



Cesar Ramos Catizane

Improving pyrolysis oil processing via electrochemistry for plastics and biomass
feedstock recycling

School of Water, Energy and Environment

PhD

Academic Year: 2022 - 2025

Supervisor: Joy Sumner
Associate Supervisor: Ying Jiang
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Abstract

The environmental pressures of plastic waste accumulation and fossil fuel dependency have driven interest in technologies that enable the sustainable conversion of waste into valuable products. Pyrolysis offers a promising route for recycling biomass and plastic feedstocks into liquid fuels and chemical intermediates. However, the resulting pyrolysis oils are typically unstable, oxygen-rich, and incompatible with existing fuel infrastructure. This thesis investigates electrochemical hydrogenation (ECH) as a low-temperature, electrically-driven method for upgrading these oils under mild conditions using water as a hydrogen source, supporting circular economy goals.

The research combines model compound studies with real pyrolysis oil experiments, using a PtRu/ACC (platinum–ruthenium on activated carbon cloth) catalyst. Benzoic acid exhibited complete selectivity for cyclohexane carboxylic acid (100%) under optimised conditions. Notably, the presence of phenol enhanced benzoic acid conversion by up to 10%, due to a novel hydrogen-bond-assisted mechanism proposed in this work. This mechanism, which facilitates adsorption and lowers activation barriers, was supported by density functional theory (DFT) calculations and represents a previously unreported pathway in electrochemical hydrogenation. When applied to real bio-oils derived from pinewood and wheat straw, ECH reduced oxygenated species and increased alcohol content in the aqueous phase potentially improving both stability and energy content.

The oily phase was treated in methanol with conductivity enhancers. While NaCl improved reactivity, it caused significant catalyst degradation. Tetrabutylammonium hexafluorophosphate (TBAHFP), initially considered less corrosive, led to greater catalyst degradation but higher conversion of identifiable compounds, highlighting a trade-off between catalyst durability and product yield. Advanced characterisation (GC-MS, FTIR, SEM, EDS, XRD, Raman) confirmed these transformations and catalyst changes.

This work offers mechanistic insight and practical guidance for advancing electrochemical upgrading of pyrolysis oils, providing a foundation for scalable, low-carbon processes that integrate waste into the energy and chemical sectors.

Keywords: Biofuels, catalysis, circular economy, density functional theory, electrochemistry, and hydrogenation.

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List of Abbreviations

ACC	Activated Carbon Cloth
AEM	Anion Exchange Membrane
BA	Benzoic Acid
CAPE	Capital Expenditures
CCA	Cyclohexane Carboxylic Acid
CEM	Cation Exchange Membrane
CSTR	Continuous Stirred Tank Reactor
CV	Cyclic Voltammetry
DCM	Dichloromethane
DES	Deep Eutectic Solvent
DFT	Density Functional Theory
ECH	Electrochemical Hydrogenation
EDS	Energy-Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FCR	Flow Cell Reactor
FE	Faradaic Efficiency
FTIR	Fourier Transform Infrared Spectroscopy
FW	Food Waste
FWSD	Food Waste Solid Digest
GC-M	Gas Chromatography-Mass Spectrometry
GGA	Generalized-Gradient Approximation
HDO	Hydrodeoxygenation
HDPE	High-Density Polyethylene
HER	Hydrogen Evolution Reaction
HHV	High Heating Values
IR	Infrared
LDPE	Low-Density Polyethylene
LSV	Linear Sweep Voltammetry
m/z	Mass-to-Charge Ratio
MEP	Minimum Energy Path
MPO	Mixed Polyolefin
NaCl	Sodium Chloride
NADES	Natural Deep Eutectic Solvent
NEB	Nudged Elastic Bands
OCP	Open Circuit Potential
OPEX	Operation Expenses
PBE	Perdew-Burke-Ernzerhof
PCW	Post-Consumer Waste

PET	Polyethylene Terephthalate
PFR	Plug Flow Reactor
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
PW	Pinewood Bio-oil
PW _{aq}	Pinewood Bio-oil aqueous phase
PW _{NaCl}	Pinewood Bio-oil oily phase with NaCl
PW _{TBAHFP}	Pinewood Bio-oil oily phase with TBAHFP
SCF	Self-Consistent Field
SDG	Sustainable Development Goals
SEM	Scanning Electron Microscopy
TBAHFP	Tetrabutylammonium Hexafluorophosphate
TMP	Trimethyl Phosphate
WS	Wheat Straw Bio-oil
WS _{aq}	Wheat Straw Bio-oil aqueous phase
WSBO	Water-Soluble Bio-oil
WS _{NaCl}	Wheat Straw Bio-oil oily phase with NaCl
WS _{TBAHFP}	Wheat Straw Bio-oil oily phase with TBAHFP
XRD	X-ray Diffraction

1 Introduction

With the increasing severity of climate change and global warming, there is growing recognition of the urgent need to mitigate carbon emissions and those of other greenhouse gases. To address these environmental challenges, several key international targets and agreements have been established, including the United Nations' Agenda 2030 and the Paris Agreement. Agenda 2030 outlines a set of Sustainable Development Goals (SDGs), key targets including promoting effective waste management, preserving ocean ecosystems, and advancing climate change mitigation efforts (SDGs 7, 12, 13 and 14).¹

These goals are important because plastic production and utilisation continue to rise, leading to waste which needs to be reused, as plastics are used in an extensive range of everyday products (Figure 2-1). Options for this excess plastic are to either recycle it into new plastic feedstock or use it as a fuel. Similarly, biomass, while renewable, must be managed efficiently to maximise its potential as a sustainable source of valuable chemicals.

The growing reliance on plastics and the need for sustainable biomass utilisation have exacerbated environmental pressures, necessitating the development of effective and comprehensive solutions, one of which is pyrolysis.^{2,3} Overall, electrochemical hydrogenation of pyrolysis oils represents a promising strategy for upgrading renewable and recycled feedstocks, such as biomass and plastic waste, into high-value fuels and chemicals. This approach aligns with global efforts to transition to a low-carbon economy, reduce reliance on fossil fuels, and address the environmental challenges associated with plastic waste. Biomass can also fulfil these needs.

Pyrolysis, the thermal decomposition of organic materials in an inert environment, transforms feedstocks such as biomass, plastic waste, and other organic residues, into valuable products such as pyrolysis oil, syngas (a mixture of gases like hydrogen, carbon monoxide, and methane), and biochar. Unlike combustion or gasification, where oxygen is present and fuels are fully or partially oxidised, feedstocks are

decomposed instead of oxidised during the pyrolysis process, resulting in a range of intermediate products that retain the majority of the feedstock's chemical energy.^{4,5}

Depending on the operational conditions, such as temperature, heating rate and duration, pyrolysis can be categorised into 3 types: conventional (slow pyrolysis), fast and flash pyrolysis. Slow pyrolysis occurs at a slow heating rate, which permits the production of solids, liquids and gases in high proportions. Conversely, fast and flash pyrolysis yields mostly liquids and gases. Other variables that affect the yield and composition of the products are particle size, alkali content, pressure, pretreatment, overall composition of the feedstock, and the use of additives.^{6–9}

Table 1-1 - Range of the main operating parameters for different pyrolysis processes.^{4,6,7}

	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Pyrolysis temperature (K)	550-950	673-873	1050-1300
Heating rate (K s ⁻¹)	0.1-1	10-200	> 1000
Particle size (mm)	5-50	<1	< 0.2
Residence time (s)	450-550	0.5-10	< 0.5

Pyrolysis has gained significant interest in applications including bioenergy production, waste management, and environmental remediation. For example, biochar produced from pyrolysis can serve as a soil amendment, improving soil fertility and sequestering carbon.⁸

Biomass pyrolysis is viewed as a promising method for renewable energy production, as it converts plant-based materials into bio-oil that can be upgraded to biofuels. Plastic pyrolysis, on the other hand, provides an effective route for recycling a range of plastic waste, converting it into liquid fuels or chemical feedstocks, thus addressing plastic pollution and reducing reliance on fossil fuels.^{10–22} However, pyrolysis oils have high water content (up to 30%), high O:C ratio and unsaturated bonds, limiting their direct use in combustion engines and industrial processes due to high viscosity and corrosivity and low HHV (high heating values). Upgrading pyrolysis oils through hydrogenation or hydrodeoxygenation, where double bonds and oxygen-containing

functional groups are reduced, is essential to improve their stability, energy density, and compatibility with existing fuel infrastructure.^{8,10,23}

Traditional pyrolysis oil upgrading is typically conducted through high-pressure catalytic processes using gaseous hydrogen, often involving precious metal catalysts and high temperatures (see Chapter 2.3). However, this method is energy-intensive and relies on outside sources of hydrogen, which involves the risks associated with hydrogen storage and can counteract the environmental benefits of using biomass and plastic waste as feedstocks.^{24–27} Electrochemical hydrogenation (ECH) offers a more sustainable alternative, by leveraging renewable electricity and using water as the in-situ hydrogen source. In an electrochemical cell, pyrolysis oil components are selectively reduced at the cathode in the presence of protons, enabling hydrogenation without the need for high-pressure hydrogen gas.^{26,28–30} The step-by-step mechanism of ECH is described in Chapter 2.3.1.

The ECH process presents several advantages compared to traditional upgrading methods (see chapter 2.3), such as the potential for ambient temperature and pressure operation, lower energy consumption, and the ability to precisely control reaction conditions, which enables selective hydrogenation of targeted functional groups.³¹ However, various challenges must be addressed before scaling this technology for industrial applications. Those key challenges include developing robust and selective catalysts capable of handling the complexity of pyrolysis oil, optimising reaction conditions for efficiency and product specificity, and understanding the interactions among the hundreds of compounds in the mixture to minimise undesired side reactions such as polymerisation, addition, and dehydration. Tailoring these reactions is crucial for improving and standardising ECH, paving the way for its industrial implementation.

A major challenge in the ECH of whole pyrolysis oils lies in the incompatibility between water-based electrolytes (such as acids, alkalis, and salts) and pyrolysis oil. While water-based electrolytes lead to low solubility of pyrolysis oil compounds, nonpolar solvents (e.g., methanol, dichloromethane) exhibit high solubility but low conductivity. Research efforts are focused on exploring alternative electrolytes, advanced catalysts such as metal alloys, transition metals, and carbon-based materials, and optimising cell designs to enhance the performance and scalability of ECH.^{23,27,32–35}

1.1 Aims and Objectives

This project aims to investigate the extent to which electrochemical hydrogenation can be utilised to upgrade pyrolysis oil, improving its stability, increasing its calorific value, and reducing its corrosivity, thereby enhancing its potential as both a biofuel and a source of valuable chemicals.

Specific objectives:

1. To characterise the complex chemical composition of the pyrolysis oil using Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR), and subsequently identify and select its key representative compounds for use as model systems in initial electrochemical hydrogenation studies.
2. To investigate the electrochemical hydrogenation of selected model compounds, both individually and in mixtures, to elucidate the potential synergistic or anti-synergistic effects of co-reactants on reaction kinetics, Faradaic efficiency, and product distribution.
3. To employ Density Functional Theory (DFT) calculations to gain mechanistic insights into the electrochemical hydrogenation of the model compounds, aiming to understand reaction pathways, identify key intermediates, and propose a reaction mechanism that can explain the observed experimental outcomes.
4. To assess the feasibility of applying the optimised electrochemical hydrogenation conditions to real pyrolysis oil, evaluating the performance of a chosen feasible electrolyte and investigating the necessity and impact of using specific additives to enhance the upgrading process for industrial application.

1.2 Thesis Structure and Overview of the Papers

The thesis is based on research presented in five papers, outlined in Table 1-2. For reference, the papers are numbered one to five, with their designations and the candidate's specific contributions detailed in Table 1-2. An overview of the analytical and modelling techniques used in this thesis is in Chapter 1.3.

A brief overview and introduction to the topics and methodologies used throughout the research are outlined in the thesis, Sections 1.2. and 1.3. A more detailed review of

the literature and an introduction to the topics specific to each paper are given within the papers themselves. A summary overview of each paper, highlighting the specific questions it sets out to answer, the paper's aims and its contributions to knowledge is given in Chapters 1.2.1 to 1.2.5.

Table 1-2 - List of research papers

Paper number	Title	Candidate's contribution to papers	Additional author's contributions to papers	Status	Journal	DOI
One	Improving plastic pyrolysis oil quality via an electrochemical process for polymer recycling: a review	The candidate conducted the literature review and was the primary author of the paper	J Sumner and Y. Jiang – supervised the research, revised the manuscript and contributed to technical content of paper	Published	<i>Energy Advances</i> , 2024, 3 , 366-388	DOI: 10.1039/D3YA00389B
Two	Mechanisms of Electrochemical Hydrogenation of Aromatic Compound Mixtures over a Bimetallic PtRu Catalyst	The candidate conducted the experimental work and analysis/imaging. The candidate was the primary author of the paper.	J. Sumner and Y. Jiang – supervised the research, revised the manuscript and contributed to technical content of paper	Published	Communications Chemistry	DOI: 10.1038/s42004-025-01413-5
Three	Hydrogen Bond Enhanced Electrochemical Hydrogenation of Benzoic Acid over a Bimetallic Catalyst	The candidate conducted the experimental work and analysis/imaging. The candidate was the primary author of the paper.	J. Sumner and Y. Jiang – Supervised the research, revised the manuscript and contributed to technical content of paper	Published	Sustainable Energy & Fuels	DOI: 10.1039/D5SE00246J
Four	Pinewood and wheat straw bio-oil aqueous phase electrochemical hydrogenation utilising a PtRu/ACC catalyst	The candidate conducted the experimental work and analysis/imaging. The candidate was the primary author of the paper.	J. Sumner and Y. Jiang – supervised the research, revised the manuscript and contributed to technical content of paper Scott Banks – provided the bio-oils, revised the manuscript and	Under review	<i>ACS Sustainable Chemistry & Engineering</i>	

			contributed to technical content of paper			
Five	Mild electrochemical hydrogenation upgrading of pinewood and wheat straw bio-oil	The candidate conducted the experimental work and analysis/imaging. The candidate was the primary author of the paper.	J. Sumner and Y. Jiang – Supervised the research, revised the manuscript and contributed to technical content of paper Scott Banks – provided the bio-oils, revised the manuscript and contributed to technical content of paper	Drafted	TBC	

When addressing ECH upgrading of bio-oils, this thesis is split into two areas: model compounds and real bio-oil. In addition, a review paper (paper 1) has been written which covers the foundations of ECH and highlights the research gap addressed in this thesis.

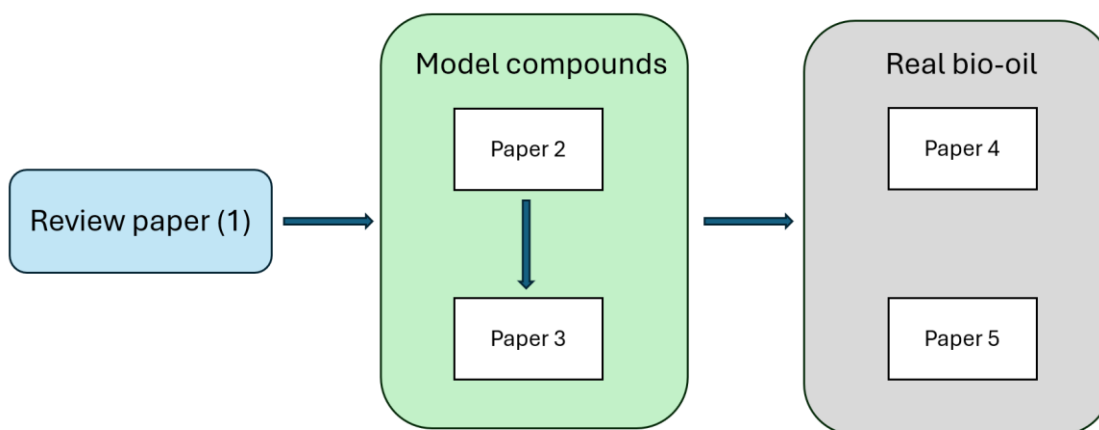


Figure 1-1 - Subject area covered by papers.

Paper 2 covers the ECH of model compounds, focusing on benzoic acid, phenol and guaiacol. The ECH of said compound mixtures was also carried out, utilising a factorial design of experiment. The findings from this study spurred the hypothesis that was the basis for paper 3; that the addition of phenol could enhance benzoic acid hydrogenation. Papers 4 and 5 focus on the ECH of real bio-oil; where paper 4 focuses on the aqueous share of the bio-oil, and paper 5 on the oily phase. Table 1-3 relates the papers and the objectives that were covered in each of them.

Table 1-3 – Objectives addressed by each paper

Paper	Chapter number	Objectives covered
Paper 1	2	1
Paper 2	3	2, 3
Paper 3	4	2, 3
Paper 4	5	1, 4
Paper 5	6	1, 4

1.2.1 Paper 1 Overview

The paper titled "Improving plastics pyrolysis oil quality via electrochemical process for polymer recycling: A review" examines the use of electrochemical hydrogenation to upgrade pyrolysis oils derived from plastics. This process is positioned as an important step towards establishing a circular economy for plastics while reducing reliance on fossil fuels.

The review investigates the inherent challenges of plastic pyrolysis oils, which are complex mixtures with high oxygen content, low pH, and high corrosivity, posing difficulties for storage, transport, and utilisation. ECH emerges as a viable alternative to traditional methods such as thermal cracking and catalytic hydrotreatment, operating under mild conditions (<80°C and 1 atm) without requiring external hydrogen supplies, offering sustainability and cost-effectiveness. Diagrams of the ECH cell configuration, setup and operation can be found in Figure 2-6, Figure 3-1, Figure 5-1 and Figure 6-1.

Advances in ECH are discussed, including the influence of variables such as cathode materials, with ruthenium and platinum-ruthenium alloys showing promise for efficient hydrogenation. The review also explores the issue of low conductivity in pyrolysis oils and proposes solutions like conductive additives or innovative solvents. The potential of ECH products for integration into fuel production and their use as chemical feedstocks is highlighted, emphasising their contribution to a sustainable plastics economy.

1.2.2 Paper 2 Overview

The study titled "Mechanisms of Electrochemical Hydrogenation of Aromatic Compound Mixtures over a Bimetallic PtRu Catalyst", explores the electrochemical hydrogenation of benzoic acid, phenol, guaiacol, and their mixtures. The work aims to advance sustainable upgrading of bio-oil-derived compounds by investigating the reaction pathways and kinetics involved in their ECH using a bimetallic on activated carbon cloth (PtRu/ACC) catalyst.

Key findings include the high selectivity of benzoic acid for cyclohexane carboxylic acid (CCA) under all tested conditions, attributed to stable parallel adsorption on the PtRu cathode surface. Phenol was the most reactive model compound, achieving high conversion and Faradaic efficiency, while guaiacol showed lower reactivity due to its complex molecular structure. When tested as mixtures, the compounds exhibited both synergistic and antagonistic effects, with phenol often dominating the reaction pathways.

The study combines experimental analysis and density functional theory calculations to reveal that the stability of benzoic acid adsorption and the interaction dynamics between the compounds contribute significantly to the observed selectivity and conversion. This research provides valuable insights into optimising the ECH process for bio-oil upgrading, highlighting the potential for sustainable fuel and chemical production.

1.2.3 Paper 3 Overview

The paper "Hydrogen Bond Enhanced Electrochemical Hydrogenation of Benzoic Acid over a Bimetallic Catalyst" investigates the co-hydrogenation of benzoic acid and phenol using PtRu/ACC as the catalyst. It focuses on how hydrogen bonding between these compounds influences reaction dynamics, enhancing the efficiency and selectivity of the electrochemical hydrogenation process.

The study highlights that hydrogen bonding between the hydroxyl group in phenol and the carboxyl group in benzoic acid improves adsorption energy and lowers activation energy barriers. This facilitates the reduction of benzoic acid to cyclohexanemethanol, a product with reduced corrosiveness, higher energy density, and improved chemical properties for biofuel applications. Experimental results show that the optimal phenol concentration in the mixture enhances conversion, Faradaic efficiency, and product yields, with the 20:5 ratio mixture achieving the best performance.

DFT calculations support the findings by revealing that the formation of a hydrogen-bonded complex increases the stability of intermediate states and decreases activation barriers, enabling more efficient and selective hydrogenation. The work provides insights into optimising ECH processes for complex bio-oil mixtures, suggesting that leveraging hydrogen bonding interactions can improve catalyst performance and product selectivity. This approach has significant implications for sustainable chemical production and biofuel upgrading.

1.2.4 Paper 4 Overview

The study titled "Pinewood and wheat straw bio-oil aqueous phase electrochemical hydrogenation utilising a PtRu/ACC catalyst" investigates the application of electrochemical hydrogenation to upgrade bio-oil derived from the slow pyrolysis of wheat straw and pinewood. The research employs PtRu/ACC as the catalyst to target the aqueous phase of

bio-oil, aiming to reduce its oxygen content and improve its chemical stability and energy density.

The findings reveal that ECH effectively reduces phenolic and carbonyl compounds while increasing the concentration of alcohols. For pinewood-derived bio-oil, significant reductions were observed in phenolic compounds such as p-cresol (62.1%) and phenol (29.3%), with an overall increase in alcohol content from 49.3% to 56.5%. Similar trends were observed for wheat straw-derived bio-oil, where alcohol concentration also increased alongside reductions in key aromatic compounds. These transformations enhance the stability and calorific value of bio-oil, making it more suitable as a renewable fuel.

The study highlights the selectivity of ECH in targeting specific functional groups, with phenols showing higher reactivity compared to carboxylic acids, which remained largely unaffected. FTIR and GC-MS analyses confirm these compositional changes, showing increased alcohol content and reduced aromatic unsaturation. The work demonstrates the potential of ECH as a milder, more sustainable alternative to conventional hydrodeoxygenation methods, providing a pathway for scaling up bio-oil upgrading processes for industrial applications.

1.2.5 Paper 5 Overview

The paper titled "Pinewood and wheat straw pyrolysis bio-oil electrochemical hydrogenation utilising a PtRu/ACC catalyst" investigates the electrochemical hydrogenation of the oily phase of bio-oils derived from the slow pyrolysis of wheat straw and pinewood. Methanol is used as the catholyte, with either sodium chloride (NaCl) or tetrabutylammonium hexafluorophosphate (TBAHFP) added to enhance conductivity while balancing electrode stability.

The research reveals that ECH selectively targets phenolic compounds, hydrogenating them into more stable and energy-dense products. Methanol effectively dissolves the hydrophobic oily phase, enabling the conversion of its compounds. However, its low conductivity necessitates the use of additives. NaCl improves conductivity and reaction efficiency but causes significant corrosion to the PtRu/ACC electrode due to chloride-induced degradation. TBAHFP, while less corrosive in theory, also damages the electrode

through unexpected interactions, leading to surface wear. This additive promotes secondary reactions, such as the formation of trimethyl phosphate, which affects product composition.

FTIR and GC-MS analyses confirm a reduction in aromatic unsaturation content and an increase in alcohol content, demonstrating the process's effectiveness in improving bio-oil properties. Despite these advancements, the study highlights trade-offs between enhanced conductivity and electrode durability, suggesting that additive choice should be tailored to desired outcomes. The research emphasises the need for developing corrosion-resistant electrodes and optimised additives to advance ECH's scalability and efficiency for renewable fuel production.

1.3 Overview of the Analytical and Modelling Techniques Adopted in the Research Programme

1.3.1 Gas Chromatography-Mass Spectrometry

GC-MS is an analytical technique that separates, identifies, and quantifies compounds. It combines the features of gas chromatography, which separates volatile and semi-volatile compounds based on their boiling points and affinities to the stationary phase, and mass spectrometry, which provides detailed structural information about the separated compounds by ionising them and analysing their mass-to-charge ratio (m/z). GC-MS is highly sensitive, capable of detecting trace amounts of substances, and can provide structural information about unknown compounds through fragmentation patterns.³⁶

However, GC-MS is limited to volatile and thermally stable compounds. The method that will be utilised during this thesis reaches a maximum temperature of 300 °C, therefore compounds which present boiling temperatures over this limit will not be quantified. Another limiting factor is the boiling temperature of the solvent, the initial cut-off temperature was set to 40°C (DCM's boiling point), hence any compounds that are more volatile than DCM were also not quantified.

1.3.2 Fourier Transform Infrared Spectroscopy

FTIR is an analytical technique used to identify and characterise materials by measuring their absorption of infrared (IR) light. When IR radiation interacts with a sample, molecules absorb specific wavelengths that correspond to the vibrational frequencies of their chemical bonds. ^{37,38}

During FTIR analysis, the absorbed IR light generates a raw data format called an interferogram, which contains all the spectral information. This data is converted into a standard IR spectrum using a Fourier transform. The resulting spectrum displays wavelengths (or wavenumbers) plotted against absorbance or transmittance, with peaks indicating the presence of bond vibrations and functional groups in the sample. Vibrational frequencies of specific chemical groups occur within defined regions, influenced by the types of atoms involved and the nature of the bonds. Reference tables exist for the primary chemical groups. Within these regions, the exact frequencies can also be affected by the local chemical environment of the groups.^{37,38}

FTIR alone cannot conclusively identify unknown compounds³⁸, as it primarily provides information about functional groups rather than complete molecular structures. However, it is useful for qualitative analysis, such as detecting specific functional groups or monitoring changes in peak areas, which can indicate variations in compound concentrations.

1.3.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy is a non-destructive imaging technique used to examine the surface morphology and composition of materials at high magnifications and resolutions. SEM employs a focused beam of high-energy electrons to interact with the sample's surface, generating signals that yield information about surface topography, crystalline structure, electrical behaviour, and chemical composition.³⁹

When the electron beam strikes the sample, it produces various signals, including secondary electrons, backscattered electrons, and characteristic X-rays. Secondary electrons are primarily utilised for topographic imaging, as they provide high-resolution details of the surface. Backscattered electrons offer contrast based on the atomic number of the elements within the sample, making them valuable for compositional analysis. Characteristic X-rays enable qualitative and quantitative elemental analysis (elemental mapping) and can be detected through energy-dispersive X-ray spectroscopy (EDS).³⁹

1.3.4 Raman Spectroscopy

Raman spectroscopy studies the inelastic scattering of light, where the inelasticity arises from an energy transfer between the incident electromagnetic radiation and the material

under investigation. This technique provides valuable insights into the vibrational states of matter, among other properties.⁴⁰

During Raman spectroscopy, a monochromatic beam of intense electromagnetic radiation, typically a laser, is focused on the sample. Most photons are elastically scattered (Rayleigh scattering), but a small fraction experiences a shift in energy by interacting with molecular vibrations, either losing or gaining energy. This inelastic scattering is termed Raman scattering. The intensity of the scattered light is measured as a function of its wavelength. The Raman spectrum typically plots intensity against the Raman wavenumber, expressed in cm^{-1} , which corresponds to the frequency difference between the scattered light and the incident radiation. Each peak in the spectrum represents specific vibrational modes, revealing information about the molecular structure, functional groups, and chemical environment.^{40–42}

1.3.5 X-ray Diffraction (XRD)

X-ray Diffraction is an analytical technique used to determine the crystallographic structure, phase composition, and other structural properties of materials. It is based on the interaction of X-rays with the atoms in a crystalline material, producing a diffraction pattern that provides a fingerprint of the material's atomic arrangement.⁴³

In XRD, a focused X-ray beam is directed at a sample, and the diffracted rays are detected at specific angles. According to Bragg's Law (1-1), constructive interference occurs when the X-rays reflect from parallel planes of atoms in a crystal, satisfying the relationship between the wavelength (λ), interplanar spacing (d), and the angle of incidence (θ). The resulting diffraction pattern is unique to each crystalline material and contains information about its lattice parameters, phase purity, and crystallite size.⁴³

$$2d \sin\theta = m\lambda \quad (1-1)$$

1.3.6 Electrochemical Measurements

Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS) are fundamental techniques in electrochemical research, each offering unique insights into redox processes, reaction kinetics, and system properties.

LSV involves sweeping the potential linearly with time while recording the resulting current and is used for identifying the onset potential of redox reactions, evaluating electrode performance, and studying the kinetics of electrochemical processes. Figure 1-2 shows a schematic of the LSV and highlights the onset point, that is, the point where the applied potential is high enough to disturb the system and signifies the reduction peak. In this study, LSV will be used to identify reduction peaks and to measure the potential of different systems at current density = -10 mA cm^{-2} vs an Ag/AgCl reference electrode. This value is related to the increased activity associated with the hydrogen evolution reaction, the competing process during ECH. The more positive this value is, the better performance the system will present, concerning Faradaic Efficiency.

44,45

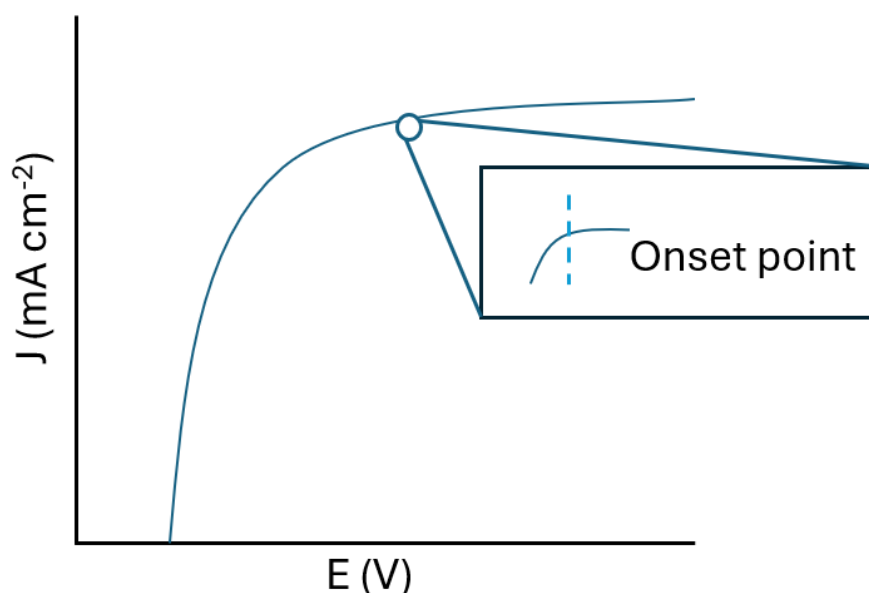


Figure 1-2 - Schematic representation of linear sweep voltammetry and a zoom-in on the onset point.

CV applies a cyclic potential sweep vs current, first in one direction and then reversing it, generating a voltammogram with forward and reverse sweeps. This technique allows detailed analysis of redox reactions, including reversibility, electron transfer kinetics, and the stability of intermediates. Key features like peak currents, peak potentials, and their separations provide insights into the electrochemical mechanisms at play. The traditional representation of a CV curve is the “duck-shaped” curve (Figure 1-3), showing both redox

peaks, however, the shape can be varied depending on the analysis parameters and the system.⁴⁶

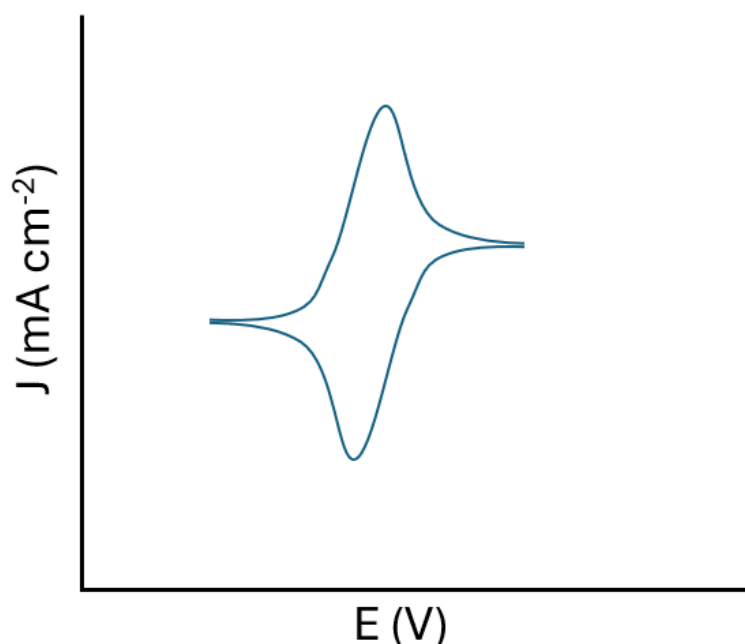


Figure 1-3 - A schematic representation of cyclic voltammetry.

Electrochemical Impedance Spectroscopy is a frequency-domain technique used to measure the impedance of an electrochemical system across a range of frequencies. Impedance is a generalised form of electrical resistance that accounts for both resistive and reactive components in a system. When a potential E is applied across a simple resistor R , a current I flows, with their relationship described by Eq. (1-2).⁴⁷

$$R = \frac{E}{I} \quad (1-2)$$

By applying a small sinusoidal potential perturbation and measuring the current response, EIS provides information on charge transfer resistance, double-layer capacitance, diffusion processes, and other system properties. The data are typically represented in the Nyquist plot (Figure 1-4) or Bode plot and can be modelled using equivalent circuits to interpret the system's physical and chemical behaviour. The distance between the onset points and the zero value on the axis is the Ohmic resistance, which represents the electric resistance of the electrolyte. In contrast, the diameter of the

curve (R_{ct}) represents the charge transfer resistance, where a larger diameter corresponds to higher R_{ct} , implying slower electron transfer at the interface.^{47,48}

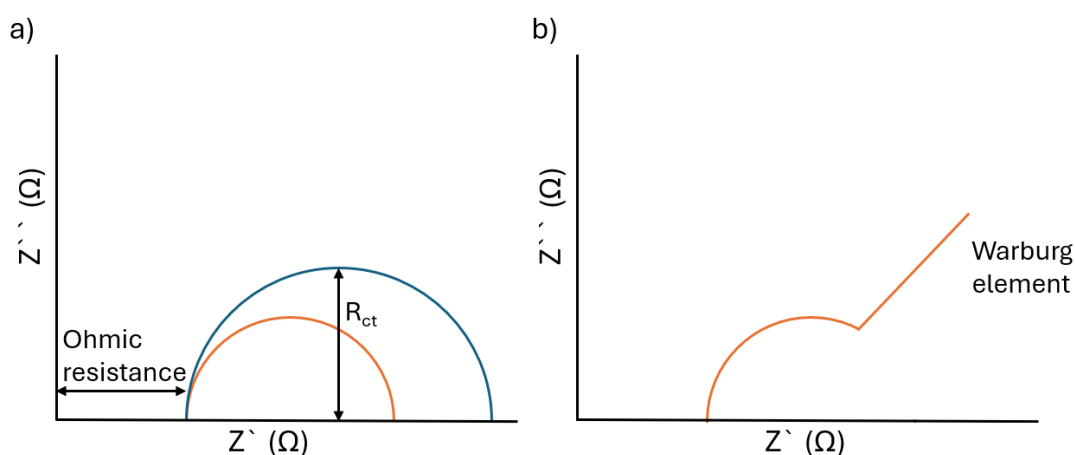


Figure 1-4 - A schematic representation of a Nyquist Plot from the EIS and (b) a representation of the presence of a Warburg element. Where R_{ct} is the charge transfer resistance.

1.3.7 Density Functional Theory Calculations

Density Functional Theory (DFT) is a quantum mechanical computational method used to study the electronic structure of many-body systems, particularly atoms, molecules, and solids. Instead of solving the complex many-electron wavefunction directly, DFT simplifies the problem by using the electron density as the fundamental variable.

In this work, particularly in papers 2 and 3, density functional theory calculations will be utilised to deepen the understanding of the interactions between model compounds and the cathode surface, as well as propose a hydrogenation mechanism for this system. Key parameters of concern in DFT calculations includes adsorption energy, Nudged Elastic Bands (NEB) and Electronic Structure and Charge Density Difference. The software utilised for these were the following:

- QuantumESPRESSO
- BurAI
- Vesta
- xCrysDen

Adsorption energy E_{ads} is defined as the difference between the energies of the initial components (calculated by the relaxation of the slab and the molecule separately) and the final system:

$$E_{ad} = E_{Total} - (E_{adsorbate} + E_{surface}) \quad (1-3)$$

Where E_{Total} is the calculated energy for the final system (slab + adsorbate), $E_{adsorbate}$ is the calculated energy of each adsorbate and $E_{Surface}$ is the energy of the bare cathode surface.

This value is important because it corresponds to the strength of the bond between the molecule (adsorbate) and the surface (adsorbent), where negative values are indicative of an exothermic and thermodynamically favourable process. A stronger bond (more negative value) is more stable, which influences reaction kinetics, selectivity, and catalyst stability.^{49,50}

NEB is a computational method used to determine the minimum energy path (MEP) and activation energy for reactions, especially those involving transitions between two stable states, such as reactants and products on a potential energy surface. In NEB calculations, a series of intermediate configurations (called "images") between the initial and final states are generated, forming a "band" along the reaction pathway. These images act as snapshots of atomic positions along the path from reactants to products. The goal of the NEB method is to adjust the positions of these images to accurately represent the lowest energy pathway between the initial and final states, identifying any transition states (saddle points) and the overall energy barrier (Figure 1-5).⁵¹⁻⁵³

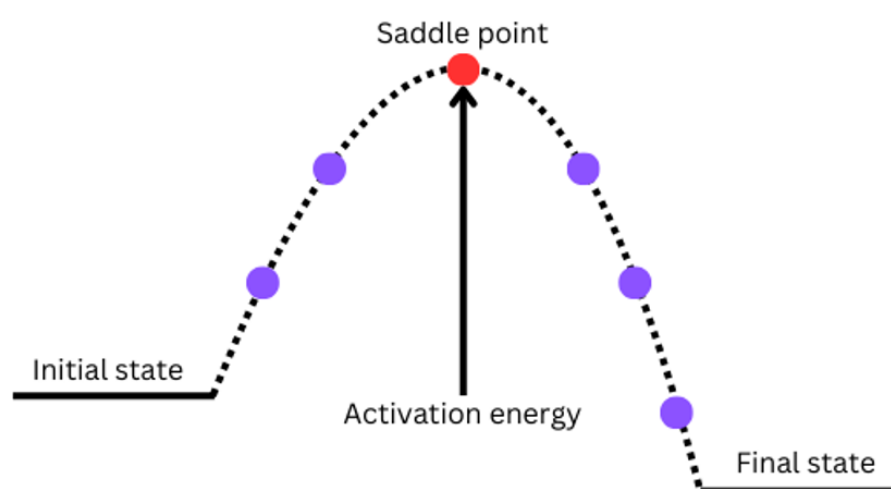


Figure 1-5 - Nudged elastic bands calculation

A series of self-consistent field (SCF) calculations are performed on each image until the set error value (eV/Å) is reached. The energy difference from the least stable image to the initial state is the energy barrier of the process. This calculation can be used to understand the reaction kinetics, such as the limiting step, as well as compare two different systems.^{51–53}

Charge density difference calculations are a tool utilised to understand changes in the electronic configuration of materials when two systems (such as adsorbent and adsorbate) interact. In this calculation, the charge density of each isolated component is calculated and subtracted from the charge density of the final system.^{54–56} Mathematically it is expressed as:

$$\Delta\rho = \rho_{adsorbate+surface} - (\rho_{adsorbate} + \rho_{surface}) \quad (1-4)$$

Where $\rho_{adsorbate+surface}$ is the electron density of the final system, $\rho_{adsorbate}$ and $\rho_{surface}$ are the electron density of the isolated adsorbate and surface, respectively.

The resulting charge density difference $\Delta\rho$ reveals where electrons are gained or lost upon interaction. Positive values of $\Delta\rho$ indicate regions where electron density has increased, suggesting electron accumulation, while negative values indicate areas of electron depletion. This spatial map of electron redistribution provides insight into the nature of the interaction.^{54–56}

2 Paper One: Improving plastics pyrolysis oil quality via electrochemical process for polymer recycling: A review

Cesar Catizane [a], Ying Jiang* [a] and Joy Sumner [a]

Abstract. Electrochemical hydrogenation (ECH) is a novel route for the upgrade of pyrolysis oil from both biomass and plastic feedstocks. Compared with conventional routes, including thermal cracking, ECH can be performed under mild conditions (<80°C and 1 atm) and without the requirement of additional H₂ supply. Successful demonstration of this application can be a critical step to enable a circular plastic economy and low-carbon fuel production. In this review we provide a critical overview of the recent advancements in understanding the variables that influence the ECH process is reviewed. In addition, we debate how this technology could be optimised and applied to plastic waste pyrolysis oil, assessing concerns such as the selection of cathode material, which needs to be resilient enough to address the complex nature of bio-oil. In addition, we present ideas on how to circumvent the challenge where the commonly used water-based electrolytes are unlikely to be suited for pyrolysis oil treatment. Finally, we discuss the possible utilisation of this product and the scalability of this process.

2.1 Introduction

With the increasing severity of climate change and global warming, there is a growing recognition of the pressing need to mitigate carbon emissions and other greenhouse gases. To address this environmental challenge, several key international targets and agreements have been established, including Agenda 2030 and the Paris Agreement. The United Nations' Agenda 2030 has outlined a set of sustainable development goals (SDGs). These goals encompass the effective management of waste, the preservation of ocean ecosystems, and the urgent undertaking of climate change mitigation efforts¹. Notably, plastic production and utilisation are becoming more prominent in daily life, as it is a material that is utilised in a huge amount of different day-to-day products, increasing plastic pollution, which demands effective and comprehensive solutions. The trend of mismanaged plastic waste is shown in Figure 2-1 ^{2,3}.

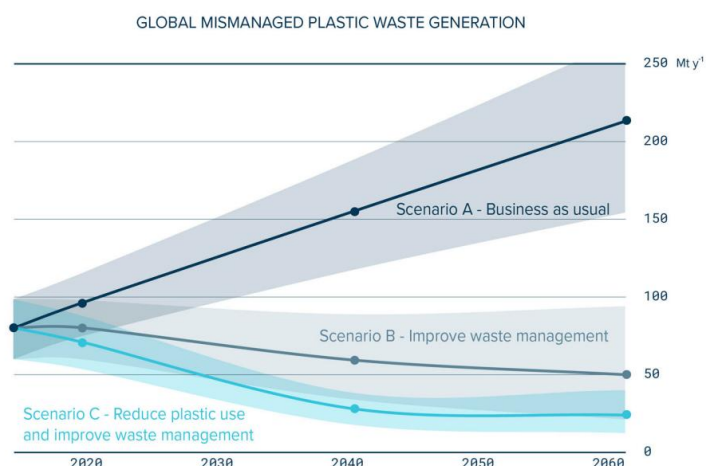


Figure 2-1 - The mismanaged plastic waste trend for three possible scenarios.²

Many of these plastic products are designed for single-use, often discarded when they are still in pristine condition ^{2,3}. In the EU for instance, in 2020, 29.5 million tonnes of post-consumer waste (PCW) plastics were collected and only 10% was sent to recycling plants, the majority of which via mechanical recycling ^{57–59}. This presents a significant challenge, as most of the plastic waste is either consigned to landfills or incinerated. There is considerable potential for expanding thermochemical recycling processes, with pyrolysis emerging as the most notable option ⁵⁸. Furthermore, the degradation and depolymerisation of plastic through weathering process leads to the production of micro and nano-plastics. These particles are ingested by animals, thereby introduced into the food chain, and causes food contamination for both animals and humans ⁶⁰.

Fast pyrolysis is a thermochemical process that occurs in an inert environment, in the range of 450 to 600°C and can be used for chemical recycling of biomass or plastic ⁸. This process products are separated in three categories: gas, wax, and oil. The resulting pyrolysis oil is a complex mixture composed of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, lignin-derived phenols, and extractible terpene with multi-functional groups ¹⁰. This is a product that potentially can be utilised as a biofuel, an alternative to petroleum-based fuels, or as feedstock for the chemical industry, which could help the creation of a circular economy ³².

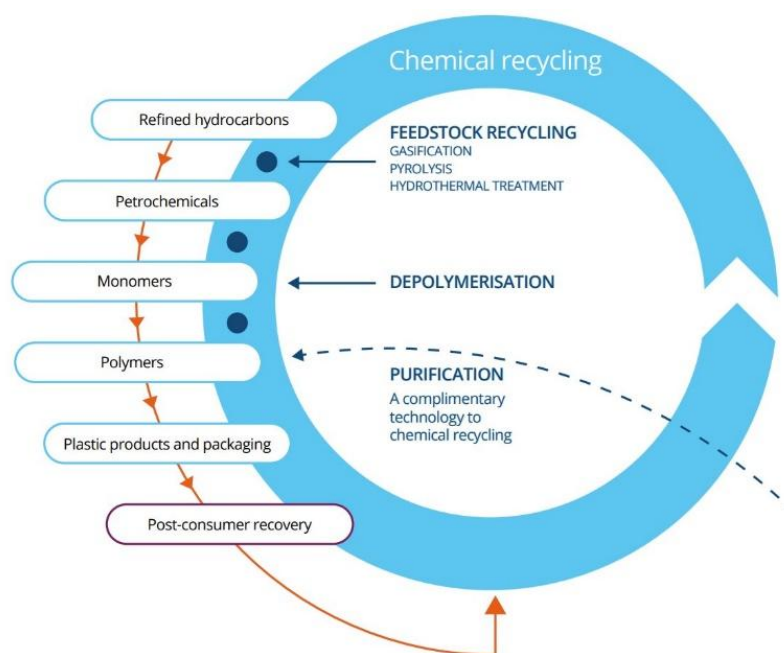


Figure 2-2 - Closed loop life cycle ⁶¹

Pyrolysis oil, however, usually has a high viscosity, low density, low pH, high water content (as high as 15–30 wt.%),¹⁰ high oxygen-to-carbon (O:C) ratio and low hydrogen-to-carbon (H:C) content ²³. All these factors make storage, transport, and utilisation of the product more difficult, due to corrosion and instability, as well as lower high heating values (HHV) (8). For effective and widespread usage, the pyrolysis oil needs to be upgraded ⁶².

2.2 Pyrolysis oil composition

2.2.1 Biomass

Biomass is renewable organic material that comes from plants and animals, it's sources include wood, agricultural crops and waste material, municipal solid waste, animal manure and human sewage. Bio-oil, derived from biomass pyrolysis, is a highly intricate mixture whose composition varies with changes in the feedstock, temperature, pressure, residence time and catalysts. Other factors that can lead to different results are pre and post-treatment of the biomass or the oil ⁶³. Typical physical-chemical properties of the biomass-derived bio-oil are summarised in Table 2-1 ²³.

Table 2-1 - Bio-oil composition matrix and associated ASTM standards ²³.

Property (ASTM Standard)	Value (avarage)
C	56 wt. %
H	6 wt. %
O	38 wt. %
N	0.2 wt. %
S	0.02 wt. %
Water content (D95, E203)	25 wt. %
pH acidity (D974, D664, D3339)	2.5
Specific gravity (density compared to water)	1.2
High heating value (D240, D4809)	17 MJ/kg
Viscosity (D88, D445, D2170)	40-100 mPa
Solids (char content)	0.10 wt. %
Density (D1298, D4052)	1.2 Kg/L

Pre-treatment is common practice in the industry that the biomass goes through several physical-chemical processes before being pyrolyzed, such as torrefaction and trituration ^{11,29}. Pyrolysis oil from a lignocellulosic (*Acacia nilotica*) raw biomass (PO-RAW) and torrefied biomass (PO-TB) are composed of furan derivatives, phenol derivatives, acids, alcohols, aldehydes, ketones, sugar derivatives, esters, and other compounds. Table 2-2 summarises the most abundant species ¹¹.

Table 2-2 - Chemical composition of pyrolysis oil identified by GC-MS analysis at optimum condition of pyrolysis of raw and TB ¹¹.

Compound	Relative content (peak area (%))	
	PO-TB	PO-RAW
Furan derivatives		
2-Furancarboxaldehyde	10.46	-
2-Furanmethanol	5.62	6.05

2(3H)-Furanone, 5-Methyl	3.52	5.02
2-Furancarboxaldehyde,-5-Methyl	-	6.45
Phenol derivatives		
Phenol, 2-methoxy	5.78	-
Phenol, 4-methoxy	-	8.72
Creosol	3.84	6.05
Phenol, 2,6-dimethoxy	9.46	9.11
3,5-Dimethoxy-4-hydroxytoluene	4.63	4.61
Phenol, 2,6-dimethoxy-4-(2-propenyl)	6.68	0.82
Acids		
n-Hexadecanoic acid	0.60	0.54
Linoelaidic acid	-	1.90
Alcohols		
1-Penten-3-ol	0.80	0.65
1,2-Benzenediol,3-methyl	-	2.15
1-Octen-3-ol,acetate	0.82	-
Aldehydes		
Benzaldehyde, 4-hydroxy-3-methoxy	-	0.8
Benzaldehyde, 4-hydroxy-3,5-dimethoxy	0.64	0.64
Ketones		
Alpha.,.beta.-crotonolactone	2.16	2.16
3-Methylcyclopentane-1,2-dione	2.86	3.93
6-Methoxycoumaran-7-ol-3-one	3.61	-
Sugar derivatives		
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	0.30	1.47
Beta.-D-Glucopyranose, 1,6-anhydro	-	6.39
Esters		
2-(Acetyloxy) Ethyl acetate	0.53	-
Diethyl Phthalate	-	0.55
Di-n-octyl phthalate	0.35	0.31
Other compounds		
1H-Pyrazole, 3,5-dimethyl	-	9.34
Benzene, 1,2,3-trimethoxy-5-methyl	3.18	1.91

Temperature is a critical factor during the pyrolysis process, significantly affecting product yields and altering the composition of the resulting oil^{12,13,29,64,65}. For example, during the pyrolysis of food waste (FW) and Food waste solid digestate (FWSD), increasing the temperature from 500 to 800°C led to a reduction in oil yield, decreasing from 19.5% to 8.2% for FW and from 15.9% to 8.3% for FWSD. Additionally, the yield of aliphatics in the bio-oil decreased from 18.91% to 16.86% for FW and from 33.78% to 25.64% for FWSD. Notably, as the temperature increased, carbon and hydrogen content in the oil increased, while oxygen content decreased. This desirable outcome for improving the oil stability and fuel quality¹². Rice husk pyrolysis oil composition was also influenced by temperature. Acids concentration varied from 7.07 wt.% at 400°C to 5.69 wt.% at 600°C, although it peaked at 8.46 wt.% at 450°C, ketones presented a similar behaviour, going from 8.65 wt.% to 4.14 wt.% for the same temperature increase. Aldehydes, phenols and nitrogenated compounds all presented a reduction in concentration¹³. Using a heavy metal contaminated mangrove as the biomass (temperatures range: 300-700°C) the main compounds found in all cases were phenol derivatives, carboxylic acids, and alcohols. Analysis on GC-MS showed that independently of the temperature, the most abundant alcohol and phenol derivative were methylpropan-1-ol and catechol, respectively, although concentrations varied. The lower temperature (300°C) led to a higher concentration of 2-methylpropan-1-ol, catechol, syringol and germanicol. For the higher temperatures (500-700°C), the most abundant compounds were the same ones. A slight variation on the concentration of 2-methylpropan-1-ol and syringol occurred (0.59 and 0.76 % variation, respectively), for catechol and germanicol, the lower temperature resulted in a noticeable higher concentration (2.80 and 2.09 % variation, respectively)¹⁴.

Phenol derivatives, lignin derivatives, benzene derivatives, alcohols and carboxylic acids are the main components of bio-oil, and account for the high oxygen concentration and instability of the oil due to low pH, when compared to conventional oils^{11,14–16,66}. The viscosity is also highly dependent on the feedstock, as reported by Luo et al¹⁵ when comparing lignocellulosic biomass fast pyrolysis bio-oils. The results of the characterisation show a total phenolic,

lignin derivatives and benzene derivatives compounds content of 32.26%, 32.36, and 15.78% respectively. All main compounds reported are oxygenated, most of which are aromatics. The results are summarised in Table 2-3.

Table 2-3 - Relative content of main compounds in organic composition of bio-oil produced from *P. indicus* ¹⁵.

Compound	Relative content (%)
Furfural	9.06
Acetoxyacetone, 1-hydroxyl	1.21
Furfural, 5-methyl	1.82
Phenol	2.55
2-Cyclopentane-1-one, 3-methyl	1.58
Benzaldehyde, 2-hydroxyl	2.70
Phenol, 2-methyl	5.04
Phenol, 4-methyl	0.51
Phenol, 2-methoxyl	0.27
Phenol, 2,4-dimethyl	9.62
Phenol, 4-ethyl	2.18
Phenol, 2-methoxy-5-methyl	4.15
Phenol, 2-methoxy-4-methyl	0.55
Benzene, 1,2,4-trimethoxyl	3.80
Phenol, 2,6-dimethyl-4-(1-propenyl)	4.25
1,2-Benzenedicarboxylic acid, diisooctyl ester	1.80
2-Furanone	5.70
Levoglucozan	6.75
Phenol, 2,6-dimethoxy-4-propenyl	3.14
Furanone, 5-methyl	0.49
Acetophenone, 1-(4-hydroxy-3-methoxy)	2.94
Vanillin	6.35
Benzaldehyde, 3,5-dimethyl-4-hydroxyl	4.54
Cinnamic aldehyde, 3,5-demethoxy-4-hydroxyl	2.19

Due to its highly complex nature, it is common to separate the bio-oil into hydrophilic, also referred to as water soluble bio-oil (WSBO) and hydrophobic shares. This process can increase the number of quantifiable compounds in the analysis, although it remains difficult to identify all components ^{16,66}. Naturally, the water-soluble fraction presents the higher concentration of water, alcohols, and carboxylic acids, due to their polar nature. Sipila *et al.* reported that WSBO from straw, pine and ensyn (hardwood) oils show a high-water content (19.9, 11.1 and 23.2% respectively), low pH (3.7, 2.6 and 2.8 respectively), and high carboxylic acid concentration (10.80, 7.30 and 6.20% respectively). Acetic and formic acids were the most significant components and the main reason for the low pH of the oils ⁶⁶. When two commercial wood pyrolysis oils (BTG and Amaron) were separated into water-soluble (WS) and hydrophobic (oil), the authors reported only 34 directly quantifiable compounds, the main components are shown in Table 2-4 ¹⁶.

Table 2-4 - Compounds Identified in the pyrolysis oils and WS fractions by GC-MS (wt.%) ¹⁶.

Compound	BTG oil	Amaron oil	BTG WS	Amaron WS
Glycolaldehyde	5.60	1.0	16.10	2.90
Acetic acid	3.90	5.50	0.40	0.70
Acetol	5.60	5.50	1.30	1.20
Levogluconan	3.50	3.00	0.20	0.20
Syringaldehyde	0.10	0.10	8.10	6.80

2.2.2 Plastics

Characterisation of plastic pyrolysis oil shows that, the composition is highly dependent on the feedstock and other pyrolysis process factors ⁶³. Dyer *et al.* studied co-pyrolysis of biomass with several types of plastic and reported on the composition of different plastic pyrolysis oils, the results are summarised on Table 2-5. These results show that PET is one of the main sources of oxygen in plastic waste, being both a highly produced plastic (10 wt.% of total resin production) ⁵⁷ and high oxygen composition (32.7%). Although polyolefins (like PE and PP) present low oxygen concentration, their major role in the plastic

production matrix (57 wt.% of all resin produced) makes it the largest contributor of oxygenated compounds in plastic oil ¹⁷.

Table 2-5 - Characteristics of the pyrolysis oil for different plastic wastes. ^a As received. ^bDry. ^cDry ash-free (HDPE: High-density polyethylene; LDPE: Low-density polyethylene; PET: Polyethylene terephthalate; PP: Polypropylene; PS: Polystyrene ¹⁷.

Proximate analysis (wt.%)	HDPE	LDPE	PET	PP	PS
Moisture ^a	0.0	0.0	0.0	0.0	0.0
Ash ^b	4.1	0.3	42.7	0.8	1.6
Volatile ^c	98.1	100.0	94.6	100.0	100.0
Fixed carbon ^c	1.9	0.0	5.4	0.0	0.0
Elemental analysis (%)					
C ^c	82.5	83.3	69.0	81.0	87.8
H ^c	13.1	12.6	5.0	11.4	9.5
O ^c	1.8	0.7	32.7	0.6	0.0
N ^c	0.1	0.1	0.0	0.1	0.0

Plastic waste pyrolysis oil usually presents a highly aromatic compounds share, when compared to bio-oil, in which can be found monoaromatics, diaromatics, naphthenoaromatics and triaromatics (51.3, 7.5, 5.9 and 2.3 wt.% respectively). Some of the main components of the aromatic share of the oil are benzene, toluene, ethylbenzene, xylene, and styrene. The detailed composition of the oil can be found in Table 2-6 ¹⁸.

Table 2-6 - Detailed composition of the plastic pyrolysis oil. Edited ¹⁸.

Component	Composition (wt.%)
Paraffins	5.0
Iso-paraffins	8.2
Olefins	12.3
Aromatics	67.1

The feedstock variation is the main factor in plastic-oil composition. In a process treating PET as feedstock, the resulting pyrolysis oil contains a high concentration of benzene derivatives (10.6 wt.%), ketones (5.90 wt.%) and acids/esters (62.0 wt.%). The most abundant compound in PET pyrolysis oil is benzoic acid and its derivatives, constituting 49.9 wt.% of the oil ¹⁹. Cit et al found similar results when comparing polyolefins (PP and LDPE) and PET, where PET pyrolysis oil's main components were benzoic acid derivatives. (benzoic acid = 23.7, 4-methyl-benzoic acid = 1.6, 4-ethylbenzoic acid = 1.3 and 4-acetylbenzoic acid = 10.3 wt.%) ²⁰. LDPE pyrolysis oil has a high share of carbon double bonds, as 39% of its composition are aromatic compounds and other unsaturated carbon molecules ²¹. A mix of LDPE and HDPE led to naphthalene derivatives as the main components (approximately 24 wt.%) in the plastic-oil, followed by p-xylene, toluene, naphthalene, benzene, 1-ethyl-4-methyl-benzene, m-xylene, 1,2,4-trimethyl-benzene, indane, indene and 1-methyl-3H-indene (approximately 19, 14, 9, 6, 3.5, 3, 2, 1.5, 1.5 and 1 wt.% respectively) ⁶⁷. For PS, monoaromatics are the main components, followed by polyaromatics and aliphatics. (77.62, 12.86 and 0.01 wt.% respectively). As expected, the main component is styrene (73.60 wt.%), other noticeable compounds are 2,4-diphenyl-1-butene (7.80 wt.%), 2,4,6-triphenyl-1-hexene (2.21 wt.%), α -methylstyrene (1.61 wt.%), and toluene (1.58 wt.%) ⁶⁸. When conducting a study on the performance of plastic pyrolysis oil as fuel, Kalagaris et al reported on the composition of the oil. The feedstock was a mixture of styrene butadiene, polyester, clay, ethylene-vinyl acetate, rosin, polyethylene, and polypropylene (47, 26, 12, 7, 6, 1 and 1 wt.% respectively). The main components of the oil are presented on Table 2-7 ⁶⁹.

Table 2-7 - Main components of plastic-oil ⁶⁹.

Compound	Composition (wt.%)
Xylene	8.80
Benzene	5.30
Chlorinated phenols	4.20
Naphthalene derivates	4.10
Cresols	3.90
Naphthalane	3.70
Cyclopentene	2.90
Toluene	2.70
Benzene derivates	1.00
Cyclobutane	0.90

The addition of different feedstocks may also change the composition of the oil, that is, the oil composition of a PS/PP mixture may not be just the sum of PS and PP oils. Many of the components found in PP pyrolysis oil, such as methylnaphthalene (8.4 wt.%), xylene (7.8 wt.%) and phenanthrene (7.6 wt.%), completely disappeared when the feedstocks were mixed. Figure 2-3 shows the oil composition for several different feedstock compositions. The ratio of each plastic in each mixture was 50/50%, in the last mixture (PS, PP, PE and PET) the ratio was 40/20/20/20%, respectively ²².

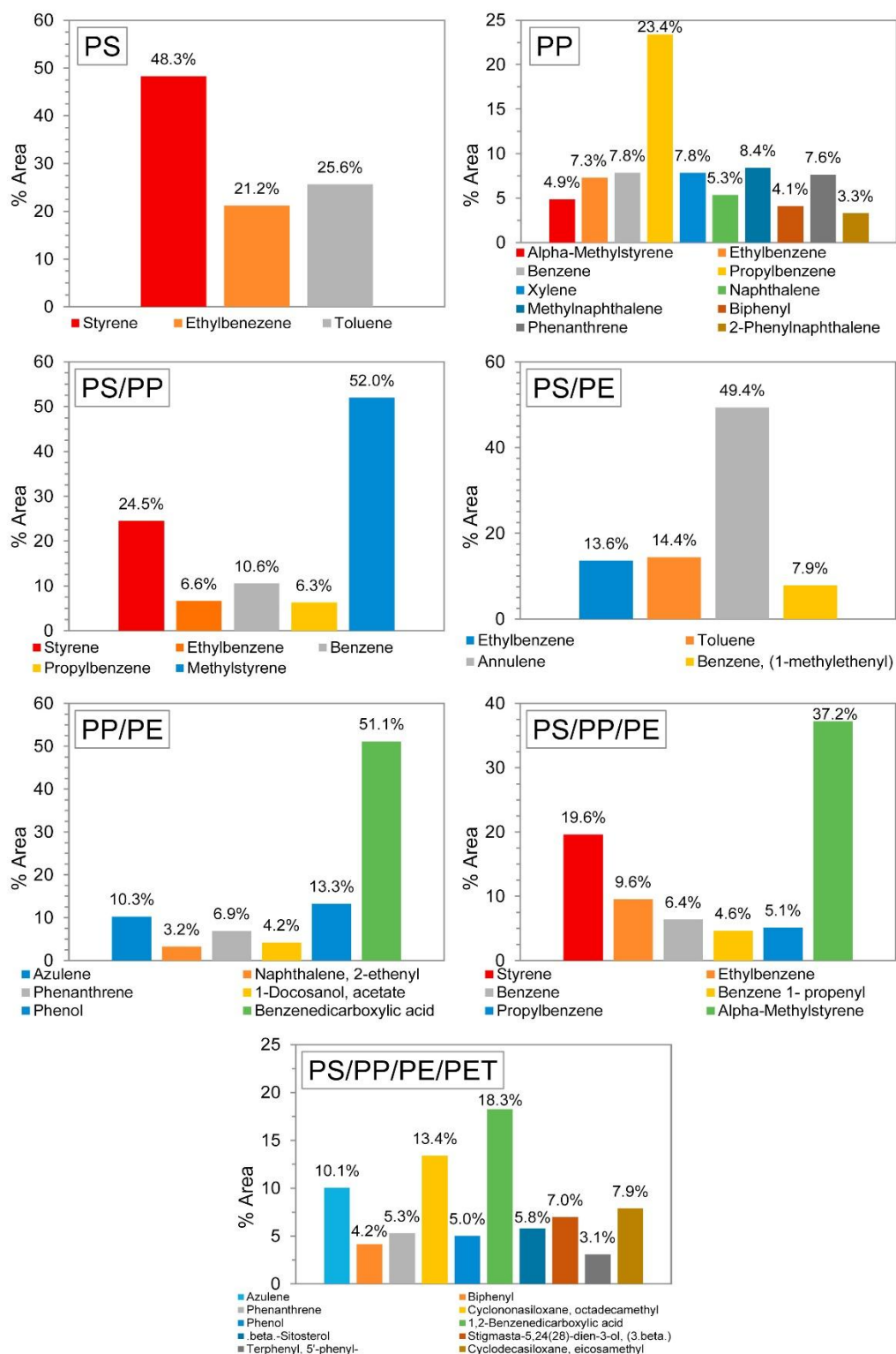


Figure 2-3 - GC-MS results of liquid oils from pyrolysis of different types of plastic waste Reprinted with permission from reference ²² Copyright 2017 Elsevier.

Both temperature and pressure are vital factors in the pyrolysis process. Pyrolysis of LDPE on different conditions (425°C / 1.60 MPa, 450°C / 2.45 MPa and 500°C / 4.31MPa) led to variation in both the class of compounds and their

concentration. The carbon chain length also changed, significantly reducing in higher temperatures/pressures. Table 2-8 shows the variation on the macro composition and Table 2-8b the specific compounds ⁷⁰.

Table 2-8a - Composition of the oil products from the pyrolysis of LDPE (% w/w oil) ⁷⁰.

Composition	425°C / 1.60 MPa	450°C / 2.45 MPa	500°C / 4.31 MPa
Naphthenes	2.69	5.56	1.50
Alkanes	46.20	31.7	17.8
Alkenes	12.40	13.1	3.58
Aromatics	12.00	22.9	68.0
Unknowns	19.10	17.9	-

Table 2-8b - Main components of the oil products from the pyrolysis of LDPE (% w/w oil) ⁷⁰.

Compound	425°C / 1.60 MPa	450°C / 2.45 MPa	500°C / 4.31 MPa
Heptane	2.26	3.16	0.46
Toluene	0.35	3.05	24.30
Octane	2.45	3.78	0.19
Ethylbenzene	0.25	0.89	3.06
p/m-Xylene	0.62	1.79	3.90
Allylbenzene	0.21	1.02	4.84
Methylnaphthalene	0.90	0.36	4.22
C ₂₁ –C ₃₀ alkanes	9.98	1.85	1.20

The same variation can be observed in the pyrolysis of PS (process conditions: 400°C / 1.14 MPa, 425°C / 1.26 MPa, 450°C / 1.47 MPa, and 500°C / 1.60 MPa). Results are summarised in Table 2-9.

Table 2-9 - Main components in the pyrolysis oil products from PS (%w/w) ⁷⁰.

Compound	400°C 1.60 MPa	425°C 2.45 MPa	450°C 4.31 MPa	500°C 4.31 MPa
Benzene	0.38	0.73	1.27	1.63
Toluene	21.70	23.10	27.00	28.40
Ethylbenzene	32.60	39.30	39.00	36.60
Styrene	1.09	0.80	0.39	0.61
Cumene	10.20	9.10	9.36	9.60
Propylbenzene	0.60	0.77	0.90	1.29
Methylstyrene	1.37	0.39	0.33	0.55
Diphenylmethane	0.91	0.83	1.00	1.61
1,2-Diphenylethane	1.44	1.16	0.60	0.37
Phenylnaphthalene	0.98	1.02	1.01	1.25
1,2-Diphenylbenzene	1.27	1.26	1.87	1.89
Triphenylbenzene	6.30	5.13	3.83	3.18

Long-chain alkanes and alkenes are common products in plastic-oil, the carbon chains can reach as high as 55 carbons (C₅₅) when the feedstock is a mixture of PP, LDPE, HDPE and styrene ^{71,72}. The carbon number range of alkanes (Table 2-10a) and alkenes (Table 2-10b) are as follows:

Table 2-10a - Carbon number range of alkane products of produced pyrolysis oil in wt.%. Adapted ⁷¹.

Feedstock	C₁₁-C₂₀	C₂₁-C₃₀	C₃₁-C₄₀	C₄₁-C₅₀
Polypropylene	2	63	0	0
LDPE	6	54	12	13
HDPE	1	67	18	0
Styrene	0	4	27	8

Table 2-10b - Carbon number range of alkene products of produced pyrolysis oil in wt.%. Adapted ⁷¹.

Feedstock	C₁₁-C₂₀	C₂₁-C₃₀	C₃₁-C₄₀	C₄₁-C₅₀
Polypropylene	9.9	8.9	0	0
LDPE	3.3	4.2	0	0.8
HDPE	0.5	6.2	1	1
Styrene	0	0	0	10

Plastic waste (polyethylene film and mixed polyolefin) pyrolysis oils blended with fossil naphtha led to an even higher carbon number range. For polyethylene film (PE-film), was C₅-C₅₅ and for mixed polyolefin (MPO) was C₅-C₅₂. The composition groups of the resulting pyrolysis oils consisted of paraffins, iso-paraffins, α -olefins, iso-olefins, diolefins, naphthenes, monoaromatics and naphthenoaromatics ⁷². Both oils also present a substantial amount of several halogen and metal contaminants, among which are found Cl, Br, Al, Ca, Cr, Cu, Fe, Li, Na, Ni, Sb, Si, Sr and Zn. Both Cl and Br can be explained from the initial composition of the feedstock, as polyvinyl chloride (PVC) is a common plastic and bromine is an element that is used in fire retardants. Metal contamination can be traced to plastic enhancers, as metals are commonly used as additives ⁷². The detailed composition of the plastic-oil and the distribution of paraffins, olefins, naphthenes and aromatics over the light, medium and heavy product fractions of all post-consumer plastic waste pyrolysis oils can be found in Table 2-11 ⁷³:

Table 2-11a - Detailed composition of the plastic pyrolysis oil in wt.%. Edited ⁷².

Composition	MPO pyrolysis oil	PE-film pyrolysis oil
Paraffins	32.2	41.9
Iso-paraffins	3.7	3.5
α -Olefins	23.5	33.0
Diolefins	5.3	4.5
Naphthenes	12.4	5.5
Monoaromatics	2.7	1.0
Naphthenoaromatics	0.2	0.1

Table 2-11b - Detailed composition of the plastic waste pyrolysis oil in wt.%. ⁷³.

Composition	Light fraction ^a	Medium fraction ^b	Heavy fraction ^c
Paraffins	28	29	44
Olefins	32	40	29
Naphthenes	18	14	17
Aromatics	19	12	11
Others	4	5	0

[a] Carbon number up to C₂₀ and boiling point up to 250 °C. [b] Carbon number up to C₃₀ and boiling point up to 450 °C [c] Carbon number > C₃₀ and FBP > 450 °C ⁷³.

2.2.3 Pyrolysis oils comparison

Although both biomass pyrolysis oil (bio-oil) and plastic pyrolysis oil (plastic-oil) share common components such as paraffins, olefins, aromatics, and oxygenated compounds, they exhibit significant differences in their composition. Notably, bio-oil's water content is much higher than plastic oil ^{8,23,71–73}. On the other hand, plastic oil presents a higher aromatic share, longer carbon chains, and various metal contaminants, which are added during its production as stabilisers and colouring, for example. The presence of long-chain alkanes and alkanes in plastic-oil can lead to a heavier and more viscous product and is a factor that will affect the upgrade process, making it slower ⁷².

For utilisation as biofuel, HHV is a vital factor. Bio-oil has a lacklustre HHV when compared to transportation fuels (bio-oil HHV: 13-19 MJ/kg compared to gasoline: 44-46 MJ/kg or coal: 25-35 MJ/kg). Plastic-oil, on the other hand, presents high HHV (41-47 MJ/kg) ⁸. The main components from both bio and plastic oil are summarised in Figure 2-4.

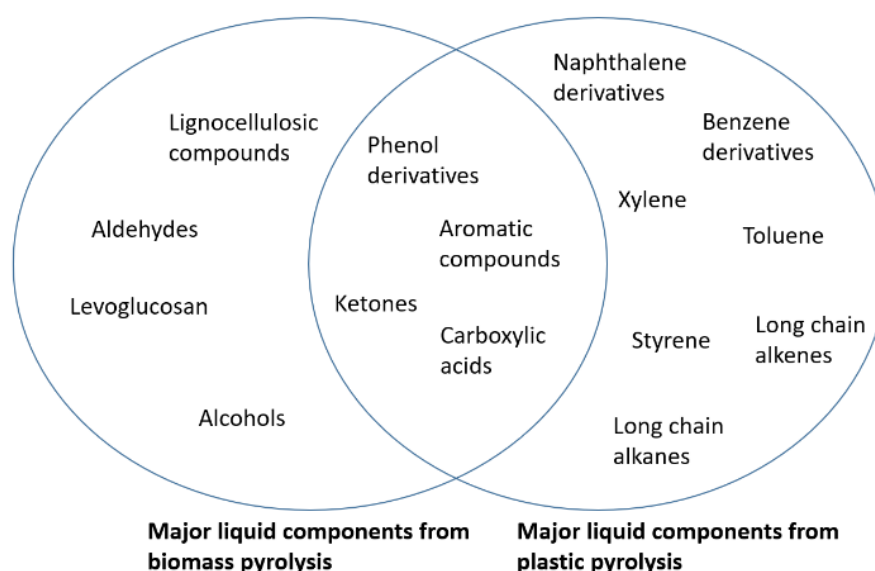


Figure 2-4 - The intersection in the composition between bio-oil and plastic-oil.

2.3 Upgrading routes

Bio and plastic oils usually present subpar physical-chemical properties when compared to traditional fuels, such as acidity, O:C and H:C ratios and, for bio-oils, low HHV. This means that for its utilisation as an alternative fuel, an upgrading process is necessary. The same is true when it comes to recycling, where these products need to be upgraded to be utilised as feedstock for the petrochemical or chemical industries. Several processes for bio-oil upgrading have been the focus of many studies throughout the years ^{10,24,25,27,28,32,33,62,74–81}. The most common method is deoxygenation, which is commonly accomplished through catalytic cracking and hydroprocessing routes such as hydrotreatment and hydrodeoxygenation ²⁷.

Upgrading routes can be separated into chemical (hydrotreating, catalytic cracking, hydrocracking, steam reforming, hydrodeoxygenation and hydrogenation) and physical (distillation, supercritical fluid extraction, liquid-

liquid extraction, and emulsification) processing. There are several advantages and disadvantages to each upgrading route, some of the disadvantages of the more traditional routes are the operational conditions, high costs and coke production. Catalytic cracking is accomplished in medium temperature and atmospheric pressure, but it leads to catalyst deactivation and the formation of carbon double bonds, which would require further improving²⁶. Decarbonylation and decarboxylation leads to the loss of valuable carbon. Hydrocracking, hydrodeoxygenation, and hydrogenation require an outside source of H₂, which is costly and difficult to store (see Figure 2-5)^{24,25}.

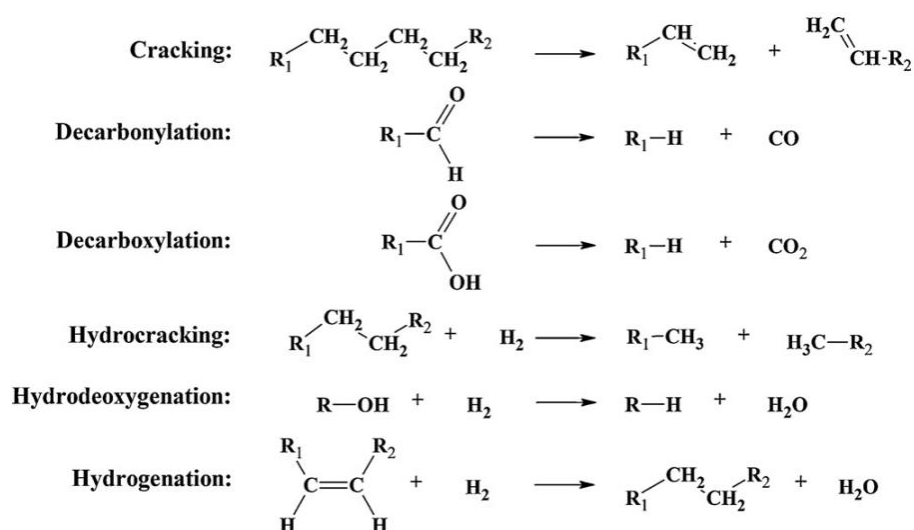


Figure 2-5 - Examples of reactions associated with catalytic bio-oil upgrading.

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2.3.1 Electrochemical hydrogenation

One recently emerging route for pyrolysis oil upgrading is electrochemical processing. Electrochemical hydrogenation (ECH) does not require H₂ from an outside source, which is produced during the process, reducing costs, and mitigating the risks associated with H₂ storage^{26,28,29}. Most setups for ECH consist of two chambers separated by a cation exchange membrane (CEM). The most prevalent cell design is H-type cells (Figure 2-6), although there are some studies utilising flow-type cells^{33–35}.

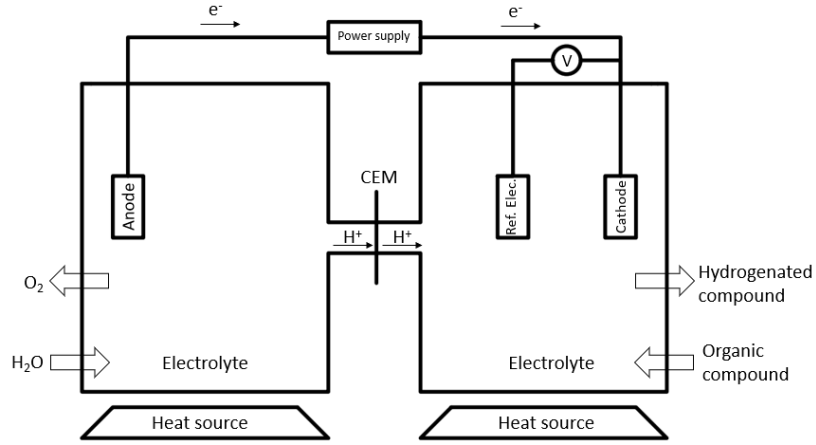
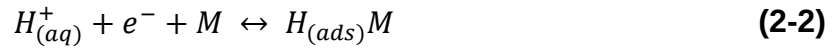
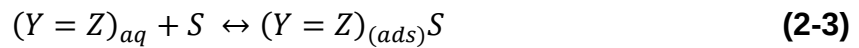
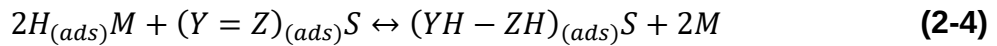
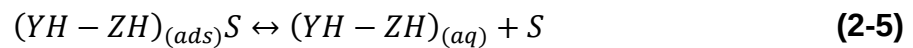
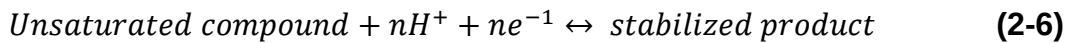


Figure 2-6 - A typical H-type cell, where the two chambers are separated by a membrane.

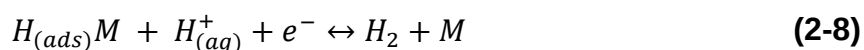
During ECH, water is oxidised at the anode (Eq. (2-1)), the resulting H^+ , that can flow through a cation exchange membrane into the cathode cell. The H^+ is then chemisorbed by the catalytic cathode (Eq. (2-2)), where M is the metal surface and $H_{(ads)}M$ is the chemisorbed hydrogen ^{30,82}.



In the cathode chamber, the organic unsaturated compound is chemisorbed onto the cathode (Eq. (2-3)), where the hydrogenation process occurs (Eq. (2-4)), followed by the desorption of the stabilised product (Eq. (2-5)). Equation (2-6) is the net reaction ^{30,82}.



Where $(Y = Z)_{aq}$ is the unsaturated compound, S is the absorption site of the cathode, $(Y = Z)_{(ads)}S$ is the adsorbed organic compound, $(YH - ZH)_{(ads)}$ is the hydrogenated product before desorption, $(YH - ZH)_{(aq)}$ is the final product and n denotes any arbitrary numerical value ^{30,82}. The hydrogen evolution reaction (HER) is a common side reaction, that can lead to the loss of hydrogen, rather than react with bio-oil, thus reducing the faradaic efficiency (FE), smaller conversion, and a poorer overall process. This reaction can occur via either the Tafel step (Eq. (2-7)) or the Heyrovsky step (Eq. (2-8)) ^{30,82}



ECH can be performed under mild conditions (<80°C and 1 atm). Lower temperatures can also avoid catalyst deactivation by coke formation and membrane fouling, potentially reducing the costs associated with catalyst purchase and recycle ³¹. However, due to high viscosity and low conductivity, it requires the utilisation of membranes, catalysts, and electrolytes to facilitate the reaction ^{27,28,32,62}. That leads to a vast spectrum of different arrangements that can be organised to optimise the process.

Table 2-12 - Methods for bio-oil upgrading comparison.

Method	T (°C)	P (bar)	H ₂ need
Cracking	330-700	1.0	No
Hydrocracking	>400	68-96	Yes
Hydrodeoxygenation	300-600	80-300	Yes
Electrochemical Hydrogenation	<80	≈1	No

2.3.1.1 Key ECH performance parameters

To understand and quantify the ECH process, the most important parameters are Faradaic efficiency (Eq. (2-9) and (2-10)), conversion (Eq. (2-11)), selectivity (Eq. (2-12)) and current density (Eq. (2-13)). Due to difficulties in measuring the surface area of the cathode and therefore the current density, some authors report this parameter as current (usually in mA), these will be highlighted in the following sections.

$$FE (\%) = \frac{(I \times T - 2 * n * F)}{(I * T)} \quad (2-9)$$

where I = current in A; T = time in s; n = mols of hydrogen; F = Faraday's constant.

This equation can also be simplified as:

$$FE (\%) = \frac{\text{Electrons used to generate products}}{\text{Total electrons passed}} * 100 \quad (2-10)$$

$$\text{Conversion (\%)} = \left(\frac{\text{Moles reactant consumed}}{\text{Initial moles reactant}} \right) * 100 \quad (2-11)$$

$$\text{Selectivity (\%)} = \left(\frac{\text{Moles desired product}}{\text{Total moles product}} \right) * 100 \quad (2-12)$$

$$\text{Current density (mA cm}^{-2}\text{)} = \frac{\text{Current}}{\text{Surface area}} \quad (2-13)$$

2.3.2 ECH reactor design considerations

2.3.2.1 Electrodes

Electrodes usually consists of conductive materials and catalysts, which play a vital part on the ECH process. Different electrodes can increase bio-oil conversion and interfere with product selectivity.²⁶ Noble metals,^{26,28} base metals,^{74,83,84} and graphite,⁸⁵ besides catalyst-coated carbon cathodes (e.g Ru/ACC)^{28,31,74} have been reported for ECH bio-oil and model compounds

upgrading. Pt, Rh, Ru, Au and Pd have been employed as cathode materials during ECH of aldehyde and phenolic model compounds ^{26,86,87}.

The choice of cathode can greatly interfere with the process, as early transition metals (e.g. Ti, Mn, Nb) and platinum group metals (Ru, Rh, Ir, and Pt) have higher affinity toward hydrogen formation, leading to more H⁺ in the solution, which increases collision probability and, in turn, leads to higher conversion ²⁶. Cathode surface coverage (or adsorption rate) can lead to the same problem of low collision probability, and is dependent on cathode/compound pairing, for example, the adsorption of phenol on Pt is stronger compared to guaiacol ^{75,88}.

Cathode selection can also influence the selectivity of the process and the desirable product yield. For the ECH of glucose, late transition metals (e.g. Fe, Cu, Pd, Ag and Au) led to higher sorbitol formation and post-transition metals (In, Sn, Sb, Pb, and Bi), Zn and Cd (d metals) favoured d 2-deoxysorbitol formation. Ni had the lowest and Pb the highest sorbitol formation potential ⁸⁹.

Platinum group metals (Pt, Pb, Ru, Rh and Ir) are commonly used in hydrogenation processes, due its stability and high affinity towards hydrogen production and have been employed in several conditions and for different compound classes ⁸⁹. For the ECH of indigo, a highly unsaturated compound that contains both oxygen and nitrogen, (reaction conditions: 1 M NaOH, 50°C, 20 mA/cm²) using Raney nickel electrodes doped with different noble metal catalysts (Pt, Pd and Pd/C), Pt coating led to both optimal conversion and FE (10.2 and 8.16% respectively), followed by Pd (8.6, 6.88%), Pd/C (4.7, 3.76%) and Raney nickel without coating (4.4, 3.5%) ⁹⁰. Nobel metals are also capable of hydrogenating phenolic compounds at high conversion and FE. ECH of phenol on several cathodes (Pt/C, Rh/C, and Pd/C) demonstrated that Rh/C exhibited the highest hydrogenation rate, the order was Rh/C>Pt/C>Pd/C ⁹¹. Du et al reported on the ECH of phenol on several different electrocatalysts: Pt, Ru, Pt₃Ru, Pt₃Sn, Ru₃Sn, and Pt₃RuSn supported on carbon cloth (reaction conditions: 0.2 M H₂SO₄ containing 10 mM phenol at -100mA, 50°C for 100 min). Pt₃Ru/CC presented the highest conversion, at 96.3%, followed by Pt₃RuSn/CC and Pt/CC (91.5 and 90.2% respectively) ⁴⁵. The concentration of the metal on the surface of the carbon can also lead to different results, although graphite alone was unable to react (reaction conditions: phenol, electrolyte 0.1

mol/L H₂SO₄ (30 mL), 30 mA, Pt sheet as anode). 1%Pt/G and 1.5%Pt/G presented the highest conversion, both 95%. The highest yield of cyclohexane and the highest FE were 30.4% and 20.3%, respectively, both occurred with the same cathode (1.5%Pt/G). The results are summarised in Table 2-13³⁰. As shown in previous sections, lignin pyrolysis oil can contain phenolic compounds (phenol, p-cresol, 4-ethylphenol, and 4-propylphenol, as well as guaiacol) which can be hydrogenated into their corresponding alkylcyclohexanols at high conversion using Ru/ACC as the catalytic cathode. The same cathode is effective on transforming model lignin monomers into cyclohexanol ³¹.

Table 2-13 - ECH of phenol on various cathodes ³⁰.

Cathode	Conversion (%)	F.E.	1	2	3	4
Pt	0	0	0	0	0	0
Ni/G	0	0	0	0	0	0
Rh/G	90	0	0	65.7	24.3	0
Pd/G	18	0	0	12.6	5.4	0
0.5%Pt/g	92	11.1	16.6	57	12	5.5
1%Pt/g	95	15.2	22.8	52.3	16.2	3.8
1.5%Pt/g	95	20.3	30.4	58.9	5.7	0
2%Pt/g	90	9.1	13.5	60.3	9	7.2
Graphite	0	0	0	0	0	0

Where [1] is Cyclohexane, [2] Cyclohexanol, [3] Cyclohexanone and [4] Benzene.

Metals outside the platinum group can also be utilised as the catalytic cathode, although it still requires more investigation. The ECH of Guaiacol and related lignin models utilising a Nickel cathode and a Co/Phosphate anode presented high selectivity towards cyclohexanol formation (>99%), with only traces of 2-methoxycyclohexanol. Other experiments were done utilising cobalt and copper as catalyst cathodes, and only Co formed trace amounts of cyclohexanol and phenol, Cu completely failed in producing these products ⁸⁴. The ECH of aldehyde compounds shows that aromatic aldehydes have a higher

conversion than aliphatic aldehydes. Au, Ag, Cu, and C catalysts exhibit the highest conversion to alcohol products ⁹².

2.3.2.2 Electrolyte

Electrolytes can affect the ECH of bio-oil in three major ways. First, the adsorption of anions from the electrolyte into the electrode can difficult the process. Second, the pH of the solution has a direct relation to product selectivity. Lastly, alcohol has been reported to reduce conversion and Faradaic efficiency ^{75,91,93}. The addition of different alcohols (methanol, ethanol, or isopropanol) to the electrolyte led to lower conversion and Faradaic efficiency as alcohol concentration increased. Carbon chain length was a factor, as the impact was greater for longer chains ⁹³.

Electrolytes are needed during ECH to increase the conductivity of the system, although they can interfere with the process. Acids, alkalis, and salts can achieve these results, and the selection of electrolytes should take into consideration both the organic compound and the cathode. Another challenge during this selection is that the electrolyte that presents the highest conversion and the one that leads to the highest FE might not be the same one. For the ECH of guaiacol (reaction conditions: 3-CE-NH₃ cathode, 80°C and 100 mA), the conversion, FE and product selectivity varied greatly. The highest conversion were NaOH (62 ± 2.4%), NaCl (64 ± 8.8%), and HCl (75 ± 3.9%). For FE, the order was NaCl (20 ± 2.2%) < NaOH (28 ± 1.0%) < HCl (30 ± 4.3%). Similar results were reported for phenol and syringol ²⁸. The pH of the system can interfere with the results, as demonstrated by the ECH of guaiacol where HClO₄ as the electrolyte led to the highest guaiacol conversion, HCl and H₂SO₄ led to moderate conversion (PtNiB/CMK-3 cathode, 0.2 M HClO₄, 0.2 M HCl and 0.2 M H₂SO₄ as electrolytes). In addition, HClO₄ achieved optimal selectivity for the desirable product (KA oil). However, increasing the concentration of sulfuric acid from 0.2 M to 0.5 M reduced the ECH activity ⁷⁵.

Different catholyte/anolyte pairings can also lead to vastly different results. Acid/acid pair (catholyte/anolyte respectively) lead to higher guaiacol conversion. (Conditions: T = 50°C, I = 300 mA (j = -109 mA cm⁻²), catalyst = 5wt% Pt/C (0.133 g), reaction time = 2h, concentration of all electrolytes = 0.2M)

followed by salt/acid and acid/alkali. Alkali/acid completely failed in generating products. ECH of phenol led to similar results ⁸⁸.

2.3.2.3 Temperature

Temperature is a factor that can greatly influence the results of ECH. FE, conversion and product selectivity have been reported to be affected by temperature ^{26,28,94}. Lower temperatures favours electrocatalytic hydrogenation, whilst high system temperature is favourable for hydrogen desorption, which leads to low ECH performance. This condition increases the water oxidation rate on the anode, which contributes to hydrogen evolution reaction (HER), a competing reaction, due to H^+ generation and transfer to the cathode²⁶. For the ECH of Indigo, increasing the temperature from 30 to 60-80°C led to an FE increase, although it substantially dropped down at higher values. The optimal reported temperature was 70°C ⁹⁰. Guaiacol (HCl as catholyte, T= 2h,100 mA) behaves in a similar way, where raising the temperature from 25°C to 50°C increased FE from 8% to 17% but further increase to 80 °C dropped it back to 10% ²⁸. Increasing temperature from 5 to 40 °C during phenol to cyclohexanol ECH upgrading significantly increased FE, upon further heating to 60 °C, FE increase was continuous, but minimal ⁹⁵.

2.3.2.4 Current and potential

Current density can have a direct impact on product selection, FE, and conversion, as it can lead to higher H_{ads} desorption from the cathode and thus become an obstacle for the main reaction ^{26,30,82}. Although higher current densities could decrease the overall process quality, insufficient current can do the same as insufficient current can lead to a lower concentration of H_{ads} on the cathode surface. This reduces collision probability and, consequently, reduces FE.²⁶ Current is directly linked to potential values, and therefore can also interfere in the reaction pathways and product selectivity. HER usually occurs by Tafel or Heyrovsky reactions (Eq. (2-7) and (2-8)) ^{26,83}. The surface coverage of H_{ads} is determined by the kinetics of Eq. (2-2 and side reactions, Eq. (2-7) and (2-8), which can be increased or decreased depending on potential. Therefore, potential is an essential factor in the ECH process ^{82,83}. For the ECH upgrading of phenol, an increase in current from the range of 10-30 to 30-70 mA slightly

lowered product yields and FE. Further increase in the current to over 70 mA highly decreased the overall process quality ³⁰. Furfural behaves in a similar way (desirable product: furfuryl alcohol and 2-methylfuran) where the increase of current density from 300 to 1200 mA/dm² led to a decrease in FE ⁸². Current density increase during the ECH of lactic acid to lactaldehyde and propylene glycol (0.01 M H₂SO₄ for 9 h at 90°C) led to a lower product yield ⁹⁶

Table 2-14 - Previous studies comparison table. *Reported as mA.

Cathode	Feedstock	Conversion	Electrolyte	Temperature (°C)	J (mA/cm²)	F.E.	Duration (h)	Ref.
Ru/ACC	Guaiacol	64 ± 8.8	NaCl	80	100*	20 ± 2.2	2	28
		75 ± 3.9	HCl			30 ± 4.3		
	Phenol	89	HCl			29		
	Syringol	58	HCl			29		
PtNiB/CMK-3	Guaiacol	>99%	HClO ₄	60	20*	86.2	2	75 84
	Raney- Ni	>99%	BK ₃ O ₃	75	8	26	6	31
Ru/ACC	Phenol	100	HCl	80	100*	20	4	90
	4-Methylphenol	100				9		
	4-Ethylphenol	98				9	6	
	4-Propylphenol	100				6		
Raney- Ni	Indigo	4.4	NaOH	50	20	3.5	-	82
Raney- Ni with Pt		10.2				8.16		
Raney- Ni with Pd		8.6				6.88		
Raney- Ni with Pd/C		4.7				3.76		45
Iron	Furfural	97 ± 1.4	NH ₄ Cl	-	6	29 ± 3.5	5	
Pt/CC		90.2				34.6		

Ru/CC		73.4				28.2	
Pt ₃ Ru/CC	Phenol	96.3	H ₂ SO ₄	50	100*	37.6	1.67
Pt ₃ Sn/CC		73.3				29.7	
Ru ₃ Sn/CC		62.3				26.7	
Pt ₃ RuSn/CC		91.5				39.5	

2.4 ECH systems for model compound and bio-oil upgrading

2.4.1 Model compounds

Zhou *et al.* proposed a new catalyst for electrocatalytic hydrogenation of guaiacol, a boron-doped PtNiB/ordered mesoporous carbon (CMK-3) cathode on a Nafion 117 membrane and IrO₂/C as the anode. The goal was the production of KA oil (a mixture of cyclohexanol and cyclohexanone) which is highly utilised as industrial feedstock⁷⁵. The working temperature was 60°C. The anolyte was 10 mL 0.2 M HClO₄ and catholyte was 10 mL 0.2 m HClO₄ with 10 mM guaiacol. Flow rate was 50 mL min⁻¹. Constant current of 20 mA for 2h. The setup is shown in Figure 2-7⁷⁵.

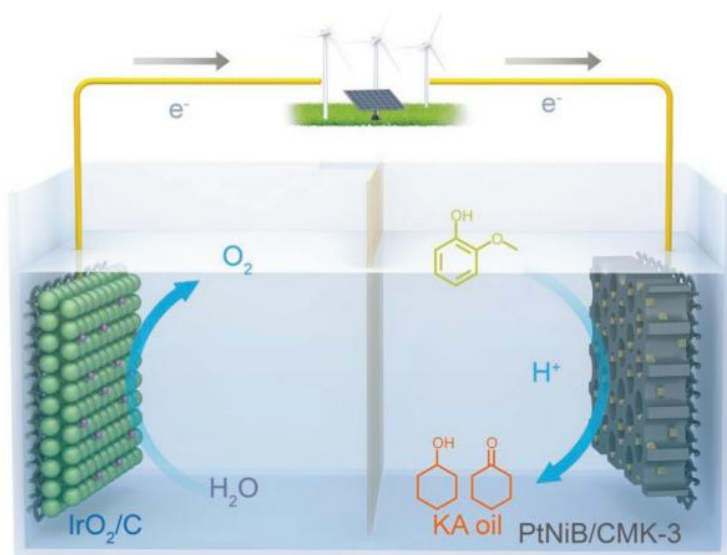


Figure 2-7 - Schematic of ECH of guaiacol into KA oil integrated with O₂ production, equipped with PtNiB/CMK-3 and IrO₂/C as the cathode and anode, respectively. Reprinted with permission from reference⁷⁵ Copyright 2019 Wiley.

The Faradaic efficiency of the process was 86.2%, in comparison to the 6.3% that was found when the reaction was carried out in a PtNi/CMK-3 cathode, that is, without boron doping. The conversion was respectively <99.0% and 11.7%. The study also reported on the ECH of other phenolic compounds using PtNiB/CMK-3. All achieved high (<95%) conversion and high (<80%) FE. The temperature increase effect on conversion and FE in

the range of 20–60 °C was positive (conversion: from 58% to 98.9% and FE: from 45% to 86.2%), but further heating to 80 °C reduced these parameters to 78% and 57% respectively ⁷⁵.

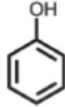
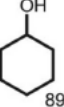
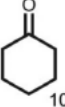
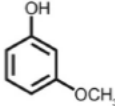
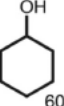
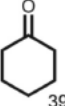
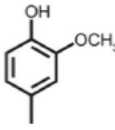
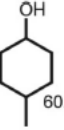
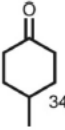
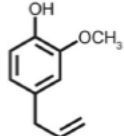
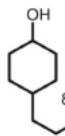
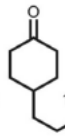
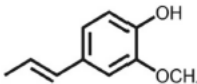
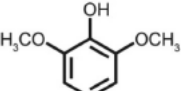
Entry	Structural formula	t (min)	Conv. (%)	FE (%)	Product (sel. %)	
1		50	97.5	90.8	 89.8	 10.1
2		60	95.8	92.6	 60.6	 39.3
3		60	95.1	88.1	 60.7	 34.4
4			90	98.7	 84.3	 12.1
5			90	97.5	 83.5	 16.1
6			90	98.6	 80.2	 11.8

Figure 2-8 - ECH of other phenolic compounds using PtNiB/CMK-3. Reprinted with permission from reference ⁷⁵ Copyright 2019 Wiley.

Garedew et al studied the ECH of phenolic compounds. Several model compounds were selected, including catechol, anisole, phenol, guaiacol, 3-methoxyphenol, 4-methoxyphenol, syringol, 1,3-dimethoxybenzene, o-cresol, m-cresol, p-cresol, creosol, vanillin, syringaldehyde, eugenol, 4-Ethylphenol, 4-propylphenol, 4-propylguaiacol and 4-ethylguaiacol ³¹.

The cell setup was a H cell, separated by a Nafion 117 membrane. The cathode was Ru/ACC and the anode a Pt wire. Catholyte was a 0.2 M HCl solution (30 mL) and the anolyte a 0.2 M phosphate buffer (30 mL). Temperature was maintained at 80 °C and the experiment was run at 100 mA. The cell setup is shown on Figure 2-9 ³¹.

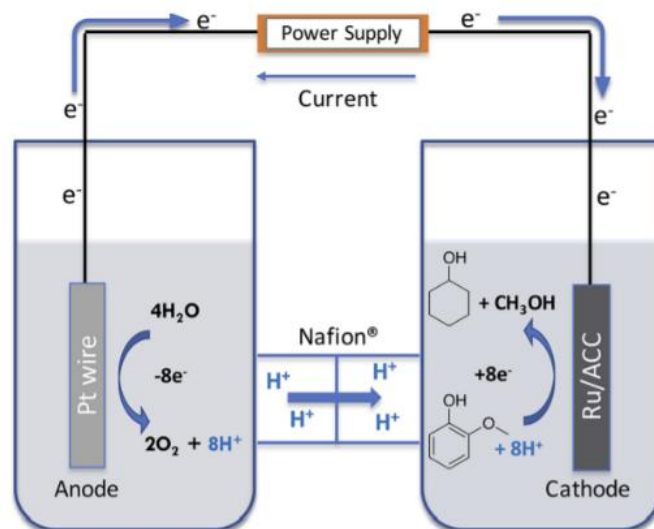


Figure 2-9 - Electrocatalytic hydrogenation in a two-chambered H cell. Reprinted with permission from reference ³¹. Copyright 2019 American Chemical Society.

The authors reported that increasing guaiacol concentration from 5 to 20 mM increased the FE and product selectivity. Further increases from 20 to 60 mM led to a steep decline in the conversion, although this was mitigated by increasing the duration of the process.

Phenol, p-cresol, 4- ethylphenol, and 4-propylphenol, as well as guaiacol, were transformed into their corresponding alkylcyclohexanols at high conversion (>98%). Carbon chain length was a determinant factor in reaction speed, as increased lengths resulted in slower conversions ³¹.

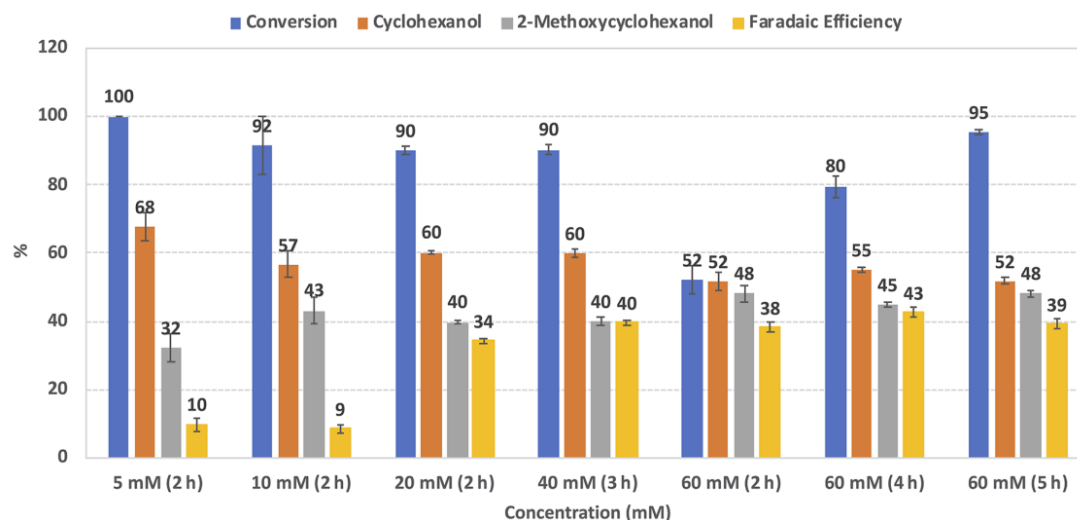


Figure 2-10 - Conversion, product selectivity, and Faradaic efficiency of guaiacol reduction using different substrate concentrations (5, 10, 20, 40, and 60 mM) at 100 mA and 80 °C. Error bars are standard errors. Reprinted with permission from reference ³¹. Copyright 2019 American Chemical Society.

2.4.2 Water soluble bio-oil (WSBO)

Li *et al.* proposed ruthenium supported on activated carbon cloth (ACC) as the catalytic cathode as the electrocatalyst. The bio-oil was mixed with water, in water to a bio-oil ratio of 4:1, with a bio-oil final concentration of 15 wt%. The mixture was then centrifuged, and the top layer was separated as the water-soluble bio-oil (WSBO) ⁹⁷. The same group proved that this cathode was capable of hydrogenating guaiacol, syringol and phenol, as shown in the previous sessions ²⁸.

Electrochemical hydrogenation of WSBO was carried out in a two-chamber glass H-cell, separated with a DuPont® Nafion117 membrane (see Figure 2-11). The reaction temperature was 27°C and the pressure was 1 atm. Anolyte consisted of 1 M sulfuric acid and Pt wire was used as the anode. A mixture of WSBO with 0.2 M NaCl served as the catholyte. The current was 480 mA ⁹⁷.

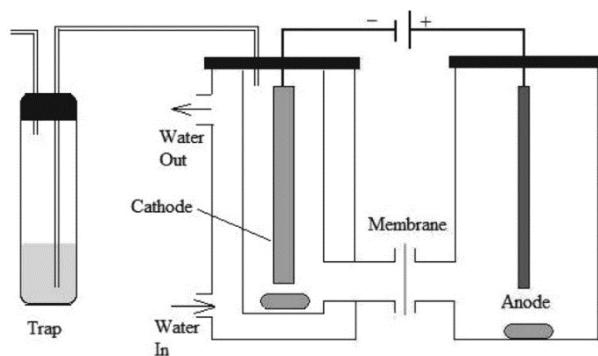


Figure 2-11 - Electrochemical hydrogenation cell setup for ECH of water-soluble bio-oil. ⁹⁷

After the 6.5h treatment, most of the organic compounds were depleted or fully converted by hydrogenation, the proposed mechanisms are shown in Figure 2-12. Removal of >50% of acetic acid is an expressive result, as it is a major contributor to bio-oil corrosiveness. No coke formation was observed. The same experiments were done using only ACC as the cathode and showed that Ru is an essential part of the proposed ECH process ²⁸.

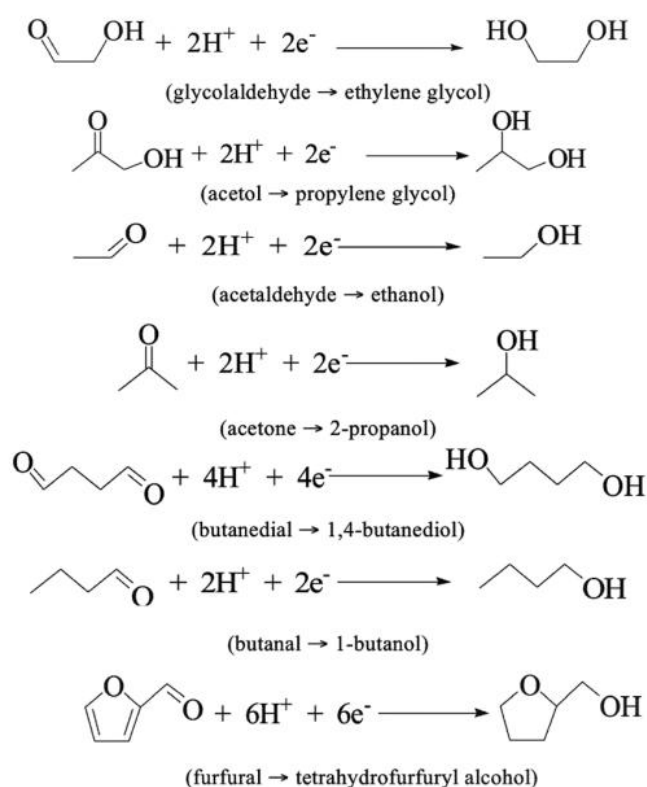


Figure 2-12 - Reduction of organic compounds in water-soluble bio-oil via ECH

97.

Although a noble metal catalyst (e.g., Pt and Ir) as the anode is normally used to ensure effective water oxidation, Zhang *et al.* found that a Fe(III)/Fe(II) redox pair can be utilised as a substitute when combined with Carbon felt as the anode. This change can make the process less expensive and can further its usage. The authors presented a Ru-based ECH cathode catalyst by uniformly embedding Ru nanoparticles into the surface of the ordered mesoporous carbon (OMC) support (noted as Ru@OMC). The catholyte solution was WSBO, duration was 3h ⁷⁴. The cell setup is shown in Figure 2-13.

The EHC treatment led to an increase in the H:C ratio and a decrease in the O:C ratio. Another result was the content reduction in several organic groups, such as acids, esters, carbonyls, phenols, sugars, and furans. The alcohol content increase was substantial, and the process elevated the selectivity of polyhydric alcohols. The results infer that this technique provides the ability to saturate unsaturated components in WSBO ⁷⁴.

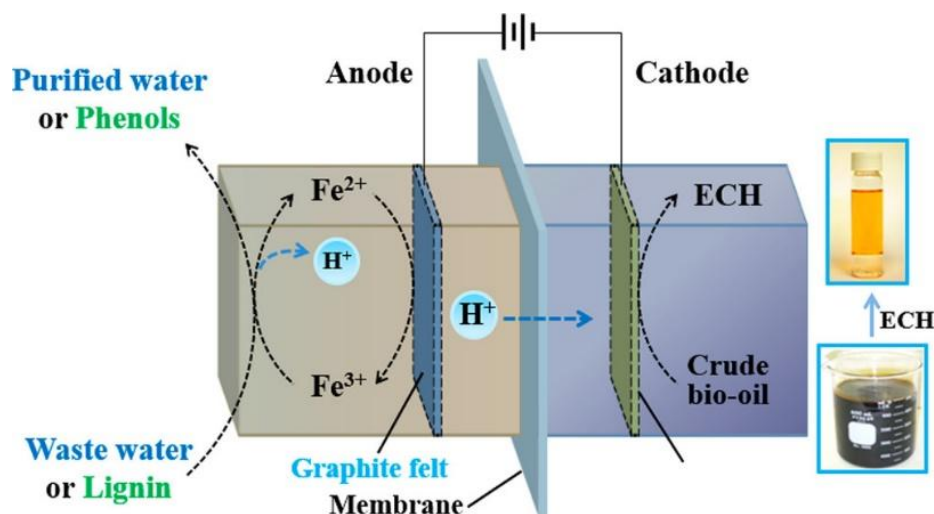


Figure 2-13 - Schematic illustration of low-energy ECH of bio-oil: experimental setup. Reprinted with permission from reference ⁷⁴. Copyright 2018 American Chemical Society

2.4.3 Whole oil

Lister et al. employed both an anion exchange membrane (AEM) and a cation exchange membrane, in what is described as a dual exchange membrane (DEM) to upgrade a whole pyrolysis bio-oil mixed with an aqueous phase containing acetic acid and formic acid. The concentrate vessel was filled with 10 mL solution of 1 M Na_2SO_4 . The oil was filtered to remove any char particles, a common product from pyrolysis. Figure 2-14 shows a diagram of the electrolysis system used in this work ³³.

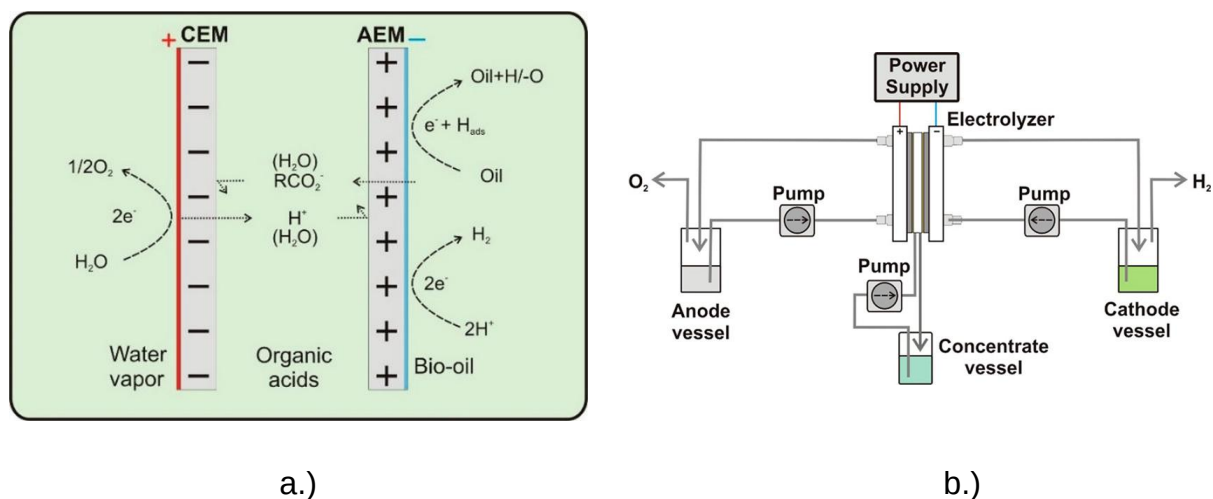


Figure 2-14 - Spatial chemical representation (a) and diagram of the separation–hydrogenation process (b). Reprinted with permission from reference ³³. Copyright 2018 American Chemical Society

The cell temperature was held at 35°C (± 2 °C), and the fluids flow rate was 2mL/min. A metal-free carbon catalytic cathode was chosen to prevent HER. The process achieved an increase in the pH from 2.6 to >4 and a significant reduction in total acid number (TAN). There were no signs of coke formation, improving carbon efficiency and catalyst lifetime. Although membrane degradation was noticed ³³.

Table 2-15 - Different setups and studies comparison table. * Reported as mA

Feedstock	Cathode	Catholyte	Anode	Anolyte	T (°C)	Duration (h)	J (mA/cm ²)	Ref.
Guaiacol	Boron-doped PtNiB/ordered mesoporous carbon (CMK-3)	0.2 M HClO ₄	IrO ₂ /C	0.2M HClO ₄	60	5	40*	75
Phenol derivatives	Ru/ACC	0.2 M HCl	Pt wire	0.2M phosphate	80	-	100*	31
WSBO	Ru/ACC	0.2 M NaCl	Pt wire	1 M H ₂ SO ₄	27	6.5	480*	97
WSBO	Ru nanoparticles on mesoporous carbon - Ru@OMC	WSBO	Fe(III)/Fe(II) + Carbon felt	Wastewater or Lignin	-	3	-	74
Resin wood (ponderosa pine) bio-oil	Metal-free (carbon)	1 M Na ₂ SO ₄	Ti sheets/ Pt coating	Purified water	35(±2)	-	-	33

2.5 Outlook from previous studies

The electrochemical approach to upgrading bio-oils is a technique that can be performed in mild temperatures ($<80^{\circ}\text{C}$) and pressure (1 atm). This is an essential condition for a cheaper product, as traditional methods are energy intensive. Also, in thermal stabilisation and deoxygenation, oxygen is released as CO_2 , CO , and H_2O . These products represent a loss of expensive carbon and H_2 ³³. The research gap that exists is on what are the ideal catalysts, membranes, cell configuration and how to increase the oil's low conductivity. Understanding the mechanism of the reaction and the behaviour of the compounds is a key part of the process, so model compound studies are necessary. Another way of simplifying the process so it can be more easily studied is utilising WSBO as a feedstock, this allows the study to circumvent the challenges brought by the complexity of a mixture that contains both polar and non-polar compounds. Most studies have focused on either model compounds or WSBO, therefore ECH of whole pyrolysis oil still needs further investigation. Zhenglong *et al* demonstrated that the separation of WSBO can lead to a higher organic compound conversion. Ruthenium was used as the basis for the catalyst cathode, this metal was also utilised by Zhang *et al.*, Zhou *et al.* and Gardew *et al.* The authors also proposed reactions for some compounds (see Figure 2-12), this shows that hydroxyl groups, such as ketones, carboxylic acids and alcohols are resistant to hydrogenation, whereas double bonds were almost depleted. Gardew *et al.* also reported that, for phenolic compounds, the double bonds inside the aromatic ring were hydrogenated, when the hydroxyl group was not (e.g., phenol was converted into cyclohexanol and cyclohexanone rather than benzene). This data was extrapolated for the main components in plastic pyrolysis oil (see Figure 2-15). It is worth noting that, although cyclohexane is a possible product of phenol hydrogenation, the process of C-O cleavage, which would involve the hydrogenation of cyclohexanol into cyclohexene ($\text{C}_6\text{H}_{12}\text{O}$

$\rightarrow \text{C}_6\text{H}_{10}$), followed by cyclohexene into cyclohexane ($\text{C}_6\text{H}_{10} \rightarrow \text{C}_6\text{H}_{12}$) would require much higher temperatures and overpotentials ⁸⁸.

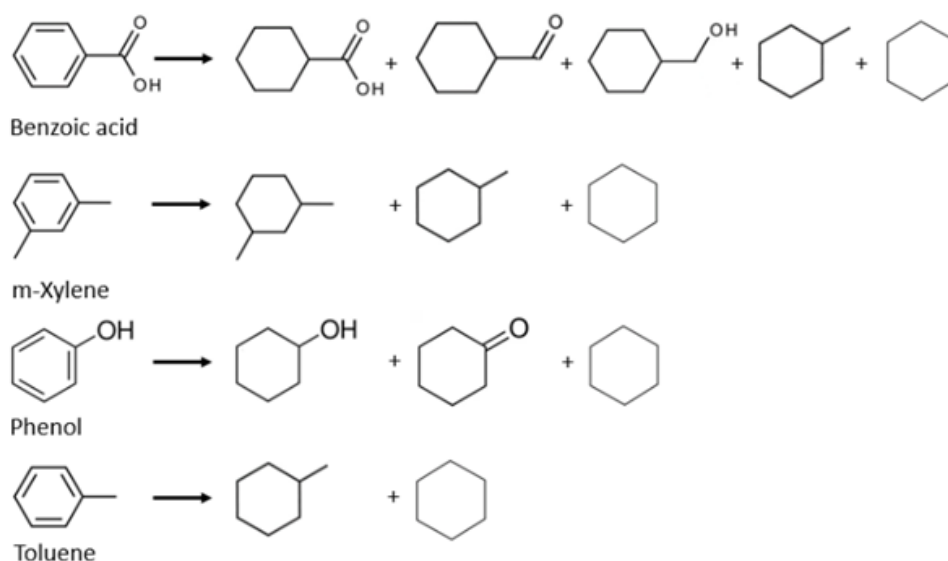


Figure 2-15 - Main components from plastic pyrolysis oil and the possible products from ECH.

Carbon loss during the ECH process was reported by Zhenglong et al, as only 80% of the carbon was retained in the cathode chamber. 6.0% was found in the anode chamber, due to migration through the membrane, 2.6% was adsorbed by the cathode and 0.2% was trapped in the downstream water trapping system. The system's total carbon loss was 11.2%. The authors suggest the rest could be inside the membrane, as it turned black after the process ⁹⁷. This exemplifies how different membranes could lead to a better result, as the carbon loss could possibly be avoided. Also, the process cost is increased by constantly changing the system's components. Zhang *et al.* showed that a cheaper anode, Fe(III)/Fe(II) redox pair, can be utilised as a substitute to the commonly used noble metal (e.g. Pt) as a way to make the overall process cheaper and more competitive.

The work of Zhou *et al* demonstrates how different catalyst cathodes can interfere with the final product, as the difference in FE and conversion were quite significant. The authors also proposed that the guaiacol upgrading was favoured by a chemisorption selectiveness to this

compound. This indicates that different feedstocks need different catalytic cathodes to be more effective. Gardew *et al* exemplified how substrate concentration can affect the FE and selectivity of the product, although it is not a direct relationship. Coke formation was not a major problem, although Zhenglong *et al* reported finding decanted materials on the cathode chamber.

To avoid the problems related to the commonly used H-type cell, Lister *et al.* proposed a carbon catalyst cathode and DEM as a cheap and effective way to achieve upgrading. Results were promising, and the product had a higher economic value, as it could be used as commodity chemicals, but the authors found that further upgrading would be necessary for utilisation as biofuel.

2.6 Plastic recycling

For the creation of a circular plastic economy, the plastic-oil needs to be upgraded into a valuable product, examples include biofuels and feedstock for industry (refined hydrocarbons, petrochemicals, or monomers). To achieve both the calorific values and chemical composition required, heteroatoms (O, S, N, etc) should be removed. Some other elements that are present in the oil were listed in previous sections.

One area where a process of generating feedstock could be helpful includes plastic recycling, where the waste product can be returned to oil and then upgraded. Taking into consideration the highly variable nature of real plastic waste, Kusenberget *et al* analysed municipal plastic waste and concluded that, to achieve industrial standards, the nitrogen concentration must be reduced by 87.7%, and oxygen by 98.0% (from 825 to 100 and 5200 to 100 ppmw respectively) ⁹⁸.

Therefore, the focus of the upgrading process are the oxygenated compounds, that is, reducing the O:C ratio of the oil. Oxygenated compounds can lead to lower stability and heating values, as well as a more corrosive product, due to carboxylic acids. Most of the oxygen content comes from PET but to accomplish an effective plastic waste recycling

process, PET cannot be excluded. Benzoic acid and its derivatives are the most common carboxylic acids in plastic-oil, therefore should be the focus of the ECH process.

2.6.1 Selecting a catalytic cathode

Catalysts can be very selective over organic functional groups, and this presents a challenge for the ECH of whole pyrolysis oil as it is a complex mixture (more than 300 compounds), therefore the cathode needs to be more versatile than the ones chosen for model compounds and be capable of hydrogenating various functional groups. Recent reports show that catalysts like alloy and carbon-metal hybrids are possible solutions ⁹⁹.

Although carboxylic acids are resistant to hydrogenation, ruthenium shows high activity for this process ¹⁰⁰. As shown in the previous section, Ru was also the chosen metal as cathode for Zhenglong et al. (Ru/ACC), Zhang et al. (Ru nanoparticles on mesoporous carbon) and Gardew et al. (Ru/ACC), which proves its effectiveness in hydrogenating WSBO and phenolic compounds, setting it as a prime candidate for the hydrogenation of whole plastic-oil. The possible mechanism for the hydronation of carboxylic acids is shown in Figure 2-16.

The hydrogenation of toluene into methylcyclohexane was carried out in a CEM system by Fukazawa et al. who found that PtRu/C was a better catalyst than individual metals such as Pt and Ru and presented high FE (>90%) ³⁵. On a later study, the same group reported on the ECH of benzoic acids into cyclohexane acids (PtRu/C catalyst) and presented high FE (99%) at a current density of 1.5mA cm⁻². The authors also reported that in less mild conditions, the carboxyl group could also be hydrogenated (see Figure 2-12). As mentioned in previous sections, Du et al also reported on the activity of different cathodes and found that Pt₃Ru/ACC led to a higher conversion than Pt and Ru separately.

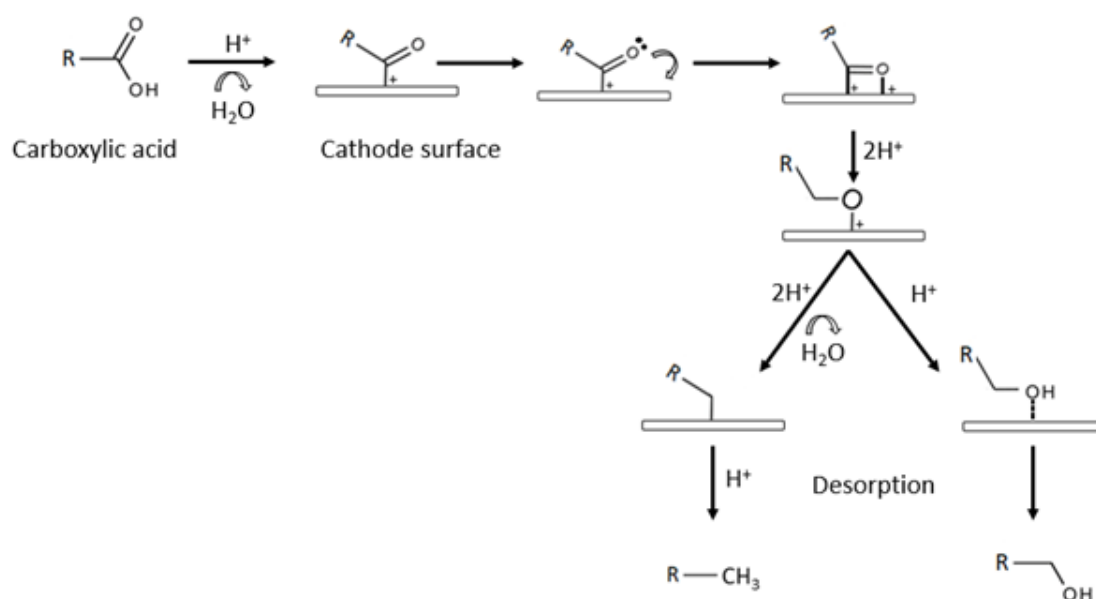


Figure 2-16 - Mechanism for the hydrogenation of carboxylic acids. Edited with permission from reference ¹⁰⁰. Copyright 2020 Wiley.

The authors suggested that this could be the result of a synergistic effect between the two metals, combining platinum's excellent hydrogenation potency and the predominant direct hydrogenolysis ability of ruthenium ⁴⁵. In addition, Salakhum et al suggested that combining both metals can facilitate the cleavage of C-O and O-H bonds, as it reduces their heterolytic activation energies ¹⁰¹. This indicates that PtRu/ACC is a prime candidate for the ECH of carboxylic acids, and therefore, a possible choice of cathode for the hydrogenation of plastic-oil ³⁴.

2.6.2 Conductivity challenge

The pyrolysis oil has low conductivity values, which is a challenge for an electrochemical process. To circumvent this, an electrolyte is used, as a way of increasing the conductivity. However, the commonly used water-based electrolytes (acid /water; alkali /water and salt /water) are unlikely to be suited for pyrolysis oil treatment, due to the large number of water-insoluble compounds. The removal of both water and the electrolyte (e.g., HCl) after the treatment is also necessary, as it lowers the quality of the

product. This would increase the costs and the complexity of the process and could render it unviable ⁹⁹.

Possible solutions are to either increase oil conductivity via additives (e.g., Tetrabutylammonium hexafluorophosphate (NBu₄PF₆); LiCl; ammonium carbonate) or use a solvent that is capable of dissolving both polar and nonpolar compounds (e.g., ionic liquids, DES (Deep Eutectic Solvents); biomass-derived organic solvents). Studies are necessary to understand the changes in the physicochemical properties of the oil and its behaviour during ECH that an additive could bring. LiCl could increase the corrosivity of the product as Li⁺ and Cl⁻ are prone to corrosion. Ammonium carbonate could lead to membrane clogging via carbonate deposition, as well as increase the nitrogen composition of the oil, and therefore, its corrosivity. NBu₄PF₆ is a chemically inert powder that is commercially available and could provide the much-needed conductivity for the system.

2.6.3 Ionic liquids and DESs

Ionic liquids and DESs are quite similar in their uses and could serve the same purpose and although DESs, especially natural deep eutectic solvents (NADES), are considered greener and cheaper, it is a very recent class of mixtures and still needs time to develop. Some of its uses are in metallurgy and electrodeposition, due to its high electrical conductivity and solubility, NADES has also been utilised as a precursor for biomass processing into more valuable chemicals ^{102–104}.

2.6.4 Biomass-derived organic solvents

Biomass-derived organic solvents are an emerging and very promising alternatives as green solvents, that are produced from renewable sources and are non-hazardous to the environment. From this class of solvents, one of the most prominent is 2-methyltetrahydrofuran (2-MeTHF), which has Levulinic acid and Furfural, two of bio-oil's main components, as its

precursors ¹⁰⁵. That sets both NADES and biomass-derived organic solvents as candidates for alternative solvents for ECH of pyrolysis oils ⁹⁹.

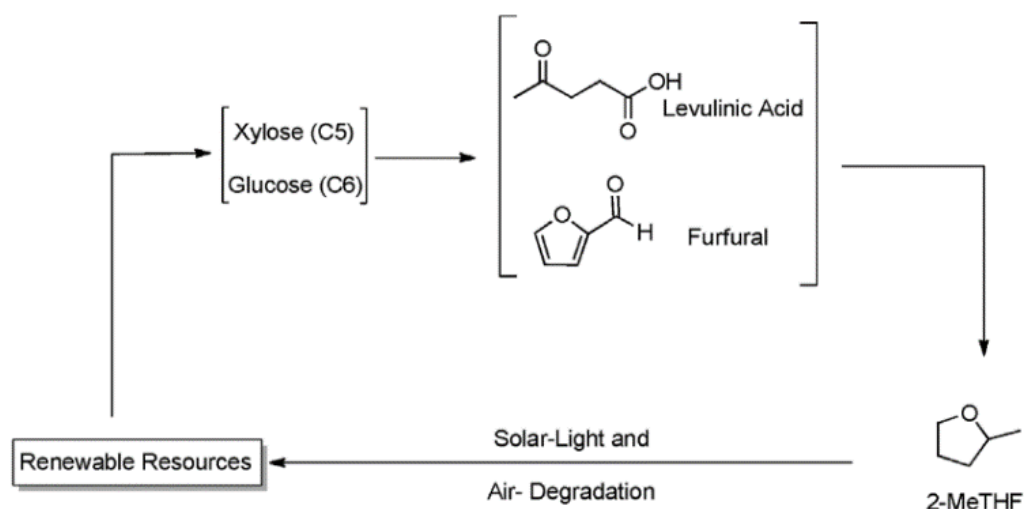


Figure 2-17 - 2-MeTHF production via renewable sources. Edited with permission from reference ¹⁰⁵. Copyright 2012 ChemSusChem.

2.6.5 Plastic oil utilisation

2.6.5.1 Biofuel

Although not an ideal solution, giving plastic waste a second life usage would be immensely beneficial for the environment as the utilisation of the upgraded plastic oil as biofuel could lower the world's consumption of petroleum. For a business-as-usual approach, global plastic waste generation will increase from 260 million tons in 2018 to 460 million tons in 2030. For the same time frame, if the amount of plastic waste collected for recycling achieves 50%, chemical recycling could be responsible for 13% of all plastic production (considering the “high adoption” scenario and oil barrel price of around \$75 dollars) ⁵⁸. This means that 59.8 million tons of plastics would go through pyrolysis, producing approximately 39.0 million tons of plastic oil (65.28 wt.% average yield from several plastic pyrolysis reactors as reported by Siu Hua Chang in 2023) ⁸. As the ECH of plastic oil still needs to be tested, the following calculations will be done using the heating value of the pre-treatment plastic oil (41-47 MJ/kg, averaged to 44

MJ/kg)¹⁰⁶. This means that approximately 476.67 TWh (terawatt-hours) per year of biofuel could be produced via ECH, which is more than the whole of Asia, Europe, and Africa combined production in 2021 (aprox. 380 TWh) and higher than the world's largest producer, The United States (399 TWh).

2.6.5.2 Plastic production

As stated in the previous sections, for the creation of a circular economy, plastic waste needs to be recycled into feedstock for plastic production. In 2019, 368 million tonnes of plastics were produced worldwide,¹⁰⁷ 16% of the waste was collected for recycling and, after accounting for losses, 12% went through mechanical recycling. Landfills were the destination for 40%, and incineration for 25%, 19% of all plastic waste produced was mismanaged⁵⁸. This means that, of all plastic waste, 65% of it, 239.2 million tonnes, was collected but not recycled. If this share went through chemical recycling, 156.15 million tonnes of plastic oil would be produced (65.28 wt.% average yield)⁸. As the ECH of plastic oil still needs to be tested, three scenarios of conversion will be considered: low, fair, and high conversion (50, 75 and 90% respectively). For low conversion, 78.08 million tonnes of plastic production feedstock would be produced. Fair and high conversion would lead to 117.11 and 140.53 million tonnes, respectively. This means that, at the current technology state, up to 38.18% of all resin could come from a sustainable source.

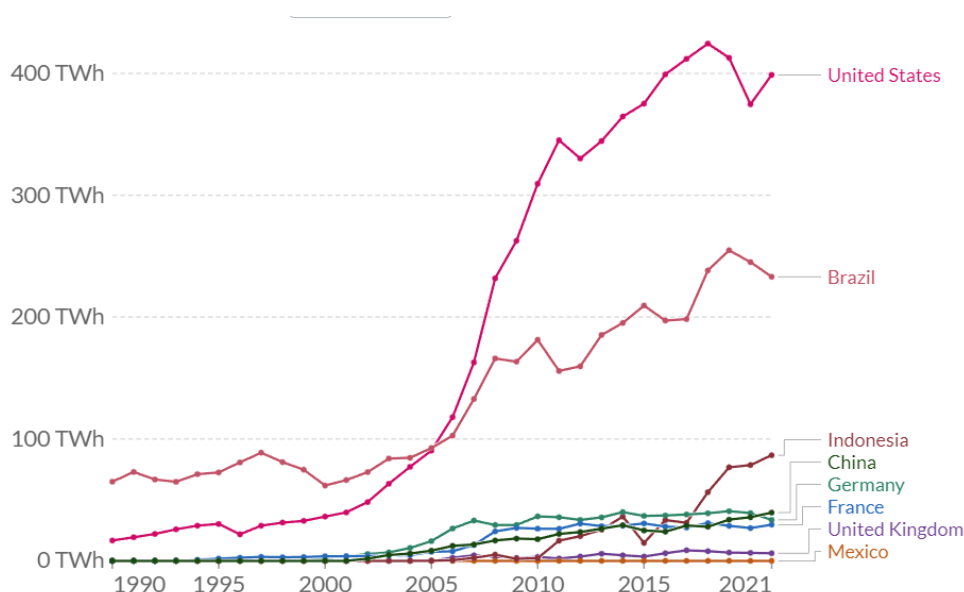


Figure 2-18 - Total biofuel production in terawatt-hours (TWh) per year. Biofuel production includes both bioethanol and biodiesel. Chart constructed by Our world in data ¹⁰⁸.

2.7 Paper 1 Conclusion

Fast pyrolysis is a thermochemical process that can be used to produce oil from both biomass and plastic. This material is a complex mixture containing acids, alcohols, aldehydes, esters, phenols, guaiacols, and a great number of other organic compounds. As it has high water content, low C:O ratios, high viscosity, and low density it needs to be upgraded for widespread usage. The Electrochemical process for bio-oil upgrading is still new and needs further study to be fully optimised. However, previous studies show that it can be done in mild conditions of temperature and pressure. ECH can be done utilising low-cost materials and can achieve high FE and conversion. ECH shows an exciting path for the upgrading process of pyrolysis oils from chemical recycling of both biomass and plastics, a low-cost, mild hydrogenation process that can help to achieve the necessary circular and greener economy. The main takeaways from this review are:

- Noble metals are reactive species for the ECH of bio-oils. Rh, Pt and Ru-loaded carbon cloth have all been reported to hydrogenate alcohols, carboxylic acids, olefins, and aromatic compounds, and presented high efficiency and FE.
- Current, potential, pH, and temperature are all essential factors in the ECH process. The fine-tuning of these variables is necessary and directly linked to the quality of the final product.
- Conductivity of the oil presents a major challenge for ECH, alternative electrolytes and additives might be required to make the process viable.
- The hydrogenation of plastic-oils is a possibility that still needs testing, although, as this technology matures, it may become one alternative for both the production of green plastics and biofuels.

2.8 Paper 1 Acknowledgements

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3 Paper Two: Mechanisms of electrochemical hydrogenation of aromatic compound mixtures over a bimetallic PtRu catalyst

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Abstract

Efficient electrochemical hydrogenation (ECH) of organic compounds is essential for sustainability, promoting chemical feedstock circularity and synthetic fuel production. This study investigates the ECH of benzoic acid, phenol, guaiacol, and their mixtures, key components in upgradeable oils, using a carbon-supported PtRu catalyst under varying initial concentrations, temperatures, and current densities. Phenol achieved the highest conversion (83.17%) with a 60% Faradaic efficiency (FE). In mixtures, benzoic acid + phenol yielded the best performance (64.19% conversion, 74% FE), indicating a synergistic effect. Notably, benzoic acid (BA) consistently exhibited 100% selectivity for cyclohexane carboxylic acid (CCA) across all conditions. Density functional theory (DFT) calculations revealed that parallel adsorption of BA on the cathode (-1.12 eV) is more stable than perpendicular positioning (-0.58 eV), explaining the high selectivity for CCA. These findings provide a foundation for future developments in ECH of real pyrolysis oil.

3.1 Introduction

Pyrolysis is the thermal decomposition of materials at high temperatures in an inert atmosphere. When applied to waste and biomass feedstocks, the condensable liquid product from pyrolysis (constitutes around 70 wt.% of the pyrolysis products), known as bio-oil is widely recognised as a low-carbon biofuel and precursor for chemical production. In the waste industry, there is significant

interest in applying pyrolysis as an enabling technology for plastic polymer recycling processes, producing pristine polymers as platform chemicals. This can potentially address the global issue of low levels of plastic recycling; currently standing at less than 10% in the European Union, most of which uses mechanical recycling routes (i.e. limited to thermoplastics).^{57–59}

Despite these potentials, bio-oil is a complex mixture containing over 300 compounds which poses significant challenges to its practical use¹⁰. Its physical and chemical properties, including viscosity, C:H C:O ratios, and thermal and chemical stability, typically cannot meet the standards of direct application as a biofuel or as feedstock for the chemical and petrochemical industries⁶². Thus, upgrading bio-oil is essential to enhance its suitability for widespread use.

A key step to improving bio-oil quality for fuel and polymer recycling applications is to increase the hydrogen-to-carbon ratio crucial for stability through hydrogenation processes. Conventional hydrogenation technologies, including catalytic cracking and hydroprocessing. Both processes involve high temperature and pressure reactions. To date, commercial applications of these hydrogenation methods are rare due to the significant operational costs, catalyst deactivation and undesirable secondary reactions, particularly tar formation^{27,32,62,109,110}. Electrochemical hydrogenation (ECH), by contrast, can be performed under milder reaction conditions at low temperatures (below 80°C) and ambient pressure to reduce reactive functionalities. Additionally, the ECH process requires no H₂ supply to the process, therefore eliminating the costs and risks associated with hydrogen storage. These advantages make ECH a promising alternative to conventional routes for sustainable bio-oil upgrading^{26,28,29}.

However, as a proof-of-concept currently, fundamental reaction kinetics and mechanisms of key bio-oil constituent compounds during ECH process are still not fully understood. As such, this study uses key compounds, including guaiacol, phenol, benzoic acid and their derivatives commonly found in both biomass and plastic-derived bio-oil^{17–19} as a model compound, to investigate their reaction mechanisms in an H-type cell set-up.

H-type cell is the most common design for electrochemical reactions. It consists of an anode and a cathode chamber, separated by a porous membrane (Figure 3-1). Cathode material selection is currently one of the most important steps in ECH research and deployment, as it can influence the conversion, Faradaic efficiency (FE), and selectivity. For phenol and guaiacol ECH, Pt, Pt/ACC (activated carbon cloth), Ru/ACC and Raney nickel have been widely reported to be effective for the ECH reactions of these compounds^{28,31,45,75,84}. However, the effective ECH of benzoic acid remains a challenge due to increasing some undesired side reactions (carboxyhydrogenation and over-hydrogenation) alongside the hydrogenation of the aromatic ring¹¹¹. A ‘bimetal’ Pt/Ru catalytic system has been reported by *Du et al*¹¹¹ and *Fukazawa et al*³⁴ for benzoic acid ECH, which performed well in promoting both hydrogenation and direct hydrogenolysis. *Salakhum et al*¹⁰¹ found that combining both metals facilitates the cleavage of C-O and O-H bonds, reducing their heterolytic activation energies, which increases ECH effectiveness.

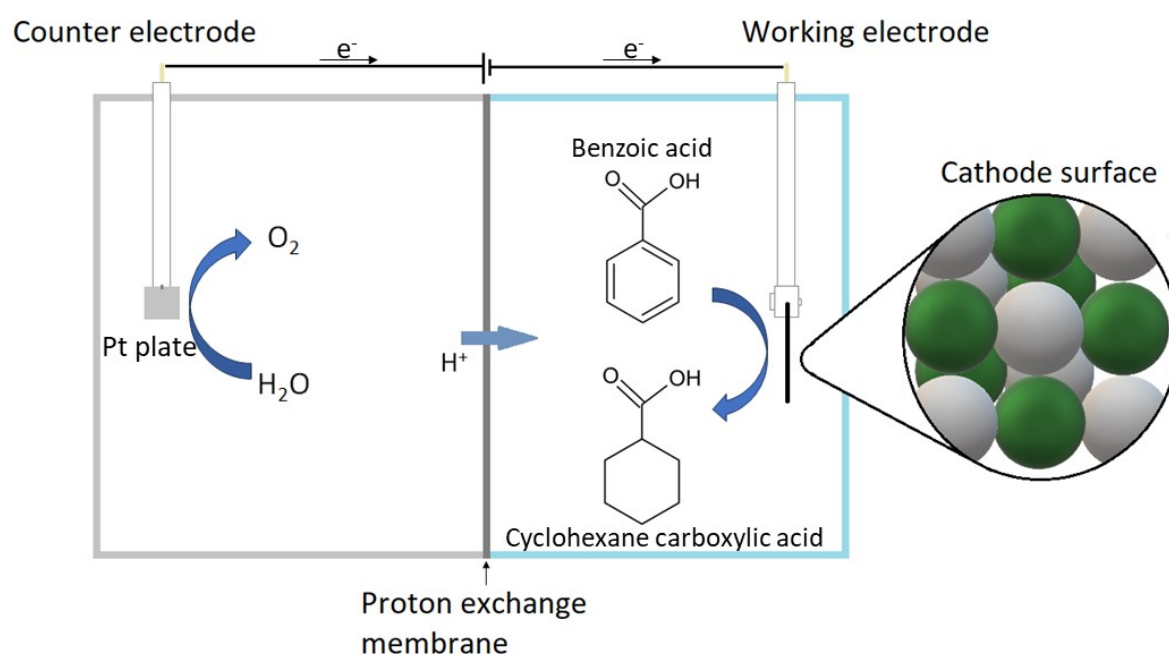


Figure 3-1 - Schematic representation of the electrochemical cell. The cathode surface represents the deposited platinum (in white) and ruthenium (in green) nanoparticles.

Understanding the complex interplay of model compounds during electrocatalytic hydrogenation is crucial for translating this process into industrial applications when dealing with real bio-oil feedstock. The presence of multiple components can significantly influence hydrogenation pathways, leading to synergistic and antagonistic effects. For instance, competition for adsorption sites can alter product distribution. Consequently, an in-depth understanding of co-hydrogenation phenomena is essential to optimise ECH processes for industrial relevance.

This study investigates the mild hydrogenation of bio-oil model compounds using a PtRu/ACC catalyst. To elucidate the complex reaction pathways and kinetics during mixtures, we adopted a full factorial experimental design to examine the co-hydrogenation of benzoic acid (BA), phenol (P) and guaiacol (G). Additionally, the ECH mechanisms of model compounds were analysed, including side reactions, adsorption energy, and molecule placement, using *in situ* electrochemical measurements and density functional theory (DFT) calculations.

3.2 Methods

3.2.1 Materials

Sulphuric acid solution (5M), benzoic acid (99%, extra pure) and guaiacol (99%) were purchased from Thermo Fisher Scientific. Phenol (liquified $\geq 89\%$) was purchased from Sigma Aldrich. All chemicals were used as received without further purification. A Nafion 117 membrane (from Ion Power) was used as the cation exchange membrane to separate the cathode and anode chambers. To ensure the activation of the membrane and optimise its ion transport capability, it was pretreated according to Peng et al ¹¹². It was treated with oxygen peroxide (H_2O_2) at 80 °C for 1h, followed by deionised water for 1h and 1.0 M H_2SO_4 for 1h at the same temperature. The membrane was washed with deionised water after each stage.

3.2.2 ECH of pure and mixed model compounds

A two-chamber electrochemical cell, separated by a proton exchange membrane (PEM) was selected for this process, where the anode was a 1x1 cm platinum

plate, the selected catalytic cathode was a commercially available 4 mg/cm² Platinum Ruthenium Black-Carbon Cloth Electrode (PtRu/ACC, Fuel Cell Store, 1:1 Pt:Ru ratio). Both cells were filled with 1.0 M sulfuric acid (H₂SO₄) as the electrolyte. The ECH tests were performed at a 90 mL (per chamber) H-type cell and run at electrostatic control and constant temperature (both at different values depending on the experiment) for 10 min without the organic compound to polarise the electrodes. Afterwards, the model compound was added to the system to obtain a set final concentration. The experiment was run for a duration which ensured the availability of sufficient electrons to convert the compounds (4 to 6 hours). Samples (1 mL) were taken in discrete time intervals, and the organic compounds were extracted with 2 mL of dichloromethane (DCM). After each experiment, the electrolyte was discarded, the cell cleaned, and the cathode was soaked in 5 mL dichloromethane (DCM) for 15 min, to ensure the desorption of any molecules on its surface.

The process of finding the optimised conditions was done utilising benzoic acid as the main model compound, and guaiacol and phenol were used to confirm the effectivity of the process in other model compounds. All tests with mixtures were carried out at the same temperature and current density as the optimised point, variations on the initial concentration were specified in the text. All tests were carried out in triplicates and the error bars are relative to the standard error.

For analysis, the samples were tested in the GC-MS Shimadzu TQ8040. The GC used a Restek Rtx-5 capillary column, 28.5 m × 0.25 mm with a 0.25 µm film thickness, a 1.18 mL min⁻¹ helium carrier gas flow rate, and a split ratio of 1:25. The injector temperature was set at 250 °C. The GC oven program started at 34°C and was held for 2 min and then heated at 50°C min⁻¹ to 300°C. Mass spectrometry was operated at m/z ranging from 50 to 500. Species associated with each chromatographic peak were identified by comparing their observed mass spectrum with the NIST library. External standards were also used to identify compounds and quantify the peaks. Results are in area %. The morphology of the electrodes and EDS (Electron Dispersive Spectroscopy) were acquired by TESCAN VEGA 3 Scanning Electron Microscope (SEM). Raman

spectroscopy was performed using a Horiba LabRAM equipped with a Red 632.8 nm laser. Samples were exposed using the following parameters: no filter, 400 μm hole, 100 μm slit, 1800 grating, 3 exposures each of 5 s. Before any samples were analysed, the Raman shift was calibrated using the known 520.7 cm^{-1} peak of a silicon reference sample.

Table 3-1. Benzoic acid ECH optimisation tests and ECH of both phenol and guaiacol at the optimised conditions

Compound	Concentration (mM)	T ($^{\circ}\text{C}$)	Current (A)
Benzoic acid	10	75	0.4
Benzoic acid	20	75	0.4
Benzoic acid	30	75	0.4
Benzoic acid	50	75	0.4
Benzoic acid	20	40	0.4
Benzoic acid	20	50	0.4
Benzoic acid	20	55	0.4
Benzoic acid	20	60	0.4
Benzoic acid	20	80	0.4
Benzoic acid	20	55	0.05
Benzoic acid	20	55	0.1
Benzoic acid	20	55	0.2
Benzoic acid	20	55	0.6
Phenol	20	55	0.1
Guaiacol	20	55	0.1

3.2.3 Factorial design of experiment

The experimental matrix was designed using JMP PRO 17, as shown in Table 3-2, where a “+” signs indicate the compound is present, and a “-” signals the opposite. Each model compound and the initial concentration were selected as independent variables (factors), and the conversion and Faradaic efficiency as

responses. The factors were set to discrete numeric values, and the model covered all main effects and two-factor interactions. Experiments with no model compounds (“-”“-”“-”) were not shown in Table 3-2, as no compounds would lead to 0% conversion. The initial concentration of each compound is always equal to the others. For all single-compound experiments, the duration was set to 4h, otherwise it was 5h. This adjustment was made to ensure enough electrons were introduced into the system, without a change in current.

3.2.4 Electrochemical measurements

Electrochemical measurements were performed using a PalmSens EmStat4s at 55°C, which consisted of a three-electrode system with the used cathode, anode, and an Ag/AgCl (in saturated KCl solution) as the working, counter, and reference electrodes, respectively. The potential vs. Ag/AgCl was converted to the potential vs. RHE (reversible hydrogen electrode) based on the Nernst equation:

$$R_{RHE} = E_{Ag/AgCl} + 0.059 * pH + E_{Ag/AgCl}^0 \quad (3-1)$$

All electrochemical measurements were carried out in 1.0 M H₂SO₄ with and without the model compounds. LSV tests were recorded at a scan rate of 5 mV s⁻¹ from -0.200 V to 0.200 V. CV was carried out from -0.200 V to 0.200 V, with a E_{step} of 5 mV and a scan rate of 5 mV s⁻¹. EIS was measured vs OCP at a max frequency of 10⁵ Hz and a min frequency of 10⁻¹ Hz, the E_{start} was set to -0.200 V. Equilibration time was 5 s.

3.2.5 Calculations

To understand and quantify the ECH process, the following equations were used:

$$F.E. (\%) = \frac{\text{mols produced} * n * F}{\text{Total electrons passed}} * 100 \quad (3-2)$$

$$\text{Conversion} (\%) = \frac{\text{Mols reactant consumed}}{\text{Initial moles reactant}} * 100 \quad (3-3)$$

$$\text{Selectivity} (\%) = \frac{\text{Mols desired product}}{\text{Total mols product}} * 100 \quad (3-4)$$

$$\text{Current density (mA cm}^{-2}\text{)} = \frac{\text{Current}}{\text{Surface area}} \quad (3-5)$$

Where F is the Faraday constant ($96\,485\text{ C mol}^{-1}$), and n is the number of electrons necessary for the hydrogenation process ($n = 6$ for the conversion of benzoic acid into cyclohexane carboxylic acid, for example).

3.2.6 DFT calculations

All calculations were carried out using QuantumEspresso/7.2-foss-2022b^{113–115} with BURAI 1.3.1 as a visualiser. VESTA was used to calculate the electronic structure. Both positive and negative isosurfaces were set to $0.06\text{ e/\AA}^3$. The generalized-gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional described the exchange-correlation energy. To enhance computational performance, all calculations were performed with a thermal smearing of 0.01 Ry and spin polarisation. A 4-Layer 4×4 PtRu (111) slab was built with a $20\text{ \AA}$ vacuum gap and two fixed bottom layers. The slab was placed at the bottom of the cell, to certify that all reactions happened on the top surface. A $(2 \times 2 \times 1)$ k-point grid was set. The test molecule was placed at a distance of $1.5\text{ \AA}$ from the surface, where it did not start the calculations with any bonds with the surface. The adsorption energy (E_{ad}) of the different adsorbates is defined as:

$$E_{ad} = E_{Total} - (E_{adsorbate} + E_{Surface}) \quad (3-6)$$

Where E_{Total} is the calculated energy for the final system (slab + adsorbate), $E_{adsorbate}$ is the calculated energy of each adsorbate and $E_{Surface}$ is the energy of the bare cathode surface.

3.3 Results

3.3.1 Electrochemical hydrogenation of model compounds

Benzoic acid electrochemical hydrogenation tests were carried out using an H-type electrochemical cell (Figure 3-1). At an initial BA concentration of 10 mM , 94.70% conversion with 100% selectivity to cyclohexane carboxylic acid (CCA)

was achieved within 4 hours at 9% Faradaic efficiency (Figure 3-2a-b). This high selectivity was consistently observed across all benzoic acid experiments in this study. Increasing the initial concentration from 10 to 20 mM resulted in a decreased conversion and increased FE (75.4% and 14%, respectively). The initial BA concentration significantly impacted both conversion and Faradaic efficiency. Increasing the concentration from 10 to 20 mM enhanced both parameters, where the higher concentration of organic compounds likely enhances the chance of interaction and reaction with existing H^+ ions. However, further concentration increases to 30 and 50 mM led to decreased conversion, despite slightly improved FEs. This suggests that at higher concentrations, the availability of electrons becomes insufficient to sustain the reaction rate. Based on this finding, the optimal initial BA concentration for this study was determined to be 20 mM and applied to other experiments across this study.

Temperature significantly influenced ECH performance. To evaluate the effect of temperature on the process, and determine the optimal condition, we tested temperatures of 40, 50, 55, 60 and 80°C (Figure 3-2c-d), maintaining the same current density at 100.0 mA cm⁻² and setting the initial concentration of BA to 20 mM. At lower temperatures (40 °C), the system's conductivity was reduced, leading to insufficient activation energy for bond cleavage^{26,28,90} and consequently lower conversion (49.8%) and Faradaic efficiency (9%). Increasing the temperature to 50-60°C enhanced both conversion and FE, with optimal performance observed at 55 °C. However, further heating to 80 °C promoted hydrogen desorption from the cathode, resulting in decreased ECH activity (78.74% conversion, 14% FE).

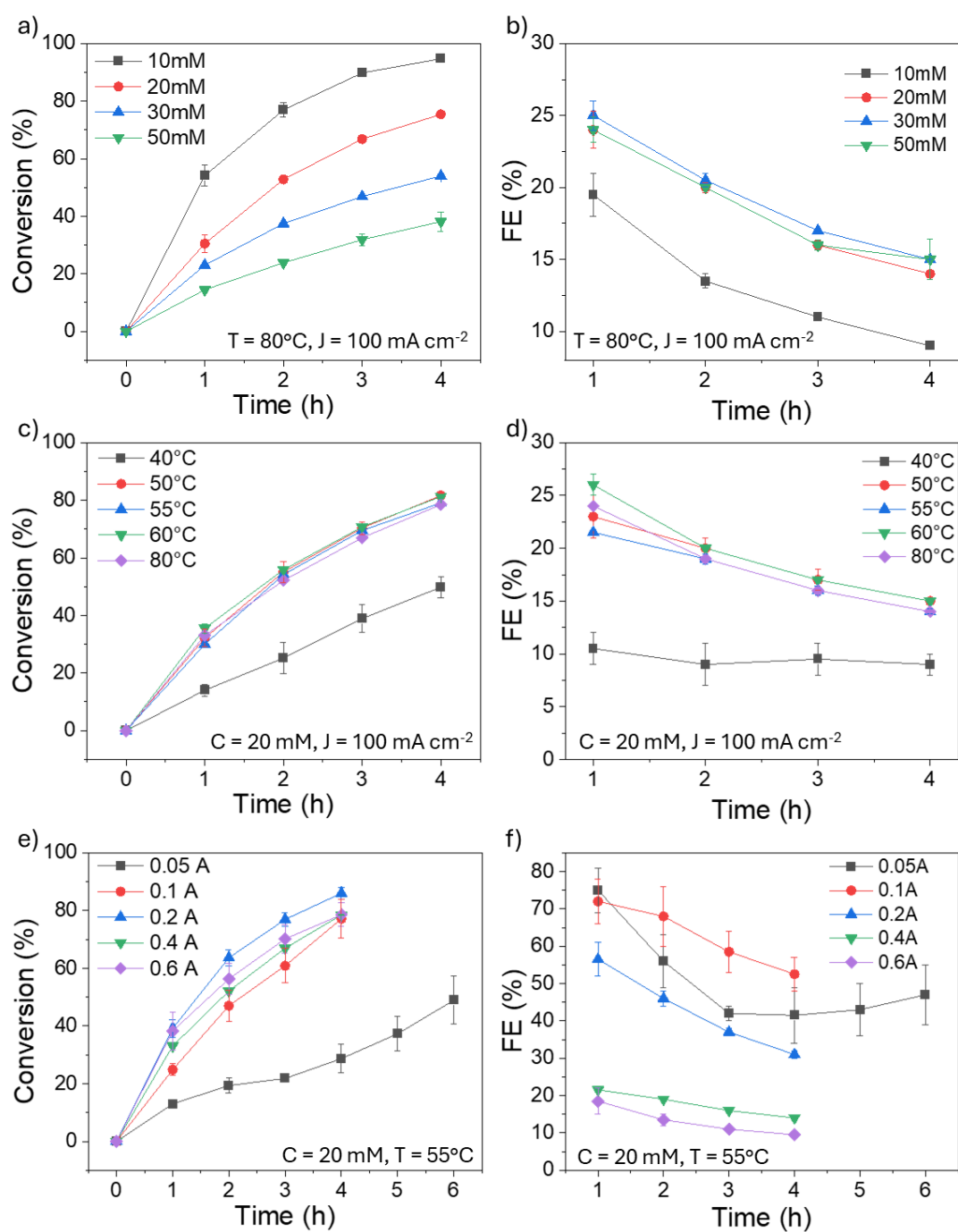


Figure 3-2 - Benzoic acid conversion to CCA over time during ECH. Charts show the impact of different initial benzoic acid concentrations (a), temperatures (c) and currents (e) and their corresponding Faradaic efficiency (b, d and f). Where T = temperature, J = current density and C = initial concentration. Error bars indicate the standard error of triplicated experimental results.

The influence of current density on ECH was investigated using five current values (0.05, 0.1, 0.2, 0.4, and 0.6 A), corresponding to current densities of 12.5, 25.0, 50.0, 100.0, and 150.0 mA cm⁻², respectively (based on a 4.0 cm² cathode area). The initial BA concentration was maintained at 20 mM, and the temperature at 55 °C. Preliminary tests at 0.05 A indicated insufficient proton generation on the cathode surface, limiting reactant collisions and hindering process efficiency.

Increasing the current density from 12.5 to 25.0 mA cm⁻² significantly improved both conversion and Faradaic efficiency. At a current density of 50.0 mA cm⁻², the conversion increased by 8.87%, but the FE reduced significantly from 56% to 31%. At higher current densities of 100 and 150 mA cm⁻², higher overpotentials are required (0.340 and 0.416 V vs Ag/AgCl, respectively), increasing HER rate and resulting in the lowest FE values observed in the experiment, at 14% and 10%, respectively. This decline in Faradaic efficiency at higher overpotentials can be attributed to several factors. First, higher overpotentials increase the likelihood of side reactions, which in this process is hydrogen evolution reaction (HER), these compete with the desired reaction and consume part of the applied current without contributing to the target product formation, reducing FE. Additionally, the rapid generation of hydrogen gas at elevated current densities can lead to the accumulation of gas bubbles on the cathode surface, which impedes effective mass transport by blocking active sites, thereby reducing the available surface area for the reaction.²⁶

To assess cathode stability, reproducibility, and process sustainability, the optimised conditions (temperature = 55 °C, current density = 25.0 mA cm⁻², initial BA concentration = 20 mM) were replicated over five consecutive cycles. The results (Figure 3-3) indicated a consistent performance of the PtRu/ACC catalyst over the five cycles of the experiment. Despite the aggressive reaction environment, there is no sign of cathode degradation, which was confirmed by scanning electron microscopy observation (Figure 3-10) in addition to assessing its consistency in performance via GC-MS. It is worth noting that the selectivity for CCA remains 100% throughout all cycles.

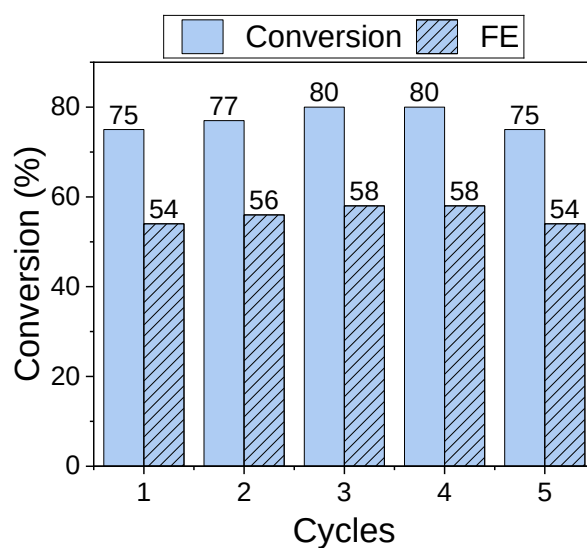


Figure 3-3 - ECH of benzoic acid in the optimal conditions for several cycles. Temperature = 55°C, current density = 25.0 mA cm⁻² and initial concentration = 20 mM of BA.

Phenol and guaiacol were subjected to ECH under the optimised conditions determined for benzoic acid. Phenol was observed to be the most effective under these conditions, achieving 88.75% conversion and 64% Faradaic efficiency with high selectivity (99%) towards cyclohexanol (Figure 3-4a-b). In contrast, guaiacol demonstrated lower activity (68.59% conversion, 59% FE) (Figure 3-4c-d) with a product distribution of 50% cyclohexanol, 46% 2-methoxycyclohexanol, and 4% 1-methoxycyclohexane, indicating a preference for demethoxylation over dehydration. Notably, complete aromatic ring hydrogenation was observed for all three model compounds, suggesting a common reaction pathway.

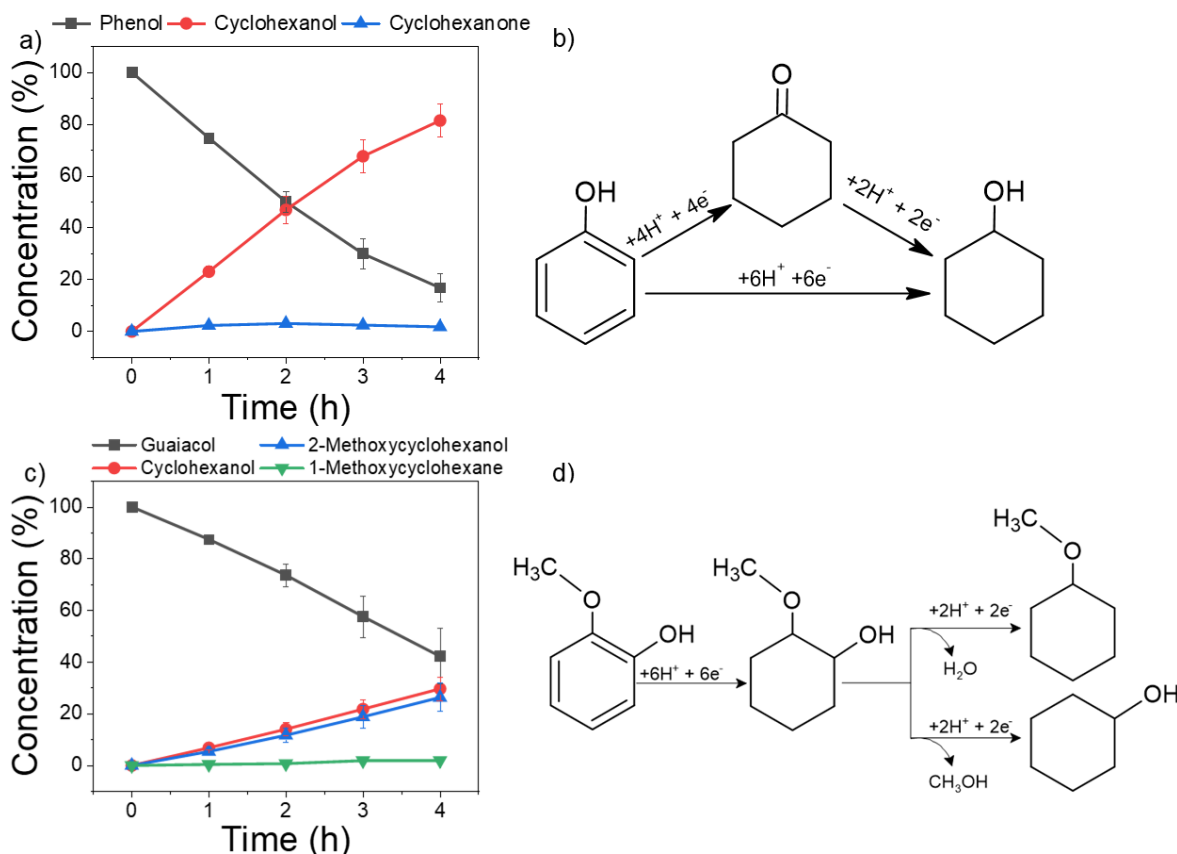


Figure 3-4 - ECH over time of guaiacol and phenol. Conversion of guaiacol (a) and phenol (b) and their respective possible hydrogenation paths (b and d). Error bars indicate the standard error of triplicated experimental results.

While higher conversion and FE for benzoic acid ECH have been reported in the literature using smaller H-type cells (25 mL vs. 90 mL) ¹¹¹, direct comparison is challenging due to differences in cell geometry. Smaller cells often exhibit lower resistance and require lower overpotentials, which in turn affects FE. Scaling up to larger H-type cells necessitates increased reactant quantities, higher currents, and overpotentials, potentially impacting efficiency and selectivity. To address these limitations, continuous flow reactors may offer advantages by mitigating mass transfer issues and enabling better process control.

3.3.2 Electrochemical hydrogenation of model compound mixtures

Understanding the effects of having more than one model compound during ECH is essential to progress bio-oil upgrading, which are inherently mixed compounds. To investigate potential interactions (synergistic and antagonistic effects) of each compound in the mixture, a factorial experimental design approach was applied as shown in Table 3-2, where a “+” signs indicate the compound is present, and a “-” signals the opposite. Notably, the applied overpotential showed minimal variance (0.003V), remaining between 0.205 and 0.208 V vs Ag/AgCl, regardless of the composition or concentration of the model compounds. This indicates that the conductivity of the system is more significantly influenced by the electrolyte and temperature rather than the model compounds, likely due to their low concentration.

Table 3-2. Results comparison for the ECH of benzoic acid (BA), phenol (P) and guaiacol (G) mixtures. Reaction parameters: current density = 25.0 mA cm⁻², temperature = 55°C, electrolyte = H₂SO₄ 1M.

Compound			Entry	Initial concentration (mM)	Conversion (%)	FE (%)
BA	P	G				
+	-	-	(1)	20	77.35 ± 2.18	56 ± 1
-	+	-	(2)	20	88.75 ± 5.57	64 ± 4
-	-	+	(3)	20	68.59 ± 5.78	59 ± 4
+	+	-	(4)	40	64.19 ± 4.51	74 ± 3
+	-	+	(5)	40	57.27 ± 2.86	66 ± 3
-	+	+	(6)	40	47.80 ± 2.69	55 ± 3
+	+	+	(7)	60	42.59 ± 1.78	73 ± 3
+	+	-	(8)	20	80.02 ± 7.28	58 ± 5
+	-	+	(9)	20	63.01 ± 0.94	46 ± 1
-	+	+	(10)	20	74.78 ± 4.41	54 ± 3
+	+	+	(11)	20	33.64 ± 1.11	24 ± 1

It was observed that increasing the number of unsaturated molecules generally decreased conversion, with the exception of mixtures containing all three compounds (Entries 7 and 11). Conversely, FE increased in runs 4, 5 and 7. Figure 3-2a shows a clear correlation between decreasing conversion and increasing initial concentration.

Notably, in entry 4, there is a significant drop in conversion from 83.05% (average of BA and P) to 64.19% in the mixture was observed, accompanied by a 13% increase in FE. This suggests a possible synergistic interaction between these two compounds, which aligns with previous studies on phenol-containing mixtures (phenol + furfural ¹¹⁶, and phenol + benzaldehyde^{117,118}), where hydrogen-bonded complex formation enhanced the hydrogenation of the co-reactant. This will be further explored in Chapter 4.

Phenol exhibited the highest conversion among the model compounds. In the BA+P mixture (Entry 4), phenol conversion reached 88.57% compared to 39.81% for benzoic acid. Similarly, phenol was preferentially converted in the G+P mixture (Entry 6) at 74.16% compared to 21.43% for guaiacol. This trend persisted in the ternary mixture (Entry 7), with phenol conversion at 75.79% exceeding those of benzoic acid (18.94%) and guaiacol (33.04%). Phenol also demonstrated the highest overall conversion efficiency as a standalone compound.

As a standalone compound, guaiacol consistently exhibited lower conversion compared to phenol and benzoic acid. This reduced reactivity is attributed to its complex molecular structure, containing both methoxy and phenolic groups, resulting in higher bond energies⁴⁵. Interestingly, in mixtures, the hydrogenation of guaiacol appears to be favoured when compared to BA. Mixing benzoic acid with guaiacol (entry 5), led to 50% and 65% conversion of each compound, respectively. This value is quite similar to pure guaiacol tests (69%, entry 3), despite the higher initial concentration. This trend was also observed for entry 7 (mixture of all three compounds). All these results are backed by the LSV (linear sweep voltammetry) analysis (see Figure 3-10), where the hydrogenation of phenol is favoured over guaiacol, which is, in turn, favoured over benzoic acid.

Setting the initial concentration to 20 mM led to similar trends to the ones observed previously. The BA + P mixture (entry 8) remains the best result for a mixture, presenting a considerably high 69.70% conversion for BA and 90.34% for phenol, very similar results to entries 1 and 2, despite the reduction in the initial concentration for each compound (from 20 to 10 mM), once again remarking to possible synergistic effects between these two compounds. Interestingly, although a slight decrease in activity is to be expected, this did not occur for phenol. Phenol also remained the most active species for ECH, achieving 91.44% conversion, compared to 58.12% for guaiacol (entry 10) and 61.60% compared to 24.33% and 26.11% for BA and guaiacol (entry 11), respectively.

Although the mixtures with guaiacol still presented inferior results, it is worth noting that P + G at 20 mM (entry 10) is far superior to P + G at 40 mM (entry 6), possibly due to guaiacol's resistance to ECH. That is, increasing guaiacol's concentration meant a greater negative interference in the process than phenol's positive one, leading to a lesser result. No phenol was detected in entry 9 (BA + G), and there was also no cyclohexane found in any of the experiments. This suggests that the concentration of these compounds may have been too low to detect, or that a larger quantity of reactant was needed to achieve the full conversion.

3.3.3 Factorial design analysis

Two models were developed to study the effects of mixture composition at low and high concentrations. In both cases, the initial model included main effects and interaction terms: BA, P, G, BA + P, BA + G, and P + G, with conversion and FE as responses.

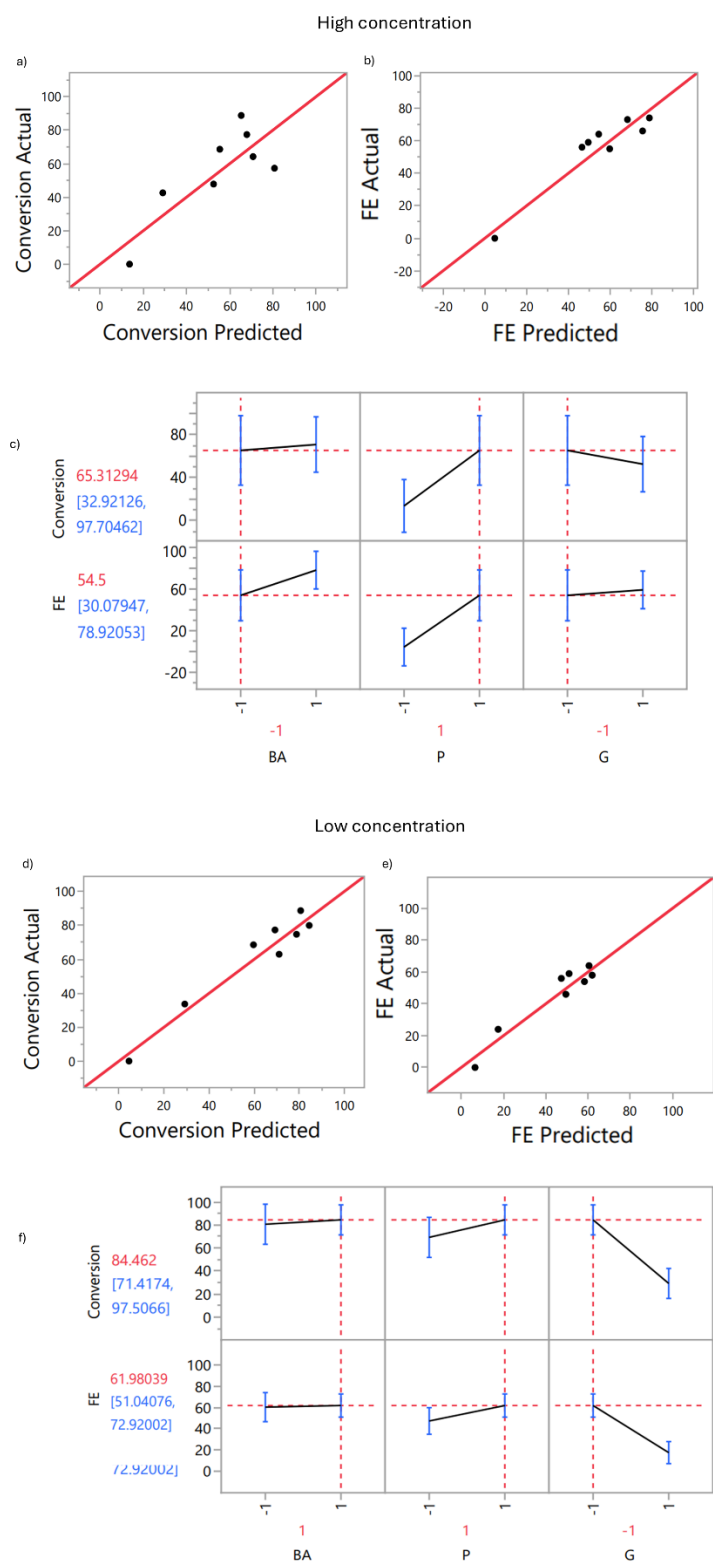


Figure 3-6 - Factorial design analysis for lower and higher concentrations. Best regression fit for the models of predicted vs real conversion (a,d) and real FE (b,e) and conversion profiler for all model compounds (c,f).

For conversion at higher concentrations (Figure 3-6a), significant contributions were observed from BA, BA $\times$ P, BA $\times$ G, and P $\times$ G, while P and G were excluded from the final model. The r^2 value for conversion was 0.7267, indicating that the model explains a moderate proportion of the variability in the response. For FE (Figure 3-6b), all terms significantly contributed, with an r^2 value of 0.9290, indicating a strong model fit.

At lower concentrations, G was excluded from the final model for conversion, while BA and G were removed for FE. The r^2 value for conversion was 0.9608 (Figure 3-6d), and for FE, r^2 was 0.9325 (Figure 3-6e), both demonstrating a high correlation with the predicted model.

The conversion profiler (Figure 3-6c and f) shows that increasing the concentration of the mixture generally leads to higher FE, with one exception. Phenol had the greatest positive impact on both conversion and FE, regardless of concentration. Conversely, Guaiacol decreased both responses in 3 out of 4 cases but led to a slight increase in FE at higher concentrations. These findings reaffirm the observed effects of these two compounds in the ECH process.

Residual plots for both models' responses showed that the residuals appeared random, with no discernible patterns or trends, confirming the model's assumptions. Additionally, no residuals exceeded control limits, indicating a good model fit. The plots of actual versus predicted responses showed a high correlation, confirming the model's predictive capability.

3.3.4 Density functional theory (DFT) calculations

DFT calculations were used to further explain the behaviour of benzoic acid on the cathode surface. The material was built with a Pt-Ru atomic ratio of 1:1, and the selected plane was (111), which was chosen to maintain cohesion with the reference utilised ¹¹¹, the slab will be herein denoted PtRu(111). BA was placed both with a parallel placement and at a 45° angle into the surface, and the structure was relaxed to find the adsorption energy. Figure 3-7 shows the interaction between them.

The lower energy value calculated for the parallel placement gives a good interpretation of the 100% selectivity of BA into CCA, whereas there is no bond between the carboxylic acid part of the molecule and the surface. The atom's placement shows that this group moves in the “z” direction, bending the molecule and moving away from the surface. That is, there is the formation of π - σ interactions between the aromatic ring and the metal surface, rather than the carboxylic group. There was also a difference in E_{ad} depending on the initial position of the compound, where placing the aromatic ring closer to ruthenium atoms (Figure 3-7b) led to a more stable system ($E_{ad2} = -1.12$ eV) than closer to platinum atoms ($E_{ad3} = -0.17$ eV, Figure 3-7c), signifying it as the preferential site.

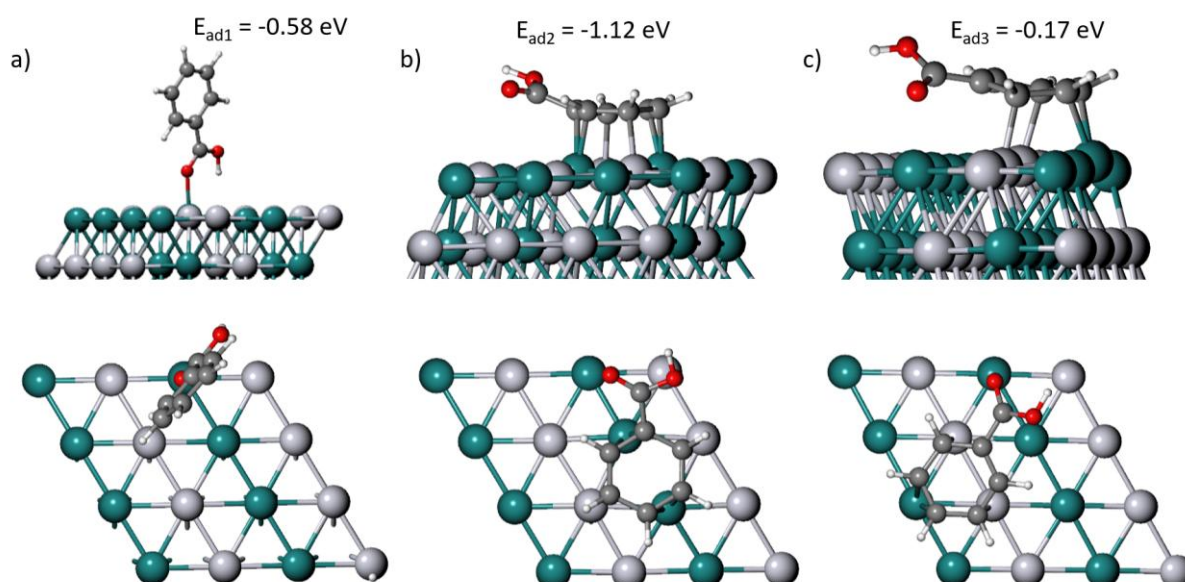


Figure 3-7 - Vertical and parallel adsorption of benzoic acid into PtRu(111). (a) Vertical placement and (b) horizontal placement into PtRu(111). (c) Adsorption into a different site. The respective top-view of the first layer is shown in the bottom images. Where the white spheres represent hydrogen, dark grey carbon, red oxygen, light grey platinum and green represent ruthenium atoms.

Interestingly, Figure 3-7b shows that a defect is created in the first layer of the cathode's surface. To accommodate the BA molecule, the two ruthenium atoms which bonded with C1, C3, C4 and C6 moved too far from each other, severing the bond. To determine whether this was a one-time event, the atoms were placed closer to each other until a bond was formed, but the relaxation process

would always lead to this defect. It is worth mentioning that from the second layer onwards, this did not occur.

The electron density difference (Figure 3-8) shows an electron accumulation (in yellow) in the interface between the adsorbed molecule and the surface, corresponding to the adsorption bonds. In contrast, the blue area shows a clear electron depletion in the aromatic ring. The carbonyl group, an electron-accepting group, pulls the electron density towards itself, degrading the electron density of the phenyl group, an electron-donating group. This creates a positively charged area which strongly adsorbs into the surface. Further accumulation of electrons around ruthenium atoms facilitates the hydrogenation reaction.

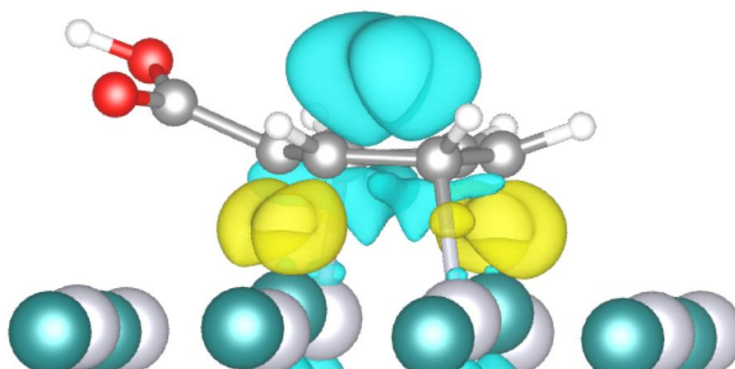


Figure 3-8 - Energy density difference of benzoic acid adsorbed into PtRu(111). Electron depletion (light blue) and electron accumulation (yellow) isosurfaces are set to $0.06 \text{ e}/\text{\AA}^3$. Where the white spheres represent hydrogen, dark grey carbon, red oxygen, light grey platinum and green represent ruthenium atoms.

It is widely acknowledged that the Langmuir-Hinshelwood (L-H) adsorption mechanism is followed by organic compounds containing an aromatic ring during ECH.¹¹¹ The process involves H^+ being quickly adsorbed into the surface, due to the synergistic effects between Pt and Ru where, in combination with an e^- , produces H_{ads} (Volmer step). The next step is the adsorption of BA in a position parallel to the catalyst surface, to form BA_{ads} . Subsequently, H_{ads} is transferred into BA_{ads} until the full hydrogenation of the aromatic ring is accomplished, followed by the desorption of the product (cyclohexane carboxylic acid). The

proposed mechanism for the ECH of benzoic acid over PtRu/ACC is shown in Figure 3-9.

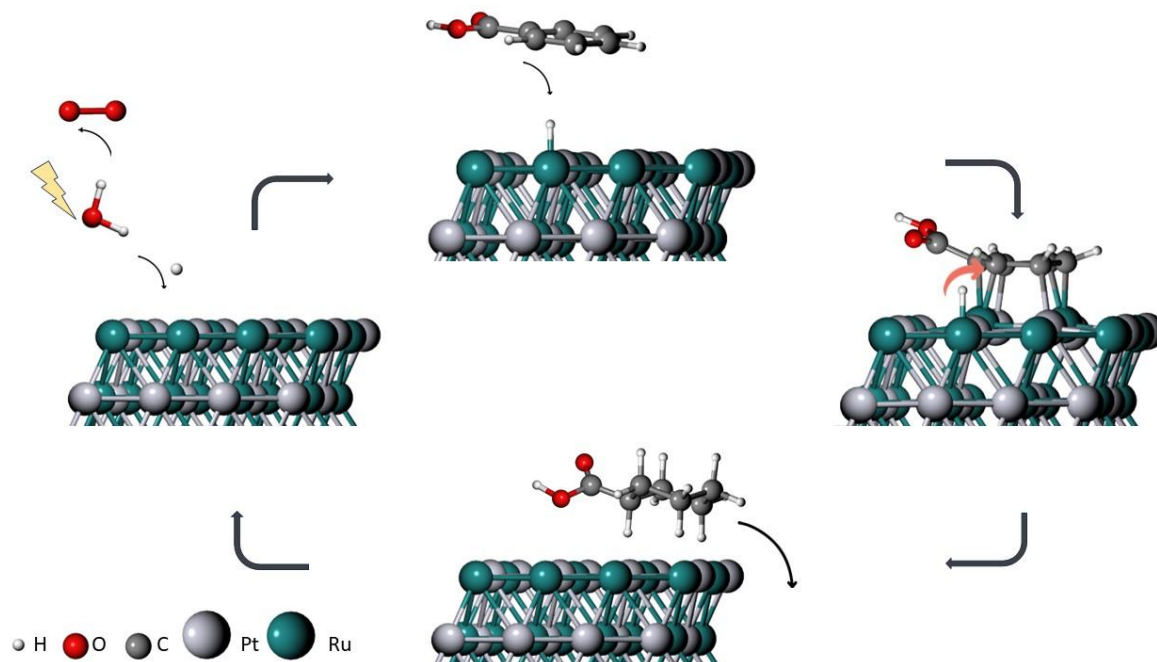


Figure 3-9 - Proposed mechanism for benzoic acid hydrogenation over PtRu/ACC. Where the hydrogenation process of BA is carried out following the Langmuir-Hinshelwood mechanism for the formation of CCA.

The hydrogenation happens in a specific order, following the most stable state of the molecule. Calculations on the one-by-one hydrogenation (Figure B-1) of BA show that the first carbon to receive an H⁺ is C1 (meta), followed by the order C2-C3-C4-C5-C6. Due to the carboxylic acid's electronegativity, a negatively charged dipole (δ^-) is formed which is close to C6, giving a good justification for why it is the least stable position for the first hydrogen (H1), and why it is the last to be hydrogenated. The positive dipole on C6 (ortho), which borders C1 and C5 (meta) and the distance from C3 to the -COOH group set them as the major candidates for H1, at a relatively small 0.056 and 0.0147 eV difference from C1 to C5 and C3, respectively. The same trend follows for the rest of the process, where the neighbouring carbon to the one that receives the hydrogen is always the least stable position until the ring is fully stabilised.

3.3.5 Material characterisation

Figure 3-10 shows the Scanning Electron Microscopy (SEM) secondary electron image for PtRu/ACC before use and after 5 cycles of the optimised BA electrochemical hydrogenation process. In both samples, the metal deposition is homogeneous throughout the surface of the carbon cloth. Elemental mapping (by energy dispersive X-ray spectroscopy) was carried out and revealed an even distribution of both Pt (in teal) and Ru (in green) across the surface; this even distribution is beneficial to optimise the reaction. No degradation of the cathode is apparent after 5 reruns, the concentration and distribution of metals remain unaltered.

XRD data (Figure 3-10g) shows peaks corresponding to carbon, platinum, and a 1:1 mixture of platinum and ruthenium, consistent with expected results. The peaks are broad and exhibit low intensity, indicating the presence of amorphous content, which complicates the interpretation of the results. The sharp peak at 18 degrees is attributed to PTFE (polytetrafluoroethylene), used in various steps of the manufacturing process of the carbon cloth, including the base cloth and the micro-porous layer (MPL). Raman spectroscopy (Figure 3-10h) presents the spectra of the cathode before (in black) and after (in red) the addition of PtRu to the carbon. The black spectrum displays two peaks around 1350 cm^{-1} and 1580 cm^{-1} , which correspond to carbon. In contrast, the red spectrum shows no apparent peaks, as both pure platinum and pure ruthenium typically do not exhibit significant Raman signals.

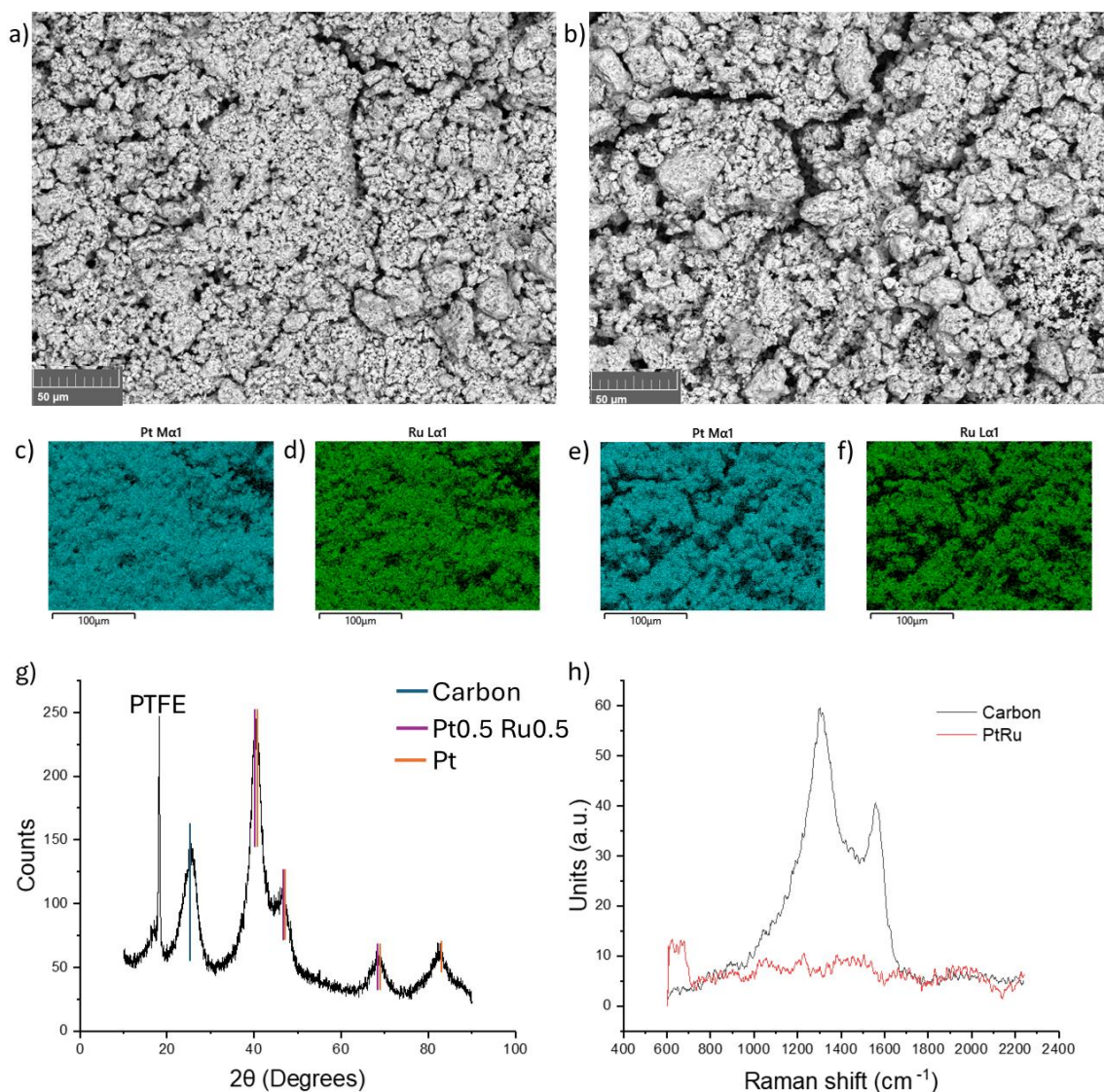


Figure 3-10 - Material characterisation via SEM, XRD and Raman. Scanning Electron Microscopy of the cathode before (a) and after 5 runs (b). Elemental mapping before (c and d) and after 5 runs (e and f). Pt was highlighted in teal and Ru in green. (g) XRD analysis, where the peaks for carbon, platinum and PtRu are highlighted in teal, purple and orange respectively. (h) Raman spectroscopy of the cathode with (in red) and without (in black) PtRu deposition.

The cyclic voltammetry (CV) data reveal that the addition of benzoic acid (in black), phenol (in red), and guaiacol (in green) to the PtRu/ACC electrode system in sulfuric acid progressively decreases the current response compared to the baseline (in yellow) established with only the electrolyte present. This trend

suggests that each compound interacts differently with the electrode surface, likely through adsorption or electron-transfer reactions that compete with or inhibit the baseline electrochemical processes involving protons, such as hydrogen evolution reaction. The yellow curve, which represents the system with only the electrolyte, shows the highest peak current, reflecting the uninhibited activity of the PtRu/ACC electrode in an acidic environment. However, with the introduction of the model compounds, the current response decreases. Phenol, while more electroactive, results in a substantial drop in current, indicating it may strongly interact with the electrode, likely due to its higher propensity for reduction. Conversely, guaiacol exhibits the lowest current, suggesting the strongest surface adsorption or passivation effect among the compounds tested. The asymmetry of the CV curves, particularly the lack of mirrored oxidation and reduction peaks, indicates that the electrochemical processes in this system are of non-reversible nature.^{44,46}

LSV analysis shows that PtRu/ACC exhibits -0.194 V vs Ag/AgCl at 10 mA cm⁻², and it becomes less negative when adding the compound, reaching -0.163 V, -0.162 V and -0.159 V vs Ag/AgCl for G, BA and P, respectively, (Figure 3-11b-c). This measurement is important for the well-known activity for HER at this current density and it is also an indication that the reactivity of the compounds for ECH is P>BA>G, which is corroborated by the empirical data.⁴⁴

The voltage change (ΔE) of $\Delta E_1 = 0.031$ V, $\Delta E_2 = 0.032$ V and $\Delta E_3 = 0.035$ V shows that the ECH of all three model compounds are prior to HER, the competing reaction, conversely. When adding P to BA, the potential went from -0.162 V to -0.155 V vs Ag/AgCl, a difference of 0.07 V, whereas when adding G to BA, there was a negative shift, going from -0.163 to -0.185 V, indicating an anti-synergistic effect. Adding P to G increased the potential from -0.163 to -0.152 V, a 0.11 V change (see Figure B-2-5).

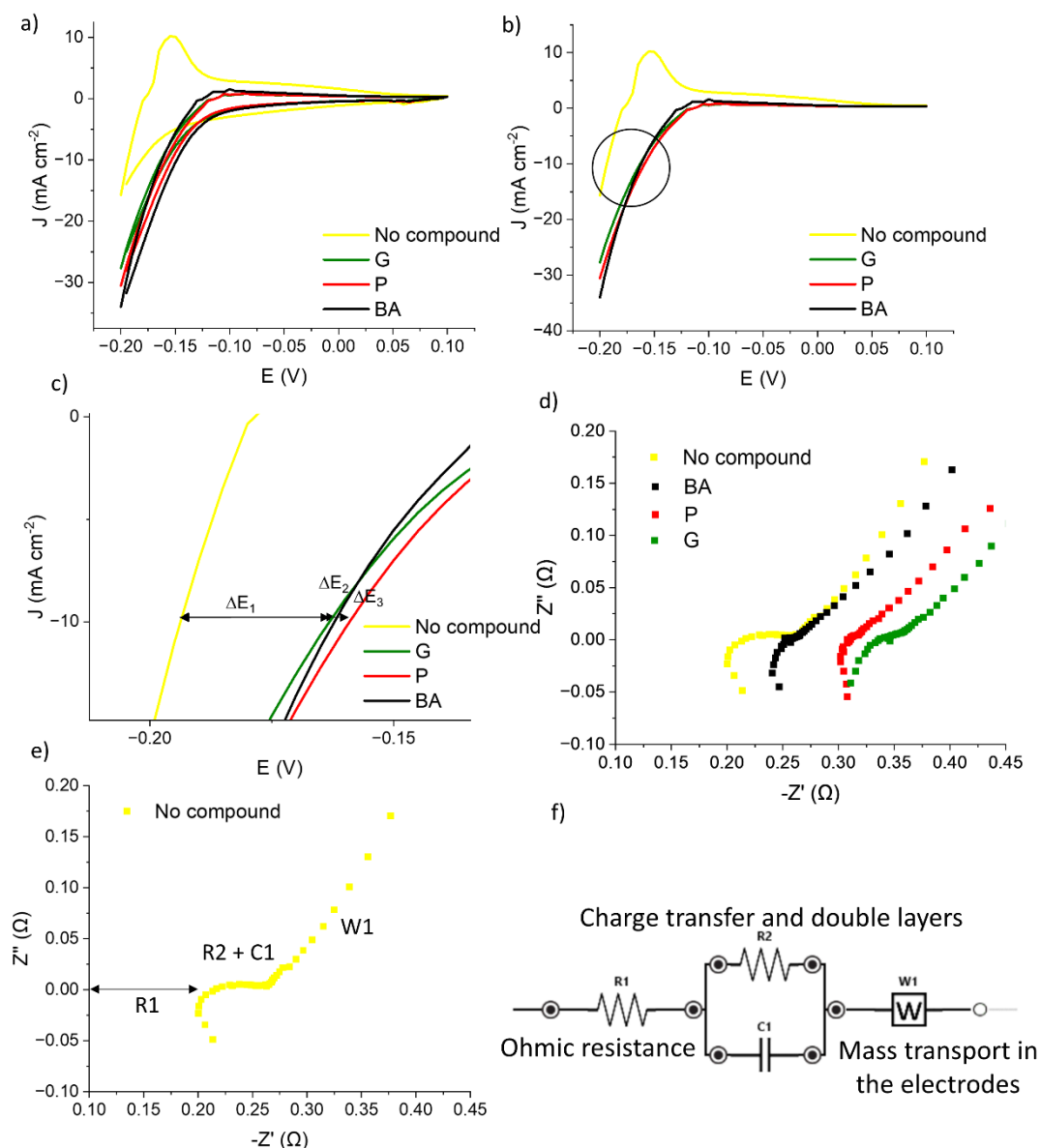


Figure 3-11 - Electrochemical analysis. Cyclic voltammetry (a) of PtRu/ACC before (in yellow) and after the addition of benzoic acid (in black), guaiacol (in green) or phenol (in red) into the system (1.0M H₂SO₄, 55°C). Linear sweep voltammetry (b) and a zoomed-in version (c). Where ΔE_1 , ΔE_2 and ΔE_3 are the differences between no added compound and G (guaiacol), BA (benzoic acid) and P (phenol) at 10 mAcm⁻² respectively. (d) EIS and zoomed-in version (e) highlighting the baseline curve. (f) Equivalent circuit for EIS fitting. All measurements are vs Ag/AgCl reference electrode.

In the Nyquist plot (Figure 3-11d), the baseline (yellow curve) represents the system before the addition of model compounds, while the black, green and red curves correspond to the presence of benzoic acid, guaiacol and phenol in the electrolyte, respectively. The EIS data reveal an increase in the ohmic resistance and the diameter of the semicircle upon the addition of the model compounds, indicating a higher charge transfer resistance (R_{ct}) in the presence of compounds. This rise in R_{ct} suggests that hydrogenation requires additional energy input, likely due to the formation of surface-bound intermediates that create an energy barrier to electron transfer. The curves also show a tail inclined at a 45° angle, which is characteristic of Warburg impedance semi-infinite diffusion layer and indicates diffusion limitations⁴⁸. These diffusion limitations likely arise from mass transport effects, such as the diffusion of hydrogen or model compound molecules to and from the electrode surface.

3.4 Discussion

In conclusion, the electrochemical hydrogenation of mixtures represents a significant advancement in the field of bio-oil upgrading. Through a factorial experimental design approach, we explored the interactions among model compounds, shedding light on both synergistic and antagonistic effects within the system. Our findings underscored the robustness of the electrochemical process, with the applied overpotential exhibiting minimal variance across different compositions and concentrations of model compounds. Notably, we observed a clear trend where increasing the number of unsaturated molecules in the system led to reduced conversion, except when all three compounds were mixed, suggesting complex dynamics at play. Phenol emerged as the most readily converted compound in most scenarios, highlighting its preferential hydrogenation over benzoic acid and guaiacol. The resistance to guaiacol hydrogenation, attributed to its complex molecular structure with methoxy and phenolic groups, posed challenges in achieving high conversion, particularly when guaiacol was present in mixtures. However, the hydrogenation of guaiacol was favoured over benzoic acid, indicating nuanced reactivity patterns influenced by compound interactions.

Furthermore, our investigation into the impact of initial concentration revealed consistent trends, with mixtures maintaining similar conversion patterns despite variations in compound concentrations. Phenol consistently demonstrated higher activity compared to benzoic acid and guaiacol, even at reduced concentrations, underscoring its significance in the electrochemical hydrogenation process.

DFT calculations demonstrated that positioning the BA molecule parallel (0°) to the surface was notably more stable compared to a 45° angle placement. This preference suggests a stronger affinity for the adsorption of the aromatic ring over the carboxylic acid component of the molecule. Such findings provide insight into the observed 100% selectivity of product formation towards cyclohexane carboxylic acid.

Overall, our study provides valuable insights into the electrochemical hydrogenation of mixtures, offering a comprehensive understanding of compound interactions and their influence on conversion and selectivity. These findings lay the groundwork for further optimisation of electrochemical processes in bio-oil upgrading, with potential applications in sustainable energy production and chemical synthesis.

3.5 Data availability

The data supporting this study's findings are available from the corresponding authors upon reasonable request. Source data are provided in [10.6084/m9.figshare.26540506](https://doi.org/10.6084/m9.figshare.26540506).

4 Paper Three: Hydrogen bond enhanced electrochemical hydrogenation of benzoic acid over a bimetallic catalyst

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Abstract

Electrochemical hydrogenation (ECH) is a sustainable alternative to traditional hydrogenation methods, offering selective reduction of organic compounds under mild conditions. This study investigates the co-hydrogenation of benzoic acid (BA) and phenol on a platinum-ruthenium on activated carbon cloth (PtRu/ACC) catalyst, with a focus on the synergistic effects arising from hydrogen bonding. Density Functional Theory (DFT) calculations reveal that the formation of a hydrogen-bonded complex between BA and phenol facilitates adsorption energy and lowers activation barrier energies compared to BA alone. Experimental results demonstrate that a 20 mM BA and 5 mM phenol mixture achieves the highest conversion (88.75%) and Faradaic efficiency (64%), significantly outperforming single-compound systems. Notably, co-hydrogenation facilitates the reduction of BA to cyclohexanemethanol, a valuable product for biofuel applications, which has reduced corrosiveness and improved energy density. These findings underscore the potential for optimising multi-compound ECH systems through targeted catalyst design and reagent concentration tuning, thus advancing the development of efficient strategies for bio-oil upgrading and sustainable chemical production.

4.1 Introduction

Electrochemical hydrogenation (ECH) has emerged as a promising technology for the selective reduction of organic compounds, offering a cleaner, safer and

more energy-efficient alternative to conventional hydrogenation methods ^{23,26–29,32,109}. By leveraging electrochemical control over hydrogen generation and reaction pathways, ECH allows for precise tunability of products under mild operational conditions. While this method has been extensively studied for single-compound systems, research into the co-hydrogenation of mixed substrates remains limited. Such studies are critical in addressing the complexities found in real-world chemical feedstocks, such as biomass pyrolysis oils, which contain multiple reactive compounds ¹⁰. Investigating co-hydrogenation is crucial not only for advancing sustainable chemistry globally but also for optimising processes that deal with complex mixtures in industrial applications. By enabling more efficient, selective transformations, ECH could reduce the need for extensive separation techniques. Thus, research in this area holds significant promise for bridging the gap between laboratory studies and real-world, large-scale applications.

It has been widely reported that the hydrogenation of aromatic compounds follows the Langmuir-Hinshelwood mechanism, that is, the compound/hydrogen interaction happens after both are adsorbed into the surface of a catalytic material ¹¹¹. This leads to competition for adsorption sites, especially if more than one compound is present simultaneously. Therefore, it is expected that anti-synergistic effects would take place in feedstock which is not pure, lowering the conversion of a particular compound, or all of them. However, previous studies on phenol-containing mixtures (phenol + furfural ¹¹⁶, and phenol + benzaldehyde ^{117,118}), showed better ECH performances after the addition of phenol, both in terms of conversion and selectivity. The authors suggest that a hydrogen-bonded complex formation enhanced the hydrogenation of the co-reactant.

In our previous study¹¹⁹, we demonstrated, for the first time, that a similar synergistic effect seemed to happen during the co-hydrogenation of benzoic acid (BA) and phenol, where this mixture led to the increase in both conversion and Faradaic efficiency, the best results amongst the ones tested. We also found that the hydrogenation of BA, regardless of condition, would lead to a 100% selectivity

towards cyclohexane carboxylic acid (CCA), in agreement with *Du et al*¹¹¹ and *Fukazawa et al*³⁴.

Herein, we explored the interactions between benzoic acid and phenol during the ECH process over a catalyst of platinum ruthenium on activated carbon cloth (PtRu/ACC) for various phenol concentrations, with the aim of better understanding the synergistic effects during co-hydrogenation. Density functional theory (DFT) calculations were performed to further elucidate the synergistic hydrogenation mechanism, including nudged elastic bands (NEB), to calculate the activation energy of each step of the hydrogenation and electronic structure calculations, and shed further light on the mechanisms of the reaction.

DFT results show a hydrogen bond enhancement during said process, increasing the adsorption energy of BA, facilitating the reaction and achieving the reduction of BA into cyclohexanemethanol. This novel observation of hydrogen bonds as a catalytic tool represents a significant advancement in the selective hydrogenation process, thus serving as a link between model compound studies and those for whole bio-oil, as well as demonstrating the complex mechanism that takes place during this process.

4.2 Experimental

4.2.1 Materials

A sulfuric acid solution (5M) and benzoic acid (99%, extra pure), were obtained from Thermo Fisher Scientific, while phenol (liquefied, ≥89%) was purchased from Sigma Aldrich. All chemicals were used as received, without any further purification. A Nafion 117 membrane (Ion Power) was employed as the cation exchange membrane to separate the cathode and anode chambers. To activate the membrane and optimise its ion transport properties, it was pretreated following the method by Peng et al¹¹². The membrane was treated in hydrogen peroxide (H₂O₂) at 80 °C, followed by deionised water and 1.0M H₂SO₄ at the same temperature, with each step lasting 1 hour. After each step, the membrane was rinsed with deionised water.

4.2.2 Electrochemical hydrogenation

A two-chamber electrochemical cell, separated by a cation exchange membrane (CEM), was used for the electrochemical hydrogenation process. The anode consisted of a 1x1 cm platinum plate, while the catalytic cathode was a platinum ruthenium black-carbon cloth electrode (Fuel Cell Store, 1:1 Pt:Ru ratio) with a loading of 4 mg/cm². Both chambers were filled with 1.0 M sulfuric acid (H₂SO₄) as the electrolyte. The ECH tests were conducted in a 90 mL (per chamber) H-type cell, operated under electrostatic control at 25.0 mA cm⁻² and a constant temperature of 55 °C for 10 minutes to polarise the electrodes without the organic compound present.

After polarisation, the model compound was introduced to achieve a set final concentration. The electrochemical co-hydrogenation of benzoic acid + phenol was carried out at different initial phenol concentrations (5, 10, 15 and 20 mM in 20 mM of BA) to investigate the effect of the presence of said model compound when mixed with benzoic acid (see Table 4-1). The experiment continued for 4 (for single model compounds experiments) or 5 hours (for mixtures), ensuring the availability of sufficient electrons for compound conversion. Samples (1 mL) were collected every hour, and the organic compounds were extracted with 2 mL of dichloromethane (DCM). NaCl was added until saturation to ensure the migration of the compounds into the DCM. After each experiment, the electrolyte was discarded, the cell was cleaned, and the cathode was soaked in 5 mL of DCM for 15 minutes to desorb any molecules from its surface. All experiments were performed twice, and where there was a standard deviation of more than 5%, a triplicate was carried out.

4.2.3 Gas chromatography-mass spectrometry (GC-MS)

The samples were analysed in the GC-MS Shimadzu TQ8040. The GC used a Restek Rtx-5 capillary column, 28.5 m × 0.25 mm with a 0.25 µm film thickness, a 1.18 mL min⁻¹ helium carrier gas flow rate, and a split ratio of 1:25. The injector temperature was set at 250 °C. The GC oven program started at 34 °C and held for 2 min and then heated at 50 °C min⁻¹ to 300°C. Mass spectrometry was operated at m/z ranging from 50 to 500. Species associated with each

chromatographic peak were identified by comparing their observed mass spectrum with the NIST library.

4.2.4 Calculations

To understand and quantify the ECH process, the following equations were used:

$$FE (\%) = \frac{\text{mol produced} * n * F}{\text{Total electrons passed}} * 100 \quad (4-1)$$

$$\text{Conversion} (\%) = \left(\frac{\text{Moles reactant consumed}}{\text{Initial moles reactant}} \right) * 100 \quad (4-2)$$

$$\text{Selectivity} (\%) = \left(\frac{\text{Moles desired product}}{\text{Total moles product}} \right) * 100 \quad (4-3)$$

$$\text{Current density (mA cm}^{-2}\text{)} = \frac{\text{Current}}{\text{Surface area}} \quad (4-4)$$

$$\text{Space – Time Yield (g m}^{-3}\text{ h}^{-1}\text{)} = \frac{\text{Moles of product}}{\text{Cell volume} * \text{Duration}} \quad (4-5)$$

Where F is the Faraday constant (96 485 C mol⁻¹), and n is the number of electrons necessary for the hydrogenation process (n = 6 for the conversion of benzoic acid into cyclohexane carboxylic acid, for example).

4.2.5 Electrochemical measurements

Electrochemical measurements were performed using a PalmSens EmStat4s at 55°C, which consisted of a three-electrode system with the selected cathode, anode, and an Ag/AgCl (in saturated KCl solution) as the working, counter, and reference electrodes, respectively. The potential vs. Ag/AgCl was converted to the potential vs. RHE (reversible hydrogen electrode) based on the Nernst equation:

$$R_{RHE} = E_{Ag/AgCl} + 0.059 * pH + E_{Ag/AgCl}^0 \quad (4-6)$$

All electrochemical measurements were carried out in 1.0 M H₂SO₄ with and without the model compounds. Linear scanning voltammetry (LSV) tests were recorded at a scan rate of 5 mV s⁻¹ from -0.200 V to 0.200 V. Cyclic Voltammetry (CV) was carried out from -0.200 V to 0.200 V, with an E_{step} of 5 mV and a scan rate of 5 mV s⁻¹. Electrochemical Impedance Spectroscopy (EIS) was measured vs Open Circuit Potential (OCP) at a max frequency of 10⁵ Hz and a min frequency of 10⁻¹ Hz, the E_{start} was set to -0.200 V. Equilibration time was 5 s.

4.2.6 DFT Calculations

All calculations were carried out using QuantumEspresso/7.2-foss-2022b^{113–115} with BURAI 1.3.1 as a visualiser. VESTA was used to calculate the electronic structure. Both positive and negative isosurfaces were set to 0.06 e/Å³. The generalised-gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional described the exchange-correlation energy. To enhance computational performance, all calculations were performed with a thermal smearing of 0.01 Ry and spin polarisation.

A 4-Layer 4 × 4 PtRu (111) slab was built with a 20 Å vacuum gap and two fixed bottom layers. The slab was placed at the bottom of the cell, to certify that all reactions happened on the top surface. A (2 × 2 × 1) k-point grid was set. The test molecule was placed at a distance of 1.5 Å from the surface, where it did not start the calculations with any bonds to the surface. The adsorption energy (E_{ad}) of the different adsorbates is defined as:

$$E_{ad} = E_{Total} - (E_{adsorbate} + E_{Surface}) \quad (4-7)$$

Where E_{Total} is the calculated energy for the final system (slab + adsorbate), E_{adsorbate} is the calculated energy of each adsorbate and E_{Surface} is the energy of the bare cathode surface.

4.3 Results

4.3.1 Electrochemical co-hydrogenation of benzoic acid and phenol

The impact of phenol concentration on the electrochemical hydrogenation of benzoic acid was systematically investigated, revealing a complex interplay

between conversion rates, Faradaic efficiency, and space-time yield (STY). ECH of benzoic acid as a stand-alone model compound achieved 77.15% conversion, 56% FE and an STY of $473.00 \text{ g m}^{-3} \text{ h}^{-1}$ (Table 4-1). Our previous study¹¹⁹ demonstrated a direct correlation between FE, STY and initial concentration. By contrast, the correlation between initial concentration and conversion rate is inversely related, that is, increasing initial concentration leads to higher FE, higher STY and lower conversion.

However, the addition of 5 mM of phenol, at a mixture ratio of 20:5, increased all three parameters (conversion = 88.75%, FE = 64% and STY = $505.68 \text{ g m}^{-3} \text{ h}^{-1}$). Higher phenol concentrations (20:10 and 20:15) increased FE at the cost of lower STY and conversion rates, at 72.05 and 63.92% conversion and 59 and 61% FE, respectively, when compared to BA alone. Interestingly, the 20:20 mixture increased the conversion rate (66.99 vs 63.92 from the 20:15 mixture) and achieved the highest FE (75%) and STY ($556.85 \text{ g m}^{-3} \text{ h}^{-1}$). In addition to the total space-time yield reported in Table 4-1, the yield of cyclohexane carboxylic acid, a product of particular interest, was quantified for each experiment. These values are 473.00, 415.14, 307.80, 250.70, and 231.49 $\text{g m}^{-3} \text{ h}^{-1}$ for benzoic acid alone, as well as for 20:5, 20:10, 20:15, and 20:20 mixtures, respectively.

At low phenol concentrations, the hydrogen-bonded complex between benzoic acid and phenol stabilises the reactants and facilitates the Langmuir-Hinshelwood mechanism, leading to improved benzoic acid conversion. However, as the phenol concentration increases, the competition for adsorption sites intensifies. Phenol, being more electroactive, outcompetes benzoic acid for active sites on the PtRu/ACC catalyst. This results in a noticeable decline in benzoic acid conversion (Figure 4-1a), from 84.91 at 5 mM phenol to 62.96, 51.28, and 47.35% at 10, 15 and 20 mM phenol, respectively, where only the 20:5 mixture achieved a higher benzoic acid conversion than BA alone. Despite this, the stronger adsorption of phenol at higher concentrations reduces the likelihood of side reactions such as hydrogen evolution, thereby improving the overall Faradaic efficiency and production rate.

Table 4-1. Results comparison for the ECH of benzoic acid (BA), phenol (P) and mixtures. Reaction parameters: current density = 25.0 mA cm⁻², temperature = 55°C, electrolyte = H₂SO₄ 1M. Where (1) = Cyclohexane carboxylic acid, (2) = Cyclohexanol, (3) = Cyclohexanone, (4) = Cyclohexane and (5) = Cyclohexanemethanol

Compound initial conc. (mM)		Total Conversion (%)	BA Conversion (%)	Phenol Conversion (%)	Total (%)	Space- Time Yield (g m ⁻³ h ⁻¹)	Selectivity (%)				
BA	P						(1)	(2)	(3)	(4)	(5)
20	-	77.15	77.15	-	56	473.00	100.00	-	-	-	-
20	5	87.33	84.91	97.01	63	505.68	86.38	13.17	0.29	-	0.15
20	10	72.05	62.96	90.23	59	476.23	82.22	17.35	0.43	-	-
20	15	63.92	51.28	80.77	61	478.67	72.57	26.31	1.12	-	-
20	20	66.99	47.35	86.63	75	556.85	65.27	32.55	1.54	0.65	-
-	20	80.75	-	80.75	64	416.63	-	99.00	1.00	-	-

Interestingly, the 20:5 and 20:20 ratios exhibit behaviour that deviates from these general trends. At the 20:5 ratio, the synergistic interaction between the two compounds is most pronounced, yielding the highest conversion of benzoic acid. At the 20:20 ratio, despite a reduced conversion of benzoic acid, the system achieves its highest STY and Faradaic efficiency. These results suggest that optimal concentrations of phenol depend on the desired outcome: higher conversion rates of benzoic acid are favoured at lower phenol concentrations, whereas higher yields and efficiencies are achieved with a more balanced ratio.

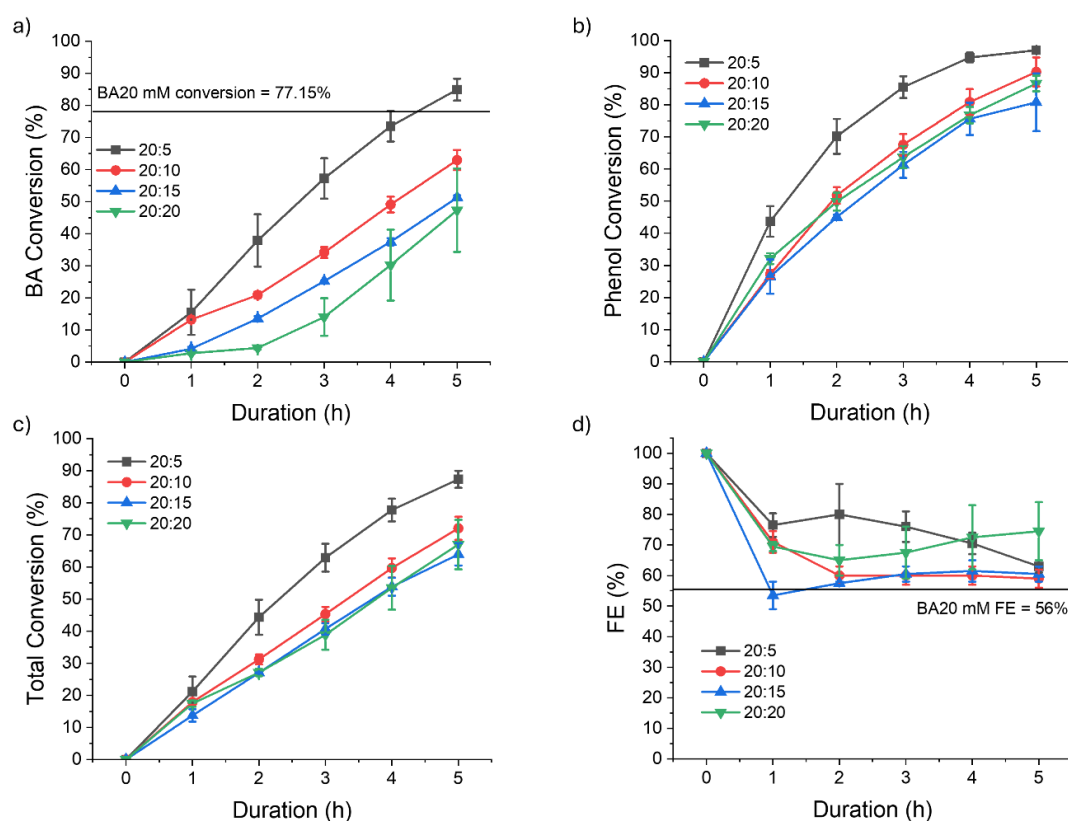


Figure 4-1 - Co-hydrogenation of benzoic acid (BA) and phenol at various phenol concentrations, the fractions are given by the number in the legend. Reaction parameters: current density = 25.0 mA cm^{-2} , temperature = 55°C , electrolyte = H_2SO_4 1M. Error bars indicate the standard error of triplicate experimental results.

The selectivity of benzoic acid towards cyclohexanemethanol during the co-hydrogenation process is a critical and novel finding of this study. Under most conditions, the reduction of benzoic acid yields cyclohexane carboxylic acid with 100% selectivity, assessed via GC-MS. However, when phenol is present at a 20:5 ratio, the reaction proceeds further, reducing CCA to cyclohexanemethanol. This transformation improves the utility of the product, reducing the corrosiveness of the carboxylic acid group and enhancing the stability, energy density, and C:O ratio of the final mixture, all important factors for the storage, transportation and widespread utilisation of bio-oil in the chemical and biofuel industries.²³ The impact of reaction time on conversion rates and product distribution is shown in Figure 4-2.²³

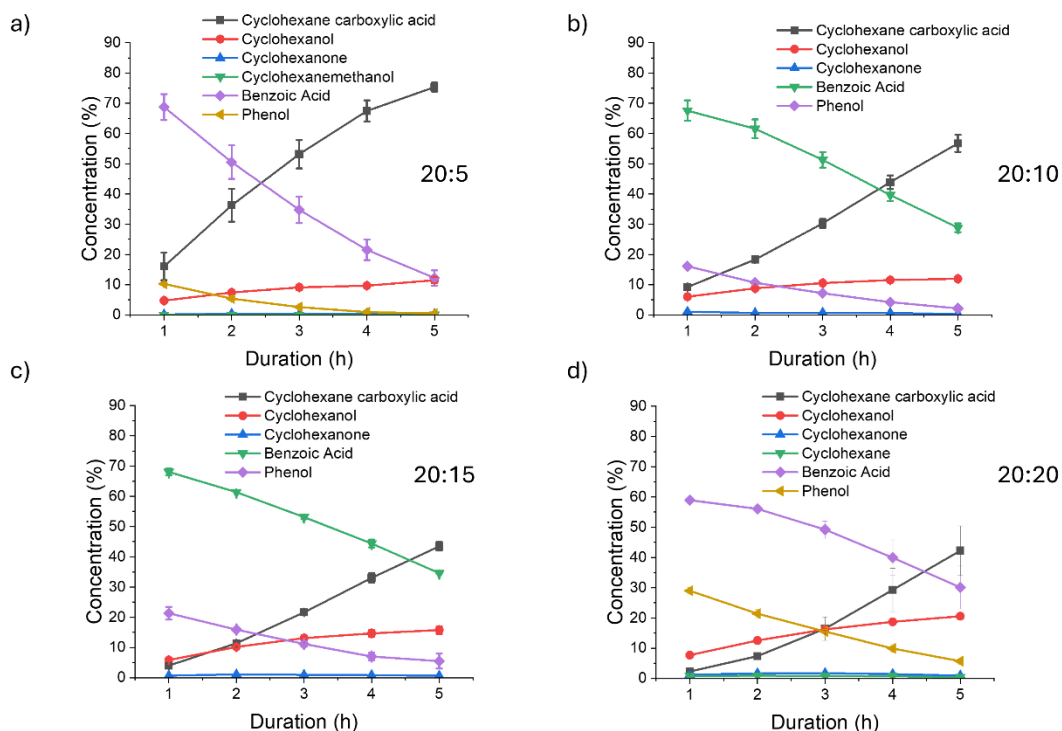


Figure 4-2 - Impact of reaction time on the co-hydrogenation of benzoic acid and phenol at various phenol concentrations, where (a) represents a benzoic acid: phenol ratio of 20:5, (b) is 20:10, (c) is 20:15 and (d) 20:20. Reaction parameters: current density = 25.0 mA cm^{-2} , temperature = 55°C , electrolyte = H_2SO_4 1M. Error bars indicate the standard error of triplicate experimental results.

The ability of the reaction to selectively produce cyclohexanemethanol at this ratio is particularly intriguing. It suggests that the phenol concentration not only influences adsorption dynamics but also alters the reaction pathways. The hydrogen-bonded complex formed between phenol and benzoic acid likely plays a key role here, stabilising intermediate states and reducing the energy barrier for the additional hydrogenation step required to convert CCA to cyclohexanemethanol. The DFT calculations corroborate this hypothesis, showing that the presence of phenol decreases the activation energy of key transition states.

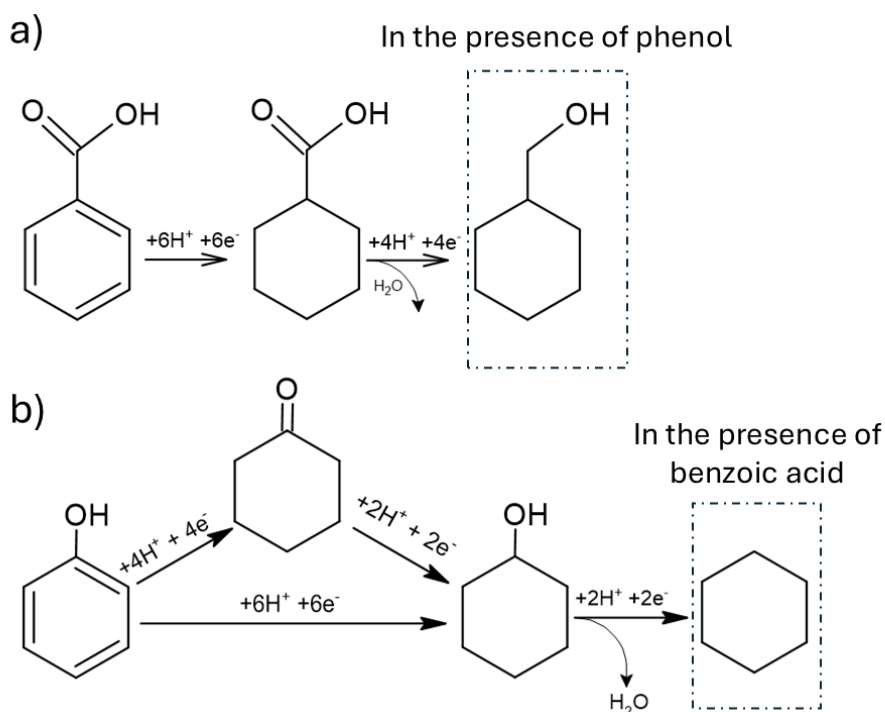


Figure 4-3 - Electrochemical hydrogenation of (a) benzoic acid and (b) phenol. The dashed square shows products that are formed only during the co-hydrogenation of benzoic acid + phenol. (b) Shows two potential routes to the formation of cyclohexanol.

The absence of cyclohexanemethanol formation at higher phenol concentrations may reflect the dominance of adsorption site competition under these conditions. At high phenol concentrations, phenol's preferential adsorption over BA limits the availability of active sites for further reducing benzoic acid intermediates.

Additionally, the increased adsorption of phenol likely shifts the reaction equilibrium, favouring the production of its own reduction products, such as cyclohexanol and cyclohexanone.

The phenol conversion at the 20:20 ratio demonstrates an intriguing aspect of the synergistic interaction between benzoic acid and phenol during co-hydrogenation. Despite the high concentration of both compounds leading to increased competition for active sites on the PtRu/ACC catalyst, phenol overall conversion remains high, achieving 86.63%. This represents an improvement over the conversion of phenol as a stand-alone model compound (80.75%), indicating that the presence of benzoic acid enhances phenol's reduction efficiency under these conditions. The combination of 20mM of BA and 20mM of phenol also led to the formation of a different product, cyclohexane. This is probably a product of the hydrogenation of phenol, rather than benzoic acid, which was achieved by increasing the concentration of phenol and focusing on that reaction (Figure 4-3b).

4.3.2 Electrochemical measurements

LSV analysis (Figure 4-4) shows that PtRu/ACC in the H₂SO₄ electrolyte exhibits -0.1940 V vs Ag/AgCl at 10 mA cm⁻², and that it becomes less negative when adding model compounds, reaching -0.1620 V or -0.1590 V vs Ag/AgCl for 20 mM of BA or phenol, respectively. After the addition of phenol to BA, the potential dislocates to less negative values, reaching -0.1537, -0.1545, -0.1555 and -0.1535 V for 20:5, 20:10, 20:15 and 20:20 mixtures, respectively.

The shift in potential (ΔE) reflects two critical phenomena. First, the observed reduction in potential indicates a decrease in competition with the hydrogen evolution reaction (HER), which is mitigated by the presence of phenol, allowing the catalytic sites to focus on the desired hydrogenation reactions. $\Delta E_1 = 0.032$ V and $\Delta E_2 = 0.035$ V show that the ECH of BA and phenol are favoured when compared to HER, the competing reaction. Second, adding phenol to BA lowers the energy required for ECH, as shown by the ΔE values for each mixture.

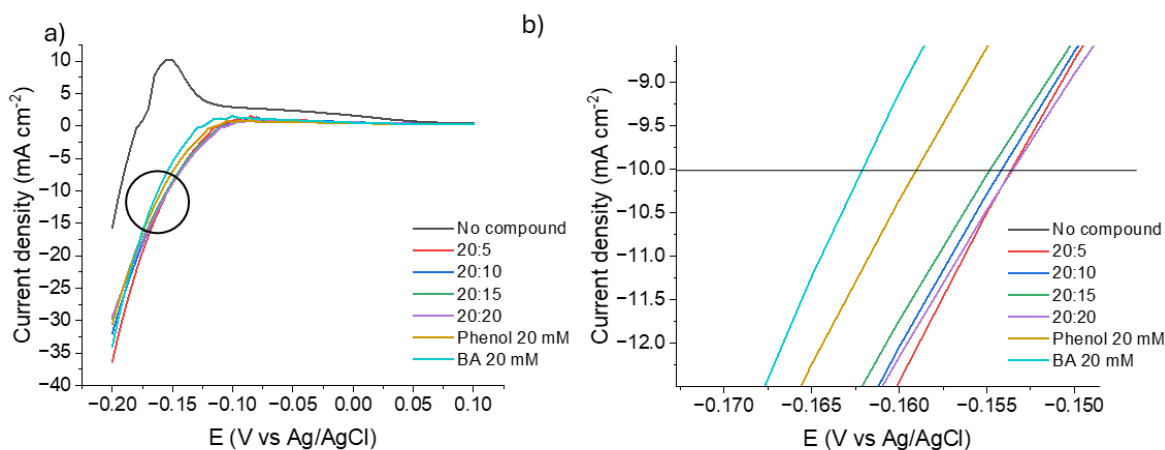


Figure 4-4 - Linear-sweep voltammetry (a) of PtRu/ACC before (in black) and after the addition of compounds to the electrolyte. Benzoic acid 20 mM (in light blue), phenol 20 mM (in yellow), 20:5 mixture (in red), 20:10 mixture (in blue), 20:15 mixture (in green) or 20:20 mixture (in purple) into the system (1.0M H₂SO₄, 55°C) and (b) a zoomed-in version to visualise the potential difference at the current density of 10 mAcm⁻². Where ΔE_1 , ΔE_2 , ΔE_3 , ΔE_4 , ΔE_5 and ΔE_6 are the differences between no added compound and BA, phenol, 20:5, 20:10, 20:15 and 20:20 mixtures at 10 mAcm⁻², respectively.

The 20:10 and 20:15 mixtures present an ΔE of 0.0395 V and 0.0385 V, respectively. The 20:5 mixture exhibits a higher ΔE of 0.0403 V, while the 20:20 mixture shows a slightly larger shift of 0.0405 V. These changes suggest that phenol facilitates the adsorption and activation of hydrogen and benzoic acid on the PtRu/ACC surface. It also supports the claim that the concentrations of 5 and 20 mM of phenol are optimal in this process. Surface characterisation techniques (SEM, XPS, XRD and Raman) were conducted on the PtRu/ACC catalyst and reported in Chapter 3.¹¹⁹

4.3.3 Density Functional Theory calculations

The addition of phenol into the mixture led to the creation of a hydrogen-bonded complex between the alcohol group in phenol and the carboxylic acid in BA (Figure 4-5c). The hydroxyl group in phenol interacts with the carboxylic group in benzoic acid, forming a stable hydrogen-bonded complex. This interaction not only increases the local concentration of reactants near the catalyst surface but

also alters the adsorption dynamics. Phenol's hydroxyl group acts as a hydrogen bond donor, while the carboxylic group in benzoic acid serves as an acceptor, redistributing electron density within the molecules. This redistribution makes the aromatic ring of benzoic acid more electrophilic, increasing the likelihood of hydrogen atoms reacting with the carboxyl group and facilitating its reduction. The hydrogen-bonded complex acts as a catalyst, facilitating the cleavage of the double bond $\text{O}=\text{C}$, leading to the reduction of the carbonyl into an alcohol group, that is, a dehydration reaction.

The charge density difference (Figure 4-5) shows an electron accumulation (in yellow) between the molecule and the catalyst surface, with (Figure 4-5b) and without (Figure 4-5a) the addition of phenol, which aligns with the adsorption bonds. Meanwhile, electron depletion (blue areas) around the aromatic ring is larger when phenol is present, indicating a stronger pull of electrons towards the carboxyl group, which makes the phenyl group more positively charged and promotes stronger adsorption. These changes in electron density enhance the catalyst's ability to adsorb BA, making the reaction more efficient and lowering the energy required for hydrogenation.

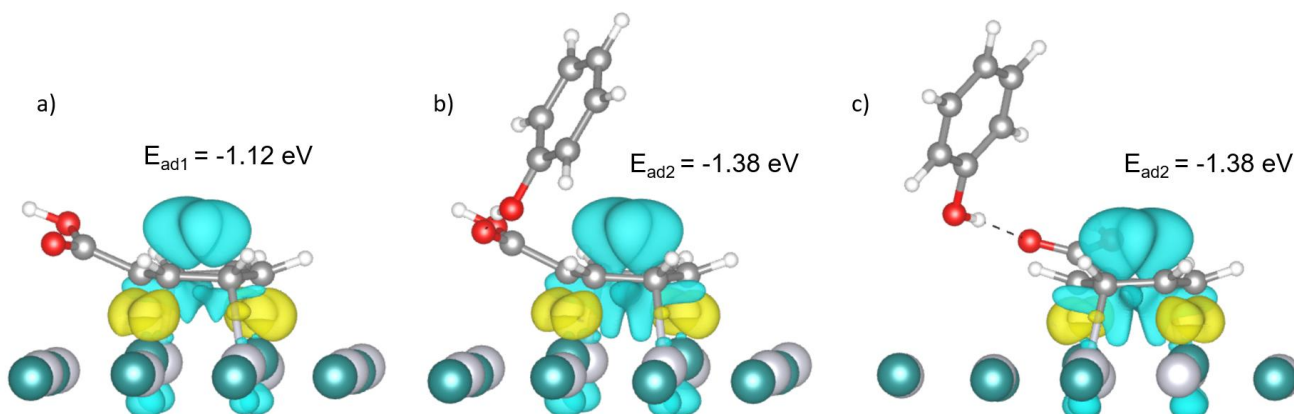


Figure 4-5 - Charge density difference of benzoic acid adsorbed into PtRu(111) before (a) and after (b) the addition of phenol. The hydrogen-bonded complex is highlighted in a rotated view (c). Electron depletion (light blue) and electron accumulation (yellow) isosurfaces are set to $0.06 \text{ e}/\text{\AA}^3$. Where the white spheres represent hydrogen, dark grey is carbon, red is oxygen, light grey is platinum and green represents ruthenium atoms.

The importance of this enhanced adsorption is highlighted by the adsorption energy (E_{ad}) calculations, which show a significant improvement in adsorption energy from -1.12 eV for benzoic acid alone to -1.38 eV in the presence of phenol. Such a strong interaction stabilises the reactants on the catalyst surface, reducing the likelihood of desorption and enabling more complete hydrogenation.

The results observed in this study align with previous literature reports of synergistic effects in other systems, such as phenol with furfural or benzaldehyde.^{116–118} These studies show that the addition of phenol increased the activity of model compounds for hydrogenation and facilitated selectivity. However, both these compounds are aldehydes that were reduced into alcohols. Therefore, the interaction between benzoic acid and phenol appears particularly effective, forming new and more hydrogenated compounds, reducing oxygen content and saturating all double bonds.

DFT calculations proceeded to identify the reason for the better catalytic effect observed for the mixtures, where the relative energy diagram is shown in Figure 4-6. Step-by-step calculation results show that for all intermediate states, that is, every intermediate state of the hydrogenation process, the mixture was more stable than the stand-alone BA. Higher adsorption energies may accelerate and facilitate the adsorption process, which plays a crucial role in the ECH process.

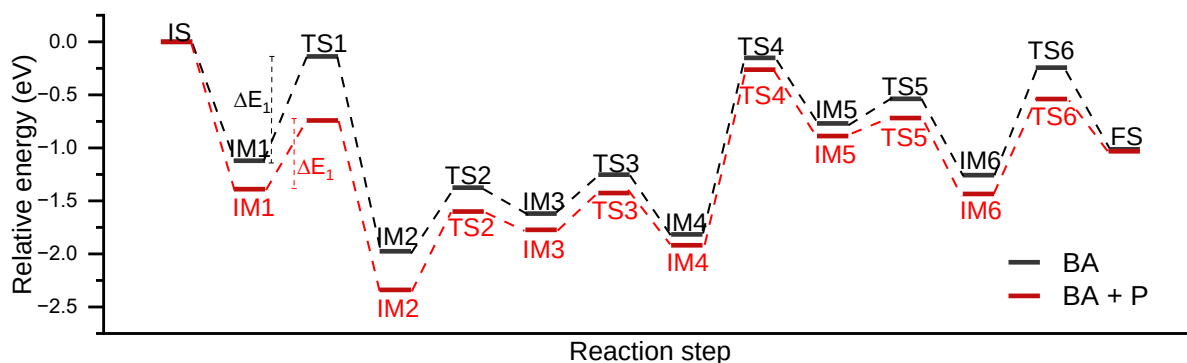


Figure 4-6 - Relative energy diagram for the ECH of BA (in black) and BA + phenol (in red). Where IS = initial state, IM = intermediate state, TS = transition state and FS = final state. All states are related to the step-by-step hydrogenation of BA. ΔE represents the calculated energy barrier for each step.

Nudged elastic bands calculations demonstrated that the energy barrier (ΔE) was also reduced when phenol was added. Table 4-2 shows the variation for each transition state activation energy. The first and fourth steps present the highest activation energies, where ΔE_4 is the limiting step of the reaction at 1.664 and 1.656 eV for the system without and with phenol, respectively.

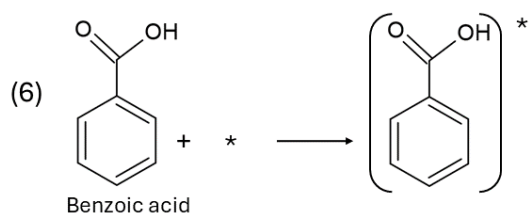
The results demonstrate that phenol can not only enhance the adsorption capabilities of benzoic acid but also reduce the activation barrier energies, facilitating the hydrogenation process and enabling the reduction of the carboxylic acid function into alcohol.

Table 4-2 - Activation energy of each step of the hydrogenation process of benzoic acid on PtRu/ACC, before and after the addition of phenol.

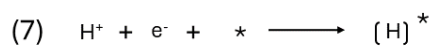
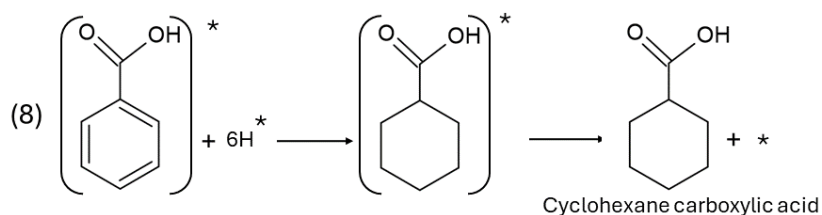
Step	Energy with no phenol (eV)	Energy with phenol (eV)
ΔE_1	0.983	0.647
ΔE_2	0.599	0.469
ΔE_3	0.367	0.346
ΔE_4	1.664	1.656
ΔE_5	0.232	0.169
ΔE_6	1.014	0.894

The process of BA hydrogenation (Figure 4-7) happens with the adsorption of benzoic acid into the surface (Eq. 6), followed by the Volmer step (Eq. 7), where an H^+ reacts with an e^- to produce H^* (adsorbed hydrogen). Subsequently, the H^* transfers into BA^* until the hydrogenation process is completed, and cyclohexane carboxylic acid is produced. The last step is the desorption from the surface (Eq. 8).

ECH mechanism without phenol:



* = adsorption site



ECH mechanism with phenol:

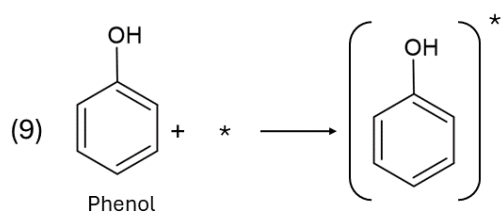
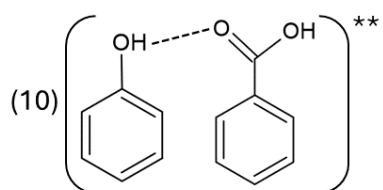
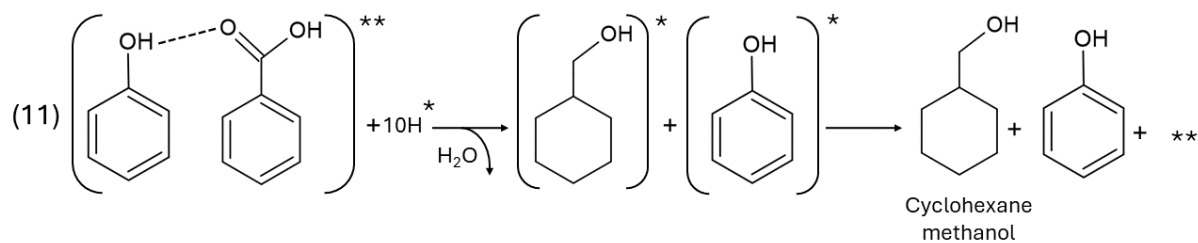


Figure 4-7 - Proposed mechanism for the ECH of BA over PtRu/ACC before and after the addition of phenol.

When phenol is added to the mixture, P^* is formed (Eq. 9), which creates a hydrogen-bonded complex with BA (Eq. 10). This complex increases the adsorption energy and lowers the activation energy of the hydrogenation process, leading to the reduction of not only the phenyl group, but also the carbonyl group. The final step is the desorption of the cyclohexanemethanol from the surface (Eq. 11).

The significance of these findings extends beyond the co-hydrogenation of benzoic acid and phenol. The ability of phenol to act as a "co-catalyst" by forming hydrogen-bonded complexes could be applied to other bio-oil components with similar functional groups, in concordance with Sanyal *et al*¹¹⁶. Moreover, the insights into reduced activation barriers suggest that catalyst design strategies could focus on promoting similar interactions.

These findings have practical implications for the optimisation of ECH processes involving complex feedstocks, such as bio-oils, which often contain phenolic and carboxylic acid compounds. Leveraging the natural synergy between such compounds can reduce energy consumption and improve product selectivity.

4.4 Discussion

This study demonstrates the significant impact of hydrogen bond enhancement on the electrochemical co-hydrogenation of benzoic acid and phenol over a platinum-ruthenium catalyst. The formation of hydrogen-bonded complexes between the hydroxyl group of phenol and the carboxyl group of benzoic acid led to stronger adsorption on the catalyst surface, as evidenced by increased electron density and improved adsorption energy. This stronger adsorption enhances the likelihood of hydrogenation, leading to higher conversion of benzoic acid.

Moreover, Density Functional Theory calculations confirmed that the addition of phenol reduces the activation energy barriers for the hydrogenation steps. These molecular changes explain the improved efficiency of the co-hydrogenation process, as well as the selectivity for cyclohexanemethanol, which was achieved due to the favourable interaction of the hydrogen-bonded complex with the

catalyst. This selectivity is particularly important for bio-oil upgrading, as the formation of alcohols reduces the corrosive effects of carboxylic acids and improves the fuel quality of bio-oil derivatives.

These findings open new avenues for optimising ECH processes, especially for handling complex organic mixtures such as those found in biomass-derived feedstocks. By leveraging hydrogen bond interactions to enhance catalytic efficiency and selectivity, this approach provides a transformative pathway for upgrading bio-oils into higher-value chemical and fuel products. Future research should focus on scaling this process and exploring its potential in real-world bio-oil systems, where the ability to selectively hydrogenate multiple reactive compounds could revolutionise the production of sustainable fuels and chemicals.

4.5 Data availability

Data for this article are available at Figshare at <https://doi.org/10.6084/m9.figshare.27940002.v1>

4.6 Author contribution

C. Catizane conducted the experimental work and analysis/imaging and was the primary author of the paper. J. Sumner and Y. Jiang supervised the research, revised the manuscript and contributed to the technical content of the paper.

5 Paper Four: Pinewood and wheat straw bio-oil aqueous phase electrochemical hydrogenation utilising a PtRu/ACC catalyst

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Abstract

Bio-oil produced from biomass pyrolysis contains a wide range of oxygenated compounds, limiting its direct use as a fuel due to chemical instability and low energy density. This study investigates the application of electrochemical hydrogenation (ECH) as an alternative to conventional hydrogenation process, to upgrade bio-oil derived from wheat straw and pinewood. Experiments were conducted in a two-chamber electrochemical cell, with ECH conditions optimised based on prior research. A platinum-ruthenium on activated carbon cloth (PtRu/ACC) was selected as the catalyst for ECH reactions. The process selectively reduced phenolic and carbonyl compounds while increasing the concentration of alcohols, as confirmed by gas chromatography-mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR) analyses. The ECH study revealed substantial reductions in phenolic compounds, notably p-cresol (62.1%) and phenol (29.3%), alongside an increase in alcohol content from 49.3% to 56.5% in pinewood-derived bio-oil. These chemical transformations demonstrate ECH's potential as a mild, sustainable alternative to traditional hydrodeoxygenation processes. This study provides

insights into the ECH process and suggests future directions for optimising bio-oil upgrading and supporting the development of renewable fuels.

5.1 Introduction

The global transition to sustainable energy sources necessitates reducing dependence on fossil fuels and mitigating greenhouse gas emissions. As concerns about climate change and resource depletion grow, biomass has been recognised as an important renewable resource for the production of fuels and chemicals. One particularly attractive product from biomass is bio-oil, generated through the pyrolysis of organic materials, including agricultural residues or woody biomass.⁸ Bio-oil is a complex liquid comprising a wide range of organic compounds, including acids, alcohols, phenols, and ketones.^{11,14–16,66} However, several characteristics of bio-oil, such as its chemical instability, high acidity, and low energy density, limit its direct use as a fuel.^{10,32}

To realise the potential of biomass derived bio-oil as a viable energy source, upgrading processes are necessary to reduce its oxygen content, thereby enhancing its chemical stability and calorific value.²³ Conventional hydrogenation techniques, including hydrodeoxygenation (HDO), require high pressures and elevated temperatures, typically around 300 bar and 700°C. Additionally, the conventional process requires the use of an external source of hydrogen gas, therefore further increasing the energy intensity and the costs of operation.^{24–29} As an alternative, electrochemical hydrogenation (ECH) has emerged as a promising approach. ECH operates under milder reaction conditions, using electricity to generate hydrogen *in situ*, which then reacts with bio-oil constituents to reduce their oxygen content. This method offers the potential for improved energy-efficiency and selectivity, enabling targeted modification of specific functional groups in bio-oil, such as phenolic compounds and carbonyl groups, which constitutes a significant proportion of its composition.^{10,23–26,28,32,74–81}

Despite its advantages, the practical implementation of ECH for bio-oil upgrading remains challenging. Key aspects, such as understanding the behaviour of various organic compounds under electrochemical conditions and optimising catalyst performance, need to be addressed to improve process efficiency.

Additionally, the high chemical diversity of bio-oil complicates the upgrading process, as each compound class may exhibit different reactivity and require tailored catalytic conditions.

Pyrolysis bio-oils can be divided into two distinct phases: the more viscous, apolar non-aqueous "oily" phase and the water-soluble "aqueous" phase. This study investigates the ECH of bio-oil derived from the slow pyrolysis of wheat straw and pinewood, with a focus on the aqueous fractions. For this application, the selected catalytic cathode needs to be versatile enough to convert a variety of compounds, unlike those designed specifically for model compound experiments. Both ruthenium and platinum have demonstrated success in facilitating the ECH process. Du et al. reported that Pt₃Ru/ACC achieves a higher conversion than either Pt or Ru alone, likely due to a synergistic effect between the two metals, where platinum excels in hydrogenation and ruthenium predominantly enhances direct hydrogenolysis.⁴⁵ Additionally, Salakhum et al. found that the combination of these metals lowers the heterolytic activation energies for cleaving C-O and O-H bonds.¹⁰¹ Based on these findings, this work employs a platinum-ruthenium on activated carbon cloth (PtRu/ACC) catalyst to hydrogenate bio-oil components, aiming to improve their composition and fuel properties. The research seeks to elucidate the impact of the ECH process on various chemical groups and assess its effectiveness in transforming bio-oil into a more stable and energy-dense product.

Through a comparative analysis of the behaviour of key compounds in both the aqueous and organic phases, conducted before and after the ECH process, this study offers valuable insights into the selectivity and efficiency of the procedure. By advancing our understanding of ECH and its application to complex bio-oil systems, this research takes a crucial step towards developing practical and scalable solutions for renewable fuel production, addressing the urgent global need for cleaner, sustainable energy alternatives.

5.2 Experimental

5.2.1 Materials

Sulfuric acid solution (5M) and toluene (99.5%) were purchased from Thermo Fisher Scientific. All chemicals were used as received without further purification. A Nafion 117 membrane (Ion Power Inc. PA, USA) was used as the cation exchange membrane to separate the cathode and anode chambers. To ensure the activation of the membrane and optimise its ion transport capability, it was pretreated according to the methodology of Peng *et al*¹¹²: treatment in oxygen peroxide (H₂O₂) at 80 °C, followed by deionised water and 1.0M H₂SO₄ at the same temperature. Each step in the pretreatment of the membrane duration was 1h, and the membrane was washed with DI water after each step. The utilised cathode is a 2x2cm, 4 mg/cm² Platinum Ruthenium Black-Carbon Cloth Electrode (PtRu/ACC, Fuel Cell Store Inc., Texas, USA, 1:1 Pt:Ru ratio).

5.2.2 Biomass pyrolysis

Slow pyrolysis experiments were conducted to generate bio-oil using a screw auger reactor with a processing capacity of 100 to 200 kg/h (subject to feedstock density). The system consists of four main sections: the feeding system, the slow pyrolysis reactor, the vapour condensation liquids collection system, and the char cooling and product outlet. The feeding system includes a metered screw-feed unit supplying a nitrogen-purged interlocked twin-valve airlock arrangement. A single-pass setup was employed to allow the collection and analysis of the gas stream (comprising nitrogen and non-condensable product gas). The experiments targeted an average pyrolysis temperature of 500 ± 5°C for pinewood and 550 ± 5°C for wheat straw, with a solid's residence time in the reactor of 20 minutes. The pyrolysis vapours and non-condensable gases exit the pyrolysis chamber at high level via trace-heated pipework to the condensation system, with char exiting via a cooling screw and a second nitrogen-purged and interlocked twin-valve airlock on the outlet.

The vapours were condensed in a recirculated and temperature-controlled spray quench column, using ISOPAR™ (Isopar V, CAS number: 64742-46-7) as the initial quenching medium, that becomes increasingly diluted with the condensed

products that accumulate in the liquid's sump. Spray condensation liquids are temperature controlled (25 and 30°C) via a separate water-cooling circuit and heat exchanger arrangement. Aerosols are coalesced in a wet-walled electrostatic precipitator operating at 12.5 kV and 0.5 mA, flushed with a combination of ISOPAR™ and condensed pyrolysis liquids. The pyrolysis liquid is gravity separated from the ISOPAR™ at the end of each experiment in the collection tank. The pyrolysis liquid separates into two distinct phases: an organic phase and an aqueous phase. These are divided by gravity using a separation funnel. After passing through the electrostatic precipitator, the remaining gases are routed via gas flowmeter to a flare.

5.2.3 Electrochemical hydrogenation

A two-chamber electrochemical cell, separated by a cation exchange membrane (CEM) was selected for the ECH process. The selected catalytic cathode was 4 mg/cm² platinum ruthenium black-carbon cloth electrode (PtRu/ACC, Fuel Cell Store), and the counter electrode was a platinum plate (1x1 cm, Ossila). The PtRu/ACC cathode was selected for its proven efficacy in facilitating hydrogenation reactions, while the constant temperature and current density were optimised based on prior studies. For all experiments, both the anode and cathode chambers were filled with 90 mL of 1M sulfuric acid.

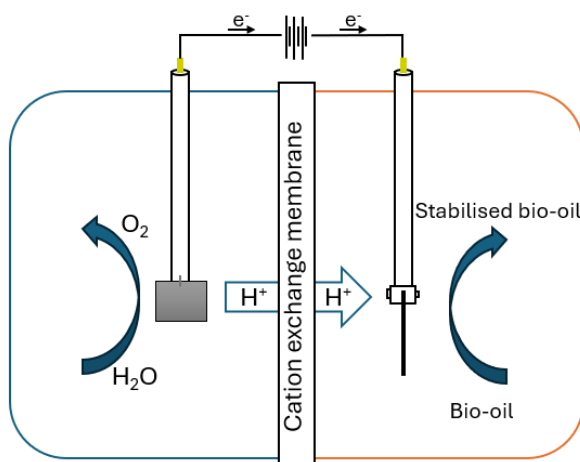


Figure 5-1 - H-type electrochemical cell utilised for ECH. The cell consists of the anode chamber, where the water oxidation happens, a cation exchange

membrane and the cathode chamber, where the hydrogenation process happens.

Each test was initiated under electrostatic control and constant temperature for 10 minutes without the organic compounds to polarise the electrodes. The aqueous phase of the bio-oil was filtered to remove any solid contaminants and reduce membrane and cathode fouling. After that, 1 mL of the prepared bio-oil was added to the system. The experiment was run for 5h to ensure the availability of enough electrons in the system for the conversion of the compounds. Samples (1 mL) were taken, and the organic compounds were extracted with 2 mL of dichloromethane (DCM). A toluene solution (0.2 mL) was added to each vial as an internal standard. After each experiment, the electrolyte was discarded, the cell cleaned, and the cathode was soaked in 5 mL DCM for 15 min, to ensure the desorption of any molecules on its surface. All experiments were run in triplicate.

A control experiment was conducted by maintaining the system under identical conditions without applying current to distinguish between electrochemical and non-electrochemical effects. To identify if evaporation was taking place, a similar control experiment was conducted where the cell, under the same conditions previously established, remained open for 5 hours. The content of the cell was weighted before and after the test.

5.2.4 Analysis

The samples were taken for analysis in the GC-MS Shimadzu TQ8040. The GC used a Restek Rtx-5 capillary column, 28.5 m × 0.25 mm with a 0.25 µm film thickness, a 1.18 ml min⁻¹ helium carrier gas flow rate, and a split ratio of 1: 25. The injector temperature was set at 250 °C. The GC oven program started at 34 °C and held for 2 min, and then heated at 50 °C min⁻¹ to 300 °C. Mass spectrometry was operated at m/z ranging from 50 to 500. Species associated with each chromatographic peak were identified by comparing their observed mass spectrum with the NIST library and then confirmed by injection of authentic samples. External standards were also used to identify compounds and quantify the peaks. Results are in area %. Fourier transform infrared spectroscopy (FTIR) was carried out in a Shimadzu IRTracer-100 and scanned in transmittance mode.

The 10 scans were made from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1} with Happ-Genzel apodisation.

5.3 Results

5.3.1 ECH of the aqueous phase

The electrochemical hydrogenation of the aqueous phase derived from the slow pyrolysis of wheat straw and pinewood (herein referred to as WS_{aq} and PW_{aq} , respectively) was performed at the optimal conditions established in our previous study¹¹⁹ (temperature = 55°C, current density = 25.0 mA cm^{-2}). The primary goal was to reduce the oxygenated and nitrogenous compounds, enhancing the hydrogen content of the bio-oil and improving its fuel properties. Figure 5-2 presents some of the primary components of both WS_{aq} and PW_{aq} before and after ECH, showcasing the chemical transformations that took place during the process.

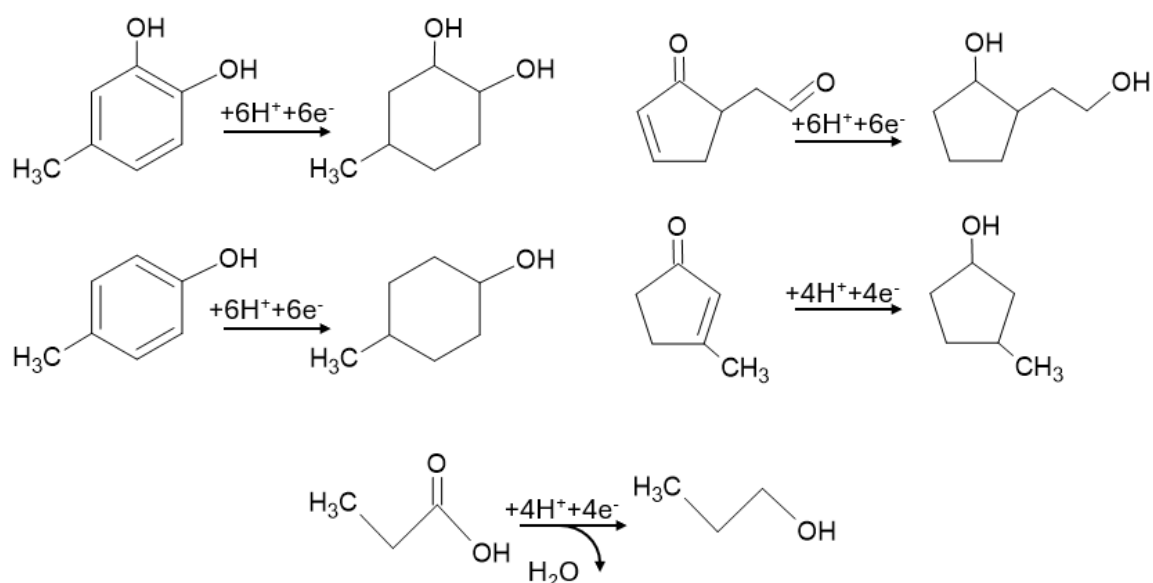


Figure 5-2 - Some of the main compounds found in the aqueous phase of bio-oils and their respective products after hydrogenation.

The hydrogenation of organic compounds over PtRu/ACC follows the Langmuir-Hinshelwood mechanism^{44,111} (Figure 5-3), where both reactants adsorb onto the catalyst surface before they react with each other, and the catalyst provides a surface that lowers the activation energy needed for the reaction. Once the

reaction occurs, the product molecules desorb from the catalyst surface and are released back into the liquid phase. Therefore, the existence of more than one molecule in the system can lead to competition for the active adsorption sites, lowering activity and hindering the hydrogenation process. If the two species (“A” and “B”) are hydrogen atoms, it could form hydrogen gas (H_2), a process known as hydrogen evolution reaction (HER), which is the competing reaction for ECH and can form bubbles that impede the adsorption process.

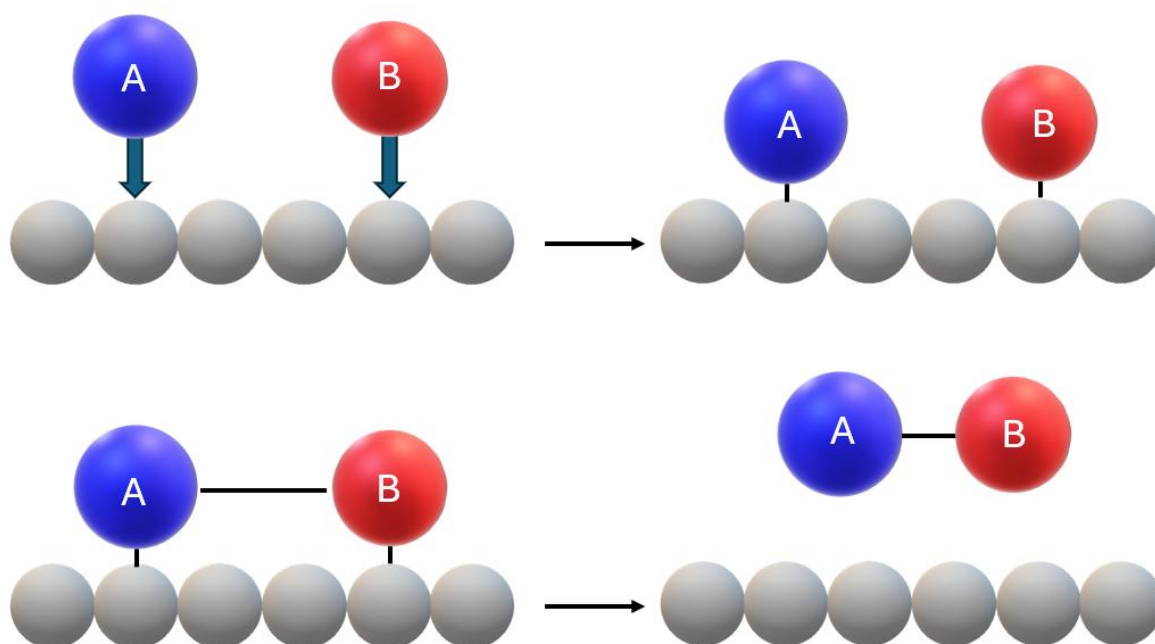


Figure 5-3 - Schematic of the Langmuir-Hinshelwood hydrogenation mechanism, which is followed by organic compounds during ECH. Where A is the organic compound and B is hydrogen.

Bio-oils are complex mixtures containing up to hundreds of compounds, therefore, only the largest peaks were identifiable and quantifiable via GC-MS. Table 5-1 shows the main peaks before and after the ECH of PW_{aq} . Toluene was used as an internal standard, so its concentration is set to 1.00. It is important to understand that the hydrogenation of compounds containing rings typically starts with the saturation of the ring, followed by the hydrogenation of any side chains. Therefore, a decrease in the concentration of phenol derivatives does not necessarily indicate a reduction in the relative concentration of alcohols. For instance, while the concentration of phenol decreased by 29.27%,

cyclohexanol—a fully saturated ring compound with an alcohol group—was found among the products resulting from phenol's hydrogenation. Signifying a reduction in phenol concentration, whereas the alcohol concentration was unaltered. The GC-MS peak, however, was not visible and was only detectable when manually searching for it.

Notable results include the conversion of p-cresol and 2-methylphenol, at 62.10 and 55.73%, respectively, and the complete depletion of 4-methyl-1,2-benzenediol and 3-methyl-1,2-benzenediol. In addition, propanoic acid presented the second-lowest conversion, at 8.23%, where the lower value was expected, as carboxylic acids are resistant to ECH.⁹⁷ For both feedstocks, on average, alcohols presented the highest tendency for reduction, followed by other oxygenated compounds, such as ketones and ethers, and carboxylic acids presented the lowest conversion.

Table 5-1 – Key composition of pine wood slow pyrolysis bio-oil aqueous phase before and after ECH.

Compound	Before ECH (relative area)	After ECH (relative area)	Reduction in relative area	Reduction in concentration
4-methyl-1,2-Benzenediol	0.172	0.000	0.172	100.00%
3-methyl-1,2-Benzenediol	0.139	0.000	0.139	100.00%
p-Cresol	0.404	0.153	0.251	62.10%
2-methyl-Phenol	0.329	0.146	0.183	55.73%
3,5-dimethyl-Phenol	0.155	0.084	0.071	46.11%
5-Hydroxymethylfurfural	0.046	0.025	0.021	44.17%
Catechol	0.302	0.169	0.133	44.12%
2,5-dimethyl-Furan	0.348	0.237	0.111	31.73%
3-methyl-2-Cyclopenten-1-one	0.180	0.123	0.057	31.66%
Phenol	0.458	0.322	0.136	29.57%
Propanoic acid	0.064	0.058	0.006	8.23%
Butyrolactone	0.075	0.071	0.004	4.74%
Toluene	1.00	1.00	-	-

Table 5-2 shows the change in concentration of the most common compounds in WS_{aq} before and after ECH. The compounds that underwent the largest change in concentration were mostly the same as in PW_{aq}, although full depletion was not achieved.

Table 5-2 – Key composition of wheat straw slow pyrolysis bio-oil aqueous phase before and after ECH.

Compound	Before ECH (relative area)	After ECH (relative area)	Reduction in relative area	Reduction in concentration
Cyclopentanone	0.0251	0.0140	0.0111	44.13%
3,5-dimethyl-Phenol	0.0533	0.0323	0.0210	39.38%
2-oxo-3-Cyclopentene-1-acetaldehyde	0.1099	0.0690	0.0409	37.20%
p-Cresol	0.2216	0.1393	0.0823	37.13%
3-ethyl-Phenol	0.0489	0.0334	0.0155	31.69%
2-methyl-Phenol	0.1353	0.0970	0.0383	28.26%
4-methyl-1,2-Benzenediol	0.0765	0.0550	0.0215	28.04%
2-methyl-2-Cyclopenten-1-one	0.0346	0.0252	0.0094	26.98%
3-methyl-1,2-Benzenediol	0.0712	0.0524	0.0188	26.41%
3-methyl-2-Cyclopenten-1-one	0.0608	0.0449	0.0159	26.12%
Butyrolactone	0.0868	0.0649	0.0219	25.22%
Phenol	0.3368	0.2620	0.0748	22.20%
2-Methoxytetrahydrofuran	0.0514	0.0403	0.0111	21.52%
4-ethyl-1,3-Benzenediol	0.0360	0.0306	0.0054	15.07%
2-Cyclopenten-1-one	0.0454	0.0395	0.0059	13.03%
Catechol	0.1733	0.1521	0.0212	12.21%
Propanoic acid	0.0624	0.0593	0.0031	4.92%
Toluene	(1.00)	(1.00)	-	-

As most of the compounds are aromatics, this explains the reduction in the number of unsaturated rings found during FTIR (Figure 5-4c-d). Other notable

results include cyclopentanone, 3,5-dimethyl-phenol and 2-oxo-3-cyclopentene-1-acetaldehyde, which were reduced by 44.13, 39.38 and 37.20%, respectively.

In addition to hydrogenation, the reduction in the concentration of identifiable compounds could be attributed to several other mechanisms. These potential pathways include the formation of undetectable compounds via polymerisation due to their insolubility and higher boiling points, preferential adsorption of certain compounds onto the cathode and membrane, and conversion to products not readily identifiable by GC-MS. Although no coke formation was observed, adsorption onto the cathode did occur, necessitating cleaning after each experiment. Table 5-3 presents the major compounds before and after the control experiment (PW_{aq} added, constant temperature, no current), revealing the presence of non-electrochemical reactions.

Most compounds showed a reduction in concentration without the application of current, although they were, generally, lower than with current. For example, phenol was still converted without an applied current, although at a lower rate, from 29.57% with current to 12.31% without. Similarly, 2-methyl-phenol, 3,5-dimethyl-phenol, catechol, and 3-methyl-2-cyclopenten-1-one, saw reductions in conversion from 55.73%, 46.11%, 44.12%, and 31.66% to 39.78%, 26.24%, 24.02%, and 4.32%, respectively.

Interestingly, both 4-methyl-1,2-benzenediol and 3-methyl-1,2-benzenediol are fully converted regardless of current input, indicating that their conversion is driven by non-electrochemical reactions. The formation of p-cresol can be the result of the 4-methyl-1,2-benzenediol dehydration reaction, where an -OH group is lost. Notably, applying an overpotential reduced p-cresol concentration by 62.10%, indicating that hydrogenation of p-cresol significantly outweighs dehydration of 4-methyl-1,2-benzenediol.

Conversely, butyrolactone showed a complete conversion, increasing from 4.74% to 100%, likely forming butanoic acid and 4-hydroxy-butanoic acid, both of which increased significantly in concentration. This suggests that current suppresses the formation of these corrosive compounds, a favourable outcome for improving the bio-oil's properties. Similar results were found when the same

experiment was conducted with WS_{aq}, including the increase in concentration of molecules containing carboxylic acid groups. These findings highlight the need for applied current to drive selective hydrogenation effectively.

Table 5-3 – Key composition of pine wood slow pyrolysis bio-oil aqueous phase before and after the blank experiment, without current input.

Compound	Before ECH (relative area)	After ECH (relative area)	Change in relative area	Change in concentration
4-methyl-1,2-Benzenediol	0.192	0.000	0.192	100.00%
3-methyl-1,2-Benzenediol	0.181	0.000	0.181	100.00%
Butyrolactone	0.131	0.000	0.131	100.00%
2-methyl-Phenol	0.546	0.328	0.218	39.78%
3,5-dimethyl-Phenol	0.249	0.183	0.066	26.24%
Catechol	0.457	0.347	0.110	24.02%
Phenol	0.719	0.631	0.088	12.31%
3-methyl-2-Cyclopenten-1-one	0.287	0.275	0.012	4.32%
p-Creosol	0.310	0.337	-0.027	-8.58%
Butanoic acid	0.123	0.167	-0.044	-35.08%
4-hydroxy-Butanoic acid	0.000	0.111	-0.111	-100.00%
Toluene	(1.00)	(1.00)	-	-

The observed decrease in the total concentration of reactants can be attributed to a combination of factors. While GC-MS analysis focuses on quantifiable changes in major compounds, the overall mass balance is influenced by (1) conversion to unidentifiable or undetectable products, (2) formation of higher molecular weight, less volatile compounds not detectable by GC-MS (potentially through polymerisation), and (3) adsorption onto the electrode. Our observations of no tar-like substance in the cathode chamber suggest a low tendency for

significant polymerisation. Tests addressing evaporation showed no significant mass change. While adsorption of reactants or products onto the catalyst surface or electrochemical cell components is another potential loss pathway, GC-MS analysis of the extract from the cleaned cathode showed no discernible peaks, and the cathode's mass change post-reaction was less than 1%. Therefore, the formation of unidentifiable compounds via GC-MS and peak overlap is likely the primary contributor to the changes in mass balance. Further studies are needed to fully quantify the contribution of each of these factors to the overall mass balance.

5.4 ECH effect on organic functional groups

5.4.1 GC-MS analysis

GC-MS analysis (Figure 5-4a) shows that the primary identifiable components in PW_{aq} are alcohols, ethers, and ketones. The increase in alcohol concentration (from 49.3% to 56.5%) after the ECH can be attributed to the reduction of ethers and ketones (from 16.3% and 18.3% to 12.2% and 13.8%, respectively), as hydrogenation of carbon-oxygen double bonds to C-OH is more easily achieved than full deoxygenation. Another notable finding is the 48% decrease in amine concentration, which is desirable since nitrogen removal is crucial in the upgrading process.

The effect of the hydrogenation process on carboxylic acids was examined in our previous study,¹¹⁹ where we showed that this group remains largely unaffected due to its stability and the specific hydrogenation mechanism. This same trend was observed in the ECH of PW_{aq} , where the process had little to no impact on the concentration of carboxylic acids. The identifiable compounds in WS_{aq} were also mostly alcohols, going from 63.2% to 64.3 % after ECH (Figure 5-4b). The concentration of ketones was reduced, while the ester concentration was slightly increased. The number of carboxylic acids, in contrast to PW_{aq} , also suffered a reduction, from 7.46 to 6.01%.

5.4.2 FTIR analysis

PW_{aq} FTIR analysis (Figure 5-4c) reveals a significant increase in the peak at 3300 cm⁻¹, associated with the vibration of O-H groups found in alcohols and phenols, following the ECH process. Additionally, there was a reduction in both the peak at 1240 cm⁻¹, linked to C-O in ether-containing compounds, and the peak at 700-750 cm⁻¹, indicating ring unsaturation vibrations. There is also a slight increase at 1640 cm⁻¹, possibly signifying the cleavage of phenyl groups into aliphatic compounds.

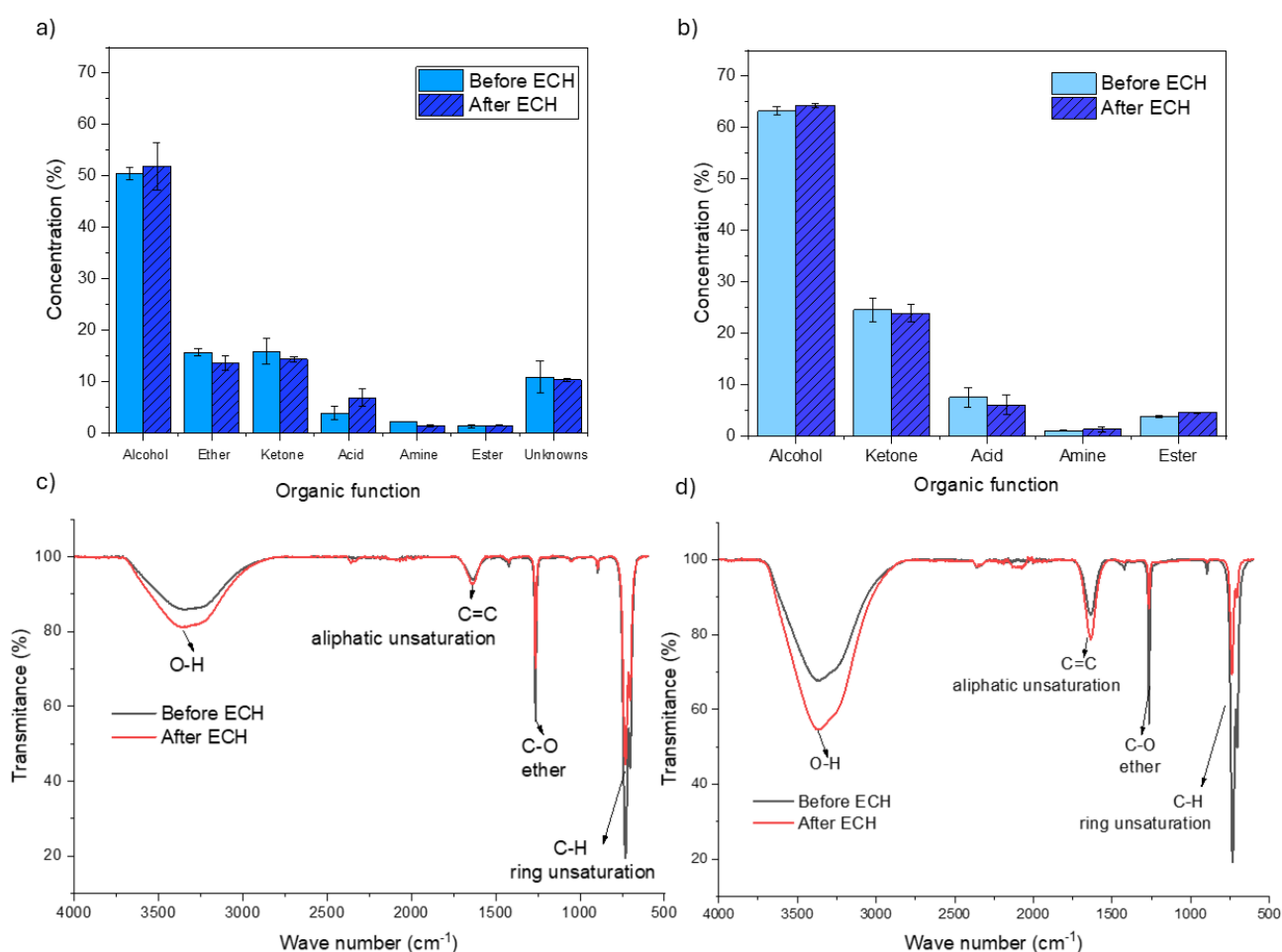


Figure 5-4 - Organic functions' relative concentration obtained by GC-MS (area %) in the slow pyrolysis of pinewood (a) and wheat straw (b) aqueous phases before and after ECH for 5h. FTIR spectrum from slow pyrolysis of pinewood (c) and wheat straw (d) aqueous phase before and after ECH process, and the main identified peaks.

Figure 5-4d shows that WS_{aq} followed the same pattern, including a noticeable reduction in the concentration of unsaturated aromatic groups, demonstrating that, although there wasn't a large change in the organic group distribution, most of the double bonds in the aromatic rings were saturated. The reduction of ethers and the increase in alcohols and aliphatic unsaturation were also higher in WS_{aq} .

While the aqueous phase itself is not suitable as a fuel due to its high water content, the changes detected by GC-MS and FTIR indicate the presence of valuable hydrogenated organic compounds. These compounds could be separated and utilised as fuel additives or feedstocks for further chemical processing towards fuel production. The reduction in oxygenated compounds, especially phenols and carboxylic acids, is beneficial for increasing the stability and calorific value of the bio-oil. By converting these compounds into more stable alcohols, the ECH process significantly enhances the overall quality of the product.

Moreover, the reduction in unsaturated aromatic rings improves the hydrogen-to-carbon ratio of the bio-oil, making it more suitable, after separation, for blending with traditional fossil fuels. The increase in alcohol content, particularly cyclohexanol and other saturated alcohols, suggests that the fuel's energy density has been enhanced, providing a cleaner-burning fuel with fewer emissions. The bio-oil's improved composition also makes it more compatible with standard refining processes, increasing its potential for commercialisation as a renewable fuel source.

5.5 Comparison with model compound behaviour

Phenol is more reactive to ECH than guaiacol¹²⁰, probably due to guaiacol's more complex molecular structure. Both methoxy and phenolic groups on adjacent carbons in guaiacol increase bond energies, making it less reactive, whereas phenol's simpler structure facilitates hydrogenation. The presence of an electronegative substituent in the ortho position (guaiacol-like) can also hinder the approach of the catalyst and/or alter the electron density of the aromatic ring, making it less susceptible to hydrogenation compared to phenol-like compounds.

In this study, the compounds in WS_{aq} and PW_{aq} were classified as either “phenol-like” or “guaiacol-like” based on their structure. All these compounds contain a phenyl group (an alcohol attached to a benzene ring). Compounds with no additional substituents or a second substituent in the meta or para position were categorised as phenol-like. In contrast, compounds with an electronegative substituent (e.g., alcohol or ether) in the ortho position were classified as guaiacol-like. Non-electronegative ortho substituents were also considered phenol-like.¹¹⁹ Although this is not an exhaustive list, most identified compounds could be categorised into these classifications. Figure 5-5 shows some of the main compounds and their classification.

The higher concentration of phenol-like compounds in PW_{aq} (1.346 vs internal standard) compared to WS_{aq} (0.831 vs internal standard) indicates why it exhibited higher activity for ECH, achieving higher conversion on average (46.51 and 25.85% respectively). These compounds, with less steric hindrance and simpler structures, were more readily hydrogenated than the “guaiacol-like”.

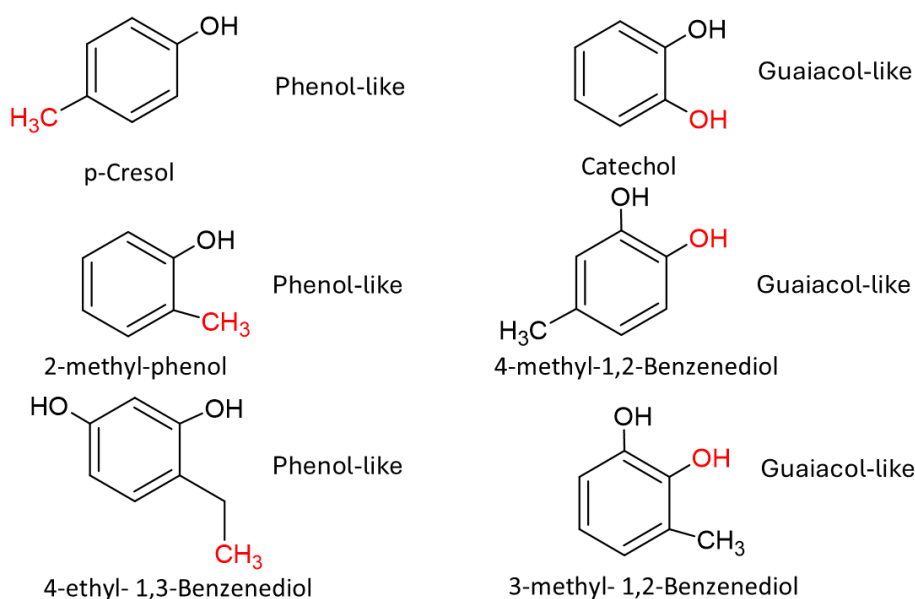


Figure 5-5 - Some of the main compounds in WS_{aq} and PW_{aq} and their classification in the system. The ramification highlighted in red indicates the classification reasoning.

The effect of the ramifications can be demonstrated by the conversion of p-cresol, 2-methyl-phenol, and catechol, where the methyl group goes from para to the ortho position, and the conversion (on average from the two feedstocks) goes from 49.61 to 42.00%, respectively. If the methyl group is substituted by an alcohol (catechol), a highly electronegative group, the conversion goes to 28.17%. Moving the methyl group from para (4-methyl-1,2-benzenediol) to meta (3-methyl-1,2-benzenediol) also led to a reduction in the conversion, from 64.02 to 63.21%.

5.6 Conclusion

This study demonstrates the application of electrochemical hydrogenation to the aqueous phase of bio-oil derived from the slow pyrolysis of wheat straw and pinewood. The ECH process resulted in a reduction of several oxygenated compounds, most notably phenols, and a concurrent increase in the concentration of alcohols, as confirmed by GC-MS and FTIR analyses. Specifically, the data indicates that ECH leads to the saturation of aromatic rings and an increase in hydrogen content, operating without the need for high-pressure hydrogen gas.

However, the data also reveals complexities and limitations in the ECH process. While a general trend of reduced oxygenated compounds and increased alcohols was observed, the extent of conversion varied among compounds. For instance, some compounds like catechol were significantly reduced under ECH conditions in WS_{aq} but not in PW_{aq} , whereas carboxylic acids generally showed limited reactivity. Furthermore, a mass imbalance in the GC-MS analysis suggests that a portion of the reactants was not accounted for by identified products, indicating the potential formation of unidentified compounds or loss through other pathways. These variations in reactivity and the mass imbalance highlight the need for further research to optimise the ECH process, improve its selectivity, and elucidate all reaction pathways.

Despite these challenges, the ECH process shows strong potential for scale-up. The lab-scale results suggest that industrial applications are feasible, particularly

given the lower energy requirements of the process compared to traditional hydrodeoxygenation methods. Future work will focus on developing pilot-scale systems that can continuously process larger volumes of bio-oil while ensuring catalyst regeneration and maintaining process efficiency. By addressing the current challenges and demonstrating scalability, ECH could become a viable method for producing renewable fuels from biomass, supporting the global shift towards cleaner energy sources.

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6 Paper Five: electrochemical hydrogenation of pinewood and wheat straw pyrolysis bio-oil utilising a PtRu/ACC catalyst

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Abstract

Electrochemical hydrogenation (ECH) is a promising technique for upgrading bio-oils by selectively hydrogenating and deoxygenating oxygen-rich compounds under mild conditions. This study investigates the ECH of the oily phase of bio-oils derived from slow pyrolysis of wheat straw and pinewood, utilising a PtRu/ACC electrode and methanol as the catholyte. Sodium chloride (NaCl) and tetrabutylammonium hexafluorophosphate (TBAHFP) were evaluated as additives to enhance electrolyte conductivity, which had detrimental impacts on electrode stability. GC-MS and FTIR analyses revealed that phenolic compounds were preferentially hydrogenated, resulting in reduced unsaturation and increased alcohol content. While NaCl improved conductivity, it caused significant cathode degradation due to chloride-induced degradation. TBAHFP, though less corrosive, led to secondary reactions, such as the formation of trimethyl phosphate, which facilitated the methylation of phenolic compounds. SEM imaging confirmed additive-specific degradation patterns on the cathode, with TBAHFP showing unexpected surface damage despite its inert properties. The findings highlight the trade-offs between additive performance and material stability, providing insights into optimising ECH conditions for bio-oil upgrading. This work underscores the potential for tailored additive selection to enhance bio-oil quality, advancing its viability as a renewable fuel alternative.

6.1 Introduction

Bio-oil, derived from the thermal decomposition of lignocellulosic biomass through fast or slow pyrolysis, represents a renewable and sustainable alternative to fossil fuels. Despite its potential as a source of valuable chemicals, bio-oil's high oxygen content, acidity, chemical instability, and propensity to polymerise present major obstacles to its direct use as a fuel.^{8,23} Overcoming these issues through selective hydrogenation and deoxygenation could significantly enhance the energy density, chemical stability, and compatibility of the resultant bio-oils with existing fuel systems. Several options exist for upgrading; however these are usually costly in terms of energy. As such, electrochemical hydrogenation (ECH) has emerged as a promising method for upgrading bio-oils into valuable chemicals or biofuel, providing a pathway to modify organic compounds under mild, energy-efficient conditions selectively.^{32,121}

ECH involves applying an electric current to a reaction system to drive the selective hydrogenation and deoxygenation of bio-oil compounds. This process utilises a catalytic cathode, where hydrogen atoms are electrochemically generated via water splitting and incorporated into the molecular structure of the target compounds (Figure 6-1).^{30,82} This avoids the costs and risks associated with hydrogen storage and utilisation.^{26,28,29} The key advantage of ECH lies in its ability to operate under ambient pressure and moderate temperatures, offering a more sustainable and scalable alternative to traditional high-pressure catalytic hydrogenation methods. By using electricity, which can be sourced from renewable energy, ECH minimises the carbon footprint of the upgrading process while achieving targeted chemical transformations. Indeed, this process has been investigated for the hydrogenation of several model compounds.^{27,31,45,75,84,90}

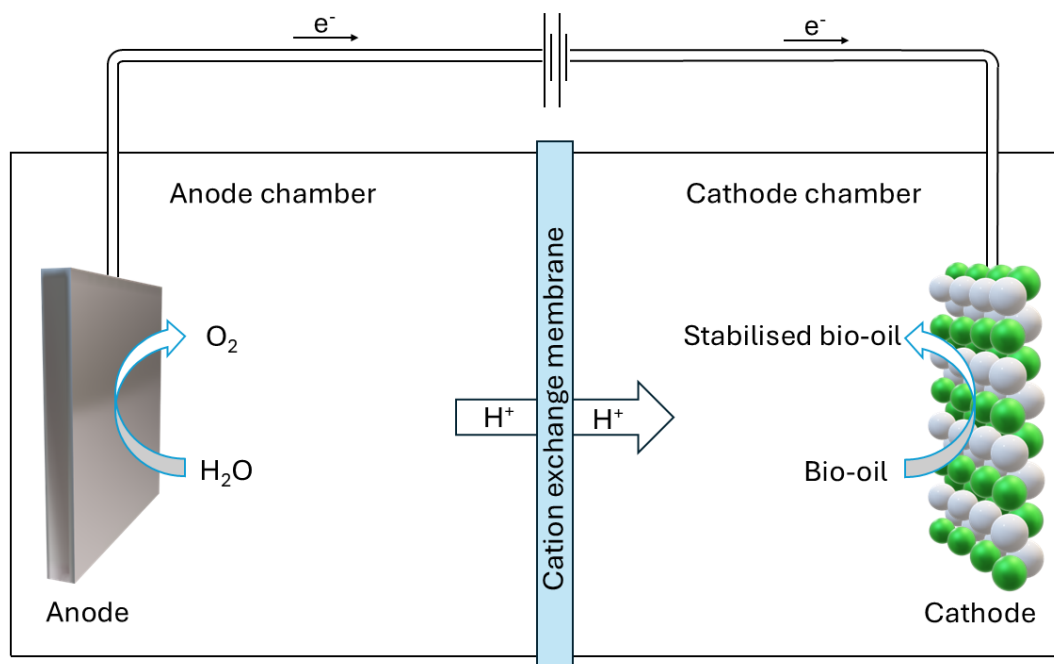


Figure 6-1 - Schematic representation of an H-type cell for ECH. The cell is composed of two chambers separated by a cation exchange membrane.

Composed of hundreds of organic compounds, bio-oils are typically separated into two distinct phases: an aqueous and an oily phase. While the aqueous phase is soluble in conventional water-based electrolytes, the oily phase is hydrophobic and poorly compatible with these systems, severely limiting the efficiency of traditional ECH processes. The oily phase, rich in aromatic and phenolic compounds, holds great promise as a precursor for renewable fuels, but its insolubility in water-based electrolytes creates technical barriers.^{99,122} Therefore, ECH of whole bio-oil presents significant challenges due to their complex chemistry, when compared to single model compound systems.

To overcome the limitations of conventional water-based electrolytes for the ECH of bio-oil, organic solvents, which are capable of dissolving the oily phase, could be utilised. Methanol offers unique advantages as an electrolyte, effectively dissolving the hydrophobic compounds of the oily phase while maintaining electrochemical compatibility with bio-oil constituents.¹²² This study represents the first application of methanol as an electrolyte for mild, low energy and low-pressure ECH of bio-oil, as no prior work in the literature has addressed this

approach. The volatility of methanol imposes limitations on the operational temperature, restricting it to approximately 60–63 °C to avoid solvent evaporation. However, this falls within the optimal temperature range for ECH, as identified in our prior work¹¹⁹. Methanol's inherently low conductivity also necessitates the use of conductive additives, introducing additional complexities.¹²³ These additives must enhance conductivity without compromising the stability or performance of the electrode material.

Sodium chloride (NaCl), a commonly employed chloride-based additive, boosts conductivity effectively but poses significant risks of electrode degradation due to its corrosive nature, especially for materials like PtRu/ACC, which, despite their resilience, remain susceptible to chloride-induced pitting and crevice corrosion. The presence of Cl⁻ anions in the system can also lead to chlorine evolution reactions, forming Cl₂ bubbles, and lowering the Faradaic efficiency. Bubbles can adhere to the cathode's surface, blocking active sites and impairing the mass transport of organic compounds from and to the surface, lowering ECH activity.^{124,125}

Conversely, quaternary ammonium electrolyte additives such as tetrabutylammonium hexafluorophosphate (TBAHFP) are generally more compatible with noble metal surfaces, including Pt and Ru. The PF₆⁻ ion is relatively inert and does not typically promote corrosion.^{124,126} TBAHFP can provide improved conductivity in organic solvents like methanol without introducing aggressive ions, making it the less corrosive option for a PtRu/ACC electrode, thus supporting electrode longevity and performance in the ECH process. However, the interaction between TBAHFP and bio-oil compounds can lead to secondary reactions, potentially forming undesired products, which was not observed with NaCl as the additive.^{124,126}

The complexity of balancing solvent compatibility, conductivity enhancement, and electrode durability underlines the main research gap in this field. In previous studies Pelosin *et al.*¹²² have focused on high-pressure and high-temperature conditions to improve bio-oil upgrading, however, these methods often conflict with green chemistry principles and are less viable for industrial applications.

There is a pressing need to develop strategies that circumvent the solubility and conductivity challenges of the oily phase while maintaining the economic and environmental advantages of ECH.

This study investigates the mild ECH of the oily phase of bio-oils derived from wheat straw and pinewood pyrolysis, with a focus on addressing the solubility and conductivity issues. Methanol is employed as the catholyte, and two conductive additives (NaCl and TBAHFP) are evaluated for their effects on reaction efficiency, electrode stability, and product composition. Using a PtRu/activated carbon cloth electrode (PtRu/ACC), the study aims to determine the trade-offs associated with each additive and provide insights into optimising ECH conditions for the oily phase. By combining chemical analysis techniques such as Gas Chromatography-Mass Spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR), and Surface Electron Microscopy (SEM), this work seeks to bridge the gap between achieving high conversion and preserving electrode integrity, advancing the feasibility of bio-oil upgrading as a renewable fuel technology.

6.2 Experimental

6.2.1 Materials

Sulfuric acid solution (5M), methanol (for HPLC), and guaiacol (99%) were purchased from Thermo Fisher Scientific. Sodium chloride (ACS reagent, $\geq 99.0\%$) and tetrabutylammonium hexafluorophosphate (purum, $\geq 98.0\%$ (CHN)) were purchased from Sigma Aldrich. All chemicals were used as received without further purification.

A Nafion 117 membrane (from Ion Power Inc. PA, USA) was used as the cation exchange membrane to separate the cathode and anode chambers. To ensure the activation of the membrane and optimise its ion transport capability, it was pretreated according to Peng *et al*¹¹². It was treated in oxygen peroxide (H_2O_2) at $80\text{ }^\circ\text{C}$, followed by deionized water and $1.0\text{M H}_2\text{SO}_4$ at the same temperature. Each step duration was 1h, and the membrane was washed with deionised water after each step.

6.2.2 Biomass pyrolysis

Slow pyrolysis experiments were conducted in a screw auger reactor with a capacity of 100–200 kg/h, depending on feedstock density. The system included a feeding unit, pyrolysis reactor, vapour condensation and collection system, and char cooling and outlet. Pinewood and wheat straw were processed at average temperatures of $500 \pm 5^{\circ}\text{C}$ and $550 \pm 5^{\circ}\text{C}$, respectively, with a 20-minute residence time. Vapours and gases exited the reactor via heated pipes to a spray quench column using ISOPAR™ as the quenching medium. Condensed products were collected and separated into organic and aqueous phases, while aerosols were coalesced in an electrostatic precipitator.

6.2.3 Electrochemical hydrogenation

A two-chamber electrochemical cell, separated by a cation exchange membrane (CEM) was selected for the ECH process. The selected catalytic cathode was 4 mg/cm² platinum ruthenium black-carbon cloth electrode and the counter electrode was a platinum plate (1x1 cm, Ossila). For all experiments, the anode chamber was filled with 90 mL of 1M sulfuric acid and the catholyte was 90 mL of methanol, and 1.5g of either NaCl or TBAHFP was added to the cathode chamber, to increase the conductivity of methanol. Lastly, 0.2g of either pinewood (PW) or wheat straw (WS) bio-oil was added to the cathode chamber.

The tests were run at the optimised conditions established in our previous work¹¹⁹ electrostatic control (25.0 mA cm⁻²) and constant temperature (55 °C) for 10 minutes without the organic compounds to polarise the electrodes. After that, 1mL of the oily phase was added to the system. The experiment was run in triplicates for 20h to ensure the availability of enough charge in the system for the conversion of the compounds. Samples (1mL) were taken, and the organic compounds were extracted with 2mL of dichloromethane (DCM). A guaiacol solution (0.1mL) was added to each vial as an internal standard.

6.2.4 Analysis

The samples were taken for analysis in the GC-MS Shimadzu TQ8040. The GC used a Restek Rtx-5 capillary column, 28.5 m × 0.25 mm with a 0.25 µm film

thickness, a 1.18 ml min⁻¹ helium carrier gas flow rate, and a split ratio of 1: 25. The injector temperature was set at 250 °C. The GC oven program started at 34 °C and was held for 2 min. Then, it was heated at 50 °C min⁻¹ to 300 °C. Mass spectrometry was operated with m/z ranging from 50 to 500. Species associated with each chromatographic peak were identified by comparing their observed mass spectrum with the NIST library and then confirmed by injection of authentic samples. External standards were also used to identify compounds and quantify the peaks. Results are in area %. Reduction in concentration was calculated according to:

$$R_c = 1 - \frac{F_c}{I_c} * 100 \quad (6-1)$$

Where R_c is the reduction in concentration, F_c is the initial concentration, and I_c is the final concentration. When the initial concentration is 0, a “-” sign will be used to refer to R_c . The reduction in relative area (R_a) is:

$$R_a = F_c - I_c \quad (6-2)$$

The morphology of the electrodes and EDS (Electron-Dispersive X-ray Spectroscopy) were acquired by TESCAN VEGA 3 Scanning Electron Microscope. Fourier transform infrared spectroscopy was carried out in a Shimadzu IRTracer-100 and scanned in transmittance mode. The scans were made 10 times from 500 to 4000 cm⁻¹ with a resolution of 4cm⁻¹ with Happ-Genzel apodization.

6.3 Results

6.3.1 Electrochemical hydrogenation

Bio-oils are complex mixtures containing up to hundreds of compounds, therefore only the largest peaks were identifiable and quantifiable via GC-MS. The oily phase of wheat straw bio-oil is a dark brown liquid, whereas the pine wood bio-oil oily phase is a viscous, paste-like, black mixture.

Table 6-1 – Key composition of pinewood slow pyrolysis bio-oil oily phase with the addition of 1.5 g of NaCl before and after ECH.

Compound	Before ECH (relative area)	After ECH (relative area)	Reduction in relative area	Reduction in concentration
2,5-dimethyl-Phenol	0.063	0.034	0.029	46.03%
4-Ethylcatechol	0.055	0.031	0.024	44.00%
Methyl propionate	0.050	0.028	0.022	43.64%
2-methylnaphthalene	0.059	0.034	0.025	42.37%
1H-Indenol	0.054	0.032	0.022	40.74%
3-ethyl-Phenol	0.159	0.100	0.059	37.11%
3,5-dimethyl-Phenol	0.300	0.190	0.110	36.67%
2,6-dimethyl-Phenol	0.123	0.078	0.045	36.59%
2-ethyl-Phenol	0.381	0.258	0.123	32.65%
p-Creosol	0.100	0.068	0.032	32.28%
1-ethyl-4-methoxy-Benzene	0.048	0.033	0.015	32.00%
2,3-dihydro-1H-Inden-1-one	0.203	0.139	0.064	31.82%
Phenol	0.049	0.033	0.016	31.53%
Cyclopentanone	0.088	0.060	0.028	31.25%
3-(1-methylethyl)-Phenol	0.050	0.036	0.014	28.00%
Naphthalene	0.099	0.072	0.027	27.27%
Butanoic acid, methyl ester	0.295	0.216	0.079	26.78%
Furfural	0.047	0.035	0.012	25.53%
3-methyl-2-Cyclopenten-1-one	0.089	0.070	0.019	21.35%
3-methyl-1,2-Benzenediol	0.102	0.082	0.020	19.61%
Catechol	0.137	0.119	0.018	13.14%
2-methoxy-Phenol	(1.000)	(1.000)	-	-

Tables 6-1 to Table 6-4 show the main peaks before and after the ECH of PW and WS with NaCl and TBAHFP, respectively, and will be referred to as PW_{NaCl}, PW_{TBAHFP}, WS_{NaCl} and WS_{TBAHFP}. Guaiacol was used as an internal standard, with

its concentration set to 1.00. Due to the heterogeneous nature of the oil, the composition of each sample may vary in both concentration and compound distribution, which is reflected in the identifiable compounds in this study.

ECH was effective in converting most identifiable compounds, although not entirely. The incomplete transformation suggests that certain reaction conditions, such as duration, could be optimised to improve conversion. Recycling unconverted products back into the reactor could also enhance efficiency by favouring sequential hydrogenation pathways. The extent of conversion observed aligns with the known reactivity trends of oxygenated compounds in ECH, where phenolic species are more readily hydrogenated than ethers and ketones, which in turn are more reactive than carboxylic acids.¹¹⁹

Phenolic compounds, which account for up to 95% of the identifiable components in the oil, contain a hydroxyl (-OH) group attached to an aromatic ring. During hydrogenation, this -OH group can be partially or fully hydrogenated, converting phenols into cyclohexanols or other hydrogenated products. This process leads to a measurable decrease in phenolic concentration without altering the overall alcohol content of the mixture. Consequently, the reduction of molecules such as phenol, catechol, and p-cresol results in a more stable and energy-dense structure, independent of FTIR analysis. Since the conversion of an aromatic ring into a fully hydrogenated one does not alter the number of hydroxyl groups, the FTIR peak corresponding to these functional groups remains unchanged.

These findings reinforce the preferential reactivity of phenolics in ECH, as observed in our previous work¹¹⁹. The selective hydrogenation of phenols over other oxygenated species has important implications for bio-oil upgrading, as it directly influences the stability and energy density of the resulting product.

Steric hindrance effects can be observed when comparing structurally similar compounds, such as 2,5-dimethyl-phenol and 2,6-dimethyl-phenol (Table 6-1). Shifting a methyl group from the para to the ortho position reduced the concentration change from 46.03% to 36.59%, suggesting that increased steric bulk near the reactive site hinders electrochemical hydrogenation. A similar trend is seen in the ECH of PW_{TBAHFP} (Table 6-2), where phenol exhibited the highest

conversion (46.75%) compared to more branched phenolic compounds, such as p-cresol (45.95%), 2-methyl-phenol (37.26%), and 2,4-dimethyl-phenol (17.69%). These results indicate that while methyl substitution does not completely prevent hydrogenation, increased steric hindrance can significantly reduce reactivity.

Table 6-2 – Key composition of pinewood slow pyrolysis bio-oil oily phase with the addition of 1.5 g of TBAHFP before and after ECH.

Compound	Before ECH (relative area)	After ECH (relative area)	Reduction in relative area	Reduction in concentration
2-Methoxy-5-methylphenol	0.0044	0.0000	0.0044	100.00%
Methanesulfonyl fluoride	0.0045	0.0013	0.0032	71.11%
Amylene hydrate	0.0583	0.0210	0.0373	63.98%
3-ethyl-Phenol	0.0018	0.0009	0.0009	50.00%
Phenol	0.0385	0.0205	0.0180	46.75%
p-Cresol	0.0766	0.0414	0.0352	45.95%
2-methyl-Phenol	0.0475	0.0298	0.0177	37.26%
Benzoic acid	0.0027	0.0020	0.0007	25.93%
2,4-dimethyl-Phenol	0.0424	0.0349	0.0075	17.69%
Phosphoric acid, trimethyl ester	0.0263	0.0910	-0.0647	-246.01%
2-methoxy-Phenol	(1.000)	(1.000)	-	-

The effect of molecular complexity is evident when comparing phenol and catechol in Table 6-1. Catechol, which has a second -OH group in the ortho position, showed a lower conversion (13.14%) than phenol (31.53%), likely due to stronger intermolecular interactions and additional electronic effects that make hydrogenation more challenging. The same trend was observed for WS_{NaCl} (Table 6-3), where phenol was converted at a higher rate (16.06%) than catechol (13.18%). These results further confirm that the number and position of functional

groups influence the efficiency of ECH, with simpler phenolic structures undergoing hydrogenation more readily.

In addition to oxygenated species, hydrocarbons were detected in the oily phase of bio-oil, which are typically not found in high concentrations in the aqueous phase ¹¹⁹. For example, 2-methylnaphthalene and naphthalene were identified in PW_{NaCl}, while 3,7-dimethyl-decane was present in both WS_{NaCl} and WS_{TBAHFP}. The presence of these hydrocarbons highlights the chemical diversity of the oily phase and its potential as a precursor for the production of valuable chemicals.

Table 6-3 – Key composition of wheat straw slow pyrolysis bio-oil oily phase with the addition of 1.5 g of NaCl before and after ECH.

Compound	Before ECH (relative area)	After ECH (relative area)	Reduction in relative area	Reduction in concentration
3-methyl-1,2-Benzenediol	0.1020	0.000	0.102	100.00%
2-ethyl-Phenol	0.0601	0.032	0.028	46.76%
3,7-dimethyl-Decane	0.0431	0.033	0.010	23.43%
2,5-dimethyl-Phenol	0.1385	0.107	0.031	22.74%
3-ethyl-Phenol	0.2178	0.173	0.044	20.57%
2-methyl-Phenol	0.2162	0.176	0.040	18.59%
2,6-dimethyl-Phenol	0.0453	0.038	0.007	16.11%
Phenol	0.3145	0.264	0.050	16.06%
Catechol	0.0979	0.085	0.012	13.18%
p-Cresol	0.3448	0.309	0.035	10.38%
2,3-dimethyl-Phenol	0.0362	0.034	0.002	6.08%
Benzofuran	0.0381	0.036	0.002	5.51%
2-methoxy-Phenol	(1.000)	(1.000)	-	-

The observed changes (Table 6-1) in the concentration of methyl propionate (43.64%), 2-methylnaphthalene (42.37%), and cyclopentanone (31.25%) demonstrates the capability of the ECH process to upgrade not only phenolic

compounds but also esters, hydrocarbons, and ketones. These results suggest that while phenolics are the most common species under these conditions, other functional groups can also undergo hydrogenation, broadening the potential applications of ECH in bio-oil upgrading.

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Due to its simpler structure, phenol undergoes electrochemical hydrogenation more readily than benzoic acid.¹¹⁹ When both compounds are present in a mixture, their reduction rates can influence each other. Specifically, at lower concentrations of phenol relative to benzoic acid, phenol facilitates the hydrogenation of benzoic acid. Conversely, when phenol is more concentrated, its own ECH is favoured. This effect is evident in PW_{TBAHFP} (see Table 6-2), where phenol, at a higher concentration, achieved a conversion of 46.75%, compared to 25.93% for benzoic acid. These results further confirm the competitive and cooperative interactions among oxygenated species in bio-oil electrochemical upgrading, reinforcing previous findings that phenols are the most electroactive species in this system.

The addition of TBAHFP led to the formation of side products, such as trimethyl phosphate (TMP) and methanesulfonyl fluoride. These compounds contain functional groups associated with PF₆⁻ and were absent in pure PW and PW_{NaCl}, suggesting that TBAHFP introduced additional reaction pathways. It is important to note that GC-MS analysis was not performed *in situ*; thus, interactions between the salt, electrolyte, and bio-oil components over time may have contributed to the formation of these new species. Additionally, the presence of these side products, relative to the main bio-oil components, may have caused peak overlap, reducing the number of identifiable compounds compared to PW_{NaCl}.

The concentration of trimethyl phosphate increased during the process (signified by the “-” sign in “change in concentration” in Table 6-2), probably due to secondary reactions with methanol as the traditional synthesis process for TMP is carried out in methanol.¹²⁷ Considering that the TPM could be separated from the mixture, this product holds great economic value, as it can be utilised in the chemical and electrochemical industries, such as in the production of flame retardants^{128,129} and sodium-ion batteries¹³⁰.

Table 6-4 – Key composition of wheat straw slow pyrolysis bio-oil oily phase with the addition of 1.5 g of TBAHFP before and after ECH.

Compound	Before ECH (relative area)	After ECH (relative area)	Reduction in relative area	Reduction in concentration
2,3-dimethyl-2-Cyclopenten-1-one	0.01800	0.0000	0.01800	100.00%
2-methyl-2-Cyclopenten-1-one	0.01731	0.0000	0.01731	100.00%
2-ethyl-Phenol	0.01651	0.0000	0.01651	100.00%
2,5-dimethyl-Phenol	0.05025	0.0121	0.03815	75.92%
Sulphuric acid dibutyl ester	0.42118	0.1770	0.24418	57.98%
3,7-dimethyl-Decane	0.06032	0.0378	0.02252	37.33%
3,5-dimethyl-Phenol	0.15153	0.1018	0.04973	32.82%
2,6-dimethyl-Phenol	0.02355	0.0184	0.00515	21.87%
p-Cresol	0.39409	0.3385	0.05559	14.11%
Phenol	0.31048	0.2947	0.01578	5.08%
2-methyl-Phenol	0.19801	0.2115	-0.01349	-6.81%
2-ethyl-4-methyl-Phenol	0.00002	0.0074	-0.00738	-100.00%
Methyl propionate	0.00002	0.0071	-0.00708	-100.00%
Phosphoric acid, trimethyl ester	0.00007	0.5485	-0.54843	-100.00%
2-methoxy- Phenol	(1.000)	(1.000)	-	-

The formation of 2-ethyl-4-methyl-phenol and the increase in the concentration of 2-methyl-phenol in 6.81% (Table 6-4) can be directly linked with the methylation of 2-ethyl-phenol and phenol as TMP can act as a catalyst for the methylation of lignin components and could have facilitated this reaction.¹³¹ This

effect can also interfere with the reduction of 2-methyl-phenol, where instead of being hydrogenated into 2-methyl-cyclohexanol, it could form 2,4-dimethyl-phenol (Table 6-3).

6.3.2 FTIR analysis

FTIR spectroscopy was employed to characterise the chemical transformations occurring during the electrochemical hydrogenation of the oily phase. The spectra (Figure 6-2) provided critical insights into functional group modifications, complementing the GC-MS findings and revealing trends in the broader chemical composition.

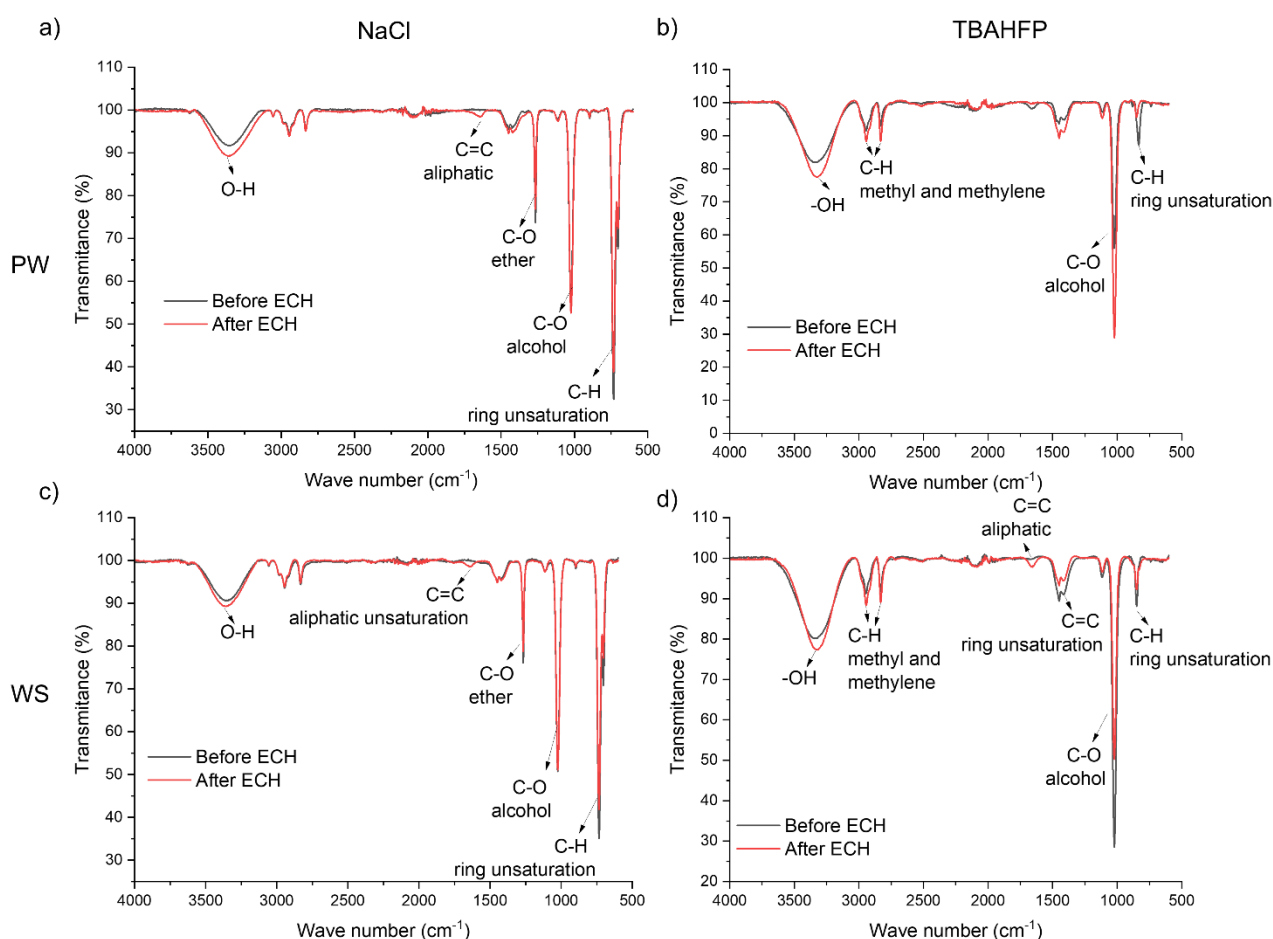


Figure 6-2 - FTIR spectra of (a) PW_{NaCl}, (b) PW_{TBAHFP}, (c) WS_{NaCl} and (d) WS_{TBAHFP} and the main identified organic functions, before (in black) and after (in red) the electrochemical process.

The most prominent observation in Figure 6-2 was the increase in the peak intensity within the 3200–3400 cm^{-1} region, associated with O-H stretching vibrations in alcohols and phenols, which was present in all four samples. This indicates the hydrogenation of ketones, ethers, esters or carboxylic acids. The reduction of C-O alcohol groups was also observed in both mixtures with TBAHFP, where the peak at 1050 cm^{-1} decreased, likely due to dehydration reactions. Both pyrolysis oil mixtures with NaCl presented a slight reduction in the peak related to C-O vibrations in ethers (1220 cm^{-1}). The hydrogenation of ethers could form -OH, contributing to the increase in alcohol content. The reduction in C:O ratio is a highly desired outcome of this process.

Another key finding was the reduction of peaks corresponding to C-H vibrations in aromatic rings at 750 cm^{-1} and 690 cm^{-1} . The observed decrease indicates that aromatic structures may have undergone partial or complete hydrogenation into cycloalkanes or other saturated products. This transformation enhances the stability and energy density of the bio-oil, providing supporting evidence that the ECH process promotes aromatic hydrogenation, as identified in the GC-MS data.

The methylation process promoted by TMP can be verified by the increase in the peaks at 2960 and 2850 cm^{-1} which are related to methyl and methylene. These are present in the mixtures with NaCl, but only underwent a significant change with the addition of TBAHFP. Another interesting finding is the peak at 1645 cm^{-1} which was non-existent in PW_{NaCl} , WS_{NaCl} and $\text{WS}_{\text{TBAHFP}}$ before the ECH process and appeared after the reaction, signifying that some aromatic compounds could have turned into acyclic carbon chains.

Table 6-5 shows all the observed changes in concentration for each functional group, assed by either GC-MS or FTIR. Notably, the FTIR peak corresponding to the C–O bond in alcohols remained unchanged in mixtures containing NaCl. In contrast, it increased in $\text{WS}_{\text{TBAHFP}}$ and decreased in $\text{PW}_{\text{TBAHFP}}$, underscoring the complexity of the electrochemical hydrogenation process.

Table 6-5 – Every observed change in the concentration of organic functional groups after the ECH of all four samples. A “-” sign signifies that the functional group was not present in the respective bio-oil.

Content	WS _{NaCl}	PW _{NaCl}	WS _{TBAHFP}	PW _{TBAHFP}
Phenolic content	Decreased	Decreased	Decreased	Decreased
Ketones	-	Decreased	Decreased	-
Ethers	-	Decreased	Decreased	-
Esters	Decreased	Decreased	-	-
Carboxylic Acids	-	-	Increased	Increased
Hydrogen Content (Ring)	Increased	Increased	Increased	Increased
Oxygen content	Decreased	Decreased	Decreased	Decreased
Alcohol (C-O)	No change	No change	Decreased	Increased
Hydroxyls (-OH)	Increased	Increased	Increased	Increased
Aliphatic C=C content	Increased	Increased	Increased	Decreased
Hydrocarbons	-	Decreased	Decreased	-
Methylation	No change	No Change	Occurred	Occurred

6.3.3 Catalyst degradation

Scanning electron microscopy was utilised to visualise the effect of both additives (NaCl and TBAHFP) on the corrosion of the catalytic cathode. Figure 6-3 shows that, even in pristine conditions, that is, before any usage, the surface of the cathode already presented some black spots. Elemental mapping (by energy-dispersive X-ray spectroscopy) revealed that black spots correspond to sites where the coverage of deposited metals (platinum and ruthenium) was low, and the bare surface of the cathode (carbon) was visible. Our previous results¹¹⁹ demonstrated that corrosion was not noticeable when the catholyte was sulfuric acid with model compounds, a more acidic media. Methanol is a mild organic solvent and should be less reactive than sulfuric acid, therefore, the observed corrosion is likely linked to the added salt.

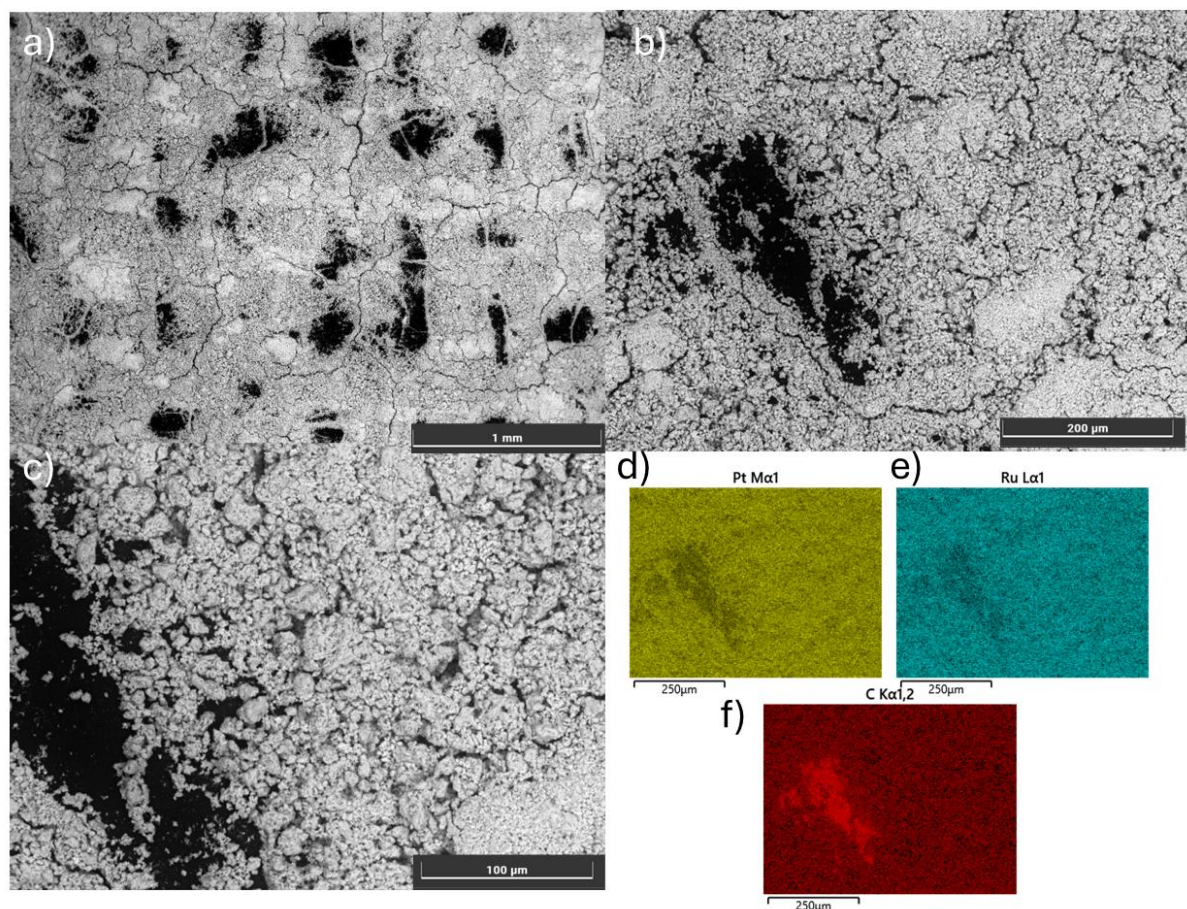


Figure 6-3 - Scanning Electron Microscopy of the cathode before the ECH process at three different magnifications (a-c) and elemental mapping of (d) platinum (in yellow), (e) ruthenium (in teal) and (f) carbon (in red).

After four ECH cycles (two with each oil) with NaCl as the additive, the catalyst surface exhibited extensive degradation. The SEM images (Figure 6-4) revealed an increase in the blackened regions, and elemental mapping confirmed a significant reduction in the platinum signal, accompanied by an increase in chlorine deposition (in pink). This suggests that chloride ions penetrated the PtRu surface, causing degradation. In elemental mapping, the peaks for Cl and Ru are quite similar (at 2.622 keV and 2.559 keV, respectively)^{132,133}, suggesting that the high concentration of chlorine may have caused the ruthenium peak to overlap and not register in the scan. However, since there is still platinum coverage on the surface, it is likely that ruthenium is present and hasn't been entirely degraded. Such degradation compromises the catalytic efficiency and

necessitates frequent electrode replacement, raising concerns about the long-term economic viability of NaCl as an additive.

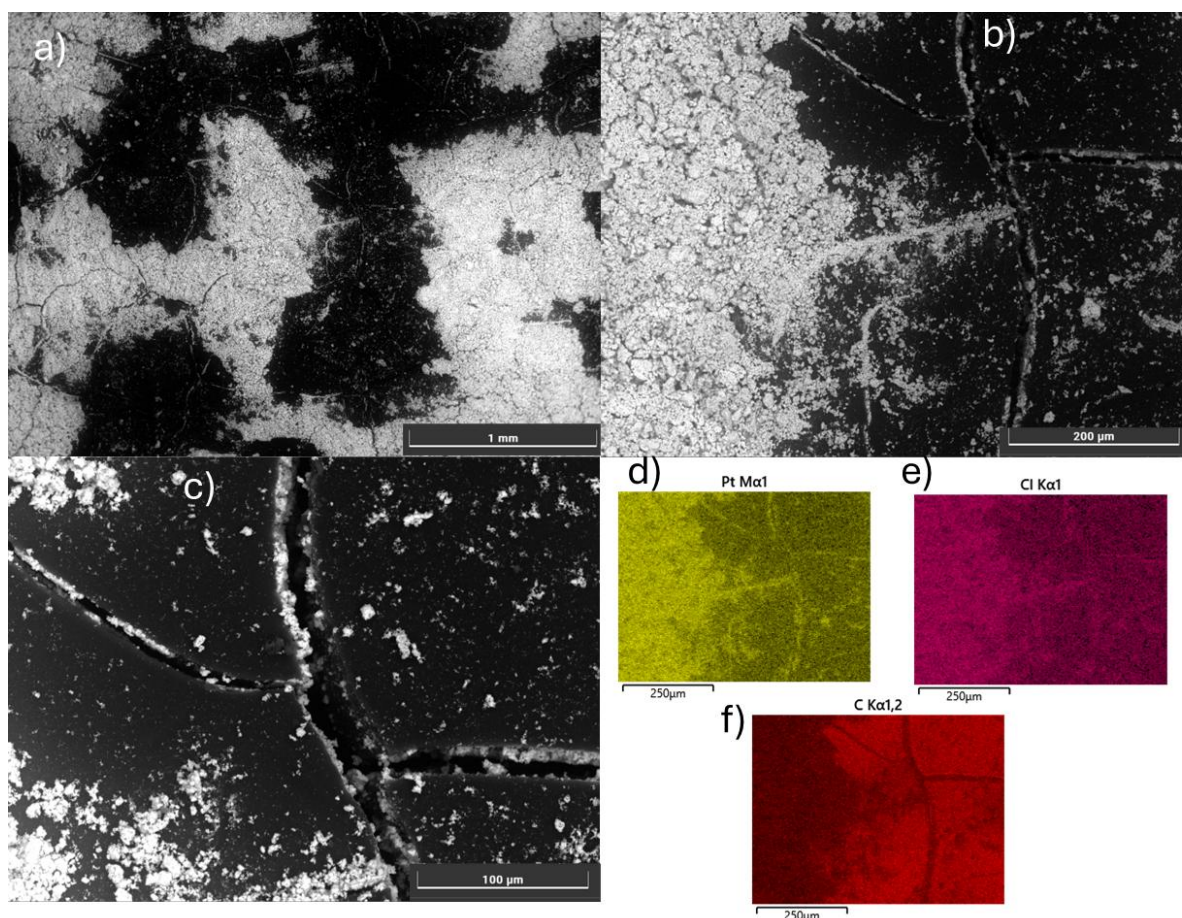


Figure 6-4 - Scanning Electron Microscopy of the cathode after four reruns (twice with PW_{NaCl} and twice with WS_{NaCl}) of the ECH process at three different magnifications (a-c) and elemental mapping of (d) platinum (in yellow), (e) chlorine (in pink) and (f) carbon (in red).

TBAHFP, despite its theoretically inert nature, also caused unexpected surface damage after four cycles. Figure 6-5 shows cracks and reduced platinum and ruthenium coverage, where only a few spots maintained PtRu deposition. It is worth noting that the cathode is built in layers, and SEM is representative of only the first layer. The cracks show that beneath the surface there is still metal coverage. However, the ECH process is a surface reaction dependent on direct contact of the metal with the unsaturated molecule, therefore, this degradation would result in the need for substitution of the material.

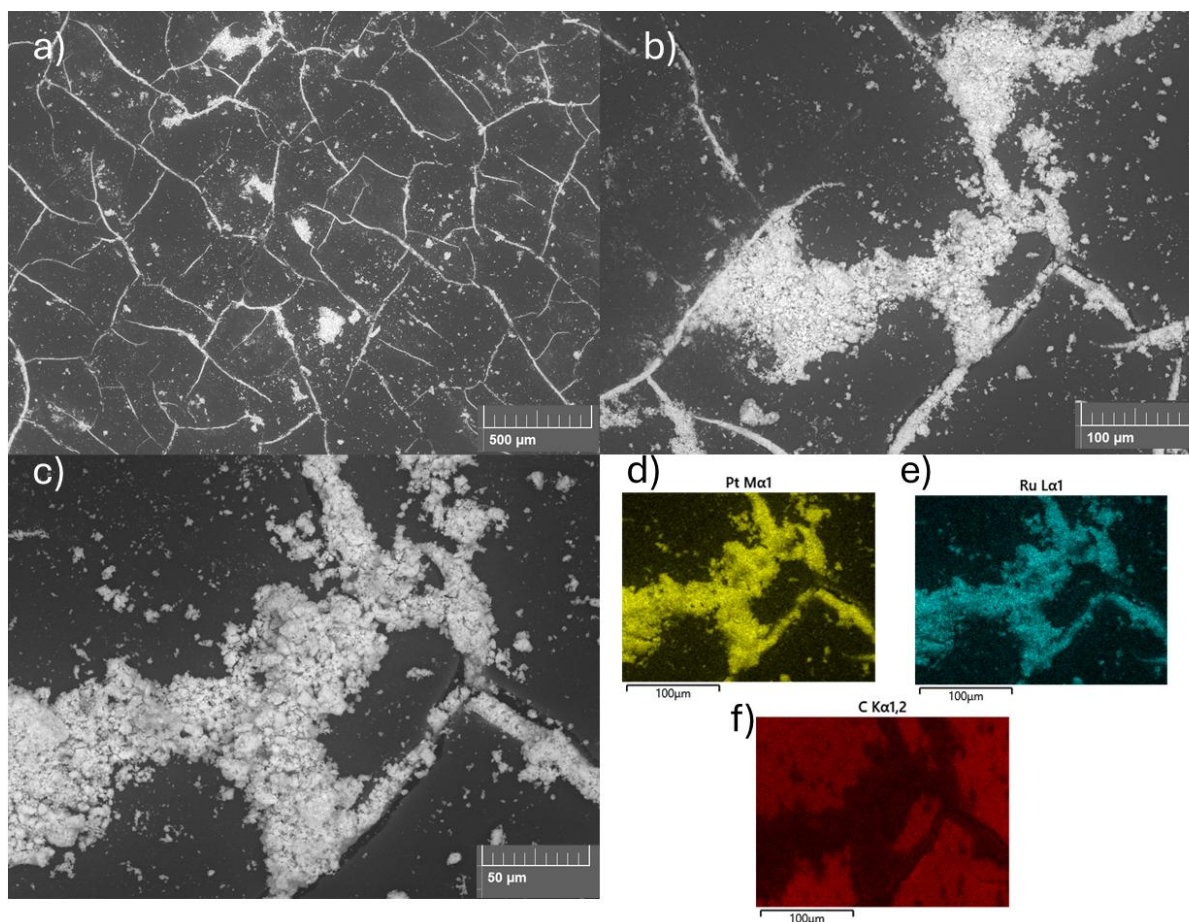


Figure 6-5 - Scanning Electron Microscopy of the cathode after four reruns (twice with $\text{PW}_{\text{TBAHFP}}$ and twice with $\text{WS}_{\text{TBAHFP}}$) of the ECH process at three different magnifications (a-c) and elemental mapping of (d) platinum (in yellow), (e) ruthenium (in teal) and (f) carbon (in red).

The degradation of the cathode found when utilising TBAHFP was surprisingly greater than when NaCl was present, which may result from secondary reactions involving PF_6^- ions. These reactions, potentially catalysed by methanol or bio-oil compounds, might weaken the metal surface or introduce reactive intermediates that accelerate wear.

However, the overall performance of $\text{PW}_{\text{TBAHFP}}$ and $\text{WS}_{\text{TBAHFP}}$ was better than their counterparts, increasing alcohol concentration and diminishing double bonds, leading to a more stable and energy-intensive product. Hence, the utilisation of each additive has drawbacks, and the choice should be tailored to the desired outcome.

6.4 Conclusion

This study explored the electrochemical hydrogenation of the oily phase of wheat straw and pinewood pyrolysis bio-oils using a PtRu/ACC catalyst and methanol-based catholytes with NaCl and TBAHFP as conductive additives. The findings provide critical insights into optimising ECH processes to address the solubility and conductivity challenges associated with bio-oil upgrading.

The results demonstrated that phenolic compounds, which dominate the composition of the oily phase, are selectively hydrogenated during ECH, producing more stable and energy-dense products. Methanol proved to be an effective catholyte for dissolving the hydrophobic oily phase, enabling the direct electrochemical conversion of its compounds. However, its low conductivity required the addition of conductive salts, highlighting a fundamental trade-off between enhanced conductivity and electrode stability. NaCl substantially improved conductivity and reaction efficiency, but its corrosive nature led to severe degradation of the PtRu/ACC electrode, as evidenced by SEM analysis. Similarly, TBAHFP caused significant surface damage to the electrode, potentially due to interactions between PF_6^- ions and the electrode or bio-oil compounds. Additionally, TBAHFP introduced secondary reactions, such as the formation of TMP, which influenced product composition and raised questions about reaction selectivity.

These findings have significant implications for the processing and conversion of bio-oils. First, the demonstrated effectiveness of ECH for transforming the oily phase addresses a critical bottleneck in bio-oil upgrading by enabling the valorisation of its more challenging, hydrophobic fraction. Second, the study underscores the need for a more nuanced approach to additive selection, balancing conductivity enhancement, electrode durability, and reaction selectivity. The formation of TMP during TBAHFP-mediated ECH suggests that secondary products could add economic value or pose challenges, depending on the desired application.

From a broader perspective, the insights gained in this study advance the feasibility of ECH as a green and scalable approach for bio-oil upgrading. By

operating under mild conditions, this process aligns with the principles of green chemistry, offering a sustainable alternative to high-pressure catalytic hydrogenation methods. However, the observed trade-offs between efficiency and material stability emphasise the importance of developing novel additives and electrode materials tailored for the specific demands of bio-oil conversion.

Future research should focus on designing conductive additives that minimise corrosion and undesired secondary reactions while maintaining high reaction efficiencies. Additionally, exploring alternative electrode materials or protective coatings could enhance durability and reduce costs, further advancing the scalability of this technology. By addressing these challenges, ECH has the potential to transform bio-oil processing, contributing to the development of renewable fuels and chemicals that align with global sustainability goals.

7 General discussion

7.1 Electrochemical Hydrogenation Overview

The electrochemical hydrogenation of simpler systems, such as single model compounds, has been extensively studied (see Chapters 2.3 and 2.4). However, these systems do not represent real bio-oils, characterised by their complex nature and consisting of hundreds of compounds. This complexity must not be overlooked, as understanding the interactions between multiple compounds during ECH is crucial for translating findings to the more intricate chemical matrices of real bio-oils.

As demonstrated in chapters 5 and 6, bio-oils can be separated into aqueous and non-aqueous (oily) phases. The aqueous phase represents a complex system, yet the hydrogenation process can be conducted using the same electrolytes as those used for model compounds. However, a key knowledge gap for both the aqueous and oily phases remained in understanding how the presence of multiple compounds influences the ECH process, including potential side reactions and competition for adsorption sites.

The oily phase presents additional challenges due to its poor solubility in the water-based electrolytes commonly used and, indeed, required due to conductivity, in electrochemistry. Addressing this requires either increasing the conductivity of non-polar solvents or employing alternative electrolytes to date. Research on both phases of bio-oils remains limited, with most studies focusing on the ECH of single model compounds.

7.2 Electrochemical Hydrogenation of Benzoic Acid

Benzoic acid and its derivatives are abundant in pyrolysis oils, but their deoxygenation is challenging. Due to this difficulty and the lack of studies on this specific molecule, it was chosen as the focus of the model compound studies in this thesis (see Chapter 2.6).

Previous studies^{34,111,134,135} reported 100% selectivity from benzoic acid towards CCA for the ECH of benzoic acid alone in the electrolyte; the same results were found in paper 2 (chapter 3). Furthermore, when utilising a CEM reactor coupled

with hydrogen gas, Fukazawa et al.³⁴ achieved 99% FE for this reaction and 100% selectivity. However, this was accomplished at a very low current density of 1.5 mA cm^{-2} and relied upon an outside source of H_2 . Low current densities restrict the flow of electrons into the system, thereby limiting the number of molecules that can be processed per unit of time. The trade-off between FE and conversion is further explored in Chapter 3.3.1. This also poses a significant challenge for scaling up the process to industrial applications, where high throughput is essential for economic viability, which will be further discussed in Chapter 7.6. Additionally, reliance on hydrogen gas poses further issues due to its high cost, the hazards associated with storage, and the limitations it imposes on the sustainability of the process. The advantages of ECH are detailed in Chapter 2.3.1.

Kong et al.¹³⁴ demonstrated how an ECH cell with benzoic acid could achieve similar results, whilst producing H_2 in situ. At a current density of 13.3 mA cm^{-2} , the conversion was 100%, and a Faradaic Efficiency of 10% was achieved, utilising a Pt/CC catalytic cathode. Later, this was improved upon by Du et al.¹¹¹, by adding ruthenium to the cathode (PtRu/CC), which increased the FE to 60% at the cost of a reduction in conversion (from 100 to 90%) at the same current density. Although not discussed within the paper, increasing the duration of the experiment would lead to higher conversion, at the cost of a lower FE. Therefore, to maximise both aspects of ECH, this was deemed the optimal point of the reaction.

An alternative was proposed by Cao et al.¹³⁵, who utilised a Ru/RuO₂ catalyst, resulting in a 100% conversion and 65% FE at a current density of 66.7 mA cm^{-2} . Herein, we demonstrated that a PtRu/ACC catalyst was employed for the same process, and the optimal results were achieved at a current density of 25.0 mA cm^{-2} , where the conversion was 77.4% and FE was 56%.

Direct comparisons between studies are challenging due to variations in cell geometry. The reactor used in this study had a volume of 90 mL, larger than those used by Kong et al. (20 mL), Du et al. (25 mL), and Cao et al. (20 mL). Smaller reactors often yield unscalable results, particularly regarding conversion and FE.

For example, when comparing two studies with the same benzoic acid concentration (10 mM) and similar cathodes (Du et al. and Chapter 3), the mass of the model compound introduced into the system differs significantly, 30.5 mg versus 109.9 mg, respectively. In the latter case, assuming the same FE, either the applied current or the experiment duration must be 3.6 times higher to ensure enough electrons are provided for the full conversion of the compounds. In practice, both adjustments are likely to reduce the conversion, FE, or both, as discussed in Chapter 3.3.1.

The reason for smaller cells generally exhibiting enhanced FE is due to their lower ohmic resistance, due to the smaller distance between electrodes, which requires lower overpotentials. However, scaling up to larger H-type cells necessitates greater quantities of reactants, higher currents, and increased overpotentials, all of which can adversely affect efficiency and selectivity, as reported in Chapter 3.3.1. Therefore, the focus of future works should be on scaling up this process to better accommodate the needs of the industry. The scaling-up process will be discussed in Chapter 7.6.

Experiments at this scale are often designed to achieve maximum conversion, however, in an industrial setting, such a goal may not be possible. Common industrial strategies, such as recycling unconverted products back into the reactor, can be implemented to increase overall conversion. Consequently, reaction optimisation for industrial applications can prioritise other factors, such as efficiency, selectivity, and cost-effectiveness.

7.3 Electrochemical Hydrogenation of Model Compounds Mixtures

The ECH of model compound mixtures revealed both synergistic and anti-synergistic effects. The selected compounds - benzoic acid, phenol, and guaiacol - are representative of key species in bio-oils. As demonstrated in Chapter 3.3.2, the behaviours observed in mixtures differed significantly from those of individual compounds. These interactions remain largely underreported in the literature, where co-hydrogenation is yet to be thoroughly investigated.

A trade-off between the conversion and Faradaic efficiency (Figure 3-2) was identified, where an increase in the initial concentration led to a decrease in the conversion but an increase in FE. For instance, adding 20 mM of phenol to a solution already containing 20 mM of benzoic acid increases the total initial concentration of molecules requiring conversion to 40 mM. Theoretically, this higher concentration should reduce the overall conversion while enhancing the FE. However, interactions between different molecules do not always follow this trend equally.

The Langmuir-Hinshelwood mechanism (Figure 5-3) dictates that molecules must first adsorb onto the cathode surface before undergoing electrochemical reduction. When multiple species are present, they compete for adsorption sites, reducing overall reaction efficiency. Consequently, anti-synergistic effects may lower the effectiveness of the ECH process. This could necessitate longer reaction times to maintain conversion, potentially reducing FE. Our results indicate that the ECH of phenol is favoured over the other compounds, followed by guaiacol and, lastly, benzoic acid (Chapter 3.3.2). If the reaction is stopped prematurely, some compounds may remain largely unconverted while others are fully hydrogenated. Therefore, careful process optimisation is essential to ensure all species reach adequate conversion when upgrading multi-component mixtures.

However, additional complications arise when the molecules interact to further complicate the cell FE response of the system. For example, the combination of phenol and benzoic acid, shown in Figure 4-1, not only increased the conversion and FE but also promoted a higher degree of hydrogenation. This resulted in transformations such as the dehydration of cyclohexane carboxylic acid into cyclohexanemethanol and cyclohexanol into cyclohexane. A similar effect was observed when coupling phenol with benzaldehyde^{117,118} and furfural¹¹⁶, where the presence of phenol led to better ECH performance, both in terms of conversion and selectivity. Furthermore, adding phenol to guaiacol also influenced the composition of the products, leading to the formation of cyclohexane. It is important to note that only a few studies^{85,136} have reported the

formation of cyclohexane for the ECH of either phenol or guaiacol. Typically, the predominant products from these processes are cyclohexanol and cyclohexanone, though guaiacol is also commonly reduced to 2-methoxycyclohexanol^[31,75,84,88,91,137–139]. In this study, the formation of cyclohexane was only observed during co-hydrogenation (see Figure 3-5).

These findings demonstrate that co-hydrogenation not only enhances the stability and energy density of the compounds by saturating double bonds but also facilitates the removal of oxygen. The deoxygenation was not observed during the ECH of single compounds. This is crucial, as the presence of oxygen increases the corrosivity and diminishes the utility of bio-oil as a valuable product.

To facilitate the understanding of why these changes in the co-hydrogenation of model compounds occurred, DfT calculations (Figure 4-5) were conducted. These demonstrated that the addition of phenol to benzoic acid forms a hydrogen-bonded complex between the alcohol and carboxylic acid groups, increasing the electronegativity of the carboxylic acid. This negative dipole (δ^-) pulls the electronic cloud from the aromatic ring, making it positively charged (δ^+), which increases the adsorption energy of benzoic acid into PtRu/ACC, an electronegative surface. This enhanced adsorption facilitates hydrogenation via the Langmuir-Hinshelwood mechanism.

Furthermore, NEB calculations (Figure 4-6, Table 4-2) revealed that, for the co-hydrogenation of phenol and benzoic acid, the energy barriers for each step of the hydrogenation process were lower. This reduction in activation energy accelerates the reaction, improving overall efficiency. Consequently, less energy is required to drive hydrogenation, which is critical for scaling up the process and improving its economic feasibility. These findings not only shed light on the dynamics of molecular competition and cooperation but also offer key insights for tackling the chemical complexity of real bio-oil systems. For example, continuously adding phenol into the system could prove desirable, if the goal is to deoxygenate the mixture.

7.4 Electrochemical Hydrogenation of Real Bio-oil

The upgrading of bio-oil via electrochemical hydrogenation presents unique challenges due to its complex composition. Unlike model compound studies, real bio-oil contains a diverse mixture of organic species, whose interactions can influence reactivity and selectivity during ECH. Understanding these transformations is essential for optimising bio-oil properties, such as stability, energy density, and compatibility with existing fuel infrastructure.

However, the analysis of real bio-oil is complicated by the presence of numerous compounds at varying concentrations, many of which may be undetectable by conventional techniques such as GC-MS. To overcome these limitations, FTIR was employed alongside GC-MS to provide a more comprehensive assessment of chemical changes, particularly for species that are difficult to resolve due to volatility constraints or peak overlap.

7.4.1 Water-soluble Bio-oil

The electrochemical reduction of the aqueous phase of bio-oil, conducted under the same conditions as model compound experiments, effectively reduced organic compounds. Phenolic species were particularly susceptible to hydrogenation, leading to an increase in alcohol concentrations. This transformation enhanced bio-oil stability by reducing oxygenated species, improving its energy density, and making it a more viable fuel source.

Analysis via FTIR and GC-MS confirmed these chemical transformations, demonstrating that ECH selectively saturates aromatic rings and increases the hydrogen content of the bio-oil. The hydrogenation behaviour observed mirrored trends from model compound mixtures, where phenolic species exhibited a higher tendency for reduction, while carboxylic acids displayed resistance to hydrogenation. This presents a challenge, as eliminating carboxyl groups is a key objective in bio-oil upgrading. Although benzoic acid underwent deoxygenation in controlled systems, the presence of multiple reactive molecules in bio-oil altered these dynamics. This shift may result from side reactions occurring during ECH

or an insufficient concentration of individual components to form the hydrogen bonds observed in Chapter 4.2.6.

However, as demonstrated in Figure 5-5, there is a strong correlation between the tendency for hydrogenation of species in model compounds and real bio-oil experiments. To be specific, simpler structures, such as phenol are more prone to reduction than more complex structures, like guaiacol. Therefore, model compound studies can be utilised as a starting point to predict the behaviour of bio-oil components with a similar structure.

Similar observations were made by Deng et al.⁸⁶ who reported both synergistic and non-synergistic interactions during the ECH of rice husk water-soluble bio-oil in an undivided cell. These interactions were consistent with the behaviour observed in model compound mixtures (Chapters 3 and 4), where the presence of polar organic compounds enhanced the hydrogenation process and was hypothesised for the real bio-oil experiments. Furthermore, prolonged processing time led to a decrease in the concentration of aromatic compounds, as unsaturated rings were hydrogenated and converted into saturated ones, which aligned with our findings. Similar results were reported by Li et al.⁹⁷ and Zhang et al.⁷⁴, where the H:C ratio increased, and both O:C ratios and unsaturated bonds decreased, further confirming the effectiveness of ECH in improving bio-oil quality. However, it is important to note that the number of published studies on this topic is limited, making comparisons challenging.

7.4.2 Water-insoluble Bio-oil

Solubility, conductivity and chemical compatibility of pyrolysis bio-oil oily phase pose a significant challenge to its mild electrochemical hydrogenation. Pelosin et al.¹²² reported on the ECH of the oily phase utilising high pressure (up to 100 bar) and a temperature of 150 and 200 °C. GC-MS results show an increase in H:C ratio and FTIR revealed a decrease in the concentration of ketones and oxygen-containing species. This solution, however, does not comply with green chemistry principles and relies on high energy consumption. Therefore, the research gap is how to achieve the conversion of the components in the oily phase of the bio-oil utilising a mild process.

To address solubility issues while maintaining a sustainable approach, methanol was chosen as the electrolyte for this process, with a temperature set at 55°C, consistent with all prior experiments. However, due to methanol's low electroconductivity, either NaCl or TBAHFP were added to increase the system's conductivity. The objective of this experiment was to evaluate whether the use of additives would be sufficient to facilitate ion migration and make the ECH process viable. Furthermore, the impact of these additives on the cathode material's durability and overall process efficiency was assessed, offering insights into the trade-offs between performance and sustainability.

Pine Wood and Wheat Straw bio-oils with NaCl and TBAHFP will be referred to as PW_{NaCl} , PW_{TBAHFP} , WS_{NaCl} and WS_{TBAHFP} respectively. Similar trends to those observed in the aqueous phase were identified, such as the high tendency of phenolic compounds to undergo hydrogenation and the low activity of carboxylic acids for the same process. In agreement with our findings, Deng et al. reported that during the ECH of rice husk bio-oil oily phase, the aromatic content was reduced significantly.⁸⁶

Of particular interest was the water-insoluble phase of PW, as both benzoic acid and phenol were detectable, providing an opportunity to directly test the hypothesised interactions between these compounds during ECH (see chapter 3.3.2). Although other external factors could interfere with both compounds, the results were as expected: phenol's conversion was higher than benzoic acid's.

TBAHFP proved less effective than NaCl in increasing methanol's conductivity, likely due to its larger ionic size and reduced dissociation efficiency. Consequently, higher overpotentials were required to achieve equivalent currents in TBAHFP-containing mixtures. However, these systems exhibited greater overall compositional changes, possibly due to side reactions involving the salt or peak overlaps that obscured certain species.

In addition to absolute conversion, the addition also resulted in changes to the compounds produced in ECH upgrading. GC-MS analysis of PW_{TBAHFP} and WS_{TBAHFP} also revealed that trimethyl phosphate (TMP) was a major product,

which is related to PF_6^- and did not appear in pure PW or PW_{NaCl} . TMP was linked to several side reactions, such as methylation.

Similarly, FTIR analysis showed an increase in the $3200\text{--}3400\text{ cm}^{-1}$ region, indicating O-H stretching from the hydrogenation of ketones, ethers, esters, or carboxylic acids. In a preliminary study, Silva et al.¹⁴⁰ observed a reduction of these peaks when performing ECH of cork pyrolysis oil, which was attributed to the reduction of furans, such as furfuryl alcohol. Dehydration reactions reduced the C-O alcohol peak at 1050 cm^{-1} in mixtures with TBAHFP. A slight reduction in the C-O ether peak at 1220 cm^{-1} was observed with NaCl, suggesting ether hydrogenation and increased alcohol content, Silva et al.¹⁴⁰ also diverged in this, reporting an increase of that peak. The reduction in C-H vibrations at 750 and 690 cm^{-1} indicates partial or complete hydrogenation of aromatic rings into cycloalkanes, enhancing bio-oil stability and energy density, as supported by GC-MS data. This analysis, when coupled with calorimeter tests and elemental analysis could provide critical data for the industry to check to determine whether the converted bio-oil meets the standards for future chemical and petrochemical applications.

Methylation, facilitated by TMP, was evidenced by the increased intensity of methyl and methylene peaks at 2960 and 2850 cm^{-1} , particularly when TBAHFP was used. Depending on the target application, this outcome could be either advantageous or undesirable. For instance, in fuel applications, branched and linear alkanes exhibit distinct combustion behaviours: branched alkanes react more readily and rapidly during the initial stages but show slower reaction rates at later stages as temperature increases¹⁴¹. This underscores the need for future studies to better understand how different electrolytes and additives influence the ECH process and tailor conditions to optimise the production of specific mixture compositions.

Another outcome that depends on the desired application is the appearance of a 1645 cm^{-1} peak after ECH, which suggests the conversion of aromatic compounds into acyclic carbon chains. In the context of jet fuels, the desired concentration of acyclic alkanes can vary from 1 to 68 wt%, and for cycloalkanes,

the range is 3 to 82 wt%¹⁴². Future research should focus on fine-tuning ECH conditions to achieve targeted compositional profiles for specific end uses.

In summary, the use of methanol as an electrolyte, combined with NaCl or TBAHFP as additives, provides a sustainable approach to the ECH of bio-oil's oily phase. While challenges such as conductivity limitations and side reactions remain, this study demonstrates the potential of ECH to enhance bio-oil quality. Continued exploration of electrolyte systems and process conditions is essential to optimise bio-oil upgrading for diverse industrial applications.

7.5 Cathode Stability

Scanning electron microscopy was utilised to assess the stability of the cathode material under different operating conditions. The cathode exhibited resistance to corrosion in acidic media (1.0M sulfuric acid) with model compounds and aqueous bio-oil. SEM revealed little to no visible change in the cathode's surface, while elemental mapping showed ample coverage of both platinum and ruthenium maintaining the electrode's catalytic integrity.

In contrast, significant degradation was observed during experiments with the oily phase of bio-oil, particularly due to the presence of salts. The damage was more pronounced with TBAHFP than with NaCl. SEM analysis revealed reduced PtRu coverage, and the appearance of regions of exposed carbon substrate, indicating a deterioration of the electrode's active surface. Elemental mapping highlighted chlorine deposition with NaCl and potential secondary effects of PF_6^- ions with TBAHFP, both of which contribute to accelerated wear.

The electrochemical hydrogenation process relies heavily on surface reactions, necessitating the adsorption of organic molecules onto the deposited PtRu layer. Any reduction in active metal coverage directly compromises the cathode's catalytic performance, significantly lowering the efficiency of the process. Given that the cathode is the costliest component of the electrochemical cell, frequent replacements due to wear would impose a substantial economic burden, particularly in pilot-scale and industrial applications.

To address this challenge, developing strategies to enhance cathode durability is essential for the scalability of the electrochemical hydrogenation of bio-oils. While protective coatings are often employed in corrosive environments, their use in this context would inhibit molecular adsorption onto the electrode surface, thereby halting the reaction. Consequently, research into alternative materials or innovative electrode designs that balance durability with catalytic performance will be critical for the commercial viability of this process.

7.6 Scale-up Considerations

Scaling up electrochemical hydrogenation requires reactor designs that balance efficiency, scalability, and process control. While H-type cells provide valuable mechanistic insights, their batch operation and mass transfer limitations hinder industrial application. Continuous systems, such as continuous stirred tank reactors (CSTRs) and plug flow reactors (PFRs), offer improved throughput and reaction control, with flow cell electrolyzers further enhancing mass and electron transfer. The following sections evaluate these reactor configurations, setting the stage for the subsequent techno-economic assessment of ECH for bio-oil upgrading.

7.6.1 H-type Cells

Although H-type cells are useful and often used for fundamental and experimental research, such as accurate measurement of potential, kinetic studies and the lack of temperature and concentration gradients, they present some drawbacks. H-type cells operate in batch mode and are limited in both mass and electron transfer rates due to their geometry. Distance from the electrodes is another important design configuration, where greater distances mean higher ohmic resistance, which should be minimised to improve electron flow.^{143,144}

These limitations make them impractical for industrial applications, where high-volume, efficient, and continuous production is necessary. Industrial-scale systems require a fundamental rethinking of the process to accommodate higher throughput and continuous operation.

7.6.2 Continuous Stirred Tank Reactor (CSTR)

The utilisation of a continuous stirred tank reactor could alleviate the need for a faster and higher-output system. CSTRs allow a constant flow of reactants and products. This leads to higher production rates and better resource utilisation compared to batch reactors, which require periodic loading, reaction, and unloading.^{145,146}

The constant addition of reactants allows this type of reactor to operate at higher concentrations, improving the reaction rate. This enables better optimisation of reaction conditions and product yield. They are also often more scalable than batch reactors, as they can easily adjust the reactor size and flow rates.^{145,146}

Due to the undivided nature of the reactor, issues similar to those in single-cell batch reactors may occur. That is, without a divider, reactants can simultaneously undergo reduction and oxidation, which leads to undesired reactions.^{143,144}

7.6.3 Plug Flow Reactor (PFR)

PFRs are continuous-flow systems in which reactants are introduced at one end and flow through the reactor, undergoing reaction along the way, before exiting at the other end. This design offers several advantages for ECH processes, including enhanced mass and electron transfer, better control of reaction conditions, and the ability to process large volumes of bio-oil. Moreover, the geometry of a PFR can be optimised to maximise the contact between the bio-oil, electrolyte, and electrode surfaces, ensuring efficient utilisation of the active catalytic material.^{143,144,147}

In a PFR, the fluid flow can be limited to move through a catalyst bed or to flow by the catalyst, the latter design is called a Flow Cell Reactor (FCR). This reduces the distance from the electrodes and minimises the ohmic resistance. Flow cell electrolyzers often employ porous electrodes, which increase the effective surface area and promote better diffusion of bio-oil compounds to the active sites.¹⁴⁴

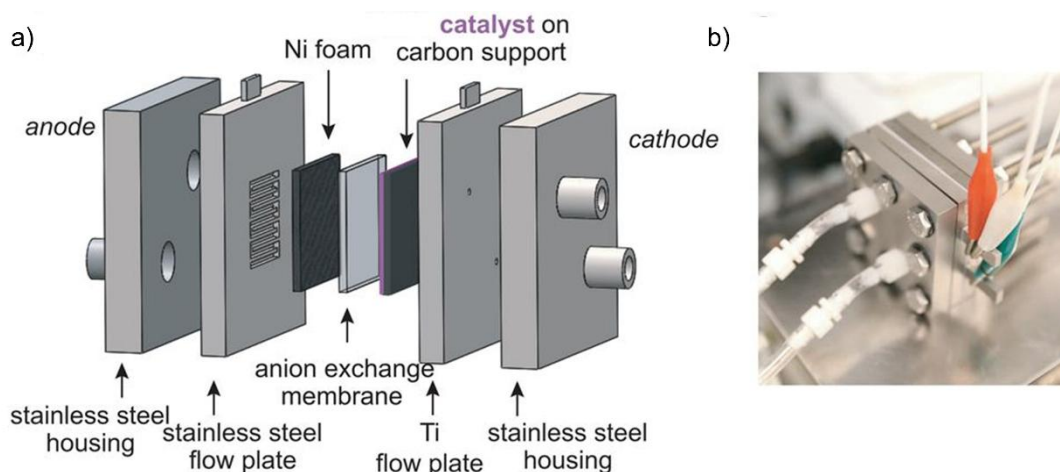


Figure 7-1 Membrane flow reactor where (a) is a diagram of the zero-gap membrane reactor and (b) is an image of the flow cell. From Ren et al.¹⁴⁸ Reprinted with permission from AAAS.

Flow cell electrolyzers can be configured with advanced designs, such as zero-gap arrangements (Figure 7-1), where the electrode and membrane are closely packed to minimise resistance and energy loss. In this configuration, the cathode exchange membrane acts as a solid electrolyte, consequently, the cell does not require a supporting electrolyte.^{34,147} This is particularly beneficial for the ECH of whole bio-oils, as it circumvents the solubility and conductivity issues raised by the non-polar nature of the oil. However, the lack of a liquid electrolyte means that there is no *in situ* production of hydrogen, hence, H_2 must be pumped into the system, negating one of the main advantages of ECH. Therefore, a refined zero-gap flow cell design that incorporates a supporting electrolyte at the cathode to enable *in situ* hydrogen production could represent an ideal approach for this application, synergistically combining efficient mass transfer and on-demand reactant generation.

Additionally, flow cells are highly modular, enabling incremental scaling by adding additional cells to meet production demands, making them an economically attractive option for industrial-scale operations.^{144,147} Another benefit of modularity lies in the ability to scale production incrementally. By adding more modules to the reactor stack, manufacturers can expand capacity without overhauling the entire system. This incremental scalability is especially

advantageous in emerging industries like bio-oil hydrogenation, where market demands and technology are evolving rapidly.

Furthermore, modular configurations simplify testing and implementation of emerging technologies, such as novel cathode materials or alternative electrolytes, allowing for gradual integration without disrupting existing operations.

The choice of reactor design will ultimately influence the economic feasibility of ECH for bio-oil upgrading. By considering process efficiency, operational costs, and scalability, the next chapter will provide a techno-economic assessment to determine the most viable path towards industrial adoption.

7.6.4 Techno-economical Assessment

7.6.4.1 Reactor Sizing

Herein the necessary size and costs for the processing of 1.0 T day⁻¹ of pyrolysis bio-oil at an industrial-scale flow cell reactor will be calculated. This means that, after the subtraction of 15-30 w.t% of water¹⁰, 700-850 kg of bio-oil would be processed daily. The average weight per molecule in pyrolysis bio-oils can vary drastically depending on the feedstock and pyrolysis process. However, it is mostly comprised of functionalised aromatics and medium to long-chain (C₈ to C₁₂) hydrocarbons which will be extrapolated to the range of 100-150 g mol⁻¹.¹⁴⁹ Hence, 4700 to 8500 mols day⁻¹ would undergo reaction.

The number of electrons necessary for the hydrogenation of each compound is different, however, we can estimate this number based on the observed composition of the bio-oil. Aromatic compounds require 6 electrons for the stabilisation of the ring. Ketones, ethers, esters and carboxylic acids would require different quantities based on the level of hydrogenation achieved. Ketones (C=O) could be reduced to either alcohol (C-OH) or undergo dehydration (C-H + H₂O), needing 2 or 4 electrons, respectively. The same can be said about ether, ester and carboxylic acid, which can require 2 to 8 electrons each. Therefore, as aromatics were the main identifiable compounds in the mixture, 8 to 14 electrons will be necessary, and as full hydrogenation is not guaranteed,

we will take 10 electrons per molecule as a nominal value required for upgrading. FCRs are directly inspired by fuel cells, and the DOE considers the current density of 300 mA cm^{-2} as the optimal point for methanol fuel cells for performance and durability.¹⁵⁰

High Faradaic efficiency is quantitatively more important in reducing production costs than selectivity¹⁵¹, FE is also related to HER and bubble formation and could hinder the process. Considering the limitations of the H-type cell in which we consistently achieved an FE > 65%, we will assume that this new configuration could operate at an FE of 80%. Applying equation (2-10), and operating at 80% FE, the FCR would need to have approximately 22 to 40 m² of cathode area.

Increasing the cathode area can lead to several issues such as mass transport limitations, uneven current distribution and increased ohmic losses. Bubble formation is also exacerbated in larger cathodes, which can block active sites, lowering mass transport effects, such as the diffusion of hydrogen or model compound molecules to and from the electrode surface.⁴⁸ EIS analysis also revealed that the PtRu/ACC cathode behaviour is characteristic of a Warburg impedance semi-infinite diffusion layer which indicates diffusion limitations (see chapter 3.3.5).⁴⁸ Structured or hydrophobic electrode surfaces could facilitate bubble detachment, while flow dynamics such as co-current or counter-current configurations in PFRs could sweep bubbles away from the electrode surface, preventing blockages. In addition, FCRs are highly modular, therefore the reactor could be composed of stacks of smaller cells, mitigating these issues.

For biofuel utilisation, the Higher Heating Value (HHV) is a crucial factor. When compared to traditional transportation fuels, bio-oil has a relatively low HHV, ranging from 13 to 19 MJ/kg, while gasoline has an HHV of 44 to 46 MJ/kg, and coal falls between 25 and 35 MJ/kg⁸. Hence, for the production of a 45 MJ/kg biofuel from a 16 MJ/kg feedstock, at a rate of 0.7-0.85 T of biofuel per day ($0.0081 - 0.0098 \text{ kg s}^{-1}$) the minimum energy input (P_{input}) is:

$$P_{inputlow} = 0.0081 \text{ kg s}^{-1} * (45 - 16) \text{ MJkg}^{-1} = 235 \text{ kW} \quad (7-1)$$

$$P_{inputhigh} = 0.0098 \text{ kg s}^{-1} * (45 - 16) \text{ MJkg}^{-1} = 284 \text{ kW} \quad (7-2)$$

In October 2024, the cost of electricity for the industrial sector in the UK was 18.2 pence per kWh,¹⁵² ergo the electrical operation would cost 1024.48 - 1240.51 pounds per day. The cost of electricity for the production of biofuel would be 1.20 - 1.77 pounds kg⁻¹. Energy costs can be responsible for up to 63% of the total OPEX¹⁵³, meaning that the final cost would be 1.90 - 2.80 pounds kg⁻¹, comparable, on the lower end, with the 1.80 pounds kg⁻¹ of gasoline. It is important to note that this is an estimate of the electrical operating costs, and does not take into consideration the cost of heating, biomass purchase or production, pyrolysis processing, storage and transporting.

Therefore, reducing the production cost of biofuel is still necessary for it to be a competitive option in the energy market. However, variations in feedstock composition, such as differing concentrations of oxygenated compounds, could affect these estimates, leading to higher or lower energy requirements.

7.6.4.2 Cost Mitigation

The opportunities, challenges, and future outlook of renewable energy adoption have been extensively reviewed elsewhere and will not be the focus of this discussion.^{154–160} Instead, this work highlights how electricity costs, a major component of operational expenses, can be mitigated.¹⁵³

Integrating renewable energy sources, such as solar or wind power, with the ECH process could significantly reduce operational costs while enhancing sustainability. However, this requires efficient energy storage systems, such as batteries or supercapacitors, to address the intermittency of solar and wind power. Another promising approach is using renewable energy to produce hydrogen, which could be fed into the reactor as a supplemental hydrogen source, further reducing reliance on grid electricity. Moreover, the shift from fossil-fuel-derived electricity to renewables could dramatically lower the carbon footprint of the ECH process, aligning it with global decarbonisation goals.

Building on these renewable energy strategies, photoelectrochemical systems represent a promising frontier in sustainable hydrogenation processes. By utilising sunlight to drive the reduction of bio-oil, these systems eliminate the need for external electricity sources. Recent advances in photoactive materials, such as perovskites and semiconductor catalysts, have shown promise in achieving high efficiencies for water splitting and hydrogenation reactions (especially CO₂ reduction). Although the technology is still in its infancy, hybrid systems combining photoelectrochemical cells with traditional electrochemical reactors could offer a transitional solution, harnessing sunlight during peak hours while relying on grid electricity as a backup.^{161–163}

The other major factor that can impact the economic feasibility of scaling up the ECH of bio-oils is cathode fouling, which was discussed in Chapter 7.5. The deterioration of the cathode material, especially when using expensive catalysts like platinum-ruthenium, directly affects both the operational efficiency and the overall cost of the process.

Without considering a discount for bulk purchases, the pricing of PtRu powder is 198.98 pounds g⁻¹, and the metal concentration on the cathode utilised was 4 mg cm⁻² or 0.04 kg m⁻². Therefore, disregarding the assembly costs, which can be considered negligible, the full cathode cost is approximately 175,000 – 318,000 pounds. In the context of CAPEX, this value is not far from a typical industrial plant of a similar size. However, in terms of operational costs, it may account for a significant percentage of expenses.

Assuming a conservative replacement interval of 6 months for an industrial-scale reactor, the annual cost of cathode replacement could reach 350,000 – 640,000 pounds. When added to other operating expenses, such as electricity (1024.48 - 1240.51 pounds per day, or approximately 374,000 – 453,000 pounds per year), the cost of cathode maintenance could rival energy consumption as the dominant contributor to OPEX. According to Das *et al*¹⁵³, in a similar configuration, the replacement of ECH stacks could be as low as 1% of OPEX.

The costs of frequent cathode replacement scales linearly with surface area, meaning that even minor increases in degradation rates could exponentially raise

operational expenses at industrial scales. However, the modularity inherent in FCR presents an opportunity to mitigate these impacts. Instead of employing a single, large cathode, industrial systems can be designed using stacks of smaller cells. This modular configuration allows for the targeted replacement of individual components rather than the entire cathode surface, significantly reducing downtime and maintenance costs. Additionally, smaller modules facilitate standardisation, which can lower manufacturing costs and improve the supply chain for replacement parts.

Mitigating cathode degradation is therefore essential for improving the economic outlook of the ECH process. Potential strategies include developing alternative electrode materials with greater durability, such as non-precious metal alloys or metal oxides (discussed in 2.3.2.1), which could provide a more cost-effective alternative without compromising performance.

Other methods for avoiding damage to the cathode, such as protective coatings, might obstruct the ECH process, as discussed in Chapter 7.5. Therefore, optimising operating conditions, such as using less corrosive additives or modifying the electrolyte composition, could extend the cathode's lifespan, without compromising conversion efficiency.

As the electrochemical hydrogenation process matures and scales, we anticipate significant reductions in both CAPEX and OPEX. Technological advancements, such as improved catalysts and more energy-efficient reactor designs, will lower the cost per unit of biofuel produced. Moreover, as economies of scale are realised, the cost of biofuel production could decrease. Government incentives for renewable energy and biofuel production could further enhance the economic feasibility, making electrochemical hydrogenation a competitive alternative to traditional biofuel production methods.

8 Overall Conclusions and Future Work

8.1 Overall Conclusions

This thesis explores the potential of electrochemical hydrogenation as a sustainable method for upgrading bio-oils derived from biomass and plastic waste pyrolysis. Through a combination of experimental studies and computational modelling, the research provides valuable insights into the mechanisms, challenges, and opportunities associated with this emerging technology.

The findings demonstrate that ECH can significantly improve the stability, calorific value, and compatibility of bio-oils with existing fuel infrastructure by selectively reducing organic compounds. The studies on model compounds established optimal conditions for ECH, highlighted the performance of PtRu electrodes, and revealed synergistic effects between certain compound mixtures. These results provided a foundation for applying ECH to real bio-oils, where similar improvements in product quality were achieved for both aqueous and oily phases.

Despite its promise, the work also identifies key challenges in scaling up ECH processes, including the solubility issues between bio-oils and water-based electrolytes, the corrosive effects of certain additives, and the need for durable catalysts capable of withstanding prolonged operation. Addressing these issues will require further advancements in catalyst design, reactor configurations, and process optimisation.

In conclusion, this thesis establishes ECH as a viable and environmentally friendly alternative to traditional hydrogenation methods for bio-oil upgrading. The research contributes to the broader goal of sustainable resource management and offers a pathway towards integrating renewable energy into chemical recycling and biofuel production.

8.2 Future Work

The electrochemical hydrogenation of bio-oils presents a promising avenue for renewable fuel production. However, several areas remain ripe for further investigation to optimise the process, enhance efficiency, and make it

economically viable for large-scale applications. The following suggestions outline key directions for future research:

8.2.1 Refinement of Theoretical Models to Account for Side Reactions

Despite the significant insights provided by the theoretical models used in this study, unanticipated side reactions, such as the formation of TMP during hydrogenation with TBAHFP, highlight the need for more comprehensive reaction models. These models, including Density Functional Theory calculations, could be expanded to predict side product formation in more complex bio-oil mixtures by modelling different configurations of the mixtures, such as different compounds, catalytic surfaces and the effect of the electrolyte composition. Future work should focus on refining these models to accurately account for the diverse range of reactions that occur in bio-oil hydrogenation. In particular, investigating the role of various electrolytes and additives in side reaction formation could help in designing more selective processes.

8.2.2 Development of More Durable Catalysts

The stability of platinum-ruthenium catalysts is a critical challenge, as catalyst degradation leads to high operational costs due to the need for frequent replacements. Future research should explore alternative catalyst materials, such as non-precious metal alloys or composite electrodes, which may offer similar catalytic activity at a reduced cost. The development of more efficient and cost-effective catalysts is essential for the commercialisation of electrochemical hydrogenation.

8.2.3 Optimisation of Electrolyte Composition for Bio-oil Hydrogenation

The use of methanol as an electrolyte, combined with additives such as NaCl and TBAHFP, has been shown to improve the conductivity of the electrolyte but also introduces challenges, such as the formation of unwanted side products. Further research should focus on optimising the electrolyte composition to balance conductivity with minimal side reaction formation. Investigating alternative electrolytes, such as ionic liquids and DESs, or additives that do not interfere with the hydrogenation process, could enhance the selectivity and overall efficiency

of the reaction. Understanding the interaction between bio-oil components and the electrolyte is also crucial for improving the reaction's performance.

8.2.4 Scaling Up to Continuous Reactors

The transition from laboratory-scale H-type cells to industrial-scale systems presents significant challenges, particularly in terms of mass transfer limitations and the continuous operation of reactors. Future studies should focus on optimising the design of continuous reactors, such as CSTRs and PFRs, for bio-oil hydrogenation. Research should investigate ways to improve mass and electron transfer, reduce energy consumption, and accommodate the complexity of bio-oil mixtures. Additionally, techno-economic assessments that consider scaling challenges, such as reactor design, installation and operational costs, will be valuable in assessing the commercial feasibility of electrochemical hydrogenation for biofuels.

8.2.5 Integration of Renewable Energy Sources

Integrating renewable energy sources, such as solar or wind power, with the electrochemical hydrogenation process could significantly reduce the operational costs associated with electricity consumption. Future work could explore hybrid systems that combine renewable energy with grid power, ensuring the process remains sustainable and cost-effective. This integration would not only lower energy costs but also contribute to the environmental sustainability of the bio-oil hydrogenation process. Further studies should assess the feasibility of coupling renewable energy with electrochemical cells in terms of energy efficiency, stability, and long-term operation.

8.2.6 Comprehensive Feedstock and Product Characterisation

Whilst this study has provided valuable insights into the electrochemical hydrogenation of bio-oils and the resultant product distribution, a more thorough understanding necessitates detailed characterisation of both the initial bio-oil feedstock and the final hydrogenated products using techniques beyond those currently employed. Future work should incorporate in-depth elemental analysis and calorimetric studies to provide crucial insights into the chemical

transformations and energy content changes occurring during electrochemical hydrogenation.

For the bio-oil itself, determining the precise elemental composition (Carbon, Hydrogen, Nitrogen, Sulphur, Oxygen) will provide a baseline for understanding the relative abundance of different elements and their potential influence on catalyst activity and side reaction pathways. Furthermore, ascertaining its calorific value (using bomb calorimetry) will establish the initial energy density, crucial for gauging the energy upgrading achieved.

Subsequently, analysing the elemental composition of the hydrogenated products will reveal the extent of hydrogen incorporation and any alterations in other elemental quantities. Similarly, measuring their calorific value will directly quantify the energy density enhancement. Correlating these findings with the electrochemical parameters employed (e.g., applied potential, current density, electrolyte composition) will aid in identifying optimal operating conditions for maximising energy upgrading and product quality.

Integrating the data from elemental analysis and calorimetry with the existing product distribution analysis will yield a more holistic comprehension of the electrochemical hydrogenation process, thereby strengthening the foundation for future optimisation and scale-up endeavours.

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Appendices

Appendix A Ethical Approval Letter



10 March 2022

Dear Mr Catizane ,

Reference: CURES/15209/2022

Title: Electrochemical bio-oil processing

Thank you for your application to the Cranfield University Research Ethics System (CURES).

We are pleased to inform you your CURES application, reference CURES/15209/2022 has been reviewed. You may now proceed with the research activities you have sought approval for.

If you have any queries, please contact CURES Support.

We wish you every success with your project.

Regards,

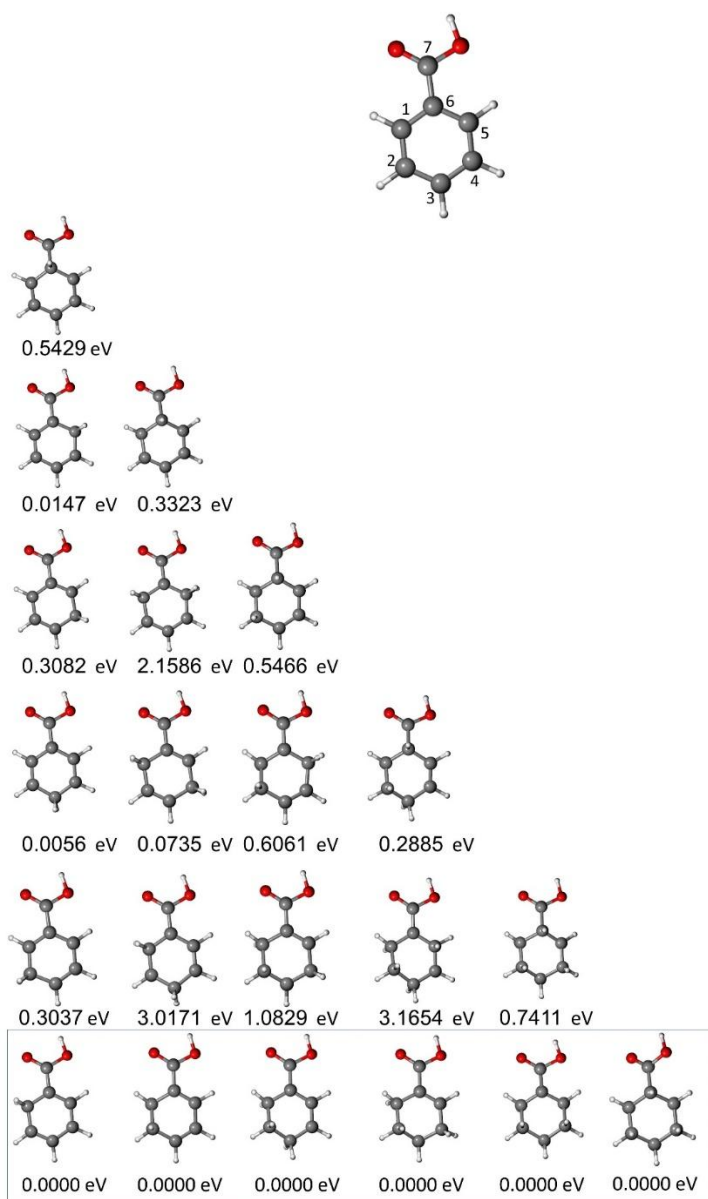
CURES Team

Appendix B

B.1 Additional Information for Paper 1

B.1.1 DFT Calculations

Figure B-1 - Relative energies of one-to-one hydrogenation step of Benzoic acid into Cyclohexane carboxylic acid. Grey spheres represent carbons, white spheres hydrogens and red oxygens. The optimal condition for each step is highlighted in blue and placed on the lower line. All energies are calculated in difference to the optimal state.



B.1.2 LSV Analysis

Figure B-2 - Zoomed in Linear-sweep voltammetry of PtRu/ACC before (in yellow) and after the addition BA (in black), P (in red) and BA+P (in light blue), into the system (1.0M H₂SO₄, 55°C). Where ΔE_2 , ΔE_3 and ΔE_4 are the differences between no added compound and BA, BA+P and P at 10 mA cm⁻² respectively. (BA = benzoic acid, P = phenol)

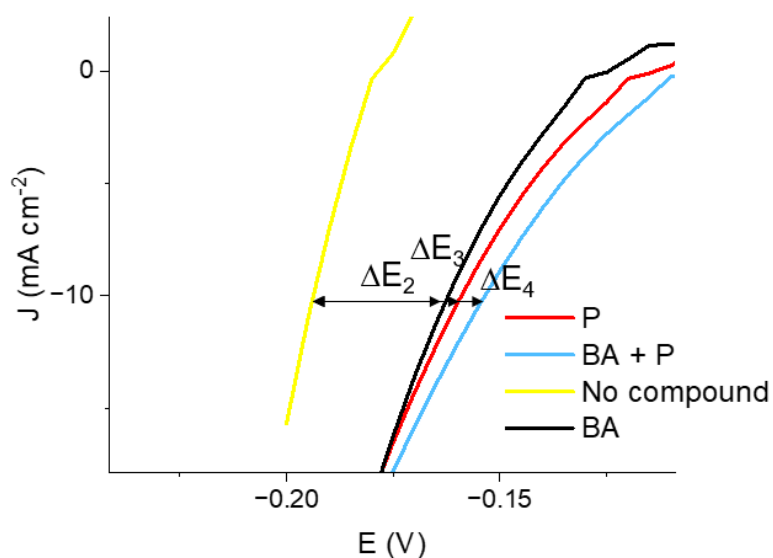


Figure B-3 - Zoomed in Linear-sweep voltammetry of PtRu/ACC before (in yellow) and after the addition of G (in green), G+P (in orange) and P (in red) into the system (1.0M H₂SO₄, 55°C). Where ΔE_1 , ΔE_3 and ΔE_5 are the differences between no added compound and G, P and G+P at 10 mA cm⁻² respectively. (G = guaiacol, P = phenol)

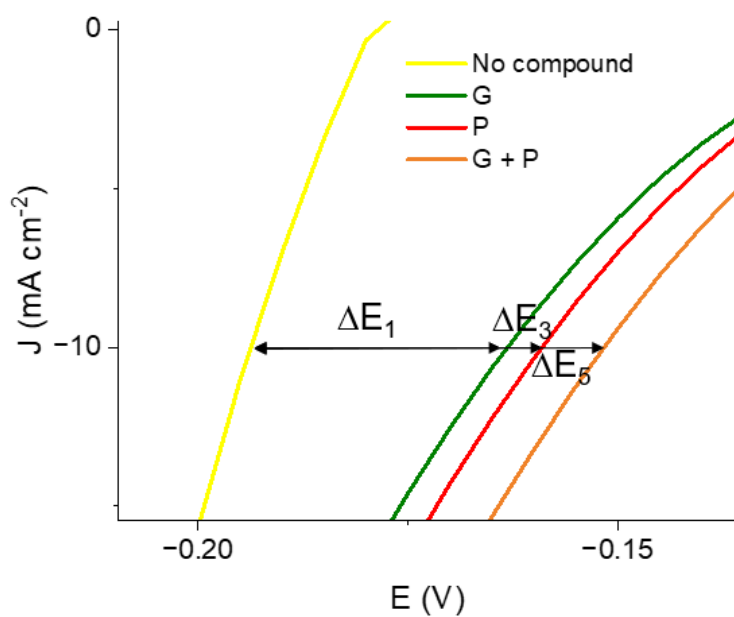


Figure B-4 - Zoomed in Linear-sweep voltammetry of PtRu/ACC before (in yellow) and after the addition of BA (in black), BA+G (in pink) and G (in green) into the system (1.0M H₂SO₄, 55°C). Where ΔE_1 , ΔE_6 and ΔE_2 are the differences between no added compound and G, BA+G and BA at 10 mA cm⁻² respectively. (BA = benzoic acid, G = guaiacol)

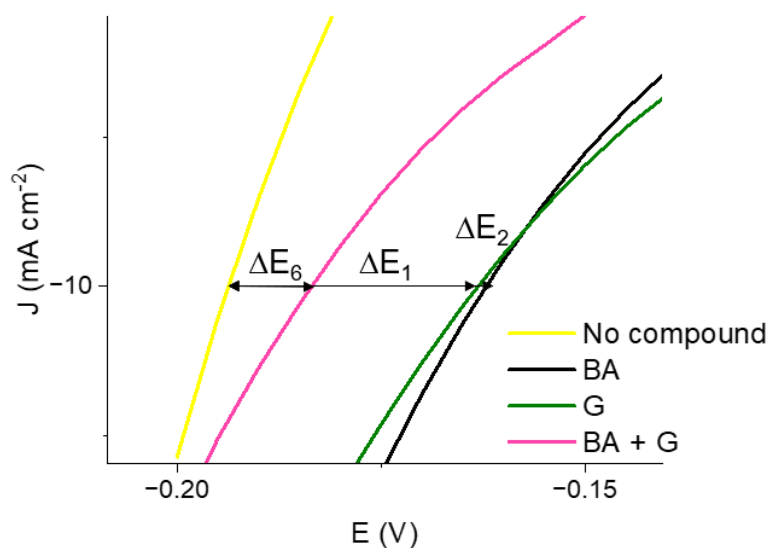
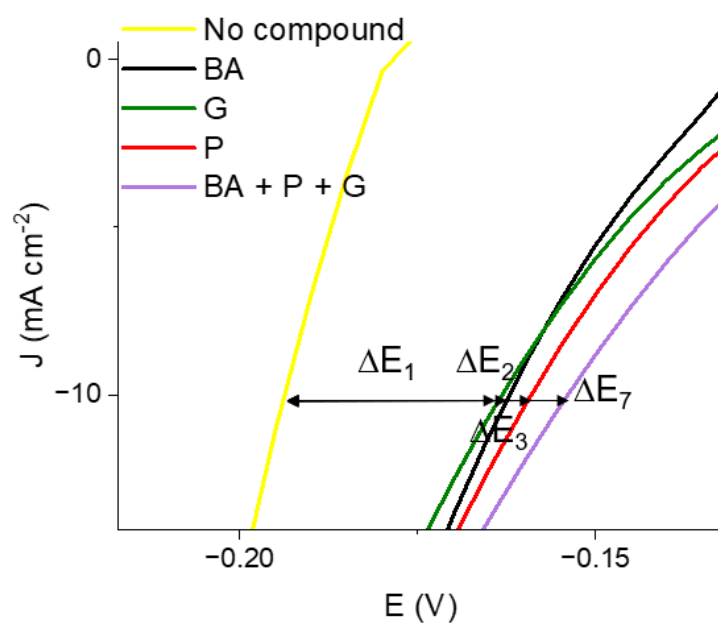


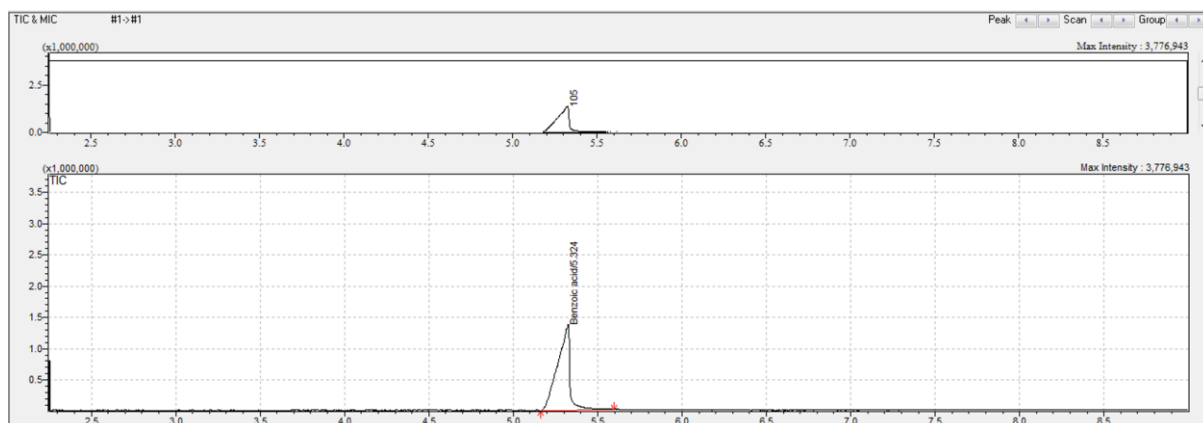
Figure B-5 - Zoomed in Linear-sweep voltammetry of PtRu/ACC before (in yellow) and after the addition of BA (in black), G (in green), P (in red) and BA+P+G (in purple) into the system (1.0M

H₂SO₄, 55°C). Where ΔE_1 , ΔE_2 , ΔE_3 and ΔE_7 are the differences between no added compound and G, BA, P and BA+P+G at 10 mA cm⁻² respectively.



B.1.3 GC-MS Spectrum

Figure B-6 - GC-MS spectrum of benzoic acid before ECH.



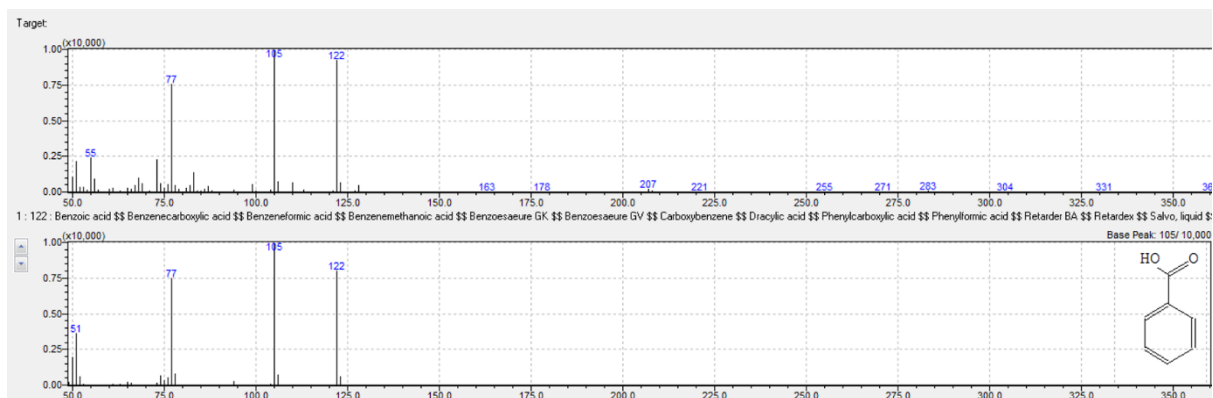


Figure B-7 - GC-MS spectrum of benzoic acid after ECH and the main product (cyclohexane carboxylic acid).

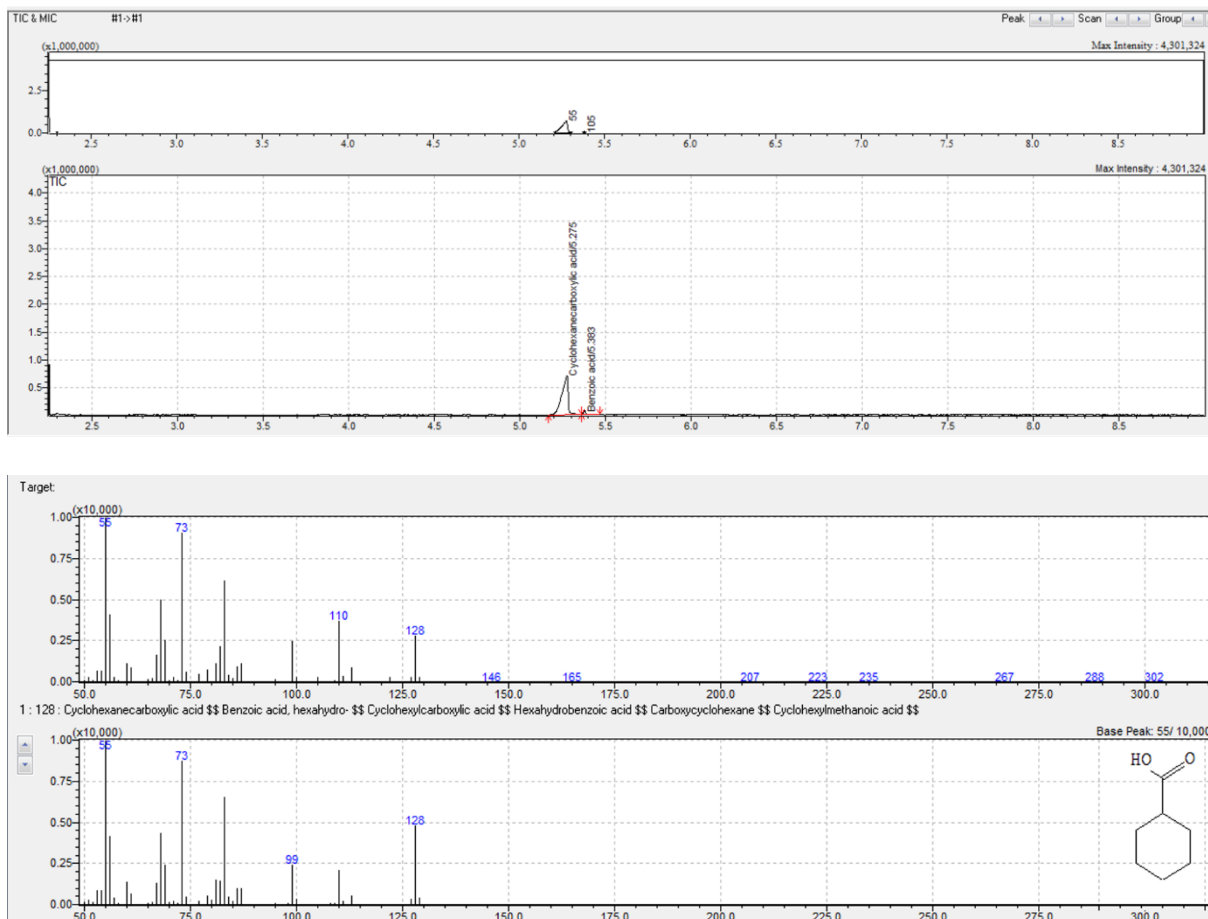


Figure B-8 - GC-MS spectrum of phenol before ECH.

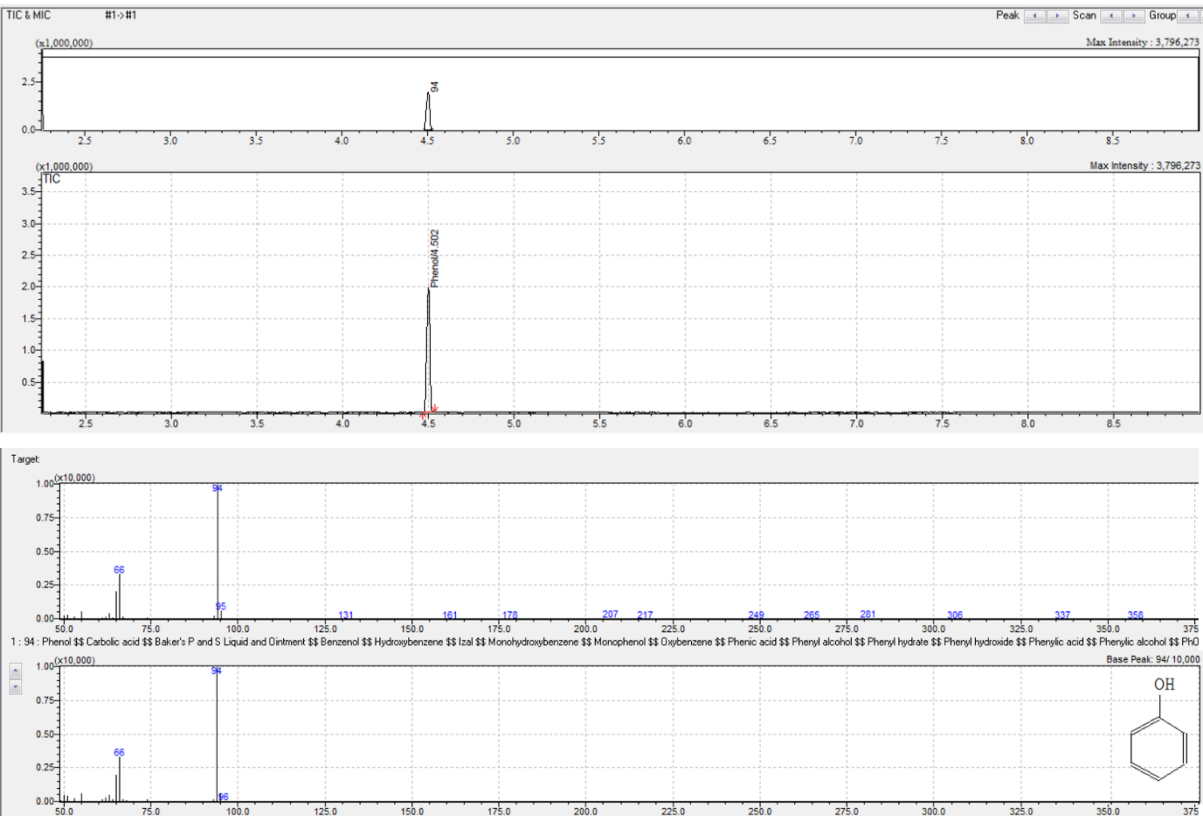


Figure B-9 - GC-MS spectrum of phenol after ECH, and the main products: cyclohexanol and cyclohexanone.

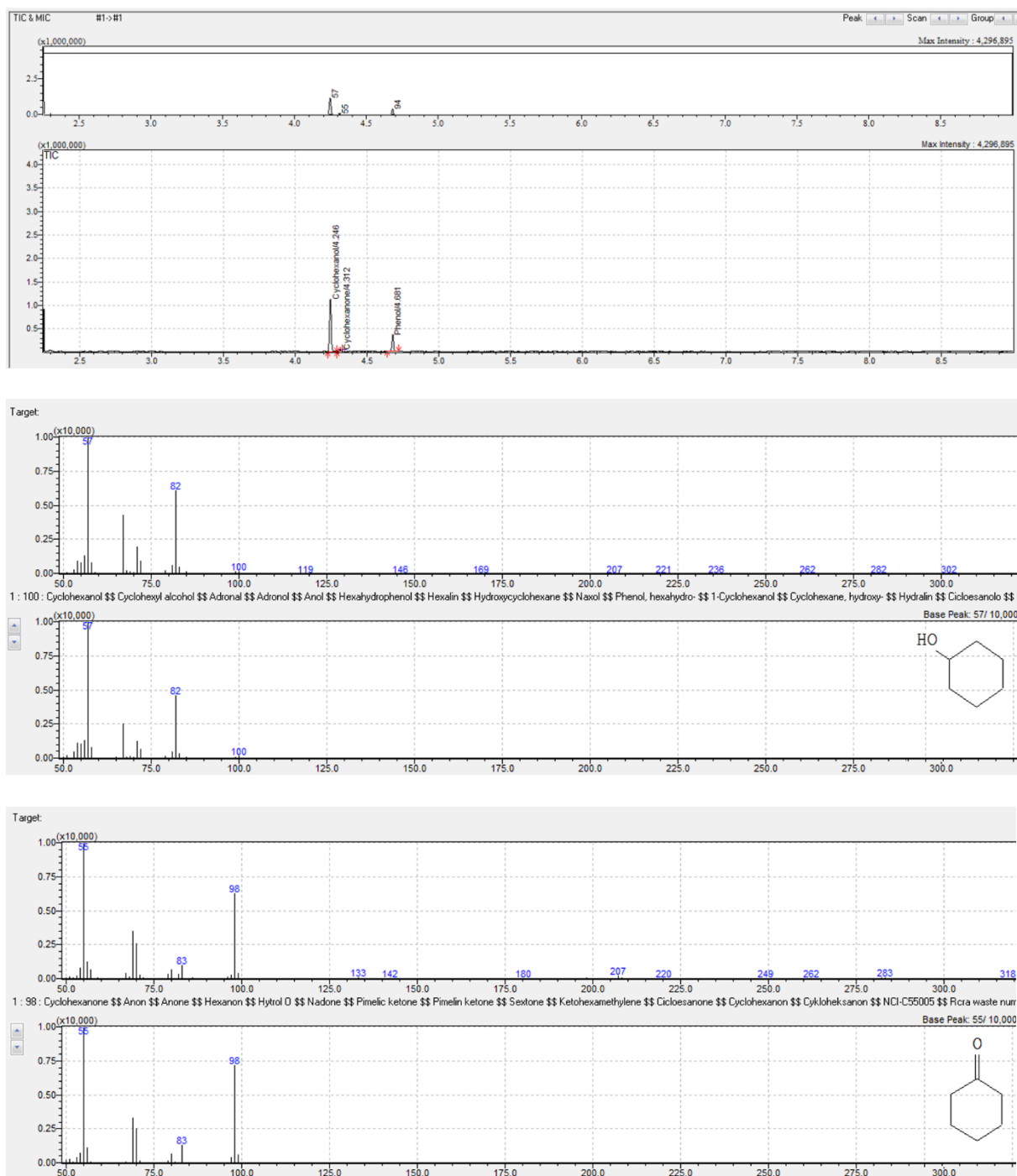


Figure B-10 - GC-MS spectrum of guaiacol before ECH.

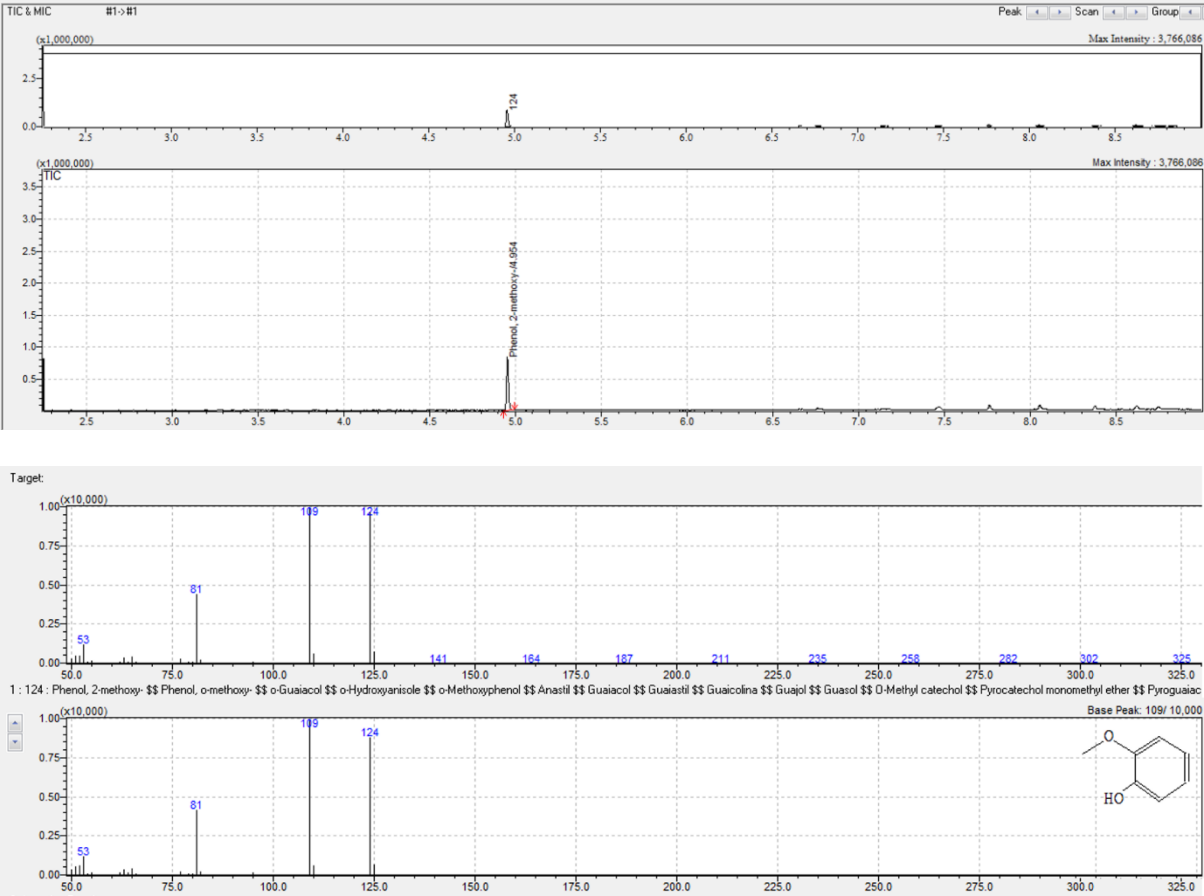


Figure B-11 - GC-MS spectrum of guaiacol after ECH and the main products: methoxycyclohexanol and methoxycyclohexane.

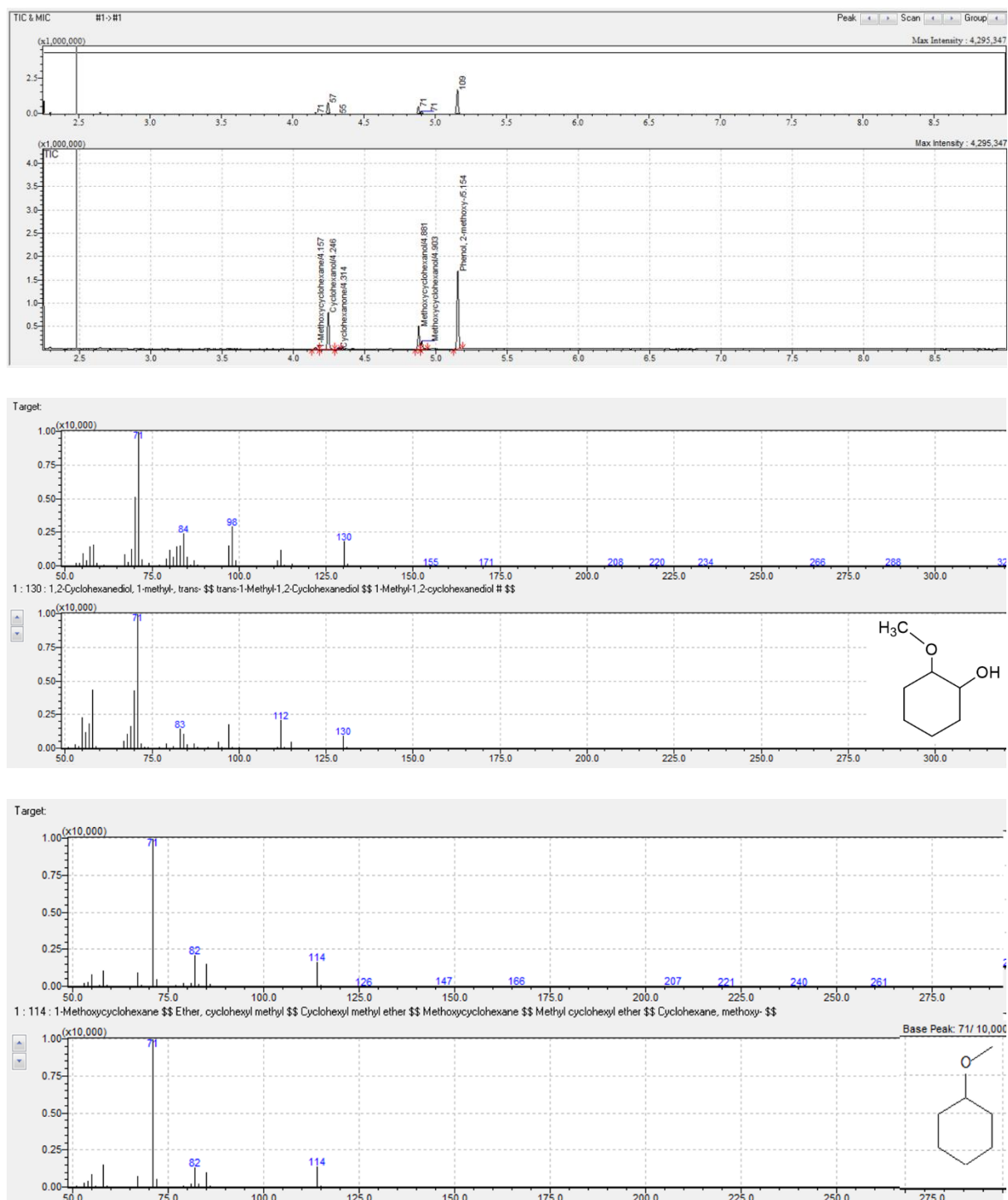


Figure B-12 - GC-MS spectrum of benzoic acid and guaiacol mixture before and after ECH, and the spectrum of cyclohexane.

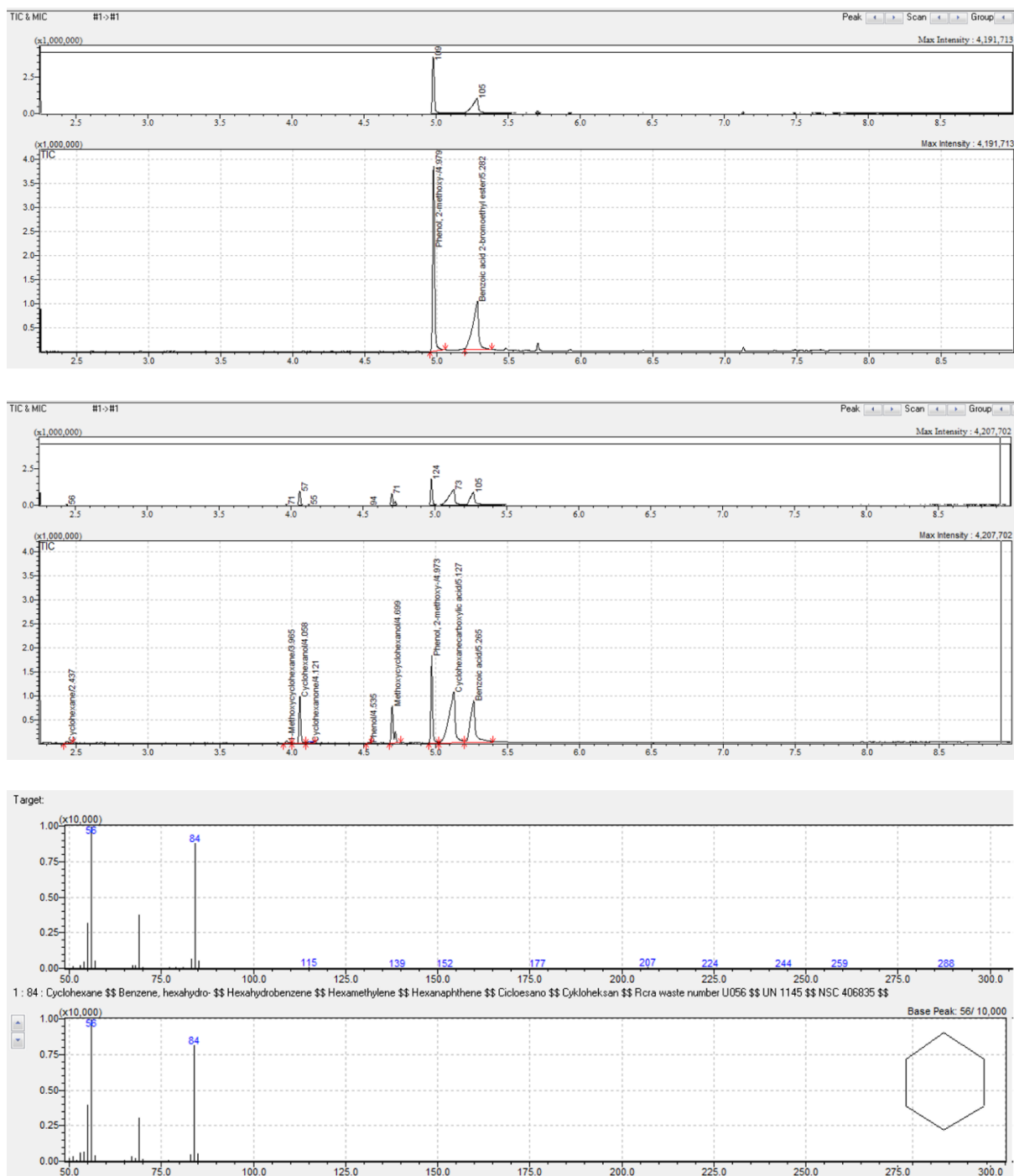


Figure B-13 - GC-MS spectrum of benzoic acid and phenol mixture before and after ECH.

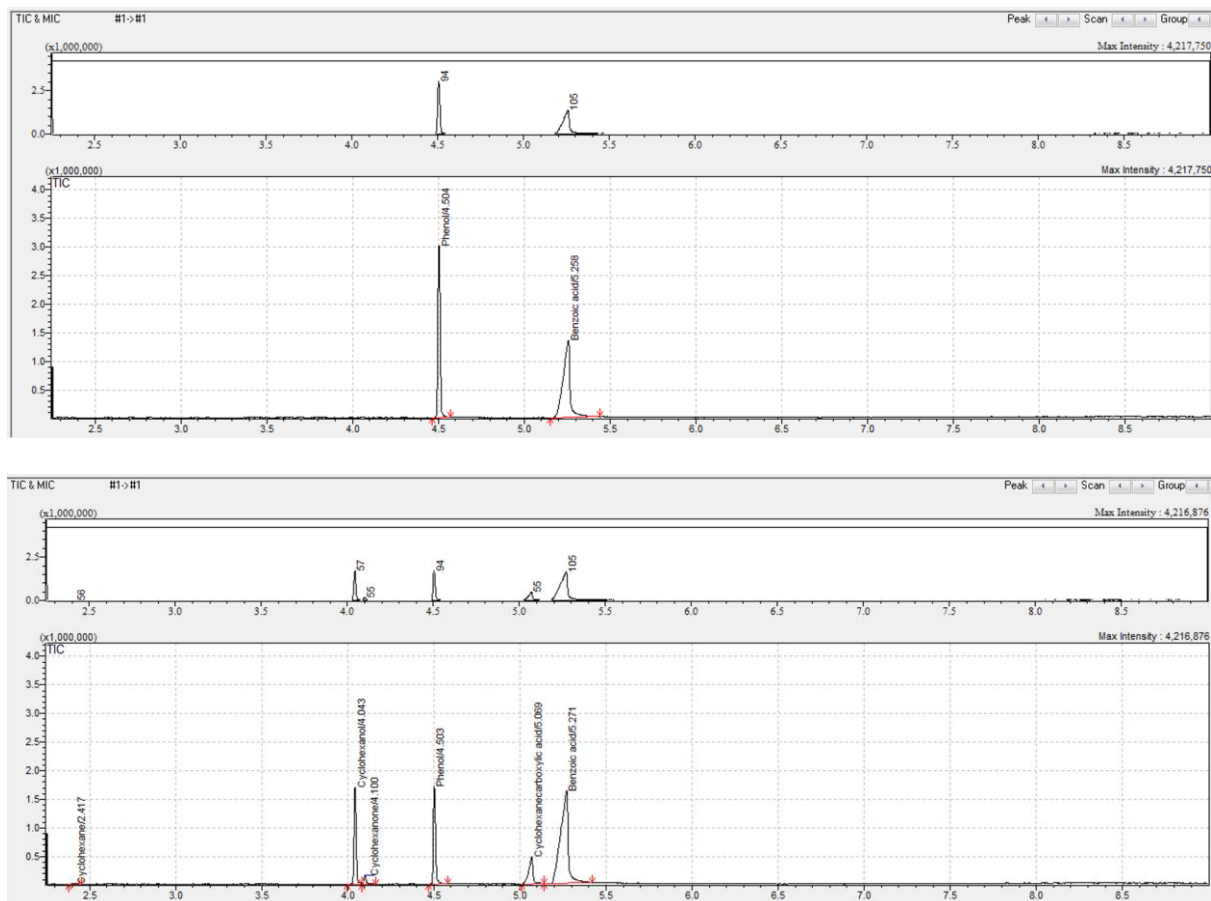


Figure B-14 - GC-MS spectrum of guaiacol and phenol mixture before and after ECH.

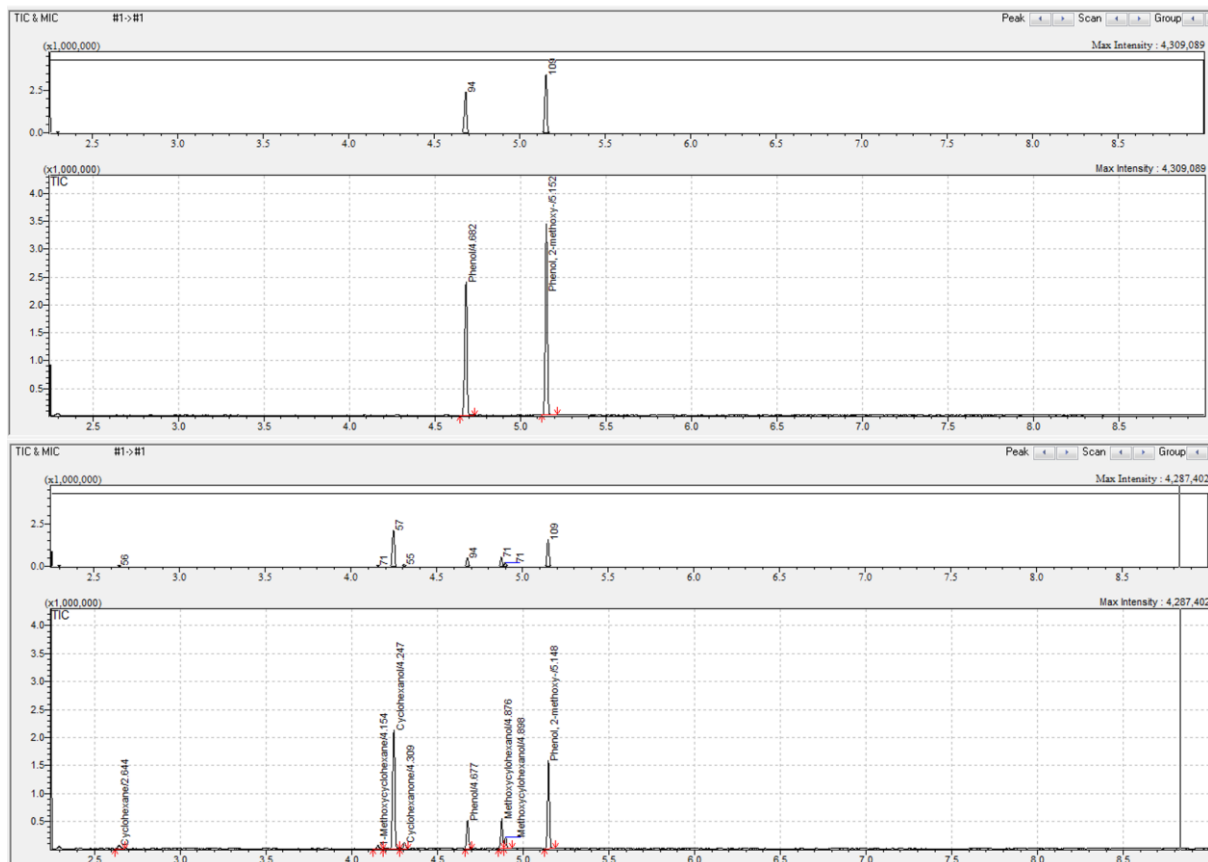


Figure B-15 - GC-MS spectrum of benzoic acid, guaiacol and phenol mixture before and after ECH.

