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Electrochemical transformations of fast pyrolysis bio-oils and related bio-oil compounds

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Electrochemical transformations of fast pyrolysis bio-oils and related bio-oil compounds

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1. Introduction

1.1. Overview

Green, sustainable and recyclable bio-based carbon is one of the central pillars of the future renewable energy mix. Industrial efforts to optimize the use of biomass-derived carbon as biofuels are rapidly maturing, leading to increasing amounts of bio-based liquid products becoming available. Research and development have led to advancements in biomass liquefaction technologies such as fast pyrolysis and hydrothermal liquefaction. However, traditional upgrading of bio-oils and bio-crudes into drop-in fuels by hydrotreatment can be expensive as it requires large-scale infrastructure and an external hydrogen source. In addition, current bio-oil hydrotreating technologies are challenged by low yields and catalyst deactivation. More recently, electrochemical processes have been considered to upgrade biomass-derived molecules to produce valuable biofuels and biochemicals. Although the research is still emerging, electrochemical processing technologies appear promising, especially if green electricity can be used.

Electrochemical processing can offer a range of advantages for valorising biomass-derived chemicals compared to traditional chemical and thermochemical processing [1-3]. These advantages include:

- Use of aqueous feedstocks and using water as an environmentally friendly solvent and source of protons.
- The conditions for electrochemical processing are typically mild and can include low voltages, low temperatures, and low pressures. Mild conditions facilitate smaller scale, distributed and possibly intermittent processing.
- Different product selectivities are possible through electrochemistry compared to traditional hydrogen-based upgrading processes.
- Scale-up is relatively easy. Typically, electrochemical cells are stacked and scaling-up is by economy of numbers. The modular design of electrochemistry cells enables integration with existing processes (e.g. pyrolysis plant, pulp mill, biorefinery) and reduction of the plant size to small distributed units at community or farm scale (Figure 1).
- Oxidising or reducing equivalents can be generated without the use of external reagents, which is aligned with green chemistry principles. For example, no external source of hydrogen is needed for electrochemical transformations, as protons and electrons are generated *in situ*, and hydrogen evolution is minimized.
- Oxidation and reduction reactions can be combined in electrochemical approaches ('paired electrolysis') to give a high degree of flexibility, selectivity, and potential for economic operation.

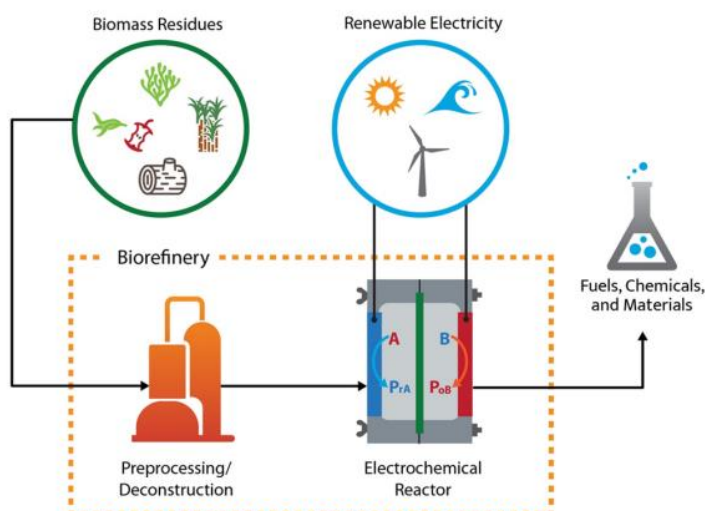


Figure 1: Integrating biorefining, renewable electricity and electrochemical catalysis for production of biofuels and biochemicals. Sourced from [1].

IEA Bioenergy Task 34 focuses on direct thermochemical liquefaction (DTL) technologies for conversion of biomass feedstocks into bioliquids (bio-oils and bio-crudes). This includes fast pyrolysis, catalytic fast pyrolysis, hydrothermal liquefaction and solvolysis technologies [4]. Fast pyrolysis is the most mature of these technologies with several commercial plants in operation or under construction. Most of the research to date on electrochemical processing of DTL bioliquids relates to fast pyrolysis bio-oils or model compounds related to compounds typically found in fast pyrolysis oil. In the broader context, several reviews recently published on the electrochemical valorization of biomass-derived feedstocks provide a more comprehensive overview of field [1-3, 5, 6]. This report has been limited in scope to the electrochemical processing of bio-oils and bio-oil compounds that are most relevant to IEA Bioenergy Task 34.

1.2. Fast Pyrolysis Bio-oils

Fast pyrolysis involves the heating of biomass in an inert environment to temperatures in the range of 450 to 600 °C to generate aerosols that can be condensed into liquid products (bio-oil), char and permanent gases (mainly CO₂, CO and CH₄). The bio-oil comprises 15–30 wt.% water and oxygenated organic compounds (water-soluble or emulsified). This bio-oil is a source of many chemicals including phenolics from the lignin and short-chain oxygenated compounds, furans and sugars derivatives from the hemicellulose and cellulose (Figure 2) [7].

The condensed bio-oil product is typically one phase; however, it can be separated into an aqueous-rich phase containing sugar-based components (such as furans, anhydrosugars, organic acids) and an oil-like phase containing partly cracked lignin-fragments. Both fractions can have a wide-ranging molecular size distribution. A simplified representation of its composition is given in Figure 2. Oxygenated organic compounds in fast pyrolysis bio-oil include [7]:

- carboxylic acids, alcohols and furans
- sugars and short-chain oxygenates
- substituted monomeric phenols, guaiacols, syringols, and other aromatics

- pyrolytic lignin
- hybrid oligomers and humins

The most abundant single chemicals present are hydroxyacetaldehyde (up to 14 wt.%), acetol (up to 9 wt.%), levoglucosan, acetic acid, and formic acid [7]. These acids and the phenolic compounds give the bio-oil a low pH (2.5–3.5).

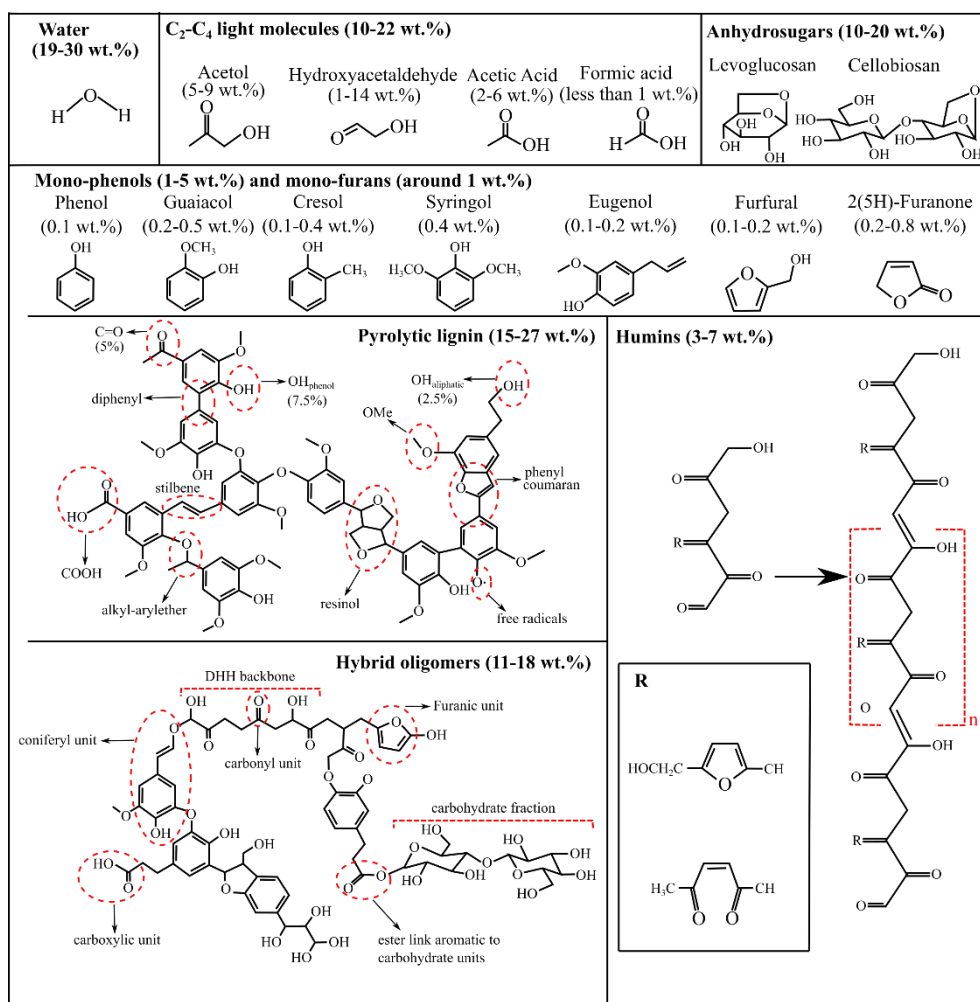


Figure 2. Representative molecules found in fast pyrolysis bio-oils. Sourced from [7].

The complex chemical composition of fast pyrolysis bio-oils makes electrochemical upgrading extremely complex and largely impractical on the whole bio-oil. Studies using model compounds or bio-oil fractions are more common (see Section 3 and 4). Before discussing these studies, some background information on electrochemical upgrading of bio-derived feedstocks is provided in Section 2.

2. Theoretical background

Electrochemical upgrading of the bio-derived feedstocks primarily involves electro-oxidation and electro-reduction reactions, generally in aqueous electrolytes (alkaline or acidic). In a typical electrolytic cell, as illustrated in Figure 3, the electro-oxidation reaction of the biomass-derived intermediates occurs at anodes, and hydrogen evolution reaction (HER) occurs at cathodes [3]. However, viable alternatives can be developed in several ways. For example, HER can be replaced by electro-reduction of biomass-derived intermediates that result in the hydrogenation of polyols,

alcohols, aldehydes, ketones, carboxyls, etc. On the other hand, the electro-reduction reactions can also combine with oxygen evolution reactions (OER) [3, 8]. However, as a result of the sluggish kinetics and low efficiency of OER, electro-oxidation of biomass-derived chemicals are nowadays preferred in the place of OER in such designs owing to its low overpotential. The electro-reduction reactions at the cathode and electro-oxidation reactions at the anode help produce value-added products from both electrodes and store energy in chemical bonds. As HER competes with electro-reduction of biomass-derived chemicals, catalysts with high HER overpotentials are commonly used to repress HER. Catalysts like Fe, Ni, Cu, Ag, and Pb can be used to achieve this [9, 10].

An experimental set-up for the electrochemical upgrading of bioderived intermediates (bio-oil/organic substrates) is shown in Figure 3. The stabilization of bio-oil by hydrogenation and HER takes place on the cathode. On the other hand, the electro-oxidation of water or organic substrates occurs on the anode. Organic substances in bio-oil that can be oxidised include acids (decarboxylation) and pyrolysis lignin (depolymerisation).

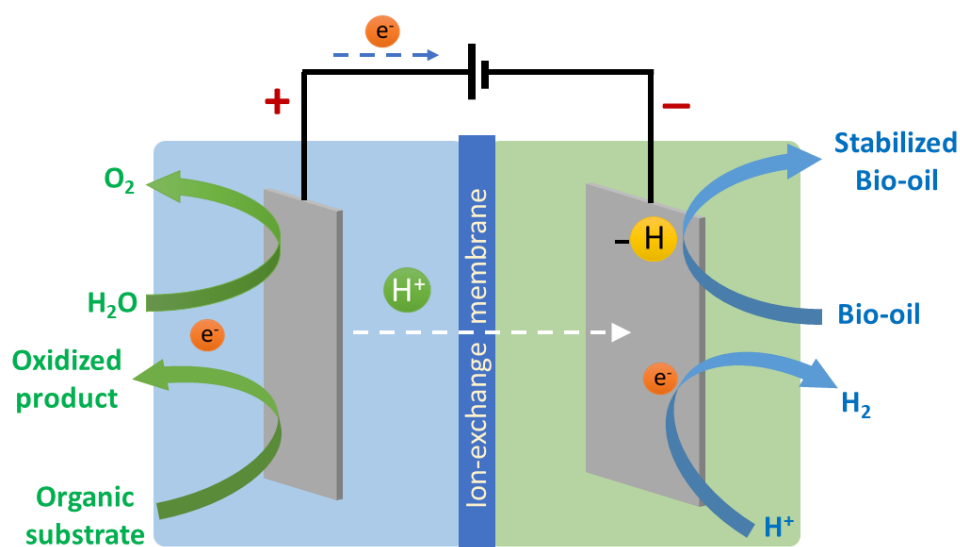


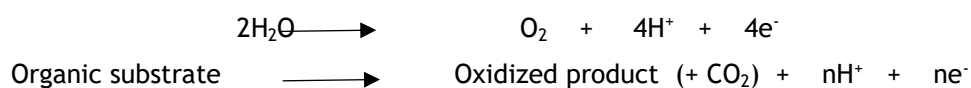
Figure 3. Experimental set-up for electrochemical upgrading of bio-derived intermediates where electrons (e^-) and protons (H^+) are generated at the anode via electro-oxidation and react at the cathode to either perform electro-reduction of bio-oil compounds or generate hydrogen. Sourced from [3].

The reactions occurring on the cathode and anode can be summarised as follows.

Cathode



Anode



The electrochemical upgrading of the bio-derived intermediates can also be carried out in organic electrolytes. This help to achieve good product selectivity due to the broad potential window and their capability to solubilise organic compounds up to a large extent [3, 8].

As numerous electrochemical reactions occur on the electrodes' surfaces, it is crucial to calculate Faradaic efficiency (% F.E.) or the current efficiency (% C.E.) by evaluating the ratio of the electrons used for the anticipated reaction over the side reaction. The % F.E. can be estimated by the equation given below,

$$\% \text{ F.E.} = \left[\frac{\text{Mol} \times F \times n}{C_{\text{total}}} \right] \times 100\%$$

where *Mol* is the moles of expected product formed, *F* is Faraday's constant (96 485 C/mol), *n* is the number of electrons essential for the redox reaction, and *C_{total}* is the total amount of charge passed in the course of the reaction.

The % F.E. becomes 100% when all of the electrons are utilized for the anticipated reaction. Nevertheless, it is very challenging to provide a comprehensive directive to raise % F.E. as it depends on various sensitive experimental parameters, including applied potential, pH, temperature, and concentration of reactants. In the case of bio-derived intermediates, the quantification of the particular product is very complex. Therefore, the experimental conditions are often initially optimized to find the utmost % F.E. by model compounds. Subsequently, the optimized experimental condition is employed to upgrade the bio-derived intermediates.

From the points mentioned above, it is evident that efficient cathode reactions are critical in the valorization of bio-oils. Several factors greatly influence these cathode reactions and are given below.

2.1. Electrodes

Properties of electrodes greatly influence the conversion and product selectivity during the electrocatalytic hydrogenation of bio-oil. Two types of electrodes are mainly utilised to carry out electrocatalytic hydrogenation reactions. They are (a) catalysts (like noble metal, base metal, alloy, and oxide) coated on conductive support (like carbon materials) and (b) metal sheets [11, 12]. The electrode's large surface area, high conductivity and stability are conducive to making the electrocatalytic hydrogenation process more efficient [12]. Regarding electro-oxidation, carbonaceous materials are likely to degrade, depending on the oxidation potential. Metallic sheets (e.g. Ti, stainless steel) and pure metal electrodes (e.g. Pt, Pd) are used instead [13-15]. Metallic thin films or nanoparticles can be deposited on the metallic sheets or electrodes to improve functionality and surface area, but they might suffer deactivation (if the oxide form is not conductive) [13, 15].

2.2. Electrolytes

Characteristics of the electrolytes significantly affect the electrocatalytic hydrogenation of bio-oils. For example, the pH of the electrolyte impacts the product composition and concentration during electrocatalytic hydrogenation [16, 17]. Some studies illustrate that the adsorption of anions from the electrolyte onto the surface of the electrode influences bio-oil conversion [12]. Apart from these, additives like alcohols in electrolytes adversely affect the electrocatalytic hydrogenation reaction as a consequence of the reduced concentration of H^+ in pure water [18].

2.3. Potential

The applied potential plays a crucial role in controlling the formation of reduction products during the electrocatalytic hydrogenation of bio-oil. For example, electrocatalytic hydrogenation of benzaldehyde in the presence of base metal catalysts generally results in benzyl alcohol and hydrobenzoin [19]. The product selectivity toward hydrobenzoin can be increased at half-cell potentials more cathodic than $-900\text{ mV vs Ag/AgCl}$ [19]. Similarly, the applied potential influences the formation of oxidation products. For example, electrochemical oxidation of carboxylic acids can be tuned with applied potential to change the product distribution from paraffins to olefins and alcohols [13, 15].

2.4. Temperature

The temperature has an effect on efficiency, product selectivity and product yield [20]. A study shows that the conversion rate of guaiacol and % F.E. of KA oil (a mixture of cyclohexanol and cyclohexanone) formation increase when temperature increases from 20 to $60\text{ }^{\circ}\text{C}$ [11]. But, a further rise of temperature to $80\text{ }^{\circ}\text{C}$ decreases both conversion rate and % F.E. Similarly, another study related to electrocatalytic hydrogenation of phenol to cyclohexane showed that enhanced temperature resulted in increased product yield within a specific temperature range (40 - $60\text{ }^{\circ}\text{C}$). A further increase in temperature to $80\text{ }^{\circ}\text{C}$ decreases the product yield, owing to the accelerated hydrogen desorption rates and volatilization of cyclohexane (boiling point is $80.7\text{ }^{\circ}\text{C}$) [20].

3. Electrochemical catalysis of bio-oil model compounds

Fast pyrolysis bio-oil is a complex mixture with hundreds of compounds (Figure 2). Its composition varies significantly based on feedstock, pyrolysis and condensation conditions, and catalysts that are used during the preparation of the bio-oil. These bio-oil compounds range in molecular weight from short-chain, simple compounds such as hydroxyacetaldehyde and levoglucosan, to complex oligomeric compounds such as pyrolytic lignin (Figure 2). A wide range of chemical functionalities are present in the bio-oil, including acids, alcohols, furans, anhydrosugars, aldehydes, ketones and phenolics [3, 7]. Insights into the capability of electrochemical catalysis for bio-oil upgrading can be gained by investigating electrocatalysis of biochemicals typically found in bio-oils. To date, most of the studies have focused on electrochemical reactions of model compounds [1-3, 6]. These studies provide information on the potential of the approach.

In general, electrochemical catalysis can reduce alkenes, aldehydes, ketones, benzene rings, and certain ethers and esters, and oxidize aldehydes, alcohols and carboxylic acids. In this section of the report, we give an overview of the capability of electrochemical catalysis to upgrade common functional groups present in bio-oils, using model compounds to illustrate the chemical reactions involved. Table 1 presents some main functional groups and their electrocatalysis products.

Table 1. Main functional groups in bio-oil derived biochemicals and their electrocatalysis. ECH represents electrocatalytic hydrogenation.

Family	Functional Group	Hydrogenation	Oxidation
Alkene			Resistant
Aldehyde			
Ketone			Resistant
Carboxylic acid		Resistant	
Alcohol		Resistant	
Benzene ring			Resistant
Ether		Aryl ethers can be cleaved via ECH	
Ester		Ester groups can be eliminated via ECH, actual products are varied case by case	

The actual reactions of each biochemical can be significantly varied when different treatment conditions are applied (e.g., catalyst, electrolyte, applied current and voltage, temperature). A brief discussion on electrocatalysis of various biochemicals is given as follows.

3.1. Acids

Acetic and formic acids are the most common acids present in bio-oils. Acids are resistant to electrocatalytic hydrogenation under ambient conditions. In contrast, electrocatalytic oxidation can convert acids via Kolbe or non-Kolbe reactions. In the Kolbe reaction the acid undergoes electro-decarboxylation to produce alkyl radicals. Alkyl radicals can combine to form alkanes (Figure 4), for example Kolbe electrocatalytic oxidation of valeric acid produces octane. The alkyl radical can lose an electron to form a carbocation as an intermediate in another pathway. The carbocation can undergo proton elimination to generate alkenes or nucleophilic attack (non-Kolbe reaction) (Figure 4). In this way, valeric acid can be oxidized to butene, 1-butanol and 2-butanol [13]. 1-Butanol can be further oxidized to butanoic acid. In addition, the butanols can react with

acids (valeric acid and butanoic acid) via esterification to generate corresponding esters. The detailed reaction pathways for different acids can be varied due to their chemical structure and electrocatalytic conditions. For formic acid, the simplest organic acid, oxidation will produce CO_2 and H_2O . As such, formic acid has been widely studied as a feedstock for fuel cells [21, 22]. It is worth noting that hydrocarbon products from oxidation of acetic acid, following the mechanisms in Figure 4, are non-condensable gases and would be released from the liquid phase.

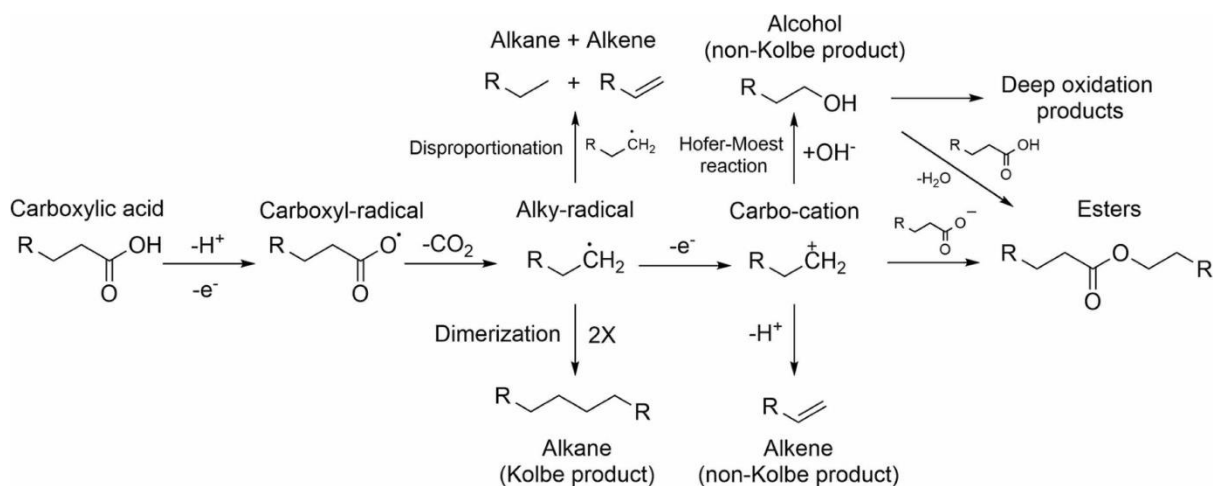


Figure 4: Electrochemical oxidation of carboxylic acids via Kolbe or non-Kolbe reactions. Sourced from [15].

3.2. Aldehydes

Aldehydes can be either reduced by electrocatalytic hydrogenation to alcohols or oxidized by electrocatalytic oxidation to carboxylic acids. For instance, reducing the aldehyde functional group of glucose mainly produces sorbitol [23], while oxidising it mainly produces gluconic acid [24]. Similarly, benzaldehyde can produce either benzyl alcohol [18, 25] or benzoic acid [26]. Electrocatalytic reduction of furfural mainly produces furfuryl alcohol [27], while oxidising it produces 2-furoic acid [28] (Figure 6), with both reactions possible in high yields (~ 90%) and F.E. (> 80-90%). Similarly, electrochemical reduction of hydroxymethylfurfural (HMF) can produce 2,5-dihydroxymethylfuran (DHMF) at near 100% yield and F.E on silver electrodes. Alternatively, complete oxidation of HMF produces 2,5-furandicarboxylic acid (FDCA), an important building block for biopolymers [29]. Benzaldehyde and furfural can also undergo electrochemical dimerization into hydrobenzoin and hydrofuroin, respectively [19]. The oxidable-reducible nature of aldehydes makes them involved in many reactions, increasing the complexity of bio-oil upgrading, while providing possibilities for achieving various biochemicals. Hydroxyacetaldehyde (glycolaldehyde) is present in lignocellulosic fast pyrolysis bio-oils in 1-14 wt.%, however electrochemical reduction of hydroxyacetaldehyde to ethylene glycol is yet to be reported.

3.3. Ketones

Ketones can be hydrogenated to corresponding alcohols but are resistant to oxidation. Acetone is the most studied model compound for electrochemical catalysis of ketones. Its electrocatalytic hydrogenation can mainly produce isopropanol [30]. However, the actual reaction mechanisms of acetone depend on the treatment conditions (applied potential and cathode catalysts), and the

other reduction products include pinacol and propane [31]. More recently, the crystalline structure of catalysts has been highlighted as another key factor, which determines the reaction pathways of electrocatalytic reduction of acetone [32]. Hydroxyacetone (also known as acetol or 1-hydroxypropan-2-one) is produced in 5-9 wt.% in lignocellulosic fast pyrolysis bio-oils and is also a dehydration product of glycerol. Hydroxyacetone can be electrochemically converted into 1,2-propanediol (propylene glycol) or acetone and isopropanol (Figure 5). Hydroxyacetone is commercially converted into 1,2-propanediol using thermochemical conditions at temperatures higher than 200 °C and hydrogen pressures up to 2 MPa. This illustrates the advantage of using an electrochemical process with milder conditions.

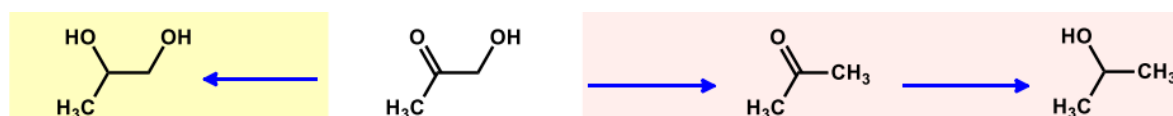


Figure 5. Electrochemical reduction of hydroxyacetone into 1,2-propanediol or acetone and isopropanol. Sourced from Lucas et al. [1].

3.4. Furans

Furfural and hydroxymethylfurfural (HMF) are common dehydration products from sugars and as such have been widely studied for electrochemical reduction and oxidation. Furfural and HMF can also be produced through biomass fast pyrolysis. Furfural has been electrochemically reduced to furfuryl alcohol and then to 2-methylfuran, a potential drop in fuel additive [33]. 2-Methylfuran can be further reduced to 2-methyltetrahydrofuran (Figure 6). Alternatively, reduction of the furan ring of furfuryl alcohol produces tetrahydrofurfuryl alcohol (Figure 6). Reductive ring-opening on Pb electrodes of furfural can produce 1,5-pentanediol, or dimerization can occur to produce hydroxyfuroin (Figure 6) [1]. Furfural can be electrochemically oxidized to furoic acid, which can be further oxidised to maleic acid (Figure 6). Conversion yields are affected by the electrode type, pH of the electrolyte and voltage potentials. The conditions for the electrochemical transformation of furfural and HMF have been recently reviewed by Lucas et al. [1].

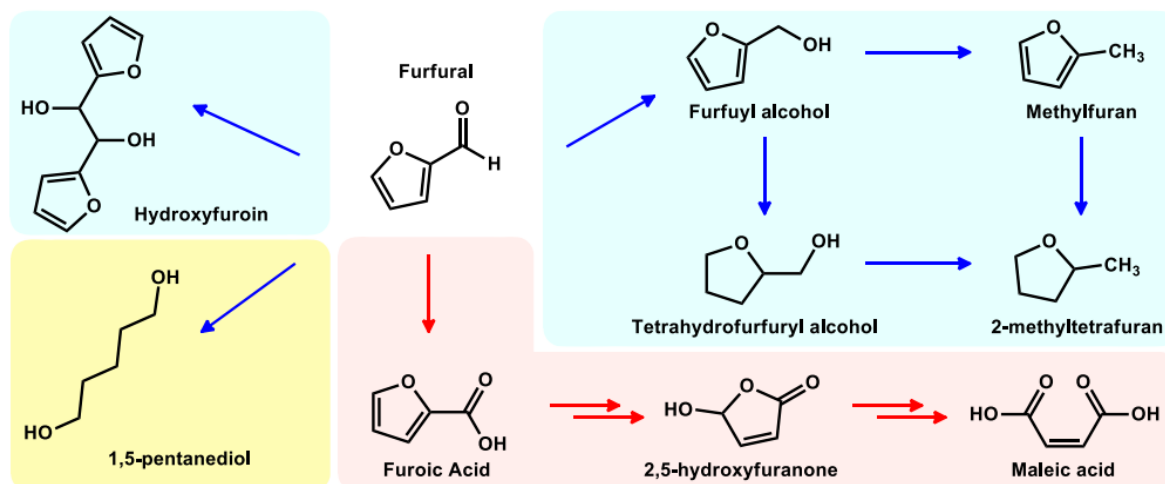


Figure 6: Electrochemical reduction and oxidation products of furfural. Sourced from Lucas et al. [1].

3.5. Anhydrosugars

Anhydrosugars make up 10-20 wt.% of fast pyrolysis bio-oils with the main compounds being levoglucosan and cellobiosan [34]. There appears to be no research to date on the electrochemical upgrading of levoglucosan or cellobiosan. Electrochemical hydrogenation of sugar monomers such as glucose and fructose has been achieved under various conditions with non-precious metal electrodes with the major product being sorbitol. Given a large variety of carbohydrates are derived from biomass and that their reactions under electrochemical treatments are not well understood, there is a significant knowledge gap yet to be filled. The electrochemical hydrogenation studies on biomass derived sugar oligomers (rich in hydrothermal biocrude) and anhydrosugars (rich in pyrolysis bio-oil) are encouraged. Electrochemical oxidation of xylose, mannose, galactose and glucose produces the corresponding xylonic, mannonic, galactonic and gluconic acids in good to high yields and selectivity. These carboxylic acids can be oxidised further to diacids and short-chain acids [35].

3.6. Alcohols

Alcohols are generally resistant to electrocatalytic reduction; however, a few examples of model compound reactions are relevant to bio-oils. These include electrocatalytic reduction of furfuryl alcohol to methylfuran, (section 3.4) and hydroxyacetone to acetone (Section 3.3). Alcohols can be more easily oxidized to aldehydes (which can be further oxidised in acids) or ketones. Methanol is a common primary alcohol in fast pyrolysis bio-oils. For the oxidation of methanol, increasing the methanol concentration will drive the reaction from total oxidation (producing CO_2) to partial oxidation (producing formaldehyde and formic acid, Figure 5) [36]. Methanol and ethanol have also been used as feedstocks in fuel cells [37, 38]. Electrochemical oxidation of glycerol to produce glyceraldehyde and various acids (e.g., glyceric acid, lactic acid) has been studied in detail, as glycerol is the main byproduct of biodiesel production [1].

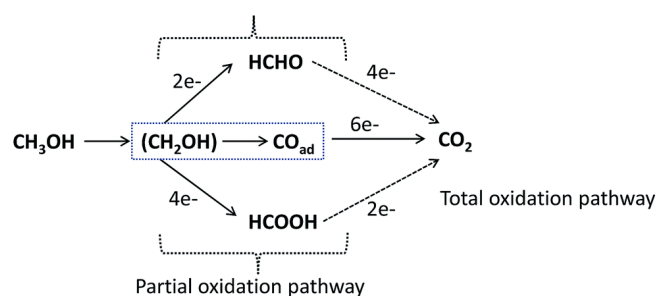


Figure 7: Partial and complete electrochemical oxidation of methanol. Sourced from [36].

3.7. Benzene rings

In fast pyrolysis bio-oils, most benzene ring-containing biochemicals are phenols or polyphenols derived from the pyrolysis of lignin [39]. The benzene ring is resistant to electrocatalytic oxidation but can be hydrogenated to the cyclohexane ring, corresponding to the addition of 3 pairs of hydrogen atoms. For example, phenol has been electrochemically reduced to cyclohexanol at a good yield (>80%) and F.E. (>90%) [40]. The reduction of more substituted phenols, such as 2-methoxy-4-propylphenol, has been achieved but at significantly lower yields (38-61%) and F.E.

(29%) [39]. The high reduction potential of benzene rings combined with the fact that lignin-derived bio-oils have relatively high heating values suggests that bio-derived phenolic compounds are promising feedstocks for electrochemical hydrogenation to liquid biofuels.

3.8. Ethers and esters

Ether bonds can be cleaved by both electrocatalytic hydrogenation and oxidation. Proof-of-concept studies have mainly involved electrochemical upgrading of lignin model compounds such as guaiacols and diaryl ethers (Figure 8). For example, guaiacol has been electrochemically reduced to a mixture of cyclohexanol, *cis/trans*-2-methoxycyclohexanol and phenol, with cyclohexanol being the major product [16]. 4-Methyl guaiacol has been electrochemically reduced to 4-methylcyclohexanol in high yield (94%) and moderate F.E. (72%) [40]. These and similar studies reviewed by Lucas et al. [1] illustrate successful ether cleavage and reduction of the benzene ring for simple lignin model compounds. The products formed are dependent on the electrochemical parameters used. The β -aryl ether linkage of dimeric lignin model compounds has been successfully cleaved by electrochemical reduction [41, 42]. However, electrochemical oxidative depolymerisation has proved more successful to date for electrochemical depolymerisation of lignin [1, 5].

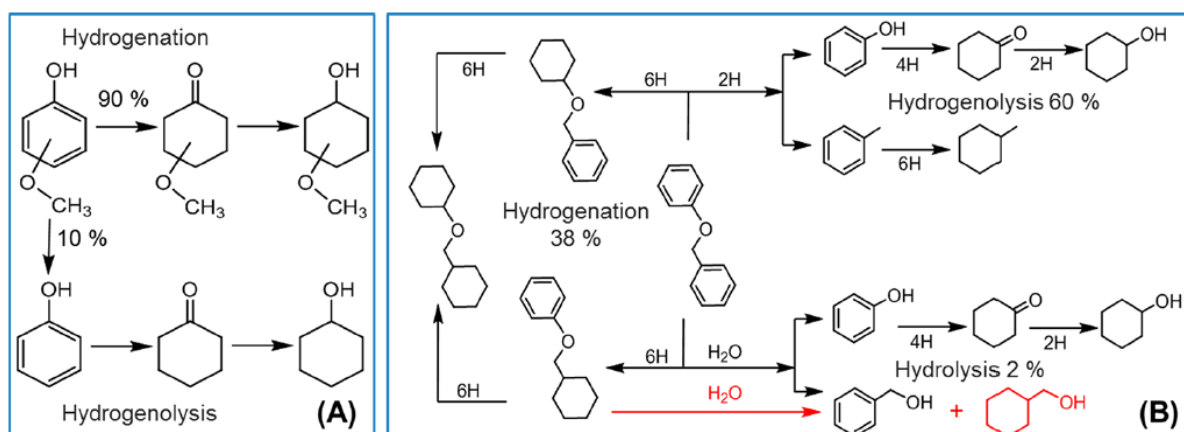


Figure 8: Reaction network for the electrocatalytic conversion of A) guaiacol and B) benzyl phenyl ether. Sourced from [43].

Esters are resistant to electrochemical oxidation, whereas electrochemical hydrogenation of esters can be achieved at room temperature. The products are varied due to the structure of feedstocks and the reaction of intermediate radicals. Some research advances have been provided in a recent review [1].

3.9. Pyrolytic lignin

Fast pyrolysis oils contain 15-27 wt.% pyrolytic lignin [7]. Studies investigating electrochemical transformation of pyrolytic lignin isolated from fast pyrolysis oil are scarcely found [44]. Some structural similarities exist despite differences between pyrolytic and other forms of lignin (alkali lignin, Kraft lignin, lignin model compounds). Therefore, literature results based on other forms of lignin can give information on potential reactions that could be achieved with pyrolytic lignin.

The earliest study on the electrocatalytic transformation of lignin can be traced back to 1946, when Bailey and Brooks treated different lignin feedstocks by electrocatalytic oxidation and hydrogenation. However, only the oxidation products of butanol lignin were identified [45]. Electrochemical oxidation has been proved to be more effective for lignin depolymerisation than electrochemical hydrogenation, with depolymerisation achieved through cleavage of ether bonds [46]. However, electrochemical oxidation is less favourable for producing liquid biofuels as the oxygen content is increased in the products, resulting in a lower energy content. Pioneering studies by Dabo et al. [47] and Wu et al. [48] have shown that electrochemical hydrogenation can cleave ether bonds in lignin model compounds. The decomposition mechanisms have been further investigated by Zhou et al. [49]. A recent review by Du et al. (2020) provides some additional examples of cleavage of ether bonds in lignin model compounds by electrochemical reduction [46]. However, depolymerisation of native lignin by electrochemical hydrogenation remains challenging, likely due to other more reducible functional groups being favoured over ether bond cleavage [50]. Recent advances in electrocatalytic hydrogenation and oxidation of lignin and its derivatives have been reported by Garedew et al. [5, 6], and the reader is referred to these reviews for detailed information. In terms of biochemicals, electrochemical oxidation of lignin and lignin derived compounds can be used to produce high value chemicals such as vanillin and aromatic acids.

Electrochemical catalysis is highly versatile and appears promising for producing selective biochemical products provided (i) starting compounds have a singular reducible or oxidable functional group, and (ii) customized treatment conditions are applied. Electrochemical catalysis works best when applied to relatively pure biochemical feedstocks. For example, levulinic acid, a dehydration product of cellulose, can be electrochemically reduced to produce valeric acid and gamma-valerolactone (GVL); both are valuable biochemicals [51]. In the case of DTL bioliquids, the bio-oil and bio-crudes are very complex starting materials with hundreds of chemicals with multiple functional groups. This mismatch makes upgrading bio-oils via electrochemical catalysis extremely challenging. A review of studies on electrochemical upgrading of bio-oils is provided in section 4.

4. Electrochemical Upgrading of Bio-oils

Based on the different types of reactions previously described, electrochemical transformation has potential for upgrading bio-oils for bioenergy applications. Electrochemical reactions leading to deoxygenation of organic compounds such as carboxylic acids, aldehydes, and phenols are likely to reduce the bio-oils' acidity while increasing its stability and energy content. This could improve the long-term storage of pyrolysis liquids, thereby enabling subsequent upgrading treatments to further improve biofuel quality. Electrochemical reactions leading to an increased degree of saturation, such as aromatic compounds, can also improve the energy content. The influence of electrochemical treatment on the degree of polymerisation and thus the viscosity of bio-oil is also a point of interest for research and development.

Only a few recent articles dealing with the whole bio-oil have reported improving several of the properties mentioned above. Key findings from these studies are discussed below, with important information listed in Table 2. In terms of chemical functionality, reduction of esters and carbonyl

groups into alcohols has been described, with carbonyl groups concentration decreased by half [19, 52]. The study by He et al. [52] also reported a decrease in phenolic content of the bio-oil. In another study, Deng et al. [44] reported a linear decrease in the concentration of phenols due to the hydrogenation of the aromatic rings. This study also noted that both depolymerisation and recombination reactions were likely to happen [44]. In a study using an undivided cell, recombination reactions led to coke formation on the anode. This resulted in enhanced oxidation reactions and reduced efficiency of the aromatic conversion [53].

Several studies have focused only on the water-soluble fraction of bio-oil. Li et al. [54] managed almost full conversion of some compounds containing aldehydes, ketones and ester groups. Ageing tests indicated that this electrochemical upgrading improved bio-oil stability. With a more modest degree of conversion, Zhang et al. [55] reported the saturation of some double bonds (aliphatic and aromatic) and the conversion of a wider range of compounds, including carbonyls, esters, phenols, sugars and furans. In both studies, the electrochemical treatment resulted in an increased concentration of alcohols. Compared to carbonyl groups, reduction of the carboxylic acid groups in bio-oil molecules appears more challenging. Although some decreases in pH and TAN of bio-oils or water-soluble fractions have been observed, this was largely attributed to the migration of some acid compounds, in the case of two-chamber configuration [52, 54, 56].

Table 2. Studies on electrochemical upgrading for bio-oils and bio-oil fractions.

Reference	Year	Bio-oil	Temperature/Ti me /Current density	Catalyst	Reactor type
Li et al. [54]	2014	water-soluble fraction of FP bio-oil	25 °C; 6.5 h; 120 mA/cm ²	Ru	A divided two-chamber cell
Zhang et al. [55]	2018	water-soluble fraction of FP bio-oil	25 °C; 3 h; 100 mA/cm ²	Ni-Ru	A divided two-chamber cell with Fe ²⁺ oxidation at the anode
Lister et al. [56]	2018	FP bio-oil	35 °C; (1-15.5) h; (1-5) mA/cm ²	Metal-free carbon	A divided two-chamber cell
Deng et al. [44]	2019	water-soluble fraction and CH ₃ OH/CH ₂ Cl ₂ extract	25 °C; (0-12) h; 10 V	Pt	An undivided cell
Mehmet Pala et al. [57]	2019	water-soluble fraction of FP bio-oil	25 °C; (0-48) h; 44 mA/cm ²	Ti, Pt, Ru, Stainless-steel, Cu-Zn	A divided two-chamber cell
He et al. [52]	2020	Zn powder pretreated FP bio-oil	25 °C; 9 h; 67 mA/cm ²	Ru	A divided two-chamber cell
Andrews et al. [19]	2020	Bio-oil diluted in isopropanol + water	25 °C; 3 min; (5-70) mA/cm ²	Pd/C and Cu/C	A divided two-chamber cell
Yuan et al. [58]	2021	FP bio-oil	0 °C; (0-24) h; 20 mA/cm ²	Graphite-felt	A divided two-chamber cell

Wang et al. [53]	2021	FP bio-oil	25 °C; 2 h; 200 mA/cm ²	Pt	An undivided cell
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Based on the complexity of bio-oil and the various types of chemical groups present, it appears challenging to find conditions suitable for the optimum conversion of most of the organic compounds in the bio-oil. Significant improvement in terms of heating value, viscosity or other fuel properties have not been widely reported. Options to obtain a simplified feedstock for electrochemical treatment include further fractionating the bio-oil or producing a more homogeneous bio-oil, by catalytic fast pyrolysis, for instance.

5. Process intensification and energy storage

5.1. Paired electrochemical transformations

Maximising the economic viability of electrochemical processing and achieving process intensification require that both the electrochemical reduction and oxidation half-reactions produce valuable products [59]. Combining the redox processes is a challenging engineering endeavour when using biomass-derived feedstocks. In one scenario, the cathode could make a valuable biochemical product by reduction, while the anode splits water to generate oxygen. Alternatively, hydrogen could be generated at the cathode, with the anode producing a valuable oxidised biochemical product. Oxygen is not a useful byproduct and, while hydrogen may be desirable, it would likely need to be used on-site [14].

It would be ideal for both electrode reactions to generate valuable biochemical products. This is very challenging and has not been done using DTL bioliquids to the best of our knowledge. One of the best examples of a paired electrochemical transformation of a biomass-derived feedstock is the simultaneous oxidation and reduction of hydroxymethylfurfural (HMF). Chadderdon et al. [60] have reported simultaneously producing 2,5-furandicarboxylic acid (FDCA) and 2,5-bishydroxymethylfuran (DHMF) from HMF. This was accomplished using an Ag cathode and a carbon felt anode. Overall, faradaic efficiency of 90% and 97% along with yields of 85% and 98% were achieved for DHMF and FDCA, respectively. This is an example of divergent paired electrolysis where the same starting material is used to make two different products in a divided cell. James et al. [61] used a tandem paired electrolysis process in an undivided cell to convert xylose into δ -valerolactone via *in-situ*, sequential, electrochemical oxidation followed by reduction. More details on paired electrochemical transformation are available in a recent review by Lucas et al. [1].

5.2. Role in energy storage

Electrochemical bio-oil upgrading can play a part in renewable energy storage when integrated with renewable electricity. Upgrading bio-oils to liquid transportation biofuels is a possible way to store and distribute energy during periods of surplus electricity production. Electrochemical bio-oil upgrading could complement hydrogen production by water splitting and act as a buffering mechanism during periods of fluctuating energy production. Highly deoxygenated biofuels could act as hydrogen carrier molecules offering long-term energy storage capacity.

Electrochemical catalysis is a promising technology from the point of view of energy storage and the production of valuable biochemicals and biofuels, particularly if sustainable electricity can be

integrated with sustainable biomass resources. The above sections of the report provide a brief overview of the field. Interested readers are referred to recent reviews for more detailed information [1, 10, 62, 63].

6. Opportunities and Challenges

Electrochemical upgrading of bio-oils is worth consideration compared with conventional bio-oil hydrotreating techniques (such as hydrogenation, hydrocracking) for a variety of reasons:

- The treatment is operated under near-ambient conditions with minimal operation risk
- The process requires no external hydrogen but can potentially produce hydrogen
- As hydrogen is produced on demand, there is no need for hydrogen transformation and storage infrastructure
- Sustainable production can be achieved if combined with sustainable biomass and power supplies. It also has the potential to produce valuable biochemicals at comparatively high concentrations.

However, the integration of pyrolysis and electrocatalysis is currently at an early stage of development. As discussed above, fundamentally, electrochemical catalysis favours single molecules transformations, while DTL bio-oils are complex mixtures of hundreds of compounds. This is considered a major challenge to the capability of electrochemical catalysis for upgrading of bio-oils. Current available studies all agree that electrochemical catalysis can upgrade bio-oils to some degree; however, the actual quality of the fuel and whether it can be used as a drop-in or blend stock fuel remains largely unknown [2, 3]. The integration of fast pyrolysis and electrochemical catalysis technologies requires further investigation and development through each step in the process before the true potential of this approach can be fully assessed.

Step 1 Pyrolysis of biomass for producing bio-oils for electrochemical catalysis

Conventional fast pyrolysis can be optimised for various purposes such as (i) improving the fuel quality and (ii) increasing the bio-oil yields and minimising the formation of char. Customised approaches are suggested when the target is preparing bio-oils for the subsequent electrochemical upgrading. We propose the following considerations:

1. The selection of feedstocks needs to be reconsidered. Compared to feeding various biomass feedstocks to pyrolysis, biomass with simpler compositions are more favoured for producing bio-oils with less complexity. For instance, lignin-rich feedstocks produce fast pyrolysis bio-oils with a high concentration of phenolics [64]. Pyrolysis of cellulose-rich feedstocks produces anhydrosugars and their derived acids and furans [65].
2. Orthodoxies in biomass pyrolysis should be challenged. Together with achieving high yields, high stabilities and/or better energy contents, the suitability of the pyrolysis oil for electrochemical upgrading should also be considered. Investigating pyrolysis conditions (e.g., atmosphere, temperature, feeding rate, catalyst) could be a way to improve its suitability. For instance, the temperature can be optimised to achieve fewer heavy

fractions, which are water-insoluble due to high molecular weight. Such heavy fractions are generally undesirable for electrocatalytic hydrogenation.

3. The quality of a bio-oil needs to be reconsidered with attention paid to its subsequent treatment by electrochemical upgrading. For instance, (i) the compatibility of bio-oil properties (compositions, dissolution behaviours in electrolytes) with electrochemical catalysis needs to be assessed, (ii) the electrochemical upgrading potentials need to be assessed based on quantitative analysis of electrochemical active sites.

Step 2 Electrochemical catalysis of bio-oils

Compared with the highly specific and targeted electrochemical catalysis of individual biochemicals, the treatment of bio-oils is very challenging. In general, electrochemical catalysts and reactors are not feedstock flexible. They are mostly finely tuned to operate on a specific, well-defined feedstock over relatively narrow operating ranges. Parameters such as temperature, applied power (current and voltage), initial concentrations can be optimised via methodological experiments. In contrast, raw DTL bio-oils are inherently heterogeneous and often incompletely characterised. Electrolytes, catalysts, and intermolecular reaction fundamentals need to be more thoroughly investigated for customised bio-oil upgrading.

1. Electrolytes. Water-based electrolytes (e.g., acid/water, alkali/water and salt/water) are unlikely to be suitable for bio-oil treatment because (i) bio-oil contains a large amount of water-insoluble compounds, (ii) water will need to be removed after treatment, increasing process cost, and (iii) the used acid, alkali and/or salts need to be removed from the upgraded bio-oils as they would be detrimental to the finished fuel product. In short, ideal electrolytes should have good electroconductivity and good compatibility with bio-oils and be easily removable from the upgraded fuel. Recently emerged biomass-derived organic solvents and deep eutectic solvents (DESs) may be potential candidates.
2. Catalysts/electrodes. Catalysts used for bio-oil upgrading need to be more versatile than those used for specific chemicals, with good performance on reducing/oxidising a number of different chemical functional groups. The development of hybrid catalysts (e.g., alloy, carbon-metal hybrids) needs further exploration.
3. Intermolecular reaction fundamentals. More research is needed on the reaction mechanisms of key biochemicals present in bio-oils. Such studies will assist the development of customised catalysts, electrodes and treatment conditions.

Step 3 Post-treatment product recovery and fuel quality assessment

Studies on post-treatment product recovery and fuel assessments represent a significant gap in the current literature for electrochemical upgrading of DTL bio-oils. Some considerations are:

1. Methods for the extraction of upgraded biofuel and electrolytes need to be developed focusing on separating the upgraded bio-oil from electrolytes and recycling of electrolytes. This is closely related to the development of electrolytes mentioned above.
2. The fuel quality (especially energy content) of electrocatalysis upgraded bio-oil remains largely unknown, despite this being the primary target of bio-oil upgrading.

Step 4 Integration of Fast pyrolysis and Electrochemical catalysis

Simply bringing the fast pyrolysis and electrochemical catalysis together is unlikely to achieve ideal performance without careful integration. Because electrocatalysis is only capable of treating certain bio-oil compounds and functional groups, some additional treatments may be needed to link fast pyrolysis with electrochemical catalysis better. These include:

1. Bio-oil fractionation. This aims to separate raw bio-oils into several fractions rich in different compounds, including fractional condensation and solvent-based fractionation. Such bio-oil fractionation could simplify the feedstock mixture and make the subsequent electrochemical processing more efficient.
2. Bio-oil stabilisation. This can be achieved via methods such as esterification, which can convert the acid functional groups to esters. This can be desirable because (i) electrochemical hydrogenation is not effective on carboxylic acid groups, and (ii) acids can react with intermediate products, leading to greater uncertainty of the effect of the electrochemical catalysis.

In addition, techno-economic assessments need to be carried out with comparison to (i) conventional hydrotreating techniques for bio-oil upgrading and (ii) other widely recognised electric power storage methods such as E2H (electricity to hydrogen) and super capacitors. The potential of storing electricity in bio-oils as an alternative energy storage method also needs to be similarly assessed.

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