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Electrobiorefineries: Unlocking the synergy of electrochemical and microbial conversions

Falk Harnisch* and Carolin Urban

Lead-in: An integrated biobased economy urges an alliance of the two realms “chemical production” and “electric power”. The concept of electrobiorefineries provides a blueprint for such an alliance agreement. Joining the forces of microbial and electrochemical conversions in electrobiorefineries allows interfacing the production, storage, and exploitation of electricity as well as biobased chemicals. Electrobiorefineries are a technological evolution of biorefineries by means of the addition of (bio)electrochemical transformations. This interfacing of microbial and electrochemical conversions will result in synergies affecting the whole process line, like enlarging the product portfolio, increasing the productivity, or exploiting new feedstock. A special emphasis is given to the utilization of oxidative and reductive electroorganic reactions of microbially produced intermediates that may serve as privileged building blocks.

1. Introduction & Motivation

Technologies that allow the preservation of scarce fossil resources and the exploitation of renewable resources, especially those which are not used today, will form the foundation of a future resource secure bioeconomy. Two main industry sectors or realms that are in transition towards a bioeconomy are *i*) electric power generation and storage and *ii*) production of chemicals, *i.e.*, commodities and fuels as well as specialty chemicals[1]. Step by step, the electrical power production switches from utilizing fossil to renewable resources, such as wind and solar energy. This leads to global gradually increasing shares of renewable energies on the overall electric energy production[2]. Various political measures are aiming to accelerate this so called decarbonization of the energy system in order to diminish the dependence on fossil resources and CO_2 emissions, for paving the way towards a more sustainable energy economy[2,3]. As a result, 2015 was the year with the largest worldwide capacity increase of renewable energy so far[2]. At the same time, endeavors for a sustainable economy based on renewable resources rather than petrochemicals are dominating the research activities[4–8]

However, so far the sectors of electric power and production of chemicals possess only very few links. Most prominently the electrolytic H_2 production and H_2 utilization in fuel cells are means for electric power storage and supply. The technologies using electricity driven reactions are currently referred to as power-to-X technologies[9], with the “X” denominating, *i.a.,* "heat", “chemicals”, “fuels” or “molecules”[9]. Power-to-X emerged in response to the fluctuating availability of renewable resources for electrical power production and temporary downtimes, *e.g.*, of solar or wind plants due to network congestion, and thus may also serve as an intermediate energy storage option[10]. Hence, power-to-X technologies are effective measures to bridge the advancements in the power sector with the efforts made towards a biobased economy.

In contrast to the auspicious promises, chemicals that are directly produced using electricity are very limited. Prominent examples of inorganic compounds are production of aluminum or chlor-alkali electrolysis that accounts for an annual production of 77×10^6 t[1,11]. The industrial synthesis of organic molecules is less widespread in terms of process and volumes. Among others, the electrosynthesis of adiponitrile from acrylonitrile by the Baizer-process with a volume of ca. 400×10^6 t per annum, representing 30% market share in 2014[1,12], is an prominent exception. However, the products that can be gained by and the feedstock that can be exploited for electrochemical conversions are currently limited. In this article, it is discussed that the electric power and the chemical sector can be linked more efficiently when unlocking the synergy of microbial and electrochemical conversions in electrobiorefineries that we define as *a facility which integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass, and which also exploits the combination of microbial and electrochemical conversions.* Thereby combining different microbial and electrochemical conversions can be used to improve existing and create new process-lines, as illustrated below.

2. Biorefineries provide a chemically challenging process environment

The dependency on the environmentally questionable and limited strategic resource petroleum as raw material has to be overcome[13,14]. This is aimed at in *biorefineries. Biorefineries* are defined as *integrated process concepts that use biomass as resource for the sustainable, ideally residue-free production of different products (including construction materials, chemicals, energy and/ or fuels*)[15]. Thus, a biorefinery (Figure 1) covers a whole process line, starting with the primary refining, usually including a biomass pretreatment and subsequent fractionation of different components (*e.g.*, sugars, plant oil, lignocellulose, gaseous products from anaerobic digestion or gasification)[14,15]. The secondary refining covers additional conversion and upgrade processes to yield the desired products[15]. Mainly, biorefineries cover the three central products biofuels, bioenergy and biobased commodities, *i.e.*, bulk and fine chemicals. Commonly, the combination of energetic and material use is realized in biorefineries, focusing on utilizing all biomass components[13,15]. Some biorefineries are on the verge to application, *e.g.*, bioethanol as fuel or plastics from poly-lactic acid as renewable commodity[6].

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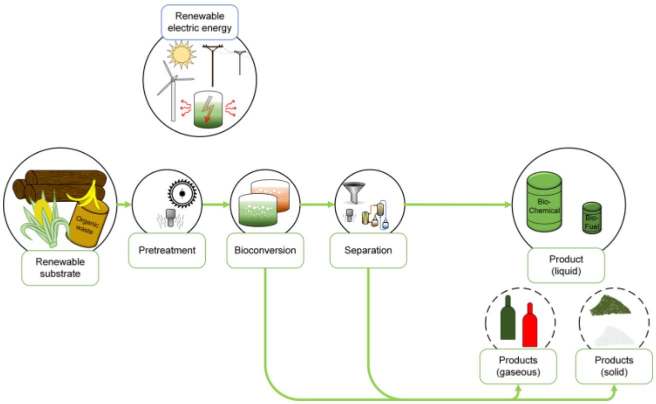

Figure 1. Simplified principle outline of a biorefinery: Renewable substrate is pretreated and the (bio)conversions yield gaseous as well as solid and liquid products, with the two latter ones possibly requiring separation. The electric energy sector is almost fully decoupled from the biochemical transformations. (Details see text.).

The coupling to the electric power sector can be only achieved via thermal use of, *e.g.*, biogas or synthesis gas as well as solids combustion.The complex field of biorefineries can be classified *via* the utilized primary feedstock[14,15] and their intermediate platform chemicals[14,15]. Among others, present prominent platform chemicals cover syngas (mainly CO and H_2, also CO_2) derived from biomass gasification, sugars, starch, lignocellulose, or plant oil[14,15]. Frequently, the primary feedstock determines the economic viability of biorefinery routes, as biobased materials often are expensive, challenging to transport over long distances, and supply routes are not yet well established[15,16]. This aspect triggered that the first biorefineries were based on energy rich plants containing easily convertible compounds and having established logistic networks, *e.g.*, sugar beet for bioethanol[5]. Yet, sustainability can only be achieved when non-food feedstock are applied, driving the research endeavors towards, for instance, algal or lignocellulosic biomass[14] as well as waste streams in general[17].

Here, linking biorefineries with the electric energy sector, which is currently mainly decoupled from chemical production, comes into play (see also Figure 3). Prior to discussing the concept of electrobiorefineries, the chemical, physical, and energetic conditions of different fractions of a biorefinery, *i.e.*, feedstock, liquid streams and gaseous streams, have to be re-called[18]. Concerning the energy content and density level, fossil resources are much more energy dense than biobased feedstock, even crops[19]. Consequently, biobased conversions need larger volumes or longer reaction times than petrochemical routes for achieving the same energy throughput. In biobased processes, also the energy density has to be increased from feedstock to products, which often leads to significant losses, *e.g.*, found as heat dissipation, which can only partly be recovered. Further, biobased feedstock possess often a relatively high water content and hence cannot be introduced in existing petrochemical plants. Consequently, either water might be the process liquid of choice or it has to be removed at high energy costs[18,20]. Thus, aqueous process liquids will play a key role in electrobiorefineries, as well, although organic solvents and ionic liquids might be applied, too. Furthermore, solid and liquid biobased feedstock is characterized by a high chemical heterogeneity that differs significantly from fossil resources. Figure 2 illustrates some examples of chemical functionalities found in petro- and biobased feedstock. Functional groups have to be treated in different ways to yield (nowadays) desired products. Whereas functional groups like hydroxyl-groups need to be introduced in petrobased processes, a (selective) removal, *i.e.*, reduction, or alteration of these is commonly desired in biobased processes. Summing up, joining bio- and electrochemical conversions faces a chemically highly challenging environment. It is characterized by high diversity (in terms of different compounds being present in parallel), high chemical heterogeneity (in terms of functional groups), as well as a narrow process window especially when water is used as solvent.

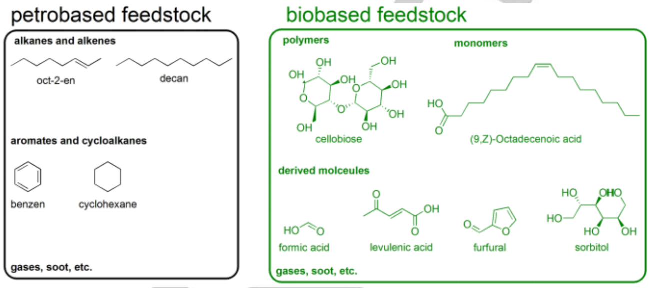

Figure 2. Selected examples for illustrating the chemical diversity and heterogeneity in petrochemical and biobased liquid process streams - adapted from [21] and [22]. For gaseous compounds, most important are the gas feeds as well as the off-gas of aerobic as well as anaerobic microbial conversions, *e.g.*, H_2, O_2, CO_2, CH_4, and more dedicated volatile intermediates and products.

3. Merging electrochemistry and microbiology in electrobiorefineries: Creating synergies

Interfacing microbial and electrochemical conversions can be achieved in primary and secondary microbial electrochemical technologies (MET) as well as hybrid systems[23].

In primary MET, the metabolism of the microorganism is immediately wired to the electrode which serves as electron acceptor/ donor. This electron exchange is based on extracellular electron transfer from the microorganism to the electrode and *vice versa*[25][26]. Secondary MET refers to processes which only indirectly influence the microbial metabolism by an electrochemical reaction, *i.e.*, producing the substrate electrochemically or regulating environmental conditions such as pH[23]. A hybrid system is based on a full spatial separation of the microbial and electrochemical conversion, *e.g.*, by feeding the off-gas of an electrolyzer cathode to a bioreactor where the H_2 serves electron donor.

In all cases, this interfacing can be of high energetic and chemical efficiency[24].

When considering the process-line of an electrobiorefinery, electrical power could be used at different stages (see also Figure 3):

Power production: Waste streams of the renewable substrate can be used for electric power production using anaerobic digestion or, more directly, microbial fuel cells[26,27].

Feedstock decomposition: Feedstock can be pretreated *via* electrochemical means in order to increase the bioavailability and hence, the corresponding bioconversion rate and efficiency. For instance, recalcitrant lignin can be pretreated by electrochemical oxidation[28] to increase its bioavailability.

Providing chemical feedstock: Using electrical power to provide feedstock for bioconversions is the essence of power-to-X-technologies. Thereby, mainly H_2 from water electrolysis is considered[29]. Yet, also C_1-compounds like formate[30,31] or C_2-compounds [32–36] or CH_4[37] can be provided using electric energy and CO_2. Here also the electrochemical oxygen evolution has to be mentioned, although it plays an only minor role, so far.

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Steering of microbial conversions: This vital field of research is denominated as microbial electrosynthesis[38,39] and covers the electrochemically driven synthesis from CO_2 as well as other precursors and the electrochemically steered fermentation[40]. Microbial electrosynthesis was first reported by Hongo and Iwahara[41] and Emde and Schink[42] for fermentations. Since its revival by the demonstration that CO_2 can serve as carbon source by Nevin *et al.*[43], numerous pure cultures, *e.g.*[44], and microbiomes, *e.g.*[45], have been exploited. The steering also holds true for electrofermentations, *e.g.* [46], where the yield is increased by interfacing the fermentation with electrodes. Interestingly, it was shown by metabolic network modeling that oxidative productions do not necessarily require anodes and reductions cathodes, respectively[47,48].

Removing products and intermediates: Bioprocesses are often limited by the accumulation of metabolites, *i.e.*, intermediates or products. These can be removed also by electricity driven methods, as most prominently demonstrated for the electricity driven extraction of carboxylic acids by several research groups[49–53].

Upgrading of intermediates: The oxidation of microbial metabolites, like H_2, for electric power production in fuel cells can be considered as upgrading. Further, if this oxidation is achieved in a secondary MET, it is even a product removal that enhances the yield, *e.g.*, of microbial fermentations limited by high partial pressures of H_2[54–56]. More specifically the products of the bioprocess can be further upgraded, both energetically and economically, using electroorganic reactions as discussed below.

In summary, all above discussed options on how to meaningfully integrate electrochemical conversions into the biobased process lines create beneficial synergies (Figure 3). Thus, electrobiorefineries may lead to improved productions in terms of yields, rates, titers, as well as to increased product purity and selectivity, or even novel production lines.

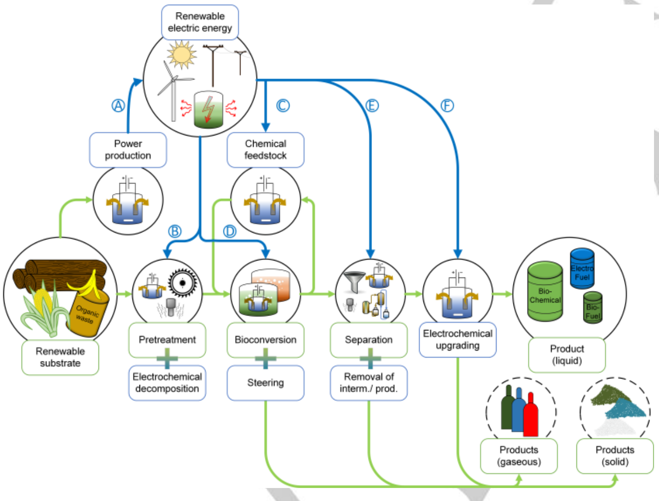

Figure 3. Principle outline of the electrobiorefinery concept: Synergies can be created by linking microbial and electrochemical conversions at different stages: A) power production, B) feedstock decomposition, C) providing chemical feedstock, D) steering of microbial conversions, E) removing products and intermediates, F) upgrading of intermediates. This leads to improved and novel processes. For details and references please see text.

3.1. Upgrading of intermediates: Electroorganic reactions of microbial products

Electroorganic reactions, *i.e.*, using electrochemistry in organic synthesis, is currently facing a renaissance[57] also with the availability of "plug-and-play" devices[58] being one important aspect. Synergies of microbial and electrochemical transformations in electrobiorefineries can be realized for several reaction types and molecular classes. Thereby, the individual weaknesses and strengths of both types of conversions as well as their interfacing have to be confronted in terms of reaction conditions, types of reaction and process as well as reactor engineering.

A plethora of electroorganic oxidation and reduction reactions have been demonstrated in the past as well as in the last years, see *e.g.* [57,59–61]. When starting from microbially produced compounds (*i.e.*, here denominated as intermediates) from biobased feedstock, we consider the electrochemical hydrogenation most straightforward and highly promising as it takes place at room temperature and ambient pressure. Figure 4 A shows a recently demonstrated electrobiorefinery processes for the production of *trans*-3-hexendioic acid, which serves as precursor of nylon-6,6 from muconic acid at high yield and selectivity as key-step[62]. Noteworthy, the muconic acid was gained by fermentation and may serve as a building block also for other important monomers, *e.g.*, adipic acid[63]. Further, it was recently demonstrated on the reduction of microbially produced itaconic acid to methylsuccinic acid[64] that the electrochemical route was superior to the chemical process based on heterogeneous catalysis using H_2. Reductive electroorganic reactions that may expand the portfolio for electrobiorefineries include for instance these of furfurals[65] and for vanillin production[66]. When considering electrochemical oxidations, the Kolbe-electrolysis is certainly the most prominent reaction for upgrading intermediates[67,68] by creating C-C-bonds from aliphatic organic acids, but also cross-coupling of other starting materials like, for instance, phenols or thiophens[69,70]. Figure 4 B shows the recent electrobiorefinery process for the conversion of corn to drop-in fuel additive utilizing the Kolbe-reaction of microbially produced middle chain carboxylic acids. Further, more particular oxidation reactions like the formation of N-N-bonds[71] or the electrochemical oxidation of olefins to enons[59] may be seized. In general, the idea is creating an electrosynthetic toolbox, *i.e.*, a set of reactions, like in "classical" synthetic organic chemistry, that allows realizing a desired reaction from scratch. Thereby, the conversions in electrobiorefineries are also promising for creating and upgrading biobased privileged building blocks or platform molecules, like the aforementioned itaconic acid, muconic acid, as well as triacetic acid lactone or furans.[72] However, this is not the *status quo* and will certainly need substantial progress in terms of science, engineering and standardization[58]. For electrobiorefineries, reactions conditions have to be considered and especially the solvent (aqueous or not) and pH-value play a key role for interfacing them directly, *i.e.*, “in one pot”. When considering process and reactor engineering, a further asset of electrobiorefineries is provided by the different reaction rates and space-time yields of bioprocesses and electrochemistry. Whereas the slower microbial conversion can run continuously, some of the fast electrochemical reactions can be operated only at times of high power production. For instance, the electrochemical feedstock decomposition or the upgrading of microbial products can take place in minutes to hours, providing for bioconversions running for days. This also allows the utilization of considerably smaller reactors and respective peripherals.

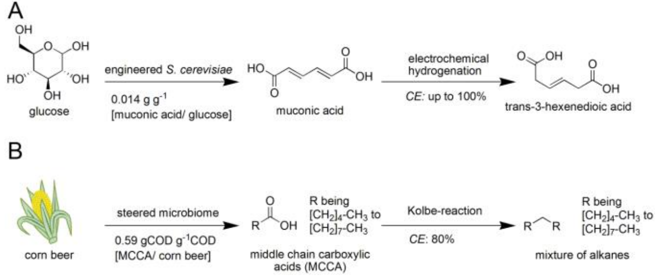

Figure 4. Examples of microbial and electroorganic conversions in electrobiorefineries: A) for the production of trans-3-hexenedioic acid from glucose being an important monomer for the production of nylon-6,6[12,62] and B) for the production of drop-in fuel additive from fermented corn[73]. When risking a look at operational expenditures for the production of nylon-6,6 the key-intermediate *trans*-3-hexendioic acid was shown be possible at costs of 2.13 US$ kg^{-1}[12] and for generation of drop-in fuel additive from ethanol and acetate as feedstock a price of 1.37 US$ L^{-1} (see SI). In both cases, the electric energy prices played only a minor role, but considerable costs like down- and upstream processing cannot be assessed at present state, which especially holds also true for the capital expenditures.

3. A look to the horizon

It was shown that by using electrobiorefineries, an alliance can be formed of the realms of electric power production and chemical production in line with the general desire to electrify chemical industry, *e.g.*, also for the NH_3-synthesis[74]. Using electric energy can allow the improved production of chemicals by different means and renewable feedstock, especially waste, can be used for electric power production. On the horizon, we see electrobiorefineries much more broad and versatile. As briefly introduced above, oxidative and reductive electroorganic reactions offer a plethora of reaction pathways that need to be explored. In addition, engineering microbial conversions by microbiomes[75] as well as pure cultures towards the production of privileged building blocks and their electrochemical upgrading seems of outstanding potential[76]. Ultimately, the economic feasibility of a given process line will certainly depend on several engineering and operation aspects, *e.g.*, the different space-time yields of electrochemical and biobased conversions, up- and down-streaming, as well as the political framework and societal spirit.

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Keywords: Electroorganic chemistry • microbial electrochemical technology • biorefinery • power storage • green chemistry

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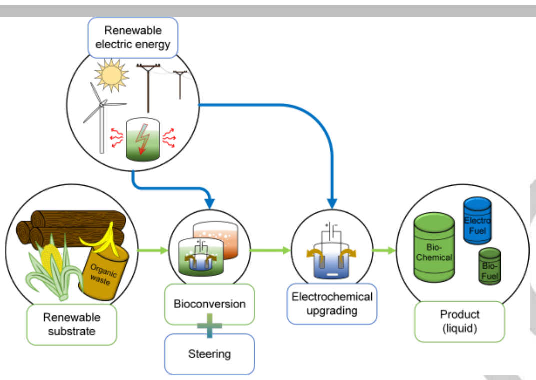
Entry for the Table of Contents

MINIREVIEW

Electrifying biorefineries: Interfacing of microbial and electrochemical conversions in electrobiorefineries can lead to synergistic benefits at multiple points of a process line. Especially joining microbial conversions and electrosynthesis is highly promising.



Falk Harnisch and Carolin Urban*

Electrobiorefineries: Unlocking the synergy of electrochemical and microbial conversions