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Biofuels through Electrochemical transformation of intermediate BIO-liquids

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Report on electrocatalysis for both value chains

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Publicity level	*Confidential, only for members of the consortium (including the Commission Services)*		
Short description	*This report shows the major results of the research on the oxidative decarboxylation (Kolbe electrolysis) of organic acid, oxidative degradation of lignin and the hydrogenation of pyrolysis done in the framework of EBIO. It contains background information, a brief summary of technical data and the main results of various electrochemical experiments.*		
Document approval	*Roman Tschentscher*	*22.12.2023*	

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Description of the deliverable content and purpose

This report describes the key results of the experimental work of WP2 - *Fundamental electrochemistry for pyrolysis and lignin value chains*, summarizing the result of D2.2, D2.4, D2.6 and D2.8 in a public matter. The focus is on the research carried out in the PhotoCatalytic Synthesis Group PCS – TNW at the University of Twente (Netherlands) and in the Waldvogel lab at Mainz University (Germany). In the framework of the EBIO project the research was supported by Process Technology, SINTEF Industry (Norway), CONDIAS GmbH (Germany) and BTG – Biomass Technology group (Netherlands).

The results of the research on optimal electrode material and operation window are divided into three subject areas (Task 2.1 – 2.3):

- Investigation on oxidative decarboxylation (Kolbe electrolysis) of organic acids
- Investigation on oxidative depolymerization of lignin (including material such as membranes and IERs and conditions for separation of oxidated compounds)
- Investigation on electrochemical hydrogenation

Within this report, we addressed the electrochemical acids conversion of black liquor, pyrolysis oil hydrogenation and oxidation. Electrochemical conversion of carboxylic acid was achieved by platinum and BDD electrodes, the conversion of acids is essential for upgraded pyrolysis oil due to its corrosive nature and detrimental to the downstream processes. The report includes the model compound (acetic acid) oxidation and influential process parameters such as pH, concentration, electrode materials and stability, supporting electrolyte effects. These important aspects of the electrochemical decarboxylation of pyrolysis oil are relevant to public interest.

The electrochemical oxidation studies were carried out on Black liquor supplied by Stora Enso. The research focused on the oxidative degradation of lignin polymeres which are contained in small amounts in black liquor to smaller oligomers and monoaromatics. The main research topics include the electrochemical setup with an autoclave especially designed to that purpose, the investigation and screening of electrode materials and electrochemical.

The electrochemical hydrogenation studies were carried out on pyrolysis oil and its fractions supplied by BTG. The hydrogenation research focused mainly on the hydrogenation of pyrolysis oil, which is a promising route to sustainable biofuel production. The main research topics include analysis of the pyrolysis oil, electrochemical setup, electrode materials and general procedures for electrochemical hydrogenation. In order to find an optimal operating window for hydrogenation, different parameters have been tested. The common goal is to develop a reaction route that will find industrial application in the future and aid Europe’s future to more sustainable transport fuels.

Content

1 Introduction

Lignin is a renewable biopolymer with a polyphenolic structure that represents a major proportion of plant-derived biomass. It accumulates as a carbon-rich side stream of the paper and pulping industries. The combustion of lignin produces increasing amounts of CO_2, which is why the selective degradation to useful monomers that can be used for other applications should be pushed towards.[1] Black liquor and pyrolysis oils derived from lignin and electrochemically depolymerized lignin have large potential as feedstocks for a possible biofuel. Within the EBIO project, research in WP2 focuses on oxidative and thermal degradation of lignin (Task 2.1) as well as on the electrochemical reduction (Task 2.3). The topic is extended by the research on the oxidative decarboxylation (Kolbe electrolysis) by University of Twente, Enschede (Task 2.2). The whole approach offers a promising route towards the sustainable production of biofuels that could find industrial application in the future.

2 Background

In the last few decades, the interest in biomass utilization for energy applications has significantly increased. Biomass can be utilized by direct combustion, syngas production or for generation of bio-oils by fast pyrolysis. Bio-oils, essentially being liquids consisting of a variety of organic compounds including carboxylic acids, alcohols, carbohydrate fractions and defragmented lignin are of interest for their potential use as fuel or feedstock in the chemical industry.[2] Acids, i.e. acetic acid decrease the pH of the bio-oil which is a significant concern for further application.[3] Technologies to improve bio-oils include catalytic hydrogenation which requires high temperatures (>200 °C) and pressures (up to 200 bar)[3] thereby negatively impacting the economic viability of bio-based fuels. With an expected surplus in electricity due to increasing renewable energy capacities, i.e. wind and solar installations, electrochemical upgrading of bio-oil operating at moderate reaction conditions, i.e. low (atmospheric) pressures and ambient temperatures, might be an appealing alternative. Kolbe/non-Kolbe electrolysis, converting acids into alkanes/alcohols and CO_2, has been previously proposed in the literature[4,5] to lower the acid content in bio-oil and is thus appealing to improving the quality of the bio-oil.

Conversion of acids from pyrolysis oil improves the stability of the bio-oil against polymerization.[6] Here, electrochemical conversion of acids is envisioned to occur which will result in the production of hydrocarbons or alcohols and H_2 which can be used for subsequent hydrogenation of pyrolysis oil.[7]

Relevant KPIs: During renewable energy conversion/storage in the form of chemicals using electrochemistry, energy losses need to be minimized. An Important parameter to estimate the electrons used for the conversion of chemical compounds in pyrolysis is the Faradaic efficiency; within the EBIO project, the threshold value of 50% Faradaic efficiency towards acid decarboxylation was aimed to be achieved at current densities of 100-500 mA/cm^2. Under specific conditions, Kolbe electrolysis, i.e. a C-C coupling reactions of formed radicals is favorable on Platinum-based electrodes. The decarboxylation of the acids on platinum electrodes occurs via adsorption of carboxylate ions forming a layer blocking the water reactions on the surface of the electrode. Compared to Pt electrodes the reaction mechanism on BDD surfaces is distinctively different and the formation of non-Kolbe/indirect oxidation products is favored.

Besides cellulose and hemicellulose, lignin as mentioned before represents a major part of plant biomass.[8] Due to the large waste stream originating from pulping processes, Kraft lignin and black liquor are of technical interest. The polyphenolic structure qualifies lignin as a potential renewable feedstock to produce bio-based products, for example aromatic fine chemicals such as vanillin, acetovanillone and guaiacol. Furthermore, lignin which is part of black liquor could also be a possible sustainable feedstock for the production of biofuels. However, due to the complexity and degradation stability of the molecular structure, the depolymerization tends to be challenging but on the other hand worthwhile. To overcome this challenges electrochemistry could be a novel approach. Electrochemical anodic oxidation of lignin is a well-known method for lignin degradation.[8–12] Nickel, cobalt, and titanium alloys, but also materials like nanoparticles based on iridium and lead are electrode materials for this reaction typ.[13,14] The major products of most of the publications is vanillin, acetovanillone and guaiacol. Promising materials for industrial lignin degradation are Ni and Co based materials. Ni or Co based materials usually leads to an outstanding selectivity regarding the formation of monoaromatic phenolic compound. Co-based materials usually suffer from corrosion in alkaline solutions which limits a technical application. Nickel based materials therefore are more stable against alkaline corrosion which makes them the most promising ones for lignin degradation as well in industrial applications.

The pyrolysis oil provided by BTG is a dark brown, highly acidic oil with a water content of up to 30%. The pyrolysis oil contains hundreds of different compounds from the degradation of lignin at high temperature. The complexity of the composition is dependent on the feedstock and the pyrolysis process.[15–17] The analysis of this unique pyrolysis oil and the clustering of components in groups is of utmost importance. There are several analytical options known in literature like NMR and GC (GCMS).[18,19]

The hydrogenation of carbonyl compounds is very important, as these compounds together with phenols, which tend to polymerize, have a negative effect on the long-term stability of the pyrolysis oil. Compared to thermochemical processes, an electrochemical approach allows to avoid petrochemically produced H2, to use mild operating temperatures and pressures and to utilize the electrode potential to tune reaction rate and product selectivity.[20] The most common approach for hydrogenation in the context of updated biomass is ECH (electrocatalytic hydrogenation).[21] It does not require a hydrogen atmosphere with high pressure and temperatures like e.g., HDO (hydrodeoxygenation)[22]. ECH uses both noble metals, which have a higher hydrogen evolution reaction (HER) competing with the hydrogenation of the compound but a better catalytic performance, and base metals.[23] The hydrogenation of the aqueous phase derived from lignin using ruthenium on carbon is already published.[24] While EHC can also hydrogenate phenolics[23], the EBIO project aims at a carbon-based reduction (preferable with BDD) of carbonyl compounds like aldehydes and ketones. The phenolics can be neglected as they most likely can be co-refined at a later stage.

BDD (boron-doped diamond) is a feasible, carbon-based electrode material. The reason for this is the enormous stability due to sp^3 hybridization. Due to its physical properties (band gap 5.45 eV at 300 K and specific resistance of 1020 Ω/cm[25]), diamond is an electrical insulator and therefore not suitable as an electrode material. Doping with boron creates a p-type semiconductor with a smaller band gap. Various support materials such as graphite, silicon or tantalum can be coated with a thin BDD layer. This multilayer is 1–15 µm thick. BDD is produced via vapor phase deposition and is mainly used to purify waste water.[26] BDD is characterized by its wide potential range from -1.1 V to 2.5 V in an aqueous, neutral medium. The high overvoltage applies for both aqueous and organic solvents. The overpotential for the hydrogen evolution reaction is reached at -1.1 V and is in a comparable range to lead or mercury electrodes.[27] The BDD electrodes for this study (15 µm on silicon with 0.08% boron) are supplied by CONDIAS GmbH.

There are three more technical requirements: scalable electrochemical conditions for industrial application, two-electrode cell design (divided or undivided)[28] and constant current. If a divided cell design is chosen, the hydrogenation of the carbonyl functionalities at the cathode and the oxidation depolymerization at the anode could take place in one cell. For initial screening, a batch process testing different cathode materials[29] (e.g. BDD, lead and lead based alloys) and (electrochemical) conditions (e.g. current density) is intended.

3 Experiments and results

Kolbe electrolysis

Kolbe electrolysis was evaluated using Platinum-based electrodes known to activate carboxylate via adsorption of carboxylate ions on its surface.[30,31] BDD was used as an alternative electrode material. The selectivity for Kolbe (hydrocarbon formation) or non-Kolbe/Hoefer-Moest (alcohol formation) on BDD and Pt electrodes was evaluated using aqueous fractions of bio-oils and model compounds.

The selectivity of BDD-based electrodes was tuned by surface functionalisation with Pt metal nanoparticles or thin film. The experiments were performed in a three-electrode batch cell coupled with gas chromatography for product analysis (GC-FID will be used to analyse both gaseous and liquid products (with headspace) and HPLC). Optimised parameters are defined based on Faradaic efficiency determination and reaction overpotentials. Batch scale investigations were translated to flow cell conditions (CONDIAS with DIACHEM electrodes on silicon and tantalum substrates). Additionally, the impact of cations was analysed to examine possible interference of cations required for acid separation from the bio-oil. Already small differences of the cations are revealed in the initial investigation, and potassium appears to be beneficial for the conversion of acetate/acid to Kolbe products.

Aqueous phase pyrolysis oil electrooxidation

Cyclic voltammetry using the aqueous phase of pyrolysis oil with Pt and BDD working electrodes revealed that half-cell potentials larger than 2.5 V are required to observe oxidative currents as shown in Figure 1. This is in good agreement with the data obtained with model compounds.[32] However, the current densities are low likely due to a high resistance induced by surface passivation by pyrolysis oil compounds and char.

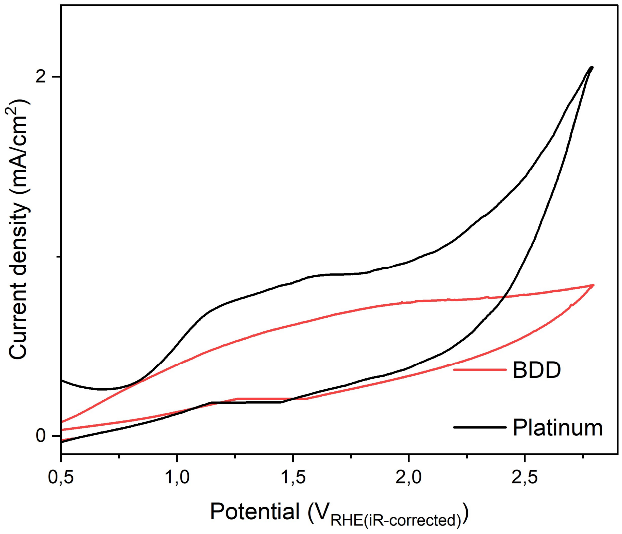


Figure 1 CV of BDD and Pt using the aqueous phase of pyrolysis oil. The pH was adjusted to pH 5.

Pyrolysis oil is a complex mixture of chemical compounds, and its complete analysis with GC-MS is cumbersome. GC-MS analysis of the aqueous phase of pyrolysis oil confirms the presence of carboxylic acid, furfural, phenolic and sugar compounds (see Figure 2 and Table 1). Though, qualitative results about the significant fraction can be obtained, the overlap of compounds due to their similar m/z ratios, renders it difficult to obtain an unambiguous assignment and quantification additional analytics are required.

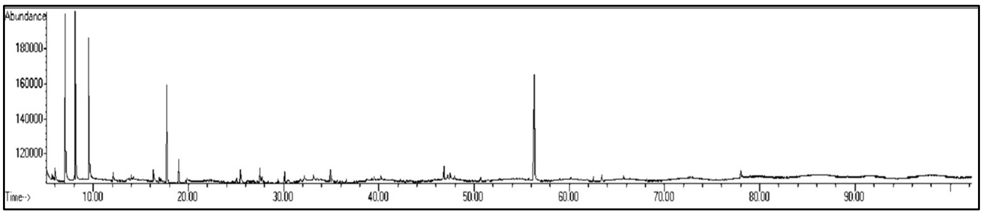


Figure 2 GC-MS spectra of aqueous fraction of pyrolysis oil before electrolysis.

Table 1 Retention time of aqueous fraction pyrolysis oil composition by GC-MS

Retention time	Component
5.4-5.8	1-propanol
5.8-7.5	Hydrazine carboxylic acid
8-8.1	Acetic acid
8.1-8.2	Formic acid methyl ester
9.1-10	1-hydroxy-2-propanone
15.9-16.7	butanediol
16.8-16.9	Cyclopentenone
17	Furfural
17.6-17.8	Diacetone from solvent
27.3-27.6	2-hydroxy 3 methyl cyclopent-1-one
29.8-30.33	Guaiacol
34.5-35.2	4-methyl guaiacol
55.9-56.9	Anhydrous mannopyranose

NMR analysis of aqueous phase pyrolysis oil

The ^{13}C NMR of aqueous pyrolysis oil before and after electrolysis performed at 25 mA/cm^2 for 60 minutes is depicted in Figure 3. Functional groups can be characterized by their chemical shift. As such a chemical shift in the range of 0–55 ppm is characteristic for short, long and branched aliphatic compounds. It can be seen that there is a rise in aliphatic compounds after pyrolysis oil electrolysis independent of the electrode used. Note that the sharp at 40 ppm is related to the solvent, DMSO-d_6. In the range of 55–95 ppm, alcohols, ethers, phenolics, methoxy, and carbohydrates are present. Clearly within this region it can be observed that multiple signals increase in intensity and additional signals appear after electrolysis.

From GC-MS data (Table 1), we found the presence of phenolics and carbohydrate sugars in the aqueous phase of pyrolysis oil and can thus tentatively assign these peaks to alcohols and ethers obtained as products of (non)Kolbe and Hofer Moest's reaction. Aromatic olefins should appear with a chemical shift of 95–166.5 ppm. However, if present in the aqueous phase of pyrolysis oil it is below the detection limit, in agreement with the GC-MS analysis. The absence of olefins before and after electrolysis is likely related to the insolubility of aromatics in water.[33]

In the range 166.5–180 ppm, carboxylic acids and esters appear. Ester formation during electrolysis likely results in the increasing intensities in this region. Aldehydes and ketones appear seem to be unaffected by the treatment (see region of 180–220 ppm). Ketones are known to be resistant to oxidation because of the absence of hydrogen atoms attached to carbonyl. Therefore, the little increment in the region could be related to other oxidation reactions that yield ketones and aldehydes.

The percentages of functional groups can be calculated based on the assumption that all carbon functionalities are detected and integrated (see Figure 4). The quantitative analysis shows no significant variation in the aliphatic C-C group. After electrolysis on both Pt and BDD, the methoxy group disappeared. Aliphatic C-O groups increase to 67% and 66% after treatment with BDD and Pt, respectively. The change is probably related to the formation of alcohols by (non)Kolbe and Hofer Moest reaction, which gives rise to an aliphatic C-O group. The higher proportion of aliphatic C-O on BDD indicates the selectivity to the alcohol group. For the aromatic C-H group, the carbon percentage decreased after electrolysis showing that it is susceptible to electrooxidation. As it is shown by GC-MS that mono phenolic compounds (guaiacol) were present in raw pyrolysis oil, that are known to be prone to oxidation, supplements the information from our analysis.[34]

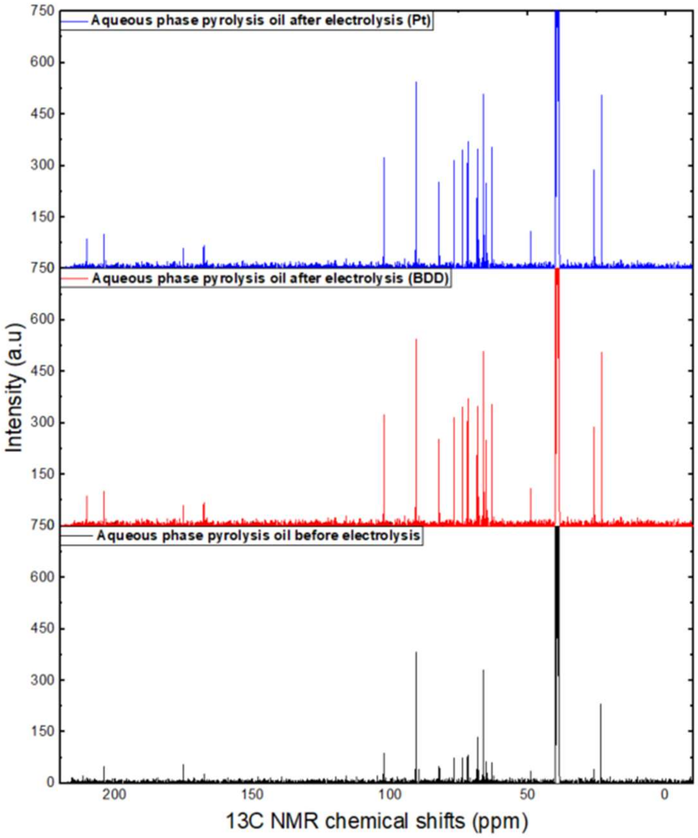


Figure 3 ^{13}C NMR of aqueous phase pyrolysis oil before (black) and after electrolysis on Pt (blue) and BDD (red) anodes at 25 mA/cm^2 for 1 hour.

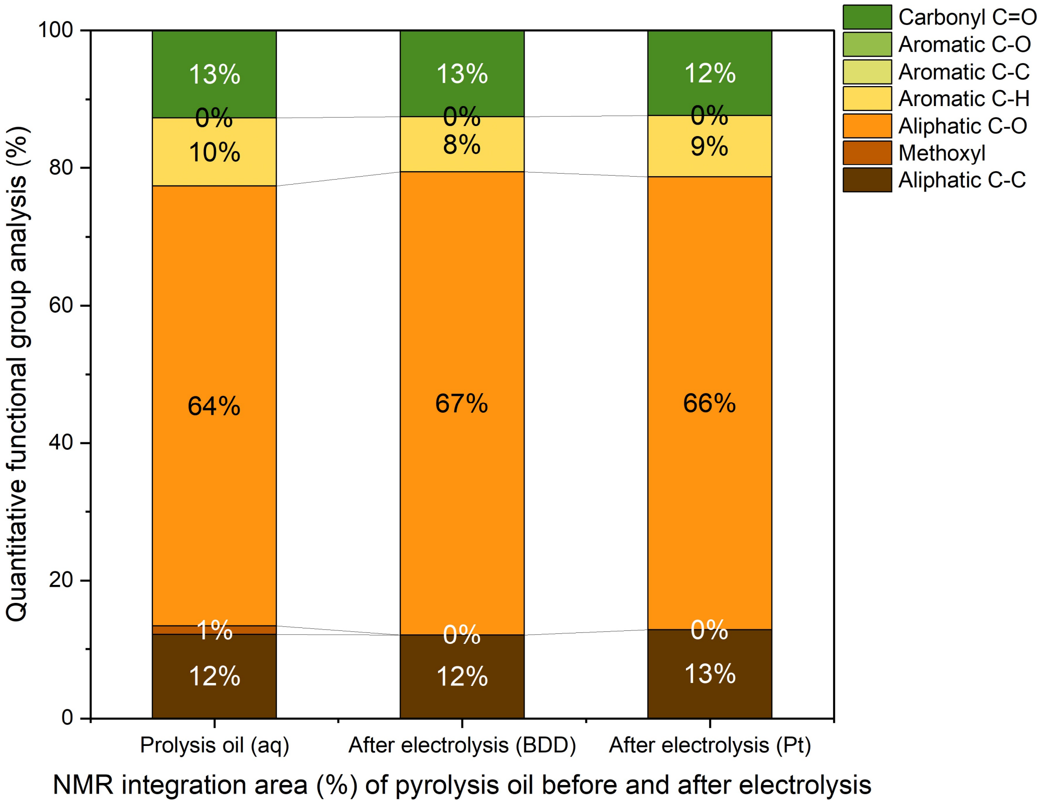


Figure 4 Integrated areas for specific carbon in specific functional group before and after electro-oxidation determined by ^{13}C NMR.

Thus, a first overview of the complex reactant and product spectrum of aqueous phase pyrolysis oil was presented clearly revealing the differences in product distribution between the electrode materials used for electrooxidation. Though this is in agreement with the model compound analysis (see below), several challenges are to be tackled to fully resolve and utilize direct electrochemical conversion of pyrolysis oil. As such prolonged electrolysis experiments resulting in more significant differences in the functional groups before and after electrolysis are required and will be addressed in ongoing work.

The use of pure pyrolysis oil will cause additional challenges. In general pyrolysis oil is a very thick and viscous liquid and cannot be used without pre-treatment in electrochemical cells. The viscosity will cause hindrance in the flow of the oil across the electrode and will likely poison the active sites of electrocatalytic material. The highly acidic pH of oil (approx. pH 2) and its low conductivity are obstacles to be overcome.[35] The complexity of pyrolysis oil due to hundreds of compounds, its composition variation due to different feedstock and the ageing process can lead to non-standard irreproducible experimental investigation. The analysis of the oil is highly complex and requires the use of multiple complementary techniques, including GC, GCMS, FTIR, Raman, LCMS, NMR, and FT-ICR. The complexity can be reduced using the aqueous fraction of pyrolysis oil (water soluble). Still the better approach is to fractionate the pyrolysis oil, extract carboxylic acids to increase the pH, and extract sugars to reduce the polymerisation probability. Our model compound analysis (below) revealed that carboxylic acids can be converted through electrochemical decarboxylation into alkanes and alcohols, simultaneously providing the protons and electrons for the electrochemical hydrogenation of pyrolysis oil. In short, from the complex analysis of pyrolysis oil before and after electrolysis it is concluded that acid separation would be advantageous for any process.

Model compound electrooxidation

Kolbe oxidation of acetic acid/acetate electrolytes (pH 5) was first investigated by cyclic voltammetry (CV) in an undivided three-electrode cell, using both Pt and BDD as working electrode (see Figure 5). For platinum electrodes, the platinum oxide formation is observed in the potential range between 0.9–1.2 V_{RHE}, subsequently leading to a rise in current at~1.6 V_{RHE} for water oxidation and likely competing acid discharge. After reaching the so-called inflection zone acetate discharge is considered to be dominant, thereby suppressing the OER, leading to methyl radical formation.[30]

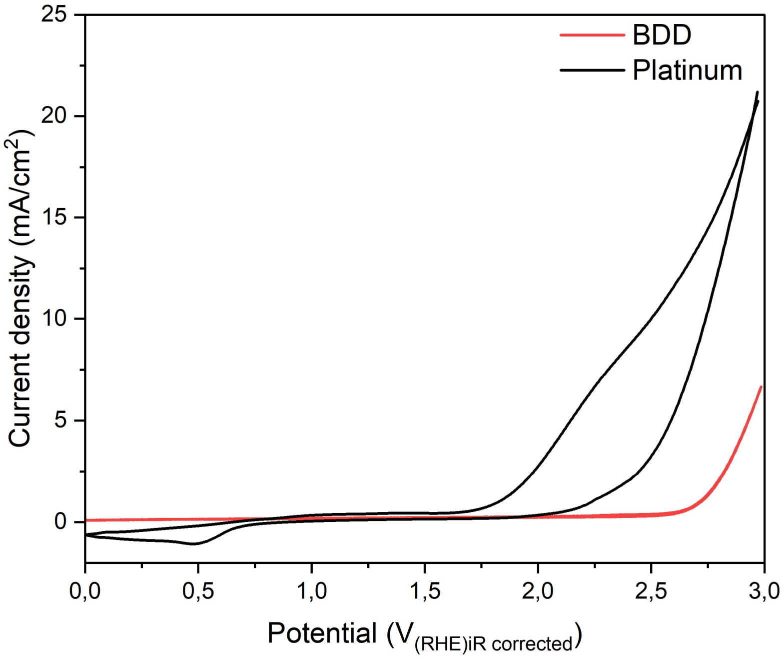


Figure 5 Cyclic voltammetry of Pt and BDD electrodes in 1M acetic acid/sodium acetate at pH 5.

The transition point between OER prevailing currents to Kolbe electrolysis lies at ~2.5 V_{RHE}, from where OER currents diminishes at 2.5 V_{RHE}. Due to the abundance of methyl radicals, dimerization is a favourable pathway forming ethane as the primary product.

In Figure 5, the characteristic CV obtained with BDD in acetate solution shows no change in electrochemical response below 2.6 V_{RHE} indicating that acetic acid is not oxidised before the onset of water oxidation.[36] The absence of a pseudo-plateau region, i.e. the inflection zone observed for Pt electrodes, suggests that oxidation on the BDD surface occurs via an indirect mechanism rather than a direct electron transfer.

Due to the larger overpotential for OER on BDD, the simultaneous water discharge leads to the formation of weakly adsorbing OH^- radicals. The reaction between methyl and OH radicals leads to methanol formation.[37] Another possibility of acetate conversion to methanol is the Hofer Moest reaction,[37,38] in which an alkyl radical is oxidized further to the carbocation which reactions with an OH anion to methanol, as shown in the Figure 6.[30]

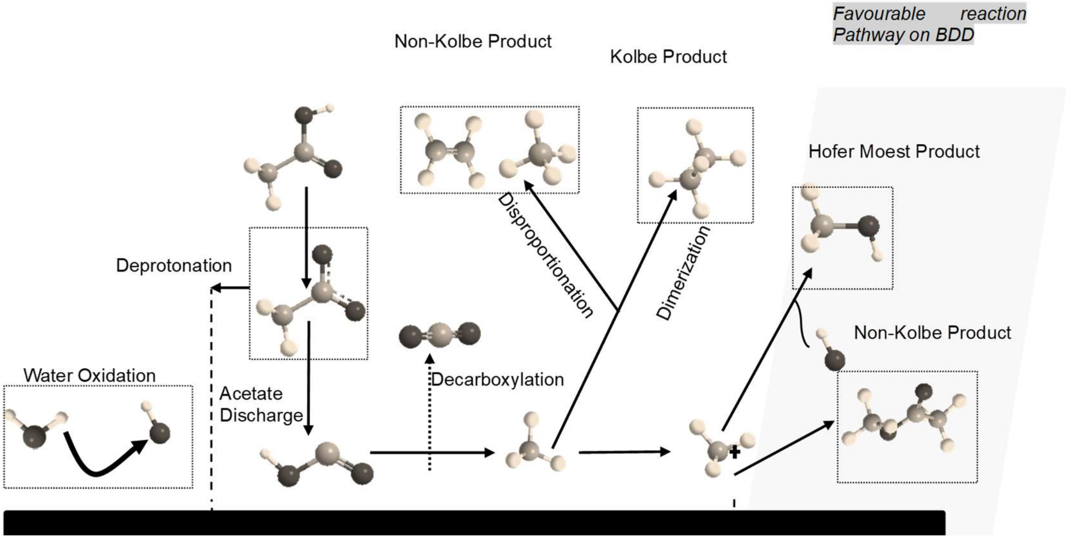


Figure 6 Reaction mechanism Kolbe electrolysis

Electrode materials

Platinum foil electrodes are highly active for the Kolbe homocoupling reaction reaching high faradaic efficiencies up to 90–99% from low current densities of 25 mA/cm^2–300 mA/cm^2 in batch cells.[32] We investigated the faradaic efficiencies towards ethane on platinum foil in flow cells also reaching >90% w.r.t time.

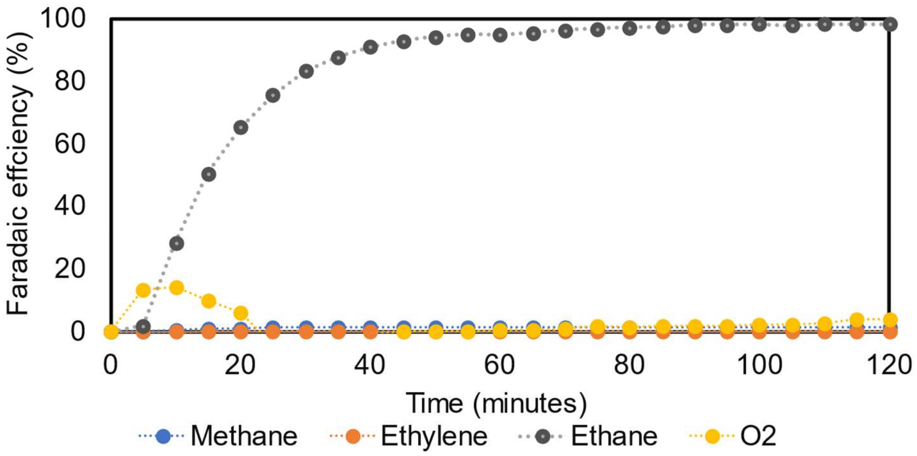


Figure 7 Faradaic efficiency towards ethane by electro-oxidation of 1M acetic acid/sodium acetate pH 5 on platinum foil in flow cell at 25mA/cm^2.

pH influence on electrooxidation of acetic acid on platinum electrode

The influence of pH and concentration significantly affects product selectivity and current efficiency. We investigated the FE to ethane in the aqueous solution of acetic acid with K acetate in galvanostatic operation at a current density of 25 mA/cm^2. The influence of pH is visible near the pKa value of acetate; the FE to ethane is higher in both 1 M and 0.5 M acetic acid/K-acetate solution (Fig 3 a) and the average FE to ethane decreases with increasing the pH. Due to the high solution resistance for electrolytes with a pH below 4 (less deprotonated acetic acid) operation of Kolbe electrolysis in the absence of supporting electrolyte is cumbersome. We observed oxygen evolution at a low concentration (0.1 M) due to fewer acetate species present in the solution (not reported here). At a high concentration (1 M), a lower FE to ethane could be a result of the autoinhibition of the oxidation reaction. If this is the case, oxidation of acetic acid will shift to a higher potential at a high concentration. In alkaline pH (8, 12), the FE to ethane was found to be lower in comparison to pH 4.7 (Fig 3 b). There is a steep decrease in FE to ethane at high pH w.r.t time due to a shift in selectivity to Hofer Moest products (methanol) at high pH and carbonates formation from the dissolved CO_2 blocking the catalyst sites for dimerization reaction.[32]

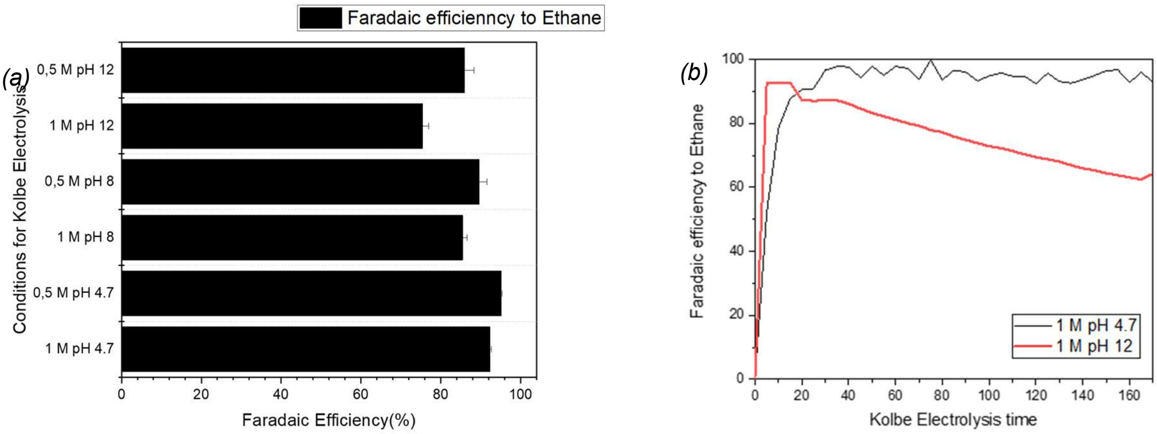


Figure 8 (a) Kolbe electrolysis of 1M K-acetate Acetic acid at different pH and conc. (b) Kolbe electrolysis of 1M K-acetate Acetic acid at different pH at 25 mA/cm^2

Supporting electrolyte cations effects

The influence of cations (Na^+, K^+, Ca^+ acetate) was analysed and it was shown that the current efficiency of the dimerization reaction is favoured in potassium containing electrolyte (FE ethane>95%).[39] the activity, i.e. in terms of the FE to ethane, increases in the order $Na^+ < Ca^+ < K^+$ (Fig 9). Although these ions are considered ‘inert’ selectivity towards specific electrochemical reactions occurs as has also been shown for other reactions (including ORR, CO_2 reduction, OER and alcohol oxidation). A similar trend has also been observed at lower current densities, where the selectivity to Kolbe products is generally observed to be detrimental, ie 80 % FE to ethane with sodium-containing electrolyte vs. up to 87% in the presence of K-cation. Its significance related to EBIO is apparent when fragmentation of pyrolysis oil compounds is required where cations, i.e. calcium are required for separation.

Our next step is to examine this trend under different conditions than optimal parameters before concluding the reason for the difference in FE to further reveal the influence of metal cations (Na, K, Cs, Li) on Kolbe electrolysis of acetic acid in aqueous solution. It will result in information on the current efficiency of Kolbe electrolysis being essential for EBIO and possible separation steps required within the process of pyrolysis oil upgrading.

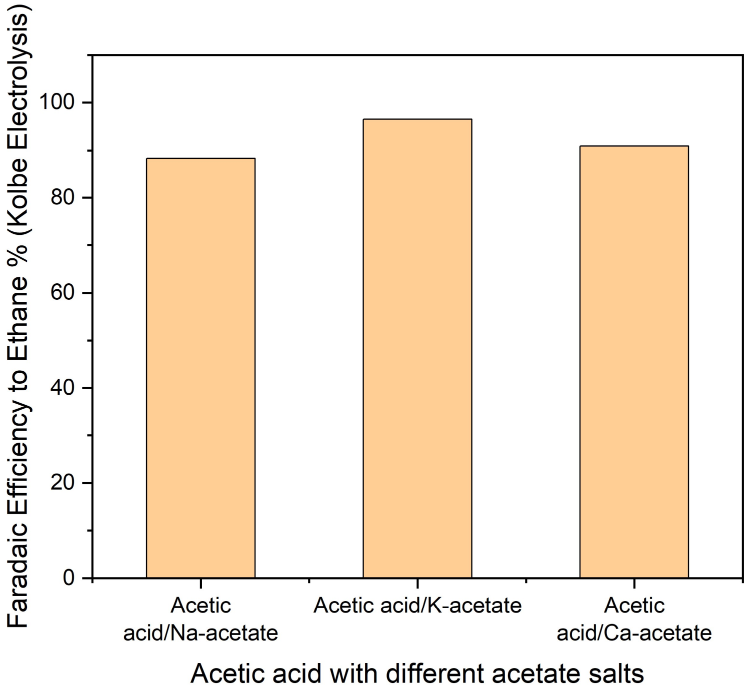


Figure 9 Kolbe electrolysis on Platinum for Acetic acid with different acetate salts at 25mA/cm^2

Other electrodes

We aimed for less costly electrode materials that can compete with the properties of Pt. Additionally, we considered the development of electrodes capable of selective non-Kolbe/Hoefer Moest product formation. Using model components in an aqueous solution or the water fraction of the pyrolysis oil, reaction mechanisms can be further understood, and product yields and selectivity determined and optimised. Catalysts/electrode composition as well as operating conditions can be changed readily.

The focus of our work was to develop and optimise metal functionalised BDD electrodes.[40] BDD and platinum foil were used for reference. Moreover, electrode functionalization of graphite, FTO and nickel foam has been investigated. Firstly, we deposited platinum nanoparticles on different substrates (BDD, Graphite, FTO and Nickel) and evaluated the faradaic efficiency towards decarboxylation. We also used thin platinum films sputtered on BDD to evaluate the selectivity of Kolbe electrolysis. BDD was used as the final electrode because it can be stable under harsh conditions (high current densities) and has a long lifetime (see also below). BDD surfaces were functionalised with different shapes of nanoparticles to shift selectivity. We found that decarboxylation on BDD produces non-Kolbe/Hoefer Moest/indirect oxidation products. Based on this study within the EBIO consortium it was agreed to use BDD for electrolysis of model compounds and complex mixtures (aqueous phase pyrolysis oil).

Stability of BDD

The stability of BDD was investigated before and after electrolysis of 1M acetic acid/sodium acetate by means of Raman spectroscopy and SEM. Overall, Raman analysis confirmed that the electrolytic corrosion on BDD is negligible during acetic acid electrolysis at low current densities (25 mA/cm^2). SEM images shows the presence of graphitised carbon on the BDD after electrolysis at high current densities ~100 mA/cm^2. The graphitised carbon can be removed by electrochemical cleaning (oxidation at 25 mA/cm^2 in 1 M $HClO_4$ for 15 minutes). Nevertheless, we conducted experiments primarily below 100 mA/cm^2.

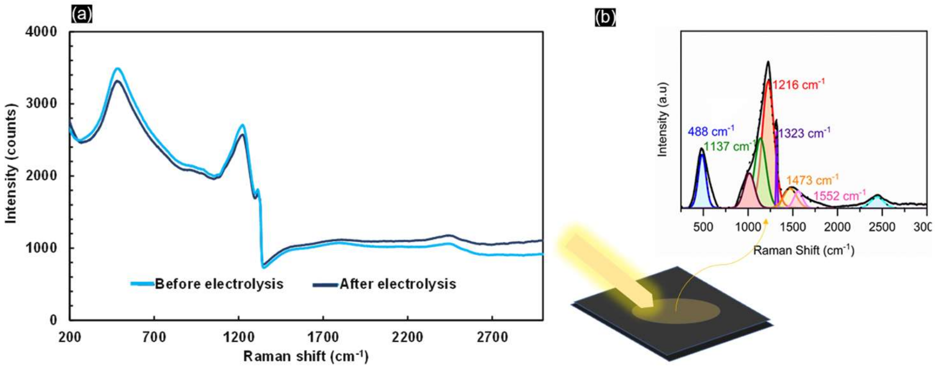


Figure 10 Raman spectra of BDD before and after 2 hrs electrolysis in 1 M acetic acid/sodium acetate pH 5 at 25 mA/cm^2.[40] The BDD electrodes used have a concentration of 2000–5000 ppm boron atoms in the lattice. (b) Deconvoluted Raman spectra of BDD reveal the position of the bands in accordance with the existing literature.

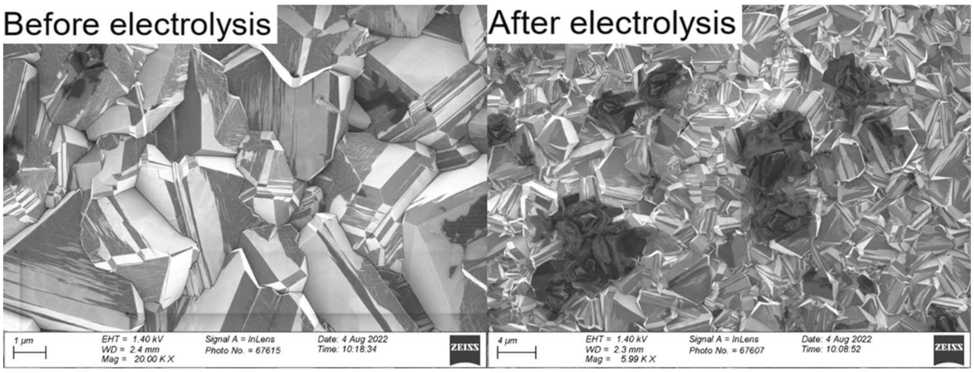


Figure 11 SEM image of BDD before and after electro-oxidation of 1M acetic acid/sodium acetate pH 5[23]

Our study contrasted the performance of boron-doped diamond (BDD) electrodes with graphite, fluorine-doped tin oxide (FTO), and nickel foam.[40] The Faradaic efficiencies shown in Figure 12, are clearly electrode material specific. Notably, Nickel Foam electrodes did not yield Kolbe electrolysis products, exhibiting a high Faradaic Efficiency (FE) for oxygen evolution (up to 95%). In contrast, FTO primarily facilitated OER, with only a minor 2% FE for hydrogen peroxide. Due to the high selectivity for OER FTO and nickel foam were not considered any further. Graphite electrodes uniquely generated methanol and methyl acetate with comparable FEs, suggesting overoxidation of the methyl radical to a carbocation, leading to Hofer Moest product formation. A potential increase observed in chronopotentiometry tests for both Graphite and FTO over a 50-minute electrolysis period indicates their instability under the tested conditions, with FTO's electrode potential reaching approximately 7 V_{RHE}. In comparison, BDD showcased notable stability, maintaining a constant potential of 3.6 V_{RHE}. Additionally, BDD electrodes demonstrated enhanced selectivity for methanol electrooxidation over graphite, making them more efficient, especially considering the challenges in separating methanol/methyl acetate azeotropes.

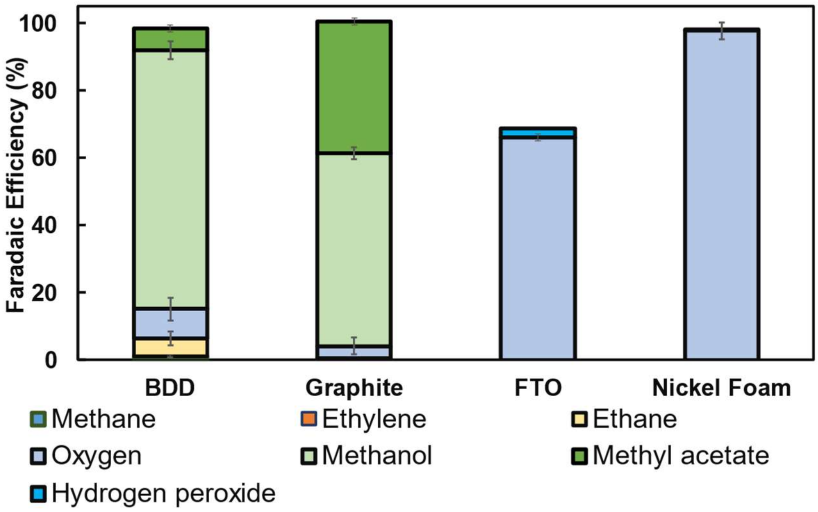


Figure 12 Average FE towards (non) Kolbe/Hofer Moest/indirect oxidation products during electrolysis of 1M acetic acid/sodium acetate for 50 minutes in the batch cell at 25mA/cm^2 and pH 5.[40]

Targeted process conditions

Firstly, the carboxylic acids will be separated from bio-oil in the form of salts (sodium/alkali metal acetate). We have found that the choice of supporting electrolyte (alkali metal salts) can influence the Kolbe reaction, i.e. $Li^+ < Na^+ < Cs^+ \sim K^+$. This is required as in presence of carbohydrates, sugars and lignin-based molecules the selectivity of acid conversion can be significantly reduced. We observed that electrochemical decarboxylation of acetic acid on the BDD electrode is lower in presence of other compounds, such as glucose (see Figure 13).

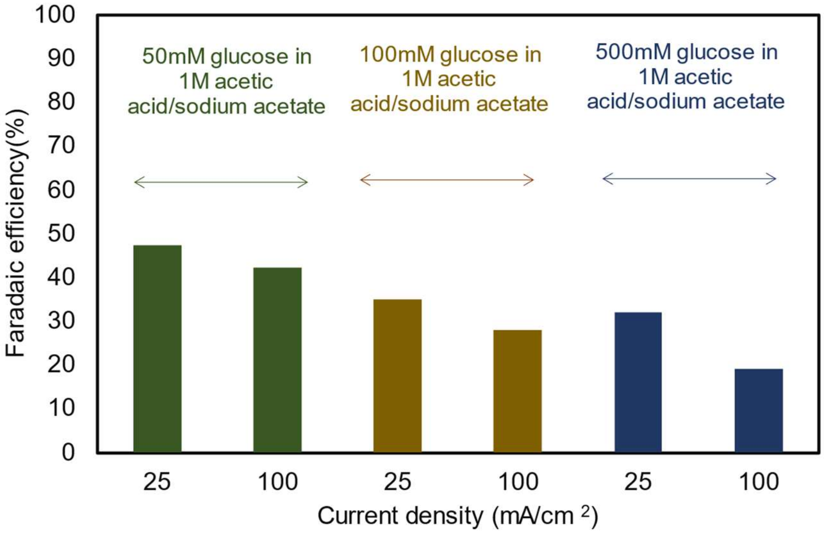


Figure 13 Effect of glucose addition with different concentration in 1M acetic acid/sodium acetate electrolysis at pH 5 on BDD electrodes with different current densities

In flow cell conditions the impact of flow rate has been evaluated using 5-350 ml/min of electrolyte flow on both anode and cathode sides, separated by an anion exchange membrane (Nafion 324). The temperature window will be between 20 and 80 °C. The electrochemical cell withstands those temperatures. The role of pressure has not yet been investigated. We observed that the flow rate only slightly influenced the faradaic efficiency but with higher flow rate a clear decrease in cell voltage has been noticed.

For the experimental tests we used DIACHEM BDD anodes with a 3.14 cm^2 active surface. A stainless-steel cathode with 5.306 cm^2 were used. The counter electrode (cathode) reaction is hydrogen evolution. The cell was operated at STP conditions with flow configuration and can reach up to 50% faradaic efficiencies to decarboxylation at 50 mA/cm^2. The oxidation reaction will be coupled with other suitable reaction for cost effectiveness in ongoing research.

Electrochemical oxidation of the Black liquor

Electrochemical anodic oxidation of lignin is a well-known method for lignin degradation.[8–12] Nickel-, cobalt- and titanium alloys, but also materials like nanoparticles based on iridium and lead are electrode materials for this reaction typ.[13,14] The major products of most of the publications is vanillin, acetovanillone and guaiacol. Promising materials for industrial lignin degradation are Ni and Co based materials. Ni or Co based materials usually leads to an outstanding selectivity regarding the formation of monoaromatic phenolic compound. Co-based materials usually suffer from corrosion in alkaline solutions which limits a technical application. Nickel based materials therefore are more stable against alkaline corrosion which makes them the most promising ones for industrial applications.

Various alloys based on nickel were under evaluation to determine their suitability for direct electrochemical degradation of lignin in Black liquor. These alloys are used in conjunction with a subsequent thermal treatment within an autoclave. In order to investigate their performance under specific conditions, properties such as chemical and thermal stability were rigorously tested. Also, various electrochemical parameters like current density, amount of applied charge, temperature, concentration of black liquor used for electrolysis, and the quantity and concentration of the solvent and sodium hydroxide, were investigated. The aim is to break down long-chain lignin polymers into shorter oligomers and monoaromatics such as vanillin, acetovanillone and guaiacol. These monoaromatics can be used, for example, in the food industry or as building blocks in chemical synthesis.

Setup of the electrochemical oxidation

To address these experiments, a specialized autoclave design developed by WALDVOGEL and co-workers was employed. This setup allows electrochemical screening at temperatures exceeding 100 °C under pressure, thereby promoting the efficient degradation of lignin within black liquor into the already described oxidation products. Following the electrochemical process, a liquid-liquid extraction was used, and the residue was characterized using gas chromatography-mass spectrometry (GC-MS), while quantification was performed using gas chromatography with flame ionization detection (GC-FID) with the aid of an internal standard.

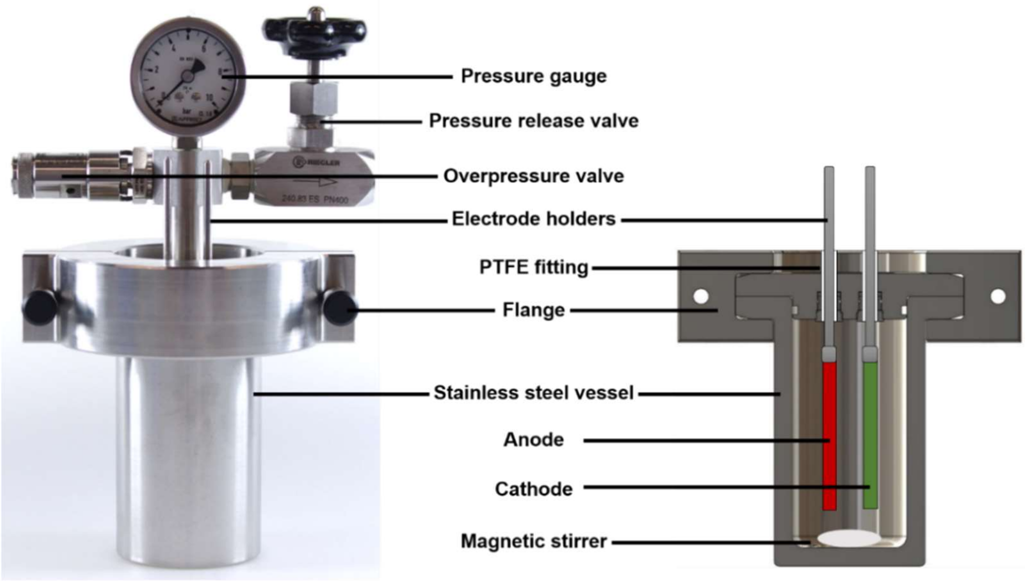


Figure 114: Autoclave design developed by Waldvogel and co-workers for lignin degradation.

Results of the electrochemical oxidation

First, we tested different electrochemical conditions as well as electrode materials. Therefore, a linear screening of single parameters to identify major influences, which impact the yield in degradation product the most was used. Based on the best working conditions of these screenings further parameters were investigated.

To verify the electrochemical degradation, the black liquor without any electrochemical treatment was analyzed. It was shown that black liquor already contains small amounts of acetovanillone (0.07 wt%) and guaiacol (0.01 wt%), but no vanillin. In the next step, the already published conditions by Waldvogel and coworkers for lignin degradation were taken and adjusted in different screenings to fit Black liquor.[8] As first parameter the current density was investigated. Therefore, significant higher amounts of acetovanillone and guaiacol but also vanillin could be obtained. It was shown that a current density of 5 $\mathrm{mA/cm^2}$ works the best so far.

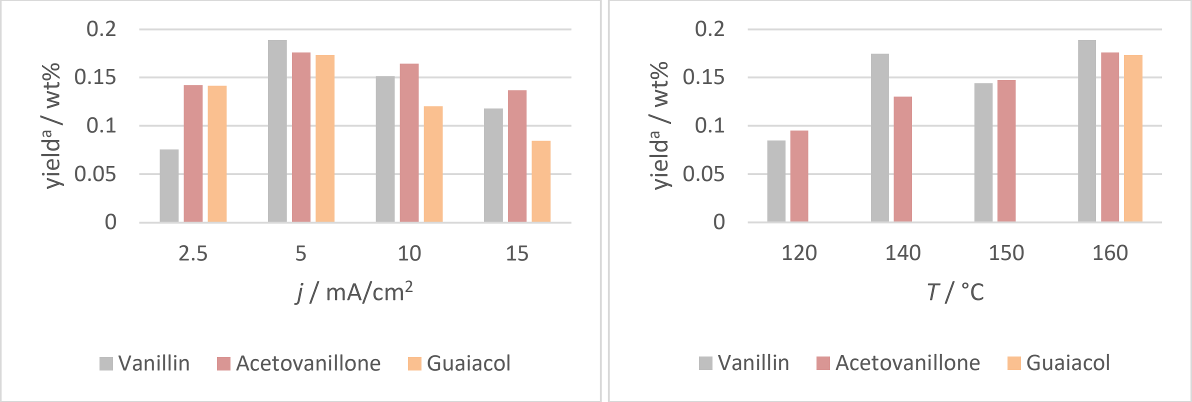


Figure 115: Left: Electro-degradation of black liquor under variation of the current density (2.4 g black liquor; 85 g 3 m NaOH; T = 160 °C; Q = 0.6 C per mg black liquor); Right: Electro-degradation of black liquor under variation of the temperature (2.4 g black liquor; 85 g 3 m NaOH; j = 5 $\mathrm{mA/cm^2}$, T = 160 °C; Q = 0.6 C per mg black liquor). a: The yield of the products vanillin, acetovanillone and guaiacol is related to the amount of starting material and was determined by GC-FID with n-dodecylbenzene as internal standard.

Temperature of the heat treatment was investigated next. Therefore, temperature was lowered from 160 °C down to 120 °C in steps of 20 °C. Therefore, a decrease in terms of the yield of degradation products was observed. It should be highlighted that a temperature of 140 °C showed a local maximum in the yield. Here, vanillin could be obtained in amounts compared to the degradation at 160 °C. Due to the lower needed temperature and the resulting improved conditions for industrial applications 140 °C was taken for further screening. Next, we focused on nickel electrodes and nickel alloys which are, as already mentioned, suitable for lignin degradation without electrode fouling or deactivation of any kind in a lab scale. Different morphologies for nickel and an alloy were tested. Ni-based alloys enabled a selective degradation of kraft lignin to vanillin and acetovanillone in good yields ranging from 0.01 to 0.17 wt% and 0.12 to 0.13 wt% respectively.

Table 2: Used electrode materials for lignin degradation in black liquor.

Electrode	Composition	Vanillin[a]	Acetovanillon[a]	Guaiacol[a]
Ni sheet	Ni99.9	0.17 wt%	0.13 wt%	-
Ni foam	Ni99.9	0.05 wt%	0.13 wt%	0.08 wt%
Waspalloy[b]	Ni59/Cr20/Co14 (traces:Mo/Ti/Al/Fe)	0.01 wt%	0.12 wt%	0.05 wt%

Electro-degradation of black liquor under variation of the electrode material (2,4 g black liquor; 85 g 3 M NaOH; T = 140 °C; j = 5 mA/cm^2; Q = 0.6 C per mg black liquor). a: The yield of the products is related to the amount of starting material and was determined by GC-FID with *n*-dodecylbenzene as internal standard; b: purchased from Goodfellow GmbH, Germany.

It turned out nickel sheet material works best for lignin degradation to vanillin and acetovanillone. This inexpensive and highly abundant electrode material showed no corrosion or loss in catalytic activity over multiple uses in the process. It is already known in literate that nickel under these conditions forms a layer of nickel oxide hydroxide.[12] Afterwards different amounts of charge were applied. A lower amount of charge however drastically lowered the yield of vanillin and lead to insufficient depolymerisation. Applying optimised reaction conditions of 2.7 C per mg lignin, good yields for both vanillin (0.52 wt%) and acetovanillone (0.26 wt%) were observed.

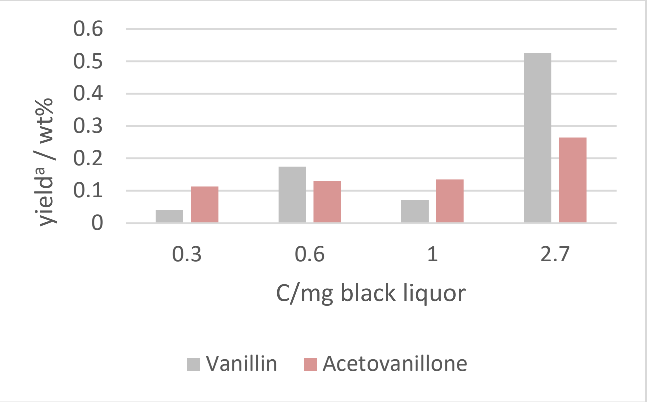


Figure 116: Electro-degradation of black liquor under variation of the applied amount of charge (2.4 g black liquor; 85 g 3 m NaOH; T = 140 °C; j = 5 mA/cm^2). a: The yield of the products is related to the amount of starting material and was determined by GC-FID with n-dodecylbenzene as internal standard.

Electrochemical reduction of the pyrolysis oil – Analysis of the pyrolysis oil

The pyrolysis oil used for all experiments was supplied by BTG Biomass Technology Group. It derives from the biopolymer lignin and contains hundreds of compounds. During the work on WP2, it was decided that the pyrolysis oil should be fractionated. This was done by phase separation leading to a heavy organic phase containing mostly lignins (lignin fraction), water phase containing mostly short acids and sugars (sugar fraction) and a middle bilayer with a lot of phenolics (phenolic fraction). The first step in WP2 was analyzing the pyrolysis oil. With SINTEF's expertise it was possible to obtain expedient results on the composition of the pyrolysis oil. Through different analyses such as gas chromatography (GC) measurements (mostly GCMS) and GPC (Gel Permeation Chromatography), it was possible to determine individual compounds of the pyrolysis oil. The major structure motifs are summarized in Table 3Table. The samples were analyzed via GCMS with a method developed by SINTEF especially for aromatic compounds in crude bioliquids. The results show the differences and similarities of the fractions with respect to aromatic compounds.

Table 3: Results of GCMS analytics showing the major structure motifs of the pyrolysis oil and its phenol and lignin fraction provided by BTG.

Biomass	Major structure motif found with GCMS
Pyrolysis oil	Substituted furans (and 3,4-Divanillyltetrahydrofuran), substituted benzofuran, phenols, short chain and vinyl esters, pyrazoles, short chain ketones/aldehydes, homovanillic acids, catechols, cresols
Phenol fraction of the pyrolysis oil	Substituted (Benzo-)furan, phenols, short chain and vinyl esters, pyrazoles, short chain ketones/aldehydes
Lignin fraction of the pyrolysis oil	Substituted furans, aldehydes, ketones, esters, triazoles, phenols, catechols, cresols, pyrimidines

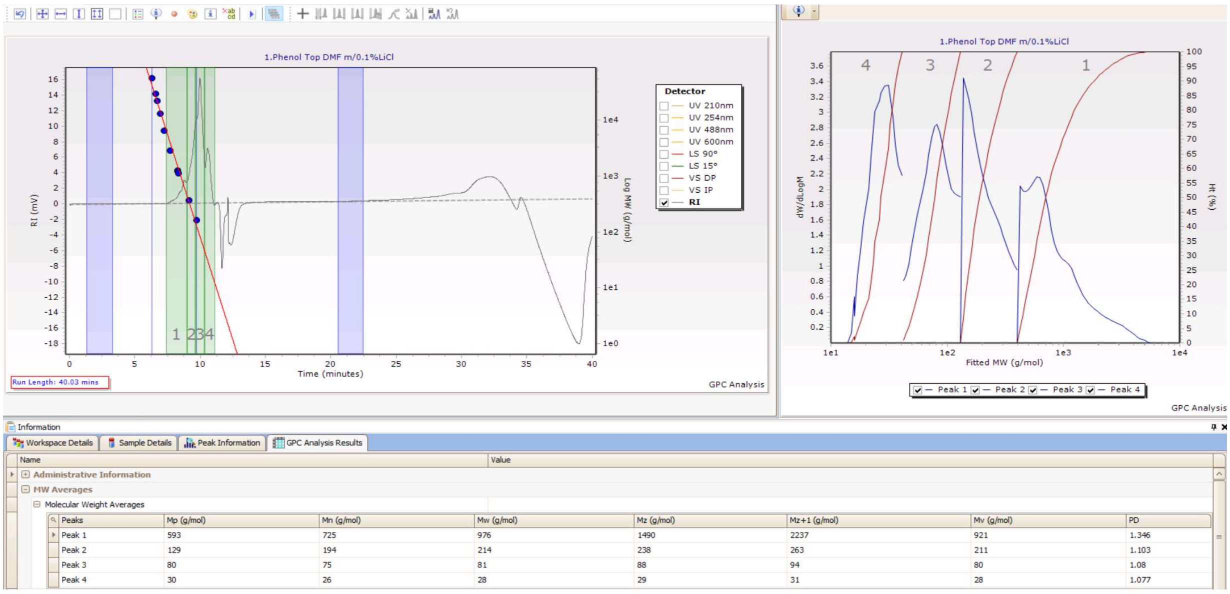
To gain information about the molecular weight of the compounds contained in the pyrolysis oil, GPC with RI detector was done by SINTEF. GPC offers a separation dependent on molecular size and is often used for the analysis of polymers.[41] The polymer content in the pyrolysis oil and its fractions were to be determined.

The molecular weight averages for each fraction on a Polargel L column (8 µm 300x7.5mm + Polargel-L Guard 8 µm 50x7.5mm; 100 – 60 000 g/mol) in DMF with 0.1% LiCl is shown in Table 4.

Table 4: Results of the GPC measurements of the pyrolysis oil fractions: PD (Polydispersity), Mn (number average) and Mw (weight average) for each fraction.

Feed stock	*Mn (g/mol)*	*Mw (g/mol)*	*PD*
Lignin fraction	2399	4139	1725
Sugar fraction	667	691	1036
Phenol fraction (top)	313	332	1061
Phenol fraction (bottom)	70	111	1586

Polystyrene was used for calibration on the Polargel L and Polargel M column (8 µm 300 x 7.5 mm + Polargel-M Guard 8 µm 50 x 7.5 mm; 1000 – 500 000 g/mol). The phenol fraction (top phase) of the pyrolysis oil as an example is exhibited in Figure 17.



Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	593	725	976	1490	2237	921	1.346
Peak 2	129	194	214	238	263	211	1.103
Peak 3	80	75	81	88	94	80	1.08
Peak 4	30	26	28	29	31	28	1.077

Figure 177: Example of the GPC measurement of the phenol fraction (top phase).

The results indicate for the top phenol fraction that most of the compounds (peak 3) have a molecular mass of around 80 – 120 g/mol with 80 g/mol at the peak maxima. The range of molecular mass of all peaks is between 20 – 8000 g/mol. The results of the other fractions are summarized in Table 5.

Table 5: GPC results of the pyrolysis oil fractions. The main peak(s) are marked in red.

Feed stock	*Mn (g/mol)*	*Mw (g/mol)*	*PD*
Lignin fraction			
Peak 1	2399	4139	1725
Peak 2	667	691	1036
Peak 3	313	332	1061
Peak 4	70	111	1586

Sugar fraction			
Peak 1	5210	6564	1260
Peak 2	755	1039	1376
Peak 3	93	185	1989
Phenol fraction (top)			
Peak 1	725	976	1346
Peak 2	194	214	1103
Peak 3	75	81	1080
Peak 4	26	28	1077
Phenol fraction (bottom)	194		
Peak 1	105475	1607	1525
Peak 2	131	169	1290
Peak 3	35	37	1057
Peak 4	6	6	1000

The GPC results concluded the hypothesis of a higher molecular weight range in the lignin fraction and compounds with lower molecular weight in the phenol fractions. The sugar fraction indicates the longest polymers with a wide range of molecular weight up to 6564 g/mol but contains mostly monomers with a median of Mw=185 g/mol.

The analysis of the pyrolysis oil and its fractions is crucial for the following electrochemical step as it is the starting material of the electrochemical conversion. It makes a comparison of the treated and the crude pyrolysis oil possible and therefore enables an evaluation of the electrochemical approach.

Setup of the electrochemical hydrogenation

The hydrogenation of pyrolysis oil was done in a galvanostatic setup in a divided cell with glass frit. In the cathodic chamber the pyrolysis oil solved in the electrolyte is electrolysed. The anodic chamber contains only the electrolyte. The setup consists of a stainless-steel carousel with up to six batch cells made from Teflon (Figure 18). A total volume of 6 mL solvent was used during the electrolysis.

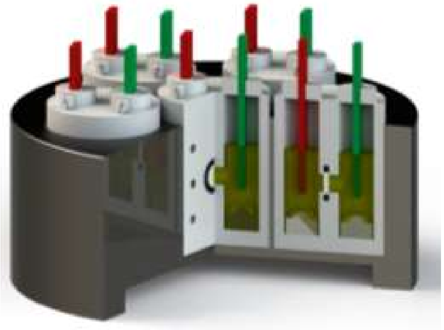


Figure 18: Cross sections of the stainless steel carousels for divided screening cells used with a total volume of 6 mL.

For the electrolysis, a general procedure to the following conditions was developed: 50 mA/cm^2, Q = 960 C (1 C/mg$_{\text{pyrolysis oil}}$), pyrolysis oil solved in methanolic H_2SO_4 (3%) in the cathodic compartment and electrolyte in the anodic compartment. Different cathode materials were tested: BDD, glassy carbon, lead, leaded alloys. During these experiments a glassy carbon anode was used.

After the electrolysis, a liquid-liquid extraction was used to neutralize the acid and remove all water-soluble compounds. The raw product mixture in the organic phase was investigated using ^{1}H, ^{13}C, 2D NMR and GC comparing the spectra before and after the electrolysis and workup.

Results of the electrochemical hydrogenation

Using this general procedure with the setup and condition mentioned above, signals deriving from major carbonylic functionalities were significantly converted and vanished in flow infrared spectrometer, ^{1}H and ^{13}C NMR spectra. This shows that electrochemical hydrogenation of most aldehydes and ketones from the pyrolysis oil is technically feasible. In Figure 1919, the spectra of the ^{1}H NMR before and after the electrolysis are presented. In the typical area of the carbonylic functionalities[42] a decrease of these groups is demonstrated.

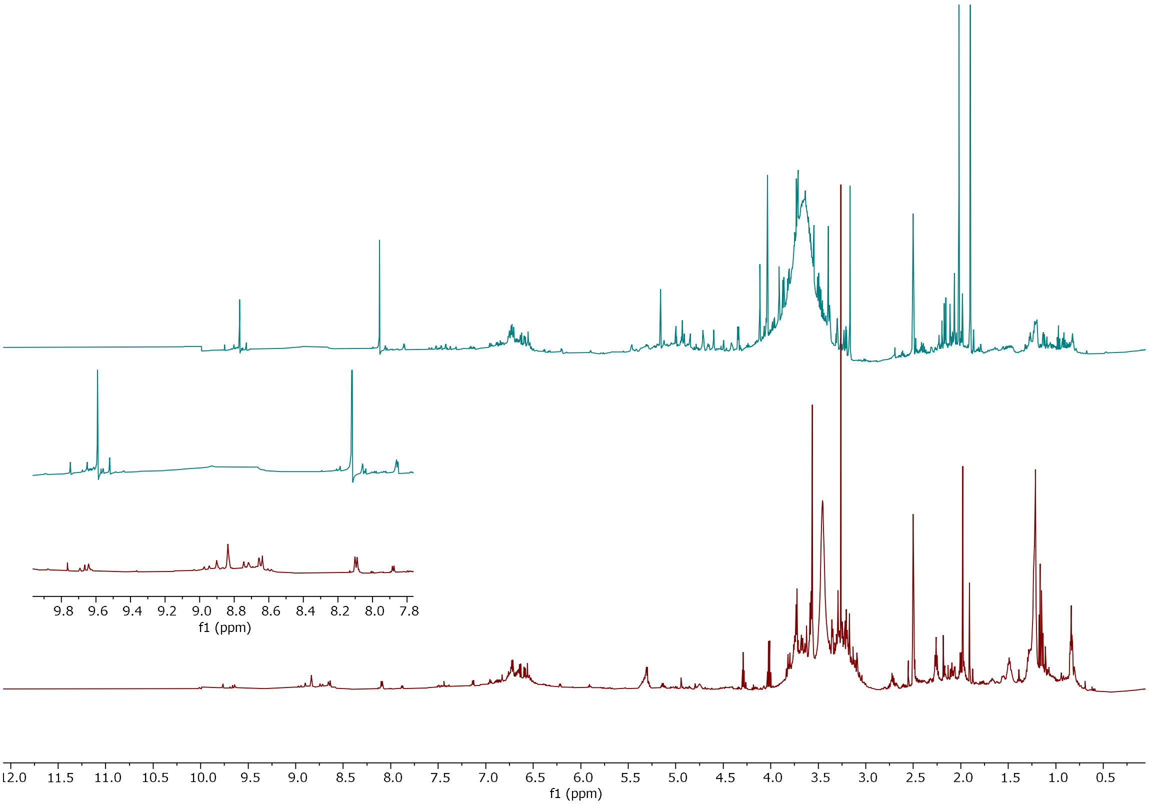


Figure 19: ^{1}H NMR (600 MHz, DMSO-d_6) of the pyrolysis oil before (blue) and after (red) the electrolysis.

The screening of the cathode materials (BDD, lead and different leaded bronze) led to the conclusion that BDD is the cathode material of choice. A screening regarding the current density was done (10 mA/cm^2 until 100 mA/cm^2 in increments of 10) and it appears due to the qualitative shift in the NMR that current densities lower than 50 mA/cm^2 are not favorable and higher current densities are favorable for the conversion of carbonylic functionalities.

Conclusion

Platinum foil electrodes have high selectivity for the Kolbe product (ethane, optimized reaction conditions 25mA/cm^2, pH 5, 1.0 M acetic acid). Oxidation of acetic acid on BDD electrode enables high selectivity towards methanol formation by an indirect hydroxyl radical driven reaction mechanism that is only slightly influenced by the electrolyte pH. BDD functionalized with platinum nanoparticles or a Pt thin film allows to alter the selectivity of hydroxyl radical mediated electrooxidation to Kolbe/non-Kolbe and Hoefer reaction. Finally, the gained knowledge was used to translate the base case measurements performed in a batch cell to the electrochemical synthesis flow cell provided by CONDIAS. Starting from simple model compounds to complex pyrolysis liquid, in the divided flow cell oxidative treatments will be performed at optimal current densities of 25–50mA/cm^2.

Table 6: The operational window for further optimisation in WPs 2 and 3

Electrode material	**BDD; possible other choices are Graphite, Platinum functionalised BDD and Pt-foil**
Current density	25-50mA/cm^2 at STP conditions
Temperature window	20–80 °C
Pressure	< 2 bar
Liquid feed rate for 3.14 cm^2 cell	5–350 mL/min

Different electrochemical parameters for the oxidation of lignin in Black liquor were investigated and optimized. Parameters like the current density, the temperature for heat treatment during electrolysis and the applied amount of charge were investigated. Therefore, a linear screening approach was used. Also a few electrode materials for the degradation were tested. Based on the results we able to define the operation window for the electrolysis as shown in Table 7.

Table 7: Summary of best working electrode material and operation window for lignin oxidation so far.

Parameter	Operation window
Current density	5 mA/cm^2
Temperature	140 – 160 °C
Amount of charge	2.7 C/ mg black liquor
Electrode material	Ni alloys

It could be shown that a current density of 5 mA/cm^2 leading to promising results, but nevertheless current densities higher than 5 mA/cm^2 are working as well. In terms of temperature, different working temperatures were investigated. A heat treatment at 140 °C during electrolysis yields in good amounts of vanillin and acetovanillone. Applying an amount of chare of 2.7 C/mg black liquor leads to a significant increase in the yield of vanillin and acetovanillone compared to lower amounts of applied charge. Increasing the amount of charge in a lab scale might not be worthwhile due to the increase of electrolysis time but could be interesting for an industrial approach. In lap scale, an increase in reaction time might lead to the risk of product consumption over time. At last, the choose of the electrode material was investigated. Here, we could show that nickel and nickel alloys serve a selective degradation of lignin.

The pyrolysis oil was analyzed concerning its composition. Regarding the electrochemical reduction it was shown that major carbonylic functionalities can be converted in a setup for batch cell experiments in a divided cell. This setup will fulfill the requirements of scale-up and therefore technical application in the future. Different analytical assays employing NMR and GC in cooperation with SINTEF were established. Results on the current densities and cathode materials for the hydrogenation of the pyrolysis oil were obtained in screening reactions. The results show that higher current densities and BDD as the cathode material appear to be favorable.

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