A Critical Review of Integration Analysis of Microbial Electrosynthesis (MES) Systems with Waste Biorefineries for the Production of Biofuel and Chemical from Reuse of CO2

Jhuma Sadhukhan¹, Jon Lloyd⁴, Keith Scott³, Giuliano C Premier⁵, Eileen Yu³, Tom Curtis² and Ian Head²

¹Centre for Environmental Strategy, University of Surrey, Guildford, Surrey, GU2 7XH, UK.
²School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, Tyne and Wear NE1 7RU, UK.
³School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, Tyne and Wear NE1 7RU, UK.
⁴Manchester Geomicrobiology Group, The University of Manchester, Oxford Road Manchester, M13 9PL, UK.
⁵Sustainable Environment Research Centre (SERC), Faculty of Computing, Engineering and Science University of South Wales, Pontypridd, Mid-Glamorgan, CF37 1DL, UK.

Abstract

Despite some success with microbial fuel cells and microbial electrolysis cells in recovering resources from wastes, challenges with their scale and yield need to be resolved. Waste streams from biorefineries e.g. bioethanol and biodiesel plants and wastewaters are plausible substrates for microbial electrosynthesis (MES). MES integration can help biorefineries achieving the full polygeneration potentials, i.e. recovery of metals turning apparently pollutants from biorefineries into resources, production of biofuels and chemicals from reuse of CO₂ and clean water. Symbiotic integration between the two systems can attain an economic and environmental upside of the overall system. We envision that electrochemical technologies and waste biorefineries can be integrated for increased efficiency and competitiveness with stillage released from the latter process used in the former as feedstock and energy resource recovered from the former used in the latter. Such symbiotic integration can avoid loss of
material and energy from waste streams, thereby increasing the overall efficiency, economics and environmental performance that would serve towards delivering the common goals from both the systems. We present an insightful overview of the sources of organic wastes from biorefineries for integration with MES, anodic and cathodic substrates and biocatalysts. In addition, a generic and effective reaction and thermodynamic modelling framework for the MES has been given for the first time. The model is able to predict multi-component physico-chemical behaviour, technical feasibility and best configuration and conditions of the MES for resource recovery from waste streams.

**Keywords:** lignocellulosic biorefinery, Gibbs free energy minimisation, thermodynamic optimisation, bioenergy, bioelectrochemistry, resource recovery from waste, MFC, BES

* Author/s to whom correspondence should be addressed: E-mail: jhumasadhukhan@gmail.com; Phone: +44 (0)1483 686642.
1. Introduction

In the most advanced sense, a biorefinery is a facility with integrated, efficient and flexible conversion of biomass feedstocks, through a combination of physical, chemical, biochemical and thermochemical processes, into multiple products [1,2]. The concept was developed by an analogy to the complex crude oil refineries adopting the process engineering principles applied in their designs, such as feedstock fractionation, multiple value-added productions, process flexibility and integration [1]. This definition of biorefinery evolved from the earlier works of the National Renewable Energy Laboratory (NREL) [3] and the Department of Energy (DOE) of the USA [4]. The products to target from lignocellulosic materials are the main question for a biorefinery system. Biorefineries are often ambiguously inferred to bioethanol or biodiesel production plants, which may or may not have accompanying combined heat and power (CHP) generation [5,6]. The most significant change occurred from 19th century through 1970s (when major uphill in the production of biofuel was observed) to today, is the use of lignocelluloses or waste materials as the feedstock [5]. However, biofuel plants are not economically feasible without subsides or guaranteed return on investment, unless high grade valuable materials from waste are coproduced. To name a few of the regulatory frameworks that support biofuel development are the “2020 climate and energy strategy” and the Renewable Energy Directive (RED) in Europe, through which the biofuel blend has been mandated with the target biofuel blend by 10% (by energy) by 2020 [7]. The Fuel Quality Directive introduced a mandatory target of a 6% reduction, by 2020, in the greenhouse gas (GHG) intensity of fuels used in road transport and non-road mobile machinery [7]. The economic return on investment of biofuel plants however fundamentally depends on the ability of coproduction of high grade valuable materials, spear-heading of which is the food and pharmaceutical ingredient, followed by composite, polymer, chemical, hydrogen, respectively. Biofuel and CHP though have high demands and production volumes, but have lower market values, compared to chemical products. 5.6% growth per year
in global chemical demand is expected, while China, India, Asia and Africa with expected gross domestic product (GDP) growth can have more than 10% growth per year in chemical demand [8]. Fig. 1 shows the targeted products for biorefineries [1]. The products at the top of the triangle have high value, but low market demand, while the base products have low value, but high demand and volume of production. A recent report disclosed that biofuel production should not be conflicted with non-fuel added-value uses of plant / agricultural / forestry residues, especially where there are markets for healthcare and food products [9]. Thus, innovative biorefineries can be designed to produce numerous high grade valuable materials alongside energy products, biofuel and CHP, to boost the overall economic gains of the biorefineries and from wastes [1]. The state of the art biofuel plants have a number of stillage streams, e.g. CO$_2$ from fermentation [10,11,12], dilute glycerol and waste streams from biodiesel plant [13,14] and effluents [15] that are being disposed of to the environment. Microbial electrosynthesis (MES) processes are suitable for sustainable conversion of stillage streams from industrial systems into added value materials [16,17,18,19]. Thus, the stillage streams from biorefineries can be a substrate for MES to produce added value products. The coupled system can achieve an overall sustainability, encompassing economic, environmental, social and technical (scale and efficiency) aspects. Thus, process integration concept is urgently needed for the sector to take complementary advantages and widen the product portfolio. To achieve the objective, integrated innovative conceptual process flowsheets and models for integration of MES are presented and discussed here. We envision that MES processes and waste biorefineries can be integrated for increased resource recovery efficiency from wastes: 1) agricultural and forestry residues and energy crops: wood, short rotation coppice, poplar, switchgrass and miscanthus; 2) grass: leaves, green plant materials, grass silage, empty fruit bunch, immature cereals; 3) oily residues: waste cooking oils and animal fat; 4) aquatic biomass: algae and seaweed; and 5) organic residues: municipal waste, manure and sewage [1]. Such symbiotic or synergistic integration can avoid loss of material and energy from waste streams, thereby increasing the overall efficiency, economics and environmental performance.
that would serve towards delivering the common goals of both systems. We envision that their relatively small scales would work in each-others favour and be complementary that could give a momentum in commercialization of these technologies.

Earlier works have considered reuse of CO$_2$ rich streams in chemical reactions to produce syngas, hydrogen, formic acid, methane, ethylene, methanol, dimethyl ether, urea, Fischer-Tropsch liquid, succinic acid, etc. as well as materials, such as epoxides acetals and orthoesters as important precursors to many polymers and carbonates through mineralisation reactions for construction applications [20,21]. CO$_2$ as a reactant in Sabatier’s reaction for methane formation, in reactions to produce calcite and succinic acid and CO$_2$ reuse for the growth of algae to produce biofuels, e.g. bioethanol and biodiesel have been analysed for techno-economic feasibility. But, this is the first review paper on CO$_2$ reduction reactions using MES. The relevant anode and cathode reactions, their Gibbs free energies and the Gibbs free energy of formations of the species participating in these reactions [22], along with the calculations of the Gibbs free energies of reactions are given in Supplementary information 1. 63 anodic and 72 cathodic reactions of metabolism and 9 metabolic pathways have been collated for future modelling for assessing technical feasibility / thermodynamic spontaneity (or constraint) of resource recovery from waste substrates and combinations of anodic and cathodic reactions using MES.

Bio fuel cells were first performed to generate electricity using organic substrate to grow the bacteria following the rules of nature [23]. The first microbial electrolysis cell reported to generate hydrogen in technologically significant quantity dates back to 1970s [24], however, the name “microbial electrolysis cell” (MEC) was coined only in 2008 [25,26,27,28] after evolving through numerous others such as H-type electrolysis cell [29], biocatalytic electrolysis cell [30] to mention amongst many others. In recent times, there have been efforts to homogenize the nomenclature in this area [31,32]. The microbial fuel cell (MFC) and MEC schematics are depicted in Fig. 2 [26,33]. Since 2010, a paradigm shift has
happened in the ability to generate organics from CO$_2$ reduction in MES [16]. Apart from organics, MES can recover functional nanomaterials such as nanocatalysts, quantum dots and nanomagnets [34].

Amongst the earlier developments in MES, electromethanogenesis is a process to reduce carbon dioxide in the cathode chamber to produce methane [35]. In principle, recovery of aromatic compounds and cyclic alkanes from organic wastes is possible. Similar to the cathode chamber, the anode chamber can also generate a number of products, bioethanol or biofuel or bulk chemical, however, relying on the specific substrate, e.g. glucose, acetate, glycerol, etc. [22]. Also, polymers can be decomposed into pyruvate, formate and fatty acids by microbial oxidation in the anode chamber. Fig. 3 shows a generic MES schematic with the range of cathode and anode substrates and products. The substrates can be similar to those reported for MFC: stillage streams from fermentation, wastewater treatment, biodiesel plants, sugar rich streams from lignocellulose fractionation, hydrogenation processes, etc. [36]. Anode can be catalysed by microorganisms or immobilised with enzymes, while cathode can be catalysed by chemical or microbial catalysts (microorganisms or enzyme immobilization). All such systems are referred as MES in this paper. Bioelectrochemical oxidation of anode substrates generates carbon dioxide and hydrogen specie or carbonic acid and hydrogen. A typical anode reaction results in hydrogen specie and electron generation. Hydrogen can pass through the electrolyte (with or without a proton exchange membrane) to cathode by the application of external voltage. With the supply of renewable electricity, wind turbines, photovoltaic cells and hydropower, etc., MES is potentially an important technology for sustainable resource recovery or polygeneration of biofuels, hydrogen or electricity, chemicals and materials, from waste [37,38,39]. It is evident that the research interest in this area is truly global with increasing number of published studies from researchers coming from different countries [18,35]. However, to achieve the full potential of polygeneration and successful commercial development of MES technologies, new modelling tools are desperately needed. Although there have already been a number of papers published on substrates [36,40] and microorganisms [41,42] and electrode material selections [17], most have
focused on design point performance evaluation (or a particular experimental set up) rather than optimisation of design and operations and modelling for systematic integration with industrial flowsheets and scale-up. Systems modelling combined with thermodynamic correlations can be a valuable tool to predict multi-component physico-chemical behaviour, providing indications of technical feasibility, identifying ways to improve efficiency and determining the best configuration and conditions for inherently integrated MES for resource recovery from waste within biorefinery systems [43,44,45]. This paper makes several novel contributions.

1) Integrated biorefinery and MES process conceptual flowsheets;

2) A plethora of added value product generation options from MES, and integrated biorefinery and MES process flowsheets;

3) Theoretical modelling framework for MES systems from the fundamental basis of the Gibbs free energy minimisation or thermodynamic optimisation of biologically relevant reactions to produce biofuels, hydrogen, energy and chemical products.

4) A market- and sustainability- driven strategy to speed up development of MES combining metabolic flux analysis, metabolic pathway analysis, thermodynamic optimisation, process simulation, dynamics and control experimentation.

The paper has been structured as follows. Section 2 gives an insightful overview of novel integrated biorefinery and MES process schemes. Section 3 gives an overview of relevant CO₂ reuse or reduction reactions. Sections 4-5 discuss the thermodynamic model formulation and future directions in integrated biorefinery and MES research. Section 6 draws on conclusions

2. **Integrated biorefinery and MES conceptual flowsheets**
Biorefineries produce a wide variety of process wastes containing degradable organics that can make good substrates for MES, specifically the anode. These wastes can be broadly divided into stillage streams from i) bioethanol plant; ii) lignocellulose fractionation based biorefinery; iii) biodiesel plant; and iv) sludge and wastewater substrates, discussed as follows. Alongside insightful integration principles between biorefineries and MES processes are illustrated. Further, some important developments in anode bacteria have been indicated.

**Bioethanol plant:** Bioethanol production from sugarcane in Brazil only utilises 38% of the cane energy, 12% is discharged as vinasse and 50% remains in the bagasse [46]. The vinasse is the effluent containing glycerol, yeast nutrients, cell debris and residual ethanol. In the United States, another large bioethanol producer, corn or corn stover is used for starch extraction with the majority produced by dry milling and only some by wet milling, which is followed by fermentation of the starch derived from them into bioethanol production [47]. The residue generated from dry and wet milling processes is quite similar in terms of constituents containing carbohydrate, glycerol and ethanol [48]. All these stillage streams make suitable substrates for MES.

**Lignocellulose fractionation followed by fermentation based biorefinery:** Lignocelluloses are a complex mixture of structural polysaccharides, mainly cellulose and hemicellulose, encased by polyphenolic lignin and are the main constituent of plant cell-wall material [49]. Lignocellulosic wastes can not be directly utilised in microbial oxidation in MES anode as lignin is recalcitrant and is resistant to hydrolysis, unlike polysaccharides and sugars. Lignin encasing cellulose in cell walls provides cell walls rigidity and strength against microbial decomposition [1]. Extraction of lignin thus reduces the cost of production of cellulosic products as well as increases utilisation using MES. Hence, lignocellulose should be fractionated or pretreated to recover cellulose and some hemicelluloses, from lignin, before being fed to the anode chamber of MES process. Pretreatment processes include mechanical, physical: steam explosion and chemical processes: organosolv (using solvent, in which lignin and some hemicelluloses
are soluble, thus separating from cellulosics, hydrothermal operation under supercritical operation and in alkaline, pH neutral and acid media etc. [50,51,52]. Pretreatment liberates cellulose microfibrills can be easily converted into glucose by enzymatic hydrolysis, followed by ethanol and chemical productions [1]. Alternatively, cellulose microfibrills can be used to form continuous phase (matrix) of composite materials [53,54,55]. Hemicellulose (C5 sugars) upon further processing: alkaline extraction, alkaline peroxide extraction, hot water/steam extraction and chemical conversion etc. gives rise to a number of chemicals, xylitol, furfural, 5-hydroxymethylfurfural, L-arabinose, furan resins and nylon, etc. [1]. Lignin can be processed into wood adhesives, epoxy resins, fuel additives, benzene-toluene-xylene, binders, carbon fiber, polyurethanes, polyolefins and specialty phenolics for high value applications, such as pharmaceuticals and fragrances (vanillin) [1]. These various routes to polygeneration from wastes (i.e. concept of multi-platform and multi-product biorefinery systems) are illustrated in Fig. 4 [1].

Fig. 5 shows plausible principles for the integration of MES process with bioethanol plants. In route 1 in Fig. 5, some pretreated lignocellulosic feedstock is diverted to produce enzyme and yeast onsite to be utilised in solid state fermentation of the rest of the pretreated lignocellulose producing bioethanol [56,57]. Research has shown that producing the enzyme and yeast on-site from the same biomass saves on operating cost and makes an economically feasible case. The cases were drawn from USA [56] and EU and Malaysia [57]. The liquid stillage streams from bioethanol purification section (consisting of distillation, molecular sieve adsorption and dehydration) are the substrates in MES. The residual solids from the bioethanol purification section primarily consisting of lignin in the configuration shown are combusted for CHP generation. However, a more economic value generation route is catalytic hydrodeoxygenation (HDO) [58] of lignin into functional phenolics, vanillin, syringol, etc. shown in Fig. 4 [1], needing hydrogen that can be sourced from MEC. This way, the two processes, bioethanol purification and MEC are integrated in both ways and additional economic value can be generated from lignin valorisation. The bioethanol plant usually has net output electricity generation for export [56,57].
Hence, lignin can be diverted from electricity generation to HDO, increasing added value product generation and lowering electricity generation until no external electricity supply is needed and energy need for the site is met. This example shows replacing low value energy generation by added value chemical production (Fig. 1).

Route 2 in Fig. 5 leads to C6, C5 and lignin platforms, which would then have a plethora of choices of products, as illustrated in Fig. 4. The two immediate integration synergies between biorefinery and MES processes can be identified: C6 and C5 sugars are used in fermentation to produce bioethanol (exploring the integration synergies in route 1) and C6 and C5 sugars utilisation as substrates for product generation using MES. The anode can microbially decompose glucose rich stream by glucose metabolism Entner-Doudoroff pathway into carbon dioxide, hydrogen species and electrons. The cathode either chemically or microbially catalysed, can generate electricity and water in open to air configuration (MFC) or hydrogen in anaerobic condition by application of voltage in an MEC (12 moles of hydrogen can be generated from 1 mole of glucose). Alternatively, carbon dioxide and hydrogen from the anode can be utilised to generate biofuel or chemical, e.g. glucose reduced into glutamate, propionate and butanol, from the anaerobic cathode in MES. Sugars are the most common substrates in bioelectrochemical systems [59]. The versatile Shewanella species for example, a functionally electrogenic niche organisms, has been shown to catabolise a variety of carbon source materials (aquatic debris) typical of their natural environments. A richer variety of carbon utilising pathways was available than had been known for Shewanella oneidensis MR-1 [60]. Cofactor expression by various engineered approaches, altering the redox chemistry [61], could provide tuned redox coupling, or enzyme expression (in e.g. Saccharomyces cerevisiae) for conversion of lignocellulosic substrates to monosaccharides [62]. Gut bacteria are primarily responsible for metabolite products. Though mixed cultures are more likely to be used, there are finite families of naturally available gut bacteria for targeted products, e.g. Butyrivibrio spp and Roseburia spp for
butyrate; methanogens for methane; acetogens for acetate; and \textit{Bacteroides} spp and \textit{Prevotella} spp for propionate [49].

\textbf{Biodiesel plant:} The biodiesel industry is one of the most prominent biofuel industries in Europe, produces wastes containing glycerol, residual fatty acids and alcohols. Their conventional purification technologies are energy intensive [13,14]. A comprehensive energy and greenhouse gas emission analysis of a cradle to gate biodiesel production system (from raw material extraction upto the production gate) has been illustrated that concludes the following [13,14].

Per 100 mass units of biodiesel production via conventional methods (\textit{e.g.} transesterification of waste oils followed by distillation):

1. 5.3 mass units of oily waste are produced and
2. 10.7 mass units of glycerol are produced;
3. 466 MJ of energy is consumed per 100 kg biodiesel produced
4. 12\% of the total energy consumed is spent in the product recovery section.

The energy lost can instead be recovered in the form of useful products and energy vectors by MES. Fig. 6 shows plausible integration schematics of MES with existing biodiesel plant utilising waste oils and oily residues. The anode microbially oxidises glycerol rich stream into bioethanol, hydrogen species and electrons. The prokaryotic pathway using \textit{Enterobacteriaceae} species primarily results in bioethanol product from the anode. The cathode, either chemically or microbially catalysed, generates electricity and water in open to air configurations of MFC or hydrogen generation by application of voltage in anaerobic condition in an MEC (1 mole of hydrogen is produced per mole of glycerol decomposed). Alternatively, carbon dioxide and hydrogen from anode can be utilised in combination with or without additional waste streams as substrate sourced from other industrial systems (\textit{e.g.} Fig. 5) to generate biofuel or chemical from anaerobic cathode in MES. Oligochemical industrial processes carry out epoxidation, sulfonation, ethoxylation, hydrogenation, etc. of fats and oils from plant and animal sources to produce chemicals,
while generating oil-laden wastes suitable as substrate for MES [37]. Food processing industries are another example of producing a wide variety of process wastes containing degradable organics [63].

A case of mass balance and productivities of the integrated flowsheet shown in Fig. 6 is illustrated in the “Supplementary material on biodiesel process flowsheet synthesis and hypothesis for MES creation”.

**Sludge and wastewater substrates:** In the last century, the activated sludge process has been the mainstay of wastewater treatment. However, it is a very energy intensive process, with approximately 0.5 kWh electrical energy consumed in treating 1 m$^3$ municipal wastewater and the total electricity consumption for wastewater treatment in the USA is 3% of the total energy usage in the USA [37,64]. Wastewater of low strength is suitable for energy generations, due to low concentration of inhibitory substances, e.g. ammonia [65]. Amongst the other wastewater streams, starch processing wastewater containing carbohydrate (2-3.5 g l$^{-1}$) and starch (1.5-3 g l$^{-1}$) also makes a good anode substrate [66].

A membrane electrolysis process involves sending the N rich stream through an anode, ammonium moves as a cation towards the cathode, where it is converted to ammonia by virtue of the high local pH [67]. The ammonia volatilises together with cathodically generated hydrogen gas. Constituent metals, e.g. K, are also recovered from the electrochemical extraction process. The membrane electrolysis process can be integrated downstream to anaerobic digester (AD). The AD effluent free of ammonium can be recycled back to the AD reactor to boost the biogas production, and to obtain a concentrated effluent stream, easier for releasing the phosphate and remaining N, and K fertilisers in marketable pellet forms [68]. Thus the integrated process offers a prospect of high-grade, valuable multi-product generations. Furthermore, resulting H$_2$/NH$_3$ from the membrane electrolysis process can be reacted to synthesize amines or alternatively recover NH$_3$ and use H$_2$ in a secondary process. The latter can be the production of methane (delivering an enriched biogas stream $>$90 vol% methane this can be used as biomethane for injection into the gas grid) or carboxylates using CO$_2$ offgases from other processes, e.g. fermentation, giving rise to an integrated multi-site biorefinery (e.g. AD, fermentation and membrane electrolysis process integration.
The options are shown in Fig. 7. Energy, and water recovery is an important aspect of sustainable manufacturing. Micro-, ultra-, and nano-filtration (MF / UF / NF), and reverse osmosis (RO) processes, downstream of the AD process can be coupled to enhance release, and recovery of nutrients, thus generating pure water, and integration with reverse electrodialysis (RED) / fuel cells (FC) using a part of the biogas for energy recovery within the integrated systems [38,69]. Biological conversion of organic wastes (sludges, animal waste, food waste, vegetal waste, effluents, and biological waste [70]) involves four fundamental phenomena: hydrolysis, fermentation, acetogenesis, and methanogenesis. Diversion to the production of a suitable precursor via any route is possible by metabolic pathway analysis, metabolic flux analysis and metabolic engineering and control, which should be pursued for reporting of more meaningful results.

Incorporating all four interlinked microbial conversion steps leads on to AD currently aimed at optimising biogas production of biomethane nature (>90% by volume) by increasing organic loading rate, and methane and energy recovery, and suppressing acetogenesis (e.g. there are 220 installations reported in the UK [71]). Acetogenesis on the other hand leads to added value volatile fatty acid production, e.g. acetate, propionate, butyrate and caproate and their accumulation inhibits methanogenesis. Shortening the solid retention time and increasing the temperature are effective strategies for driving microbial communities towards controlled production of high levels of specific volatile fatty acids [72] that can generate much higher value for AD operational industries.

**Anodic catalysts:** Extensive reviews of substrates used in anodic oxidation reactions in microbial cells that have potential in product generation are available. Electrogenic bacteria used in anodes include: *Geobacter sulfurreducens* [73,74] and *Shewanella oneidensis* [75], which are capable of extracellular electron transfer [76,77,78]. However, the substrate fed to an anode under non-sterile conditions, as would be expected with biorefinery waste streams, influences not only the bacterial community formation in the anode biofilm, but also power density and Coulombic efficiency as well as recovery efficiency of
metals, nutrients, chemicals or biofuels [79]. Immobilised enzyme catalysed bio fuel or electrolysis cells on the other hand suffer from enzyme instability and lower electron transfer rate and enzyme loading [80,81]. Whole microorganisms offer added advantages, self-generation and adaptation to various substrates and desired productivity. The key transfer mechanism is extracellular electron transfer by microorganisms, which has to be made efficient. In some cases this can be affected without diffusion of a mobile redox component into and out of the cell and from or towards an insoluble electron donor or acceptor [82]. An indirect method of electron transport involves the production of electron shuttles such as phenazines, which are formed as secondary metabolites by organisms [82,83] or primary metabolites such as flavins [84,85] as well as humic substances not produced by the cell. Rabaey and Rozendal provide an excellent review on the mechanisms of direct and indirect transfer in electrogenic microorganisms [16]. The electrogenic microorganisms are much less prevalent for anodes being fed non-sterile waste streams as substrate. They may be more relevant in clean cathode-based processes.

3. Cathodic metal and CO₂ reduction process and substrates

Cathodic processes using organic substrates in MES to reduce CO₂ to produce targeted products are at an early stage of development. Industrial, municipal and agricultural wastewaters are potential sources of metals, acids, bases and salts, which could be recovered, while chemicals and biofuels could be synthesised by CO₂ reuse in electrochemical reactions in the cathode [86]. Apart from the potential metal recovery by MES, Lu et al. also discussed the role of metal ions in enhancing the performance of MES [87]. With increasing metal ions concentration the conductivity of the electrolyte was increased and so is the desalination and biocatalyst performance, lowering the internal resistance.

The inherent challenge to sustainable resource recovery is to develop a strategy that is less destructive (i.e. recovery of constituents of a substrate at milder and safer conditions), disruptive (easy to integrate
with existing processes) and game changing. Conventional methods, e.g. metal recovery technology from wastewater using chemical precipitation, filtration and solvent extraction, have low efficacy, high start-up or operating costs and low metal selectivity. They can also cause secondary pollution from metal enriched sludge, from which it may not be technically feasible to recover metals. The flow of current in such cells can also enable selective ionic movement to recover salts, acid and base using electrodialysis and electro-hydrolysis respectively [88]. Further efforts could be in the synthesis of functional nano-scale materials ranging from catalysts to novel inorganic antimicrobials, nanomagnets, remediation agents and quantum dots for electronic and optical devices [89].

Earlier works considered CO$_2$ as a reactant in chemical reactions to products [21]. Further, methods to harness reducing power from wastewater, possibly supplemented from renewable energy sources, can also be developed for the synthesis of chemicals and biofuels from reuse of CO$_2$. CO$_2$ is believed to participate in the cathodic reduction reactions via HCO$_3^-$ or higher chain carboxylic acids. Such relevant reactions that have been proven at lab scale are shown here. In terms of the thermodynamic spontaneity, the following electron-accepting, hydrogen consuming or hydrogenation reactions and CO$_2$ reuse in the form of HCO$_3^-$ or carboxylation from energy metabolism via C1-C2 molecule synthesis at the cathode, are shown [22].

\[
\begin{align*}
\text{HCO}_3^- + H^+ + 4H_2 &\rightarrow CH_4 + 3H_2O & \Delta G^o_{r,\text{cathode}} = -135.6 kJ \\
2\text{HCO}_3^- + 2H^+ + 4H_2 &\rightarrow CH_3COOH + 4H_2O & \Delta G^o_{r,\text{cathode}} = -64.6 kJ \\
\text{HCO}_3^- + H^+ + 3H_2 &\rightarrow CH_3OH + 2H_2O & \Delta G^o_{r,\text{cathode}} = -23 kJ \\
\text{HCO}_3^- + H^+ + 2H_2 &\rightarrow HCHO + 2H_2O & \Delta G^o_{r,\text{cathode}} = 21.8 kJ \\
\text{HCO}_3^- + H^+ + H_2 &\rightarrow HCOOH + H_2O & \Delta G^o_{r,\text{cathode}} = 38.5 kJ
\end{align*}
\]

$\Delta G^o_{r,\text{cathode}}$ is the Gibbs free energy for the cathode side reaction under standard conditions (25°C temperature and 1 atm pressure) and pH 7.
The starting point should thus be the identification of chemicals that can be sourced from a waste stream, from which the processing steps that present the closest match to their theoretical recovery limits, can be defined. This was further evidenced in a study of 20 different valuable products screened from anaerobic electrically enhanced fermentation [90]. It was found that an increase in a product formation by electrical enhancement is not as much dependent as on the metabolic pathway producing it. The compounds studied were those produced at an industrial scale such as succinic acid, lysine and diaminopentane as well as new bio-commodities such as isoprene, para-hydroxybenzoic acid and para-aminobenzoic acid, etc. Furthermore, it was shown that electron transport mechanism has an influence on biomass and product yields. Future models in this area should thus include electron transport and energy conservation equations relating to metabolic pathways. Furthermore, if a robust model can be developed, it can be used for validation against experimental performance and optimisation of configurations and operability to achieve targeted product formations. Some more examples of successful production of products using MES at lab scale are as follows.

Wheat bran, sugar cane bagasse, coffee husk, pineapple waste and carrot processing waste amongst others, are sources of citric acid, a suitable anode substrate for undergoing the reaction in equation 1. An example follows: Solid state fermentation (combined saccharification and fermentation) of agricultural residues, using Aspergillus niger on an amberlite inert support [91], gives citric acid in a manner free from heavy metal inhibition [92]. The citric acid formed is a useful anode substrate for microbial oxidation into succinic acid, carbonic acid and proton generation through the citric acid cycle. Succinic acid can be separated from the anode chamber as a product. The proton can be reduced to hydrogen and recovered in the cathode chamber in MEC. Alternatively, the following reaction in the cathode chamber leads to the production and recovery of formic acid in MES.

\[ \text{HCO}_3^- + H^+ + H_2 \rightarrow \text{HCOOH} + H_2O \]
Similarly, acetic, propionic, butyric, lactic, acrylic, malic and fumaric acids can be generated from \( \alpha \)-keto acids (e.g. pyruvate\(^{-}\)), \( \alpha,\beta \)-unsaturated acids and hydroxy acids as potential substrates in the cathode [93]. Recently, medium chain fatty acids such as caproate and caprylate were produced from acetate at a biocathode using mixed microbial cultures (where Clostridium kluyveri was the predominant microorganism) [40]. The maximum concentrations of reduced organics from 100 mM acetic acid were 739 mg l\(^{-1}\) for caproate, 263 mg l\(^{-1}\) for butyrate, 36 mg l\(^{-1}\) for caprylate and 27 mg l\(^{-1}\) for ethanol. The cathode reactions to caproate and butyrate are as follows:

\[
3C_2H_3O_2^- + 2H^+ + 4H_2 \rightarrow \text{Caproate}(C_6H_{11}O_2^-) + 4H_2O \quad \Delta G_{r,\text{cathode}}^{\circ} = -96.6 \text{ kJ}
\]

\[
2C_2H_3O_2^- + H^+ + 2H_2 \rightarrow \text{Butyrate}(C_4H_7O_2^-) + 2H_2O \quad \Delta G_{r,\text{cathode}}^{\circ} = -48.3 \text{ kJ}
\]

These compounds are liquid at room temperature which makes the product recovery relatively easy. Broadly, homoacetogenesis by Clostridium thermoaceticum converting hydrogen and carbon dioxide into acetate; succinate formation from glycerol by Actinobacillus succinogenes; reverse \( \beta \) oxidation for chain elongation of ethanol and acetate to \( n \)-butyrate; and ethanol and \( n \)-butyrate to \( n \)-caproate by Clostridium kluyveri are proven cathode carboxylation reactions [94].

\[
4H_2 + 2CO_2 \rightarrow C_2H_3O_2^- + H^+ + 2H_2O \quad \Delta G_{r,\text{cathode}}^{\circ} = -94.96 \text{ kJ}
\]

\[
\text{Glycerol} + CO_2 \rightarrow \text{Succinate}^{2\text{\textsuperscript{-}}} + 2H^+ + H_2O \quad \Delta G_{r,\text{cathode}}^{\circ} = -44.5 \text{ kJ}
\]

\[
\text{Ethanol} + \text{Acetate}^- \rightarrow \text{Butyrate}^- + H_2O \quad \Delta G_{r,\text{cathode}}^{\circ} = -193 \text{ kJ}
\]

\[
\text{Ethanol} + \text{Butyrate}^- \rightarrow \text{Caproate}^- + H_2O \quad \Delta G_{r,\text{cathode}}^{\circ} = -194 \text{ kJ}
\]

The ability of microorganisms to use electrons donated from an electrode to reduce CO\(_2\) to simple organic acids such as acetic acid using the acetogenic microorganism Sporomusa ovata proceeding through acetyl-coenzyme A (CoA) is proven [42]. Acetyl-CoA is a central intermediate (Wood-Ljungdahl pathway) for the production of a diverse suit of organic molecules including those relevant to biofuels and platform chemical, storing electrical energy in chemical bonds.
The microbial processes can be engineered for optimal microbial growth to alter length, functionality, the degree of fatty acid saturation and branching to maximise fuel effectiveness. In contrast to fatty acids, higher alcohols have higher energy contents. Butanol, a key component of gasoline contains 84% of its energy content and is immiscible with water [95]. These molecules are easy to use as drop-in fuels in existing transportation fuel infrastructure and can be used as 100% pure. Engineered microbial technologies for the synthesis of higher alcohols (e.g. butanol, isobutanol) as biofuels and copolyesters (e.g. poly(3-hydroxybutyrate-co-4-hydroxybutyrate) as biopolymers, are reaching the pilot scale of development [96,97,98]. Comparing these technologies to engineered microbial processes that use exogenous electron donors to supply electrons in-situ within MES reactor, several advantages can be described: (i) no infrastructure for the supply of hydrogen is required, (ii) in-situ electron supply at the right cathode potential might result in locally high hydrogen partial pressures, which are favorable for the reaction, and (iii) the electron donor is renewable when renewable electricity is used [40].

**Cathodic catalysts:** The cathode reduction process can be affected by a chemical catalytic process (a metal catalyst at the cathode) as opposed to a microbial oxidation process in the anode in MFC / MEC, or indeed microbially catalysed reduction at the cathode. The reduction of carbon dioxide in aqueous solution using a metal catalyst has been demonstrated [99]. The use of ruthenium [100], gallium arsenide [101] and RuO₂-TiO₂ mixed cathodes [102] have been reported for methanol synthesis through carbon dioxide reduction. However, all these catalysts have shown instability compared to enzymatic fixation of carbon dioxide in organic molecules. For example, the electrochemical synthesis of methanol from CO₂ reduction has been demonstrated using formate dehydrogenase and methanol dehydrogenase [103]. The use of enzymes in electro-reductive fixation of CO₂ to yield isocitrate from α-oxoglutaric acid and malate from pyruvic acid has been demonstrated [99]. Such enzymatic electro-reductive fixation of CO₂ is possible using a photochemical reaction in the cathode and shows higher energy efficiency compared to corresponding metal cathodes with and without metallocomplexes as the electrocatalysts [103,104,105].
In recent times, there has been an upsurge in the application of microorganisms as opposed to enzymes, specifically for resource recovery from wastes in MES. This is because the self-renewing microbial growth which is almost unavoidable in the presence of waste substrates and which extracted enzymes cannot achieve [106]. Laccase as an isolated enzyme has been studied for oxygen reduction in MFC by its immobilisation on the cathode [107]. Many microorganisms, such as *Shewanella putrefaciens*, *Pseudomonas aeruginosa*, *Acinetobacter calcoaceticus*, *Acidithiobacillus ferrooxidans*, *Chlamydomonas reinhardtii* were also identified as biocatalyst for oxygen reduction in MFC cathode [108,109]. The known microorganisms, which have the ability to take up electrons from an electrode and use them in the production of H\(_2\), formate or acetate, include most Gram-negative bacteria such the *Shewanella* and *Geobacter* species, and some Gram-positive bacteria. The catalyst performance in terms of open circuit potential was found to be in the following order: laccase > microorganisms > Pt catalyst [106]. The different catalysts were loaded on identical plain carbon cloth electrodes of MFC. Apparently, the laccase-immobilised cathode direct electron transfer can produce a potential much closer to the thermodynamic equilibrium potential of the oxygen reduction reaction, compared to microbial and Pt catalysed cathodes. The low open circuit potential of the Pt catalyst may be attributed to a lower relative Pt loading and the formation of PtO on the catalyst surface. However, the maximum power density shows a different trend: Pt catalyst > laccase > microorganisms, and this is attributed to higher conductivity and greater affinity of Pt to oxygen. Pioneering researchers in the field agree that the cell configuration, specific architecture, electrode spacing and internal resistance have a more significant effect on performance than the type of catalyst for MES. For example, methanogens and some acetogens can utilise the produced H\(_2\) or formate as electron donors for anaerobic reduction of carbon dioxide to produce methane or to form higher tier organic fuels such as 2,3-butanediol, lactate, butyrate, and butanol [106]. The need to establish the energetic favourability of the processes is of paramount importance for all these conversions, as the reduction of CO\(_2\) / organics proceeds at low redox potentials [16]. In order to assess
whether the MES has all the advantageous compared to metabolic systems, the thermodynamic correlations to estimate the applied voltage can prove to be useful. Hence, the general equations (i.e. a generic model) [22,43,44,45,110,111,112,113], are discussed to determine the thermodynamic favourability of the MES reactions.

4. Model formulation and parametric analysis

The anode side oxidation of substrate can be expressed as in equation 1, generating the substrates of interest for the cathode side.

\[ C_xH_yO_z + (3x - z)H_2O \rightarrow xHCO_3^- + wH^+ + we^- + \frac{y+5x-w-2z}{2}H_2 \]

\[ \forall (3x - z) > 0, (y + 5x - w - 2z) \geq 0, \text{and } w,x,y,z > 0 \] (equation 1)

The Gibbs free energy (\( \Delta G^{o'}_{r,anode} \)) of the anode reaction in equation 1 can be expressed in terms of the Gibbs free energy of formation of the species (\( \Delta G^{o'}_{f,i} \) \( \forall i \in \{HCO_3^-, H^+, H_2O, C_xH_yO_z\} \)) under standard conditions (25°C temperature and 1 atm pressure) and pH 7, as shown in equation 2.

\[ \Delta G^{o'}_{r,anode} = x\Delta G^{o'}_{f,HCO_3^-} + w\Delta G^{o'}_{f,H^+} - (3x-z)\Delta G^{o'}_{f,H_2O} - \Delta G^{o'}_{f,C_xH_yO_z} \] (equation 2)

By substituting the \( \Delta G^{o'}_{f,i} \) values of \( HCO_3^-, H^+, H_2O, -586.85, -39.9, -237.178 \) \( \frac{kJ}{mol \text{ of substrate}} \) respectively [22], into equation 2, the following expression is obtained for the specific anode reaction case, generating \( HCO_3^-, H^+, H_2 \). Upon simplification, equation 3 is obtained.

\[ \Delta G^{o'}_{r,anode}(in \frac{kJ}{mol \text{ of substrate}}) = -586.85x - 39.9w + 237.178(3x - z) - \Delta G^{o'}_{f,C_xH_yO_z} \]

\[ \Delta G^{o'}_{r,anode}(in \frac{kJ}{mol \text{ of substrate}}) = 124.684x - 39.9w - 237.178z - \Delta G^{o'}_{f,C_xH_yO_z} \] (equation 3)
Cathode side reduction of oxygen in MFC results in the formation of water. Hence, the Gibbs free energy of 0.5 mole of oxygen reduction into 1 mole of water formation is equal to the Gibbs free energy of formation of 1 mole of water subtracted from the Gibbs free energy of formation of 2 $H^+$ species under the standard conditions and pH 7 (equation 4a). Note that $w$ number of $H^+$ specie is responsible for electricity generation from MFC.

$$\frac{w}{4}O_2 + wH^+ + we^- = \frac{w}{2}H_2O$$

$$\Delta G_{r,cathode}^{o'} \left( \frac{kJ}{mol \ of \ substrate} \right) = \frac{-237.178 + 79.8}{2}w = -78.689w \quad \text{(equation 4a)}$$

In the case of MEC, the cathode side reduction of $H^+$ species results in the formation of molecular hydrogen, as follows. Thus, $\Delta G_{r,cathode}^{o'} \left( \frac{kJ}{mol \ of \ substrate} \right)$ results in equation 4b.

$$wH^+ + we^- = \frac{w}{2}H_2$$

$$\Delta G_{r,cathode}^{o'} \left( \frac{kJ}{mol \ of \ substrate} \right) = 39.9w \quad \text{(equation 4b)}$$

Hence, the net energy generation from the MFC and the net energy consumption by the MEC is the summation of the Gibbs free energies between the cathode reaction and the anode reaction, shown in equations 5a and 5b, respectively. Negative value of $\Delta G_{r,cell}^{o'}$ for MFC indicates that this is an energy generation from the MFC and positive value indicates energy consumption by the MEC.

$$\Delta G_{r,cell}^{o'} = \Delta G_{r,cathode}^{o'} + \Delta G_{r,anode}^{o'}$$

$$\Delta G_{r,MFC}^{o'} \left( \frac{kJ}{mol \ of \ substrate} \right) = 124.684x - 118.589w - 237.178z - \Delta G_{f,c,H_yO_z}^{o'} \quad \text{(equation 5a)}$$

$$\Delta G_{r,MEC}^{o'} \left( \frac{kJ}{mol \ of \ substrate} \right) = 124.684x - 237.178z - \Delta G_{f,c,H_yO_z}^{o'} \quad \text{(equation 5b)}$$

Equations 5a-b can be presented in terms of 1 eV potential generation from MFC or 1 eV consumption by MEC as shown in equations 6-7 respectively, from the substrate of $C_x H_y O_z$ formula in the anode.

$$\Delta G_{r,MFC}^{o'} \left( \frac{kJ}{1 \ electron \ transfer} \right) = \frac{124.684x - 118.589w - 237.178z - \Delta G_{f,c,H_yO_z}^{o'}}{w} \quad \text{(equation 6)}$$
\[
\Delta G'_{r,\text{MEC}} \left( \text{in} \frac{kJ}{1 \text{ electron transfer}} \right) = \frac{124.684x - 237.178z - \Delta G'_{f,CH\text{HyOz}}}{w} \quad \text{(equation 7)}
\]

In the case of MES with cathode reactions for the formation of products, the energy needed must take account of the Gibbs free energy of electron-accepting hydrogenation or reduction reactions in the cathode. As an example, for \( \text{HCO}_3^- + H^+ + 4H_2 \rightarrow CH_4 + 3H_2O \) reaction, the Gibbs free energy of the MES cathode can be derived from the negative of equation 3, with \( x=1, w=1 \) and \( z=0 \), as follows [22].

\[
\Delta G'_{r,\text{cathode}} \left( \text{in} \frac{kJ}{\text{mol of hydrogen}} \right) = -84.784 + \Delta G'_{f,CH_4} = -135.6 \quad \Delta G'_{f,CH_4} = -50.8
\]

Thus, as the cathode reaction becomes endogenous, the thermodynamic spontaneity of the MES system reduces. The methodology can be followed to calculate \( \Delta G'_{r,\text{cathode}} \left( \text{in} \frac{kJ}{\text{mol of substrate}} \right) \) and equation 3 can be applied to calculate \( \Delta G'_{r,\text{anode}} \left( \text{in} \frac{kJ}{\text{mol of substrate}} \right) \) for different types of substrates in MES reported in [22]. Thus, \( \Delta G'_{r,\text{MES}} \left( \text{in} \frac{kJ}{\text{mol of substrate}} \right) = \Delta G'_{r,\text{cathode}} + \Delta G'_{r,\text{anode}} \) can be estimated for various combinations of anode and cathode reactions to examine the overall energy performance and feasibility.

The methodology is adaptable for given substrates or waste streams as long as their chemical formulae are predicted (e.g. by elemental analysis: proximate and ultimate analyses).

The model is further useful to link to economic profitability and environmental impact analysis. A comparative life cycle analysis will be useful to determine the most feasible combinations of substrate and target products and anode and cathode reactions. This will be a novel and smart approach for screening of best options before experimental based approaches [114]. Without this aspect, commercialisation of MES will be a long process.

The Gibbs free energy change across the cell under actual conditions prevailing can be obtained from the molar Gibbs free energy change at standard condition and pH = 7. Equation 8a can be used to estimate the Gibbs free energy change for MFCs, where oxygen reduction occurs in the cathodic chamber [115].

\[
\Delta G'_{r,\text{MFC}} = \Delta G'_{r,\text{MFC}} - RT \ln \left( \frac{1}{[O_2]^{0.5}[H^+]^2} \right) \quad \text{(equation 8a)}
\]
\( \Delta G_{r, MEC} \) is the molar Gibbs free energy change as a function of temperature \((T)\) and pressure \((P)\).

\( R \) is the universal gas constant, 8.314 J mol\(^{-1}\) K\(^{-1}\).

\([O_2]\) is the partial pressure of oxygen; \([H^+]\) is equal to \(10^{-7}\) M/l when pH = 7.

Equation 8b can be used to estimate the Gibbs free energy change for MECs, where \(H^+\) reduction occurs in the cathodic chamber [115]. \([H_2]\) is the partial pressure of hydrogen.

\[
\Delta G_{r, MEC} = \Delta G_{r, MEC}^{o'} - RT \ln \left( \frac{[H_2]}{[H^+]^2} \right) \quad \text{(equation 8b)}
\]

A generic thermodynamic equation for the Gibbs free energy change for multi-component systems should be applied. However, it is necessary to replicate the case in reality as far as possible. A generic thermodynamic equation for the Gibbs free energy change across the cell under the cell conditions thus can be applied as shown in equation 9 [1,116].

\[
\Delta G_{r, cell} = \Delta G_{r, cell}^{o'} + \sum_{j=1}^{N_{react}} n_jRT \ln \left( \frac{n_j}{n_T} \right) - \sum_{j=1}^{N_{pd}t} n_{j'}RT \ln \left( \frac{n_{j'}}{n_{T'}} \right) \quad \text{(equation 9)}
\]

\( n_j \) is the stoichiometric number of moles of reactant \(j\) in the overall reaction equation of the cell and \(n_T\) is the total number of moles of reactants and products in the overall reaction equation of the cell. \( n_{j'} \) is the stoichiometric number of moles of product \(j'\) in the overall reaction equation of the cell. \( N_{react} \) is the total number moles of reactants in the overall reaction equation of the cell and \( N_{pd}t \) is the total number of moles of products in the overall reaction equation of the cell.

The theoretical maximum voltage corresponding to the Gibbs free energy change across the cell is given by the Nernst equation, shown in equation 10. The Gibbs free energy change is related to the process operating conditions, in this case, cell temperature, pressure and the difference in pH between the anode and cathode compartments.

\[
E = -\frac{\Delta G_{r, cell}}{n_e F} \quad \text{(equation 10)}
\]
\( n_e \) is the number of electrons transferred in the overall reaction of the cell, and \( F = 96,485 \ \text{C mol}^{-1} \) is Faraday’s constant. For hydrogen generation, thus the adjusted potential required for MEC at 298 K = \( \frac{39.9 \times 1000}{96485} = 0.414 \ \text{V} \).

The voltage calculated using equation 10 is the theoretical maximum voltage obtained corresponding to reversible process that results in minimum Gibbs free energy change. However, the actual voltage is less than the theoretical voltage in MFC and more than the theoretical voltage in MEC. This is due to the three types of polarisation effects, which are universal to all types of electrochemical cells: activation, ohmic and concentration potentials in equations 11-16.

Activation overpotentials are a result of resistance to electrochemical reaction kinetics occurring in the anode and cathode. According to the general Butler–Volmer equation, the respective theoretical activation overpotentials of the anode and cathode can be calculated as shown in equations 11-12 [1,113,117].

\[
V_{\text{activation, anode}} = \frac{2RT}{n_e F} \sinh^{-1} \left( \frac{i}{2i_0,\text{anode}} \right) \quad \text{(equation 11)}
\]

\[
V_{\text{activation, cathode}} = \frac{2RT}{n_e F} \sinh^{-1} \left( \frac{i}{2i_0,\text{cathode}} \right) \quad \text{(equation 12)}
\]

\( V_{\text{activation, anode/cathode}} \) is the voltage loss due to activation overpotentials in anode / cathode.

\( i_{0,\text{anode/cathode}} \) is the anode / cathode exchange current density.

Ohmic overpotentials (\( V_{\text{ohmic}} \)) are due to the resistance to conduction of ions through the electrolyte, electrons through the electrodes and current collectors and by contact, resistance between cell components, shown in equation 13 [1,118].

\[
V_{\text{ohmic}} = i \left( \frac{L_{\text{electrolyte}}}{\sigma_{\text{electrolyte}}} + \frac{L_{\text{anode}}}{\sigma_{\text{anode}}} + \frac{L_{\text{cathode}}}{\sigma_{\text{cathode}}} + \frac{L_{\text{interconnect}}}{\sigma_{\text{interconnect}}} \right) \quad \text{(equation 13)}
\]

\( L_k \) is the thickness, \( \forall k \in \{\text{electrolyte, anode, cathode, interconnect}\} \)

\( \sigma_k \) is the electronic or ionic conductivity in \( k \), \( \forall k \in \{\text{electrolyte, anode, cathode, interconnect}\} \), which is a function of temperature in K shown in equation 14a-b [1,118].
\[ \sigma_k = \frac{C_1 k}{T} \exp \left( \frac{C_2 k}{T} \right) \quad \forall k \in \{ anode, cathode, interconnect \} \quad \text{(equation 14a)} \]

\[ \sigma_k = C_1 k \exp \left( \frac{C_2 k}{T} \right) \quad \forall k \in \{ electrolyte \} \quad \text{(equation 14b)} \]

\( C_{1,k} \) and \( C_{2,k} \) are the constants.

Concentration overpotentials caused by mass transfer limitations from the substrate and through the electrode result in further voltage loss, shown in equations 15-16 [118].

\[ V_{\text{concentration, anode}} = -\frac{RT}{n_e F} \ln \left( 1 - \frac{i}{i_{i, anode}} \right) \quad \text{(equation 15)} \]

\[ V_{\text{concentration, cathode}} = -\frac{RT}{n_e F} \ln \left( 1 - \frac{i}{i_{l,cathode}} \right) \quad \text{(equation 16)} \]

\( V_{\text{concentration, anode/cathode}} \) is the voltage loss due to concentration overpotentials in anode / cathode.

\( i_{i,anode/cathode} \) is the limiting current density of the anode / cathode, assumed constant.

The net voltage thus obtained is the Nernst theoretical voltage (equation 10) minus the voltage losses (equations 11-16), shown in equation 17 [1,43].

\[ V = E - V_{\text{activation}} - V_{\text{ohmic}} - V_{\text{concentration}} = E - \frac{RT}{n_e F} d_1 \quad \text{(equation 17)} \]

where,

\[ d_1 = 2 \sinh^{-1} \left( \frac{i}{2 i_{i, anode}} \right) + 2 \sinh^{-1} \left( \frac{i}{2 i_{i, cathode}} \right) \]

\[ + \frac{i n_e F}{RT} \left( \frac{L_{\text{electrolyte}}}{\sigma_{\text{electrolyte}}} + \frac{L_{\text{anode}}}{\sigma_{\text{anode}}} + \frac{L_{\text{cathode}}}{\sigma_{\text{cathode}}} + \frac{L_{\text{interconnect}}}{\sigma_{\text{interconnect}}} \right) \]

\[ - \ln \left( 1 - \frac{i}{i_{l, anode}} \right) - \ln \left( 1 - \frac{i}{i_{l, cathode}} \right) \]

In the case of MFCs, the Nernst theoretical voltage and the net voltage, \( E \) and \( V \), respectively, with \( E > V \), are positive, indicating energy generation from MFCs.
In case of MEC, $E$ and $V$ are negative with $|V| > |E|$, indicating that a higher voltage would be needed by the MEC than the Nernst theoretical voltage provides.

To determine the conditions for maximum net energy generation (MFC) or minimum net energy consumption (MEC) by thermodynamic analysis, the activation overpotential is the most important contributor in decreasing the Nernst theoretical voltage. The activation overpotential is a function of current density and exchange current density. The higher the current density, exchange current density and their ratio, the greater is the activation overpotential. This is illustrated in Figs. 8a-b: current densities in logarithmic ($\log_{10}$) scale on y-axis versus activation overpotentials in linear scale on x-axis. The current density was varied from 1 to 16 A m$^{-2}$ for two exchange current densities of 3.33 and 1.67 A m$^{-2}$. As a result, the activation overpotential increased to 153 and 42 mV, respectively. The concentration overpotential increases with increasing current density, decreasing limiting current density and increasing ratio between them, as shown in Fig. 9. However, while activation overpotential contributes to $\sim$84% of the polarisation effect, the concentration overpotential only contributes to the remaining proportion of the polarisation effect, $\sim$16%. The ohmic overpotential can be overcome by increasing conduction of ions through the electrolyte, electrons through the electrodes and current collectors and by contact between cell components and hence would have negligible polarisation effect.

Amongst the various substrates identified for MFC, acetogenesis is the least hassled or the easiest metabolic process to control / occur and acetate is the most established substrate for which consistent data are available in literature [119]. Thus, the results [119] are used to validate the model. Equations 5a and 10-17 were used to predict the performance of acetate as substrate at various concentrations, 0.15, 0.5 and 1 g l$^{-1}$ and compared against the experimental results, in terms of power density and potential ($V$ in equation 17) with respect to current density, as shown in Figs. 10a-b, respectively. For the net potential ($V$ in equation 17), the Nernst theoretical potential was first estimated from $\Delta G^o_{r,MFC}$ using equation 5a and then overpotentials estimated using equations 11-17, are subtracted.
For Acetate$^-$, \( x = 2, w = 2, z = 2 \) and \( \Delta G_{f,Acetate}^{\circ} = -369.41 \) kJ mol\(^{-1}\)

\[
\Delta G_{r,MFC}^{\circ} = -92.756 \text{ kJ mol}^{-1}
\]

Thus, the Nernst theoretical potential calculated per mole of acetate is calculated to be 0.9614 V.

The best values of exchange current densities, limiting current density and effective surface area per reactor volume for closest match of the net potential to the experimentally measured potentials [119], alongside other reactor geometric parameters and conductivities for equations 13-14 are given in Table 1.

The coefficient of determination (R-squared) of this generalised model (equations 5 and 10-17) is greater than 0.96. The R-squared value could also be affected by the fact that the experimental values were read from the published graphs rather than from the measurements [119]. Next, the distributions of the ratio of cathode surface area to reactor volume (m\(^2\) m\(^{-3}\)) for the three concentrations of acetate (shown in Fig. 11) are estimated to transform the value of \( V \times i \) or the power density, in W m\(^{-3}\). The power density was shown as a linear function of the cathode specific surface area for the case where wastewater used as substrate [119].

The generalised model (equations 5 and 10-17) can be applied to predict energy performance of MES systems for the synthesis of biofuels or chemicals or polymers (Fig. 3). This is a pragmatic and robust way to determine whether a plausible integration schematic of MES in terms substrate inputs is feasible. The maximum oxidation of anode substrate and the maximum reduction of cathode substrate and the product chemicals need to be determined in order to hypothesise the overall balanced anode and cathode reaction stoichiometry. The overall balanced reaction equation can be developed for multi-component systems. From the balanced reaction equations, the Gibbs free energies of anode and cathode reactions and thereby the overall reaction can be calculated. These steps are shown in equations 1-5 for the simpler forms of anode and cathode reactions in MFC and MEC. Once the Nernst theoretical potential is estimated from the Gibbs free energy of the overall reaction, it can be deducted or increased by the overpotentials (equation 17) calculated using equations 11-16. The model is suitable to best fit
experimental data as well as for predicting optimal factors: electrode specific surface area (influencing power density), substrate concentration (influencing overall reactions and potential) and current densities, conductivity and reactor geometry (influencing overpotentials and thereby potential and power density) for the highest feasible energy performance, as applied generically for performance estimation, analysis and optimisation of other fuel cell systems [120,121,122,123]. The model is not as data intensive as computational fluid dynamics [124], but adequate for screening of substrates for MES and for the estimation of energy performance and thereby avoided environmental impacts from MES [125]. Equally, the model that uses reaction controlled charge transfer, the Butler-Volmer equation and has a general basis in non-equilibrium thermodynamics can be applied to smaller dimensions to predict performances of finite elements that can be compiled for up-scaled systems [113]. The analysis of metabolic pathways to expand the source of feedstock, engineer microorganisms and to tune the properties of products [126,127,128,129,130,131] is another thread of research should be explored for optimising MES process design.

5. Future research directions

Biorefinery simulation frameworks on the other hand are established having been developed for more than a decade [1]. A few of the earliest works in the field, much well ahead of the times, looked at the added value production (arabinoxylans) in bioethanol plant to increase the number of platform and product, hence economic viability using process integration tools [10,11,12]. The process integration tools developed by a group of process engineers at ICI in 1970s to dramatically increase the energy efficiency of crude oil refineries and combat against drastic depletion of finite fossil resources are now proving to be effective for integration within and between systems [1,58,132] and for CO₂ reduction system [21,133] and thus are desperately needed for MES integration within and to link up
industrial systems, e.g. biorefinery systems, for overall sustainability. Process flowsheet simulation software such as Aspen Plus™ has been effectively used for modelling of both electrochemical and biorefinery systems using a modular approach and thermodynamic optimisation methodology to estimate detailed mass and energy balance analysis [1,44,45]. The advantage of the software is the in-built thermodynamic property packages needed to take account of the non-ideality of the flows / mixtures / blends concerned, which are complex and heterogeneous [134]. Aspen Plus™ v7.1 offers the following base-property methods [135]:

1) Peng-Robinson equation of state,
2) Braun K-10 for petroleum applications,
3) Chao Seader correlation with Lee-Kesler enthalpy,
4) Electrolyte non-random two liquid (NRTL) model with Redlich-Kwong (RK) equation of state for aqueous and mixed solvent systems,
5) Ideal property method using Rault’s law and Henry’s law,
6) NRTL,
7) Peng-Robinson equation of state,
8) Polymer NRTL with RK equation of state,
9) Henry’s law for polymer solutions,
10) Soave-Redlich-Kwong (SRK) equation of state,
11) Predictive Redlich-Kwong-Soave (RKS) equation of state,
12) Solids property method for general solids and pyrometallurgy applications,
13) UNIFAC with RK equation of state and Henry’s law,
14) Wilson with ideal gas and Henry’s law,
15) UNIQUAC with ideal gas and Henry’s law and
16) Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) property method for copolymer system.

Any of the above property packages can be selected based on the type of the system under consideration. For the electrochemical systems, the most relevant ones are Peng-Robinson equation of state and Electrolyte NRTL methods. The package then leads to a collection of estimation methods of several thermodynamic (fugacity, enthalpy, entropy, Gibbs free energy, and volume) and transport (viscosity, thermal conductivity, diffusion coefficient, and surface tension) properties. The key results of mass and energy balance analysis and stream properties of the integrated flowsheet once simulated using a thermodynamic package are validated against practical results. Different thermodynamic packages may need to be examined for the selection of the best thermodynamic package that gives the closest match. The overall system performance will then be optimized for highest productivity, purity, economic and environmental performances. Such tools allow engineering of real plant configurations, optimisation of design and operability and definitive and detailed estimates of economics, such as using Aspen Icarus software, needed for feasibility [1,136]. We are now in a position to test this aspiration technologically. This way the right innovations and options for advanced integration can be supported. Research efforts should be more on the metabolic flux and pathway analyses to reduce the number of experimental trials and optimise the experimental strategy [126,127,128,129,130,131]. It is time to make use of computer-aided analytical tools to increase the search efficiency and speed up the commercial uptake of MES technologies, as shown in Fig 12. Finally, the targeted chemicals are listed in Table 2 and the targeted polymers are shown in Fig. 13, respectively, [1]. Both MES and biorefinery process units can be coupled to target such products.

6. Conclusions
A comprehensive overview of integration between waste biorefinery and MES system has been presented. The biofuel and biorefinery industries are currently facing the challenges resulting from increasing volume of stillage streams representing unconverted lignocellulose, fermentation / fractionation / transesterification / and hydrogenation byproducts, which are discharged to the environment. However, these should not be directly disposed of to the environment due to increasing concerns over land, aquatic and atmospheric emissions. MES can help recover these biorefinery pollutants as resources and thereby eliminate discharges to the environment. Biorefineries and MES systems may be symbiotically integrated to increase product yields and selectivities and thereby overall efficiency to resolve the key issues with up-scaling of both the technologies.

By the virtue of different reduction potentials, selective synthesis of biofuels and chemicals is possible in MES utilising carbon sources from waste streams. Realizing the full polygeneration potentials, i.e. simultaneous recovery of metals (apparently pollutants from biorefineries), production of biofuels and chemicals from reuse of CO₂, and synergistic integration within biorefineries, is imperative to attain an economic and environmental upside of novel electrochemical synthesis processes.

Furthermore, a generalised model based on classical thermodynamics and linear flux has been discussed with a view to optimise operation of the MES. The total Gibbs free energy change summed over each reaction step correlated to the molar compositions can be minimized. This determines the optimal molar distributions and thus yields, and physico-chemical behaviour, providing indications of technical feasibility and identifying the best conditions to achieve highest efficiency, reduced overpotentials and mass transfer losses incurred in a cell. The thermodynamic modelling, as discussed in this paper is applicable to multi-component systems. The model takes account of the specific surface area of electrodes, substrate concentration, current densities, conductivities and reactor geometry, in predicting highest feasible energy performance. The model can be used to estimate the best substrate or combinations of substrates with appropriate number of electron transfers in the reaction steps of the
electrochemical cell. The anode and cathode exchange and limiting current densities can also be updated for a specific set up. Furthermore, the operating and design parameters, such as anode and cathode exchange and limiting current densities, anode, cathode, electrolyte and interconnect thickness and conductivity constants, can be defined for a specific experimental design to estimate the overpotentials that must be deducted from the Nernst theoretical potential, estimated for overall balanced reactions of the cell. Current research must be complemented by process integration research to facilitate commercialisation of MES technologies.

Acknowledgement: The authors gratefully acknowledge the financial support of the Natural Environmental Research Councils (NERC), UK Grant NE/L014246/1.

References


[68] Enhancement and treatment of digestates from anaerobic digestion. WRAP. <http://www.wrap.org.uk/sites/files/wrap/Digestates%20from%20Anaerobic%20Digestion%20A%20review%20of%20enhancement%20techniques%20and%20novel%20digestate%20products_0.pdf> [accessed on 10.08.15].


[70] <http://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do> [accessed on 10.08.15].

[71] <http://www.biogas-info.co.uk/resources/biogas-map/> [accessed on 10.08.15].


