Electro-privileged transformations of bio-derived molecules: Progress and roadmap

Cong Tian[1,2,10], Roham Dorakhan[2,10], Joshua Wicks[2,10], Zhu Chen[2], Kyoung-Shin Choi[3], Nirala Singh[4], Joshua A. Schaidle[5], Adam Holewinski[6], Aleksandra Vojvodic[7], Dionisios G. Vlachos[8], Linda J. Broadbelt[9], Edward H. Sargent[1,2*]

Affiliations:

[1]Department of Chemistry and Department of Electrical and Computer Engineering, Northwestern University, Evanston, IL 60208, USA.

[2]Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

[3]Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

[4]Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136, USA

[5]Bioenergy Science & Technology Directorate, National Renewable Energy Laboratory, Golden, Colorado 80401, USA

[6]Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80303, USA

[7]Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

[8]Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19711, USA

[9]Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, USA

[10]These authors contributed equally: Cong Tian, Joshua Wicks, Roham Dorakhan.

Abstract

Biomass incorporates carbon captured from the atmosphere and can serve as a renewable feedstock for producing valuable chemicals and fuels. Here we look at how electrochemical approaches can impact biomass valorization, focusing on identifying electro-privileged chemical transformations. First, we recommend that the field explore widening the spectrum of platform chemicals derived from bio-feedstocks, thus offering new pathways to molecules that have historically been derived from petroleum. Second, we identify opportunities in electrocatalytic production of energy-dense fuels from biomass that utilize water as the hydrogen source and renewable electricity as the driving force. Finally, we look at the potential in electrochemical depolymerization to preserve key functional groups in raw feedstocks that would otherwise be lost during harsh pre-treatments in traditional depolymerization routes. Based on these priorities, we suggest a roadmap for the integration of biomass and electrochemistry and we offer milestones required to tap further into the potential of electrochemical biomass valorization.

Introduction

Biomass represents a large source of already-fixed carbon that is globally available, its input CO_2 already partially-reduced. It is derived from diverse sources, including residue and bio-waste from crops and algae. The estimated global supply of dry biomass from agriculture and forestry is ~ 12 gigatons per year (Gt/y), while waste biomass constitutes >100 Gt/y when one totals up industrial, municipal, and food waste. [1] Given its ~ 50 wt% carbon content, [2] waste biomass corresponds to the rough equivalent ~150 Gt of CO_2 fixed/year. The valorization of biomass holds potential in the sustainable production of biofuels, bio-based chemicals, and bio-materials. One prominent application is in the production of sustainable aviation fuels[3], where a transition away from petrochemical feedstocks will contribute to reducing the carbon footprint of aviation.

We summarize the biomass processing landscape in **Fig. 1A**, rating feedstocks based on their H_{adj}/C ratio, where H_{adj} is the adjusted hydrogen content representing the difference in the number of hydrogen and oxygen atoms, and the generation of feedstock. We show different product categories along with processes used to obtain them and rank the processing energy input (PEI) required to produce each category from specific processes. For example, lignocellulosic biomass feedstock (with an H_{adj}/C=0.2) can be used in a pyrolysis process to produce pyro-oil with a relatively high PEI of 5/6. The pyro-oil product category has a H_{adj}/C range of ~ 1-1.4 (length of product category along the y-axis), and can be converted to furans, short chain aliphatics, benzylics and C_{7+} paraffins/olefins through hydroprocessing and corresponding separation. The product categories made through this route also have a significant PEI of 5/6, with C_{7+} paraffins/olefins having the highest H_{adj}/C (>1.6), followed by aromatics, aliphatics, and furans. Transformations with higher PEI will consequently have a higher energy demand and potentially higher carbon intensity associated with the process.

Today's biomass valorization landscape evidences a number of limitations. A first concern is that many biofuels today rely on first-generation edible feedstocks that may compete with food supply and may alter land use and increase food cost. [4-5] To illustrate, the production of approximately 42 million tons of bioethanol in US consumes 120 million tons of sugar- and starch-rich plants. [1] Transitioning towards second-generation feedstocks such as lignocellulosic biomass seeks to address this issue; however, these feedstocks are today more energy intensive to process. This can be seen in **Fig. 1A** where the production of furans, aliphatic and aromatics through Pyrolysis/HTL/hydroprocessing has a much higher PEI (5/6) when lignocellulosic biomass is used as the feed, compared to when sugar and starch crops are used. As of today, their share in the biomass market remains minute, with the contribution of lignocellulosic ethanol to total bioethanol production residing below 1%.[5] The use of biomass-derived products will, in the long run, rely on the transition toward these second-generation feedstocks.

A second concern for existing biomass conversion processes (as shown in **Fig. 1A**) is their high PEI, linked to a demanding set of operating conditions in temperature (as high as 1300 °C in

gasification) [6-7] and pressure (ranging from 20 to 300 bar). [8-11] These necessitate specialized infrastructure and typically militate against a modular approach to plant design. [12] Higher PEI also increases the carbon intensity of the product. This impacts both cradle-to-grave carbon intensity and cost.

These considerations motivate interest in alternative processes for biomass valorization, among which electrochemical processes[13-14] – ideally ones that minimize energy consumption and contribute to decreasing overall carbon intensity – are candidates. Electrochemistry provides both oxidative and reductive chemical transformations[15], each of interest in biomass processing. [16] Its reliance on increasingly available renewable electricity – expected to continue its growth and decline further in electricity's carbon intensity (C.I., gCO_2e/kWh) – will create opportunities for lowered-C.I. biomass-derived products. Precedents for scalable and industrialized electrochemical processes include the chloralkali process [17-18] and, increasingly, green H_2 production, with electrification of biomass valorization an open challenge and opportunity. [19]

Here we define electro-privileged transformations on biomass-derived molecules (**Fig. 1B**) as those that 1) utilize renewable electricity as a low-C.I. energy source, H_2O as hydrogen source and/or CO_2 as carbon source; 2) proceed under mild conditions that are suitable for modular deployment; 3) selectively produce the desired product range with minimal side reactions (electro-privileged molecules).

In this Perspective we offer three priorities in biomass electrochemical valorization to meet the need for carbon- and energy-efficient chemicals production and provide a roadmap for net-zero emission: 1) broaden the scope of biomass-derived feedstocks and electrochemically valorized products; 2) identify opportunities in electrochemical transformation of biomass to energy-dense fuels and 3) pursue direct electrochemical depolymerization of raw biomass feedstocks.

Observation #1: Platform chemicals: an intensive focus by electro-biotransformation researchers has led to rapid progress on a set of compelling reactions and bioderived chemicals

Biomass platform chemicals[20] are building blocks produced by biomass pretreatments and ready for further valorization. In contrast with the case of fossil-derived chemicals, rich oxygen-containing functional groups naturally formed in biomass are preserved in these molecules, eliminating the need for downstream capital-intensive oxidation processes. [21] In particular, the aromaticity of molecules in lignin is preserved, obviating the need for costly and energy-intensive aromatic catalytic reforming of naphtha in the petroleum industry. [22] Similarly, amino groups found in biomass can be preserved in platform chemicals to circumvent downstream amination processes.

Electrochemical approaches can offer mild reaction conditions, their oxidation and reduction potentials and electrolytes finely tuned to oxidize or reduce only a desired functional group. This includes the selective oxidation of only a secondary alcohol of polyols (e.g. glycerol), [23] preferentially oxidizing an alcohol group instead of an aldehyde group (or vice versa), [24] and oxidizing an alcohol group only to an aldehyde group without further oxidizing to a carboxylic group. [25] The reductive valorization of aromatic molecules and unsaturated hydrocarbons presents opportunities for electrochemical reduction toward fuels, fuel additives, and other hydrocarbon products. [26] Both electrochemical oxidative and reductive conversion of these biomass platform chemicals can retain desirable functional groups while modifying the chemical structure to obtain diverse downstream products with a high selectivity. A range of electrochemical biomass platform chemical valorization pathways published in the recent decade are mapped out in **Fig. 2**.

When evaluating candidate chemicals, we look at three groups of biomass feedstocks: bio alcohols (glycerol and ethanol), bio-acids (formic acid and levulinic acid), and furans (HMF and furfurals). Each class of platform chemical has a variety of valuable derivatives with large and growing markets (**Table 1**). Valorization of these platform chemicals could lead to products that

serve as drop-in replacements for legacy petrochemicals; or, it might instead replace them with chemicals that can be further processed to provide similarly useful physical and chemical properties. Certain chemicals can be obtained through electrochemical transformations with high selectivity, energy efficiency and reaction rate; such biomass-derived products are referred to as electro-privileged.

Glycerol, a by-product of biodiesel with multiple hydroxyl functional groups, can be oxidatively upgraded to valuable chemicals[23] having market sizes larger than that of glycerol. Electro-oxidation of glycerol produces a range of carboxylic acids, ketones and aldehydes that can be used as C1-C3 feedstocks in polymers, medicines and food. [27-28] Mechanistic studies[29] of glycerol oxidation assisted by *in-situ* spectroscopy, reveal stabilization of certain reaction intermediates and deprotonation during C–C cleavage as critical steps in influencing product selectivity. Hence, discriminative stabilization of certain intermediates and controlling deprotonation kinetics can help enhance product selectivity.

5-Hydroxymethylfurfural (HMF) has been considered a versatile biomass platform chemical for its multi-functional groups capable of oxidative upgrading toward various products. HMF is potentially also an electro-privileged molecule due to a reduction of carbon footprint using electrochemical processing steps. The electro-oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) has attracted attention as a biomass-derived replacement for terephthalic acid (TPA) in producing commercial polymers[30]. Employing wind-generated electricity, FDCA could reach a carbon footprint of as low as 0.3 kg-CO_2/kg-FDCA; [31] while TPA suffers from a cradle-to-gate carbon footprint of 2.6 kg-CO_2/kg-TPA.

Furfural has also been examined as a biomass derived building block inclined to both oxidative and reductive valorizing transformations. [32] Furfuryl alcohol and furoic acid are some of the products accessible from furfural[33] of interest for their application in furan resins and FDCA[34-35] respectively. Recent works have studied the pH-dependent selectivity shift between furfural alcohol and 2-methylfuran, as well as the benefit of aqueous-organic co-solvents to inhibit side-production of humins. [36]

Lignin monomers represent a variety of oxygenated molecules generated from lignin depolymerization. [2] These renewable aromatic feedstocks can be unstable due to the presence of unsaturated oxygenates such as alkenyl, aldehydes, ketones and carboxylic acids, and need further valorization before being used as fuels and chemicals. Electrocatalytic hydrogenation (ECH) offers mild reaction pathways to produce diverse chemicals including phenol, guaiacol, syringol and cyclohexane. [37]

Recommendation #1: Broaden the scope of biomass-derived electrochemically valorized feedstock platform chemicals and accessible products

In light of these concrete examples in electrified biomass valorization, we recommend that the field further widen the spectrum of electrochemically valorized chemicals, which should encompass both diversity in biomass-derived reactants and products. We provide examples of how diversity in feedstock and/or product range can be achieved.

Bioethanol is widely used as a fuel additive[4, 38], but also provides a suitable platform (when sourced from non-edible lignocellulosic feedstocks) for chemicals production[39]. It is used as a drop-in fuel, due to its high energy density and availability, in internal combustion engines and fuel cells, with the latter gaining much interest in recent years. [40] We recommend a further focus on the electrochemical valorization of bioethanol into acetic acid, [41] a commodity chemical with applications in paints, adhesives and plastics, [42] having a market size of $20 billion/year and 86 million tonnes/year (Table 1). Its volume is comparable to that of bioethanol, today coming from fossil fuel-derived methanol and carbon monoxide through carbonylation routes.

HMF is one of the most versatile platform chemicals, being able to serve a variety of products through oxidative and reductive treatments. However, it has mostly been the object of research for electrochemical transformation to FDCA (**Figure 2**). We recommend focusing on its upgrading intermediates and processes to control and diversify electrochemical products. For example, by leveraging *operando* spectroscopies and quantum mechanical simulations[24, 30, 43], researchers have gained mechanistic insight into the electrooxidation of HMF: key intermediates

of 2,5-diformylfuran (DFF) and 5-hydroxymethylfuran-2-carboxylic acid (HMFCA) have been identified and mechanisms have been proposed including hydrogen atom transfer (HAT) and hydride transfer. [44] These insights assist in developing catalysts and systems that target non-FDCA products and diversify the product range of HMF feedstocks.

Levulinic acid, a C5 bio-acid formed by cellulose hydrolysis[45], can be valorized to valeric acid, γ-valerolactone and 4-hydroxyvaleric acid (precursor to biodegradable polyhydroxyalkanoates, PHAs) via electrochemical reduction reactions. [46] Recently, neo acids, a new class of platform chemicals conventionally produced from petroleum-derived olefins, have been synthesized from biomass-derived levulinic acid via hydroxyalkylation/alkylation and further hydrodeoxygenation (HDO) [47]. We suggest the development of a tandem system that integrates thermocatalytic hydroxyalkylation and ECH reactions to produce the desired neo acids.

Exploring new electro-privileged transformations does come with challenges specific to electrochemistry. Most biomass feedstocks contain multiple functional groups, some of which need to be selectively targeted during oxidation/reduction, without other groups being affected. Operating at sufficient current densities is of importance to minimize capital expenditure (CAPEX). However, the high voltages applied to generate sufficiently high current densities may result in the overoxidation of feedstock to CO_2 and an increase in competing oxygen evolution reactions (OER) during electrooxidation, as well as hydrogen evolution reaction (HER) in the case of reduction. In case of reduction reactions, suitable complementary oxidation reaction will need to be identified to mitigate the need for high voltage OER or sacrificial anodes, whereas oxidation reactions can be paired with HER to simultaneously produce green hydrogen. These challenges motivate opportunities to focus on: 1) sequential oxidation-reduction reactions in one-cell electrochemical reactors; 2) study of reaction mechanisms by theoretical and spectroscopic techniques; 3) surface engineering for novel and efficient/selective heterogeneous catalysts; 4) electrolyzer design as a means to minimize side-reactions.

Observation #2: Biomass reduction reactions enable increasing H_{adj}/C ratio via hydrogenation, hydrogenolysis and deoxygenation, producing energy-dense hydrocarbons and fuels

Biomass derived fuels (biofuels) such as bioethanol and biodiesel are already being deployed as low-carbon transportation fuels and additives[38, 48]. Biofuels require high energy density to offset their production cost and become feasible fuels. The drawbacks associated with the distributed nature of biomass feedstocks and the transportation costs will be lower per unit energy for biofuels that are higher in energy density and manufactured close to their source.

Energy dense hydrocarbons require a high H:C ratio with low O:C.[26] This traditionally has called for transforming oxygenated biomass feedstocks using thermochemical processes to increase the H_{adj}/C (**Fig 1A**). The transformations constitute both removal of oxygen atoms and addition of hydrogen atoms, through hydrogenation and/or hydrodeoxygenation (HDO), increasing the H_{adj}/C ratio and overall energy density of the molecule. Hydrogenation involves addition of hydrogen atoms to increase saturation of C–C or C–O bonds. HDO can constitute (i) cleavage of C–O bonds and formation of C–H bonds through hydrogenolysis, (ii) decarbonylation/decarboxylation or (iii) dehydration to form unsaturated C–C bonds. We term the electrochemical counterparts of hydrogenation as electrocatalytic hydrogenation (ECH), the hydrogenolysis category of HDO is termed electrocatalytic hydrogenolysis (ECHy) and other HDO categories ((ii) and (iii)) are termed electrocatalytic deoxygenation (ECDO). The target product range of these processes should possess a H_{adj}/C ratio of >1 and an LHV of >30 MJ/kg. This highlights the importance of aromatics, aliphatic and C_{7+} paraffins/olefins as important target fuels.

Jet/diesel range (C_8-C_{22}) high carbon alkanes can be synthesized from lignocellulosic biomass via C–C coupling of monomers, followed by HDO to increase their lower heating value (LHV)[49]. Various coupling reactions of biomass derived furans, including hydroxyalkylation, alkylation and aldol condensation, can deliver high yields of long chain hydrocarbons that are suitable for fuels, lubricants and detergents.[50] However, HDO reactions typically require harsh

reaction conditions that lead to high energy consumption and undesirable C–C cleavage. Therefore, electrochemical reduction reactions hold potential to replace HDO and produce similar high carbon biofuels.

Biomass gasification followed by Fischer-Tropsch and hydroprocessing allows access to energy dense product streams, at the expense of high PEI attributed to harsh gasification conditions.[51] Hydrolysis offers a lower PEI option; however, the corresponding products are of a lower energy density. Pyrolysis and hydrothermal liquefaction can be performed in milder conditions than gasification, but the significant separation cost of the resulting complex pyro-oil mixture limits its technoeconomic feasibility to date. Hydroprocessed esters and fatty acids (HEFA) are a low PEI alternative, but they are limited to oil seeds and other lipid-rich feedstocks, the former a first-generation feedstock competing with food resources. All these reactions require access to considerable H_2 as reductant and suffer from its associated carbon footprint and energy cost, depending on the production method. The reaction conditions of these processes suggest the potential to scale economically, while the distributed nature of second-generation biomass feedstocks is slated to benefit from a modular transformation processes.

Water-based electrolytes, as a proton source, lead to the hydrogen evolution reaction as a side-reaction, requiring dedicated catalyst design to suppress HER and enhance selective ECH without reducing its efficiency. Although H_2 may prove useful in biomass conversion processes, having careful control over the selectivity of ECH is important for energy efficiency. An understanding of what materials or sites catalyze ECH or HER is needed. As an example, for Pt and Rh, the terrace sites are active for ECH of phenol[52] while step sites are not, and so using electrocatalysts with a higher fraction of terrace sites increases the selectivity to ECH.

A challenge for reductively upgrading biomass - compared to the reduction of water, CO_2, or N_2 – originates from the fact that biomass-derived molecules often have multiple functional groups that can be reduced. Each functional group may undergo reduction reactions mentioned above (i-iii) in a competitive manner. Thus, selectively reducing only a specific functional group, and to a prescribed degree, is critical to obtaining a desired product with a high selectivity.

Electrochemical approaches combine tunable applied potential with bespoke electrolyte composition (pH, with specific cations and anions to regulate reduction mechanism). Mechanisms specific to electrochemical reduction may further offer pathways to increase the diversity and selectivity to products: for example, the hydrogenation of an aldehyde group to an alcohol group is not an initial step of the hydrogenolysis of the aldehyde group to an alkane. Instead, the hydrogenation of the aldehyde group and the hydrogenolysis of the aldehyde group are competing reactions preferring different hydrogenation mechanisms. This means that both the alcohol product and the alkane product can be obtained with a high selectivity by electrochemically controlling the competing mechanisms under ambient conditions.

Understanding reaction mechanism through a combination of spectroscopy and kinetic studies[53], including studying the effect of reaction conditions on activity and selectivity[54], is foundational to pursuing such electrochemically orthogonal reaction pathways, as well as for designing more active catalysts and reaction conditions for each pathway. Another potential method to control selectivity is using temperature. Although most studies for ECH are done at room temperature, there can be benefits to operating at different temperatures such as increasing the temperature to increase catalyst activity or controlling the temperature to promote desired reactions over undesired ones. For typical electrochemical reactors that use polymer exchange membranes (e.g., Nafion), reaction temperature can readily be increased up to 80 °C.

Understanding the impact of electrocatalytic conditions such as temperature and voltage on catalyst lifetime is essential due to potential deactivation issues in biomass mixtures. While ECH operates at lower temperatures than thermocatalytic hydrogenation, it can encounter problems such as deactivation from byproduct build-up[55], or the applied potential may induce catalyst dissolution. By comprehending these deactivation modes and testing various mechanisms, catalyst stability can be enhanced. Electrocatalysis also offers methods to control deactivation; adjusting temperature or electrochemical potential can protect catalysts from poisoning and reduce leaching[56], thereby extending electrocatalyst lifespan.

Recommendation #2: Use of low-PEI thermochemical pathways in conjunction with downstream electrochemical hydrogenation, hydrogenolysis and deoxygenation for the transformation of biomass to fuels

The feasibility of ECH, hydrogenolysis (ECHy) and deoxygenation (ECDO) have been demonstrated using certain biomass platform chemicals as feedstock. [44, 57] Current studies focus on the transformation of single platform chemicals into more hydrogenated forms. We propose to expand the feedstock list of ECH, ECHy, and ECDO to encompass not only platform chemicals, but also low/mid-PEI chemical mixtures that suffer from low H_{adj}/C e.g. pyro-oil and sugar/furane mixtures from cellulose hydrolysis (**Fig. 1A**). Theses mixtures would be ideal targets for low-PEI electrochemical reduction reactions such as ECH, ECHy and ECDO, forming a low-PEI and low-C.I. biomass transformation network to increase product H_{adj}/C and produce fuels. The modularity of electrochemical systems, their independence from pressurized hydrogen gas, and their ability to controllably hydrogenate mixture feedstocks make them an ideal technology for biofuel production and rendering the fuels generated via this method electro-privileged products. The chemical variety present in feedstock mixtures poses a challenge for catalyst and system design, a challenge that requires progress in materials synthesis, separation and reaction engineering. We thus highlight the importance of exploring mixtures as feedstocks, where potentially a sequence of ECDO, ECHy and ECH are needed in specific orders to enable production of a high H_{adj}/C fuel. An example would be the reduction of HMF, where although the feedstock is not mixed, reaction conditions can facilitate either ECH, ECHy or both, depending on the reaction pH[44, 58]. This also highlights the importance of site-specific ECDO strategies, that could cleave ECHy-susceptible oxygen species prior to ECH, eliminating ECHy side-products.

Another avenue is the exploration of a wider product range from platform chemical reduction. Opportunities exist where competing reactions that produce multiple products, each with moderate H_{adj}/C, can have their products co-reacted to produce a unified product stream with higher H_{adj}/C and energy density. Cellulose and hemicellulose-derived bio-acids such as lactic acid and levulinic acid can be converted to fuel-grade long chain alkanes and cycloalkanes with high

energy density using ECH. There, the myriad of products, each not a suitable fuel, can be cross-reacted with each other to produce octane, a valuable and energy dense fuel. This inspires the study of side-reactions and potential opportunities to produce product mixtures that can be transformed to energy dense fuels with a low PEI thermo-/electro-chemical process. These recommendations are summarized in **Fig. 3B** where the sequential combination of thermochemical biomass treatment with downstream ECH, ECDO and ECHy can lead to products with higher energy densities with lower energy expenditure.

Advancements in electrochemical reduction reactions will require deepened understanding of mechanistic pathways. Clarifying the reaction mechanism can direct catalyst and system design to achieve those goals. In case of ECH reactions, there are key differences between electrochemical pathways and their thermocatalytic counterparts. Unlike thermocatalytic hydrogenation processes that rely on H–H cleavage in H_2, electrochemical hydrogenation (ECH) can utilize H_2O directly to produce adsorbed hydrogen (H*) or drive direct proton-coupled electron transfer (PCET) from the solution. [58-60] ECH reactions have been demonstrated for transformation of biomass platform chemicals to fuels[26] and can benefit from better PEI than thermocatalytic alternatives. We recommend a focus on three additional mechanistic questions with particular relevance to ECH of biomass species: 1) what catalysts and reaction conditions achieve selective ECH while minimizing other competing reduction reactions (e.g. ECDO and ECHy)?; 2) how do interactions between the different molecules in biomass mixtures affect their conversion through ECH?; and 3) what are the mechanisms of catalyst deactivation in conversion of biomass products? ECH and ECHy are known to be competitive in nature, requiring careful reaction environment control selectively produce ECH or ECHy products. The diverse pool of molecules and functional groups present in ECH gives rise to intricate interactions that complicate conversion prediction. While competitive adsorption between reactants is common[61-62], conditions sometimes favor faster ECH rates for mixed molecules, hinting at enhanced conversion possibilities[63-64]. [26] Identifying conditions where mixtures may enhance conversion is a potential opportunity for ECH. An implication of the difficulty of converting biomass mixtures is that it is unclear whether the best

process will use a single type of catalyst that converts multiple molecules effectively or a diverse set of catalysts that can convert different types of molecules. Identifying which route is preferred will require a greater understanding of ECH in these mixed streams.

In addition to direct ECH, ECHy or ECDO for fuel production, electrocatalysis can assist in processing steps that are up-/downstream of the reduction process. CO_2 can be a common by-product in biomass transformation, which may be directly converted to energy dense hydrocarbons by using CO_2 electroreduction systems well-developed in the last decade. [13, 65] Biogas, another chemical stream available in biomass processing units containing mainly CO_2 and methane[66], can be utilized for electrochemical reduction to synthetic natural gas and other chemicals for further upgrading. Lastly, SO_x and NO_x impurities produced during biomass gasification can be removed by selective reduction/oxidation using electrocatalytic systems. [67]

Observation #3: Pretreatment strategies to exploit lignocellulosic biomass have, until now, relied heavily on pyrolysis and gasification

Lignocellulose, regardless of source (unlike starch), can be diverted for chemical and fuel production without affecting nutrition supplies and act as a carbon-neutral feedstock for replacing fossil-derived chemicals. [68] However, due to its complex chemical structure, strong hydrogen bonds and resistance to solvents, lignocellulosic feedstocks require harsh pretreatments such as enzymatic catalysis, pyrolysis, gasification, or hydrolysis prior to their upgrade to useful intermediates and building block chemicals, hindering their broad utilization as feedstocks. [69] Lignin depolymerization can occur through reductive and/or oxidative cleavage of C–O and C–C bonds across monomeric groups, preserving aromatic functional groups[70]. In nature, this is done via oxidative and hydrogenative enzymes[71] designed to drive enzymatic lignin depolymerization. In industry, the processing of bio-polymers is mostly done through thermochemical methods such as pyrolysis and gasification, where thermal energy is used to cleave bonds non-selectively, or oxidize them via addition of an oxidizing agent e.g. O_2[72]. Cellulose depolymerization is markedly less energy intensive through hydrolysis, however upstream separation of lignin from cellulose in

lignocellulosic feeds adds to the energy cost of the processes. There is a need for strategies that can process lignocellulosic biomass efficiently, ideally without the need for upstream lignin separation, and utilize the lignin for chemical production.

Enzymes, mostly from bacterial and fungal species, have been used for catalytic lignin depolymerization due to their mild reaction conditions and high product selectivity. However, enzymatic degradation generates large amounts of CO_2, releasing the bio-immobilized carbon and reducing overall carbon utilization. On the other hand, high temperature conditions required for pyrolysis lead to poor selectivity, producing a wide range of products that raise separation costs. Specifically, catalytic pyrolysis induces radical formation, and in turn eliminates many desired functional groups. Gasification[73] eliminates all functional groups, making for a circuitous production path via syngas, which inevitably will suffer from high energy costs and low overall energy efficiency. This low energy efficiency also reduces the net energy gain from downstream fuel synthesis processes. High temperatures are necessary in both pre-treatment and the process itself: devolatilization and gasification of the produced char at 700 - 1300°C. Hydrolysis processes[45] are energy intensive and destroy valuable functional groups contained in the feedstock. Moreover, most thermal hydrolysis processes require strong acids and harsh reaction conditions, making the process and acid recovery economically unfeasible.

Recommendation #3: Electrochemistry could contribute by increasing product selectivity in electrochemical depolymerization of raw biomass feedstocks, with a particular focus on conserving valuable chemical functional groups

Electrochemistry[74] offers a route to pre-treat lignocellulosic feedstocks under mild conditions (**Fig. 3C**). Particularly when lignin-derived chemicals are used, electrochemical depolymerization can proceed at the anode to deliver various bio-acids that preserves valuable carboxylic groups, or the cathode to conduct selective reductive C–C cleavage in lignin linkages[74]. One way to understand the mechanism of electrochemical depolymerization in lignocellulosic feedstocks is to study the degradation of lignin fragment dimers, as the selective cleavage of

linkages is critical to understanding how to preserve valuable benzene rings and functional groups.[75] Aromatic monomers, include phenol, guaiacol, and syringol, can be obtained via ECH of lignin dimers, with various reports indicating mixed product distributions using single-metal catalyst materials. Moreover, the tunable oxidative/reductive capacity of electrochemistry through voltage control can potentially be used to selectively treat cellulose and lignin in mixed lignocellulosic feedstocks, alleviating the need for costly upstream separation of the two.

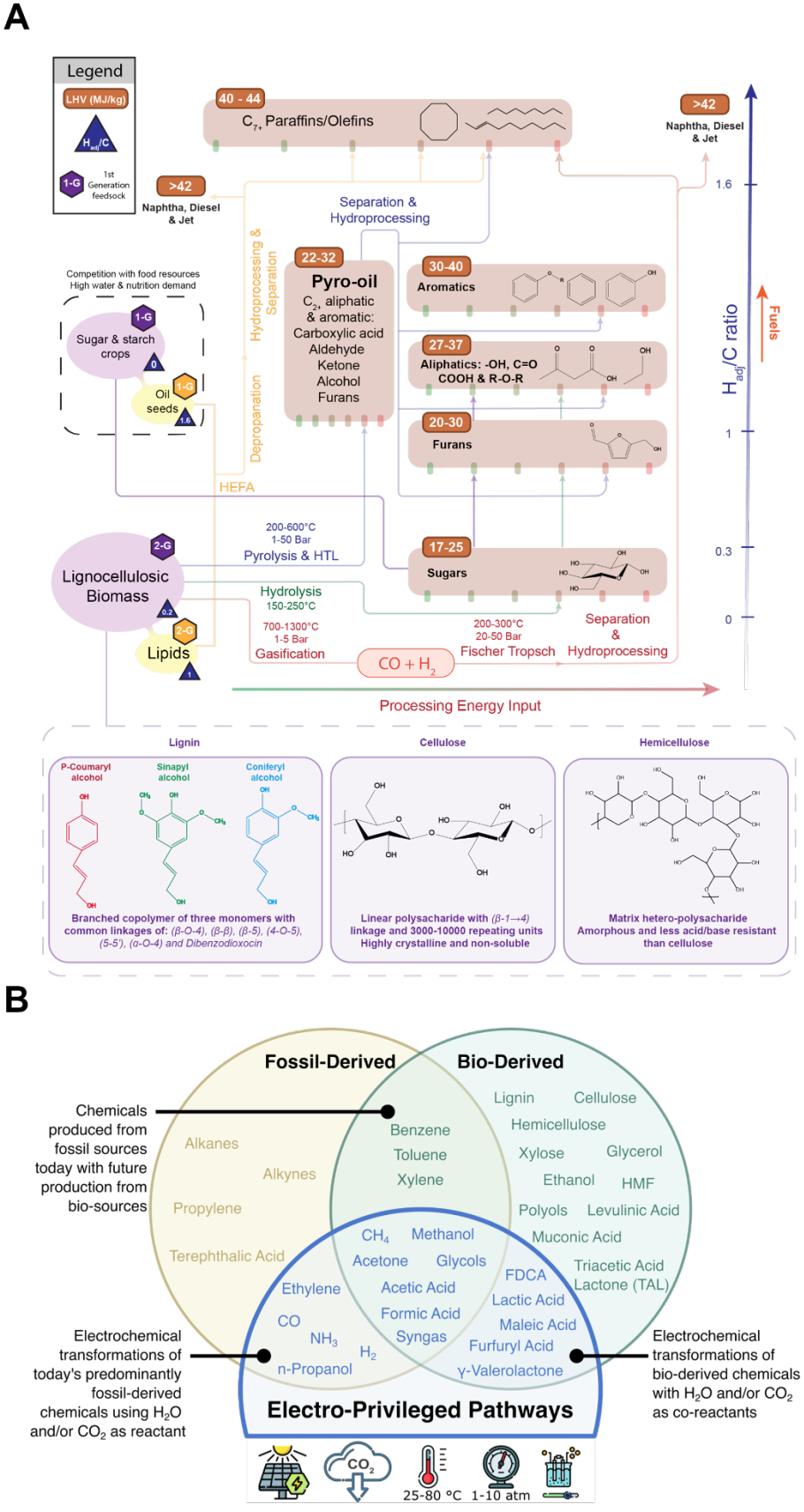
Challenges[76-78] remain for the evolving field of electrocatalytic lignin depolymerization. Reactants can be subjected to overoxidation in electrochemical system and lead to undesired CO_2. Biopolymers may not easily dissolve; limited interaction between electrode surface and polymers restricts reactivity; reactants can be subjected to overoxidation in electrochemical system and lead to undesired CO_2. Thus, optimizing pH and identifying an appropriate co-solvent that can maximize the solubility of the biopolymers without affecting the rate of oxidation and product selectivity is needed. Designing electrochemical reactors that overcome the issues with the restricted interaction between the polymer structure and the electrode and overoxidation are essential. For example, a recently reported electrochemical membrane reactor[77] expels chopped-off depolymerized fragments from the anolyte. This can help the core portion of the biopolymer come into contact with the electrode surface more frequently. The depolymerized fragments are removed from the anolyte, so they cannot undergo overoxidation before the depolymerization of the core part is completed. When such or further improved reactor designs (i.e. reactors that can allow cascade reactions) are coupled with new electrocatalysts that can achieve selective depolymerization, based on the strategies developed for other electrocatalytic reactions like alloying and catalyst surface modification, interesting new opportunities will emerge for the selective depolymerization of raw biomass feedstocks to useful chemicals.

Another strategy that can be used to address the restricted interaction between the polymer structure and the electrode is to use redox-mediators, [76, 79] which allows the depolymerization of biopolymers without them directly contacting the electrode. Product selectivities achieved by the use of redox-mediators can be different from those obtained by heterogeneous catalytic electrodes,

increasing the product diversity. For the practical use of redox-mediators, the synthesis of robust, inexpensive, and easy-to-recover mediators may be needed depending on the reaction conditions and the desired product type with customized design of reactors for the oxidation and recovery steps.

Outlook

The ever-decreasing carbon intensity of electricity provides new avenues to pair electrochemistry with biomass-derived feedstocks. However, electrochemical biomass valorization has largely been limited, until now, to fundamental studies. In **Fig. 4**, we summarize milestones along which the union of electrochemistry and biomass valorization can contribute to net-zero decarbonization goals. Phase I aims to highlight a near-term accomplishment of each priority pathway, Phase II maps to a corresponding deliverable that signals the translation of research into industrial application, and Phase III describes the way in which each priority contributes to our net-zero in 2050 outcome. Comprehensive research, including aspects from electrochemistry, materials science, and systems engineering, will be needed to address the challenges above.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C2+ aliphatic & aromatic:
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Aldehyde
Ketone
Alcohol
Furans
30-40
Aromatics
27-37
Aliphatics: -OH, C=O COOH & R-O-R
20-30
Furans
17-25
Sugars
Competition with food resources
High water & nutrition demand
1-G
Sugar & starch crops
0
1-G
Oil seeds
1.6
HEFA
2-G
Lignocellulosic Biomass
0.2
2-G
Lipids
1
200-600°C
1-50 Bar
Pyrolysis & HTL
Hydrolysis
150-250°C
700-1300°C
1-5 Bar
Gasification
CO + H2
200-300°C
20-50 Bar
Fischer Tropsch
Separation & Hydroprocessing
Processing Energy Input
Hadj/C ratio
1.6
1
0.3
0
Fuels
Lignin
P-Coumaryl alcohol
Sinapyl alcohol
Coniferyl alcohol
Branched copolymer of three monomers with common linkages of: (β-O-4), (β-β), (β-5), (4-O-5), (5-5'), (α-O-4) and Dibenzodioxocin
Cellulose
Linear polysaccharide with (β-1→4) linkage and 3000-10000 repeating units
Highly crystalline and non-soluble
Hemicellulose
Matrix hetero-polysaccharide
Amorphous and less acid/base resistant than cellulose
B
Fossil-Derived
Bio-Derived
Chemicals produced from fossil sources today with future production from bio-sources
Alkanes
Alkynes
Propylene
Terephthalic Acid
Benzene
Toluene
Xylene
Lignin
Cellulose
Hemicellulose
Xylose
Glycerol
Ethanol
HMF
Polyols
Levulinic Acid
Muconic Acid
Triacetic Acid Lactone (TAL)
CH4
Methanol
Acetone
Glycols
Ethylene
Acetic Acid
Formic Acid
Syngas
FDCA
Lactic Acid
Maleic Acid
Furfuryl Acid
γ-Valerolactone
CO
NH3
H2
n-Propanol
Electrochemical transformations of today's predominantly fossil-derived chemicals using H2O and/or CO2 as reactant
Electrochemical transformations of bio-derived chemicals with H2O and/or CO2 as co-reactants
Electro-Privileged Pathways
CO2
25-80 °C
1-10 atm

Fig. 1. Process analysis for biomass valorization and electro-privileged transformation. (A) The processing energy required in biomass chemical transformations varies significantly as a function of biomass feedstock and corresponding processes to achieve high energy density and H:C ratio in desired products. Multi-step reactions and harsh reaction conditions are needed and typically result in high overall energy input. The PEI values in this figure are semi-quantitative and are based off of processing temperature, pressure, and separation energy. **(B)** Interfacing electro-privileged pathways with present-day fossil-derived and future bio-derived carbon sources.

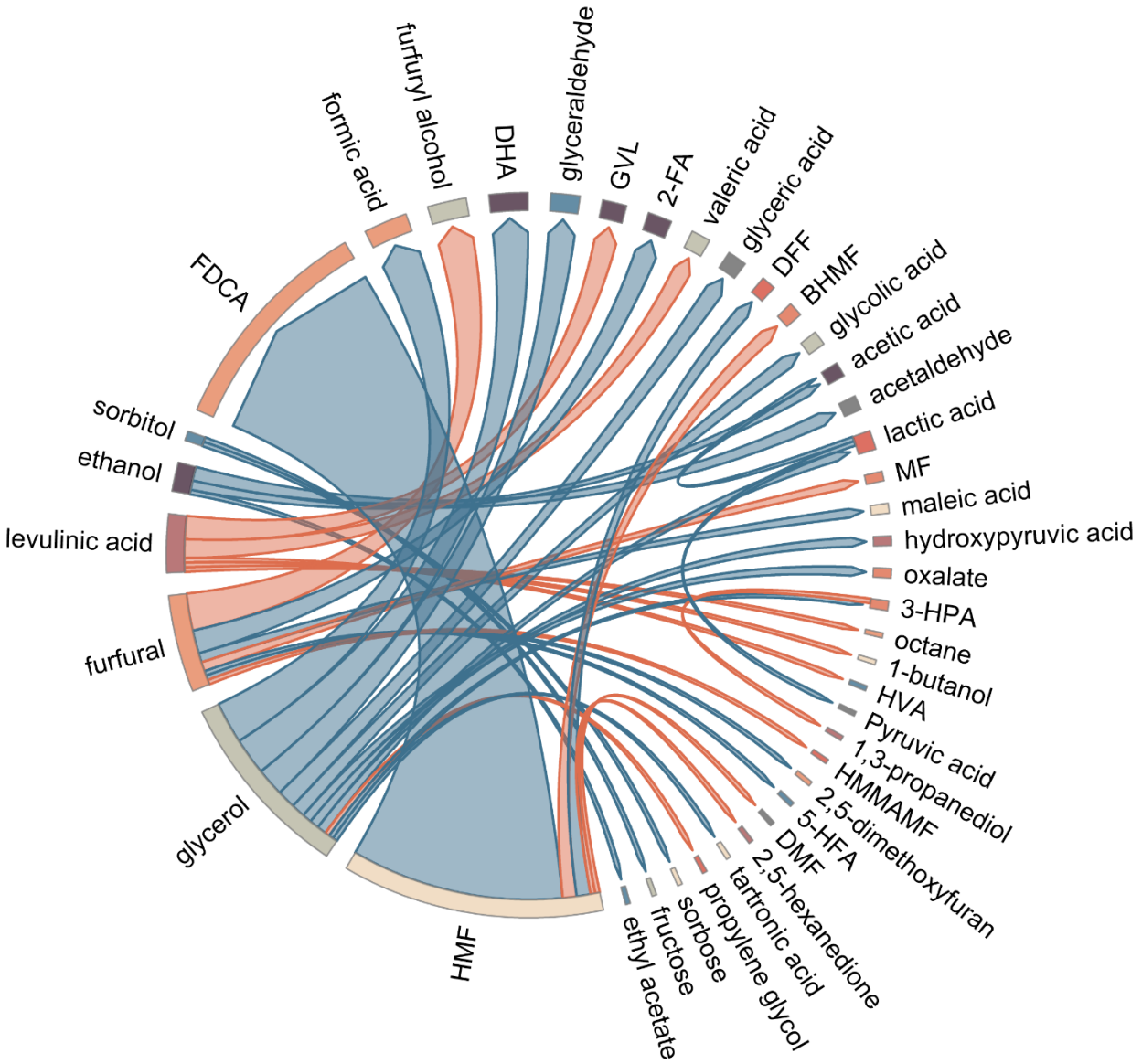

Fig. 2. Reactant molecules from biomass and the products formed using electrochemical biomass valorization in publications from the last decade. Reduction reactions are indicated in red and oxidation reactions are indicated by blue. 2,5-furandicarboxylic acid (FDCA), dihydroxyacetone (DHA), γ-valerolactone (GVL), 2-furoic acid (2-FA), furandicarboxaldehyde (DFF), 2,5-Bis(hydroxymethyl)furan (BHMF), 2-methylfuran (MF), 3-hydroxypropionic acid (3-HPA), 4-hydroxyvaleric acid (HVA), 2,5-dimethylfuran (DMF), 2-hydroxymethyl-5-(methylaminomethyl)furan (HMMAMF) and 5-hydroxyfuroic acid (5-HFA). Size of the label corresponds to the number of reports in total of 138 publications.

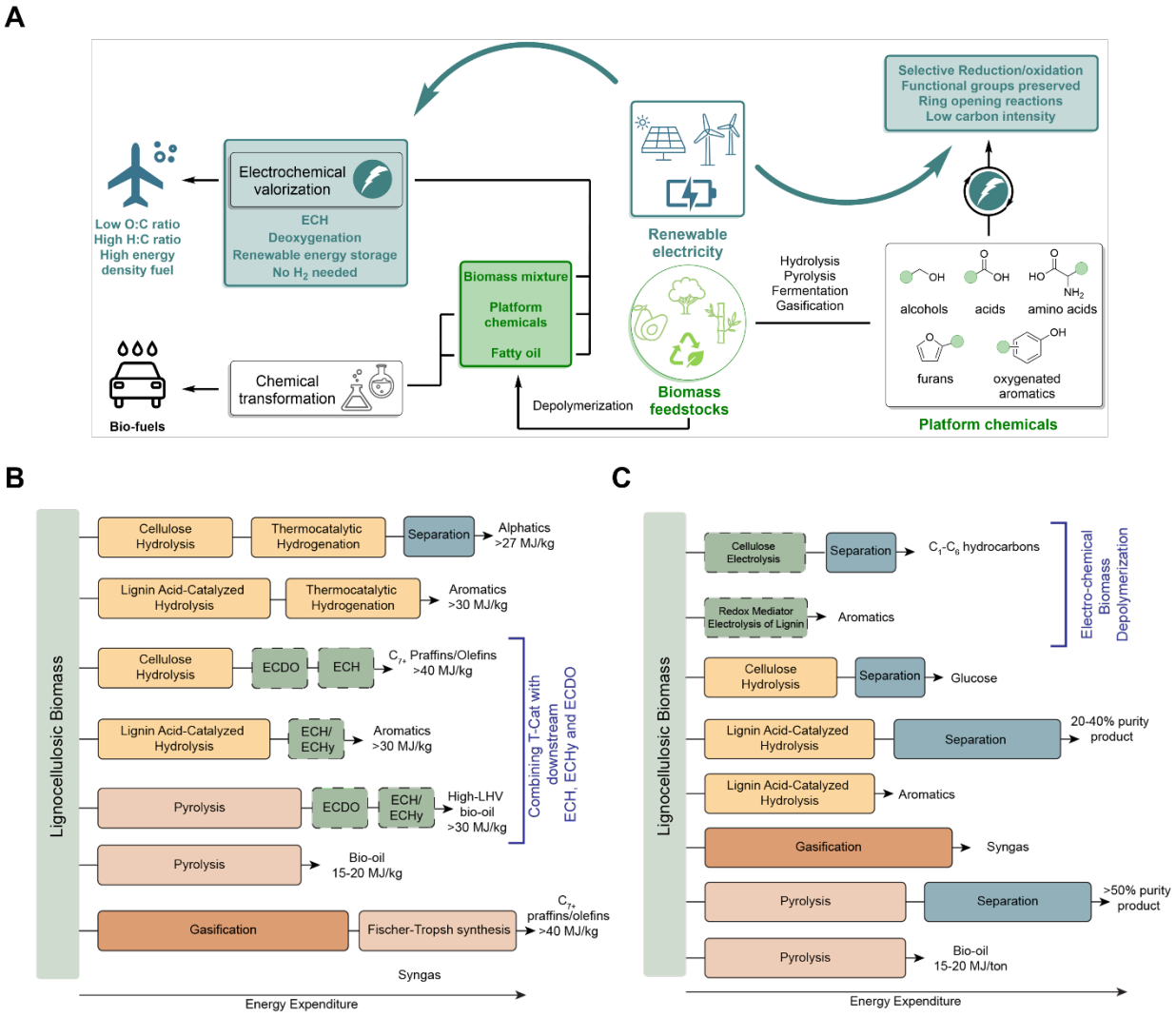

Fig. 3. Electrochemical biomass valorization pathways. (A) Electro-privileged valorization starts from electrochemical feedstock depolymerization to fuels that storage renewable energy and to valorized chemicals via biomass platform chemicals. **(B)** Energy expenditure of conventional pathways and electrochemical alternatives in biomass valorization for fuel production. **(C)** Energy expenditure of conventional pathways and electrochemical alternatives in cellulose and lignin depolymerization.

Reactant	Product	FE (%)	Total Current Density (mA/cm^2)	Today's Market Size of Product ($)	Reactant global production volume (tonnes/year)	Product global production volume (tonnes/year)
Bio-ethanol	Acetic acid	100	598	20 billion	86 million	20 million
Lactic Acid	Propylene Glycol	0.002	4	4.3 billion	1.4 million	1.9 million
HMF	FDCA	100	200	441 million	n/a	82 million *
Furfural	Furfuryl Alcohol	89	50	473 million	0.3 million	0.2 million
Glycerol	L-Lactic acid	72	570	2.9 billion	2.8 million	1.4 million
Glycerol	Formic Acid	99	10	1.8 billion	2.8 million	0.7 million

Table 1. Bio-derived precursors and potential products via electrocatalytic upgrading. Ethanol is a promising bio-derived precursor for chemical manufacture due to its high global production volume, whereas increased lactic acid production would enable access to the large propylene glycol market using electrochemistry. HMF, furfurals and glycerol are the most researched biomass-derived chemicals in electrochemistry due to the large market size and their application potentials.

*Production volume of terephthalic acid, which can be replaced by FDCA.

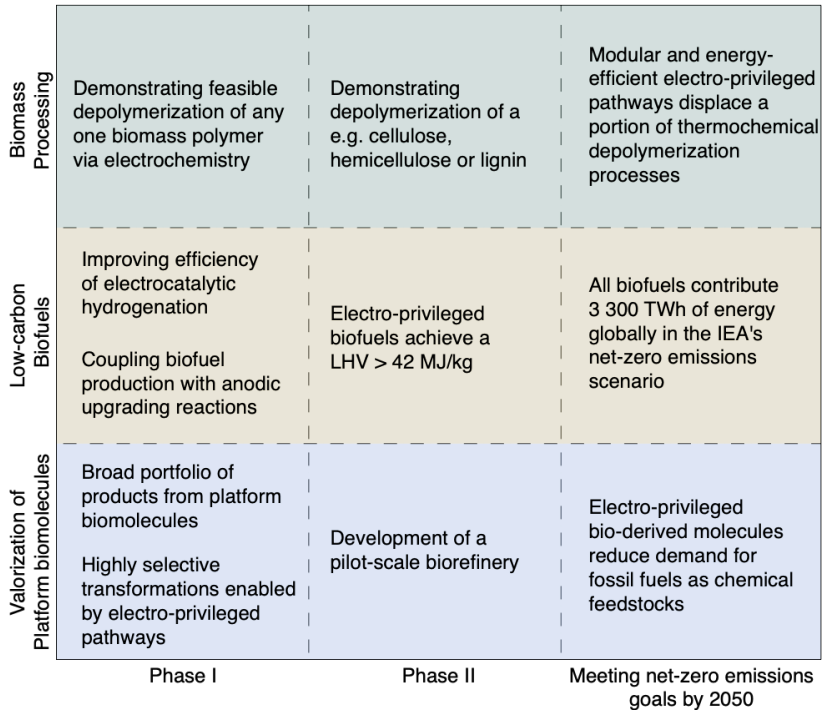

Fig. 4. Roadmap to contribute to net-zero. A roadmap charting the development of electro-privileged biomass transformations across three pillars: biomass processing, low-carbon biofuels, and the valorization of platform bio-molecules.

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