RESEARCH ARTICLE

Electrochemical lignin depolymerization - effects of electrolyte composition and electrode materials

[version 1; peer review: 1 approved with reservations]

Chloe Roux[1], Cassandre Ecrabey[1], Linda Mezule[2], Sabarathinam Shanmugam[3], Timo Kikas[3], Roman Tschentscher[1]

[1]Department of Process Technology, SINTEF AS, Oslo, Oslo, 0373, Norway
[2]Water Research Laboratory, Riga Technical University, Riga, Riga, LV-1048, Latvia
[3]Institute of Forestry and Engineering, Estonian University of Life Sciences, Tartu, Tartu County, 51006, Estonia

v1 **First published:** 09 Jun 2025, **5**:157
https://doi.org/10.12688/openreseurope.19060.1
Latest published: 09 Jun 2025, **5**:157
https://doi.org/10.12688/openreseurope.19060.1

Abstract

Background

Lignin, a significant by-product of the pulping industry, accounts for up to a third of the biomass weight. Despite its potential as a renewable alternative to petroleum, it is primarily burned onsite. Targeting the valorization of future lignin streams, this study focuses on the optimization of electrochemical depolymerization of lignin from black liquor, examining the influence of electrolyte composition and electrode materials.

Methods

The effects of adding water, white liquor (an aqueous solution of sodium salts), and various alcohols are investigated, alongside the testing of different metals, including nickel (Ni), copper (Cu), lead (Pb), and stainless steel as electrode materials. The experiments were conducted in batch mode applying lab-scale undivided flow-through cells with an active electrode area of 3.1 cm^2. The electrolytes were prepared by dissolving sodium salts in water, to which industrial Kraft lignin and alcohols were added. The experiments consisted of chronoamperometric test protocols spanning the voltage range of 1-3V. Selected samples were analyzed with respect to their molecular size distribution applying size exclusion chromatography.

Results and conclusions

Open Peer Review

Approval Status ?

	1
version 1 09 Jun 2025	? view

1. **Xabier Erdocia**, University of the Basque Country Language and Speech Laboratory, Vitoria-Gasteiz, Spain
University of the Basque Country UPV/EHU, Donostia-San Sebastián, Spain

Any reports and responses or comments on the article can be found at the end of the article.

The results indicate that diluting black liquor with water and white liquor effectively enhances the solution's properties, including conductivity, viscosity, and the formation of deposits. Additionally, the utilization of alcohols as capping agents prevents oxidative repolymerization of lignin. Under optimized conditions, nickel electrodes are applied, and the electrolyte consists of a mixture of intermediate black liquor, water, white liquor, and alcohol in a volumetric ratio of 20:7.5:7.5:5, resulting in stable operation. The addition of alcohols as well as activation of the Ni anode by growing a NiOOH layer does not improve the performance.

Plain Language Summary

Lignin is a major by-product of the pulp- and paper producing industry, making up about a third of the weight of the feedstock materials used. Although it has the potential to be a renewable alternative to oil, it is usually just burned on-site. This study looks at potential options for lignin utilization by focusing on developing a process called electrochemical depolymerization, which breaks down lignin into smaller, useful parts. The study explores how different ingredients in the solution, like water, a salts containing liquid used in paper processing (called white liquor), and various alcohols, affect the electrochemical process. It also tests different metals, such as nickel, copper, lead, and stainless steel, to evaluate which works best as electrode material. The findings show that adding water and white liquor improves the solution’s ability to conduct electricity, reduces its viscosity, and helps to prevent formation of unwanted deposits. Using alcohols also helps stop the lignin from forming undesired products. At optimized conditions identified, nickel electrodes are used, and the solution is a mix of black liquor, water, white liquor, and alcohol in a ratio of 20:7.5:7.5:5.

Keywords

Black liquor, lignin, electrochemistry, depolymerization

H2020 This article is included in the Horizon 2020 gateway.

Corresponding author: Roman Tschentscher (roman.tschentscher@sintef.no)

Author roles: Roux C: Conceptualization, Data Curation, Investigation, Methodology, Validation, Visualization, Writing – Original Draft Preparation; **Ecrabey C**: Conceptualization, Investigation, Methodology, Writing – Original Draft Preparation; **Mezule L**: Funding Acquisition, Project Administration, Resources, Supervision, Writing – Original Draft Preparation; **Shanmugam S**: Formal Analysis, Methodology, Resources, Writing – Original Draft Preparation; **Kikas T**: Funding Acquisition, Investigation, Project Administration, Resources, Supervision; **Tschentscher R**: Conceptualization, Funding Acquisition, Investigation, Methodology, Project Administration, Writing – Original Draft Preparation, Writing – Review & Editing

Competing interests: No competing interests were disclosed.

Grant information: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No [101006612] (Biofuels through Electrochemical transformation of intermediate BIO-liquids [EBIO]). This work has also received funding from EEA Grants/Norway Grants EEZ/BPP/VIAA/2021/7
The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

How to cite this article: Roux C, Ecrabey C, Mezule L *et al.* **Electrochemical lignin depolymerization - effects of electrolyte composition and electrode materials [version 1; peer review: 1 approved with reservations]** Open Research Europe 2025, **5**:157 https://doi.org/10.12688/openreseurope.19060.1

First published: 09 Jun 2025, **5**:157 https://doi.org/10.12688/openreseurope.19060.1

Introduction

Industrial lignin production

Lignocellulosic biomass is expected to play a major role in the provision of materials, chemicals and energy carriers[1–4]. Specifically lignin as the second most abundant polymer on earth is a valuable source of aromatic platform chemicals[4–14].

The primary industrial source of lignin is the pulp and paper industry, which generates approximately 50–70 million tons of lignin annually[15]. In 2021, the global pulp and paper market was valued at $351.5 billion, with the Asia-Pacific region leading in market share (38%), followed by North America (27%) and Europe (22%)[16].

Lignin separation is primarily achieved through two methodologies: chemical pulping and mechanical pulping. Chemical pulping involves dissolving wood chips in an aqueous solution under high temperature and pressure[17,18]. The chemical treatments can be categorized as alkaline (sulfate process) or acidic (sulfite process). In contrast, mechanical pulping employs physical processes such as refining, grinding, mechanical shearing, and disintegration to isolate individual fibers[6]. The primary lignin extraction methods—Sulfite, Sulfate, Soda, and Organosolv—are outlined in Figure 1. This report focuses on the sulfate process, widely known as the Kraft process, which is the predominant method for extracting lignin from lignocellulosic biomass[19].

Despite the substantial quantity of dissolved lignin produced, much of it is not utilized externally. Instead, it serves as an internal fuel source within pulp mills, where it is combusted to generate heat for the pulping process and to recover cooking chemicals. However, ongoing advancements in pulp mill technologies have enabled partial separation and valorization of lignin dissolved in cooking liquors. In optimized Kraft mills, approximately 20% of lignin can be extracted for external applications. This percentage may increase with the adoption of heat pumps and renewable energy sources. Ethanol production by hydrolysis of lignocellulose also provides a secondary source of lignin-rich residues.

Kraft pulping process

The Kraft process involves cooking wood chips for approximately two hours at temperatures between 150–170°C and pressures of 800 kPa, using a highly alkaline solution known as white liquor (pH > 12). This method offers several advantages, including the production of high-strength paper, energy and chemical recovery during pulping, and its applicability to both softwoods and hardwoods as raw materials[9]. The recovery of chemicals is a crucial feature of this process, enabling recycling and enhancing cost efficiency.

The core chemical cycle of the Kraft process is the sodium cycle (Figure 2). In this cycle, wood undergoes pre-treatment, digestion, and washing to extract cellulose and produce pulp, which is later bleached to manufacture paper. During cellulose separation, a mixture of lignin and hemicellulose, referred to as "weak" black liquor, is collected. This liquor is processed through a series of evaporators to remove water and concentrate the solids, resulting in "strong" black liquor. The strong black liquor is then combusted in boilers to generate steam, power, or heat. The remaining residue, termed green liquor, is recycled through the calcium cycle by reacting with calcium hydroxide ($Ca(OH)_2$) to regenerate white liquor, which contains sodium hydroxide (NaOH) and sodium sulfide (Na_2S)[5].

Globally, approximately 1.3 billion tons of weak Kraft black liquor (BL) are produced annually[6]. The composition of BL varies depending on wood type and operational conditions but generally consists of highly viscous, dark brown alkaline aqueous

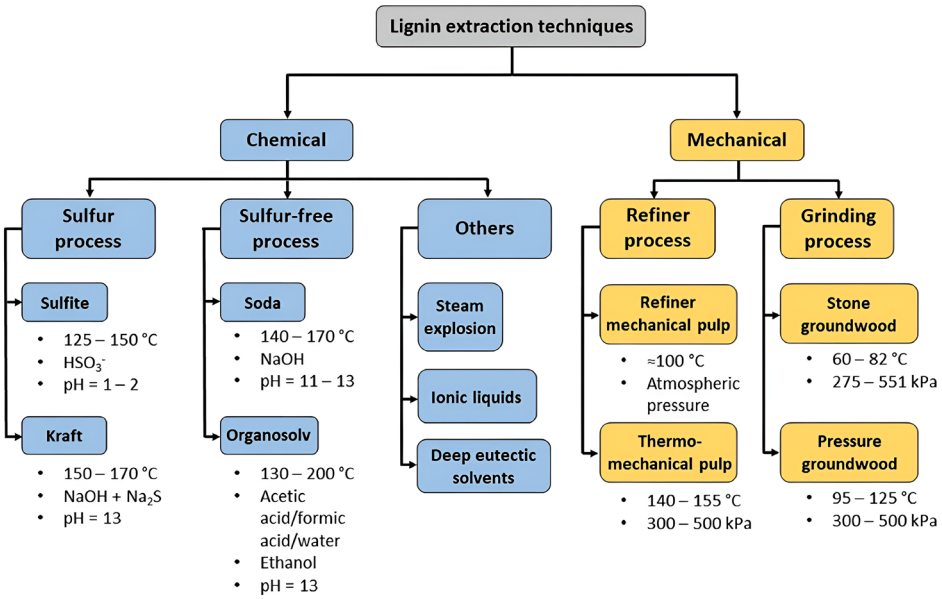

Figure 1. Lignin extraction technologies including process conditions, based on information provided by 20.

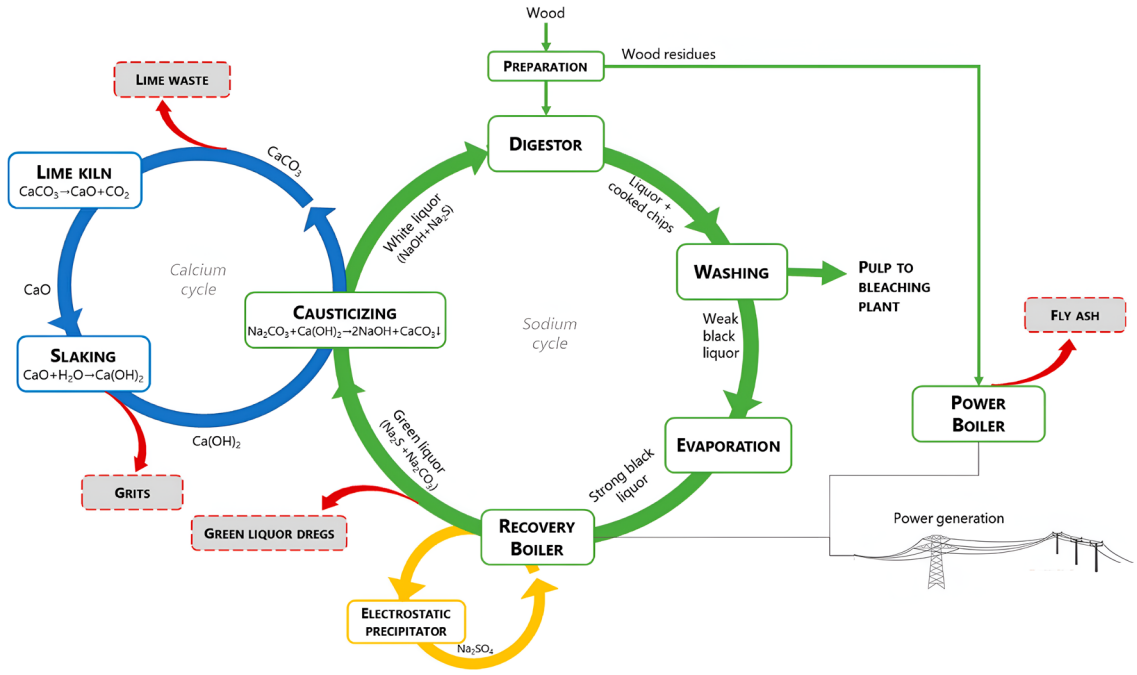

Figure 2. The Kraft process cycle to obtain pulp and generate energy. Reused from 21 with permission from MDPI.

solutions. It has a significant organic content (e.g., lignin, soaps, tall oil) and inorganic content (e.g., pulping chemicals such as Na_2CO_3, NaOH, and Na_2S). Its primary elemental composition includes carbon, oxygen, and sodium. Weak BL contains roughly 15% solids, whereas strong BL can reach up to 65% solids[19].

Instead of directing weak BL to boilers, it can undergo lignin precipitation through acidification (e.g., using dissolved CO_2), followed by filtration and washing to extract solid lignin. This approach could produce lignin feedstock and alleviate the load on the recovery boiler, a known bottleneck in the Kraft process, thereby enhancing pulp production capacity[16]. However, the harsh alkaline conditions of the Kraft process result in significant lignin degradation and repolymerization, yielding highly condensed lignin with a reduced number of β-O-4 bonds, which compromises its potential for valorization[8]. Consequently, it is preferable to convert lignin while it remains dissolved in Kraft BL[22].

Conversion processes of lignin

Several lignin conversion processes are currently under investigation[21,23–27].

a. **Thermal Processes**: Methods such as pyrolysis, gasification, and combustion effectively depolymerize lignin but require extreme conditions, typically exceeding 400°C and high pressures[9,10].

b. **Biological Processes**: These involve lignin-degrading enzymes produced by fungi and bacteria, including biofunneling pathways. Biological methods are appealing due to their mild conditions, eco-friendliness, and specificity. However, their efficiency is hindered by lignin's complex and heterogeneous structure[26].

c. **Chemical Processes**: Catalytic reactions offer controlled reaction conditions and high product selectivity under mild conditions. However, the primary challenges are catalyst recovery and degradation, which add costs and necessitate additional purification steps[3,19,24].

Electrochemical depolymerization

Electrochemical conversion represents a promising alternative to conventional approaches. This method is reagent-free and operates under mild and safe conditions, enhancing both eco-friendliness and economic feasibility[27,28].

In this report, an electrochemical approach will be explored. The process involves direct electrooxidation of lignin and its chemical oxidation via reactive oxygen species (ROS) generated at the anode[20]. Electrocatalytic oxidation occurs at the anode, producing oxygen, while electrocatalytic hydrogenation takes place at the cathode, using electrons as the reagent and producing hydrogen (Figure 3). This dual reaction system could provide an efficient pathway for lignin depolymerization and valorization.

Several critical factors influence the efficiency of electrochemical depolymerization of lignin: the surface area of the electrode, the solubility of lignin, proton/electron conduction, and the stability of the electrolyte[9]. The two main competing reactions during this process are surface functionalization (e.g., α-carbonylation) and the cleavage of C-C and C-O bonds. The cleavage of β-O-4 linkages, which are the most abundant

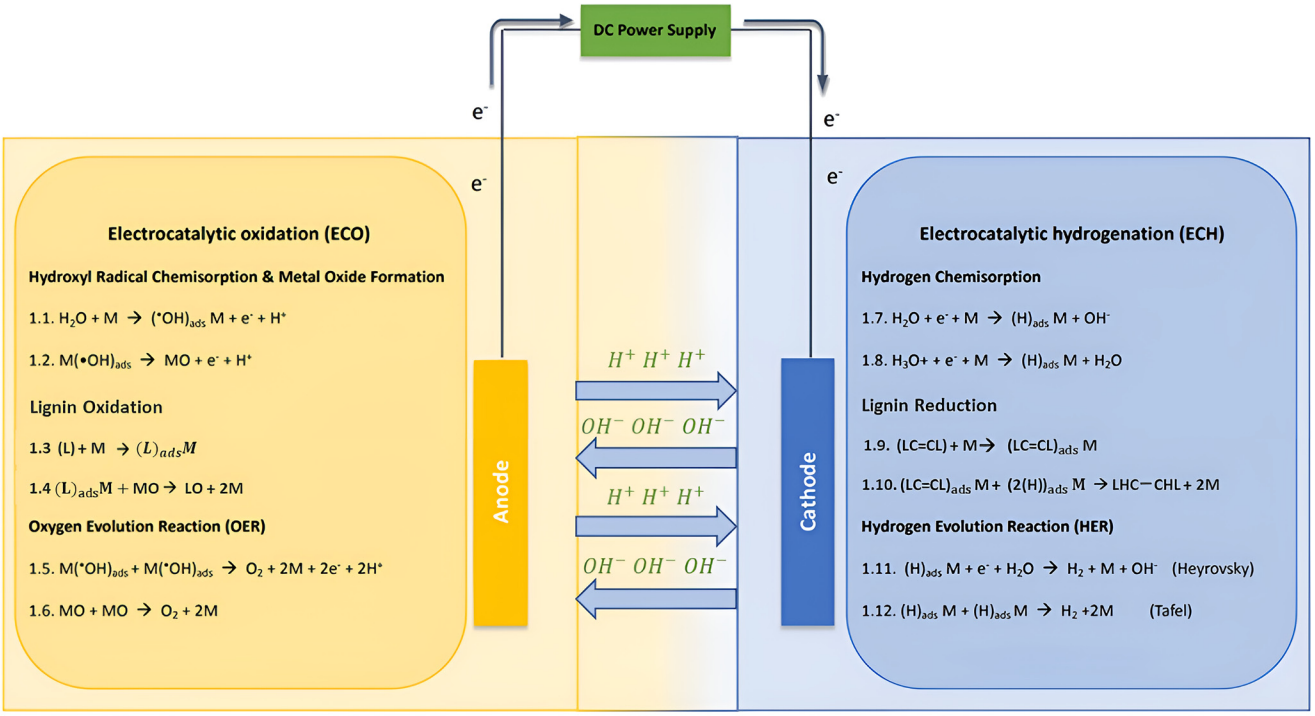

Figure 3. Simplified reaction scheme of electrocatalytic oxidation and electrocatalytic hydrogenation and water splitting. Adapted from 27 with permission from the Royal Society of Chemistry.

bonds in lignin, is identified as the rate-determining step of lignin depolymerization[27,29].

However, repolymerization of lignin through intermolecular condensation or radical coupling reactions poses a significant challenge, especially under high-temperature conditions, as these reactions diminish product quality[20,30].

To frame the study, a detailed review of electrode materials and electrolytes was conducted. A schematic overview is shown in Table 1.

Based on this analysis, experiments are designed to test diluted Kraft black liquor using various cathode materials (Nickel, Copper, Stainless Steel, and Lead), with Nickel serving as the anode. The study's objective is to optimize the electrochemical depolymerization reaction of lignin in Kraft black liquor through chronoamperometry using a small-scale electrochemical cell.

Methods

Experimental setup

The chronoamperometry step tests are performed with a PC-controlled power supply to track the obtained curent over time on the Test Bridge software[1]. The voltage applied to the electrochemical cell follows a sequence of constant steps in the range of 1 to 3V, whose duration varies between 20 and 80 minutes.

The experimental setup, shown in Figure 4, consists of an electrochemical cell through which a BL electrolyte flows thanks to a pump. The cell is connected to a power supply (Aim-TTi QPX600DP) that is PC-controlled to apply a defined voltage and produce current. The electrolyte is stored in a bottle (100 mL) which is heated by an oil bath, and the temperature of both is measured with probes. A valve outlet enables to manually collect BL samples.

Electrolyte preparation

The electrolyte used in the experiments is an intermediate Kraft black liquor (BL) sourced from Stora Enso's Sunila pulp mill in Finland. This BL has been pre-concentrated through evaporation, resulting in a solid content of 30%, with tall oil soaps removed. The BL is diluted with water, white liquor (WL), and alcohol in various ratios.

- **White Liquor (WL)**: WL enhances the conductivity of the solution. Its composition is detailed in Table 2.
- **Alcohols**: The alcohol acts as a capping agent, reacting with intermediates to prevent repolymerization. A range of alcohols tested is provided in Table 3.

The prepared electrolyte has a total volume of 40 mL and is heated to 90°C (or lower, depending on the boiling point

[1] https://www.aimtti.com/resources/test-bridge-software

Table 1. Overview of electrochemical lignin conversion eletrolytes and electrode materials.

			Advantages	Disvantages
Electrolyte	Kraft Black Liquor		Largely available, by-product of the pulping industry Can be integrated to the Kraft process. Simultaneous hydrogen production at the cathode	Other compounds than lignin: analysis is difficult
	Lignin dissolved in:	Alkaline solutions[31]	Good solubility for lignin High electron/ion conductivity	Destroy several chemical functionalities of lignin Further oxidations to undesired organic acids and carbon dioxide High pH: limits the use of metals as electrodes Low yields at mild conditions Poor selectivity
		Ionic liquids (IL)[31,32]	High lignin solubility Thermal stability Good proton and ion conductivity Easily regenerated Promoting free radical reactions Selective formation of monomers Non-volatile, chemical inertness, low viscosity	High cost. Low amount of lignin required: limited for industrial scale High viscosity Possible toxicity Difficult formulation
		Deep eutectic solvents (DES)[29]	Easier to formulate than IL, less toxic Low price Can act as both solvent and catalyst Easily recoverable and recyclable	High viscosity
		Aqueous suspensions[30,33–35]	Simple, green solvent	Limited by formation of oxygen Suspensions require higher potentials because of inhibition of the charge transfer
	Sub- and supercritical fluids(not electrochemical)		Requires less toxic, recyclable, and easily recoverable solvents Use water and CO2 : cheap, non-flammable, eco- friendly, recyclable Act as catalyst at high pressure -> minimize the use of catalyst	Requires high temperature and pressure Requires special and costly instruments
Electrode	Carbon	RVC cathode[36]	Inexpensive, easy construction High corrosion resistance Good catalytic activity Good selectivity High volume/area ratio	Fragile
		Boron doped Diamond[35,37]	High potential for the oxygen evolution reaction Inert surface with low adsorption capacity Chemical stability and corrosion resistance	Bad Eco-toxicity of heavy-metal electrodes
	Metal/Metal Alloy	Ni[22,30,38]	Low cost High stability in alkaline media High selectivity towards vanillin	Passivation of the electrode due to the adsorption of lignin on the active sites of the electrode
		Co-based alloy[22]	High electrocatalytic activity of Cobalt High yields of vanillin High selectivity towards vanillin	Corrosion instability -> loss of electrocatalytic activity
	Noble metal	Pt[30,34,38]	High electrocatalytic activity Better catalytic activity than Ni	Expensive, limited availability
		Silver[33]		Overoxidation products
	Metal Oxide	PbO2-based[39]	High conductivity and corrosion resistance High electrocatalytic activity Low cost, easy preparation	Toxicity (Pb): limited by environmental regulations
		TiO2-based[34]		
		Ir02-based[40,41]		

of the alcohol used). The heating is maintained using an oil bath set at 140°C. During the reaction, the electrolyte flows at a rate of 0.28 g/s and is continuously stirred at 260 rpm to ensure uniform mixing.

Electrochemical cell

The electrochemical cell comprises two metal electrodes (each with an electrode surface area of 3.14 cm^2), separated by a Teflon layer that defines the liquid volume between them. The assembly is enclosed by stainless steel walls, which are screwed tightly to ensure the system is leak-proof. To prevent short circuits, the electrodes are oriented perpendicularly to the inlet and outlet of the electrolyte[42]. The anode is constructed of nickel (Ni), while the cathode is made from one of the following metals: nickel (Ni), copper (Cu), lead (Pb), or stainless steel (SS, AISI 304).

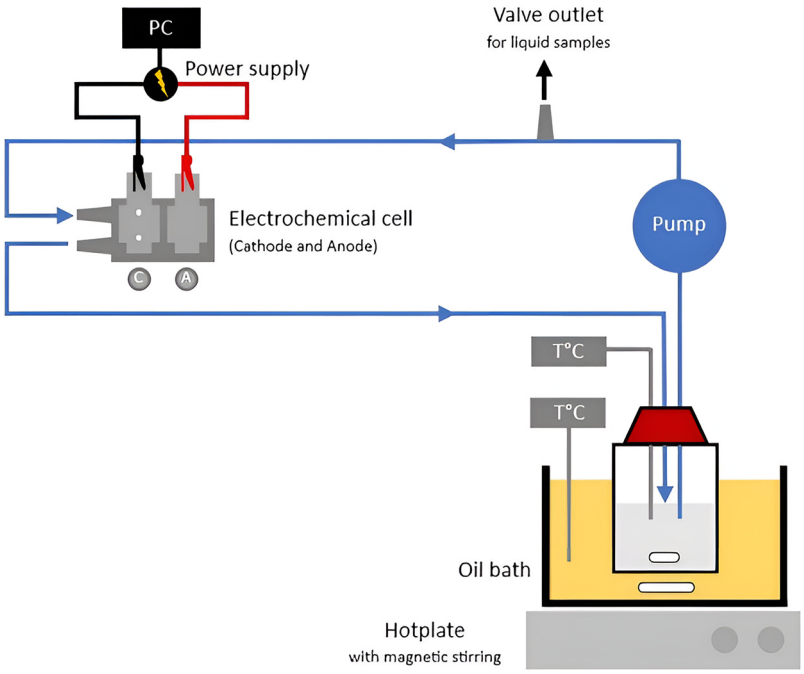

Figure 4. Scheme of the experimental setup showing the electrolyte flow and connections to the electrochemical cell.

Table 2. Composition of white liquor (aqueous solution of Na salts).

Component	CAS No.	Supplier	Catalogue number	Concentration (g/L)
NaOH	1310-73-2	Merck	567530	122,62
Na_2S	1313-82-2	Merck	407410	45,57
Na_2CO_3	497-19-8	Merck	223530	44,42
Na_2SO_3	7757-83-7	Merck	239321	9,82
Na_2SO_4	7757-82-6	Merck	238597	20,89
$Na_2S_2O_3$	7772-98-7	Merck	217263	15,39

Table 3. List of alcohols used to dilute BL with corresponding physical state and boiling point (bp).

Alcohol	State at room T	Bp (°C)
Glycerol	liquid	290
1-Butanol	liquid	118
Propan-1-ol	liquid	97
Ethanol	liquid	78
Phenol	solid	182
Methanol	liquid	65

Electrode preparation

In one experiment, the nickel anode undergoes pre-treatment to deposit a layer of nickel oxyhydroxide (NiOOH). This is achieved through two potentiometric cycles, each consisting of 12 steps (60 seconds per step, with 5-second breaks between steps) at 2.35 V, corresponding to a current density of 2.2 $mA{\cdot}cm^{-2}$.

During this pre-treatment, the anode is placed opposite a nickel cathode in a beaker containing an electrolyte composed of 0.05 M nickel sulfate hexahydrate (Merck, catalogue no. 227676), 0.1 M sodium acetate (Merck, catalogue no. 241245) and 0.005 M sodium hydroxide (Merck, catalogue no. 567530).

The solution is stirred at 180 rpm throughout the process to ensure uniform conditions (Figure 5).

Analysis

Molecular weight distribution by GPC. The molecular weight distribution of the samples is assessed using Gel Permeation Chromatography (GPC), a form of Size Exclusion Chromatography (SEC) that separates molecules by size. The analysis is performed on an Agilent HPLC 1100 instrument equipped with a guard column and two PL aquagel-OH SEC columns (300 × 7.5 mm, particle size 8 µm) arranged in series to minimize diffusion. The eluent is an aqueous solution containing 0.27 g/L NaN_3 (Merck, catalogue no. 8.22335) and 0.2 g/L NaOH (Merck, catalogue no. 567530). Samples are dissolved in the eluent at a 1:9 mass ratio and analyzed at 30°C with a flow rate of 1 mL/min. Detection is performed using a Refractive Index Detector (RID) and a Diode Array Detector (DAD) operating in the 190–400 nm range[43].

Detection of monomers in HPLC. Lignin monomers are detected using the same HPLC system, equipped with a guard column and a Kinetex C18 RP column (100 × 3 mm, particle size 2.6 µm), designed for high-resolution detection of smaller molecules. The method is based on Fischer *et al.*[43], employing an eluent gradient of 0.15M formic acid (Merck, catalogue no. 5.33002) in water (Merck, catalogue no. 270733) and methanol(Merck, catalogue no. 34860), transitioning from 9:1 to 1:1. Samples are dissolved in the 9:1 eluent at a 2:8 mass ratio, then filtered through a 0.2 µm membrane prior to injection. Key conditions include: Detection: DAD at 230 nm, Temperature: 40°C, Flow rate: 0.4 mL/min, Injection volume: 5 µL.

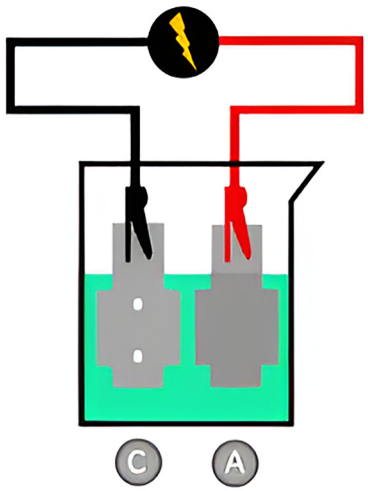

Figure 5. Scheme of the experimental setup for the deposit of a nickel hydroxide layer on the nickel cathode (C) with a nickel anode (A).

Monomers identification by GC-MS. To identify monomers generated during depolymerization, a Gas Chromatograph coupled to a Mass Spectrometer (GC-MS) is used, specifically an Agilent 5975C TAD GC×GC-MS system. Samples are prepared by dissolving them in methanol at a 1:9 mass ratio, followed by filtration through a 0.2 µm membrane (). A splitless injection method is employed to maximize peak signals and improve identification accuracy.

Results and Discussion

Effects of electrolyte composition

Diluting BL with water and white liquor. Chronoamperometry experiments conducted in the voltage range of 1 to 3 V reveal that diluting black liquor (BL) with water (W) and white liquor (WL) enhances both electrical conductivity and electrode stability, reducing the formation of deposits. Transitioning from intermediate to weak BL further improves conductivity, lowers viscosity, and decreases the diffusion layer thickness. The optimal electrolyte composition for achieving current stability was found to be a volumetric ratio of BL:W:WL = 2:1:1 (Figure 6). This ratio facilitated the formation of xylene, confirmed by GC-MS analysis. . Additionally, diluting BL (resulting in lower lignin concentrations) increased the ratio of depolymerized lignin to repolymerized lignin. However, increasing salt content in the electrolyte showed diminishing returns beyond a certain threshold, as ion clusters and aggregates began to form. Despite these observations, GPC and HPLC analyses indicated no significant change in molecular weight distribution or composition.

Effect of adding alcohols. The utilisation of alcohols as capping agents effectively prevented oxidative repolymerization of lignin fragments. Among the tested alcohols, ethanol and 1-propanol exhibited the highest current density and stability (Figure 7). However, the operational voltage range could not be extended beyond 2.25 V during continuous operation. Cathodic hydrogenolysis of lignin fragment intermediates and alcohols produced aromatic hydrocarbons, including toluene and xylene, as identified by GC-MS.

Importance of electrode material

Cathode materials selection. The choice of cathode material significantly influences the electrochemical depolymerization process. Copper demonstrates high current density and efficient monomer formation at 2 V. However, repolymerization occurs around 2.25 V, and above 2 V, the current

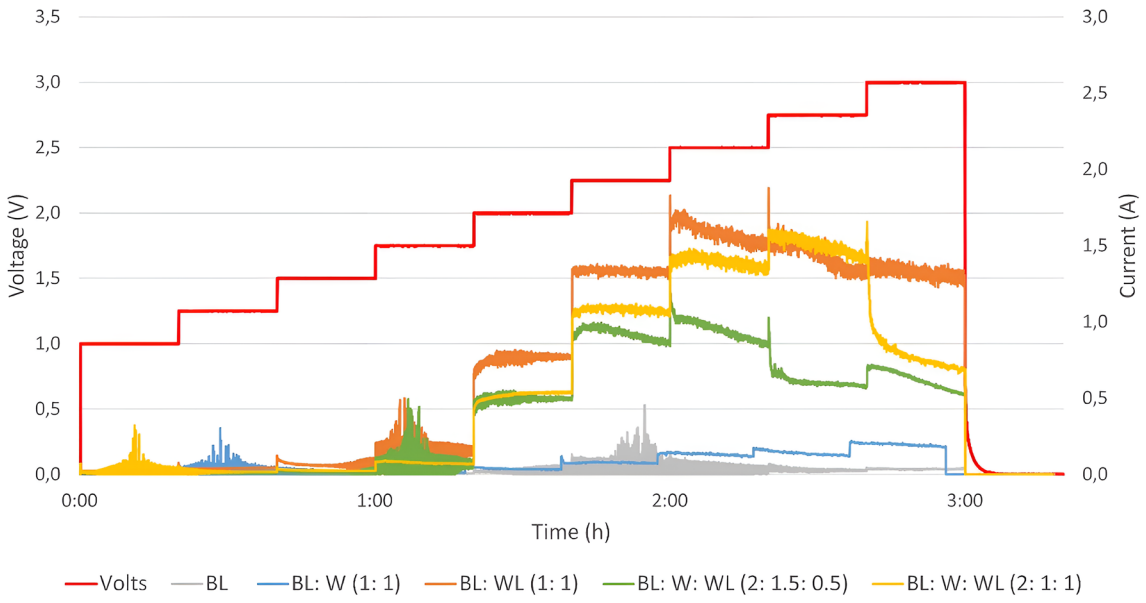

Figure 6. Chronoamperometry step test for BL: W: WL in different ratios with Ni electrodes.

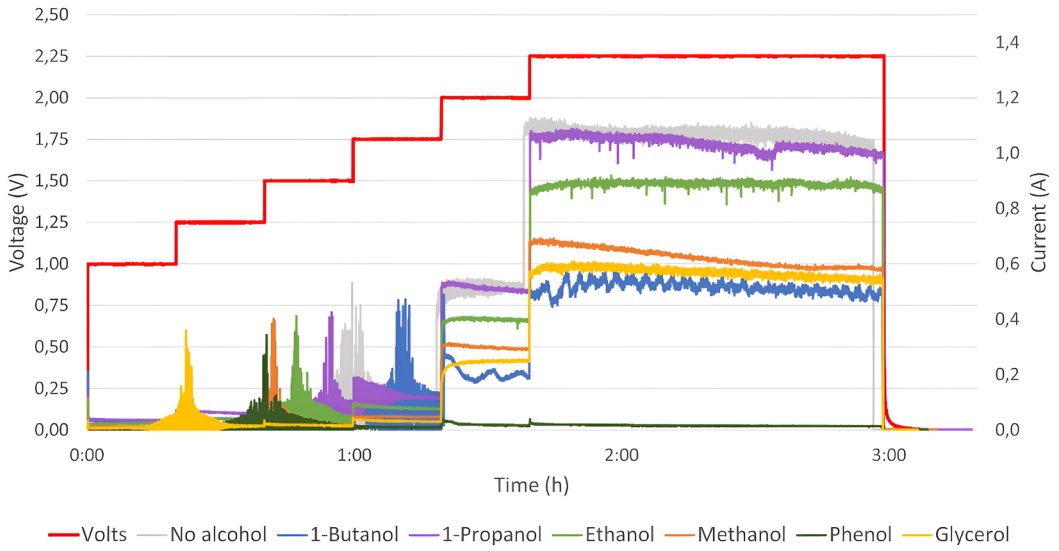

Figure 7. Chronoamperometry step test for BL: W: WL: Alcohol (20: 7.5 :7.5 :5) for different alcohols with Ni electrodes.

becomes highly unstable. In contrast, lead exhibits low and unstable currents across the entire voltage range, making it unsuitable for stable operation. Stainless steel (AISI 304) offers a more stable performance compared to copper or lead, but it has lower activity for lignin oxidation than nickel, as reported by Oliveira *et al.*[37]. Nickel, on the other hand, provides the most stable current across the voltage range and results in minimal deposit formation on the electrode surface, preventing reaction inhibition. Moreover, nickel is advantageous due to its low cost, making it the most promising cathode material for this process. These comparative performances are illustrated in Figure 8.

Inspection of the spent electrodes did not show any deposits for the case of Nickel and stainless steel electrodes. Copper and lead electrodes, instead show significant deposits, indicating that the current fluctuations and the current drop over time are a result of the layer formation. This shows that among the tested materials only Nickel and stainless steel are suitable cathode materials.

Modification of nickel anode. A NiOOH layer is successfully formed on the nickel anode, as indicated by the black deposit observed on its surface (Figure 9, left). This modified anode is then placed in the electrochemical cell, and the

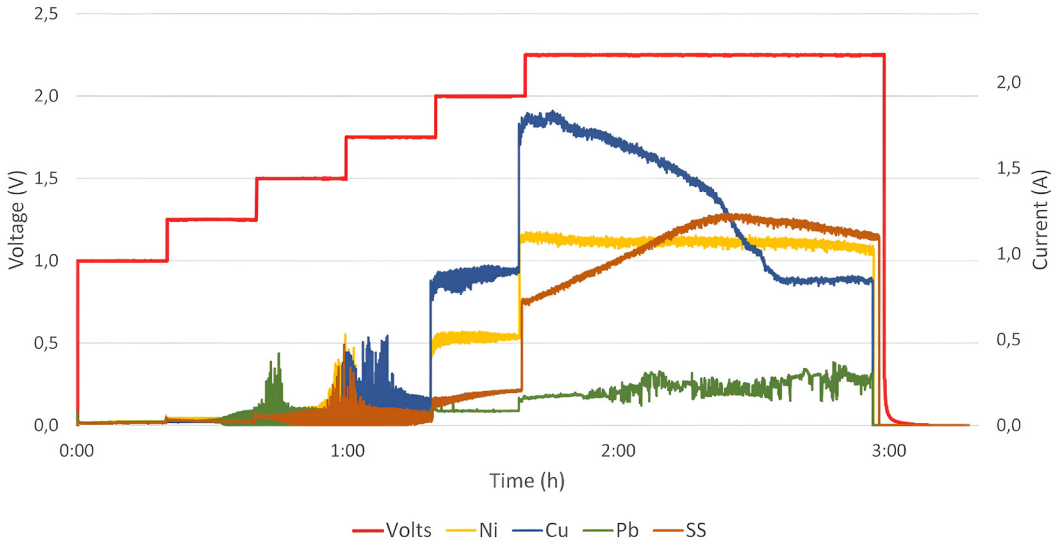

Figure 8. Chronoamperometry step test for different cathode materials, with BL: W: WL (2: 1: 1) and Ni anode.

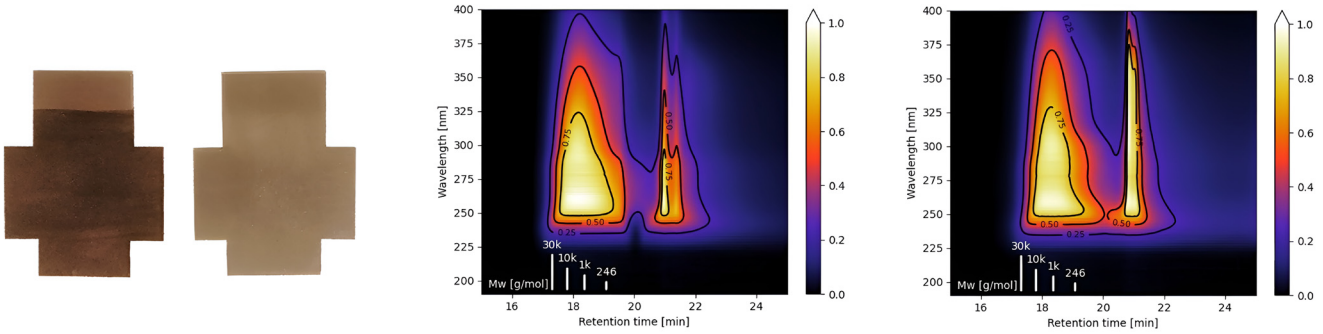

Figure 9. Visual aspect of electrodes after electrolysis test(left), and molecular weight distribution 3D DAD spectra of depolymerisation products, with NiOOH layer (middle) and without (right) showing the formation of low molecular weight products after 20 min of retention time.

experiment is conducted. The DAD spectra show that the formation of monomers is reduced when the preliminary NiOOH layer is applied to the nickel anode (Figure 9, right). Therefore, with this specific electrolyte, the application of the nickel oxide layer does not enhance depolymerization relative to repolymerization. One potential explanation for this observation is that the NiOOH layer is not sufficiently homogeneous when formed using this method. Furthermore, while the current stability is similar whether or not the NiOOH layer is applied, a current drop occurs sooner when the NiOOH layer is present, as shown in Figure 10.

Conclusion

The influence of electrode materials and electrolyte composition on the electrochemical depolymerization of lignin from Kraft black liquor has been investigated using a small-scale electrochemical cell. The study demonstrated that diluting black liquor with water and white liquor improves both electrical conductivity and electrode stability. Adding alcohols such as ethanol and 1-propanol effectively promotes lignin depolymerization over repolymerization, leading to the formation of aromatic monomers such as toluene and xylene. Regarding cathode materials, nickel showed the best performance, offering the most stable current and the least deposit formation compared to copper, lead, and stainless steel.

Overall, the optimal results in terms of depolymerization efficiency and current stability were achieved with nickel electrodes and an electrolyte composed of black liquor, water, white liquor, and ethanol or 1-propanol in a volumetric ratio of 20:7.5:7.5:5. The objectives outlined at the beginning of this study were successfully met. However, there are still opportunities for further optimization of the electrochemical depolymerization process.

To improve the analysis of reaction products, LC-MS should be used to combine monomer detection by liquid chromatography (currently achieved by GPC or HPLC) with their identification through mass spectrometry (currently performed with GC-MS). This combined approach would address the

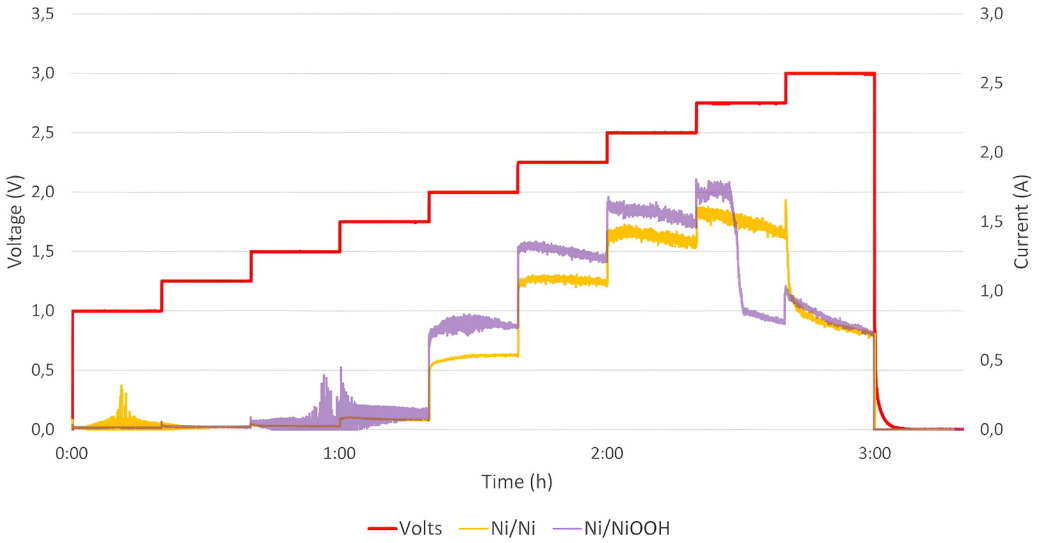

Figure 10. Chronoamperometry step test for BL: W: WL (2: 1: 1) with and without a NiOOH layer on the anode.

challenge of associating low-molecular-weight molecules with their structures, as current analytical methods are divided and do not provide quantitative monomer results. Additionally, phenolic monomers have not yet been detected.

An online-GC system could also be implemented to monitor the formation of gases such as oxygen and hydrogen in real-time during the experiment. Although the online-GC system was connected to the setup, missing equipment, such as a flowmeter for calibrating the nitrogen flow, prevented its proper use.

Finally, extended chronoamperometry tests at a constant voltage should be conducted to evaluate long-term stability. A redesigned electrochemical cell with a larger electrode surface area could improve performance, and a longitudinal design might lead to a more uniform flow of electrolyte. A pilot reactor for the system has already been constructed and will facilitate further optimization and scaling up of the reaction.

Ethics and consent

Ethical approval and consent were not required.

Data availability

ZENODO: EBIO Repository. Lab journal Chloe Roux - Electrochemical lignin conversion., Doi: https://doi.org/10.5281/zenodo.14230852[42]

The project contains the following underlying data:

- Digital Lab Journal 2023 SINTEF

(Detailed description of electrochemical experiments performed, including electrolyte composition, process parameters, voltage and current recordings over time).

References

1. Trebostad M: **Renewable chemicals from lignin – a conceptual evaluation of thermochemical processes for production of valuable chemicals from lignin**. Norwegian University of Life Sciences, Ås, 2016.
Reference Source
2. Dahmen N, Lewandowski I, Zibek S, *et al.*: **Integrated lignocellulosic value chains in a growing bioeconomy: status quo and perspectives.** *Glob Change Biol Bioenergy.* 2019; **11**(1): 107–117.
Publisher Full Text
3. Brandt A, Gräsvik J, Hallett J, *et al.*: **Deconstruction of lignocellulosic biomass with ionic liquids.** *Green Chem.* 2013; **15**(3): 550–583.
Publisher Full Text
4. Isikgor FH, Remzi Becer C: **Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers.** *Polym Chem.* 2015; **6**: 4497–4559.
Publisher Full Text
5. Pettersen RC: **The chemical composition of wood.** *The Chemistry Of Solid Wood.* 1984; **207**: 57–126.
Publisher Full Text
6. Mazela B, Perdoch W, Peplińska B, *et al.*: **Influence of chemical pretreatments and ultrasonication on the dimensions and appearance of cellulose fibers.** *Materials (Basel).* 2020; **13**(22): 5274.
PubMed Abstract | **Publisher Full Text** | **Free Full Text**

7. Hu LS, Fang XZ, Du MH, *et al.*: **Hemicellulose-based polymers processing and application.** *Am J Plant Sci.* 2020; **11**(12): 2066–2079.
Publisher Full Text

8. Deshavath NN, Veeranki VD, Goud VV: **Chapter 1 - Lignocellulosic feedstocks for the production of bioethanol: availability, Structure, and composition**. In: *Sustainable Bioenergy*. Guwahati, India, 2019; 1–19.
Publisher Full Text

9. Jönsson AS: **5 - membranes for lignin and hemicellulose recovery in pulp mills**. In: *Membrane Technologies for Biorefining*. Lund, Sweden, 2016; 105–133.
Publisher Full Text

10. Lisý A, Ház A, Nadányi R, *et al.*: **About hydrophobicity of lignin: a review of selected chemical methods for lignin valorisation in biopolymer production.** *Energies.* 2022; **15**(17): 6213.
Publisher Full Text

11. American International Forest Products: **Hardwood vs. softwood: understanding the difference**. April 11, 2022; [Accessed 14 July 2023].
Reference Source

12. Lourenço A, Pereira H: **Compositional variability of lignin in biomass**. In: *Lignin - Trends and Applications*. InTech, 2018; 65–98.
Publisher Full Text

13. Suota MJ, Da Silva TA, Zawadzki SF, *et al.*: **Chemical and structural characterization of hardwood and softwood LignoForce™ lignins.** *Ind Crops Prod.* 2021; **173**: 114138.
Publisher Full Text

14. Kai D, Chow LP, Loh XJ: **Chapter 1: lignin and Its properties**. In: *Functional Materials From Lignin*. World Scientific, 2018; 1–28.
Publisher Full Text

15. Tran MH, Phan DP, Lee EY: **Review on lignin modifications toward natural UV protection ingredient for lignin-based sunscreens.** *Green Chem.* 2021; (13): 4633–4646.
Reference Source

16. Precedence Research: **Pulp and paper market**. June 2022; [Accessed 25 July 2023].
Reference Source

17. Lu X, Gu X, Shi Y: **A review on lignin antioxidants: their sources, isolations, antioxidant activities and various applications.** *Int J Biol Macromol.* 2022; **210**: 716–741.
PubMed Abstract | Publisher Full Text

18. Norgren M, Edlund H: **Lignin: recent advances and emerging applications.** *Curr Opin Colloid Interface Sci.* 2014; **19**(5): 409–416.
Publisher Full Text

19. Pola L, Collado S, Oulego P, *et al.*: **Kraft black liquor as a renewable source of value-added chemicals.** *Chemical Engineering Journal.* 2022; **448**: 137728.
Publisher Full Text

20. Mboowa D: **A review of the traditional pulping methods and the recent improvements in the pulping processes.** *Biomass Conv Bioref.* 2024; **14**(1): 1–12.
Publisher Full Text

21. Kim KH, Kim CS: **Recent efforts to prevent undesirable reactions from fractionation to depolymerization of lignin: toward maximizing the value from lignin.** *Front Energy Res.* 2018; **6**: 92.
Publisher Full Text

22. Zirbes M, Schmitt D, Beiser N, *et al.*: **Anodic degradation of lignin at active transition metal-based alloys and performance-enhanced anodes.** *ChemElectroChem.* 2019; **6**(1): 155–161.
Publisher Full Text

23. Cai J, He Y, Yu X, *et al.*: **Review of physicochemical properties and analytical characterization of lignocellulosic biomass.** *Renew Sustain Energy Rev.* 2017; **76**: 309–322.
Publisher Full Text

24. Roy R, Rahman MS, Amit TA, *et al.*: **Recent advances in lignin depolymerization techniques: a comparative overview of traditional and greener approaches.** *Biomass.* 2022; **2**(3): 130–154.
Publisher Full Text

25. Zhou N, Wass Thilakarathna WPD, He QS, *et al.*: **A review: depolymerization of lignin to generate high-value bio-products: opportunities, challenges, and prospects.** *Front Energy Res.* 2022; **9**: 758744.
Publisher Full Text

26. Wang H, Peng X, Li H, *et al.*: **Recent biotechnology advances in bio-conversion of lignin to lipids by bacterial cultures.** *Front Chem.* 2022; **10**: 894593.
PubMed Abstract | Publisher Full Text | Free Full Text

27. Garedew M, Lam CH, Petitjean L, *et al.*: **Electrochemical upgrading of depolymerized lignin: a review of model compound studies.** *Green Chem.* 2021; **23**: 2868–2899.
Publisher Full Text

28. Du X, Zhang H, Sullivan KP, *et al.*: **Electrochemical lignin conversion.** *ChemSusChem.* 2020; **13**(17): 4318–4343.
PubMed Abstract | Publisher Full Text

29. Di Marino D, Stöckmann D, Kriescher S, *et al.*: **Electrochemical depolymerisation of lignin in a deep eutectic solvent.** *Green Chemistry.* 2016; **18**(22): 6021–6028.
Publisher Full Text

30. Di Fidio N, Timmermans JW, Antonetti C, *et al.*: **Electro-oxidative depolymerisation of technical lignin in water using platinum, nickel oxide hydroxide and graphite electrodes.** *New J Chem.* 2021; **45**(21): 9647–9657.
Publisher Full Text

31. Reichert E, Wintringer R, Volmer DA, *et al.*: **Electro-catalytic oxidative cleavage of lignin in a protic ionic liquid.** *Phys Chem Chem Phys.* 2012; **14**(15): 5214–5221.
PubMed Abstract | Publisher Full Text

32. Dier TKF, Rauber D, Durneata D, *et al.*: **Sustainable electrochemical depolymerization of lignin in reusable ionic liquids.** *Sci Rep.* 2017; **7**(1): 5041.
PubMed Abstract | Publisher Full Text | Free Full Text

33. Stecker F, Malkowsky IM, Fischer A, *et al.*: **Method for producing vanillin by electrochemical oxidation of aqueous lignin solutions or suspensions**. Germany, Patent US20130040031A1, August 08, 2012.
Reference Source

34. Chang X, Van der Zalm J, Thind SS, *et al.*: **Electrochemical oxidation of lignin at electrochemically reduced TiO_2 nanotubes.** *J Electroanal Chem.* 2020; **863**: 114049.
Publisher Full Text

35. Griesbach U, Fischer A, Stecker F, *et al.*: **Method for electrochemically cleaving lignin on a diamond electrode**. Patent WO 2009/138368, (19.11.2009 Gazette 2009/47).
Reference Source

36. Friedrich JM, Ponce-de-Léon C, Reade GW, *et al.*: **Reticulated Vitreous Carbon as an electrode material.** *J Electroanal Chem.* 2004; **561**: 203–217.
Publisher Full Text

37. Oliveira RCP, Buijnsters JG, Mateus MM, *et al.*: **On the electrooxidation of kraft black liquor on boron-doped diamond.** *J Electroanal Chem.* 2022; **909**: 116151.
Publisher Full Text

38. Oliveira RCP, Mateus M, Santos DMF: **Chronoamperometric and chronopotentiometric investigation of Kraft black liquor.** *Int J Hydrogen Energy.* 2018; **43**(35): 16817–16823.
Publisher Full Text

39. Shao D, Liang J, Cui X, *et al.*: **Electrochemical oxidation of lignin by two typical electrodes: Ti/Sb-SnO_2 and Ti/PbO_2.** *Chem Eng J.* 2014; **244**: 288–295.
Publisher Full Text

40. Zhu H, Wang L, Chen Y, *et al.*: **Electrochemical depolymerization of lignin into renewable aromatic compounds in a non-diaphragm electrolytic cell.** *RSC Adv.* 2014; **4**(56): 29917–29924.
Publisher Full Text

41. Tolba R, Tian M, Wen J, *et al.*: **Electrochemical oxidation of lignin at IrO_2-based oxide electrodes.** *J Electroanal Chem.* 2010; **649**(1–2): 9–15.
Publisher Full Text

42. Roux C: **Lab journal Chloe Roux - Electrochemical lignin conversion.** http://www.doi.org/10.5281/zenodo.14230852

43. Fischer K, Höffler S: **RP-HPLC analysis of phenolic lignin monomers with DAD and coulometric array detection.** *J Chromatogr Sci.* 2021; **59**(4): 312–324.
PubMed Abstract | Publisher Full Text

Open Peer Review

Current Peer Review Status: ?

Version 1

Reviewer Report 23 September 2025

https://doi.org/10.21956/openreseurope.20625.r59475

?

Xabier Erdocia
[1] University of the Basque Country Language and Speech Laboratory, Vitoria-Gasteiz, Basque Country, Spain
[2] Applied Mathematics, University of the Basque Country UPV/EHU, Donostia-San Sebastián, Basque Country, Spain

The manuscript entitled “Electrochemical lignin depolymerization-effects of electrolyte composition and electrode materials” investigates the optimization of lignin depolymerization from Kraft black liquor using electrochemical methods. The study focuses on how electrolyte composition and electrode materials influence the efficiency and stability of the depolymerization process. The authors tested various electrolyte formulations by diluting black liquor with water, white liquor, and alcohols in various ratios, and evaluated different cathode materials (nickel, copper, lead, and stainless steel), while keeping nickel as the anode. Following depolymerization, the reaction products were thoroughly analyzed GPC, HPLC and GC/MS, allowing the authors to assess molecular weight distribution and identify aromatic monomers. The authors concluded that alcohols such as ethanol and 1-propanol were found to prevent oxidative repolymerization and promote depolymerization. In addition, they stated that nickel emerged as the most promising cathode material due to its stable performance and minimal deposit formation. Additionally, the authors explored the effect of modifying the nickel anode with a NiOOH layer, but they claimed that this did not enhance depolymerization efficiency. The study concluded that the optimal setup involves nickel electrodes and an electrolyte composed of black liquor, water, white liquor, and alcohol (ethanol or 1-propanol) in a volumetric ratio of 20:7.5:7.5:5. Finally, the authors suggest that future studies should incorporate LC/MS to combine monomer detection and identification in a single platform, improving analytical resolution. They also propose implementing online-GC for real-time gas monitoring and redesigning the electrochemical cell to enhance the performance and obtain a more uniform flow of electrolyte. Furthermore, they report that a pilot reactor has already been constructed to support further development and scale-up of the process.
The scope of the study is clearly defined and highly relevant to the field of lignin valorization. In addition, a wide range of analytical techniques were employed, providing a thorough characterization of the depolymerization products. The manuscript is well-written and logically

structured, with a clear discussion of the results. Moreover, the comparison of different cathode materials is well-supported and offers practical insights for electrochemical cell design. However, there are also some weaknesses that should be addressed. Based on these considerations, minor revision of the article is recommended.

To improve the clarity of the manuscript, the authors might want to address the following comments:

1. Although aromatic monomers are identified, no quantitative data on monomer yields are provided. Some results of HPLC and CG/MS analysis should be included in the main article.

2. Were the chronoamperometry experiments performed in triplicate to ensure reproducibility? If so, could you include average values and standard deviations?

3. The NiOOH layer did not improve performance, but the reasons for this are not deeply explored, nor are alternative approaches suggested. Some explanation should be included.

4. The authors selected a volumetric ratio of 20:7.5:7.5:5 for the electrolyte, but no justification or comparison with other ratios is provided. Could the authors clarify whether other compositions were tested and why this specific ratio was chosen?

5. Was the pH of the electrolyte monitored or controlled during the experiments? Given the alkaline nature of black liquor and white liquor, it would be helpful to understand whether pH variations could have influenced the depolymerization efficiency or electrode stability.

6. Table 2 contains a formatting issue: the decimal values in the last column are separated by commas instead of periods. The authors should correct this.

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
No

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Biomass. Lignin. Statistics.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.