Hydrogen from Water is more than a Fuel: Hydrogenations and Hydrodeoxygenations for a Biobased Economy

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Abstract: Worldwide a hydrogen-based economy is on the political agenda. Its centre forms molecular hydrogen (H₂) that should serve mainly as energy carrier and fuel. However, currently and foreseeable in the future H₂ is playing its main role as reactant in the chemical industry. Electrolytic generation and storage of H₂ gas is energy demanding and may hardly become economically at the large scale. We argue that in the overall transition towards an economy that is based on biomolecules and CO₂ as carbon feedstock electrochemical hydrogenations and hydrodeoxygenations in aqueous solutions need to be moved in the centre. Departing from the well-known fact that electrochemistry allows creating reactive hydrogen species from water, i.e. hydrogen in statu nascendi (H*), at ambient temperature and pressure we illustrate the existing diversity of reactions based thereon. We focus on examples of model compounds from thermal biomass pretreatment and products from real thermal biomass pretreatment (bio-oil). Consequently, we advocate that electrochemical hydrogenations and hydrodeoxygenations have to be further explored and interweaved into existing process lines.

Keywords: electrosynthesis, electrochemistry, hydrogenation, statu nascendi, power-to-chemicals, power-to-molecules, bio-oil

1. Seizing the Upheaval – A Grand Opportunity for Organic Electrosynthesis

The search for alternative sources that replace fossil resources in a future biobased and circular economy continues to rise. This pursuit is not only fuelled by the foreseeable decline in their supplies, but societal awareness of the dire environmental impact from their utilization. Surrogating the material foundation of our fossil-based economy for a biobased economy, needs sustainable feedstock that can meet the demand for providing energy, fuels and commodities. The use of renewables for a more sustainable production of electric energy, e.g. wind turbines or photovoltaics, is experiencing a rapid deployment and their share in total electric energy production is increasing. On the materials site, in addition to the use of CO₂ as carbon source, the effective use of renewable biomass as material feedstock meaning as a source of carbon, nitrogen etc. will be the cornerstone. There are several technologies for the conversion of biomass into industrially relevant building blocks. These technologies include enzymatic, chemocatalytic and thermochemical conversions for the transformation of diverse polymeric and monomeric biomass feedstock such as lignocellulose, saccharides, furans, alcohols, aldehydes, and acids into building blocks. Among the plethora of technologies, the ones that can be summarized as Power-to-Chemicals or Power-to-Fuels have gained special attention. Commonly they are based on the electrochemical upgrading of compounds or electrochemical supply of intermediates for bioconversion and thus allow combining utilization of electric energy with biobased feedstock.
exemplified the applicability of Power-to-Chemicals on the upgrading of bio-oil (gained by thermochemical conversion of biomass) by means of electrochemical hydrogenation and hydrodeoxygenation.

In industry, electric power is utilized mainly indirectly, e.g., for the generation of process heat or cooling. It is clear that this is not necessarily efficient and, hence, the direct utilization of electric energy for chemical conversions is of paramount importance and can be realized in electrochemical synthesis. Electrochemical synthesis is currently facing a renaissance albeit it was already forecasted in the 1960s that electrons may replace chemical oxidants and reductants. Successful examples for industrial implementation are the chlor-alkali process or the Baizer process. However, generally Power-to-Chemicals represents only a very minor share of established industrial processes and Power-to-Fuels is currently negligible. When it comes to Power-to-Chemicals and Power-to-Fuels the use of electric energy from renewables will represent a further advantage beyond the conversion of electric to chemical energy as follows. The production of renewable electric energy is often characterized by temporal fluctuations and spatial separation of source and sink that is creating a demand for storage and conversion technologies. We envisage a future in which electrical power production based on renewable resources – especially from local peak productions – can be converted into chemical energy carriers and commodities. To achieve this goal technologies and process lines including Power-to-Fuels and Power-to-Chemicals from biobased resources that are referred to as electrobiorefineries will have to allow to be tuned on the respective peak production of electric energy. This will allow to valorise peak electric power (which cannot be achieved currently) and at the same time enable to stabilize the electric grid. Yet, we are aware that this requires a sustainable and balanced interweaving of the sectors of chemical synthesis and fuel production with electric power management and a tailoring or re-building of our current grids and pipelines. In this promising perspective of an electrified biobased economy, organic electrosynthesis plays a central role by creating the bridge needed to use clean electric energy for production of consumer items (Figure 1). First steps on the less travelled paths in this direction have been done by several researchers for different feedstock, products and types of electroorganic reactions.

2. Organic Electrosynthesis – from a Toolbox to a Process Step in the 21st Century

The multifaceted toolbox of organic electrosynthesis allows a high variety of electrochemical transformations (Scheme 1). Recently, Pollok and Waldvogel have presented a comprehensive overview and put these in perspective on how the remarkable developments achieved up to date are contributing to opening new frontiers in organic electrosynthesis.

They show that these transformations are compatible with a wide range of substrates, such as alcohols, alkenes, alkynes, amines, allenes, arenes, carbon monoxide, carboxylic acids, isocyanides, unsaturated and saturated aliphatic substrates, biogenic substrates, and functionalized compounds carrying azide, chloride, bromide, trifluoromethyl, phosphonate, nitrile, secondary and tertiary amino moieties. This versatility enables organic electrosynthesis prospectively finding applications in different areas. Some examples comprise industrial processes, such as the electro-organic racemization in the synthesis of an

![Figure 1](image)
active pharmaceutical ingredient (API) by Bayer and the electro-conversion of amino acids to synthesize nylon precursors. Figure 2 depicts the use of electrochemical transformations as key for the synthesis of complex molecular structures, natural products and APIs, as well as asymmetric synthesis and electro-valorisation of renewable, biobased feedstock.

From this extensive repertoire of reactions in organic electro-synthesis, electrochemical hydrogenations (ECH) and hydrodeoxygenations (ECHDO) seem of highest relevance to us. As illustrated in the following ECH and ECHDO possess an enormous potential for its future use in chemical industry based on biogenic feedstock. As general approximation hydrogenations and hydrodeoxygenations by organic electrosynthesis can be defined as the reaction of molecules and hydrogen atoms that are formed at a cathode. These electroorganic reactions allow for the generation of either reduced compounds, i.e. more saturated hydrocarbons (hydrogenation), or a more deoxygenated product when an oxygenated feedstock is used (hydrodeoxygenation). Based on the feasible electron and proton transfer mechanisms, ECH and ECHDO can proceed via two different pathways. Direct electro-reduction, also sometimes referred as electrohydrogenation, starts with the initial electron transfer between the organic substrate and electrode surface, followed by a protonation step in aqueous solution with water as the proton donor (Scheme 2A). On the other hand, electrocatalytic hydrogenation in aqueous media involves first the formation of chemisorbed hydrogen by reduction of water or protons at the cathode. The adsorbed hydrogen atom that is electrochemically generated in situ at the electrode surface can be seen as an immobilized and highly redox-active reagent catalysing the hydrogenation of the organic compound (Scheme 2B). Electrochemical hydrodeoxygenation might proceed either following pathway A, B, or a combination of both depending the structural complexity of the substrate (Scheme 2C). However, when developing organic electrosynthesis based on ECH and ECHDO, the exact pathway is most often not addressed or even deciphered.

Within this article “ECH” refers to “electrochemical hydrogenation” without distinction on the specific hydrogenation pathway the process might undergoes (see below). To avoid any misunderstanding, please be aware that this abbreviation is also used in the literature to refer to electrocatalytic hydrogenation, only.
Unlike petrochemical raw materials, biogenic compounds are usually highly functionalized (see section 4.1). In consequence, whereas functionalities like hydroxy groups need to be introduced in petrochemical platform chemicals, a selective removal or transformation of functional groups is required for biogenic compounds in order to make them a suitable feed for existing process lines of the chemical industry. Biogenic feedstock usually comes in aqueous medium and thus using water as source of hydrogen for ECH and ECHDO seems a perfect match. As protic solvent, using water can allow circumventing the harsh conditions of, for example, elevated temperatures and hydrogen gas pressures, typically used in conventional (catalytic) hydrogenation/hydrodeoxygenation.25

Figure 2. Selected examples of organic electrosynthesis applications. A: complex molecular architecture formation; B: asymmetric synthesis; C: electro-valorisation of renewable feedstock; D: key transformations towards natural products and E: active pharmaceutical ingredients (APIs).

Scheme 2. Simplified schematic of pathways for electrochemical hydrogenations and hydrodeoxygenations.

2.1. Water is the Prime Solvent for Electroorganic Hydrogenations and Hydrodeoxygenations

The use of water as reaction environment for an electrochemical conversion of biogenic compounds creates several synergies that are extensively discussed by Harnisch and Schröder.3a Most important an easy separation of water-insoluble products can be achieved, as well as the integration of processing of wet and highly diluted feedstock and even bioelectrosynthesis is feasible (not discussed in this article, see e.g.26). Additionally, in contrast to conventional organic synthesis, electrosynthesis requires an ionically conductive reaction medium, and in general, the conductivity of aqueous electrolyte solutions is significantly higher than that of organic electrolyte solutions (Table 1).
From an application perspective, aqueous solutions are ideal electrochemical reaction environments, since the high conductivity of aqueous solutions – especially of acidic or alkaline solutions – result in low potential losses, reducing the power losses (see also Table 1). Thus, we can only emphasize as advocated previously that water is the prime reaction medium for transition of the chemical industry from fossil to renewable and biogenic resources.

### Table 1. Electrolytic conductivities of selected aqueous and non-aqueous electrolyte solutions, measured at a temperature of 25 °C and the derived Ohmic losses.*

| Aqueous reaction media | Specific conductivity, η [mS cm\(^{-1}\)] | Ohmic loss* [V] | Ohmic loss* [W cm\(^{-2}\)] |
|------------------------|------------------------------------------|----------------|---------------------------|
| Water (pure)           | 10\(^{-2}\)–10\(^{-3}\)                 | 2.9            | 2.9                       |
| 1 M H\(_2\)SO\(_4\)    | 346                                      | 4.5            | 4.5                       |
| 1 M KOH                | 223                                      | 11.6           | 11.6                      |
| 1 M NaCl               | 86                                       | 1.2            | 1.2                       |
| 5.68 M HCl             | 849                                      |                |                           |
| Organic reaction media |                                          |                |                           |
| 0.66 M LiClO\(_4\) (propylene carbonate) | 5 | 200          | 200                       |
| 1.16 M LiClO\(_4\) (DMF) | 22           | 45.5          | 45.5                      |
| 1.6 M LiAsF\(_6\) (tetrahydrofuran) | 16    | 62.5          | 62.5                      |

* Across an electrolyte solution layer of 1 cm thickness and at a current density of 1 A cm\(^{-2}\) that can be considered as benchmark for industrial relevance (table adapted from [3a]).

3. **Hydrogen in Electrochemistry Beyond use as Energy Carrier**

The use of hydrogen can be split in two main categories: material use that is exploiting hydrogen as a chemical feedstock, and energetic use that is utilizing hydrogen as an energy vector. Especially the latter is the essence of what is now publicly perceived as a hydrogen economy, for instance in Germany as “green H\(_2\)”.[28] However, nowadays the material use of hydrogen is certainly of higher importance, as the chemical industry constitutes the largest producer and consumer of H\(_2\).[29] Thus, about 55% of the H\(_2\) produced around the world is used for ammonia synthesis, 25% in refineries and about 10% for methanol production. The other applications account for only about 10% of global hydrogen production (Figure 3).[30] Promising applications in the energy sector are currently emerging for the use of H\(_2\) as energy carrier for transport and stationary use, mainly by chemical fuel cells. We are confident that using hydrogen as chemical feedstock will remain of highest importance and we may even speculate that on the long run it will be of higher importance than its role as energy carrier. In any case, to day H\(_2\) is mainly generated by catalytic reforming of fossil oil and gas at high temperatures and pressures, whereas H\(_2\) production by electrolysis is still of very minor industrial importance (Figure 3).[30] This current scenario might find its turning point, when electrochemical water electrolysis at technical scale is widespread and at low cost.[31]

As shown in Scheme 2, electrochemistry allows creating reactive hydrogen species from water, i.e. hydrogen molecules but especially hydrogen in *statu nascendi* being hydrogen radicals (H\(^*\)), at ambient temperature and pressure. These reaction conditions differ substantially from catalytic reforming. Noteworthy, when using electrochemically generated H\(_2\)
and $\text{H}_2^*$, in addition to the environmental and energetic benefits also an increased workplace safety can be realized as no feed of $\text{H}_2$ gas and no pressurized reactors are needed. Thus, we advocate that ECH and ECHDO reactions may be further explored as they allow creating process steps that can be interweaved into existing process lines. Examples of ECH or ECHDO reactions in aqueous solutions include the reduction of biomass-derived liquids containing compounds with oxygen functionalities and unsaturated carbon bonds. This was shown, for instance, for the production of stable, energy-dense, chemical-grade hydrocarbons.\textsuperscript{[33]} Table 2 compiles representative studies on the ECH or ECHDO of biomass-derived oxygenates and different model compounds that are discussed further in the following sections.

4. Electrochemical Hydrogenations and Hydrodeoxygenations of Biomass and Biomass Derived Molecules

4.1. Composition of Bio-oil and Their Need for Hydrogenations and Hydrodeoxygenations

Within many types of biorefineries, especially those being based on thermochemical conversion of biomass, one of the main concerns is the stabilization of the produced bio-oil. The small aldehydes and ketones as well as sugars and phenolic compounds that are gained from complex feedstock, can easily undergo polymerization and condensation with time.\textsuperscript{[41]} These reactions are changing the chemical composition and hence compromising the stability and “quality” of the bio-oil.\textsuperscript{[42]} Among the most common bio-oil upgrading strategies like hydrotreatment, hydrocracking, catalytic cracking, steam reforming, etc.,\textsuperscript{[40]} ECH and ECHDO stand out.

Bio-oils are rich in oxygenated compounds.\textsuperscript{[40]} Here, ECH and ECHDO find a potential application for the sustainable

### Table 2. ECH and ECHDO of biomass-derived oxygenates and model compounds.$^*$

| feedstock             | conditions                                                                 | cathode material | products                                    | F.E.** (%) | Ref. |
|-----------------------|-----------------------------------------------------------------------------|------------------|---------------------------------------------|------------|------|
| glucose               | $-1.5$ to $0 \text{ V vs Ag/AgCl, pH } < 7$, $1 \text{ atm, RT, 0.1 M Na}_2\text{SO}_4$ | Ni, Fe, Co, Cu, Pd, Au, Ag; Pb, Zn, Cd, Sn, In, Sb, Bi Cu | sorbitol; sorbitol and 2-deoxyosorbital FA***; MF*** | N.A.       | [34] |
| furfural              | $-1.1$ to $1.8 \text{ V vs Ag/AgCl, pH } < 7$, $1 \text{ atm, RT, 20 vol\% acetonitrile and 0.5 M H}_2\text{SO}_4$ | Fe, Ni, Cu, Pb; Co, Ag, Au, Cd, Sb, Bi; Pd, Pt, Al, Zn, Sn, In, Sb | DHMF***; DMDHF***; DMDHF*** | 52.2       | [35] |
| 5-HMF***              | $-1.5$ to $0 \text{ V vs Ag/AgCl, pH } < 7$, $1 \text{ atm, RT, 0.5 M H}_2\text{SO}_4$ | Ni, Fe, Co, Cu, Pd, Au, Ag; Pb, Zn, Cd, Sn, In, Sb, Bi Cu; Fe, Ni, Cu, Pb; Co, Ag, Au, Cd, Sb, Bi; Pd, Pt, Al, Zn, Sn, In, Sb | DHMF***; DMDHF***; DMDHF*** | N.A.       | [36] |
| hydroxyacetone        | $-1.5 \text{ V vs Ag/AgCl, pH 2, 1 atm, RT, 0.5 M Na}_2\text{SO}_4$            | 1 mg cm$^{-2}$ Pr/C | sorbitol; sorbitol and 2-deoxyosorbital FA***; MF*** | 20.0       | [37] |
| levulinic acid        | $-1.8 \text{ V vs Ag/AgCl, pH } < 7$, $1 \text{ atm, 8°C, 0.5 M H}_2\text{SO}_4$ | Pb | valeric acid | 27.0       | [38] |
| 2,7-octane-dione      | $-1.8 \text{ V vs Ag/AgCl, pH } < 7$, $1 \text{ atm, 8°C, 0.5 M H}_2\text{SO}_4$ | Pb | n-octane | 11.2       | [38] |
| guaiacol              | $-8 \text{ mAm}^{-2}$, pH 8, $1 \text{ atm, 75°C, 0.1 M borate buffer}$       | Raney-nickel     | cyclohexanol, phenol | 18–26      | [33b] |
| 2-ethoxyphenol        | $-8 \text{ mAm}^{-2}$, $75°C$, $0.1 \text{ M pH 8, potassium borate buffer and 0.5 mM triethyramidonium bromide, CoP anode for water electrolysis}$ | Raney-nickel     | cyclohexanol, phenol | 23         | [33b] |
| benzaldehyde          | $-0.9 \text{ V vs Ag/AgCl, pH 5, 1 atm, 25°C, acetate buffer}$                | Raney-nickel     | cyclohexanol, phenol | 99         | [39] |
| phenol                | $-0.08 \text{ V vs Ag/AgCl, pH } < 1$, $1 \text{ atm, 55°C, 0.1 M silico-tungstic acid water solution}$ | 5 % Pd/C         | benzyl alcohol | 98         | [13] |
|                       |                                                                                 | 10 wt % Pd/C     | cyclohexane | 98         | [13] |

$^*$ Table adapted from\textsuperscript{[40]} with permission from \textit{American Chemical Society} (journal: \textit{Energy & Fuel})

$^1$ For conversions at constant potential (chronoamperometry) it is provided in volt (V), and for constant current (galvanostatic) operation the current density in mA cm$^{-2}$ is shown.

$^*$ F.E.: faradaic efficiency or current efficiency, usually estimated based on substrate consumption and not (as should be preferred) on product harvest.

$^***$ 5-hydroxymethylfurfural (5-HMF); furfuryl alcohol (FA); 2-methylfuran (MF); 2,5-dihydroxymethylfuran (DHMF); 2,5-dimethyl-2,3-dihydrofurcan (DMDHF).
production of fuel and chemicals. The feasibility of applying ECH and ECHDO therefore has been shown for simple model compounds, validating the conversion of aldehydes and ketones to alcohols,[43] furfural to furfuryl alcohol to furans,[44] and the reduction of the aromatic ring of phenolic compounds.[34]

4.2. Hydrogenations and Hydrodeoxygenations of Model Compounds

During ECH the carbonyl groups can be transformed into alcohols or diols, preventing condensation (Scheme 3).[43] In cases where the resulting hydroxy group is conjugated or the conversion is performed in the presence of a strong acid, the product of ECH may further dehydrate to yield an olefin, which can then be hydrogenated to yield an alkane. This commonly occurs with furfural, in which the first hydrogenated product (furfuryl alcohol, FA) undergoes an acid-catalysed dehydration followed by a second ECH step to render 2-methylfuran (MF) (Scheme 3).

Among all bio-oil compounds furfural has attracted special attention due to its low-toxicity and high accessibility. Different conditions have been tested for the ECH of furfural in aqueous electrolyte solutions. For instance, it was shown that depending on the pH the use of sacrificial nickel anodes leads to the selective production of either FA or MF.[35,45] Another furan-type constituent of bio-oils is 5-hydroxymethylfurfural (5-HMF). Interestingly, it was shown that the presence of glucose at neutral pH accelerated the ECH of 5-HMF to 2,5-dihydroxymethylfuran (DHMF), presumably due to changing the onset potential of generation of DHMF to less negative values.[46] Furthermore, it was shown that in acidic conditions the used electrodes can be differentiated on their product distributions between DHMF and 2,5-dimethyl-2,3-dihydrofuran (DMDHF) into three groups of metals (Scheme 4).[36] This model study might suggest that the inherent presence of glucose (usual constituent of bio-oil from biopolymers), as well as the high acidity in raw bio-oil are proper conditions for favouring the ECH of 5-HMF present in bio-oils to a more saturated product, hence supporting the suitability of applying ECH for bio-oil upgrading.

Other examples include the production of valeric acid from levulinic acid (Scheme 5).[7a] Valeric acid can be considered as a biogenic platform molecule that can, for instance, be further converted to the drop-in fuel additive n-octane.[47]

Degradation of cellulose and hemicellulose during bio-oil production yields various monosaccharides. Among these monosaccharides is especially glucose a valuable monomer that can be converted into sorbitol by means of ECH.[48] The electrocatalytic hydrogenation of glucose using 30 different metal electrodes at neutral pH allowed their classification into two reactive groups, as depicted in Scheme 6. The same investigation concluded that the product selectivity is mediated by the catalyst, with a minor influence of the applied potential and the pH.[34]

Aromatic compounds represent a high portion of the bio-oil composition, which is mainly constituted for phenol, guaiacol, syringol, and derived molecules.[49] The ECH of

Scheme 3. Examples of ECH of soluble carbonyl compounds present in aqueous fraction of bio-oil. A: conversion to alcohols; B: conversion to diols; C: reduction of aromatic aldehydes.
aromatic bonds has, so far, been only accomplished using precious metals, such as Pt,\textsuperscript{[13,33c]} Rh,\textsuperscript{[49]} and Ru,\textsuperscript{[33d,50]} and some of the skeletal abundant metals, such as Raney-nickel.\textsuperscript{[33a,b,51]}

Among different aromatic compounds, guaiacol and syringol have been widely used as the model feedstock towards ECH and ECHDO of bio-oil. Electrochemical treatment of methoxy phenolic compounds, such as in guaiacol, can proceed via two different pathways. It proceeds either as demethoxylation followed by aromatic hydrogenation to produce cyclohexanol, or via direct ECH of the aromatic ring to yield 2-methoxycyclohexanol.\textsuperscript{[33a,d,49a,b,50,52]} The experimental data support that the hydro-cleavage of the aryl C-O bond takes place during the aromatic hydrogenation, because it has

Scheme 4. Electrocatalytic hydrogenation of 5-HMF at acidic conditions. Depending on the used cathode a selective reaction pathway can be achieved. A: metals mainly forming DHMF; B: metals forming DHMF and DMDHF depending on the applied potentials; C: metals forming mainly DMDHF. DHMTHF was observed on all metal catalysts as a minor product.

Scheme 5. Electro-valorisation of levulinic acid through hydrodeoxygenation reaction in aqueous solutions. Subsequently, valeric acid can be electrochemically converted via Kolbe reaction or other reaction pathways to \textit{n}-octane.

Scheme 6. ECH of glucose using different cathode materials. A: metals producing selectively sorbitol; B: metals producing sorbitol and 2-deoxysorbitol; C: metals favouring hydrogen evolution reaction (HER) over glucose reduction, no ECH and ECHDO of glucose occurs.
been shown that aliphatic alcohols, for example, 2-methoxy-cyclohexanol, cannot be demethoxylated to yield cyclohexanol. The conversion by ECHDO of syringol to guaiacol also undergoes through a demethoxylation step, although it at a lower rate.

4.3. Hydrogenations and Hydrodeoxygenations of Bio-oil

As discussed above, ECH and ECHDO have been broadly studied using model compounds being representative for biomass-derived molecules. Yet, only a few studies have explored the electrochemical upgrading of bio-oil and components in the aqueous phase formed during bio-oil formation that are summarized in Table 3. These studies have been hampered for technical issues (lack of equipment for biomass liquefaction for bio-oil production) and challenges in chemical analysis, but especially to the difficulties in producing bio-oil with consistent quality, and the aforementioned challenges of bio-oil storage.

However, the quantification of the organic substrate for hydrogenation in a bio-oil is hardly possible and mostly not reported. Thus, instead of assessing the F.E. other approaches are required for quantification. Commonly, the carbonyl concentration (CON, amount of carbonyl groups determined via potentiometric titration) and total acid number (TAN, acid components determined via titration) are used. From an application perspective the stability of bio-oil in the pre- and post-upgraded stages is determined by measuring the extent of polymerization during storage using gel permeation chromatography (GPC).

Pioneering research was performed by Li et al. for the stabilization of bio-oil by means of an ECH. A two-chamber H-cell was implemented in bench-scale for the reduction of small carbonyl compounds to its corresponding alcohols and diols at activated carbon cathodes with Ru as electrocatalyst. Further, acetic acid was removed from the cathode compartment presumably by migration to the anode compartment. Zhang et al. used a similar setup and electrocatalyst. In their case the system allowed to ECH the small carbonyls and the aromatics and enabled the spontaneously reductive upgrading of bio-oil. On the other hand, Lister et al. exploited the migration of organic-acid anions across a membrane as means to neutralize the acidity of bio-oil. Despite the witty use of a dual-membrane cell (three chamber system) for removing acetic acid and formic acid from the bio-oil in the cathode chamber and trapping them in a middle chamber between cathode and anode, the ECH rate was very low. Further investigations have to be conducted for the cathode catalysts in order to improve the applicability for bio-oil upgrading.

Andrews et al. used a fixed-bed continuous-flow cell setup to examine a series of metals as cathode and showed that only Pd and Cu were effective in ECH of benzaldehyde to benzyl alcohol in the presence and absence of bio-oil. Interestingly, when a bio-oil sample was added to the catholyte, only Pd cathode managed to decrease the CON, whereas Cu was deactivated. The learned lesson is that the study of model compounds can be highly interesting for revealing the reaction mechanism. Yet, they may not be adequate to predict the outcome of ECH of bio-oil. The study of Deng et al. revealed that in an undivided electrochemical cell when the light organic and aromatic compounds undergo ECH treatment at the same time, the aromatic content rapidly declines. This suggests that some constituents have an adjuvant effect in the hydrogenation of the aromatics. The results of these studies imply the existence of interactions among bio-oil components during ECH that certainly need further investigation.

The effective use of ECH and ECHDO in the endeavour of a bio-based economy, requires the systematic study of different parameters and setups that cannot be covered in detail in this personal account. In a recent review Akhade et al. provide an in-depth analysis on parameters for electrochemical efficiency and understanding the complexity of the composition. This is crucial towards a systematic engineering of synthesis from simple feedstock to complex process streams. Other experimental considerations are presented in a current review about electrocatalytic hydrogenation in aqueous conditions, as well as, in a mini-review on bio-oil upgrading via ECH. Furthermore, recent advances in hydrodeoxygenation including ECHDO of biomass-derived oxygenates are covered by Kim et al.
5. A Plea for Changing the Paradigm

We do not want to carry coals to Newcastle when stating that electrochemistry is a key scientific discipline for the turnaround of the fossil based to a biobased industry. For this turnaround the electrochemistry of hydrogen will play a key role. Most prominently for the conversion of electric energy by water electrolysis into H₂ for its use as feedstock or fuel. Beyond this energetic use hydrogen in electroorganic synthesis will be of vital importance as we have illustrated on numerous examples (vide supra). In electroorganic synthesis hydrogen and hydrogen radicals that are produced in situ allow their instant use for chemical reactions that are ECH and ECHDO. This circumvents the need of storage of chemicals and electric power and increases workplace safety. Further the specific examples discussed here, interweaving electrochemical technologies with the effective use of fluctuating electric power from renewables to make value-added chemicals will be a game-changer for the future of the chemical industry. However, this can only be achieved, if fascinating examples at laboratory scale are developed into economically competitive technologies.

The main economic parameter for a widespread application of electroorganic synthesis are their operational expenditures (opex) and here the costs of electric power. Without the need to discuss different trends and shares of renewables and their specific prices for countries or regions it is very clear that the capacities have increased and the costs of renewable electric power have decreased in the last decades (see Figure 4). For instance, the global photovoltaic power capacity has multiplied by almost 20 in the last decade. The international energy agency (IEA) expects that only during the next 5 years the global production of renewable electric energy will grow another 50 %. Further the specific examples discussed here, interweaving electrochemical technologies with the effective use of fluctuating electric power from renewables to make value-added chemicals will be a game-changer for the future of the chemical industry. However, this can only be achieved, if fascinating examples at laboratory scale are developed into economically competitive technologies.

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For example, we already have presented proof-of-concept of a electrobiorefinery for high yield production of drop-in fuels or fuel additives from complex biomass using combined anaerobic fermentation, pertraction and Kolbe electrolysis. The product gained at a technology readiness level of 2-3 was not only shown to fulfil the legal requirements for fuels to a great extent, but also to be produced at costs of 1-2 €L⁻¹. For ECH beyond the upgrading of bio-oil this was demonstrated for the conversion of muconic acid gained by sugar fermentation using yeast to produce trans-3-hexenedioic acid, that serves as a precursor for a Nylon-6,6-like polymer at prospected costs of 2-3 €kg⁻¹. Petrochemicals still have a great economic advantage over electrochemical conversions due to their well-established position in the existing chemical infrastructure. Regarding large scale industrial applications, low-cost electrocatalysts composed of earth abundant elemental need to be developed that are available using inexpensive methods. Further to that, other technological aspects like design and operation of reactors have to be targeted. Only a concerted endeavour involving different disciplines will allow to bring electroorganic synthesis from the lab bench via technical scale to reality in industrial process lines. As mentioned above, this will require creating economic incentives for the needed innovation. We see this incentive especially needed for re-structuring production lines and for developing the needed infrastructure there-
fore. The economic advantage for running a specific process from biobased feedstock and with renewable electric power rather than with petrochemicals may be inherent or even allow to provide a green premium. This impulse for a wiser use of energy and weaving it into a thread with bio-friendly production lines is a mission that we as electrochemists can accomplish, and we’ve got to do that.2

6. A Glance in the Future

Verifying the in situ electrochemical hydrogenation / hydrodeoxygenation at technically relevant scale to be a universal tool will lead a paradigm shift. A fundamental change that may contribute securing the fate of the chemical industry of biogenic platform chemicals. Water will be made a sustainable, safe and secure universal source of hydrogen for synthesis, enabling refinery processes using electrons instead of H2 as the reductant at mild temperatures and pressures. In a greater scope, in-water electrochemistry will allow for the valorisation of different raw materials but also energy savings, pollution abatement, recycling, improvement of working conditions and the benefits to be gained from developing new technologies, even though they are not yet economical.

Up to date, the studies on model compounds has demonstrated that ECH and ECHDO can convert carbonyls compounds present in bio-oil into alcohols and diols, as well as to transform methoxylated aromatic monomers into cyclic aliphatic constituents, and to attain neutralization by selectively removing acidic compounds. This research will pave the way to the comprehensive use of ECH and ECHOD for upgrading diverse feedstock while applying clean energy sources. In line with the concept of electrobiorefineries6[6] modular and energetically autarkic equipment will permit locating electrochemical production facilities close to abundantly carbon resources (e.g., biomass, waste, and CO2), and the upgrading by ECH and ECHDO of feedstock will leverage unprecedented synergies.

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