteen and ten times less CO_2 than conventional processes as suggested by GWR values greater than one. Regarding ethanol, DeCicco *et al.* (2016) showed that using a fermentation production process to produce biofuels emitted more CO_2 than the one used. It was shown that for a 7 year period this would result to 27% more carbon emissions than gasoline (DeCicco et al. 2016). This study suggested that producing ethanol from CO_2 using MES could be more beneficial as there was no production of major carbon hiding co-products (e.g. carbon remaining in a corn plant). Producing propionic acid (0.19) and acetic acid (0.04) yielded a positive global warming potential and had GWR values less than one showing that conventional method of producing the acids released less CO_2. This is a consequence of the energy required for purification after microbial synthesis. Results in this study as mentioned earlier were limited to only the consideration of CO_2 emissions from energy use.

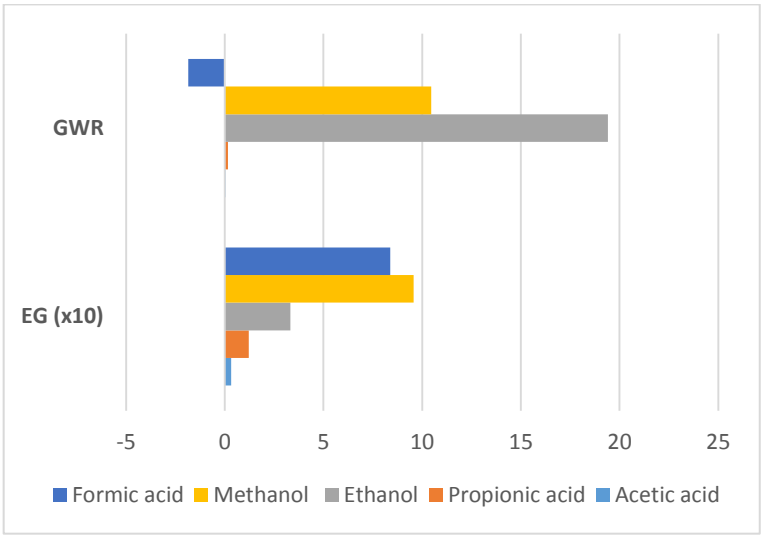


Figure 41: EG and GWR values of formic, acetic and propionic acids, methanol and ethanol from MES.

5.3 Conclusion

Comprehensive energy and global warming analysis of MES have been presented. The assessment showed that using gaseous CO_2 as a substrate offers environmental benefits when formic acid is synthesized. Product formation and purification have high energy demand due to CO_2 thermodynamic properties and formation of water molecules during synthesis. EG values for MES suggested that the energy efficiency of the process has to be optimized to rival conventional processes. Methanol and formic acid synthesis using MES should be the focus of the optimization effort as their energy demand was found to be marginally higher than conventional processes. MES as a technology has been shown to have the ability to decrease green-house gas emissions for formic acid production if deployed on a large scale.

Chapter 6: Environmental assessment of microbial electrosynthesis

6.1 Introduction

6.1.1 Life Cycle Assessment Software's

Life cycle assessment (LCA) can be both a complex and time consuming task therefore to ease the difficulty several LCA software's have been developed. These software's usually come with essential inbuilt inventory data designed for LCA calculations. This makes them attractive alternatives to undertaking the assessment using conventional data analysis software's such as MS excel and Matlab. The process is further simplified as key material and process information can be obtained using these software's. Most LCA software's are ISO 14040 and 14044 compliant but also have the flexibility of being deployed for more simpler applications (Speck *et al.*, 2015). LCA software's can be widely and commercially available (e.g SimaPro and GaBi) or be propriety to be used only by certain groups.

Comparison of Life Cycle Assessment Software's

GaBi and SimaPro are usually the software's of choice for conducting LCA in academic research (Herrmann and Moltesen, 2015; Speck *et al.*, 2015; Speck *et al.*, 2016). They are commercially available appearing on the market in 1992 and 1990 respectively. GaBi was developed by a German company PE International while SimaPro a Netherlands based company PRe consultants (Herrmann and Moltesen, 2015). Speck and co-workers verified the wide usage of these software's by analysing the number of scientific articles published using LCA software's in three Journals between the year 2010 and 2013 (See Figure 42). During these years the total number of scientific articles published using GaBi and SimaPro increased exponentially when compared with other LCA software's. Scientific research rarely uses more than one LCA software for analysis due to several factors such as time and cost. Therefore researchers have to compare the different available LCA software and make a decision on which one would be suitable for their research.

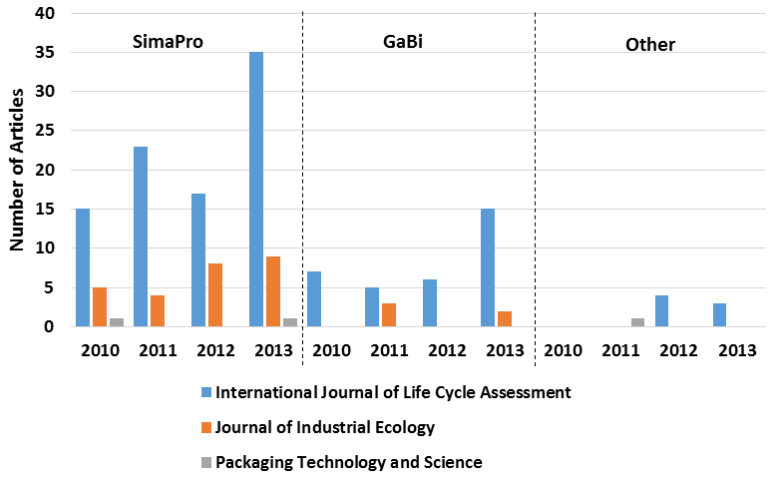


Figure 42: Journal articles using LCA software for analysis; Adapted from (Speck et al., 2015)

Several researchers have attempted to aid the choice of LCA software by comparing and contrasting the different available software's. The first of such analysis was done by Specks and co-worker when the LCA software's Compass, simaPro and Gabi were used to model packaging containers (Speck *et al.*, 2015). They found that there were significant discrepancies in the results for four impact categories; greenhouse gas emissions, eutrophication, fossil fuel energy and water depletion. The same effect was seen in more complex assessment done specifically for GaBi and simaPro by (Speck *et al.*, 2016) and (Herrmann and Moltesen, 2015). However it is worth noting that for most of the impact categories there was a less than 20 percent discrepancy. Seto and co-researchers approached the problem of LCA software choice differently as three important criteria for user friendliness were evaluated using a custom questionnaire (See Appendix D1 for questionnaire)(Seto *et al.*, 2017). The quality of five software's were analysed using flexibility, sophistication and complexity of analysis and usefulness of output as guides. A weighted score was given to each of the software packages with GaBi software recording the highest with a score of 44 out of 48. SimaPro came a close second with a score of 41 out of 48. The quality of both GaBi and simaPro over other software's was highlighted in this study as no other software scored more than 33. Their evaluation however focused on implementation of the software's for LCA in the Canadian concrete industry and as such could be considered limited. This led to their findings being challenged due to its specific nature in a letter to the editor in chief of the international journal of life cycle assessment (Heijungs, 2017). The difference between the main LCA software's GaBi and SimaPro is inconsequential as both have proven capable of handling complex LCA research. This study made use of GaBi software for the LCA as it has established competency in LCA research.

6.1.2 Overview of GaBi Life Cycle Assessment Software

As mentioned previously GaBi is a commercially available life cycle assessment modelling application that is fully compliant with the ISO 14010 and 14044 standards. GaBi provides comprehensive life cycle inventory (LCI) and inventory assessment (LCIA) through its comprehensive database. Product life cycles in the software are modelled as plans comprising of process, material and energy flows creating a clear and transparent (Thinkstep, 2017). GaBi has the ability to imbed plans into one another if needed with tracking of material, emissions and energy flows done automatically. Conveniently costs, working hours and social matters can also be accounted for in GaBi. The software calculates individual balances which are basically lists of all inputs and outputs then assists in result clarification and analysis. GaBi has one of the largest internal LCA database having the ability to incorporate other externally available commercial databases (Takano *et al.*, 2014). The thinkstep team responsible for programming has compiled using accurate primary sourced data more than ten thousand LCI over 20 years for the software. In GaBi individual modules for the LCI, LCIA and weighting models are separated making them easy to manage. They are only put together when result balances are measured and displayed in easy to understand tables. As mentioned previously transparency is one of the main advantage of GaBi as hot spots in a life cycle analysis can easily be identified. This is because different balance levels can be individually calculated and tracked back to the source process. GaBi is known for its user friendliness (see Appendix D1) as the software has an open, flexible and transparent this alongside other reasons was why the software was chosen for this study.

Modelling of the life cycle of a Systems with GaBi

GaBi database structure comprises of balances, plans, processes, flows and quantities (See Appendix D2). Single processes are combined together to form plans. These plans determines the various stages of a products life cycle. Each process is characterised by its flows which in turn is defined by quantities considered to be its properties. In GaBI results are display as a list of all the input and output flows of the various processes known as balances. The fundamentals of life cycle assessment (goal and scope definition, life cycle inventory, life cycle assessment and life cycle interpretation) are used to describe how GaBi can be used to model the life cycle of a system effectively.

Goal and Scope Definition

The goal of an LCA states the reasons and intended audience of the study. The scope on the other hand defines the function, functional unit, system and system boundaries, methodology

and impact assessment and final result presentation. Complying with the ISO 14044 standards for goal and scope definition is made convenient by GaBi as it was programmed with this as a priority. Goals and scopes of projects can conveniently be documented in written format in the software. GaBi also enables numerous projects to use the same goal and scope defined as balances, plans, processes and flows are automatically allocated to any active project.

Life Cycle Inventory

Life cycle inventory involves the collation and quantification of all inputs and outputs through the life cycle of a system. GaBi provides a transparent database and access to crucial data to enable the easy completion of this phase of the life cycle frame work. The software helps with all the calculations associated with this phase arranging results in an orderly manner. LCI data is efficiently managed due to GaBi's database structure consisting of flows, processes, plans and balances (See Appendix D2).

A flow shows specific materials or energy used by processes in GaBi. A list of comprehensive flows in the form of a flow group hierarchy arranged by type can be found in the database of GaBi. Users can create new flows as not all possible flows can be found in its comprehensive database. Values are assigned to materials and energy flows for specific processes during modelling. These values are summed up by GaBi during its balance calculations. Flow group hierarchy is advantageous because it helps to identify incomplete models.

GaBi processes shows actual processes, technical procedures or collection of procedures for a system. ISO 14044 terms them as unit processes and in GaBi are also hierarchy grouped like flows. This enables processes to be designed by users and reused for other modelling tasks. GaBi's database already has pre designed processes such as electricity generation and distribution. This makes it easier to model as needed predefined data can be available. Processes can have multiple outputs bring a unique problem where inputs have to be allocated appropriately. Allocation involves distributing the different input flows to their respective output flow. This task is made easy in GaBias this can be done without changing the process.

Plans in GaBi are basically different processes grouped together to form the stages of a systems life cycle. They are basically process road maps with all the relevant sub sections displayed. Plans in GaBi can be inputted in other plans in the same way as processes in plans. In order to complete the life cycle analysis however balances have to be calculated from produced plans. Balances compares all inputs with their respective outputs and are basically the results of life cycle inventory. Balances can be displayed in different ways using category

filters and selected impact categories. Therefore it can be said that they can be used to do life cycle inventory, life cycle impact analysis and interpretation.

Life Cycle Impact Assessment

Potential environmental impacts have to be evaluated in order for life cycle assessment of a system to be considered complete. According to ISO 14044, assessment are divided into two sub categories which are classification and characterization respectively. Classification is the allocation LCI data into selected categories while characterization involves modelling these data within impact categories. GaBi is able to perform these two classifications simultaneously in the balance window. The user is able easily to move between LCI variables such as energy allocations and impact categories such as ozone depletion potential.

Life cycle Interpretation

This step of the life cycle framework involves analysing and summarising LCI data and LCIA in order to reach informed conclusions. GaBi makes sure that all the tests done before coming to this important decision are well documented including the goal and system boundaries. The software also has the ability to conduct sensitivity analysis and error calculations if needed

Life cycle assessment is used to compare and evaluate the environmental performance of products and services which could cover entire or limited production and value chains (Volkart *et al.*, 2013). Microbial electrosynthesis (MES) which is a relatively new technology has shown the ability to utilize CO_2 and produce value added chemicals leading to a reduction in carbon emission (Finn *et al.*, 2012; Bajracharya *et al.*). It is essential therefore that using these technologies does not lead to a shift of burden where there is an increase in other negative environmental impacts. This may mitigate the positive effects of using the technology therefore a comprehensive assessment of other environmental burdens is required. This chapter focuses on LCAs for the application of MES in the production of acetic, formic and propionic acids, methanol and ethanol using the GaBi educational LCA software. The life cycle methodology used in this chapter followed the ISO standards 14040 and 14043 (ISO, 2006a; ISO, 2006b).

General Hypothesis

The hypotheses for this chapter is that “MES scaled up beyond the laboratory for the synthesis of chemicals could be environmentally beneficial using United Kingdom national grid as an energy source”

Objectives

The objectives associated with this hypothesis are;

- To assess the environmental sustainability of producing chemicals using MES when the United Kingdom national grid is used as energy source.
- To assess the environmental sustainability of producing chemical using abiotic electrochemical reduction.
- To compare the environmental effects of producing chemicals using MES with that of abiotic electrochemical reduction.
- Identify the environmental trade-offs of MES implementation.

6.2 LCA goal and scope definition

This LCA study aims to analyse and understand the potential environmental impacts of MES through a process based LCA model. The environmental impacts of the process from cradle to gate was assessed and environmental burdens characterised using the ILCD (International Life Cycle Data System) method in GaBi. The functional unit as stated in the methodology section still remains 1000 tonnes of products per year synthesized from CO_2. The gas was assumed to be captured from a coal fired plant fitted with post combustion capture system. Environmental credit from the CO_2 captured is accounted for in the overall calculations. This study assumes that the electricity supplied to the system is from the UK national grid. Potential environmental impacts in this analysis is the net impact calculated by deducting the environmental credit gained from CO_2 used by the process.

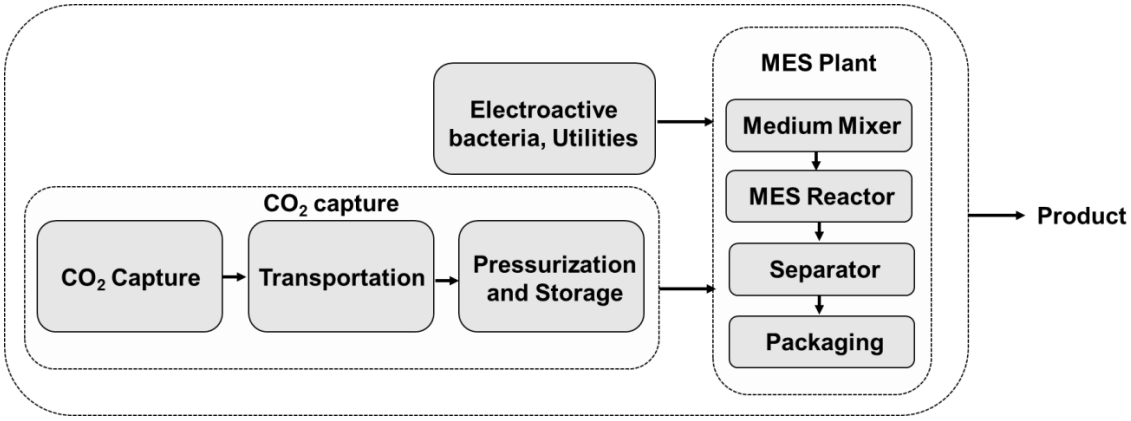


Figure 43: System boundary for 1000t/yr MES plant for formic, acetic and propionic acids, methanol and ethanol production

Figure 43 shows a simplified system boundary of the LCA model (See methodology section for the detailed system boundary). The process is divided into phases to ease analysis including CO_2 capture, purification and transportation, product formation, separation and

packaging. All MES plant unit operations (mixer, MES reactor, gas separator and rectification unit) and parameters that make up the MES plant remained the same as those described in the methodology section.

Table 14: Comparing abiotic electrochemical reduction and microbial electro synthesis (Adapted from (Chen *et al.*, 2018))

	Abiotic electrochemical reduction	**MES**
Catalyst	Noble metal, Transition metal oxide, Heteroatom doped carbon material	Electro active bacteria
Main products	Carbon monoxide, formate, Methane, Ethylene, Ethanol	Acetate, Methane
Cathodic potential	-700 to -1800mV vs Ag/AgCl	-300 to -1100mV vs Ag/AgCl
Productivity	5 to 20$gL^{-1}day^{-1}$	0.2 to 2$gL^{-1}day^{-1}$

Additionally a comparison is done between a standalone industrial sized biotic and abiotic reactor capable of reducing CO_2 to useful products using the same functional unit. Abiotic electrochemical reduction of CO_2 follows the same principles as MES without the use of micro-organisms as catalyst (See Table 14). As with MES CO_2 and protons are synthesized to products at the cathode with water oxidized to oxygen and protons at the anode(Tao *et al.*, 2017). Abiotic CO_2 reduction pathways have been shown by researchers to yield acetic acid, formic acid, methanol and ethanol using specific type of catalysts (Endrődi *et al.*, 2017). An evaluation was conducted to compare the effects of using abiotic and biotic catalysts on the environmental burdens.

6.3 Life cycle inventory analysis

6.3.1 MES Plant

A conceptual design is implemented in the life cycle analysis software GaBi according to a 1000 tonnes commercial plant size (See Appendix D3 for flowsheets sample). Gabi as described previously can be used to estimate the output of particular processes (in terms of greenhouse gas and other environmental burdens produced). Table 15 summarizes the material and energy consumed each year for each of the products evaluated. Process description and associated assumptions remains the same and have been described in the methodology section therefore would not be stated here.

Table 15: Parameters used in the life cycle analyses of product synthesized using MES

Parameter	**Acetic acid**	**Formic acid**	**Propionic acid**	**Methanol**	**Ethanol**
Energy consumed capturing and processing CO_2 (GJ/yr)	379.68	247.68	461.65	355.80	494.89
Process water consumed (m^3/yr)	740.81	483.28	930.52	1319.66	1448.42
Energy consumed by MES plant (rectification unit, bioreactor and gas separator) (GJ/yr)	95457.09	8844.97	92211.75	31779.49	41051.51
Energy consumed for packaging (GJ/yr)	126.70	109.00	134.67	167.92	168.58

6.3.2 Reactor Evaluation

Standalone MES reactors capable of generating 1000 tonnes of products per year was evaluated and compared with abiotic electrochemical reactors (AER). This was done to ascertain if there is any benefit of replacing MES reactors with AER in the simulated plant. Figure 44 shows a diagram of components that differ in each of the reactors. Materials used in manufacturing the reactors as well as energy inputs are accounted for in the assessment. This section gives a description of the assumptions made in comparative analysis. Detailed inventory data for the AER reactor can be found in Table 17 and that for MES in Appendix D4.

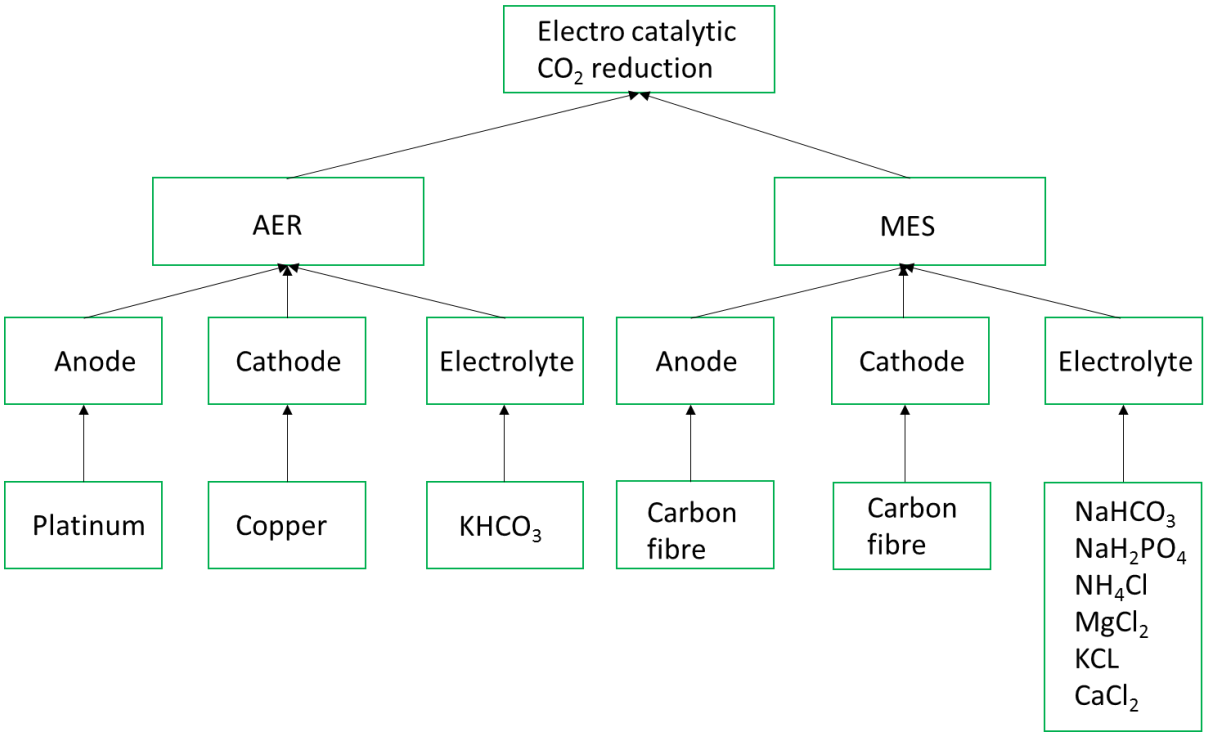


Figure 44: Component differences between the MES and AER reactors analysed

As can be seen from Figure 44 the anode and cathode for each reactor differed. In the AER reactor the anode was assumed to be platinum while the cathode copper. Platinum was selected because it is the most widely used anode for water oxidation in AER (Endrődi *et al.*, 2017; Evangelisti *et al.*, 2017). The baseline AER anode for this study was pure platinum being the same size as the cathode. Lower more practicable platinum loading was investigated in the sensitivity analysis. Most of the world's platinum is produced in South Africa and Russia (Evangelisti *et al.*, 2017), therefore the inventory data for the metal was collated from Ecoinvent 3.0 assuming mining is done underground in Russia. Copper was chosen as the cathode and therefore the abiotic electro catalyst. Selection was based on its unique ability to produce a wide variety of products specifically hydrocarbons similar to products assessed in the simulated MES plant (Kuhl *et al.*, 2012). However over potential required for the reaction is relatively high when compared to other abiotic catalysts and MES (See Table 16). Catalytic stability problems leading to gradual degradation due to carbon deposits and other toxic elements was not taken account in this study (Qiao *et al.*, 2014). Electrodes for the MES reactors are biotic, similar to the design analysed previously as a MES plant unit operation. Biotic anode and cathode MES reactor design have proved effective for electro catalytic CO_2 reduction by (Marshall *et al.*, 2013) and (Giddings *et al.*, 2015). Carbon fibre made from polyarcylonitrile was considered as the MES reactor electrode material. Inventory data for

copper and carbon fibre was collated from Ecoinvent 3.0 and (Shemfe *et al.*, 2018) respectively.

Table 16: Reaction balances and cell potential for CO_2 reduction into acetic acid, formic acid, methanol and ethanol

Product	**Overall reaction**	**AER Potential (V vs SHE) (Kuhl *et al.*, 2012)**	**MES potential (V vs SHE)**
Acetic Acid	$2CO_2 + 4H_2O \rightarrow \ CH_3COOH + 2H_2O + 2O_2$	-1.857	-1.210
Formic Acid	$CO_2 + H_2O \rightarrow \ HCOOH + 0.5O_2$	-1.677	-1.217
Methanol	$CO_2 + 3H_2O \rightarrow CH_3OH + H_2O + 1.5O_2$	-1.937	-1.207
Ethanol	$2CO_2 + 6H_2O \rightarrow \ CH_3CH_2OH + 3H_2O + 3O_2$	-1.867	-1.152

Electrolytes are needed for electro catalytic reduction of CO_2 because it aids the transfer of electrons and protons to and from the electrodes. Electrolytes used for CO_2 reduction in AER reactors could be aqueous, ionic or organic (Zhang *et al.*, 2017). This study assumes an aqueous electrolyte (0.1M $KHCO_3$) as it is comparable to those used in MES reactors. Aqueous electrolyte are also cheap due to water usage but has the disadvantage of low CO_2 solubility (0.03M in 25^{o}C) and competing hydrogen evolution reaction reducing faradaic efficiency (Tao *et al.*, 2017).

The MES reactor aqueous medium still remains the mix analysed previously. The database of GaBi and Ecoinvent 3.0 accounted for the chemicals used in the electrolytes. Sodium carbonate, sodium phosphate and potassium carbonate were used as proxies for sodium bicarbonate, sodium dihydrogen phosphate and potassium bicarbonate due to lack of life cycle data. Conversion rates were assumed to be 58.8% for both reactors with the unreacted gas recycled back. Faradaic efficiency for product formation in the AER was assume to be 30% using experimental results obtained by (Kuhl *et al.*, 2012). The faradaic efficiency for MES reactors still remained 69%. All reactors were assumed to be made of stainless steel with sizes varying due to the amount of process water needed to synthesize 1000 tonnes of the specific products.

Table 17: Life cycle inventory of a standalone abiotic reactor for 1000t of product

	Material	Unit	Acetic acid	Formic acid	Methanol	Ethanol
Reactor						
Cathode	Copper	kg	54.91	41.30	68.90	85.85
Anode	Platinum	kg	131.45	98.87	164.95	205.53
Construction	Stainless steel	kg	579.08	435.57	726.65	905.44
Current collector	Copper	Kg	1.08E-04	8.11E-04	1.35E-04	1.68E-o4
Medium						
Water		m^3/yr	740.81	483.28	1319.66	1448.42
0.1M $KHCO_3$		Kg/yr	14831.85	9675.67	20848.61	28998.89
Energy						
Conversion energy		GJ/yr	40577.30	11952.93	59497.28	79767.41
Heat treatment		GJ/yr	56.00	36.53	79.43	78.71
CO_2 capture						
CO_2		t/yr	1677.32	1094.22	1571.84	2186.31
Capture energy		GJ/yr	294.87	192.36	276.33	384.35
Total weight		Kg	786.50	591.59	986.93	1229.77
Total energy		GJ/yr	40928.17	12181.80	59852.30	80261.3

6.4 Life cycle impact assessment and interpretation

6.4.1 MES plant

Climate change

The assessment of the MES plant gives a positive greenhouse gas emissions for all the products (acetic acid, formic acid, propionic acid, ethanol and methanol) analysed. This is similar except in the case of formic acid (-3,420,564 kg CO_2 eqv) to the values observed when natural gas was assumed as the energy source in chapter 5 (See Table 18). Formic acid (2,200,000 kg CO_2 eqv) which had a negative value with natural gas as the energy source has turned positive. However, it was found to emit comparatively the lowest quantity of greenhouse gas (CO_2) to the atmosphere. This is mainly due to the fact that the generation and transmission of electricity in UK produces more than three times as much greenhouse gas emissions per GJ of electricity generated than natural gas (50 kg CO_2 eqv per GJ). Table 18 also shows the amount of contribution to climate change by the greenhouse gases. The most prevalent greenhouse gas in all the different product is carbon dioxide with the next potent greenhouse being methane due to its high CO_2 equivalent value.

Table 18: Greenhouse gases emissions from acetic acid, propionic acid, formic acid, ethanol and methanol MES plant (1000t/y) modelled using GaBi (Electricity from UK national grid) compared with emissions using natural gas as electricity

Products	**Greenhouse gases**				**GWP (Electricity from UK national Grid) (Kg CO_2 eqv)**	**GWP (Electricity from burning natural gas) (Kg CO_2 eqv)**
	Carbon dioxide (kg)	**Methane (Kg)**	**Nitrous Oxide (Kg)**	**Sulfur Hexafluoride (Kg)**		
	1 Kg CO_2 eqv	**25 Kg CO_2 eqv**	**298 Kg CO_2 eqv**	**22800 Kg CO_2 eqv**		
Acetic Acid	81,202,757	117,719	905	1.03E-07	67,800,000	66,406,463
Propionic Acid	84,170,610	135,435	1,114	1.08E-07	67,700,000	58,360,062
Ethanol	59,703,004	144,018	1,421	1.52E-07	42,100,000	382,324
Methanol	45,635,880	108,934	1,321	1.15E-07	33,200,000	1,587,815
Formic Acid	12,304,698	27,852	271	3.24E-08	2,200,000	-3,420,564

Figure 45 shows the climate change contributions of the different unit operations of the MES plant for acetic, propionic acid and formic acid, methanol and ethanol. Acetic and propionic

acids relatively high amount of contribution to climate change is mainly due to their energy intensive rectification unit. Rectification of acetic (50,700,000 Kg CO_2 eqv) and propionic acid (44,233,895 Kg CO_2 eqv) contributed 75 and 65 percent respectively to climate change. Formic acid rectification contributed 55 percent while that of methanol and ethanol contributed less than 6 percent to climate change. Evaluating the five MES reactors it was observed that only formic acid (-170,773.81 Kg CO_2 eqv) had a negative climate change contribution. The MES reactors of ethanol and methanol contributed significantly to climate change accounting for 92 and 90 percent respectively. This can be attributed to the large amount of energy needed for microbial electro-synthesis (380,371 GJ for ethanol and 286,479 GJ for methanol) compared to other unit operations. Acetic acid (16,000,000 Kg CO_2 eqv) and propionic acid (22,100,000 Kg CO_2 eqv) MES reactors contributed less than 30 percent to climate change. Results indicates that without supporting unit operations standalone MES reactors still has a net positive global warming potential. Formic acid is a notable exception as it was observed to be the best performing reactor having a negative global warming potential.

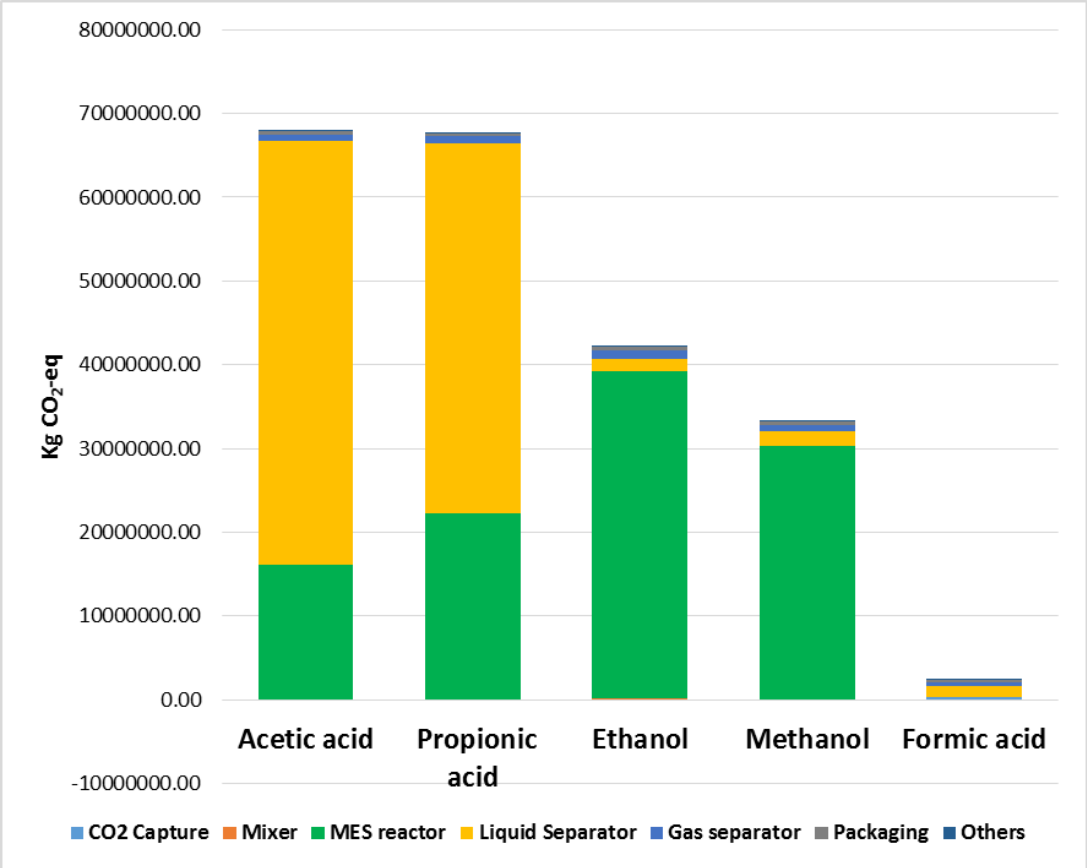


Figure 45: Climate change contributions of MES plant for the production of acetic, propionic and formic acids, methanol and ethanol

Other Environmental Burdens

Eight midpoint indicators were selected for a more detailed analysis from thirteen indicators of the ILCD methods. The indicators chosen included ozone depletion (OD, in Kg R11-Eqv), human toxicity cancer effects (HT, in CTUh), particulate matter (PM, in PM2.5 Eqv), ionising radiation (IR, in U235 Eqv), photochemical ozone formation (POF, in Kg NMVOC Eqv), acidification (AC, in Mole of H+ Eqv), freshwater europhication (FE, in Kg P Eqv) and ecotoxicity (EC, in CTUe). The remaining midpoint indicator results and raw data for the MES plants can be seen in Appendix D5. The results are displayed relative to the maximum value in each of the midpoint impact category.

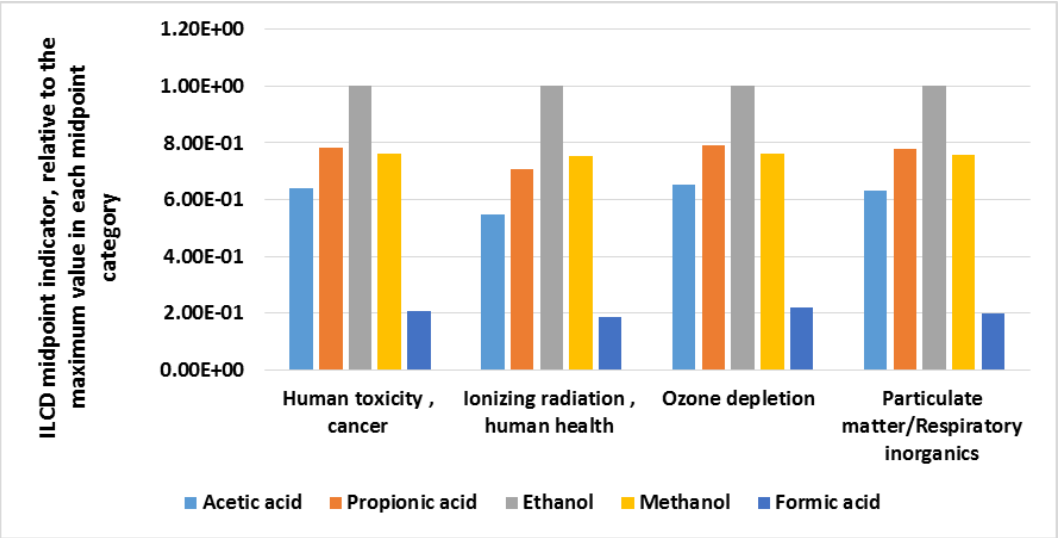


Figure 46: Life cycle environmental burdens (Human toxicity, ionizing radiation, ozone depletion and particulate matter) of the MES plant for the production of acetic, propionic and formic acids, ethanol and methanol using ILCD method. Results are displayed relative to the maximum value in each impact category.

Data obtained from the analysis shows that all MES plants has overall negative impact on the environment in all the impact category. This indicates that the environmental benefits of CO_2 utilization cannot compensate for the generation of other environmental burdens. Figure 46 and Figure 47 shows that formic acid contributes the lowest in the selected impact categories as its relative values to the maximum is always less than 30 percent. Ethanol was observed to have the maximum value in all of the selected impact categories differing from results obtained for climate change (See Figure 45). Propionic and acetic acid gave very similar results in all the selected impact categories as they were found to always have a relative value more than 50 percent to the maximum (ethanol).

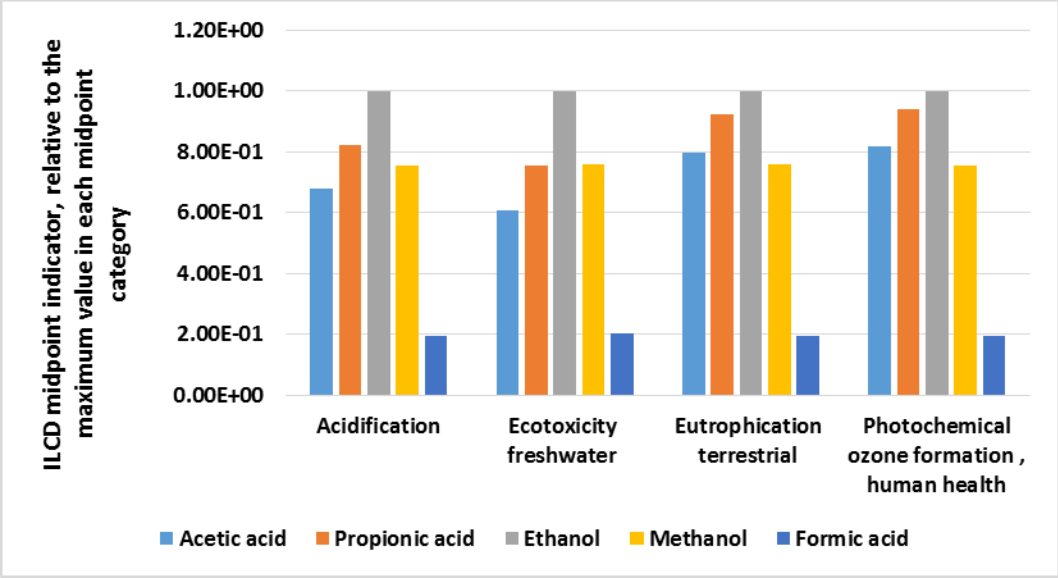


Figure 47: : Life cycle environmental burdens (Acidification, ecotoxixity, eutrophication and photochemical ozone formation) of the MES plant for the production of acetic, propionic and formic acids, ethanol and methanol using ILCD method. Results are displayed relative to the maximum value in each impact category.

The cradle to gate environmental impacts are further assessed in terms of plant unit operation. Electricity used for synthesis of products in the MES reactors had relatively large environmental impact contributions in most impact categories. Assessing ethanol which had the most energy intensive MES reactor it was observed that synthesis of the chemical takes up between 94.5 and 98.2 percent in the selected impact categories. Similar results were seen in methanol and formic acid which alongside ethanol had relatively low rectification energy duty. Assessing formic acid specifically it was observed that its MES reactor takes up 88.9% of AC, 81.8% of EC, 76.7% of FE, 80.2% of HT, 92.3% of IR, 76.1% of OD, 86.3% of PM and 87.7% of POF. Process steam needed to heat the reboilers of acetic and propionic producing MES plants contributed on average 15 percent in the selected impact categories. Analysing acetic acid which uses the most energy for rectification it was observed that the unit operation takes up 20.4% of AC, 9.7% of EC, 4.9% of FE, 14.9% of HT, 1.0 % of IR, 16.1% of OD, 14.1% of PM and 34.6% of POF. This was found to be always less than its MES reactor in all impact categories except climate change. Rectification of formic acid, ethanol and methanol contributed less than 4 percent in all impact categories apart from climate change. All other unit operations (CO_2 capture, mixer and gas separator) contribute less than 5 percent in all selected impact categories for each product analysed. Therefore it can be concluded that the hot spot of the modelled MES plant in terms of unit operation is the MES reactor.

Flue gas from the gas separator and incineration of filtered biomass could also contribute to the environmental burdens of the MES plants. As the selectivity of CO_2 to products (88 percent) and faradaic efficiency (69 percent) of the MES reactors are not 100 percent there may be undesired by-products formed. This would have to be vented off to the atmosphere alongside oxygen as CO_2 is being recycled back to the MES reactor. The impurities in the flue gas would most likely be mainly hydrogen and trace methane. The use of 2-bromoethanesulfonate (see table 6) in biofilm development should help suppress methanogenic bacteria growth hence its expected minimal quantity. Vented Hydrogen gas can affect the upper atmosphere due to a build-up of water vapour. This can cause ozone depletion and its undesired consequences (Tromp et al., 2003). Methane on the other hand contributes to climate change and POF environmental burdens (Sadhukhan et al., 2014). Incineration of biomass would take place twice each year away from the plants hence transportation environmental burdens needs to be taken into account. Municipal waste incineration is known to contribute about 360 $KgCO_2$ eqv/ton to global warming (Havukainen et al., 2017). This value should be what is expected when the filtered bacteria cells are incinerated. As the MES plants would be incinerating just a few grams of bacteria cells per year, this waste treatment method should not significantly affect climate change and other environmental burdens results of the MES plants.

6.4.2 Reactor evaluation

Climate change

Table 19 shows the global warming potential associated with the construction and operation of a standalone MES and AER reactors for ten years. The operation of the reactors contributed the most to climate change as the impact of construction is calculated only at start-up. MES reactors had lower global warming potential both for construction and operation than AER reactors for all the products analysed. This is mainly due to the negative climate change effect of producing platinum used as the anode and the low faradaic efficiency of copper electrodes (30 percent). Product specific it was observed that formic acid production had the lowest global warming potential for both construction and operation in both MES and AER reactors. The chemical production through MES reactors (162,665 Kg CO_2 eqv) was found to be 52 times better than AER reactors (8,604,502 Kg CO_2 eqv). This was however not the case for all reactors as acetic acid (16,500,000 $KgCO_2$ eqv), ethanol (39,800,000 $KgCO_2$ eqv) and

methanol(30,701,535 $KgCO_2$ eqv) were only around 3 times better than their respective AER reactors.

Table 19: Comparing climate change standalone MES and AER electro catalytic reactors

Products	**MES (Kg CO_2 eqv)**		**AER Kg CO_2 eqv)**	
	Construction	Operation	Construction	Operation
Acetic acid	1,370	16,500,000	8,500,000	48,900,000
Ethanol	2,150	39,800,000	13,300,000	107,000,000
Methanol	1,720	30,701,535	10,700,000	80,304,049
Formic acid	1,030	162,665	6,390,000	8,604,502

Other Environmental Burdens

For the assessment of the other environmental burdens of the standalone MES reactor and AER reactor, the same impact categories are chosen as those used in the commercial grade MES plant. The complete midpoint results and raw data are provided in Appendix D5. It was observed that the environmental burdens associated with the construction and operation of AER ethanol producing reactor alternatively had the maximum value in all the impact categories selected. The construction of the reactor had the maximum value in five (AC, EC,FE, POF and PM) of the selected impact categories while operation in four (HT, IR and OD). In the case of construction this is because the reactor needed to generate 1000tonnes of ethanol per year is the largest due to the amount of aqueous medium needed for the reaction. Platinum usage as the anode is 99 percent responsible for the large construction environmental burdens of the AER reactors. Industrial use of pure platinum would be unsustainable and low platinum loading on large surface area electrodes such as carbon fibre could be optimum.

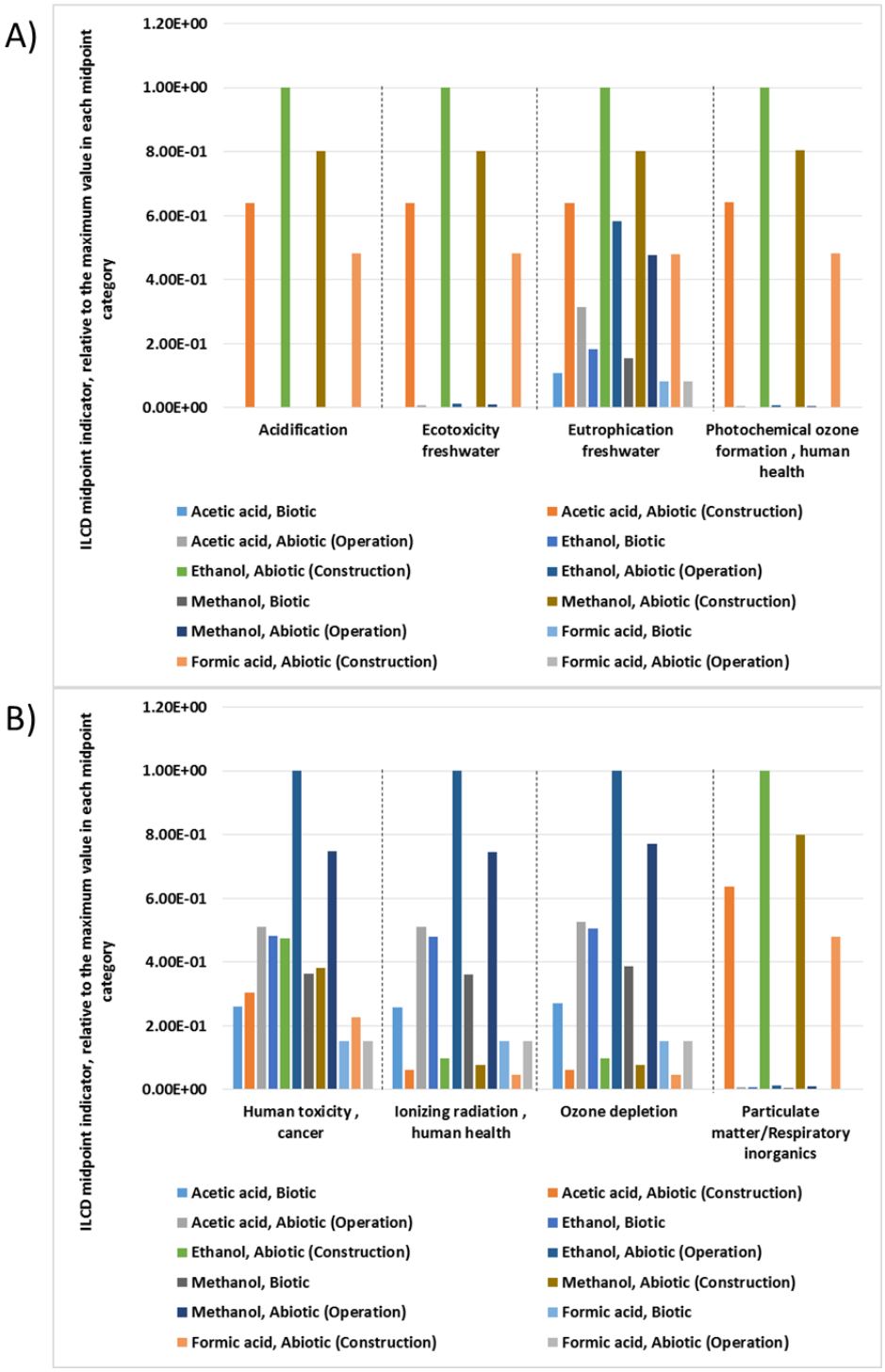


Figure 48: Life cycle environmental burdens of the MES and AER reactor using ILCD method. A) Acidification, ecotoxicity, eutrophication and photochemical ozone formation B) Human toxicity, ionizing radiation, ozone depletion and particulate matter. Results are displayed relative to the maximum value in each impact category.

6.4.3 Sensitivity Analysis

MES plant

A sensitivity analysis has been carried out by exploring two MES plant parameters changes. CO_2 conversion and faradaic efficiency were examined to see the environmental impact variations resulting from the changes in these parameters. Alternative scenarios different to the base case where these parameters are set at 40 and 100 percent respectively were assessed. The scenario analysis results of the different CO_2 conversion and efficiency are shown in Figure 49 for climate change and Figure 50 for other environmental burdens.

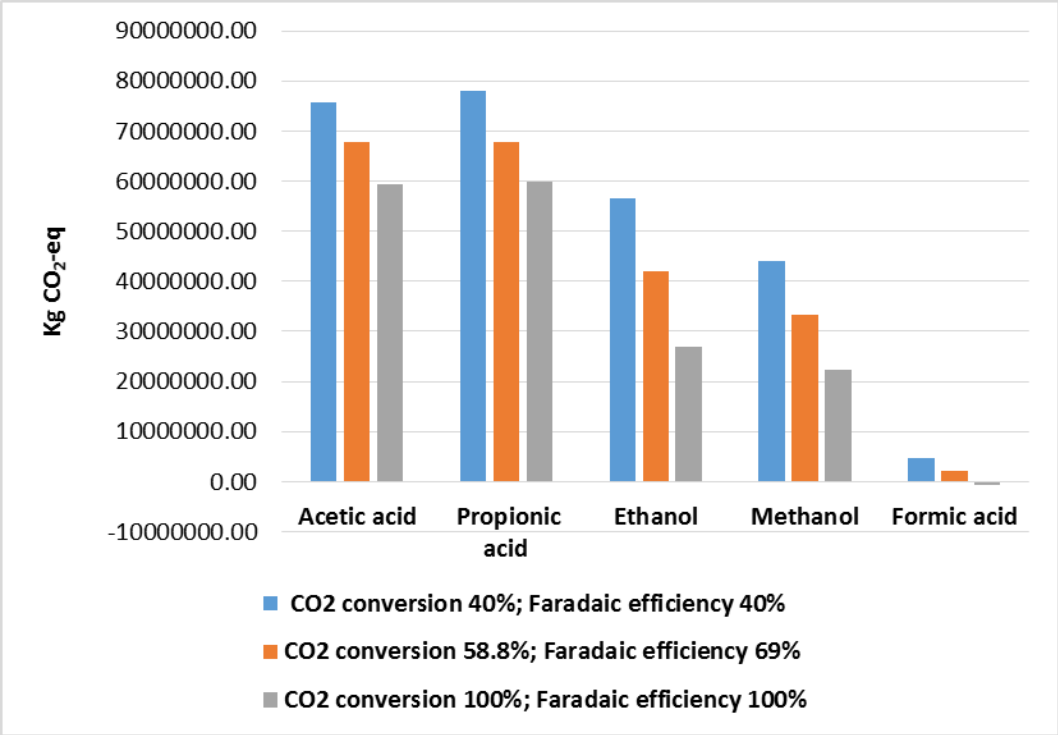


Figure 49: Scenario analysis of CO_2 conversion and faradaic efficiency

From Figure 49, it was observed that when the CO_2 conversion and faradaic efficiency are reduced a higher environmental impact in terms of climate change is seen. The reverse is seen when these parameters are reduced. This can be explained by the change in the energy requirements for the MES reactor and gas separator. An energy requirement change of between 25-30 percent is seen in the MES reactor for each of the products analysed when the CO_2 conversion and faradaic efficiency is changed to the selected percentages. In terms of the gas separator a CO_2 conversion of 100 percentage eliminates the need for the unit operation as oxygen can be vented off to the atmosphere directly from the MES reactor. A reduction to 40 percentage increases the energy requirement by more than two times in the case of all products analysed. It can be seen from Figure 49 that only the global warming potential of

formic acid (-734000 $KgCO_2$ eqv) becomes negative when the CO_2 conversion and faradaic efficiency is set at 100 percent. Comparatively low rectification and MES reactor energy requirements are the main reason for this change yielding a positive results. This indicates that low synthesis and rectification energy requirements are necessary for good conversion and efficiency values seen in experimental research to yield positive global warming reduction for a commercial grade MES plant.

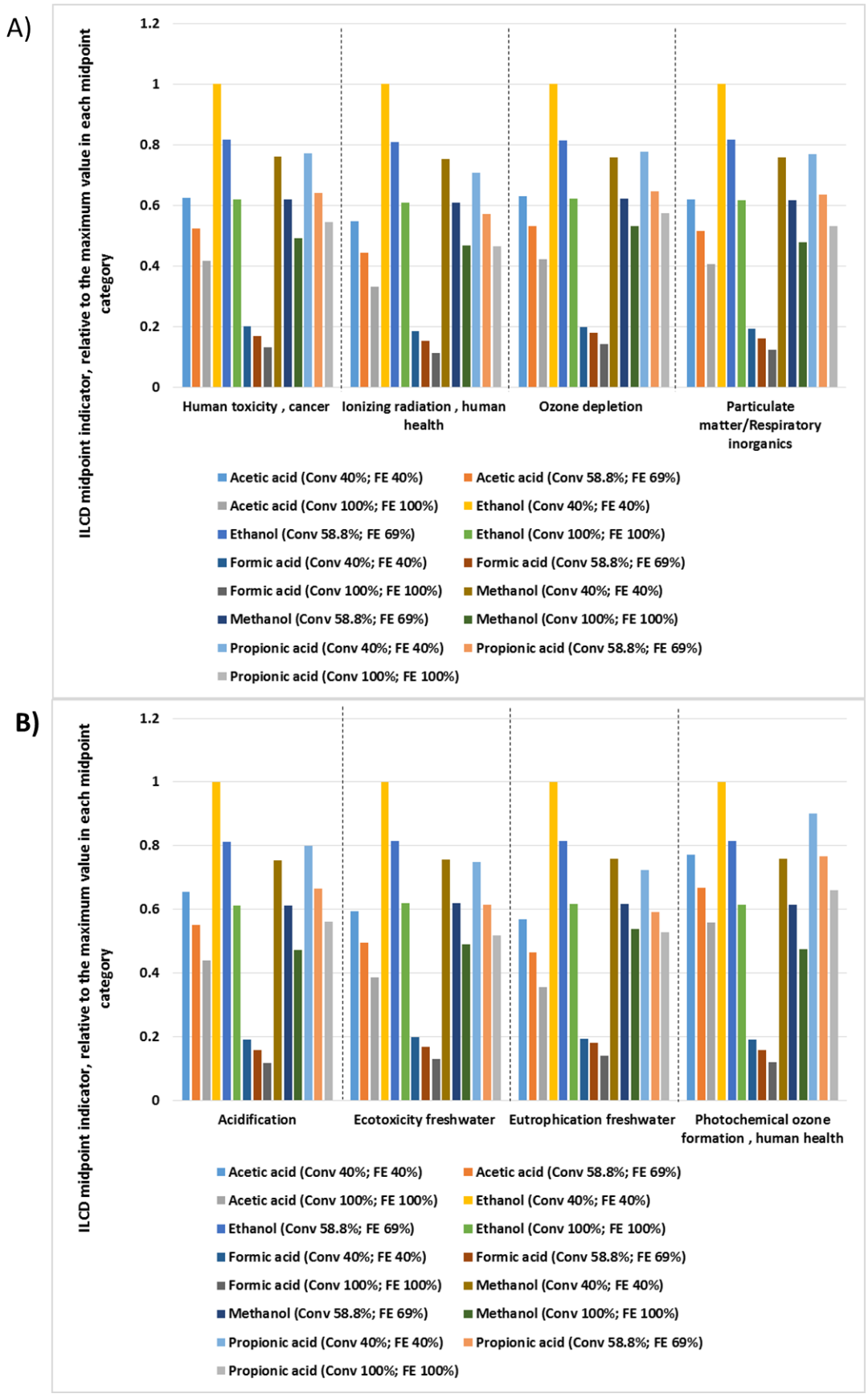


Figure 50: Scenario analysis of CO_2 conversion and faradaic efficiency A) Life cycle environmental burdens (Human toxicity, ionizing radiation, ozone depletion and particulate matter) B) Life cycle environmental burdens (Acidification, Ecotoxicity, eutrophication and photochemical ozone formation)

Figure 50 shows the sensitivity analysis results for other environmental impact burdens when the CO_2 conversion and faradaic efficiency differed from the base scenario. It was observed that for all selected impact categories a variation of between 5 and 40 percent occurred. Ethanol at 40 percent CO_2 conversion and efficiency as with the base scenario was observed to have the maximum value in all (HT,IR,OD,PM,AC,EC FE, and POF) of the selected impact categories. The base scenario was surpassed marginally by acetic acid and methanol at 40 percent CO_2 conversion and faradaic efficiency. Formic acid still had the lowest effect on the environment for all impact categories even though the parameters were adjusted to the worst case scenario.

Reactor analysis

A sensitivity analysis was carried out which takes into account a reduction in the platinum used in the anode (75 percent) and 100 percent conversion and faradaic efficiency in the AER reactor. Figure 51 shows the greenhouse emissions from these scenarios compared with the baseline abiotic and MES reactors operated for one year. A reduction of platinum loading or increase in conversion and faradaic efficiencies gives a proportional reduction in global warming potential as well as other impact categories of the AER reactors. Comparing the two method that can be used to reduce environmental burdens. It was observed that reducing the platinum loading gives between 30 -75 percent reduction in climate change for all products analysed. This shows that the main hot spot of AER reactors are the environmental burdens associated with the use of rare metals as counter electrodes.

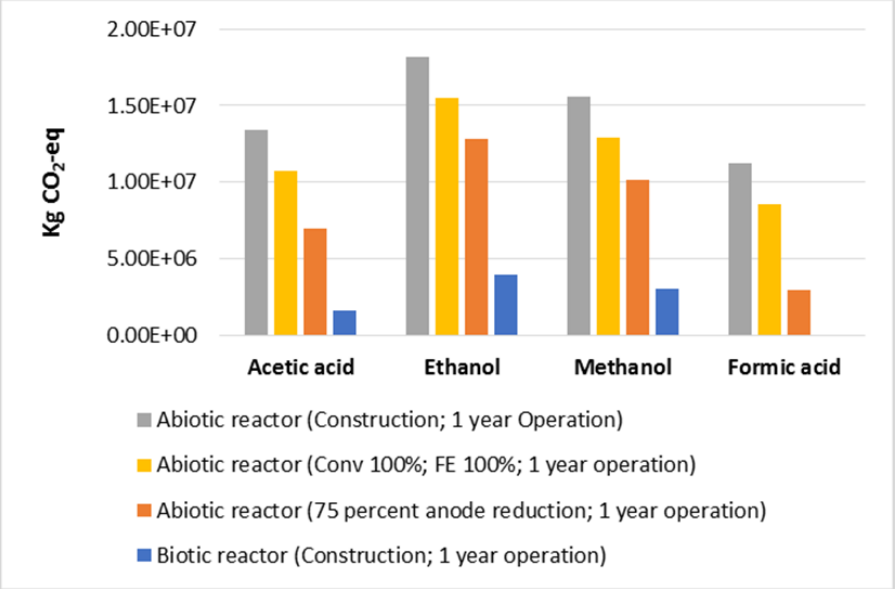


Figure 51: Scenario analysis for climate change comparing AER and MES reactors

Conclusion

To facilitate the commercial application of MES a cradle to gate life cycle analysis was performed in this study. Environmental impact variations were performed for MES plants capable of producing acetic, propionic and formic acid, ethanol and methanol. The results show that formic acid production have relatively low environmental impacts in the various environmental categories. The low environmental impacts was mainly due to the lower energy requirement for its reactor and rectification unit. The reduction of greenhouse gas emissions due to MES of formic acid can only be achieved at high conversion and faradaic efficiencies using electricity from UK national grid. However there is always a trade-off in other environmental burdens than climate change. Depending on the product generated, conversion and faradaic efficiencies there can be climate change benefit of using MES for synthesis of chemicals. Choice of catalyst has an effect on the environmental burdens as biotic catalyst performed better than abiotic when compared. As there is still need for more research on the industrial application of MES, this LCA study provides an initial assessment serving as a basis for future LCA studies on large scale application of MES and other BES based technology. Based on the conclusions, the production of formic acid is of particular interest and is the best suited product for MES to provide environmental benefits if applied industrially.

Chapter 7: Environmental assessment of formic acid manufacturing routes

Formic acid is a colourless corrosive acid which is totally miscible with water and numerous polar solvents. It is mainly used in the textile, pharmaceuticals and food industry with the leather and tanning industry being it largest user in 2003 (Reutemann and Kieczka, 2000; Bulushev and Ross, 2018).This has however been overtaken recently by its use as an additive and preservative in animal feed which accounts for as at 2014 around 34% of global formic acid usage (Aligoli, 2014). The total amount of formic acid manufactured worldwide is estimated to be 0.95 mega tonnes per year with the price set at between $0.60 and $0.70 per Kg in the first half of 2014. Demand for the chemical is set to increase by around 6 percent in 2019 because of its ever expanding use cases (Bulushev and Ross, 2018). Formic acid can be used to store hydrogen due to its good properties and simple dehydrogenation (Bulushev and Ross, 2018).

Conventionally formic acid can be manufactured through oxidation of hydrocarbons, hydrolysis of formamide, preparation of free formic acid from formate and hydrolysis of methyl formate (Reutemann and Kieczka, 2000). In the oxidation of hydrocarbons to produce formic acid, methane and methanol can be employed. Methanol oxidation yield formaldehyde which in turn is oxidized to formic acid in a two step process (Andrushkevich *et al.*, 2014). Methane on the hand is oxidized to formic acid using heterogeneous catalysts. Using methane is advantageous because oxidation occurs at low temperatures (60^{o}C) even though yields are low (Hutchings, 2016). Comparing the different ways formic acid can be produced conventionally Hydrolysis of methyl formate is currently the main way the chemical is manufactured. The route accounts for around 90 percent of all formic acid installation production facilities. It occurs in a two stage process where 95 percent carbon monoxide and 30 percent methanol are initially reacted to produce methyl formate which is then hydrolysed to synthesize formic acid (Saavalainen *et al.*, 2017).

Electrocatalytically formic acid has been shown to be produced through biotic (Reda *et al.*, 2008; Srikanth *et al.*, 2014) and abiotic catalysts (Gupta *et al.*, 2016). In the case of biotic catalyst the chemical is produced through microbial electrosynthesis by supplying suitable bacteria or biomolecules electrons and CO_2 for synthesis (Srikanth *et al.*, 2017). Abiotically the chemical can be produced either through homogenous and heterogeneous abiotic catalysts (Gupta *et al.*, 2016). Formic acid production through MES has previously been shown to have relatively low environmental burdens when compared to other chemicals that can be synthesized by the process. This chapter focuses on comparing the environmental impacts of

MES with three other formic acid production routes using the Gabi educational LCA software. The formic acid production routes analysed were the main conventional (hydrolysis of methyl formate) and two other carbon utilizing routes that makes use of abiotic catalysts. The life cycle methodology used in this chapter followed the ISO standards 14040 and 14043 (ISO, 2006a; ISO, 2006b).

General Hypothesis

The hypotheses for this chapter is that "MES scaled up beyond the laboratory for the synthesis of formic acid could be environmentally beneficial than conventional and abiotic electrochemical means of production"

Objectives

The objectives associated with this hypothesis are;

- To assess the environmental sustainability of producing formic acid using methyl formate hydrolysis.
- To assess the environmental sustainability of producing formic acid using homogenous abiotic catalysts.
- To compare the environmental effects of producing formic acid using MES with that of both abiotic electrochemical reduction and conventional routes.

7.1 LCA goal and scope definition

This LCA study aims to compare the potential environmental impacts of producing formic acid through a process based LCA model. Four ways of manufacturing the chemical are analysed in this study using the ILCD (International Life Cycle Data System) method in GaBi. The options consisted of three processes that utilizes CO_2 (Microbial electrosynthesis (MES), Abiotic electrochemical reduction (AER) and Hydrogenation of carbon dioxide (HCD) and a conventional benchmark (Hydrolysis of methyl formate (HMF)). Assessment for the MES plant was based on analysis done in chapter 6. AER plant assessment were partly based on the analysis done for a standalone abiotic electrochemical reactor and simulations using GaBi. Additional AER plant unit operation such as mixer, liquid and gas separator were based on assumptions similar to that of the MES plant. Data for the HCD formic acid producing plant were obtained from literature through the research of (Pérez-Fortes *et al.*,

2016). Comparative analysis between the three CO_2 utilizing formic acid production routes described above and a conventional route was done in this study. The functional unit used for this comparison was 1000 tonnes of formic acid generated at a commercial grade concentration of between 90 and 99 percent. The database of Ecoinvent 3.0 and Gabi LCA software was used to conduct this study with electricity supplied for each plant assumed to be from the UK national grid.

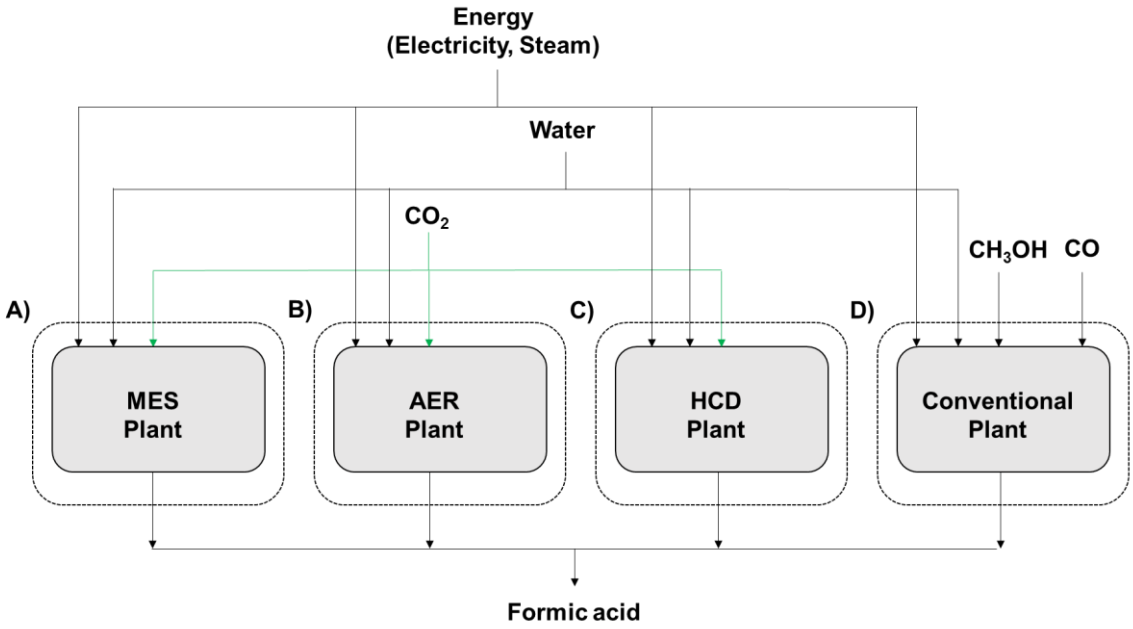


Figure 52: System boundary for 1000t of formic acid production: A) MES B) AER C) HCD and D) HMF plants

Figure 52 shows the system boundaries of the LCA models for the four alternative formic acid production routes. As can be seen from the diagram methanol and carbon monoxide are raw materials needed only in the conventional plant (HMF). CO_2 on the other hand is used as raw material in the three other production plants as the technology used in these plants needed CO_2. Utilities such as water, electricity and steam are used in each of the formic acid production routes. However this would differ in magnitude depending on the needs of each individual plant. Assumptions for the MES and AER plants are the same as described in the methodology section. The assumptions associated with the HCD and HMF plants are described in the subsections below;

7.1.1 HCD plant

Formic acid production from a HCD plant were evaluated and compared with other ways of generating the chemical. The plant was assumed to be located at Newcastle Upon Tyne, UK. CO_2 needed for plant operation was assumed to be supplied at 0.1758 GJ per tonne from a coal fired plant 30km away (Bhown and Freeman, 2011). The transportation of the gas to the plant site was done by a diesel powered truck from the database of GaBi. Energy required to compress CO_2 from atmospheric pressure to that required by the plant is allocated to the HMF plant overall energy duty. As stated previously an electrolyser is required for production of hydrogen needed by the plant. It is assumed that the required hydrogen needed to operate the main reactor is supplied by an electrolyser situated onsite. Inventory data needed for modelling of the HCD plant was obtained from the work of (Pérez-Fortes *et al.*, 2016) and the database of Gabi (See appendix E1 for flowsheet).

7.1.2 HMF plant

Methyl formate hydrolysis was used as the bench mark conventional process because of its wide industrial application (Saavalainen *et al.*, 2017). The process involves two stages with the first being methanol carbonylation for the formation of methyl formate. Methyl formate is then hydrolysed to produce formic acid in the second stage. Methanol and carbon monoxide which are the main raw materials needed by the plant is assumed to be supplied from a production facilities 30 Km from the plant site. Inventory data for the HMF plant was collated from database of Ecoinvent 3.0 and Gabi (See appendix E1 for flowsheet).

7.2 Life cycle inventory analysis

7.2.1 MES and AER plants

Life cycle inventory was performed based on results obtained in chapter 6 for formic acid producing MES and AER plants. Process description and all assumptions apart from construction energy and any associated environmental burdens are the same. The methodology section describes the full assumptions and therefore would not be stated here. Table 20 shows a summary of the life cycle inventory of the four formic acid production routes assuming 1000 tonnes per year of formic acid is synthesized. The values summarized in the table are grouped into raw materials, product, output and energy consumed by the plants. For the three CO_2 utilizing plants unreacted CO_2 and water are assumed to be perfectly recycled back into the plant with the analysis done for a ten year time frame.

Table 20: Life cycle inventory of the formic acid production routes analysed

	Unit	MES Plant	AER Plant	HCD Plant	HMF Plant
Reference		**Chapter 6**	**Chapter 6**	**(Pérez-Fortes *et al.*, 2016)**	**(Sutter, 2007)**
Raw material					
CO_2	t/yr	1094	1094	830	-
H_2O	t/yr	483	483	560	600
CO	t/yr	-	-	-	614
CH_3OH	t/yr	-	-	-	40
Product					
HCOOH	t/yr	1000	1000	1000	1000
Output					
O_2	t/yr	348	348	480	-
Energy					
CO_2 capture energy	GJ/yr	192	192	146	-
Plant electricity	GJ/yr	7183	11989	14652	1044
Steam	GJ/yr	1771	1771	10030	19500
Total energy	GJ/yr	8954	13761	24682	20544

It can be seen from Table 20 that the main contributors to climate change and other environmental burdens is expected to be plant electricity and steam usage. Electricity consumed by the three CO_2 utilizing plants ranged between 14652 GJ/yr and 7183 GJ/yr while that of the HMF plant was 1044 GJ/yr. The relative difference is mainly due to electricity being used to undergo formic acid synthesis in the reactors of the MES, AER and HCD plants. The HMF plant (19500 GJ/yr) showed the highest consumption of steam for the production of 1000 tonnes per year of formic acid while the HCD plant (10030 GJ/yr) was the highest for the CO_2 utilizing routes. Analysing raw material used it can be observed that both

the MES and AER plants (1094 t/yr) used the most CO_2 obtaining the maximum allocated environmental credit associated with CO_2 use. The HMF plant does not use CO_2 and therefore no environmental credit was given to the process. All plants analysed used comparable process water with the HCD plant using water in an electrolyser to produce H_2 which would be feed into its main reactor.

7.3 Life cycle impact assessment and interpretation

7.3.1 Plant Evaluation

Climate Change

An assessment of four formic acid producing plants was done using GaBi. The assessment gives a positive greenhouse gas emissions for the all the formic acid producing plants analysed. However the MES plant (2,120,000 kg CO_2 eqv) was found to emit the least amount of greenhouse gases about eight times lower than the HMF plant (18,400,000 kg CO_2 eqv). Interestingly a CO_2 utilizing plant had a higher global warming potential than the conventional plant analysed. This shows that the environmental credit associated with CO_2 use may not be sufficient to rival conventional processes.

Table 21: Greenhouse gases emissions from MES, AER, HCD and HMF plants (1000t/y) modelled using GaBi (Electricity from UK national grid)

Plant	**Greenhouse gases**				**GWP (Electricity from UK national Grid) (Kg CO_2 eqv)**
	Carbon dioxide (kg)	**Methane (Kg)**	**Nitrous Oxide (Kg)**	**Sulfur Hexafluoride (Kg)**	
	1 Kg CO_2 eqv	**25 Kg CO_2 eqv**	**298 Kg CO_2 eqv**	**22800 Kg CO_2 eqv**	
MES	12,220,560	28,172	273	3.19E-08	2,120,000
AER	19,396,736	45,875	449	5.05E-08	9,820,000
HCD	28,806,454	60,000	560	6.13E-08	22,200,000
HMF	17,378,430	33,374	149	1.02E-08	18,400,000

Table 21 also shows the amounts of greenhouse gases emitted by each of the formic acid producing routes. The most prevalent greenhouse gas in all the four plants analysed was CO_2 with the next potent greenhouse being methane. The HCD plant emitted the most carbon dioxide (28,806,454 kg CO_2 eqv) alongside the other greenhouse gases assessed. Emission amounts were between 44 and 83 percent that of the HMF plant. It was observed that the HMF plant emitted the least amount of sulphur hexafluoride (1.02E-08 kg CO_2 eqv) and nitrous oxide (149 kg CO_2 eqv) while the MES plant carbon dioxide (12,220,560 kg CO_2 eqv) and methane (28,172 kg CO_2 eqv). Comparing the three carbon utilizing routes, MES released the least amount of all greenhouse gases, significantly lower than the AER and HCD plants. As MES had the lowest global warming potential amongst the plants analysed and released comparably low amounts of each greenhouse gases, producing formic acid through this route in terms of climate change is beneficial over the routes analysed.

Other Environmental Burdens

Eight midpoint indicators were selected for a more detailed analysis from thirteen indicators of the ILCD methods. The indicators chosen included ozone depletion (OD, in Kg R11-Eqv), human toxicity cancer effects (HT, in CTUh), particulate matter (PM, in PM2.5 Eqv), ionising radiation (IR, in U235 Eqv), photochemical ozone formation (POF, in Kg NMVOC Eqv), acidification (AC, in Mole of H+ Eqv), freshwater europhication (FE, in Kg P Eqv) and ecotoxicity (EC, in CTUe). The remaining midpoint indicator results for the formic acid producing plants can be seen in Appendix E2. The results are displayed relative to the maximum value in each of the midpoint impact category (see Appendix E2 for raw data).

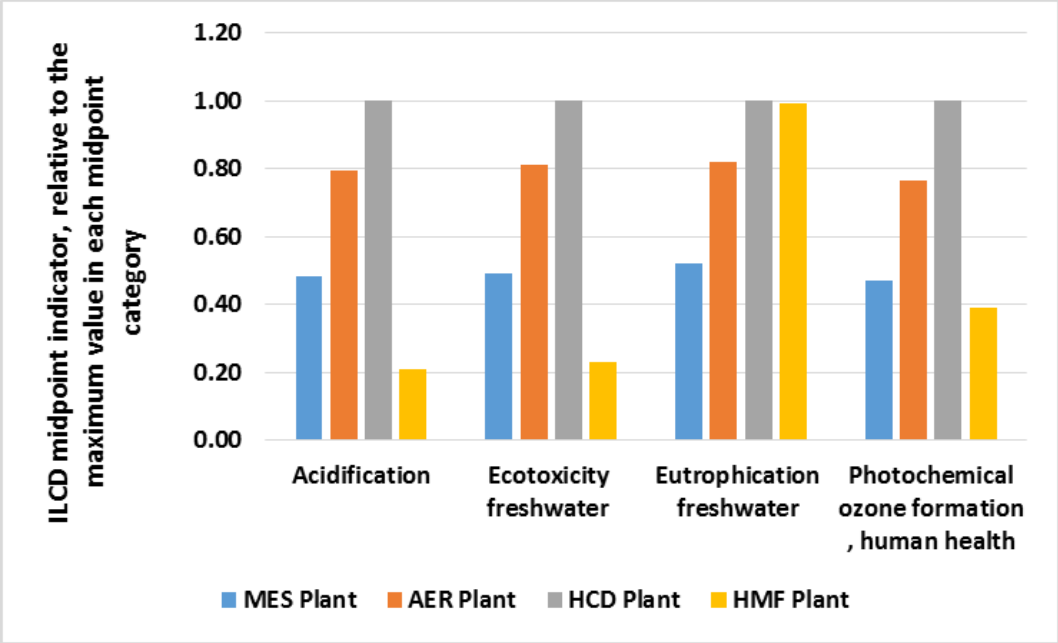


Figure 53: Life cycle environmental burdens (Acidification, ecotoxixity, eutrophication and photochemical ozone formation) of MES, AER, HCD and HMF plants using ILCD method. Results are displayed relative to the maximum value in each impact category.

Data obtained from the analysis shown in Figure 53 and Figure 54 indicates that the CO_2 utilizing HCD plant contributes the most in all the selected impact categories. It was on average more than 20 percent higher than the next worst plant for the impact categories analysed. The conventional formic acid production plant (HMF) performed better than all assessed plants in six (AC,EC, POF,HT,IR and PM) of the selected ILCD impact categories. This may be due to the use of mostly steam (19500 GJ/yr) instead of electricity (1044 GJ/yr) for energy. Steam usage in the HMF contributes 42.5 percent to AC, 17.1 percent to EC, 45.2 percent to POF, 27.9 percent to HT, 4.1 percent to IR and 34.7 to PM. The HMF plant was also seen to be marginally better than the HCD plant in the EF environmental impacts category. Using MES for the generation of formic acid had the lowest environmental impact in the EF and OD impact categories. The plant was observed to always have a relative value in each impact category less than 60 percent of the maximum which was the HCD plant. Results presented here showed than the use of CO_2 as raw material does not guarantee environmental benefit as other factors such as amount of energy needed for production should be considered. The use of an electrolyser in the HCD plant places large energy burden on the plant and if eliminated could reduce energy consumption by around 92 percent (Pérez-Fortes *et al.*, 2016). This makes the use of MES particularly attractive over other CO_2 utilizing routes as it used comparatively low amounts of energy (7183 GJ/yr) hence the relatively low

environmental impact. However in most impact category this was not sufficient to show value over the conventional process.

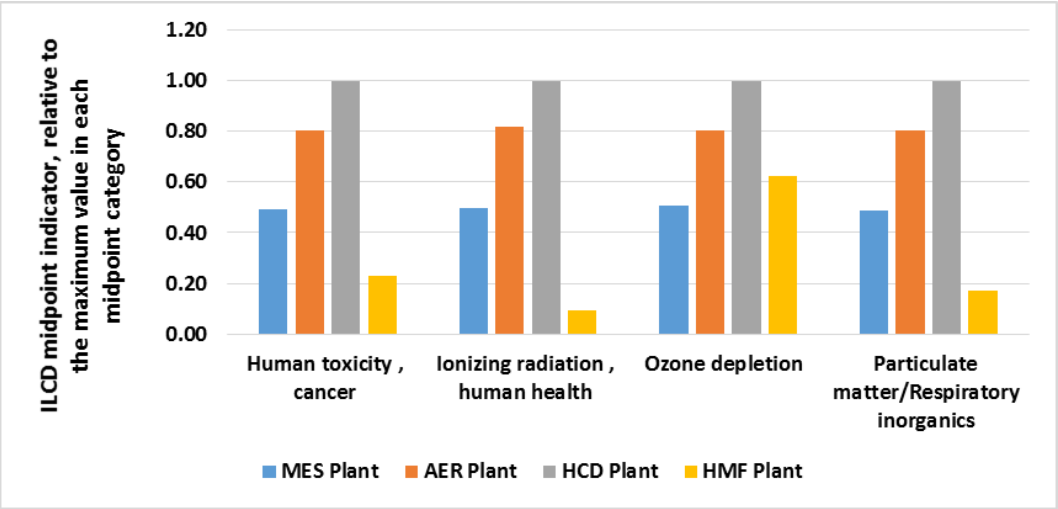


Figure 54: Life cycle environmental burdens (Human toxicity, ionizing radiation, ozone depletion and particulate matter) of MES, AER, HCD and HMF Plants using ILCD method. Results are displayed relative to the maximum value in each impact category.

Environmental impacts are further assessed in terms of raw materials. For the HMF plant carbon monoxide production using synthetic gas contributes 42 percent to EC, 84.2 percent to EF, 39.7 percent to HT and 69.4 percent to OD. It is the highest contributor in these impact categories and in all the impact category analysed was consistently above 15 percent. Comparing this with the environmental burdens of capturing CO_2 from a coal fired plant for MES. It was observed that the environmental burdens did not exceed 2.6 percent in all impact categories other than climate change. Overall in MES electricity for synthesis contributed the highest in all the impact categories. This shows that CO_2 capture energy is not the main environmental hot spot for implementation of MES technology in the manufacturing of formic acid on a commercial scale.

Looking at the market, formic acid is sold at different concentrations. These concentration vary between 85 - 99 weight percent with 85 percent formic acid concentration being the most traded (Pérez-Fortes et al., 2016). Assessing the MES plant, a change in formic acid concentration delivered to the end users would affect specifically the rectification unit of the plant. The concentration of formic acid after synthesis in the MES reactor is 45 percent hence the need for rectification. Energy required for the rectification of the chemical contributes 55 percent to climate change but only less than 4 percent in the other selected impact categories. This is because natural gas is used to supply the needed energy instead of the UK national grid. Any change in the formic acid concentration delivered to the end user by the plant would

therefore affect mainly climate change. Comparative results shown here already indicates that the MES plant is more beneficial than all the other plants analysed in this environmental category. Therefore, a concentration change should not affect results presented here. In the case of other environmental burdens due to the relatively insignificant effect of the rectification unit a change in formic acid concentration to 85 percent would not be able to make the MES plant rival the conventional plant in the AC,EC, POF,HT,IR and PM impact categories.

7.3.2 Electricity Source Evaluation

Different electricity sources were evaluated for the production of formic acid in MES, AER, HCD and HMF plants. A good mix of fossil fuel (coal, oil and gas) and renewable sources (Hydro, biogas, wind and photovoltaic) were chosen. Environmental impacts in terms of climate change and other burdens are analysed in the below subsections.

Climate Change

Table 22 shows the global warming potential associated with using fossil fuel and renewable sources to generate electricity for the MES, AER, HCD and HMF plants. The MES plant global warming potential remained positive when powered by coal (9940000 Kg CO_2 eqv) and oil (9367374 Kg CO_2 eqv) but turned negative when natural gas (-615000 Kg CO_2 eqv) was used. This is consistent with results obtained in chapter 5 as natural gas is often seen as a cleaner form of fossil fuel based electricity source and has been shown to emit less greenhouse gases than coal and oil (Jaramillo *et al.*, 2007; Burnham *et al.*, 2012). Negative global warming potential are also recorded when renewable energy sources were used. This shows that the choice of energy source for the synthesis of formic acid using biocatalysts is important. However renewable energy should be favoured as it consistently had a lower global warming potential than natural gas. Using renewable energy decreased the global warming potential in the base scenario (UK national grid) by on average more than 9,000,000 Kg CO_2 eqv while that of natural gas by 2,735,000 Kg CO_2 eqv. Comparing coal (9,940,000 Kg CO_2 eqv) and oil (9,367,374 Kg CO_2 eqv) with the base scenario (2,120,000 Kg CO_2 eqv) it was observed that there is no climate change benefit to their use. The global warming potential of the conventional route analysed (HMF plant) still remained positive even though renewable energy sources are used. This is because 71.1 percent of its global warming potential value is accounted to the steam (10,030 GJ/yr) used by the plant.

Table 22: Global warming potential from the eight different electricity sources analysed for production of 1000 tonnes formic acid using MES, AER, HCD and HMF plants

Plant	GWP (Kg CO_2 eqv)							
	Coal	**Gas**	**Oil**	**Nuclear**	**Hydro**	**Biogas**	**Wind**	**Photo voltaic**
MES	9940000	-615000	9367374	-9600000	-9550000	-5780000	-9581263	-8686566
AER	22700000	5308619	21797173	-9530645	-9453813	-3220000	-9500000	-8023609
HCD	37931962	16755618	36786615	-1271750	-1178412	6390000	-1240000	559000
HMF	19500000	18032956	19448326	16759161	16765756	17300000	16800000	16900000

Looking at the HCD plant it was observed to have negative global warming potential when nuclear (-1271750 Kg CO_2 eqv), hydro (-1178412 Kg CO_2 eqv) and wind (-1240000 Kg CO_2 eqv) are used. However, it had a positive global warming potential when biogas (6390000 Kg CO_2 eqv) and photovoltaic (559000 Kg CO_2 eqv) are used as electricity sources. This was however between 60 and 98 percent lower than values seen for fossil fuels usage. Results outlined here show that there is climate change benefit of using renewable energy source to power formic acid synthesis plants that utilizes CO_2.

Other Environmental Burdens

For the assessment of other environmental burdens associated with producing formic acid from MES using other sources of electricity, the same impact categories as used above was employed. The complete midpoint results for MES and the other two CO_2 utilizing plants (AER and HCD) are shown in appendix E2.

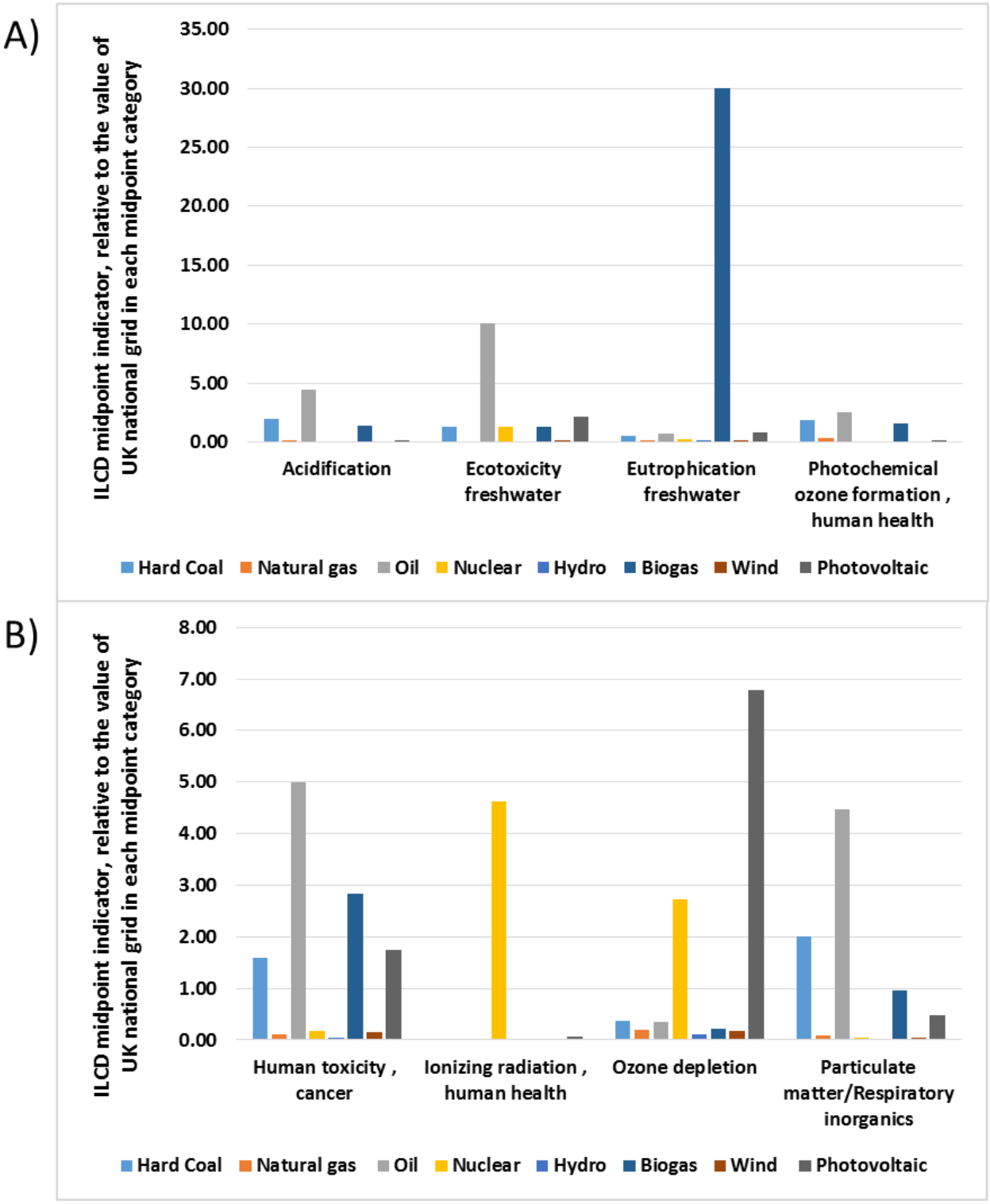


Figure 55: Life cycle environmental burdens of the MES plant for eight different electricity sources using ILCD method. A) Acidification, ecotoxicity, eutrophication and photochemical ozone formation B) Human toxicity, ionizing radiation, ozone depletion and particulate matter. Results are displayed relative to the value of the UK national grid in each impact category.

Figure 55A and Figure 55B shows the results for other environmental impact burdens when electricity source differed from that of the base scenario (UK national grid). It was observed that for all the impact categories using coal, oil, nuclear, biogas and photovoltaic means of electricity generation was higher than the base scenario for the MES plant. Coal and oil had more negative environmental impact in five (AC, EC, FE, HT, PM and POF) of the eight selected categories. Nuclear, biogas and photovoltaic also had more negative impact in three (EC, HT and PM), one (FE) and three (EC, HT and OD) midpoint indicators respectively. Natural gas and the remaining renewable energy sources (Hydro and wind) consistently had lower negative environmental impact than the base scenario. However in the case of hydro electricity generation finite resource (water) usage is an issue earning a more negative environmental impact in the resource depletion impact category (See appendix E2). Results obtained here are comparable to the other two CO_2 utilizing plants (AER and HCD) analysed (see appendix E2). Electricity generation by wind turbines shows good promise when both climate change and other environmental burdens are assessed. The technology was consistently lower than the base scenario for the CO_2 utilizing plants in all ILCD impact categories.

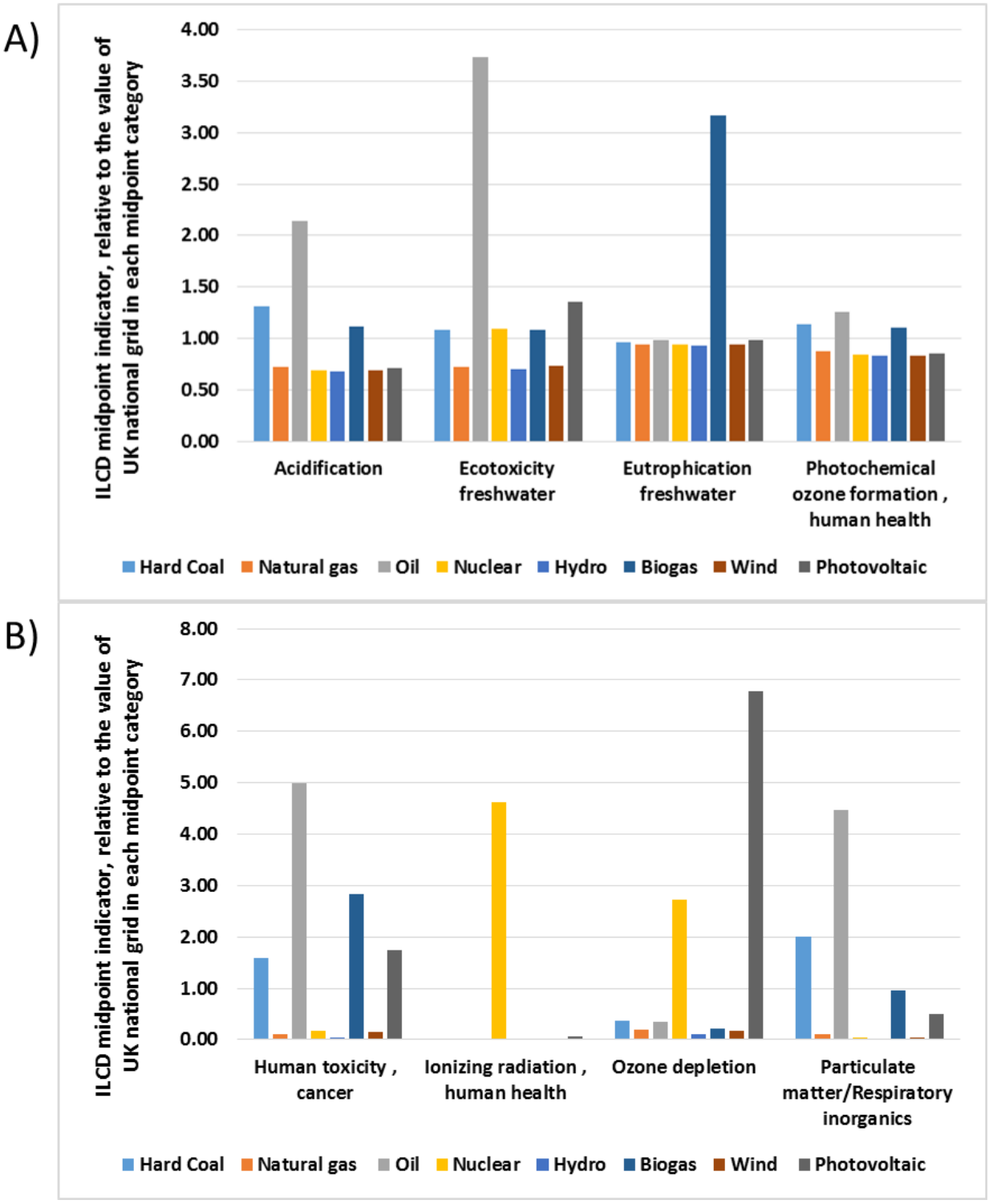


Figure 56: Life cycle environmental burdens of the HMF plant for eight different electricity sources using ILCD method. A) Acidification, ecotoxixity, eutrophication and photochemical ozone formation B) Human toxicity, ionizing radiation, ozone depletion and particulate matter. Results are displayed relative to the value of the UK national grid in each impact category.

The same impact category was used to assess the other environment burdens of using different electricity sources on the conventional plant (HMF). It was observed that coal and oil was higher than the base case in five of the eight selected impact categories. Nuclear, biogas and photovoltaic have more environmental burdens in three, one and three impact categories respectively. This showed similar trend to what was observed for the CO_2 utilizing plants. However in the AC, EC, FC and POF impact categories environmental burdens did not go lower than 60 percent the value of the base scenario differing from what was observed in the MES plant. Generation of electricity was also found to be lower than the base scenario in all ILCD impact categories. Wind energy usage for formic acid production has been shown to be environmentally better than the UK national grid for both CO_2 utilizing and conventional plants. UK is an island nation therefore energy from both onshore and offshore wind turbines can be relatively easy to harness when compared to landlocked countries. However offshore wind farms should be favoured as it has been proven marginally beneficial in terms of global warming (Kaldellis and Apostolou, 2017).

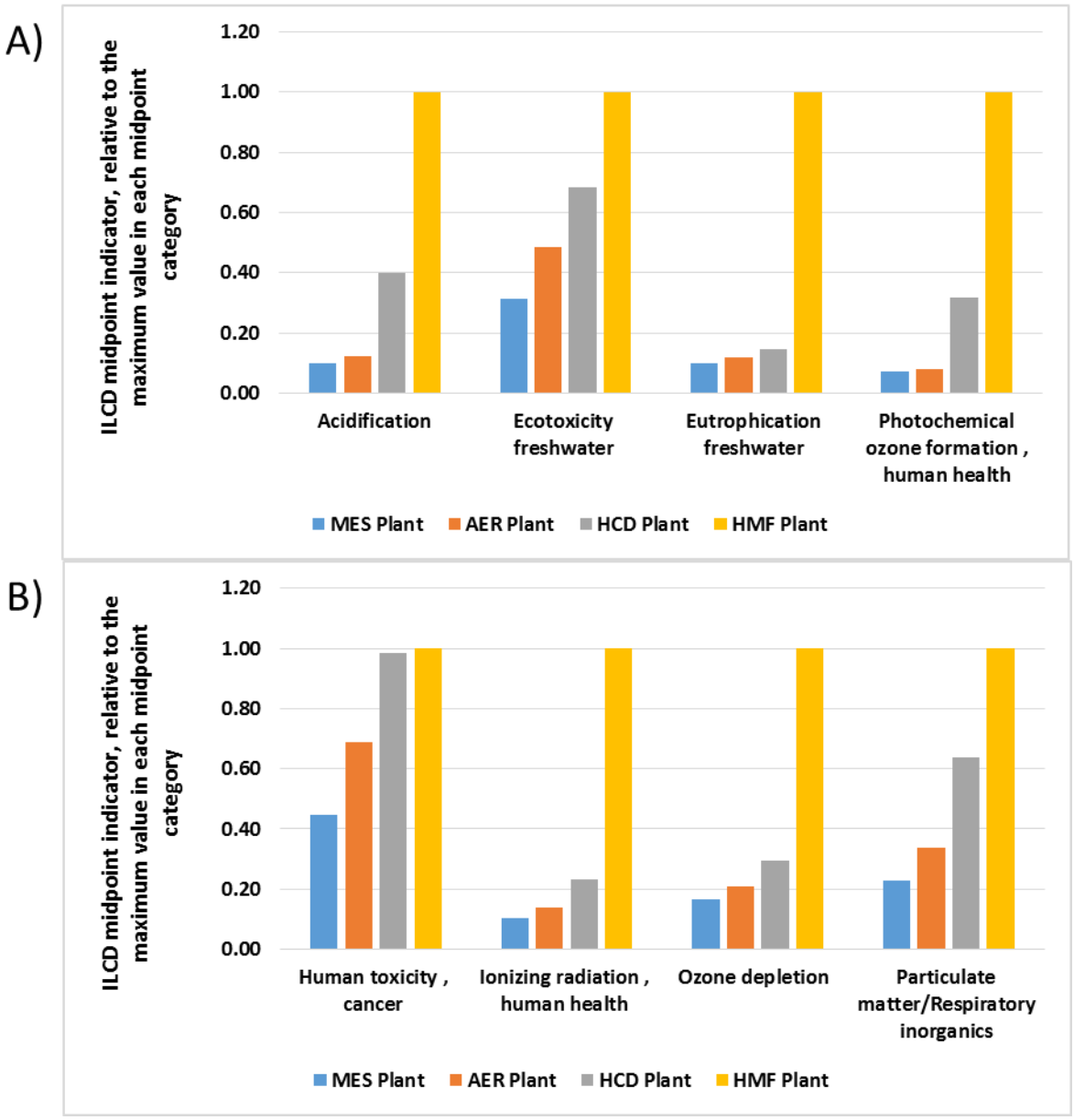


Figure 57: Life cycle environmental burdens of the MES, AER, HCD and HMF plant for eight different electricity sources using ILCD method. A) Acidification, ecotoxixity, eutrophication and photochemical ozone formation B) Human toxicity, ionizing radiation, ozone depletion and particulate matter. Results are displayed relative to the maximum value in each impact category.

Figure 57 compares the four plants analysed if electricity used was generated using wind turbines. Values displayed are relative to the maximum value in each impact category. It was observed that wind energy usage relegated the HMF plant to having comparatively the worst impact on the environment than all CO_2 utilizing routes. This could be because the impact of a change to a more environmentally friendly source of electricity is relatively small for the HMF plant as steam is mostly used. The HCD plant which previously had the highest impact in most categories is on average 55 percent better when wind energy is used instead of the base scenario. These analysis and results suggests that MES should be deployed on an industrial level favouring electricity generated from wind for synthesis.

7.4 Conclusion

Life cycle assessment of four types of formic acid production routes, a MES, an AER, a HCD and HMF plant was developed in this study. The use of HMF for the production of formic acid was shown to be environmentally beneficial than the three CO_2 utilizing technologies analysed when electricity used was generated from the UK national grid. Analyses of other sources of energy showed that renewable energy helps reduce climate change in both CO_2 utilizing and conventional plants. However in the case of biogas and photovoltaic energy generation environmental burdens shifted to the EC and OD impact categories. Generation of electricity through wind turbines is of particular interest as it had the ability to reduce environmental burdens in all ILCD impact categories when compared with the UK national grid. This helped mitigate the comparative negative impact of deploying MES, AER and HCD on a large scale. Synthesis of formic acid through MES using wind generated electricity provides huge benefits and should be employed when MES is industrially applied.

Chapter 8: Conclusion and future work

The main aim of this thesis was to environmentally evaluate and empirically investigate the synthesis of useable chemicals from CO_2 through MES. The aim of this research was achieved by satisfying the objectives set out at the beginning of this study. The main objectives of each chapter are outlined below;

- To evaluate the performance of a stable cathodic biofilm in BES to synthesize products over a long period of time.
- To evaluate the energy requirement of scaling up the MES process.
- To assess the global warming potential of producing chemicals using MES.
- To assess the environmental sustainability of producing chemicals using MES when the United Kingdom national grid is used as energy source.
- To compare the environmental effects of producing formic acid using MES with that of both abiotic electrochemical reduction and conventional routes.

The experimental part of this thesis used mixed culture to assess bio production in MES using anaerobic sludge as inoculum. Different poise potentials and temperatures were assessed in order to determine the effects of changes to these parameters on chemical synthesis. Environmental impacts of producing chemicals through MES were also examined by modelling a simulated industrial plant. This was done to help reveal environmentally beneficial products that should be targeted when MES is commercially scaled. Acetic acid, propionic acid, formic acid, ethanol and methanol manufacturing MES plants were considered using two sources of energy (natural gas and UK national grid), one at a time for a ten year plant life. This gave specific and detailed scenarios that allowed comparison of the environmental impacts. Below are outlined the major findings addressing the research objectives summarized according to chapters provided in the thesis.

Chapter 4 “Investigation of bioproduction using mixed culture” aimed to develop a stable microbial electro synthesis performing biofilm from mixed culture. Enrichment of a bio cathode from anaerobic sludge operated for 288 days in batch mode was discussed in this chapter. This work concentrated on monitoring the effects of changes to poise potential and temperature on a mixed culture biofilm. Poise potential was varied intermediately between -

797mV vs Ag/AgCl and -1397mV vs Ag/AgCl with two temperatures (27 ^{O}C and 40^{O}C) also used. Acetic acid, propionic acid, formic acid, isobutyric acid, methane and hydrogen were detected at the applied conditions. The maximum rate of producing these chemical was 3633 µM/day at cathode potential of -1397mV vs Ag/AgCl and temperatures of 40^{o}C. Overall the reactors were able to consistently use CO_2 to synthesize high economic significant products.

Chapter 5 "Energy and global warming assessment of using carbon dioxide in microbial electrosynthesis" sought to assess the net energy and CO_2 emissions associated with the production of 1000 tonnes per year of acetic acid, propionic acid, formic acid, ethanol and methanol. Energy gained and global warming potential was used to compare the simulated plant with conventional methods. Formic acid offered environmental benefits when CO_2 assumed to be obtained from a coal fired plant is used as substrate. Synthesizing of the chemical using MES proved more environmentally beneficial in terms of global warming than conventional processes. This was mainly due to the low energy demand especially for rectification of the chemical from water. These findings reveal that MES as a technology has the ability to decrease greenhouse gas emissions for formic acid production if deployed on a large scale.

Chapter 6"Environmental assessment of microbial electro synthesis" aimed to assess other environmental burdens than global warming for MES plants capable of producing 1000 tonnes per year of acetic acid, propionic acid, formic acid, ethanol and methanol. These was also compared with synthesis using abiotic catalysts were applicable. The results show that formic acid production have relatively low environmental impacts in the various environmental categories. The low environmental impacts was mainly due to the lower energy requirement for its reactor and rectification unit. The reduction of greenhouse gas emissions due to MES of formic acid can only be achieved at high conversion and faradaic efficiencies using electricity from UK national grid. However there is always a trade-off in other environmental burdens than climate change. Depending on the product generated, conversion and faradaic efficiencies there is significant climate change benefit of using MES for synthesis of chemicals. It was also discovered that choice of catalyst for synthesis is important as biotic catalyst performed environmentally better that abiotic catalysts when compared. Overall production of formic acid should be targeted as it provided the best environmental benefits for MES applied industrially.

Chapter 7"Environmental assessment of formic acid manufacturing routes" aimed to compare the environmental sustainability of producing formic acid using MES and other manufacturing routes. Two other CO_2 utilizing routes and the main conventional means of producing the chemical was evaluated using life cycle assessment. Results show that formic acid production using methyl formate hydrolysis was environmentally beneficial than the three CO_2 utilizing technologies analysed when electricity used was generated from the UK national grid. Renewable energy should be employed as it helped mitigate climate in both CO_2 utilizing and conventional plants. Generation of electricity through wind turbines is of particular interest as it had the ability to reduce environmental burdens in all impact categories analysed when compared with the UK national grid. This helped mitigate the comparative negative impact of deploying MES, AER and HCD on a large scale. Synthesis of formic acid through MES using wind generated electricity provides huge benefits and should be employed when MES is industrially applied.

Future research

The following recommendations are highlighted for future work

- The effect of different parameters on bioproduction was analysed using mixed culture for a lab scale experimental setup. Experiments on larger scale MES reactors should be undertaken to gain valuable insight on the behaviour of the bio cathode scaled up. This would provide more accurate data for future environmental assessments.

- Recently MES have been shown to be capable of producing higher alcohols such as isobutanol, n-butanol and n-hexanol (Vassilev *et al.*, 2018). Comparative environmental analysis should be undertaken on these product. This would give insight on any environmental benefits of using MES to synthesize them.

- Biotic and abiotic standalone reactors were compared in this study. Copper was selected as the heterogenous abiotic catalyst because of its ability to produce a wide range of chemicals like MES. Environmental analysis should be carried out on other types of abiotic catalysts.

- This study analysed energy yield and global warming potential of acetic acid, propionic acid, formic acid, ethanol and methanol. However, only formic acid was selected for further analysis and compared with conventional process. Environmental impact assessment should be conducted on the remaining products to ascertain any environmental benefit other than climate change when compared with conventional processes.

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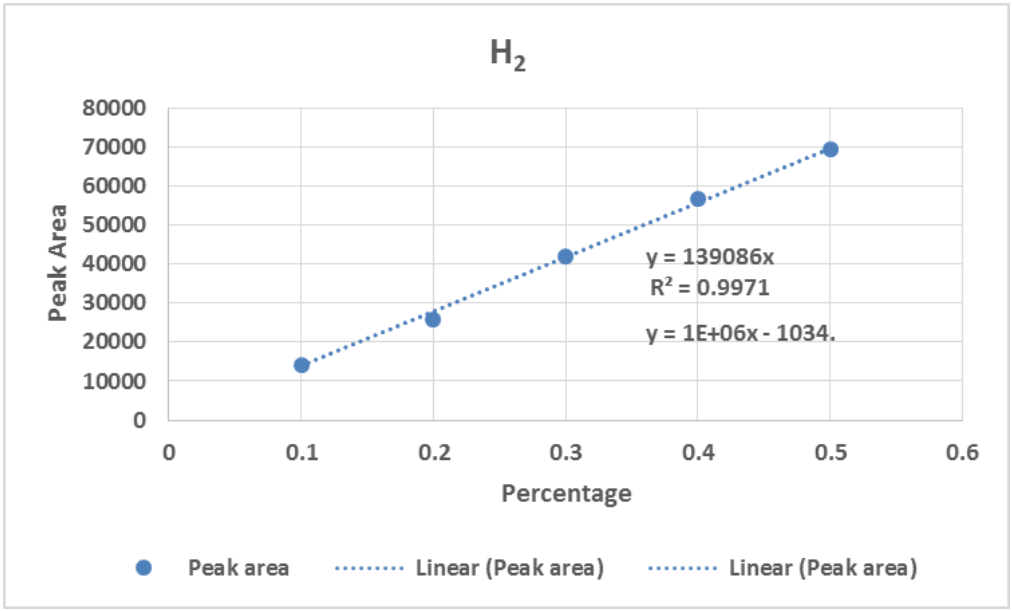
Chapter 9 Appendixes

A1- Wolfe vitamin and mineral solution

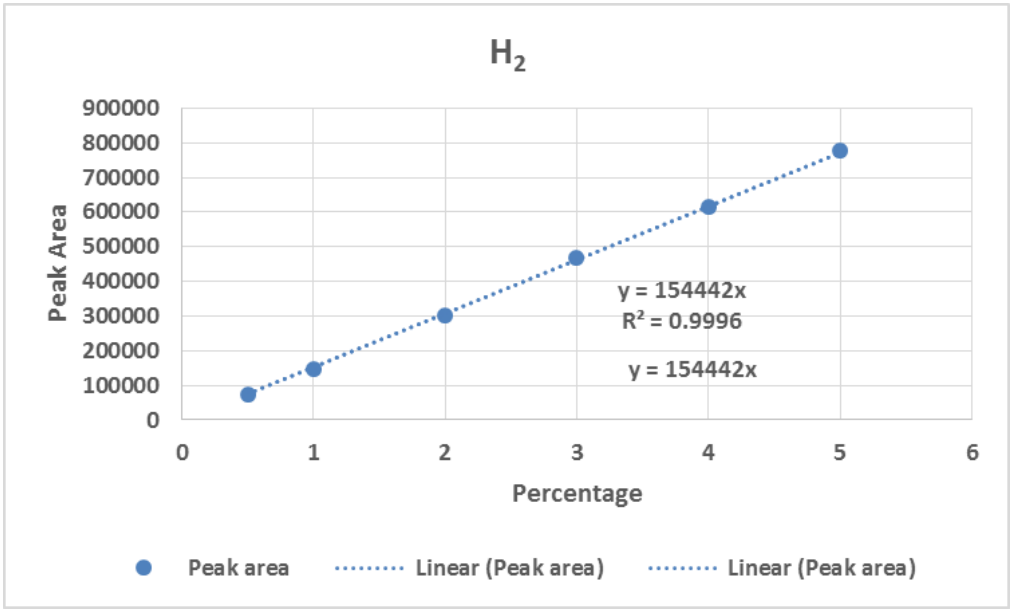
Wolfe Vitamin solution stock composition per litre

S/N	Chemical	Mass (mg)
1	Pyridoxine HCL	10.00
2	p-Aminobenzoic acid	5.00
3	Lipoic acid	5.00
4	Nicotine acid	5.00
5	Riboflavin	5.00
6	Thiamine HCL	5.00
7	Calcuim DL-pantothenate	5.00
8	Biotin	2.00
9	Folic acid	2.00
10	Vitamin B12	1.00

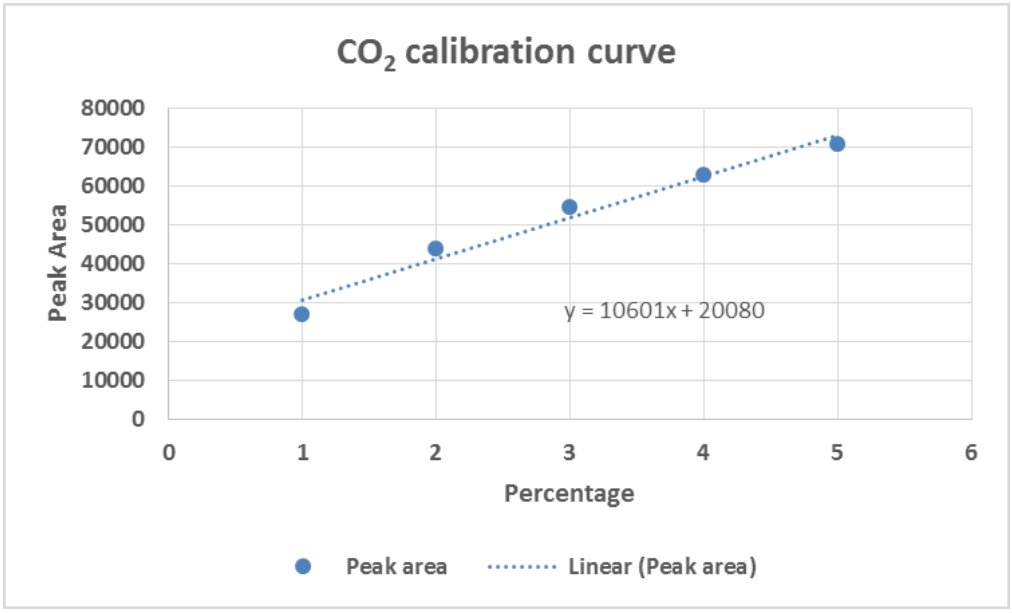
A2- Gas Calibration Curve



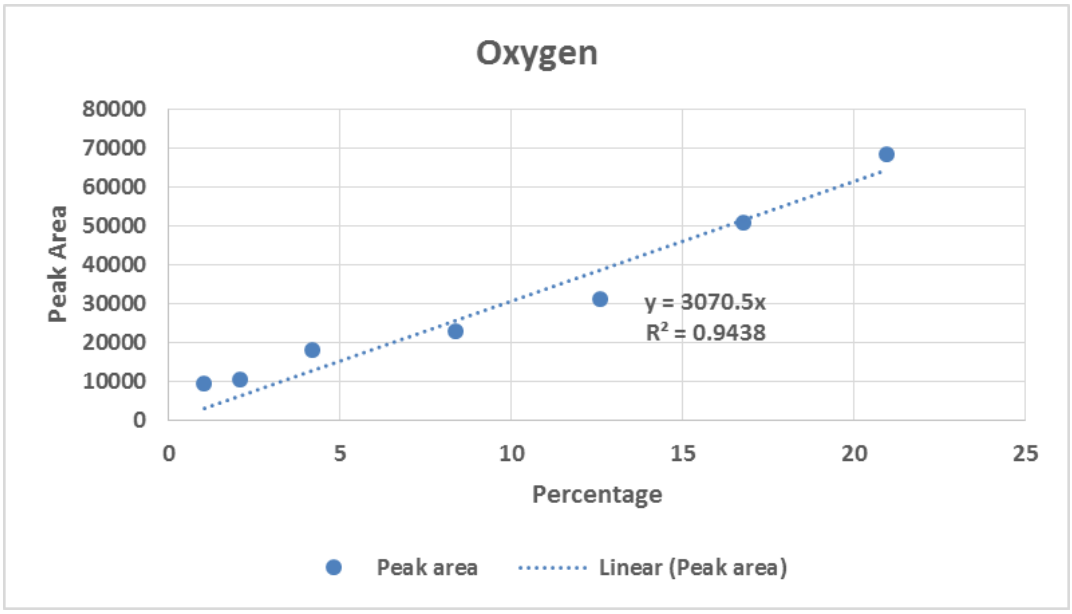
Calibration Curve of Hydrogen (0 -0.6 percent)



Calibration curve of Hydrogen (0-6 percent)



Calibration curve of Carbon dioxide



Calibration curve of Oxygen

A3- Details and assumptions used for the environmental analysis

Process Units	Details and assumptions	Equations	References
Mixer	Tank size (Varies with product); 20 minutes required to mix each batch; 3 blade hydrofoil impellers used.	Impeller Power= Power number X density of fluid X rotational speed^3 X Diameter^5	(McGraw-Hill Higher Education, 2003; Deglon and Meyer, 2006)
Microbial electrosynthesis (MES) reactor	4 membrane-less reactor reactors; Total electrode size 775.2 Kg per 1000 tonne production (based on lab scale experiments); titanium wires used as contactors; Negligible biofilm detachment; Biofilm thickness 25 microns; Wastewater strength 4000mg COD/L; Bacteria Effluence 2-5%.	Q =mcΔT (Assumption: c=4.2 J/g, mass of medium (m) varies with product) Q = ((mol × no of e^- × C) × 1.31 × E) × 0.000278 (Assumptions= 69% Coulombic efficiency for product formation, E is the applied potential, Units= kWh)	(McGraw-Hill Higher Education, 2003; Reda *et al.*, 2008; Marshall *et al.*, 2013; CEAE, 2014; Blanchet *et al.*, 2015)
Gas separator/ membrane	Membrane used for separation; gas contains CO_2 and O_2; CO_2/O_2 selectivity assumed to be 50; Single stage membrane separation; Capture efficiency 99.9 %; Simulation results shows 0.4GJ is needed to capture 30 mol% CO_2 from flue gas; Downstream vacuum pump is used instead of upstream compression.		(Bounaceur *et al.*, 2006; Brunetti *et al.*, 2010)
Rectification	Rectification unit simulated using Aspen Plus V86	Aspen Software, (McGraw-Hill Higher Education, 2003)	Aspen Plus V86 Software; (Li and Bai, 2012)
Storage tank	Tank assumed to hold Two batches worth of product (20 tonnes); assuming tank is always above melting point of product	(McGraw-Hill Higher Education, 2003)	(McGraw-Hill Higher Education, 2003)
Packaging	Steel drums (208L each); Sheet thickness (mm) (1.2/0.9/1.2); Weight 36.7 Lbs(16.6 kg)		(Rietveld and Hegger, 2014)
CO_2 capture	From coal fired plant; 0.1758 GJ/ tonne of CO_2 captured		(Bhown and Freeman, 2011)
Transportation to MES plant	Distance 30km; Transportation via trucks (capacity 60 tonnes); total number of trips varies with product		(SunEarthTools, 2016)
CO_2 Compression and Storage	CO_2 was assumed to be obtained at 25^{o}C and 1 atm from flue gas; Tank assumed to hold 60 tonnes of CO_2 (truck capacity); Tank size 63m^3.	Work = pressure * Volume * in [initial pressure/ final pressure]	
Pump to reactor from mixer	Flowrate assumed to be 0.5 tonnes/ minute; Pumping time estimated to be approximately 4 minutes per batch; Pump efficiency assumed to be 100 percent	Power= flowrate * density of fluid * gravity * differential head	(TheEngineering ToolBox, 2016)
Pump to intermediate storage tank from reactor	Assumed constant flow rate throughout the year; pump running for 8000 hours a year;	Power= flowrate * density of fluid * gravity * differential head	(TheEngineering ToolBox, 2016)

	flowrate is 30m^3/hr		
Pump to rectification unit from intermediate storage tank	Assumed constant flow rate throughout the year; pump running for 8000 hours a year; flowrate is 0.3m^3/hr	Power= flowrate * density of fluid * gravity * differential head	(TheEngineering ToolBox, 2016)
Pump to storage tank from rectification unit	Assumed constant flow rate throughout the year; pump running for 8000 hours a year; flowrate is 0.12m^3/hr	Power= flowrate * density of fluid * gravity * differential head	(TheEngineering ToolBox, 2016)
Chemicals Purchased	Sodium Bicarbonate (2.5g/L) Sodium Dihydrogen Phosphate (0.6g/L) Ammonium chloride (0.25g/L) Magnesium chloride (0.212g/L) Potassium chloride (0.1g/L) Calcium chloride (0.03g/L); Vitamin and mineral solution negligible		(Cefic, 2014; Eurostat, 2014)
Transportation to Incinerator	Distance 50km; Transportation via petrol car; total number of trips 2		(SunEarthTools, 2016)
Incineration	Using UK Municipal solid waste as reference (10MJ/kg generated)		(DEFRA, 2013)
Steel Equipment	Steel assumed to be made from 100 % scrap metal at 1600^{o}C; energy required to produce is 1.289 GJ/tonne		(Fruehan *et al.*, 2000a)

A4- Equations used for the MES plant unit operations

Process Units	Equations
Mixer	$E_{impeller} = Power\ Number * Fluid\ Density * Speed^3 Diameter^5$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{impeller}$
MES reactor	$E_{Temp\ Change} = Medium\ Mass * Specific\ Heat\ Capacity * Temperature\ change$ $E_{reaction} = (moles\ involved * number\ of\ electrons * Faradays\ constant * 1.31 * Applied\ potential)$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * (E_{Temp\ Change} + E_{reaction})$
Gas separator/ membrane	$E = 0.4 \frac{GJ}{Tonne} * Tonne\ of\ gas\ separated$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E$
Rectification unit	Simulated using Aspen Plus V86
Stainless steel equipment	$E = 1.289 \frac{GJ}{Tonne} * Steel\ Density * Steel\ Volume$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E$
Packaging	$E = 20 \frac{GJ}{Tonne} * Container\ Number * Weight\ per\ container$ $\text{GW} = 0.03247721 \frac{\text{Tonnes}}{\text{GJ}} * Container\ Number$
CO_2 capture	$E = 0.1758 \frac{GJ}{Tonne} * Tonne\ of\ CO2\ captured$ $GW = -(Tonne\ of\ CO2\ captured)$
Transportation to MES plant	$E_{transportation} = (Trips\ per\ year * Distance *$ Fuel consumed $*$ Fuel energy) $E_{compression} = Tank\ Pressure * Tank\ Capacity * \ln(\frac{Initial\ Pressure}{Final\ Pressure})$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * (E_{Transportation} + E_{compression})$
CO_2 Compression and Storage	$E_{compression} = Tank\ Pressure * Tank\ Capacity * \ln(\frac{Initial\ Pressure}{Final\ Pressure})$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{compression}$
All Plant Pumps	$E_{Pump} = flowrate * density\ of\ fluid * gravity * differential\ head$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{Pump}$
Chemicals Purchased (*vitamins and minerals are assumed negligible)	$E_{chemicals} = 7.0116289 \frac{GJ}{Tonne} * Tonne\ of\ Chemicals\ used\ per\ year$ $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{chemicals}$

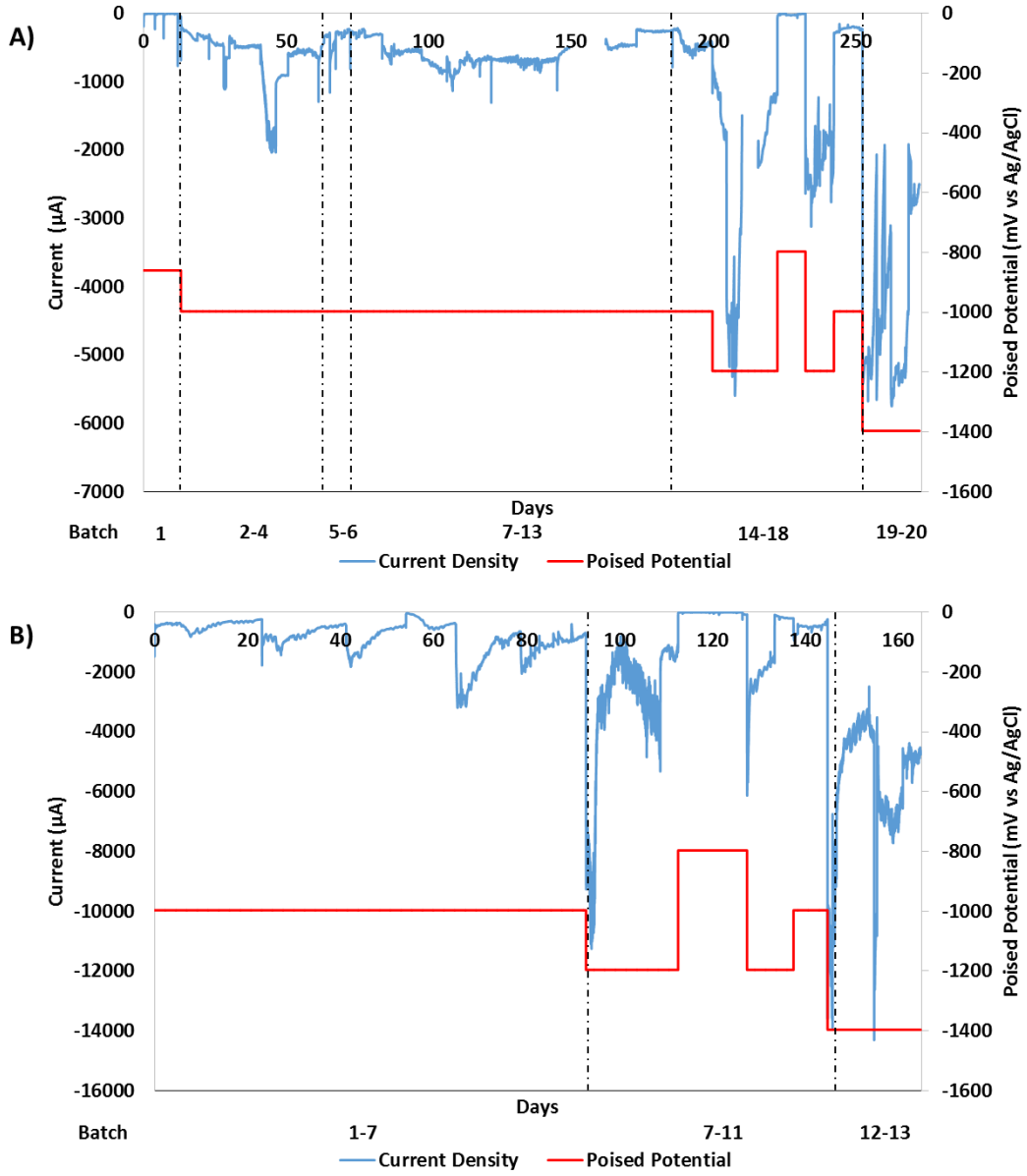
Transportation to Incinerator	$E_{Transportation} = (Trips\ per\ year * Distance *$ Fuel consumed $*$ Fuel energy $\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{Transportation}$
Incineration	$E_{Incineration} = 10 \frac{GJ}{Tonne} * Tonne\ Bacteria\ Effluence$ $\text{GW} = \text{Tonne Bacteria Effluence} * 1 \frac{Tonne\ CO2\ eqv}{Tonne\ Waste}$

A5- Composition of medium used for environmental analysis

Composition of electrolyte	**Formula**	**Concentration (mg/L)**
Sodium bicarbonate	$NaHCO_3$	2500
Sodium phosphate	$NaH_2PO_4 \cdot H_2O$	600
Ammonium chloride	NH_4Cl	250
Magnesium chloride	$MgCl_2$	212
Potassium chloride	KCl	100
Calcium chloride	$CaCl_2$	30
Composition of vitamin solution		
Biotin (d-biotin)	$C_{10}H_{16}N_2O_3S$	0.002
Folic acid	$C_{19}H_{19}N_7O_6$	0.002
Pyridoxine HCl	$C_8H_{12}ClNO_3$	0.010
Riboflavin	$C_{17}H_{20}N_4O_6$	0.005
Thiamine HCl 1.0 H2O	$C_{18}H_{18}Cl_2N_4OS$	0.005
Nicotinic acid	$C_6H_5NO_2$	0.005
d-pantothenic acid, hemicalcium salt	$C_9H_{16}NO_5$. 1/2Ca	0.005
Vitamin B12	$C_{63}H_{88}CoN_{14}O_{14}P$	0.0001
p-aminobenzoic acid	$C_7H_7NO_2$	0.005
Thioctic acid	$C_8H_{14}O_2S_2$	0.005
Composition of mineral solution		
Nitrilotriacetic acid (dissolve with NaOH to pH 8)	$C_6H_9NO_3$	1500
Magnesium sulfate heptahydrate	$MgSO_4$ $7H_2O$	3000
Manganese sulfate monohydrate	$MnSO_4$ H_2O	500
Sodium chloride	NaCl	1000
Ferrous sulfate heptahydrate	$FeSO_4$ $7H_2O$	100
Calcium chloride dihydrate	$CaCl_2$ $2H_2O$	100
Cobalt chloride hexahydrate	$CoCl_2$ $6H_2O$	100
Zinc chloride	$ZnCl_2$	130
Cupric sulfate pentahydrate	$CuSO_4$ $5H_2O$	10
Aluminum potassium disulfate dodecahydrate	$AlK(SO_4)_2$ $12H_2O$	10

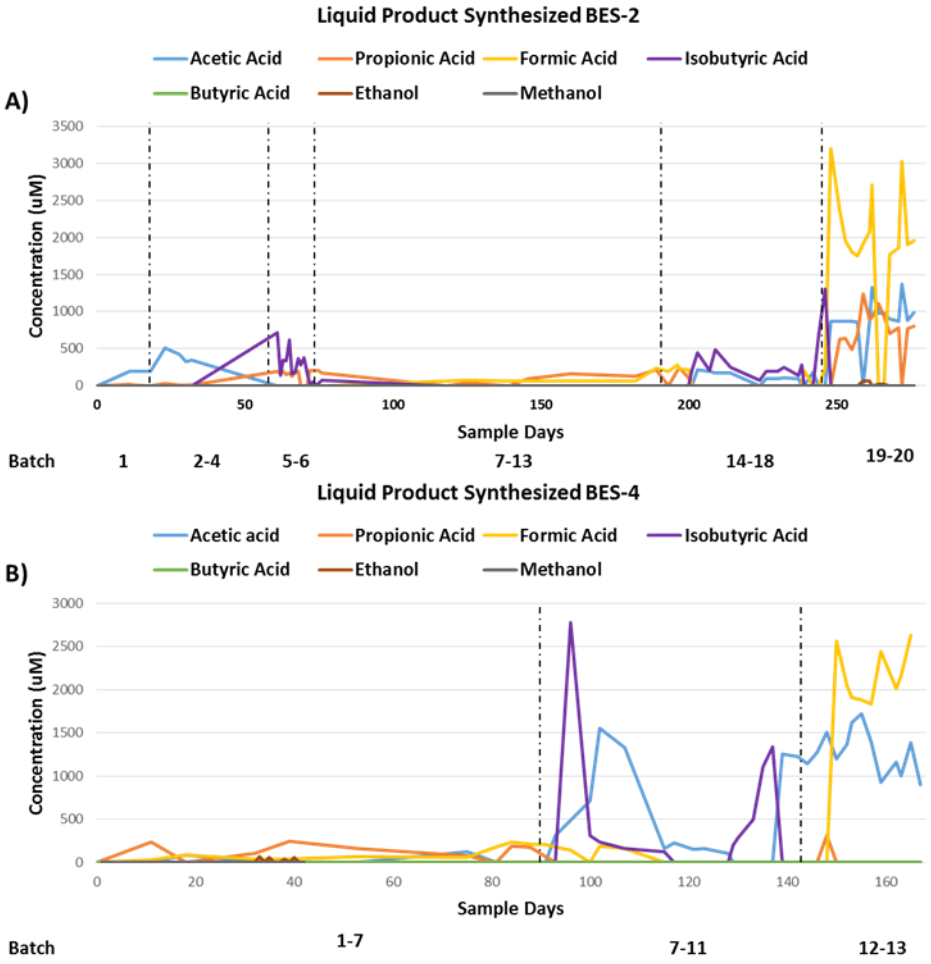
Boric acid	H_3BO_3	10
Sodium molybdate dihydrate	Na_2MoO_4 $2H_2O$	25
Nickel chloride hexahydrate	$NiCl_2$ $6H_2O$	24
Sodium tungstate	Na_2WO_4 $2H_2O$	25

B1- Current Density and Poised Potential for BES-2 and BES-4



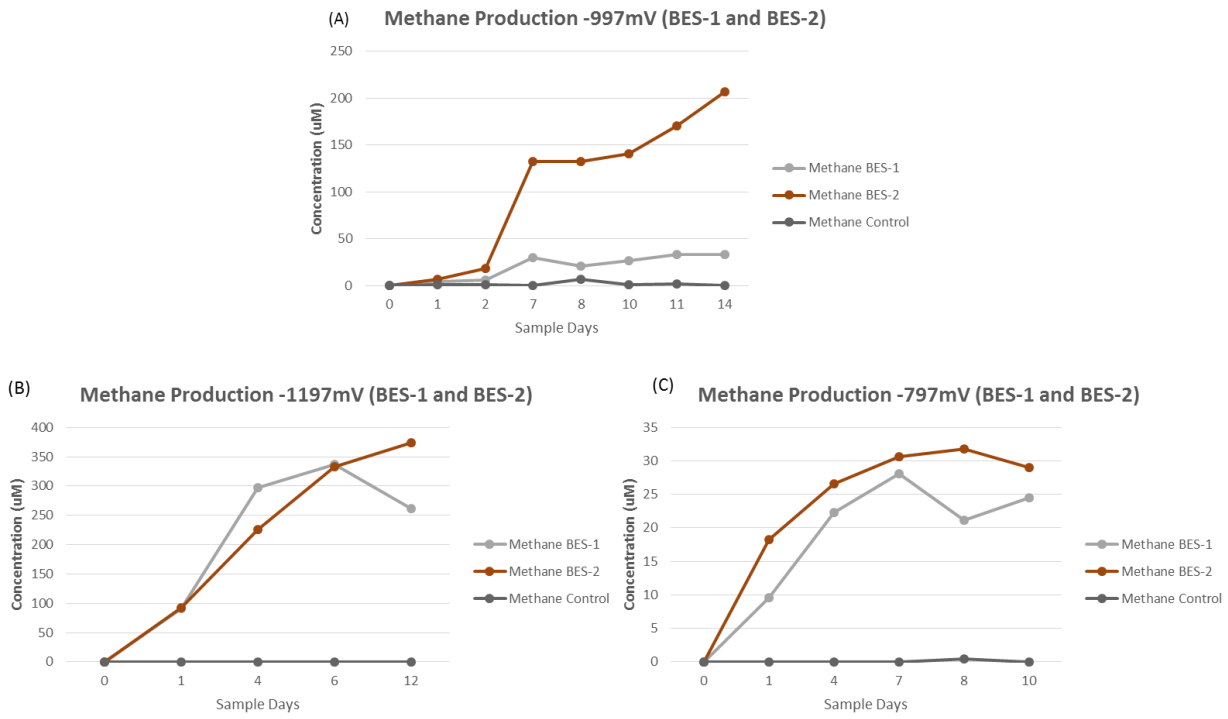
Current Density and Poised Potential for A) BES-2 (290 days) and B) BES-4 (172 days)

B2- Liquid Products Synthesized for BES-2 and BES-4

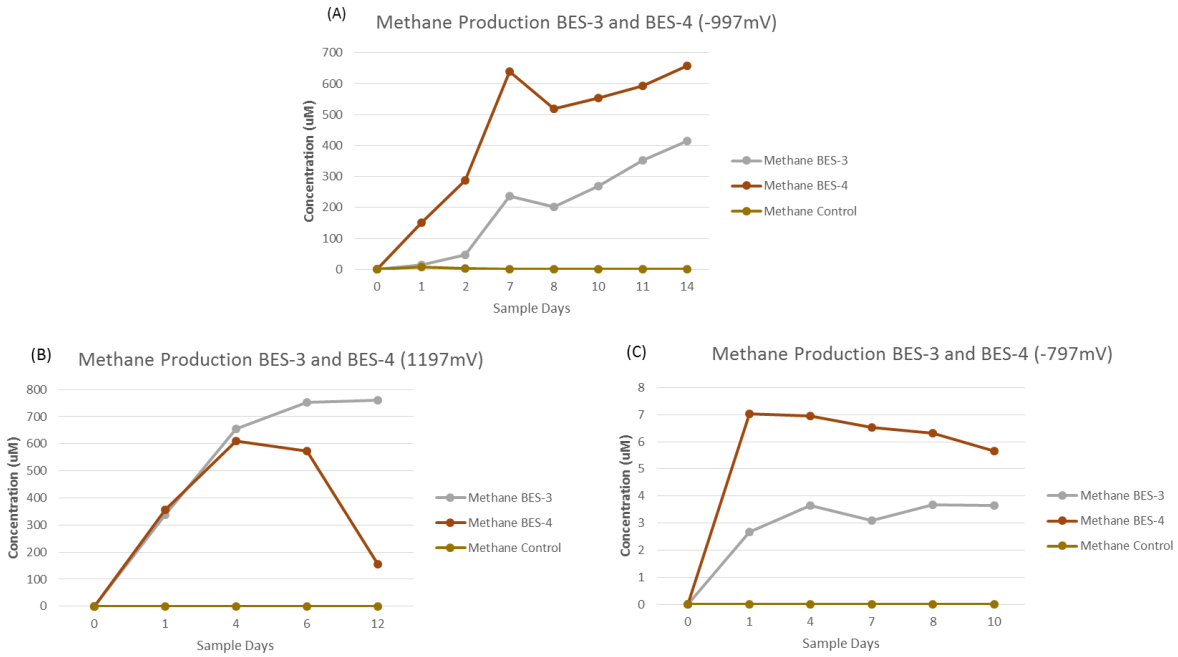


Liquid product synthesized from A) BES-2 and B) BES-4

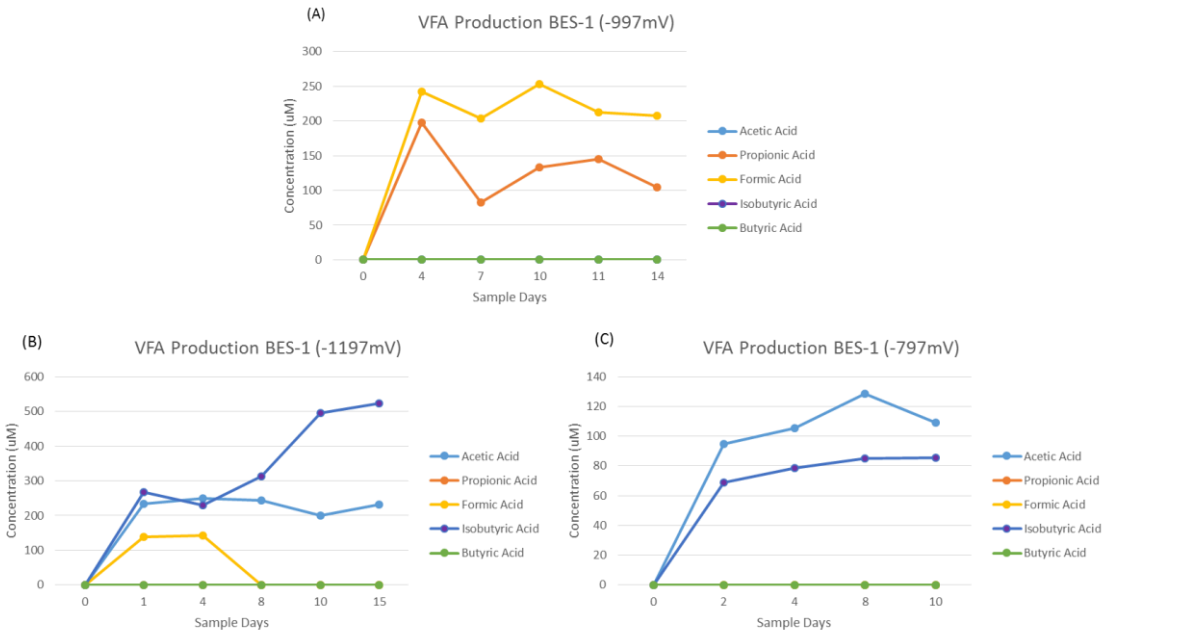
B3- Synthesis variations due to poise potential change



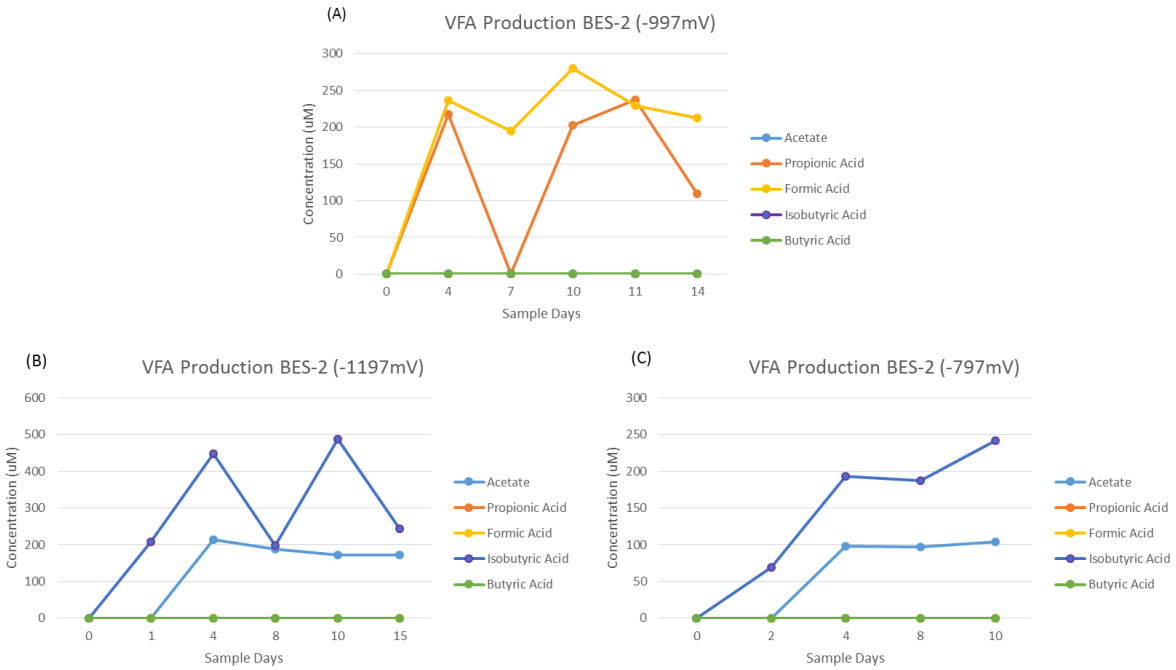
Methane detected in BES-1 and BES-2 A) -997mV B) -1197mV C) -797mV



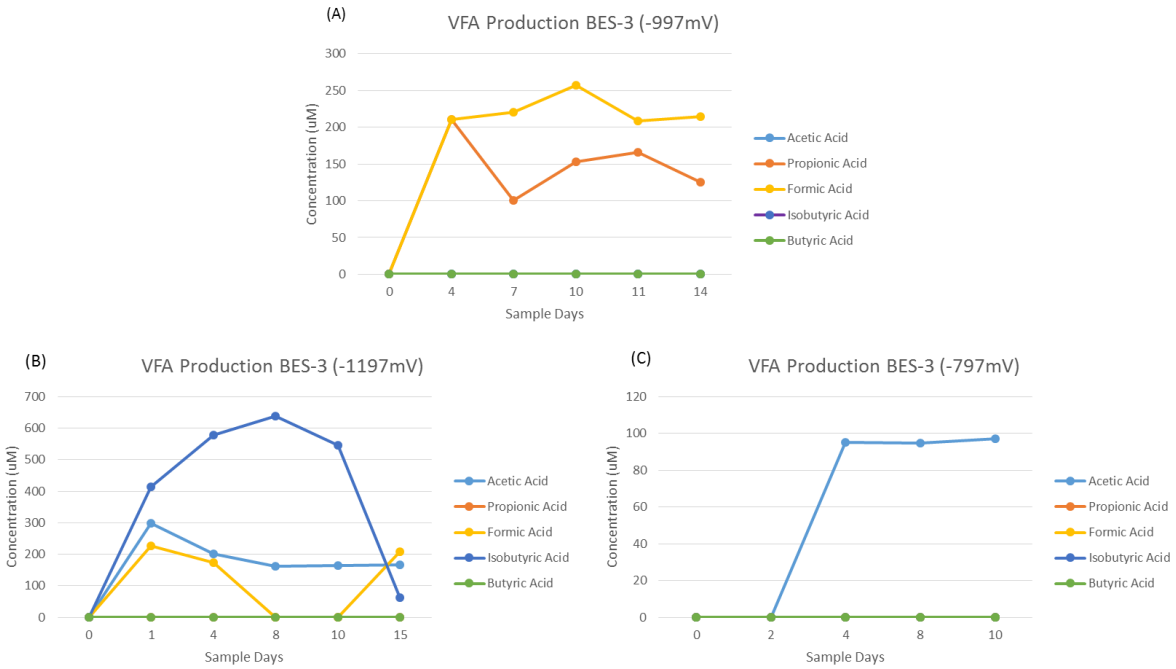
Methane detected in BES-3 and BES-4 A) -997mV B) -1197mV C) -797mV



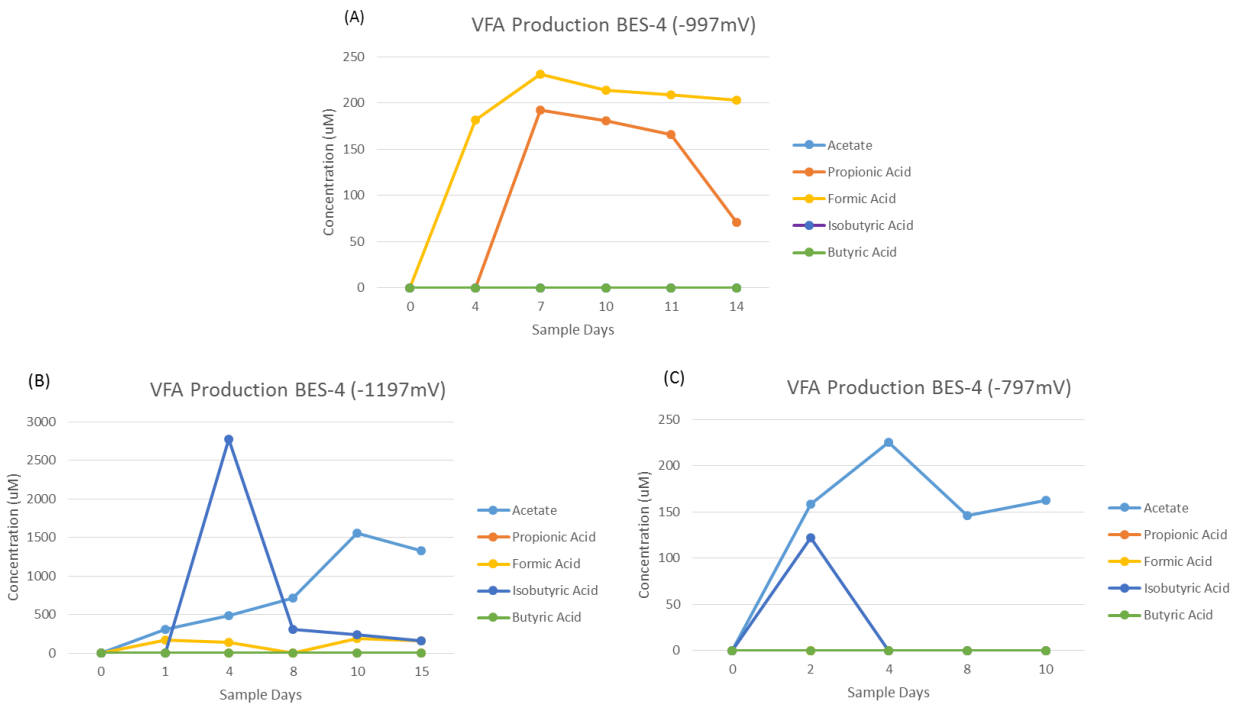
VFA detected in BES-1 A) -997mV B) -1197mV C) -797mV



VFA detected in BES-2 A) -997mV B) -1197mV C) -797mV



VFA detected in BES-3 A) -997mV B) -1197mV C) -797mV



VFA detected in BES-4 A) -997mV B) -1197mV C) -797mV

C1- Energy and global warming value for each MES plant unit operation

Process Units	Acetic Acid		Formic Acid		Propionate Acid		Ethanol		Methanol		Equations	References
	Energy (GJ)	GW (tonnes CO_2 eqv)	Energy (GJ)	GW (tonnes CO_2 eqv)	Energy (GJ)	GW (tonnes CO_2 eqv)	Energy (GJ)	GW (tonnes CO_2 eqv)	Energy (GJ)	GW (tonnes CO_2 eqv)		
Mixer	670	30	170	10	1100	60	2040	100	600	30	$E_{impeller} = Power\ Number * Fluid\ Density * Speed^3 Diameter^5$ $\mathrm{GW} = 0.0502988 \frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E_{impeller}$	(McGraw-Hill Higher Education, 2003; Deglon and Meyer, 2006; EIA, 2016)
MES reactor (Cathode energy load)	66740	3360	22330	1120	70070	3520	111390	5600	93100	4680	$E_{Temp\ Change} = Medium\ Mass * Specific\ Heat\ Capacity * Temperature\ change$ $E_{reaction} = (moles\ involved * number\ of\ electrons * Faradays\ constant * 1.31 * Applied\ potential)$ $\mathrm{GW} = 0.0502988 \frac{\mathrm{Tonnes}}{\mathrm{GJ}} * (E_{Temp\ Change} + E_{reaction})$	(McGraw-Hill Higher Education, 2003; Reda *et al.*, 2008; Marshall *et al.*, 2013; CEAE, 2014; Blanchet *et al.*, 2015; EIA, 2016)
MES reactor (Total energy load)	204301	10276	67208	3380	265225	13340	380372	19132	286479	14410		
Gas separator/ membrane	4670	230	3050	150	5680	290	6090	310	4370	220	$E = 0.4 \frac{GJ}{Tonne} * Tonne\ of\ gas\ separated$ $\mathrm{GW} = 0.0502988 \frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E$	(Bounaceur *et al.*, 2006; Brunetti *et al.*, 2010; EIA, 2016)
Rectification unit	1440400	72450	75980	3820	1289320	64850	48500	2440	47930	2410	Simulated using Aspen Plus V86	Aspen Plus V86 Software; (Li and Bai, 2012)
Stainless steel equipment	5.885	0.296	5.567	0.28	6.462	0.325	6.45	0.324	6.135	0.309	$E = 1.289 \frac{GJ}{Tonne} * Steel\ Density * Steel\ Volume$ $\mathrm{GW} = 0.0502988 \frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E$	(Fruehan *et al.*, 2000a; EIA, 2016)

Packaging	1267	124	1090	107	1347	132	1686	165	1679	164	$E = 20\frac{GJ}{Tonne} * Container\ Number * Weight\ per\ container$ $\mathrm{GW} = 0.03247721\frac{\mathrm{Tonnes}}{\mathrm{GJ}} * Container\ Number$	(Rietveld and Hegger, 2014)
CO_2 capture	2950	-16770	1920	-10940	3590	-20390	3840	-21860	2760	-15720	$E = 0.1758\frac{GJ}{Tonne} * Tonne\ of\ CO2\ captured$ $GW = -(Tonne\ of\ CO2\ captured)$	(Bhown and Freeman, 2011)
Transportation to MES plant	380	20	250	10	460	20	490	30	350	20	$E_{transportation} = (Trips\ per\ year * Distance *$ Fuel consumed $*$ Fuel energy) $E_{compression} = Tank\ Pressure * Tank\ Capacity * \ln(\frac{Initial\ Pressure}{Final\ Pressure})$ $\mathrm{GW} = 0.0502988\frac{\mathrm{Tonnes}}{\mathrm{GJ}} * (E_{Transportation} + E_{compression})$	(EIA, 2016; SunEarthTools, 2016)
CO_2 Compression and Storage	470	20	310	20	570	30	610	30	440	20	$E_{compression} = Tank\ Pressure * Tank\ Capacity * \ln(\frac{Initial\ Pressure}{Final\ Pressure})$ $\mathrm{GW} = 0.0502988\frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E_{compression}$	(EIA, 2016)
All Plant Pumps	3.3	0.16	2	0.11	2.9	0.14	5.4	0.32	2.63	0.13	$E_{Pump} = flowrate * density\ of\ fluid * gravity * differential\ head$ $\mathrm{GW} = 0.0502988\frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E_{Pump}$	(EIA, 2016; TheEngineeringToolBox, 2016)
Chemicals Purchased (*vitamins and minerals are assumed negligible)	11.7	0.6	5.1	0.26	15.8	0.8	22.9	1.15	11	0.55	$E_{chemicals} = 7.0116289\frac{GJ}{Tonne} * Tonne\ of\ Chemicals\ used\ per\ year$ $\mathrm{GW} = 0.0502988\frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E_{chemicals}$	(Cefic, 2014; Eurostat, 2014; EIA, 2016)
Transportation to Incinerator	5.2	0.3	5.2	0.3	5.2	0.3	5.2	0.3	5.2	0.3	$E_{Transportation} = (Trips\ per\ year * Distance *$ Fuel consumed $*$ Fuel energy $\mathrm{GW} = 0.0502988\frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E_{Transportation}$	(EIA, 2016; SunEarthTools, 2016)
Incineration	Negligible										$E_{Incineration} = 10\frac{GJ}{Tonne} * Tonne\ Bacteria\ Effluence$ $\mathrm{GW} = \mathrm{Tonne\ Bacteria\ Effluence} * 1\frac{Tonne\ CO2\ eqv}{Tonne\ Waste}$	(DEFRA, 2013)

C2- Formic acid sample calculation

Formic acid Sample calculation

S/N	Key calculation input	Amount	Unit
1	Amount of Product synthesized	1000	Tonnes/year
2	Molar Mass	46	g/mol
3	Mole of CO_2 per mole of products	1	Mol
4	Mole of H_2O per mole of products	2	Mol
5	Mole of H_2O in products	1	Mol
6	Mole of O_2 in products	0.5	Mol
7	Amount of electrons needed	2	Electrons
8	CO_2 selectivity	88	%
9	CO_2 conversion rate	58.8	%
10	H_2O selectivity	90	%
11	H_2O conversion rate	90	%
12	CO_2 released for electricity Generation	0.0502988	tonnes/GJ
13	Energy required to produce stainless steel	1.289	GJ/tonnes

CO_2 capture energy

Using,

$$E = 0.1758\frac{GJ}{Tonne} * Tonne\ of\ CO2\ captured$$

Where the Tonne of CO_2 captured calculated using,

$$Tonne\ of\ CO2\ captured = \left(\frac{Amount\ of\ product}{Molar\ mass\ of\ formic\ acid}\right) * (CO2\ number\ of\ moles * molar\ mass\ of\ CO2)$$

$$Tonne\ of\ CO2\ captured = \left(\frac{1000}{46}\right) * (1 * 44.01) * \frac{100}{88} * \frac{58.8}{100}$$

$$Tonne\ of\ CO2\ captured = 1847.97\ Tonnes$$

According to the system boundary excess CO_2 is recycled therefore;

$$CO2\ per\ batch = \frac{1847.97}{100} = 18.47\ Tonnes$$

$$CO2\ output\ per\ batch = 18.47 * \left(\frac{100 - 58.8}{100}\right) = 7.61\ Tonnes$$

$$New\ CO2\ needed\ per\ batch = 18.47 - 7.61 = 10.87\ Tonnes$$

$$New\ CO2\ needed\ per\ year = 10.87 * 99 = 1074.74\ Tonnes$$

$$Tonne\ of\ CO2\ captured\ if\ recycled = 18.47 + 1074.74 = 1094.22\ Tonnes$$

Therefore;

$$CO2\ capture\ energy = 0.1758 * 1094.22 = 192.36\ GJ/yr$$

Global warming from captured energy

Using,

$$GW = -(Tonne\ of\ CO2\ captured)$$

Therefore,

$$GW = -1094\ tonnes\ CO2\ eqv/yr$$

CO_2 transportation, pressurization and storage

S/N	Key calculation input	Amount	Unit
1	Distance to MES plant	30	Km
2	Amount of fuel (petrol) consumed	0.15	Litres/Km
3	Amount of energy per litre of fuel	9.7	KWh
4	Amount of CO_2 produced per Km	345	CO_2 g/Km
5	Truck capacity	60	Tonnes
6	Truck tank Pressure	24.13	bar
7	Truck tank volume	156.13	m^3
8	CO_2 input temperature	20	^oC
9	Tank temperature	25	^oC
10	Tank pressure	64.35	bar
11	Density of liquid CO_2 at tank temperature	709.7	Kg/m^3
12	Density of gaseous CO_2 at tank temperature	243.4	Kg/m^3

Energy for transportation to MES plant,

Using,

$$E_{transportation} = (Trips\ per\ year * Distance * \text{ Fuel consumed} * \text{Fuel energy})$$

Where,

$$Trips\ per\ year = \frac{1094.22}{60} = 18.24 = 18\ trips$$

Therefore,

$$E_{transportation} = (30 * 0.15 * 9.7 * 18) * (3600 * 0.000001) = 2.87 GJ/yr$$

Global warming for fuel used in truck

Using,

$$\text{GW} = (\text{Distance} * \text{CO2 produced per Km} * \text{Trips per year}) = (30 * 345 * 18) * 0.000001 = 0.189\ \text{Tonnes CO2 eqv}$$

Therefore,

$$\text{GW} = (30 * 345 * 18) * 0.000001 = 0.189\ \text{Tonnes CO2 eqv/yr}$$

Energy for compression in truck tank

$$E_{compression} = Tank\ Pressure * Tank\ volume * \ln(\frac{Initial\ Pressure}{Final\ Pressure})$$

Therefore,

$$E_{compression} = \left(24.13 * 156.13 * \ln(\frac{1.013}{24.13})\right) * \left(\frac{1}{10000}\right) = 1.19\ GJ$$

$$E_{compression} = 1.19 * 18 = 21.79\ GJ/yr$$

Global warming for transportation to MES plant

Using,

$$\text{GW} = \left(0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * (E_{compression})\right) + GW\ fuel$$

Therefore,

$$\text{GW} = \left(0.0502988 * (21.79)\right) + 0.189 = 1.28\ \text{tonnes CO2 eqv/yr}$$

Energy for pressurization and storage

Using,

$$E_{compression} = Tank\ Pressure * Tank\ volume * \ln(\frac{Initial\ Pressure}{Final\ Pressure})$$

Where,

$$Tank\ Volume\ = \frac{CO2\ mass}{CO2\ Density} = \frac{60 * 1000}{709.7 + 243.4} = 62.95\ meter\ cube$$

$$E_{compression} = \left(64.35 * 62.95 * \ln(\frac{1.013}{64.35})\right) * \left(\frac{1}{10000}\right) = 1.68GJ$$

Therefore Energy required to compress gas in tank for a year,

$$E_{compression} = 1.68 * 18 = 30.67\ GJ/yr$$

Global warming for pressurization and storage at MES plant

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * (E_{compression})$$

Therefore,

$$\text{GW} = 0.0502988 * (30.67) = 1.54\ \text{tonnes CO2 eqv/yr}$$

Mixer

S/N	Key calculation input	Amount	Unit
1	Rotational speed of impellers	5	rps
2	Power Number	0.3	-
3	Density of fluid (water)	1000	Kg/m^3
4	Mass of all chemicals used in mixer	3568.15	Kg/year
5	Average energy to manufacture chemicals	7.011	GJ/tonne
6	Flow rate of pump from mixer to reactor	0.5	m^3/min

Water used for Mixer

$$Tonne\ of\ water\ used = \left(\frac{Amount\ of\ product}{Molar\ mass\ of\ formic\ acid}\right) * (water\ number\ of\ moles * molar\ mass\ of\ water)$$

$$Tonne\ of\ water\ needed = \left(\frac{1000}{46}\right) * (2 * 18.015) * \frac{100}{90} * \frac{90}{100}$$

$$Tonne\ of\ water\ needed = 966.46\ Tonnes/yr$$

According to the system boundary excess water is recycled therefore;

$$water\ per\ batch = \frac{966.46}{100} = 9.66\ Tonnes$$

$$water\ output\ per\ batch = \left(9.66 * \left(\frac{100-90}{100}\right)\right) + \left(\frac{\left(\frac{1000}{46}\right) * (1 * 18.015)}{100}\right) = 4{,}88\ Tonnes$$

$$New\ water\ needed\ per\ batch = 9.66 - 4.88 = 4.78\ Tonnes$$

$$New\ water\ needed\ per\ year = 4.78 * 99 = 473.61\ Tonnes$$

$$Tonne\ of\ water\ needed\ if\ recycled = 9.66 + 473.61 = 483.27\ Tonnes/yr$$

Energy used in Mixing

Using,

$$E_{impeller} = Power\ Number * Fluid\ Density * Speed^3 Diameter^5$$

Determining mixer size assuming size of initial batch plus 5% contingency;

Since 1 tonne of water occupies 1m^3

$$Mixer\ Size = 9.66 + (0.05 * 9.66) = 10.15$$

Therefore size of mixer is 10.15 m^3

Determining diameter of impeller;

$$Impeller\ Diameter = Mixer\ size^{\frac{1}{3}} * 0.6$$

It is assumed that the impeller is 60% of tank diameter

$$Impeller\ Diameter = 10.15^{\frac{1}{3}} * 0.6 = 1.30m$$

Therefore;

$E_{impeller} = 0.3 * 1000 * 5^3 1.3^5 =$ 138698.83 J/S

Assuming 20 minutes mixing per batch;

$$E_{impeller} = (138698.83 * 1200 * 100) * 0.000000001 = 16.64\ GJ/yr$$

Global warming from Mixing

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{impeller}$$

Therefore,

$$\text{GW} = 0.0502988 * (16.64) = 0.84 \text{ tonnes CO2 eqv/yr}$$

Energy from Pump (Mixer to MES reactor)

Using,

$$E_{Pump} = flowrate * density\ of\ fluid * gravity * differential\ head$$

Determining differential head,

Assuming pump is into top of MES reactors therefore differential head is height of reactor. There are four reactors able to together hold one batch.

$$differential\ head = height\ of\ MES\ reactor = \left(\frac{water\ per\ batch}{4}\right)^{\frac{1}{3}} = \left(\frac{9.66}{4}\right)^{\frac{1}{3}} = 1.34m$$

Therefore,

$$E_{Pump} = 0.5 * 1000 * 9.81 * 1.34 = 6581.82\ J/min$$

For one batch;

$$E_{Pump} = 6581.82 * \left(\frac{9.66}{0.5}\right) = 127220.81\ J/batch$$

Assuming 100 pump efficiency energy of pump for the year;

$$E_{Pump} = (127220.81 * 100) * 0.000000001 = 0.0127\ GJ/yr$$

GW from Pump (Mixer to MES reactor)

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{Pump}$$

Therefore,

$$\text{GW} = 0.0502988 * (0.0127) = 0.0006399 \text{ tonnes CO2 eqv/yr}$$

MES Reactor

S/N	Key calculation input	Amount	Unit
1	Reactor inlet temperature	16	^oC
2	Reactor outlet temperature	25	^oC
3	Applied potential	1.217	V
4	Coulombic efficiency	69	%
5	Mass of product per batch	10	tonnes
6	Mass of medium per batch	9.66	tonnes
7	Number of MES reactors	4	reactors
8	Specific capacity of water	4200	J/ Kg ^oC
9	Faradays constant	96485	C/mol
10	Flow rate of pump from mixer to reactor	0.5	m^3/min
11	Density of formic acid	1220	Kg/m^3

Energy required for MES reactor

Using,

$$E_{MES\ reactor} = E_{Temp\ Change} + E_{reaction}$$

Calculating energy required for MES temperature change,

$$E_{Temp\ Change} = Medium\ Mass * Specific\ Heat\ Capacity * Temperature\ change$$

Therefore,

$$E_{Temp\ Change} = (9.66 * 1000000) * 4.2 * (25 - 16)$$

$$E_{Temp\ Change} = 365320177.7\ J$$

Calculating energy for MES reaction,

$$E_{reaction} = (moles\ involved * number\ of\ electrons * Faradays\ constant * 1.31 * Applied\ potential)$$

Therefore,

$$E_{reaction} = \left(\left(\frac{10 * 1000000}{46}\right) * 2 * 96485 * 1.31 * 1.217\right)$$

$$E_{reaction} = 66842746741\ J$$

Calculating total energy for a batch,

$$E_{MES\ reactor} = (365320177.7 + 66842746741) * 0.000000001)$$

$$E_{MES\ reactor} = 6.721\ GJ/batch$$

Therefore for one year (100 batches);

$$E_{MES\ reactor} = 6.721 * 100\ GJ/yr$$

$$E_{MES\ reactor} = 6721\ GJ/year$$

Global warming from MES reaction

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * (E_{MES\ reactor})$$

Therefore,

$$\text{GW} = 0.0502988 * 6721 = 338.05\text{tonnes CO2 eqv/yr}$$

Energy from Pump (MES reactor to distillation storage tank)

Using,

$$E_{Pump} = flowrate * density\ of\ fluid * gravity * differential\ head$$

Determining differential head,

Assuming pump is into top of distillation storage tank which can hold two batches therefore differential head is height of tank.

$$differential\ head = height\ of\ Distillation\ storage\ tank = \left((water\ output\ per\ batch + product\ output\ per\ batch) * 2\right)^{\frac{1}{3}}$$
$$= (29.76)^{\frac{1}{3}} = 3.10m$$

Determining density of fluid,

$$density\ of\ fluid = \frac{(water\ output\ per\ batch * Density\ of\ water) + (Product\ output\ per\ batch * Density\ of\ Product)}{(water\ output\ per\ batch + Product\ output\ per\ batch)}$$

$$density\ of\ fluid = \frac{(4.88 * 1000) + (10 * 1220)}{(4.88 + 10)}$$

$$density\ of\ fluid = 1147.84\ Kg/m3$$

Therefore,

$$E_{Pump} = 0.5 * 1147.84 * 9.81 * 3.10 = 17447.71\, J/min$$

For one batch;

$$E_{Pump} = 17447.71 * \left(\frac{14.88}{0.5}\right) = 519262.88\, J/batch$$

Assuming 100 pump efficiency energy of pump for the year;

$$E_{Pump} = (519262.88 * 100) * 0.000000001 = 0.0519\, GJ/yr$$

GW from Pump (MES reactor to distillation storage tank)

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{Pump}$$

Therefore,

$$\text{GW} = 0.0502988 * (0.0519) = 0.002611 \text{ tonnes CO2 eqv/yr}$$

Energy from Pump (Distillation storage tank to Distillation Column)

Using,

$$E_{Pump} = flowrate * density\ of\ fluid * gravity * differential\ head$$

Determining flowrate,

Assuming pumps runs for 8000 hours a year

$$flowrate = \frac{\left(\frac{1000}{1.22}\right) + \left(\frac{488}{1}\right)}{8000}$$

$$flowrate = 0.16\, m3/h$$

Where differential head is the height of the distillation column. Simulation using Aspen determined that the height of the column is 28.04m and the feed stage is the first tray.

Therefore;

$$E_{Pump} = 0.16 * 1147.84 * 9.81 * 28.04$$

$$E_{Pump} = 44965.13\, J/min$$

For one batch;

$$E_{Pump} = 44965.13 * \left(\frac{14.88}{0.16}\right) = 4093242.426\, J/batch$$

Assuming 100 pump efficiency energy of pump for the year;

$$E_{Pump} = (4093242.426 * 100) * 0.000000001 = 0.41\, GJ/year$$

GW from Pump (Distillation storage tank to Distillation Column)

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{Pump}$$

Therefore,

$$\text{GW} = 0.0502988 * (0.41) = 0.021 \text{ tonnes CO2 eqv/yr}$$

Incineration

S/N	Key calculation input	Amount	Unit
1	Distance from MES plant to incinerator	50	km
2	Amount of fuel (petrol) consumed	0.15	Litres/Km
3	Amount of energy per litre of fuel	9.7	KWh
4	Amount of CO_2 produced per Km	345	CO_2 g/Km
5	Number of trips per year	2	Trips

Energy for transportation to Incinerator,

Using,

$$E_{transportation} = (Trips\ per\ year * Distance * \text{Fuel consumed} * \text{Fuel energy})$$

Therefore,

$$E_{transportation} = (50 * 0.15 * 9.7 * 2) * (3600 * 0.000001) = 0.5238 GJ/yr$$

Global warming for fuel used in car

Using,

$$\text{GW} = (\text{Distance} * \text{CO2 produced per Km} * \text{Trips per year})$$

Therefore,

$$\text{GW} = (50 * 345 * 2) * 0.000001 = 0.0345 \text{ Tonnes CO2 eqv/yr}$$

Gas separator

S/N	Key calculation input	Amount	Unit
1	Membrane capture energy	0.4	GJ/tonne
2	Capture efficiency	99	%
3	CO_2/O_2 membrane selectivity	50	-
4	Mole percent of CO_2	0.6143	%
5	Mass percent of CO_2	0.6865	%

Estimating CO_2 output from MES reactor;

$$CO2 \ output \ per \ batch = \ 18.47 * \left(\frac{100 - 58.8}{100}\right) = 7.61 \ Tonnes$$

Therefore CO_2 output per year;

$$CO2 \ output \ per \ year = 7.61 * 100 = 761.36 \ tonnes/yr$$

Estimating O_2 output from MES reactor;

$$Tonne \ of \ O2 \ separated = \left(\frac{1000}{46}\right) * (0.5 * 32)$$

Therefore O_2 output per year;

$$Tonne\ of\ O2\ separated = 347.63\ tonnes/yr$$

Energy for gas separation

Using,

$$E = 0.4\frac{GJ}{Tonne} * Tonne\ of\ gas\ separated$$

Therefore,

$$E = 0.4 * (761.36) = 304.54\ GJ/yr$$

Global warming from separation

Using,

$$\text{GW} = 0.0502988\frac{\text{Tonnes}}{\text{GJ}} * E$$

Therefore,

$$\text{GW} = 0.0502988 * (304.54) = 15.32\ \text{tonnes CO2 eqv/yr}$$

Liquid separator (Distillation column)

Distillation column simulated using Aspen. The below table shows some important parameters

S/N	Key calculation input	Amount	Unit
1	Number of trays	40	trays
2	Diameter of column	1.5	m
3	Height of column	28.04	m
4	Condenser duty	237300	KJ/h
5	Reboiler duty	202200	KJ/h

Energy for Liquid separation

Using,

$$Energy = Condenser\ duty + Reboiler\ duty$$

Therefore,

$$Energy = (237300 + 202200) * 8760 * 0.000001$$

$$Energy = 7597.67\ GJ/yr$$

GW for liquid separation

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E$$

Therefore,

$$\text{GW} = 0.0502988 * (7597.67) = 382.15 \text{ tonnes CO2 eqv/yr}$$

Energy from Pump (Distillation column to storage tank)

Using,

$$E_{Pump} = flowrate * density\ of\ fluid * gravity * differential\ head$$

Determining differential head,

Assuming pump is into top of storage tank therefore differential head is height of the tank. Tank can hold two batches.

$$differential\ head = height\ of\ storage\ tank = Tank\ volume^{\frac{1}{3}}$$

Calculating tank volume

$$Tank\ volume = \left(\frac{Product\ per\ batch}{Molar\ mass}\right) * 2 = 16.39m3$$

Therefore,

$$differential\ head = (16.39)^{\frac{1}{3}}$$

$$differential\ head = 2.54m$$

$$E_{Pump} = 0.102 * 1220 * 9.81 * 2.54 = 3115.08/min$$

For one batch;

$$E_{Pump} = 3115.08 * \left(\frac{10}{0.1025}\right) = 304031.72\ J/batch$$

Assuming 100 pump efficiency energy of pump for the year;

$$E_{Pump} = (304031.72 * 100)\ * 0.000000001 = 0.030403\ GJ/yr$$

GW from Pump (Distillation column to storage tank)

Using,

$$\text{GW} = 0.0502988 \frac{\text{Tonnes}}{\text{GJ}} * E_{Pump}$$

Therefore,

$$\text{GW} = 0.0502988 * (0.0304) = 0.001529 \text{ tonnes CO2 eqv/yr}$$

Packaging

S/N	Key calculation input	Amount	Unit
1	Capacity of steel drum	208	Litres
2	Energy to produce Steel drum	20	MJ/Kg
3	CO_2 emission from manufacturing one steel drum	0.0324	Tonnes
4	Weight of one steel drum	16.6	kg

Calculating number of drums required;

$$\text{Number of drums} = \left(\left(\frac{1000}{1.22}\right) * 1000\right)/208$$

$$\text{Number of drums} = 3940.73 = 3941 \text{ drums}$$

Assuming drums recycled monthly;

$$\text{Number of drums} = \frac{3941}{12} = 328 \text{ drums}$$

Energy to produce drums

Using,

$$E_{drum} = \ Number\ of\ drums * \ Energy\ to\ produce\ drum * weight\ of\ drum$$

Therefore,

$$E_{drum} = (328 * \ \ 20 * 16.6) * 0.001$$

$$E_{drum} = 108.90\ GJ/yr$$

GW from producing drums

Using,

$$\mathrm{GW} = 0.0324 \frac{\mathrm{Tonnes}}{\mathrm{GJ}} * E_{drum}$$

Therefore,

$$\mathrm{GW} = 0.0324 * 108.90$$

$$\mathrm{GW} = 3.53\ \mathrm{tonnes\ CO2\ eqv/yr}$$

Equipment Steel

S/N	Key calculation input	Amount	Unit
1	Surface area of CO_2 tank	94.95	m^2
2	Surface area of mixer	28.13	m^2
3	Surface area of reactor	27.22	m^2
4	Surface area of rectification column	80.92	m^2
5	Surface area of main storage tank	38.72	m^2
6	Energy to produce stainless steel	1.289	GJ/tonne
7	Density of stainless steel	8000	Kg/m^3
8	Thickness of stainless steel	2	mm

Energy to produce steel

Using,

$$E = 1.289\frac{GJ}{Tonne} * Steel\ Density * Steel\ Volume$$

Where,

$$\text{Steel Volume} = \text{Total Surface area} * Steel\ thickness$$

$$\text{Steel Volume} = (94.95 + 28.13 + 27.22 + 80.92 + 38.72) * 0.002$$

$$\text{Steel Volume} = 0.54\ m^3$$

Therefore,

$$E = 1.289 * 8000 * 0.57 * 0.001$$

$$E = 5.567\ GJ$$

GW from steel production

Using,

$$\text{GW} = 0.0502988\frac{\text{Tonnes}}{\text{GJ}} * E$$

Therefore,

$$\text{GW} = 0.0502988 * 5.567$$

$$\text{GW} = 0.28\ \text{tonnes CO2 eqv}$$

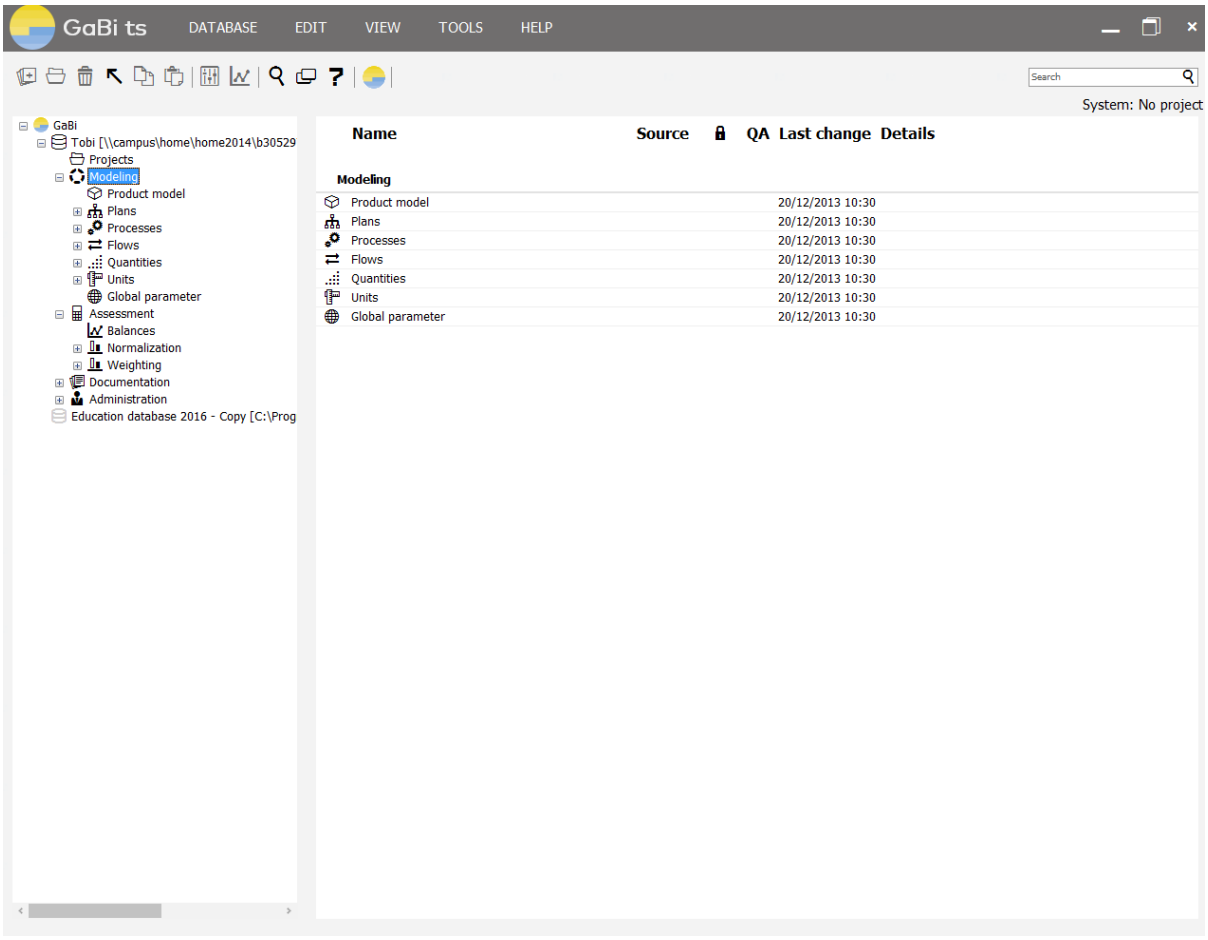
D1- LCA Software Questionnaire

Questionnaire comparing LCA software's (Seto et al., 2017)

S/N	Primary Criteria Addressed	Questions and Sub-Questions	High way	BEES	GaBi	Suite	Sima Pro 7
Goal and Scope Definition							
1.1	Flexibility	Can system boundaries be defined by the user?	1	0	2	1	2
1.2	Flexibility	Can user input any functional unit that they want?	0	0	1	1	1
Life Cycle Inventory Analysis							
2.1	Complexity	Does the software include a database of inventory information for life cycle processes?	2	2	2	2	2
2.2	Flexibility	Can additional databases be added	0	0	2	1	2
2.3	Complexity	Is the data updated regularly?	1	1	1	1	1
2.4	Complexity	Can the use stage of a product be modelled?	2	0	2	2	2
2.5	Complexity	Can the disposal phase of a product be modelled?	1	1	2	2	2
Life Cycle Impact Assessment							
3.1	Complexity	Does the tool include impact assessment methods?	1	2	2	1	2
3.2	Complexity	Do the impact assessment methods support weighting?	0	2	2	1	2
3.3	Flexibility	Can the default weighting be modified?	0	2	2	0	2
3.4	Flexibility	Can you set a cut off point for what impacts are included?	0	2	2	0	2
3.5	Complexity	Can you incorporate other impacts besides environmental ones?	2	2	2	2	2
Interpretation							
4.1	Output	Does the software generate graphical representation of results?	2	2	2	2	2
4.2	Output	Are the quantitative or physical data outputs readily available?	1	2	2	0	2
4.3	Complexity	Can the software be used to perform sensitivity analysis?	1	1	2	1	2
4.4	Output	Can the software be used to compare alternatives?	2	2	2	2	2

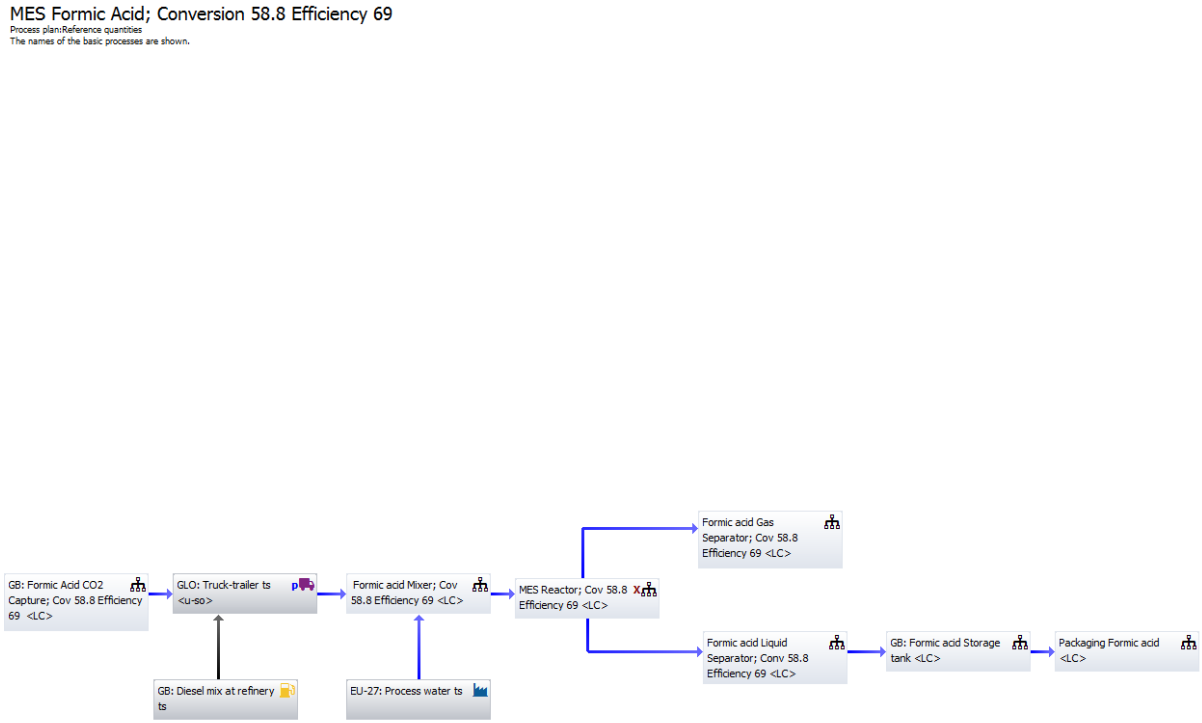
General User-Friendliness							
5.1	Complexity	How intuitive is the data entry?	1	2	2	2	1
5.2	Complexity	How transparent is the process?	0	0	2	1	2
5.3	Complexity	Does the software have a good user interface?	0	2	2	2	1
5.4	Flexibility	How easy is it to compare alternative by making small changes?	1	2	2	2	2
5.5	Complexity	Is support provided for users of the software?	0	1	2	1	1
Total (Maximum Possible Score =42 Points)			**18**	**28**	**40**	**27**	**37**

D2- Gabi Database Structure

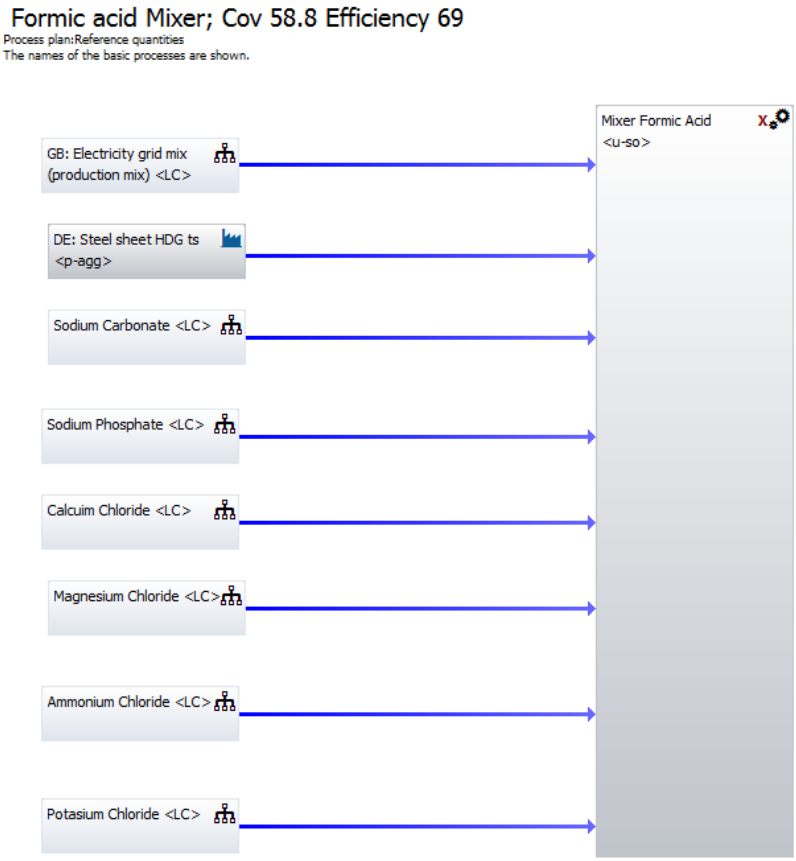


Gabi Database Structure

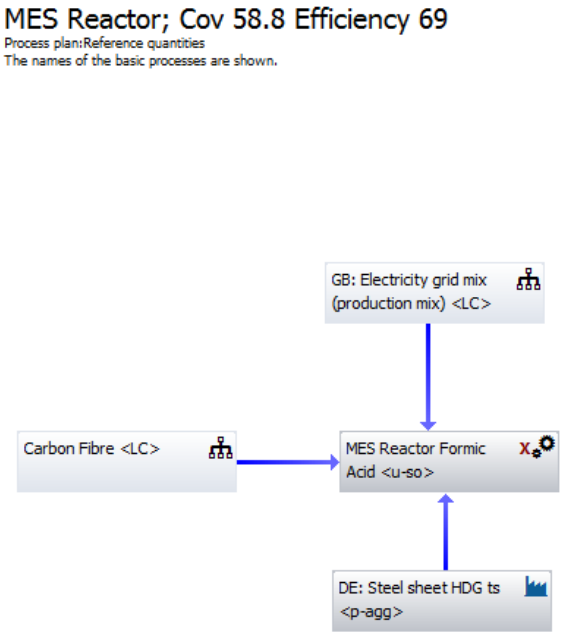
D3- GaBi Flowsheets



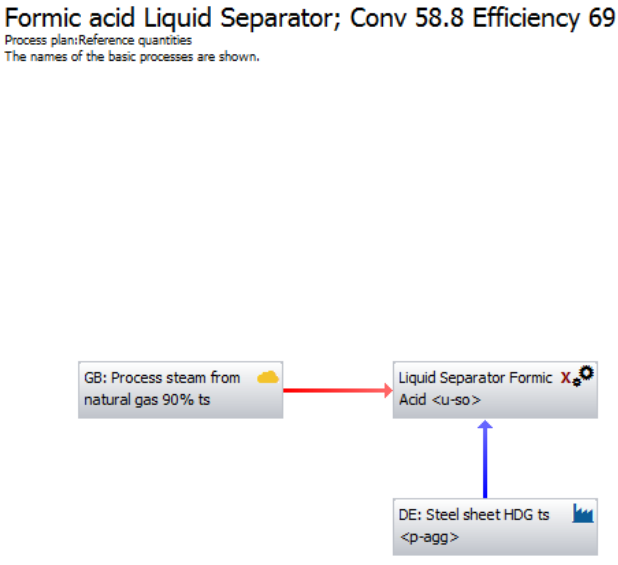
Gabi flowsheet for base scenario for formic acid production through MES



Gabi flowsheet for mixer of base scenario for formic acid production through MES



Gabi flowsheet for MES reactor of base scenario for formic acid production through MES



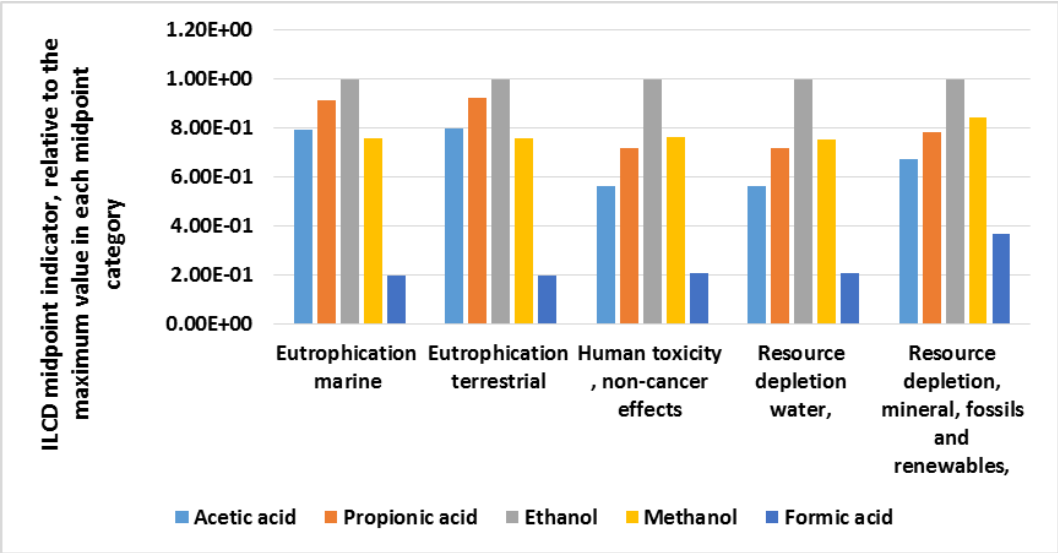
Gabi flowsheet for Liquid rectification unit of base scenario for formic acid production through MES

D4- Life cycle inventory of standalone MES reactor

Life cycle inventory of a standalone MES reactor for 1000t of product per year

	Material	**Unit**	**Acetic acid**	**Formic acid**	**Propionic acid**	**Methanol**	**Ethanol**
Reactor							
Cathode	Carbon fibre	kg	10.95	8.25	13.85	13.76	17.15
Anode	Carbon fibre	kg	10.97	8.25	13.85	13.76	17.15
Construction	Stainless steel	kg	579.08	435.57	731.09	726.64	905.44
Current collector	Copper	Kg	0.0173	0.0173	0.0173	0.0173	0.0173
Medium							
Water		m^3/yr	740.81	483.27	930.52	1319.66	1448.42
Sodium Bicarbonate		Kg/yr	3703.70	2416.14	5253.95	5206.17	7241.40
Sodium Dihydrogen Phosphate		Kg/yr	888.89	579.87	1260.95	1249.48	1737.94
Ammonium chloride		Kg/yr	370.37	241.61	525.40	520.62	724.14
Magnesium chloride		Kg/yr	314.07	204.89	445.54	441.48	614.07
Potassium chloride		Kg/yr	148.15	96.65	210.16	208.25	289.66
Calcium chloride		Kg/yr	44.44	28.99	63.05	62.47	86.90
Energy							
Conversion energy		GJ/yr	20430.12	6720.81	26522.50	28647.85	38037.15
Heat treatment		GJ/yr	56.00	36.53	79.43	78.71	109.48
CO_2 capture							
CO_2		t/yr	1677.33	1094.22	2039.49	1571.84	2186.32
Capture energy		GJ/yr	294.87	192.36	358.54	276.33	384.35
Total weight		**Kg**	622.10	467.94	785.40	780.63	972.70
Total energy		**GJ/yr**	20781.99	6949.70	26960.47	29002.89	38530.98

D5- midpoint impact category data



Life cycle environmental burdens of the MES plant for the production of acetic, propionic and formic acids, ethanol and methanol using ILCD method. Results are displayed relative to the maximum value in each impact category

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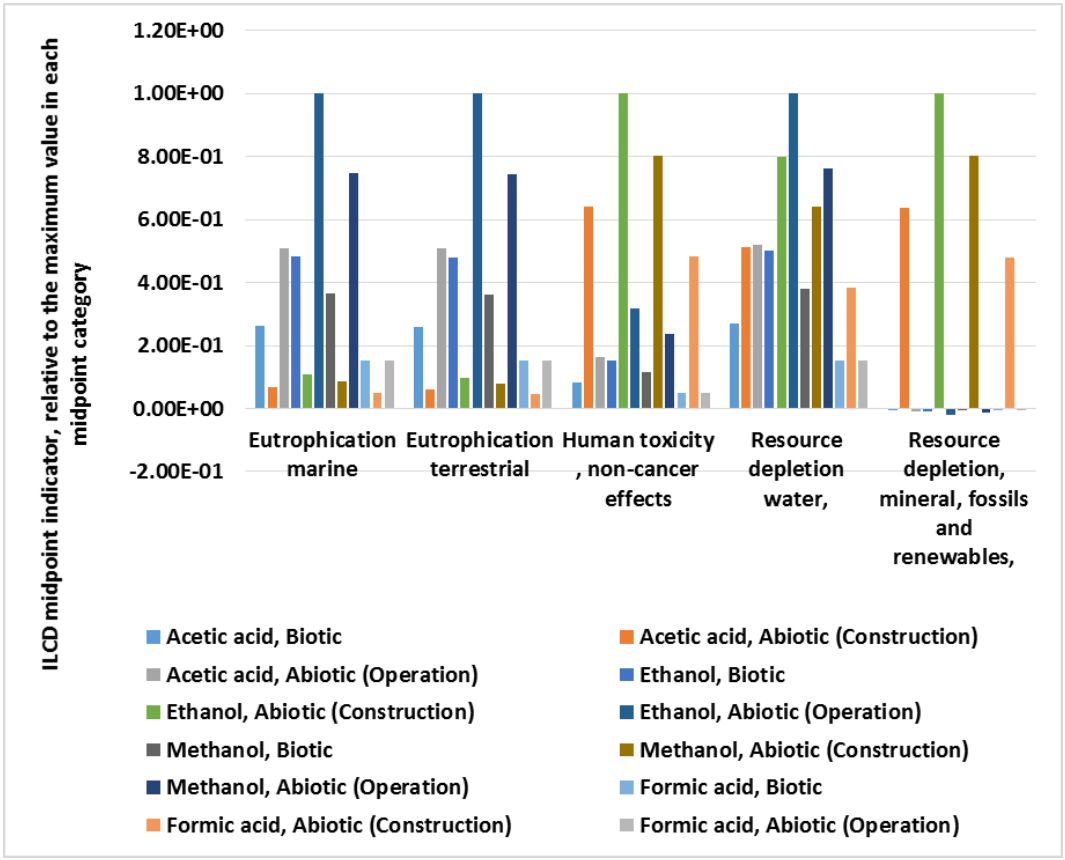
Life cycle environmental burdens of the MES plant for the production of acetic, propionic and formic acids, ethanol and methanol using ILCD method

Indicators		**Acetic acid**	**Propionic acid**	**Ethanol**	**Methanol**	**Formic acid**
Acidification	[Mole of H+ eq.]	1.43E+05	1.73E+05	2.11E+05	1.59E+05	4.08E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	8.46E+07	8.81E+07	6.40E+07	4.89E+07	1.31E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	6.78E+07	6.77E+07	4.21E+07	3.32E+07	2.20E+06
Ecotoxicity freshwater	[CTUe]	1.04E+06	1.29E+06	1.71E+06	1.30E+06	3.52E+05
Eutrophication freshwater	[kg P eq]	13.8	17.6	24.2	18.3	5.34
Eutrophication marine	[kg N-Equiv.]	3.72E+04	4.30E+04	4.70E+04	3.56E+04	9.30E+03
Eutrophication terrestrial	[Mole of N eq.]	4.04E+05	4.68E+05	5.06E+05	3.83E+05	9.94E+04
Human toxicity , cancer	[CTUh]	0.0241	0.0295	0.0376	0.0286	0.00783
Human toxicity , non-cancer effects	[CTUh]	0.871	1.11	1.55	1.18	0.32
Ionizing radiation , human health	[kBq U235 eq]	5.09E+06	6.57E+06	9.31E+06	7.01E+06	1.75E+06
Ozone depletion	[kg CFC-11 eq]	0.000123	0.00015	0.000189	0.000144	4.17E-05
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	6.43E+03	7.93E+03	1.02E+04	7.71E+03	2.01E+03
Photochemical ozone formation , human health	[kg NMVOC]	1.08E+05	1.24E+05	1.32E+05	9.96E+04	2.57E+04
Resource depletion water,	[m^3 eq.]	4.91E+04	6.29E+04	8.75E+04	6.60E+04	1.82E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	112	130	166	140	60.8



Other Life cycle environmental burdens of the MES and AER reactor using ILCD method.

Life cycle environmental burdens of a standalone MES reactor for the production of acetic, propionic and formic acids, ethanol and methanol using ILCD method

		Construction					Operation				
Indicators		**Acetic acid**	**Propionic acid**	**Ethanol**	**Methanol**	**Formic acid**	**Acetic acid**	**Propionic acid**	**Ethanol**	**Methanol**	**Formic acid**
Acidification	[Mole of H+ eq.]	5.65E+00	7.07E+00	8.84E+00	7.09E+00	4.25E+00	1.12E+05	1.46E+05	2.08E+05	1.57E+05	3.76E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	1.37E+03	1.72E+03	2.14E+03	1.72E+03	1.03E+03	3.33E+07	4.32E+07	6.17E+07	4.65E+07	1.11E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	1.37E+03	1.72E+03	2.15E+03	1.72E+03	1.03E+03	1.65E+07	2.27E+07	3.98E+07	3.07E+07	1.63E+05
Ecotoxicity freshwater	[CTUe]	3.37E+02	4.09E+02	5.27E+02	4.23E+02	2.54E+02	8.96E+05	1.16E+06	1.66E+06	1.25E+06	3.01E+05
Eutrophication freshwater	[kg P eq]	2.15E-03	2.71E-03	3.36E-03	2.70E-03	1.62E-03	1.35E+01	1.75E+01	2.51E+01	1.91E+01	4.77E+00
Eutrophication marine	[kg N-Equiv.]	2.30E+02	2.30E+02	3.60E+02	2.89E+02	1.73E+02	2.47E+04	3.21E+04	4.59E+04	3.45E+04	8.28E+03
Eutrophication terrestrial	[Mole of N eq.]	1.22E+01	1.51E+01	1.91E+01	1.53E+01	9.17E+00	2.69E+05	3.49E+05	4.98E+05	3.75E+05	9.01E+04
Human toxicity , cancer	[CTUh]	7.31E-06	9.22E-06	1.14E-05	9.17E-06	5.50E-06	1.95E-02	2.52E-02	3.61E-02	2.72E-02	6.53E-03
Human toxicity , non-cancer effects	[CTUh]	3.30E-04	4.16E-04	5.15E-04	4.14E-04	2.48E-04	7.98E-01	1.04E+00	1.48E+00	1.11E+00	2.67E-01
Ionizing radiation , human health	[kBq U235 eq]	2.57E+01	3.12E+01	4.02E+01	3.22E+01	1.93E+01	4.99E+06	6.47E+06	9.24E+06	6.96E+06	1.66E+06

Ozone depletion	[kg CFC-11 eq]	2.55E-08	3.21E-08	3.98E-08	3.19E-08	1.91E-08	1.03E-04	1.34E-04	1.92E-04	1.47E-04	3.63E-05
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	9.24E-01	1.16E+00	1.44E+00	1.16E+00	6.95E-01	5.36E+03	6.95E+03	9.93E+03	7.48E+03	1.79E+03
Photochemical ozone formation , human health	[kg NMVOC]	3.72E+00	4.66E+00	5.82E+00	4.67E+00	2.80E+00	6.96E+04	9.02E+04	1.29E+05	9.71E+04	2.32E+04
Resource depletion water,	[m^3 eq.]	2.92E+00	3.67E+00	4.56E+00	3.66E+00	2.19E+00	4.85E+04	6.30E+04	9.02E+04	6.83E+04	1.69E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	3.49E-01	4.40E-01	5.45E-01	4.38E-01	2.62E-01	5.55E+01	7.20E+01	1.03E+02	7.75E+01	1.85E+01

Life cycle environmental burdens of a standalone abiotic reactor for the production of acetic, propionic and formic acids, ethanol and methanol using ILCD method

		Construction					**Operation**				
Indicators		**Acetic acid**	**Propionic acid**	**Ethanol**	**Methanol**	**Formic acid**	**Acetic acid**	**Propionic acid**	**Ethanol**	**Methanol**	**Formic acid**
Acidification	[Mole of H+ eq.]	2.03E+07		3.18E+07	2.55E+07	1.53E+07	2.21E+05		4.34E+05	3.24E+05	6.59E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	8.51E+06		1.33E+07	1.07E+07	6.40E+06	6.57E+07		1.29E+08	9.61E+07	1.96E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	8.50E+06		1.33E+07	1.07E+07	6.39E+06	4.89E+07		1.07E+08	8.03E+07	8.60E+06
Ecotoxicity freshwater	[CTUe]	9.99E+06		1.56E+07	1.25E+07	7.51E+06	1.76E+06		3.44E+06	2.57E+06	5.22E+05

Eutrophication freshwater	[kg P eq]	3.04E+00		4.75E+00	3.81E+00	2.28E+00	2.58E+01		4.89E+01	3.80E+01	7.43E+00
Eutrophication marine	[kg N-Equiv.]	6.53E+03		1.02E+04	8.19E+03	4.91E+03	4.87E+04		9.55E+04	7.13E+04	1.45E+04
Eutrophication terrestrial	[Mole of N eq.]	6.43E+04		1.01E+05	8.07E+04	4.84E+04	5.29E+05		1.04E+06	7.73E+05	1.57E+05
Human toxicity , cancer	[CTUh]	2.28E-02		3.56E-02	2.86E-02	1.71E-02	3.83E-02		7.50E-02	5.61E-02	1.14E-02
Human toxicity , non-cancer effects	[CTUh]	6.22E+00		9.72E+00	7.80E+00	4.68E+00	1.58E+00		3.09E+00	2.31E+00	4.69E-01
Ionizing radiation , human health	[kBq U235 eq]	1.20E+06		1.87E+06	1.50E+06	9.00E+05	9.85E+06		1.93E+07	1.44E+07	2.93E+06
Ozone depletion	[kg CFC-11 eq]	2.35E-05		3.68E-05	2.95E-05	1.77E-05	1.99E-04		3.79E-04	2.93E-04	5.76E-05
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	9.50E+05		1.49E+06	1.19E+06	7.15E+05	1.06E+04		2.07E+04	1.55E+04	3.15E+03
Photochemical ozone formation , human health	[kg NMVOC]	1.28E+06		1.99E+06	1.60E+06	9.59E+05	1.37E+05		2.69E+05	2.01E+05	4.09E+04
Resource depletion water,	[m³ eq.]	9.20E+04		1.44E+05	1.15E+05	6.92E+04	9.34E+04		1.80E+05	1.37E+05	2.75E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	-7.34E+03		-1.15E+04	-9.21E+03	-5.52E+03	1.10E+02		2.15E+02	1.60E+02	3.27E+01

		Construction (Platinum reduction)					Operation (100 percent conversion and efficiency)				
Indicators		**Acetic acid**	**Propionic acid**	**Ethanol**	**Methanol**	**Formic acid**	**Acetic acid**	**Propionic acid**	**Ethanol**	**Methanol**	**Formic acid**
Acidification	[Mole of H+ eq.]	5.09E+06		7.95E+06	6.38E+06	3.83E+06	1.31E+05		2.56E+05	1.91E+05	3.93E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	2.13E+06		3.33E+06	2.67E+06	1.60E+06	3.89E+07		7.61E+07	5.68E+07	1.17E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	2.13E+06		3.32E+06	2.67E+06	1.60E+06	2.22E+07		5.43E+07	4.11E+07	7.91E+05
Ecotoxicity freshwater	[CTUe]	2.50E+06		3.91E+06	3.13E+06	1.88E+06	1.04E+06		2.03E+06	1.52E+06	3.11E+05
Eutrophication freshwater	[kg P eq]	7.60E-01		1.19E+00	9.54E-01	5.72E-01	1.56E+01		2.89E+01	2.31E+01	4.43E+00
Eutrophication marine	[kg N-Equiv.]	1.63E+03		2.55E+03	2.05E+03	1.23E+03	2.89E+04		5.64E+04	4.21E+04	8.65E+03
Eutrophication terrestrial	[Mole of N eq.]	1.61E+04		2.52E+04	2.02E+04	1.21E+04	3.13E+05		6.12E+05	4.57E+05	9.38E+04
Human toxicity , cancer	[CTUh]	5.70E-03		8.91E-03	7.15E-03	4.28E-03	2.27E-02		4.43E-02	3.32E-02	6.79E-03
Human toxicity , non-cancer effects	[CTUh]	1.55E+00		2.43E+00	1.95E+00	1.17E+00	9.34E-01		1.83E+00	1.36E+00	2.80E-01
Ionizing radiation , human health	[kBq U235 eq]	2.99E+05		4.68E+05	3.75E+05	2.25E+05	5.83E+06		1.14E+07	8.51E+06	1.75E+06
Ozone depletion	[kg CFC-11 eq]	5.90E-06		9.23E-06	7.40E-06	4.44E-06	1.20E-04		2.24E-04	1.77E-04	3.43E-05
Particulate matter/Respiratory	[kg PM2,5-	2.38E+05		3.71E+05	2.98E+05	1.79E+05	6.26E+03		1.22E+04	9.14E+03	1.88E+03

inorganics	Equiv.]										
Photochemical ozone formation , human health	[kg NMVOC]	3.19E+05		4.98E+05	4.00E+05	2.40E+05	8.13E+04		1.59E+05	1.19E+05	2.44E+04
Resource depletion water,	[m³ eq.]	2.30E+04		3.60E+04	2.89E+04	1.73E+04	5.61E+04		1.07E+05	8.24E+04	1.65E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	-1.83E+03		-2.87E+03	-2.30E+03	-1.38E+03	6.50E+01		1.27E+02	9.48E+01	1.95E+01

Life cycle environmental burdens of a different scenarios for the MES plant for the production of acetic, ethanol and formic acid using ILCD method

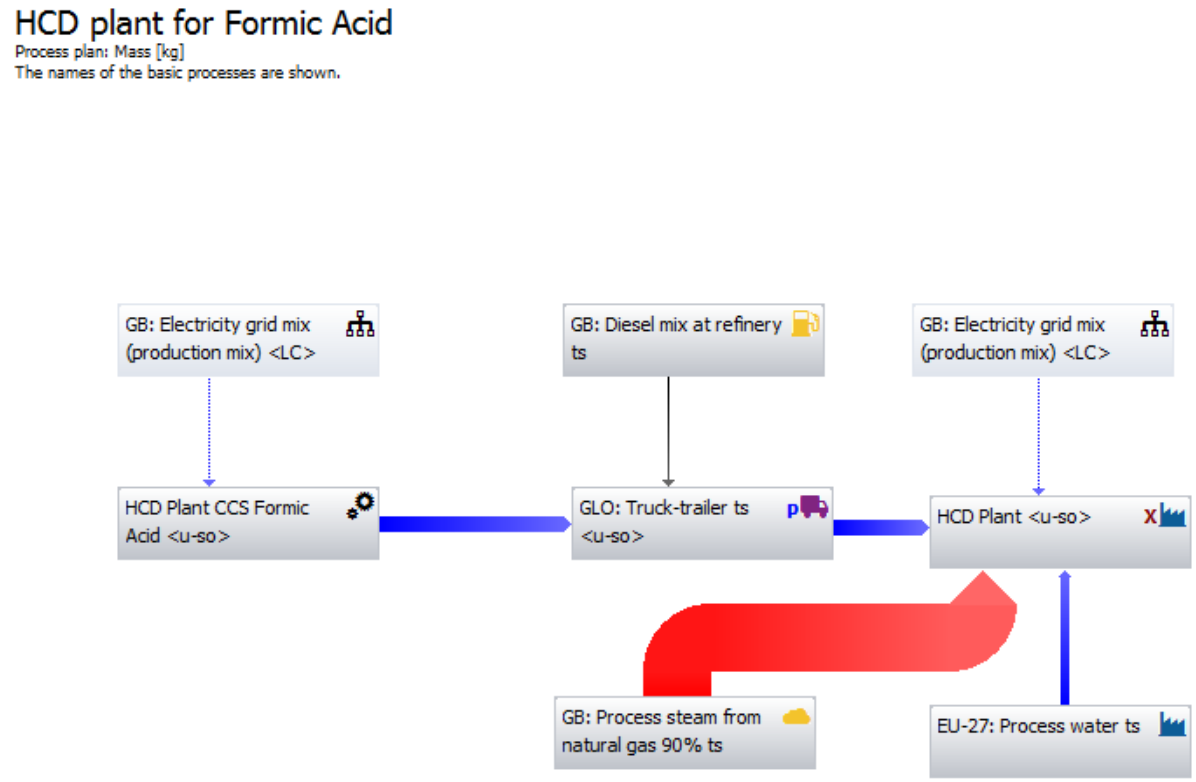
		Acetic acid			**Ethanol**			**Formic acid**		
Indicators	**Conversion**	40	58.8	100	40	58.8	100	40	58.8	100
	Efficiency	40	69	100	40	69	100	40	69	100
Acidification	[Mole of H+ eq.]	1.70E+05	1.43E+05	1.14E+05	2.60E+05	2.11E+05	1.59E+05	4.93E+04	4.08E+04	3.06E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	9.27E+07	8.46E+07	7.61E+07	7.86E+07	6.40E+07	4.87E+07	1.57E+07	1.31E+07	1.01E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	7.57E+07	6.78E+07	5.93E+07	5.65E+07	4.21E+07	2.69E+07	4.68E+06	2.20E+06	-7.34E+05
Ecotoxicity freshwater	[CTUe]	1.25E+06	1.04E+06	8.09E+05	2.10E+06	1.71E+06	1.30E+06	4.15E+05	3.52E+05	2.72E+05
Eutrophication freshwater	[kg P eq]	1.69E+01	1.38E+01	1.06E+01	2.97E+01	2.42E+01	1.83E+01	5.73E+00	5.34E+00	4.19E+00
Eutrophication marine	[kg N-Equiv.]	4.32E+04	3.72E+04	3.09E+04	5.78E+04	4.70E+04	3.56E+04	1.11E+04	9.30E+03	7.07E+03
Eutrophication terrestrial	[Mole of N	4.70E+05	4.04E+05	3.36E+05	6.23E+05	5.06E+05	3.82E+05	1.19E+05	9.94E+04	7.51E+04

	eq.]									
Human toxicity , cancer	[CTUh]	2.88E-02	2.41E-02	1.92E-02	4.61E-02	3.76E-02	2.86E-02	9.24E-03	7.83E-03	6.08E-03
Human toxicity , non-cancer effects	[CTUh]	1.06E+00	8.71E-01	6.67E-01	1.90E+00	1.55E+00	1.18E+00	3.81E-01	3.20E-01	2.48E-01
Ionizing radiation , human health	[kBq U235 eq]	6.30E+06	5.09E+06	3.82E+06	1.15E+07	9.31E+06	7.00E+06	2.14E+06	1.75E+06	1.30E+06
Ozone depletion	[kg CFC-11 eq]	1.46E-04	1.23E-04	9.77E-05	2.32E-04	1.89E-04	1.44E-04	4.57E-05	4.17E-05	3.28E-05
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	7.73E+03	6.43E+03	5.07E+03	1.25E+04	1.02E+04	7.71E+03	2.42E+03	2.01E+03	1.53E+03
Photochemical ozone formation , human health	[kg NMVOC]	1.25E+05	1.08E+05	9.03E+04	1.62E+05	1.32E+05	9.94E+04	3.11E+04	2.57E+04	1.94E+04
Resource depletion water,	[m^3 eq.]	6.04E+04	4.91E+04	3.73E+04	1.08E+05	8.75E+04	6.61E+04	2.04E+04	1.82E+04	1.39E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	1.25E+02	1.12E+02	9.77E+01	1.91E+02	1.66E+02	1.41E+02	6.48E+01	6.08E+01	5.57E+01

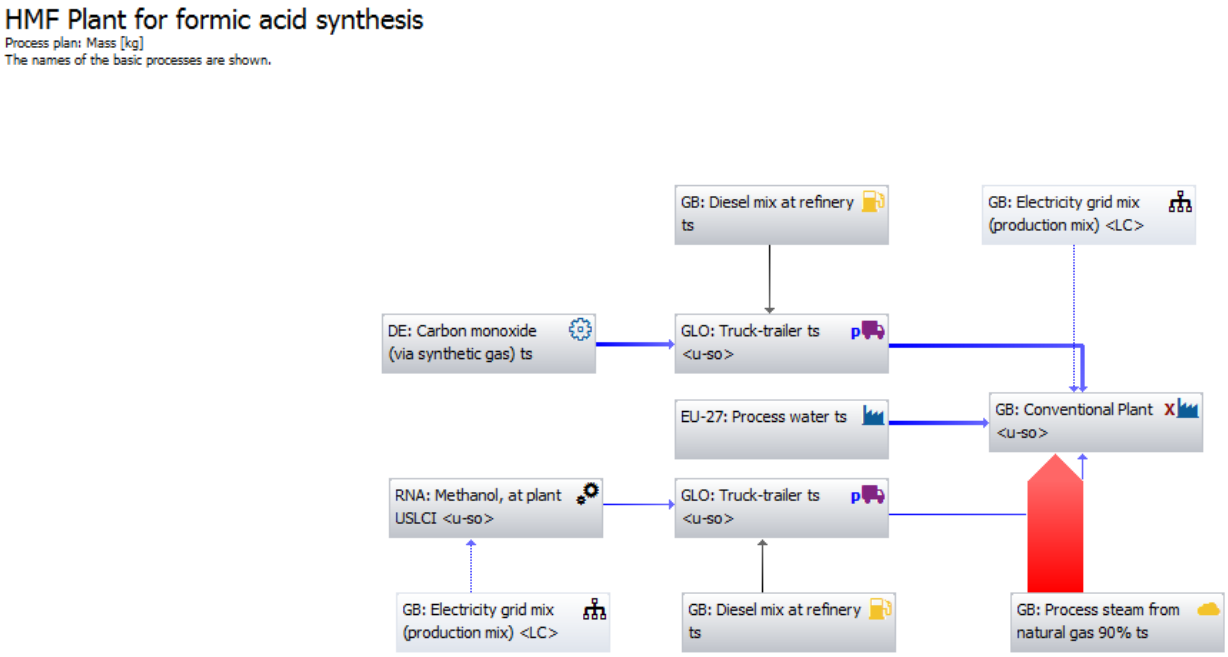
		Methanol			**Propionic acid**		
Indicators	**Conversion**	40	58.8	100	40	58.8	100
	Efficiency	40	69	100	40	69	100
Acidification	[Mole of H+ eq.]	1.96E+05	1.59E+05	1.23E+05	2.08E+05	1.73E+05	1.46E+05
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	5.99E+07	4.89E+07	3.81E+07	9.85E+07	8.81E+07	7.99E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	4.40E+07	3.32E+07	2.24E+07	7.79E+07	6.77E+07	6.00E+07
Ecotoxicity freshwater	[CTUe]	1.59E+06	1.30E+06	1.03E+06	1.57E+06	1.29E+06	1.09E+06
Eutrophication freshwater	[kg P eq]	2.25E+01	1.83E+01	1.60E+01	2.15E+01	1.76E+01	1.57E+01
Eutrophication marine	[kg N-Equiv.]	4.37E+04	3.56E+04	2.77E+04	5.08E+04	4.30E+04	3.71E+04
Eutrophication terrestrial	[Mole of N eq.]	4.71E+05	3.83E+05	2.98E+05	5.52E+05	4.68E+05	4.04E+05
Human toxicity , cancer	[CTUh]	3.50E-02	2.86E-02	2.26E-02	3.56E-02	2.95E-02	2.51E-02
Human toxicity , non-cancer effects	[CTUh]	1.44E+00	1.18E+00	9.22E-01	1.36E+00	1.11E+00	9.21E-01
Ionizing radiation , human health	[kBq U235 eq]	8.65E+06	7.01E+06	5.38E+06	8.14E+06	6.57E+06	5.34E+06
Ozone depletion	[kg CFC-11 eq]	1.76E-04	1.44E-04	1.23E-04	1.80E-04	1.50E-04	1.33E-04

Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	9.47E+03	7.71E+03	5.98E+03	9.60E+03	7.93E+03	6.63E+03
Photochemical ozone formation , human health	[kg NMVOC]	1.23E+05	9.96E+04	7.70E+04	1.46E+05	1.24E+05	1.07E+05
Resource depletion water,	[m^3 eq.]	8.13E+04	6.60E+04	5.50E+04	7.74E+04	6.29E+04	5.44E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	1.59E+02	1.40E+02	1.23E+02	1.48E+02	1.30E+02	1.24E+02

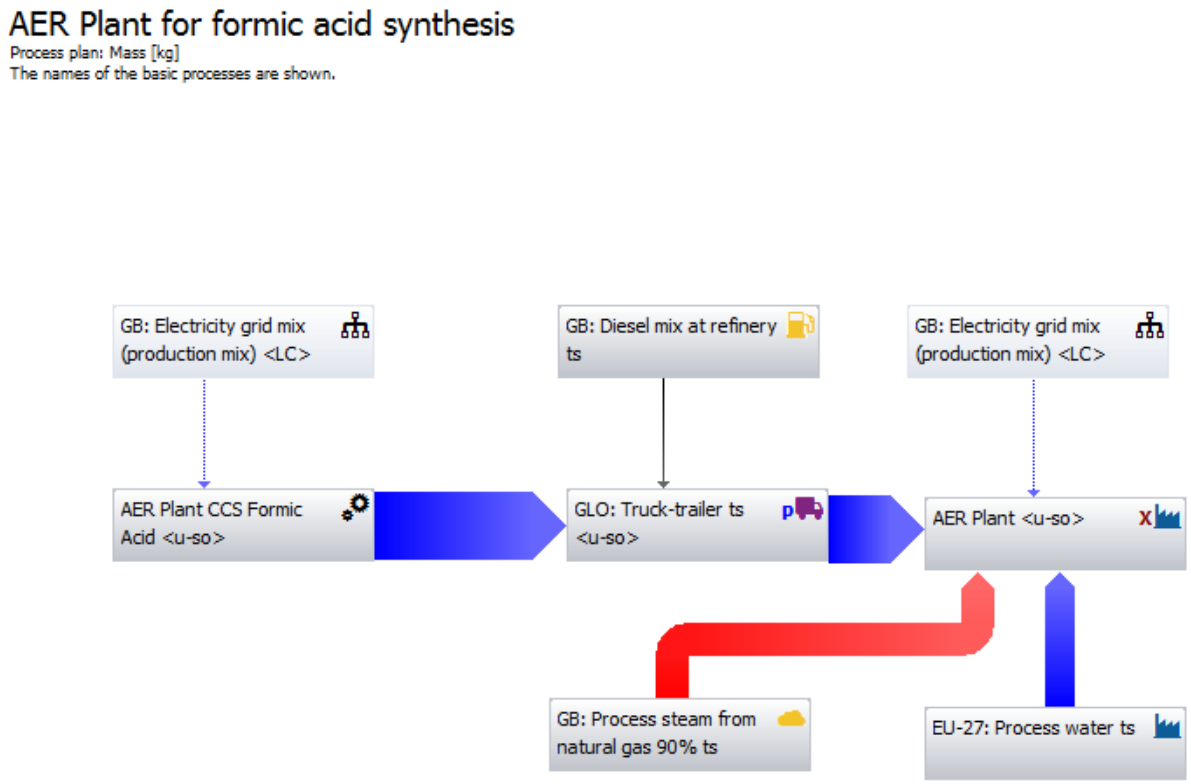
E1- GaBi flowsheets



Gabi flowsheet of base scenario for formic acid production through HCD

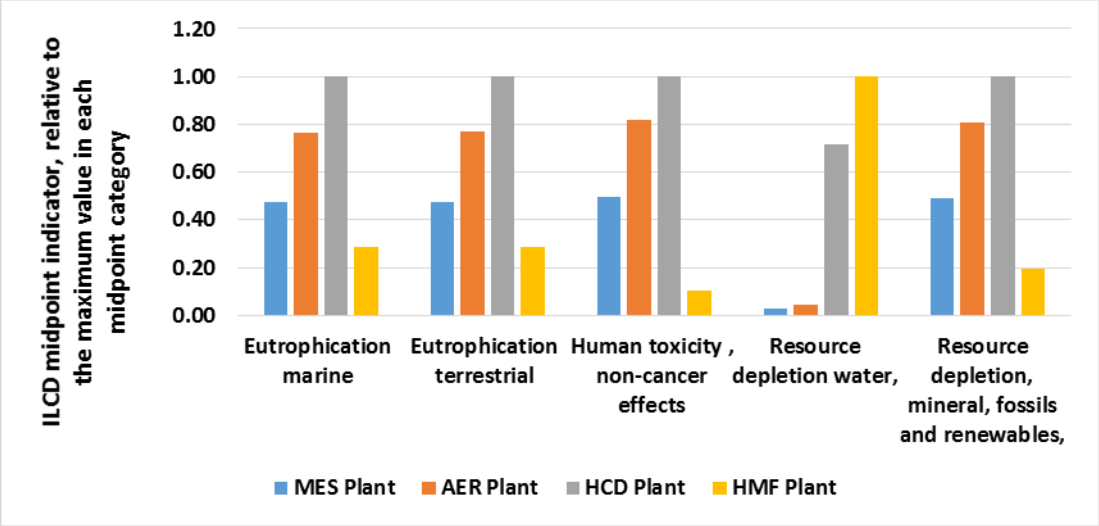


Gabi flowsheet of base scenario for formic acid production through HMF



Gabi flowsheet of base scenario for formic acid production through AER

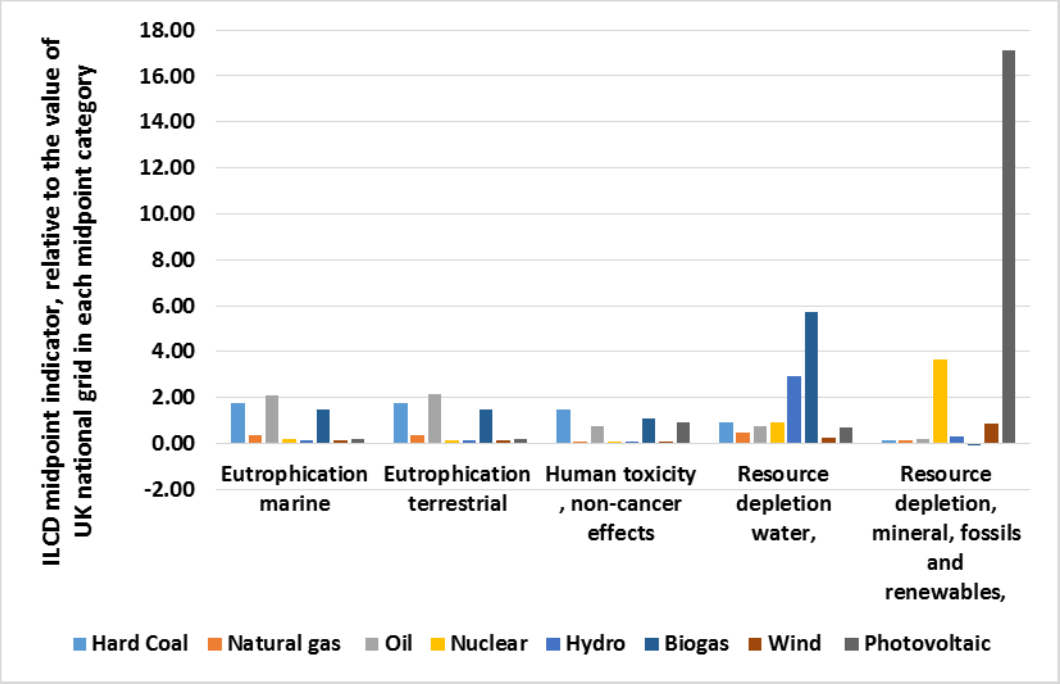
E2- midpoint impact category data



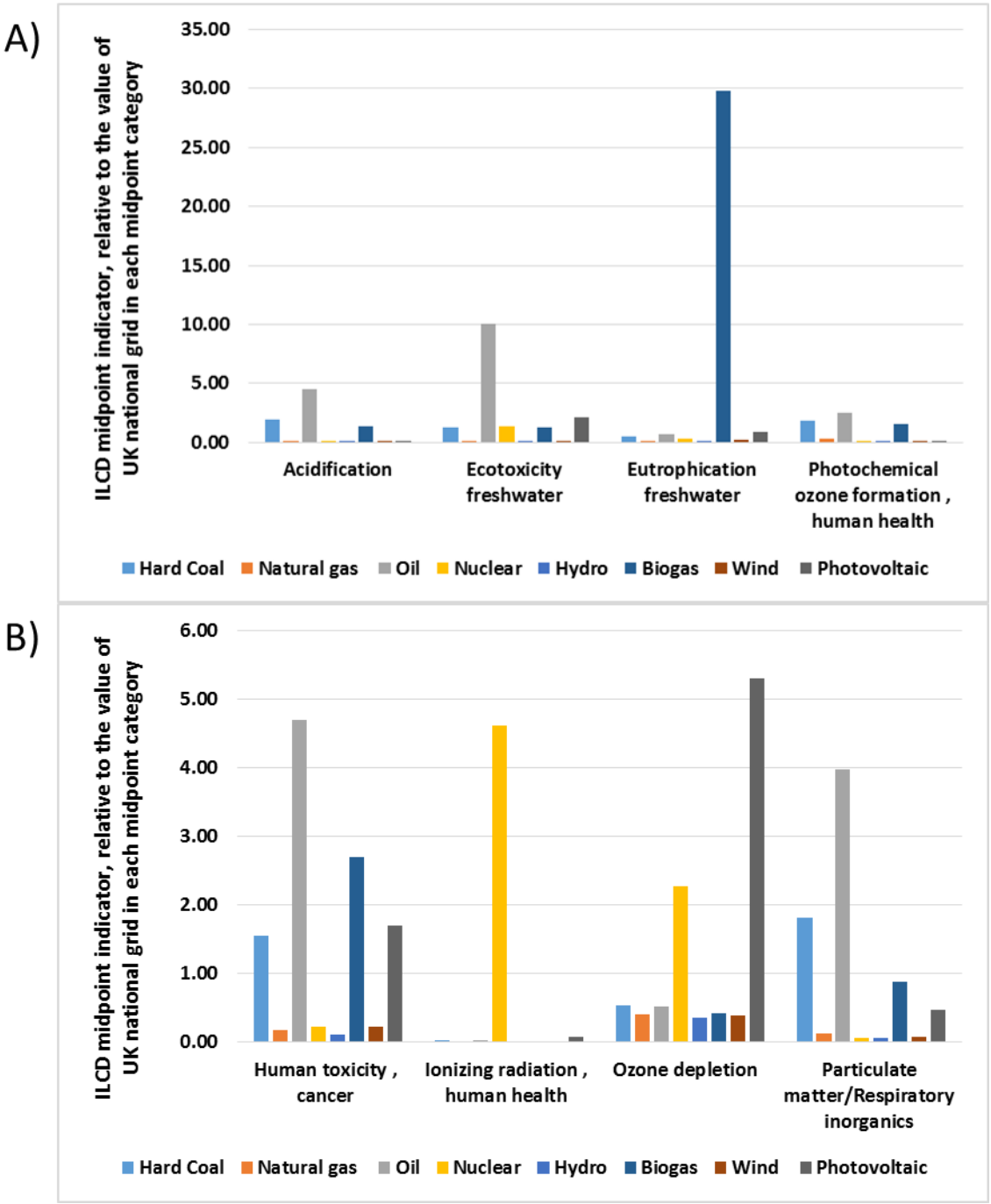
Life cycle environmental burdens of the MES, AER, HCD and HMF plant for the production of formic acid using ILCD method. Results are displayed relative to the maximum value in each impact category

Life cycle environmental burdens of the base scenario for MES, AER, HCD and HMF plants producing formic acid using ILCD method

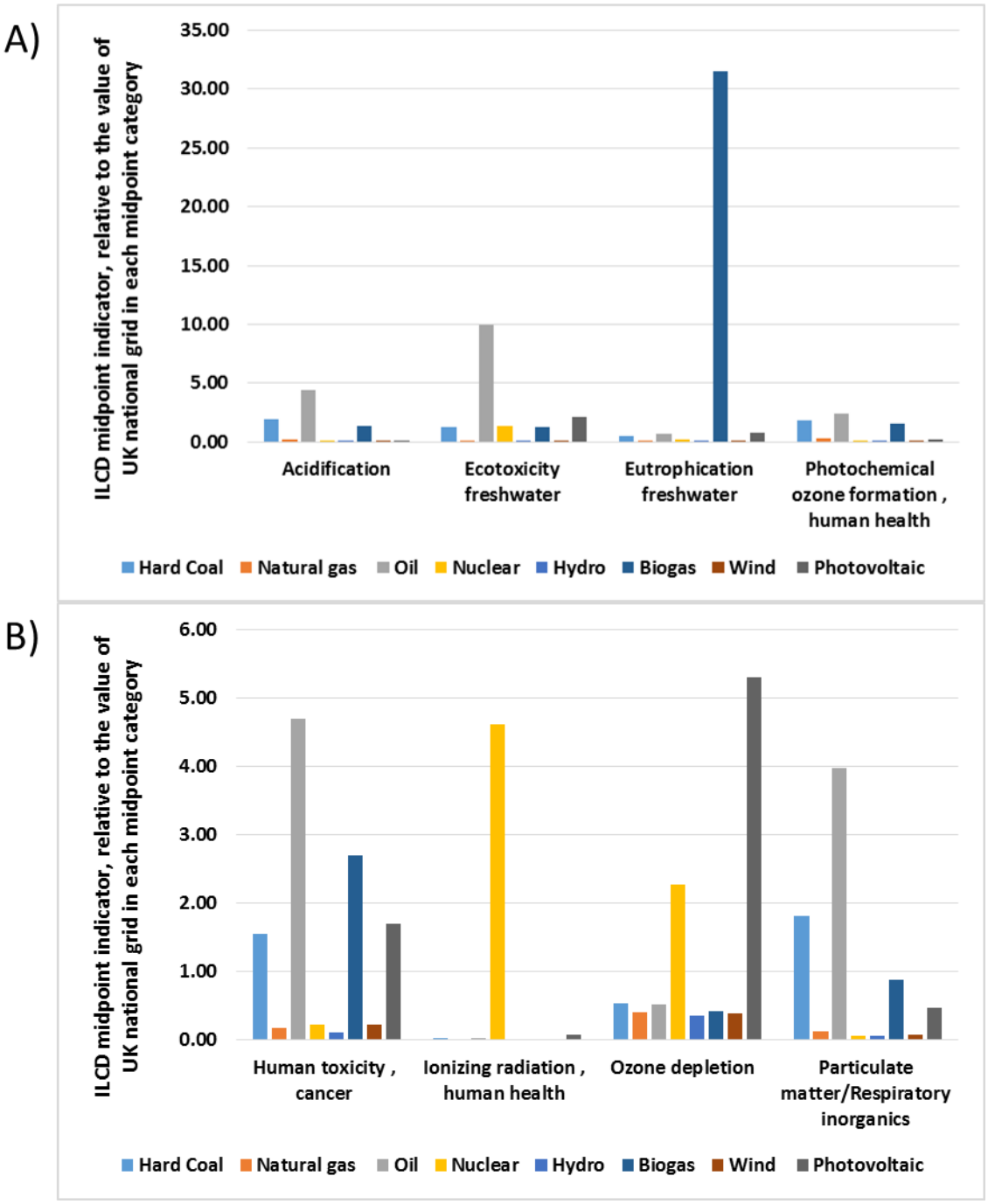
Indicators		**MES Plant**	**AER plant**	**HCD plant**	**HMF Plant**
Acidification	[Mole of H+ eq.]	4.07E+04	6.66E+04	8.40E+04	1.77E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	1.31E+07	2.08E+07	3.06E+07	1.84E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	2.12E+06	9.82E+06	2.22E+07	1.84E+07
Ecotoxicity freshwater	[CTUe]	3.21E+05	5.27E+05	6.50E+05	1.51E+05
Eutrophication freshwater	[kg P eq]	5.10E+00	8.03E+00	9.78E+00	9.69E+00
Eutrophication marine	[kg N-Equiv.]	9.11E+03	1.48E+04	1.93E+04	5.54E+03
Eutrophication terrestrial	[Mole of N eq.]	9.89E+04	1.61E+05	2.09E+05	6.04E+04
Human toxicity , cancer	[CTUh]	7.07E-03	1.16E-02	1.44E-02	3.32E-03
Human toxicity , non-cancer effects	[CTUh]	2.85E-01	4.70E-01	5.73E-01	6.03E-02
Ionizing radiation , human health	[kBq U235 eq]	1.78E+06	2.93E+06	3.57E+06	3.33E+05
Ozone depletion	[kg CFC-11 eq]	3.89E-05	6.16E-05	7.68E-05	4.78E-05
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	1.93E+03	3.17E+03	3.95E+03	6.74E+02
Photochemical ozone formation , human health	[kg NMVOC]	2.57E+04	4.19E+04	5.48E+04	2.14E+04
Resource depletion water,	[m^3 eq.]	1.75E+04	2.82E+04	4.42E+05	6.19E+05
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	2.00E+01	3.29E+01	4.08E+01	7.98E+00



Life cycle environmental burdens of the MES plant for eight different electricity sources using ILCD method. Results are displayed relative to the maximum value in each impact category



Life cycle environmental burdens of the AER plant for eight different electricity sources using ILCD method. A) Acidification, ecotoxixity, eutrophication and photochemical ozone formation B) Human toxicity, ionizing radiation, ozone depletion and particulate matter. Results are displayed relative to the value of the UK national grid in each impact category.



Life cycle environmental burdens of the HCD plant for eight different electricity sources using ILCD method. A) Acidification, ecotoxixity, eutrophication and photochemical ozone formation B) Human toxicity, ionizing radiation, ozone depletion and particulate matter. Results are displayed relative to the value of the UK national grid in each impact category.

Life cycle environmental burdens of other electricity sources for MES plant producing formic acid using ILCD method

Indicators		**Hard Coal**	**Natural gas**	**Oil**	**Nuclear**	**Hydro**	**Biogas**	**Wind**	**Photo voltaic**
Acidification	[Mole of H+ eq.]	7.93E+04	6.05E+03	1.82E+05	1.48E+03	9.13E+02	5.51E+04	1.23E+03	5.05E+03
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	2.09E+07	1.03E+07	2.03E+07	1.34E+06	1.39E+06	5.25E+06	1.36E+06	2.23E+06
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	9.94E+06	-6.15E+05	9.37E+06	-9.60E+06	-9.55E+06	-5.78E+06	-9.58E+06	-8.69E+06
Ecotoxicity freshwater	[CTUe]	4.05E+05	2.29E+04	3.23E+06	4.24E+05	7.00E+03	4.08E+05	3.44E+04	6.91E+05
Eutrophication freshwater	[kg P eq]	2.67E+00	7.23E-01	3.74E+00	1.42E+00	6.68E-01	1.53E+02	8.96E-01	4.30E+00
Eutrophication marine	[kg N-Equiv.]	1.70E+04	2.48E+03	2.06E+04	6.51E+02	3.66E+02	1.43E+04	4.37E+02	1.05E+03
Eutrophication terrestrial	[Mole of N eq.]	1.84E+05	2.75E+04	2.25E+05	5.73E+03	4.02E+03	1.51E+05	4.77E+03	1.14E+04
Human toxicity , cancer	[CTUh]	1.13E-02	8.18E-04	3.53E-02	1.18E-03	2.51E-04	2.00E-02	1.10E-03	1.23E-02
Human toxicity , non-cancer effects	[CTUh]	4.20E-01	4.89E-03	2.17E-01	1.24E-02	4.18E-03	3.16E-01	1.53E-02	2.60E-01
Ionizing radiation , human health	[kBq U235 eq]	3.03E+04	1.35E+04	3.02E+04	8.24E+06	4.78E+03	1.83E+04	8.49E+03	1.29E+05
Ozone depletion	[kg CFC-11 eq]	1.45E-05	7.62E-06	1.39E-05	1.06E-04	4.55E-06	8.75E-06	7.09E-06	2.64E-04
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	3.88E+03	1.88E+02	8.62E+03	6.71E+01	3.48E+01	1.85E+03	9.51E+01	9.44E+02
Photochemical ozone	[kg	4.74E+04	7.70E+03	6.52E+04	1.56E+03	1.07E+03	4.09E+04	1.27E+03	3.96E+03

formation , human health	NMVOC]								
Resource depletion water,	[m^3 eq.]	1.55E+04	6.11E+03	1.22E+04	1.52E+04	5.76E+04	1.17E+05	1.62E+03	1.11E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	2.38E+00	1.77E+00	3.05E+00	7.48E+01	5.39E+00	-2.27E+00	1.75E+01	3.55E+02

Life cycle environmental burdens of other electricity sources for AER plant producing formic acid using ILCD method

Indicators		**Hard Coal**	**Natural gas**	**Oil**	**Nuclear**	**Hydro**	**Biogas**	**Wind**	**Photo voltaic**
Acidification	[Mole of H+ eq.]	1.30E+05	9.45E+03	3.01E+05	1.91E+03	9.71E+02	9.05E+04	1.49E+03	7.80E+03
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	3.37E+07	1.62E+07	3.27E+07	1.41E+06	1.49E+06	7.86E+06	1.43E+06	2.88E+06
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	2.27E+07	5.31E+06	2.18E+07	-9.53E+06	-9.45E+06	-3.22E+06	-9.50E+06	-8.02E+06
Ecotoxicity freshwater	[CTUe]	6.65E+05	3.45E+04	5.34E+06	6.97E+05	8.22E+03	6.71E+05	5.35E+04	1.14E+06
Eutrophication freshwater	[kg P eq]	4.01E+00	7.97E-01	5.78E+00	1.94E+00	7.05E-01	2.53E+02	1.08E+00	6.70E+00
Eutrophication marine	[kg N-Equiv.]	2.78E+04	3.88E+03	3.38E+04	8.54E+02	3.82E+02	2.33E+04	5.00E+02	1.51E+03

Eutrophication terrestrial	[Mole of N eq.]	3.02E+05	4.30E+04	3.69E+05	7.02E+03	4.19E+03	2.47E+05	5.43E+03	1.63E+04
Human toxicity , cancer	[CTUh]	1.85E-02	1.23E-03	5.82E-02	1.83E-03	2.97E-04	3.29E-02	1.70E-03	2.03E-02
Human toxicity , non-cancer effects	[CTUh]	6.94E-01	7.16E-03	3.58E-01	1.96E-02	5.99E-03	5.21E-01	2.43E-02	4.29E-01
Ionizing radiation , human health	[kBq U235 eq]	4.73E+04	1.96E+04	4.71E+04	1.36E+07	5.19E+03	2.75E+04	1.13E+04	2.10E+05
Ozone depletion	[kg CFC-11 eq]	2.13E-05	9.90E-06	2.02E-05	1.72E-04	4.81E-06	1.18E-05	9.02E-06	4.34E-04
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	6.39E+03	2.94E+02	1.42E+04	9.36E+01	4.02E+01	3.04E+03	1.40E+02	1.54E+03
Photochemical ozone formation , human health	[kg NMVOC]	7.76E+04	1.21E+04	1.07E+05	1.92E+03	1.12E+03	6.69E+04	1.45E+03	5.89E+03
Resource depletion water,	[m^3 eq.]	2.50E+04	9.43E+03	1.94E+04	2.45E+04	9.44E+04	1.92E+05	2.00E+03	1.77E+04
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	3.77E+00	2.77E+00	4.88E+00	1.23E+02	8.75E+00	-3.90E+00	2.88E+01	5.86E+02

Life cycle environmental burdens of other electricity sources for HCD plant producing formic acid using ILCD method

Indicators		**Hard Coal**	**Natural gas**	**Oil**	**Nuclear**	**Hydro**	**Biogas**	**Wind**	**Photo voltaic**
Acidification	[Mole of H+ eq.]	1.62E+05	1.45E+04	3.68E+05	5.36E+03	4.22E+03	1.13E+05	4.86E+03	1.25E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	4.63E+07	2.51E+07	4.51E+07	7.07E+06	7.16E+06	1.49E+07	7.10E+06	8.85E+06
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	3.79E+07	1.68E+07	3.68E+07	-1.27E+06	-1.18E+06	6.39E+06	-1.24E+06	5.59E+05
Ecotoxicity freshwater	[CTUe]	8.19E+05	5.21E+04	6.49E+06	8.58E+05	2.02E+04	8.25E+05	7.52E+04	1.39E+06
Eutrophication freshwater	[kg P eq]	4.89E+00	9.92E-01	7.04E+00	2.38E+00	8.82E-01	3.08E+02	1.34E+00	8.16E+00
Eutrophication marine	[kg N-Equiv.]	3.50E+04	5.95E+03	4.23E+04	2.28E+03	1.71E+03	2.96E+04	1.85E+03	3.08E+03
Eutrophication terrestrial	[Mole of N eq.]	3.81E+05	6.61E+04	4.62E+05	2.24E+04	1.89E+04	3.14E+05	2.04E+04	3.37E+04
Human toxicity , cancer	[CTUh]	2.29E-02	1.86E-03	7.11E-02	2.59E-03	7.24E-04	4.04E-02	2.43E-03	2.50E-02
Human toxicity , non-cancer effects	[CTUh]	8.45E-01	1.08E-02	4.37E-01	2.59E-02	9.37E-03	6.34E-01	3.17E-02	5.23E-01
Ionizing radiation , human health	[kBq U235 eq]	6.28E+04	2.93E+04	6.26E+04	1.65E+07	1.17E+04	3.88E+04	1.92E+04	2.60E+05
Ozone depletion	[kg CFC-11 eq]	2.77E-05	1.39E-05	2.64E-05	2.11E-04	7.73E-06	1.62E-05	1.28E-05	5.29E-04
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	7.86E+03	4.52E+02	1.74E+04	2.08E+02	1.43E+02	3.79E+03	2.64E+02	1.97E+03

Photochemical ozone formation , human health	[kg NMVOC]	9.83E+04	1.86E+04	1.34E+05	6.25E+03	5.27E+03	8.51E+04	5.68E+03	1.11E+04
Resource depletion water,	[m^3 eq.]	4.38E+05	4.19E+05	4.31E+05	4.37E+05	5.22E+05	6.41E+05	4.10E+05	4.29E+05
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	5.48E+00	4.27E+00	6.84E+00	1.51E+02	1.15E+01	-3.84E+00	3.59E+01	7.13E+02

Life cycle environmental burdens of other electricity sources for HMF plant producing formic acid using ILCD method

Indicators		**Hard Coal**	**Natural gas**	**Oil**	**Nuclear**	**Hydro**	**Biogas**	**Wind**	**Photo voltaic**
Acidification	[Mole of H+ eq.]	2.32E+04	1.28E+04	3.78E+04	1.22E+04	1.21E+04	1.98E+04	1.22E+04	1.27E+04
Climate change, excl biogenic carbon	[kg CO2-Equiv.]	1.95E+07	1.80E+07	1.94E+07	1.67E+07	1.68E+07	1.73E+07	1.67E+07	1.69E+07
Climate change, incl biogenic carbon	[kg CO2-Equiv.]	1.95E+07	1.80E+07	1.94E+07	1.68E+07	1.68E+07	1.73E+07	1.68E+07	1.69E+07
Ecotoxicity freshwater	[CTUe]	1.63E+05	1.09E+05	5.64E+05	1.66E+05	1.07E+05	1.63E+05	1.10E+05	2.04E+05
Eutrophication freshwater	[kg P eq]	9.35E+00	9.07E+00	9.50E+00	9.17E+00	9.07E+00	3.07E+01	9.10E+00	9.58E+00
Eutrophication marine	[kg N-Equiv.]	6.65E+03	4.60E+03	7.16E+03	4.34E+03	4.30E+03	6.27E+03	4.31E+03	4.39E+03
Eutrophication terrestrial	[Mole of N eq.]	7.26E+04	5.03E+04	7.83E+04	4.72E+04	4.70E+04	6.78E+04	4.71E+04	4.80E+04
Human toxicity , cancer	[CTUh]	3.92E-03	2.44E-03	7.33E-03	2.49E-03	2.35E-03	5.16E-03	2.47E-03	4.07E-03

Human toxicity , non-cancer effects	[CTUh]	7.95E-02	2.06E-02	5.07E-02	2.16E-02	2.04E-02	6.46E-02	2.20E-02	5.67E-02
Ionizing radiation , human health	[kBq U235 eq]	8.56E+04	8.32E+04	8.56E+04	1.25E+06	8.20E+04	8.39E+04	8.25E+04	9.96E+04
Ozone depletion	[kg CFC-11 eq]	4.43E-05	4.33E-05	4.42E-05	5.72E-05	4.29E-05	4.35E-05	4.32E-05	7.97E-05
Particulate matter/Respiratory inorganics	[kg PM2,5-Equiv.]	9.51E+02	4.27E+02	1.62E+03	4.10E+02	4.05E+02	6.63E+02	4.14E+02	5.34E+02
Photochemical ozone formation , human health	[kg NMVOC]	2.45E+04	1.88E+04	2.70E+04	1.80E+04	1.79E+04	2.35E+04	1.79E+04	1.83E+04
Resource depletion water,	[m^3 eq.]	6.19E+05	6.18E+05	6.19E+05	6.19E+05	6.25E+05	6.33E+05	6.17E+05	6.18E+05
Resource depletion, mineral, fossils and renewables,	[kg Sb-Equiv.]	5.49E+00	5.40E+00	5.58E+00	1.58E+01	5.91E+00	4.83E+00	7.64E+00	5.55E+01

F1- List of Disseminations

1. Oral presentation

Conference: Scotland and North of England Electrochemistry Symposium

Organizer: Royal Society of Chemistry

Location/date: Glasgow, 20th April, 2016

Title: Bioelectricity generation using mixed culture from anaerobic sludge in dual chambered bioelectrochemical system

Conference: 6th International Congress on Green Process Engineering

Organizer: GPE

Location/date: Toulouse, 3-6 June 2018

Title: A comparative study on sustainability analysis of microbial electrosynthesis and abiotic electrochemical reduction
(In absentia, presented by Dr Sharon Velasquez-Orta).

2. Poster presentation

Conference: Scotland and North of England Electrochemistry Symposium

Organizer: Royal Society of Chemistry

Location/date: St Andrews, 26th April, 2017

Title: Sustainability assessment of using carbon dioxide in microbial electrosynthesis

3. Articles published

Christodoulou, X., Okoroafor, T., Parry, S. and Velasquez-Orta, S.B. (2017) 'The use of carbon dioxide in microbial electrosynthesis: Advancements, sustainability and economic feasibility', Journal of CO2 Utilization, 18, pp. 390-399

Okoroafor, T. and Velasquez-Orta, S.B. (2018) ‘A comparative study on sustainability analysis of microbial electrosynthesis and abiotic electrochemical reduction', In: 6th International Congress on Green Process Engineering, Toulouse, France.

4. Courses Attended

Course: Advanced electrochemistry Course

Organizer: Birmingham University

Location/date: Birmingham, January, 2016