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Kraft lignin oxidative valorization via electrochemical methods

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Abstract

Lignin is one of the most abundant waste biomasses from the pulp and paper industry and the largest natural source of aromatic chemicals. Due to its complex polymeric structure, Kraft lignin is under-utilized and usually burnt for heat generation, thus, resulting in CO₂ emission in the Kraft process. To valorize lignin with renewable electricity and to convert it into value-added aromatic chemicals, efficient electrochemical methods need to be discovered not only based on its apparent yield of certain chemicals, but also based on its energy efficiency. In this study, the electro-oxidative performance of six different metals is systematically evaluated. The results showed that the synthesized Ni-based catalyst can increase the vanillin and vanillic acid apparent yield by 50-60% compared to when no Ni-based catalyst is used. In conventional electrochemical oxidation reactions, the tests are usually performed before the oxygen evolution reaction (OER) region to avoid competing for electron supply. This requires applying a smaller voltage; thus, a smaller reaction rate is also expected. However, with the newly proposed notion of charge efficiency, we found that the OER serves more than a competing reaction where the oxygen generated from the anode could synergistically help oxidize the lignin for more aromatic products. We showed that, utilizing a thinner layer of Ni catalyst balances the OER and the oxidative reaction of lignin to improve the charge efficiency.

Résumé

La lignine est l'une des biomasses de déchets les plus abondantes de l'industrie des pâtes et papiers et la plus grande source naturelle de produits chimiques aromatiques. En raison de sa structure polymère complexe, la lignine Kraft est sous-utilisée et généralement brûlée pour générer de la chaleur, ce qui entraîne des émissions de CO₂ dans le procédé Kraft. Pour valoriser la lignine avec de l'électricité renouvelable et la convertir en produits chimiques aromatiques à valeur ajoutée, des méthodes électrochimiques efficaces doivent être découvertes non seulement sur la base de son rendement apparent de certains produits chimiques, mais également sur la base de son efficacité énergétique. Dans cette étude, les performances électro-oxydantes de six métaux différents sont systématiquement évaluées. Les résultats ont montré que le catalyseur à base de Ni synthétisé peut augmenter le rendement apparent de vanilline et d'acide vanillique de 50 à 60 % par rapport à l'absence de catalyseur à base de Ni. Dans les réactions d'oxydation électrochimique conventionnelles, les tests sont généralement effectués avant la région de réaction de dégagement d'oxygène (OER) pour éviter la concurrence pour l'apport d'électrons. Cela nécessite d'appliquer une tension plus faible ; ainsi, une vitesse de réaction plus faible est également attendue. Cependant, avec la notion nouvellement proposée d'efficacité de charge, nous avons constaté que l'OER sert plus qu'une réaction concurrente où l'oxygène généré par l'anode pourrait aider de manière synergique à oxyder la lignine pour des produits plus aromatiques. Nous avons montré que l'utilisation d'une couche plus mince de catalyseur Ni équilibre l'OER et la réaction oxydative de la lignine pour améliorer l'efficacité de la charge.

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Content

1	Introduction	1
2	Literature review	4
2.1	Lignin overview	4
2.2	Vanillin production from lignin	5
2.3	Lignin Electrochemical Valorization Catalysts.....	8
2.3.1	Nickel-based catalysts	8
2.3.2	Lead-based catalysts	9
2.3.3	TiO ₂ -based.....	11
2.3.4	Stainless steel and silver	12
2.4	Non-electrochemical metallic catalysts.....	12
2.5	Schematic of the reaction pathway.....	13
3	The objective of the thesis.....	14
4	Materials and methodology	15
4.1	Chemicals.....	15
4.2	Catalyst synthesis	15
4.3	Reactor setup.....	16
4.4	Electrochemical Characterization.....	17
4.4.1	Cyclic Voltammetry	17
4.4.2	Electrochemical Active Surface Area (ECSA).....	17

4.4.3	Chronoamperometry (CA).....	18
4.5	Product analysis.....	18
4.5.1	Liquid-Liquid Extraction and Rotary Evaporation.....	18
4.5.2	GC-FID/GC-MS	20
4.5.3	HPLC-UV	23
5	Results and discussion	24
5.1	Proposed schematic for lignin reaction	24
5.2	Electrochemical characterization of electrode materials	25
5.3	Chemical species identification.....	27
5.4	The apparent yield of the targeted chemicals	30
5.5	ECSA Normalized yield.....	33
5.6	Effects from the OER and charge efficiency.....	36
6	Conclusion	42
7	Limitations and Future Directions	43
7.1	Limitations	43
7.2	Reaction under elevated temperature	43
7.3	HPLC-MS product identification	44
7.4	Lignin structure and reaction kinetics characterization.....	44
7.5	Multi-Metallic systems.....	45
7.6	Apply model compound results on real lignin	46
7.7	Closing Remarks	46

8	References	47
9	Appendix	52

List of Figures

Figure 1 Monolignols and their residues presented in lignin. Adapted from Calvo-Flores et al. ²²	4
Figure 2 Typical linkages between the lignin units. Adapted from Li et al. ²³	5
Figure 3 Synthesis vanillin from guaiacol ²⁵	6
Figure 4 Borregaard's oxidation of lignosulfonate to vanillin, adapted from M.Lersch, 2009 ²⁶	7
Figure 5 Scheme of the flow cell system combined with ultrafiltration unit, adapted from Stiefel et al. ³⁴	9
Figure 6 A schematic for lignin valorization using Pb/PbO ₂ catalyst and Cu cathode, adapted from Liu et al. ¹⁶	11
Figure 7 H-cell configuration for Kraft lignin oxidation with 1 M KOH on both sides of the cell	16
Figure 8 Lignin solution acidified with an equal volume of 1 M H ₂ SO ₄ , before (A) and after (B) centrifuge.....	18
Figure 9 Separation funnel with aqueous phase (product solution from centrifuge) on top and organic phase (dichloromethane) at the bottom.....	19
Figure 10 Overview of the rotary evaporation system	20
Figure 11 GC-FID Calibration A: Vanillin B: Syringaldehyde C: Guaiacol	22
Figure 12 Proposed simplified lignin oxidative depolymerization for aromatic chemical production.....	24
Figure 13 A: Cyclic Voltammetry of tested physical vapor deposited metallic catalysts with 200 nm thickness in 1 M KOH from -0.5 V to 1 V vs Ag/AgCl B:	

Chronoamperometry test for tested physical vapor deposited metallic catalysts and YLS carbon paper base with 10 g/L Kraft lignin under 1 V	26
Figure 14 Vanillin and Vanillic acid increase for different anode materials. A: Original concentration in ppm B: normalized to YLS base. The lines are for better visualization for comparison for electricity effects (air) and metallic catalyst effects (YLS carbon paper).	30
Figure 15 HPLC Chromatogram A: 200 nm Ni before reaction and after 1500 s reaction B: 1 cm x 1 cm Ni foam, after 1, 2, and 3 hours of reaction. Both with 10 g/L Kraft lignin in 1 M KOH and the reaction were under 1 V vs Ag/AgCl. Only the two targeted products were labeled in the HPLC chromatogram.....	31
Figure 16 Vanillin and Vanillic acid yield comparison for 200nm Ni and 100nm Ni samples	35
Figure 17 CV scans with 200 nm Ni with (orange) and without (black) Kraft lignin.....	36
Figure 18 Vanillin yield difference due to applied potential difference.....	37
Figure 19 Vanillin production due to the purge of nitrogen gas with 100nm Ni under 1 V for 1500 s	38
Figure 20 Total charge transfer for 200nm Ni sample and 100nm Ni sample	40
Figure 21 Vanillin and vanillic acid increase after 1500s reaction under 1V	52
Figure 22 A: Double-layer capacitance plot for 100 nm Ni B: ECSA scans for 100 nm Ni	53
Figure 23 A: Double-layer capacitance plot for 200 nm Ni B: ECSA scans for 200 nm Ni	54
Figure 24 A: Double-layer capacitance plot for Ni foam B: ECSA scans for Ni foam	55
Figure 25 GC-MS Chromatogram for Kraft Lignin before and after reaction under 1V for 10 hours with 1cm x 1cm Ni foam	56

Figure 26 HPLC calibration curve for vanillin and vanillic acid	57
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List of Abbreviations

ACT – 4-Acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl
BHT – butylated hydroxytoluene
CO₂ – Carbon Dioxide
COD – Chemical Oxygen Demand
CV – Cyclic-voltammetry
DFT – Density Functional Theory
ECSA – Electrochemical Surface Area
FE – Faradaic Efficiency
FID – Flame Ionization Detector
FT-IR – Fourier-Transform Infrared Spectroscopy
GC – Gas Chromatography
HPLC – High Power Liquid Chromatography
HSQC-NMR – Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance
LSV – Linear Sweep Voltammetry
MS – Mass Spectrometry
NIST – National Institute of Standards and Technology
NMR – Nuclear Magnetic Resonance
OCP – Open Circuit Potential
OER – Oxygen Evolution Reaction
PVD – Physical Vapor Deposition
RDE – Rotating Disk Electrode
TEMPO – (2,2,6,6-tetramethylpiperidin-1-yl)-oxyl
TOC – Total Organic Carbon
UV – Ultraviolet
UV-Vis – Ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

1 Introduction

As climate change becomes a more and more important issue for human society, fuel consumption by humanity is shifting from massively relying on fossil fuels to renewable energy sources. Biobased products such as biofuels and biochemicals are considered one of the most promising sustainable chemical sources as they often involve underutilized agricultural and forestry wastes thus reducing the dependence on petroleum for chemical production.¹

Lignin, among all the types of lignocellulosic biomass, takes up to 15%-30% by weight, and 40% by energy, making it the largest renewable source for renewable aromatic bioproducts.^{2,3} However, traditionally in the pulp and paper industrial application, the black liquor which contains the Kraft lignin, is usually incinerated for power generation in the Kraft process,⁴ resulting in CO₂ emission from the pulp and paper industry, albeit its low heat efficiency.

Numerous methods have been investigated for lignin valorization,⁵ such as pyrolysis,⁶ bacteria treatment,⁷ and traditional thermal catalysis methods to yield bio-oil and bio-char, which can be applied as the replacement fuel for coals for existing industrial boilers,⁸ as well as yielding valuable organic small molecular products and carbon-based gas products.

Among all the methods to valorize lignin, electrochemical degradation and valorization has become a promising route for its usage of green electricity, which is often from renewable sources,⁹ and more importantly, the reaction can be controlled by adjusting the applied current, applied voltage, and supplied charge for better yield and selectivity of the value-added products, as well as by optimizing the reaction conditions.

Researchers have been performing studies on the topic of electrochemical valorization of lignin using different catalysts manufactured from different synthesis methods with various experimental setups. Nickel-based material has been the most tested catalyst for its outstanding activity towards biomass oxidation as well as its stability against corrosion.¹⁰ Ni and Co nanoparticles were deposited on a Pt disk electrode using the water-ethanol dispersion method and tested for lignin reaction in a typical three-electrode setup.¹¹ Ni-Co catalysts were also prepared by electrodeposition on a 1.5 cm × 1.5 cm titanium foil in a typical three-electrode setup for softwood alkali lignin oxidation.¹² In another three-electrode setup, nickel foam was tested for organosolv lignin oxidation.¹³ Several commercially available Ni, Co, Fe, and Ti-based alloys as well as black liquor activated Ni foam were tested for Kraft lignin degradation.¹⁰ For higher overall product yield, high-temperature electrolysis was performed in a sealed three-electrode cell with nickel foam and nickel sheet as the working electrode.⁹ Besides Ni-based anodes, PbO₂-based catalysts were also tested for BHT (butylated hydroxytoluene) production from black liquor lignin.¹⁴ PbO₂-based catalysts were also tested with Aspen lignin for 4-Methylanisole production¹⁵ and discussed different cathode pairing for bamboo lignin¹⁶, rice straw lignin¹⁷, corn stover lignin from paper-making black liquid,¹⁸ and cornstalk lignin¹⁹ in a single-cell reactor. To develop a more uniform deposition of PbO₂ nanoparticles and avoid surface defects, a deposition method with a multi-wall nanotube on a rotating disk electrode (RDE) was developed and tested for lignin depolymerization.²⁰

However, due to different catalyst preparation methods, catalyst sizes, reaction conditions such as temperatures and pressures, reaction time, and lignin types, results were reported in various styles, making it difficult for scientific researchers to compare the characteristics of the catalyst itself. Moreover, to the best of our knowledge, most literature used undivided

cells for lignin electrolysis which mixes both oxidation and reduction processes, making it difficult to distinguish the effects from oxidation to reduction. The exact structure of lignin is still unknown, as well as the exact reaction mechanism. Consequently, monitoring the charge transfer for each product and calculating the Faradic efficiency (i.e., electron selectivity and electrical efficiency) is extremely difficult.

In this project, I utilized a divided H-type cell reactor to focus only on the Kraft lignin oxidation process under room temperature and pressure with several pure metal catalysts prepared through the same method. Instead of optimizing the product yield by recycling the reactant flow or having a longer reaction time, we propose novel normalization metrics for catalyst comparison for their energy efficiency.

2 Literature review

2.1 Lignin overview

Lignin is a polymer mixture whose composition changes with respect to plant types. However, it is generally believed that all lignin is made of three basic phenolic monolignols: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol and their aromatic residues accordingly are named p-hydroxyphenol (H), guaiacyl (G), and syringyl (S) units.²¹ Their structures are shown below in Figure 1.

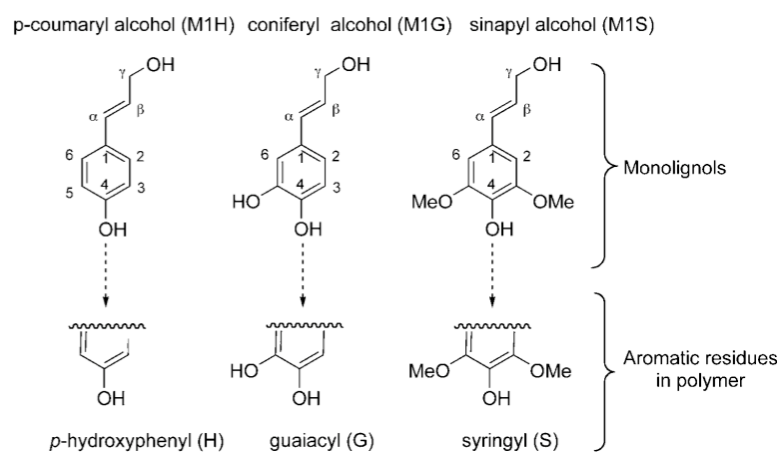


Figure 1 Monolignols and their residues presented in lignin. Adapted from Calvo-Flores et al.²²

Lignin structure is constructed with the three aforementioned monolignols with various linkages, such as β -O-4, α -O-4, β -1 and many other linkages in Figure 2 as well as more linkages to be discovered by future researchers.

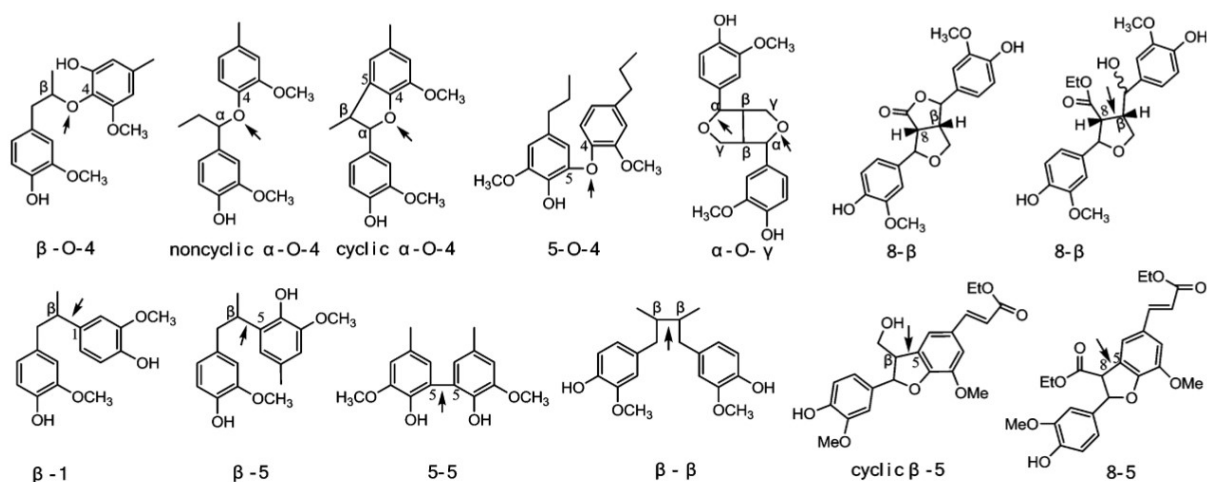


Figure 2 Typical linkages between the lignin units. Adapted from Li et al.²³

2.2 Vanillin production from lignin

Vanillin is naturally extracted from vanilla beans and is used for scent and flavoring in the food, pharmaceutical and cosmetic industries. However, natural vanilla only constitutes less than 5% of the global market demand and as a result, artificial vanillin is needed to meet the world's demand.²⁴

The use of liginosulfonates for vanillin production was the dominant procedure for artificial vanillin. According to the literature, a pulp and paper mill in Ontario took the global market share for synthetic vanillin by 60%. However, due to the number of waste effluents and the cost of the effluent treatment, the vanillin production from pulp and paper mills was closed gradually.²¹ A competing process, the Kraft process, has been implemented in the pulp and paper industry for energy which burns the waste black liquor stream that contains a great amount of lignin for energy generation.²⁴

With the development of the petrochemical industry, a synthesis route from petrochemical guaiacol²⁵ took over 85% of the global market share of synthetic vanillin and only 15% of the market share is from lignin. Figure 3 depicts the vanillin synthesizing route from guaiacol by adding the aldehyde group onto an aromatic ring. The condensation reaction of guaiacol with glyoxylic acid is followed by the oxidation of the resulting mandelic acid, resulting in the phenyl-glyoxylic acid. Then the phenyl-glyoxylic acid is put through decarboxylation which gives vanillin.²⁵

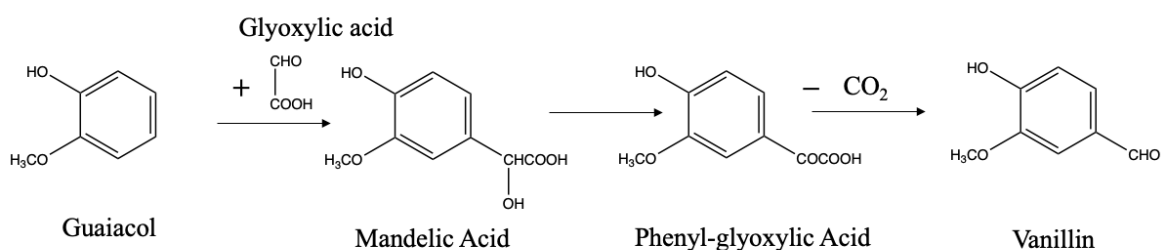


Figure 3 Synthesis vanillin from guaiacol²⁵

As a result, the global artificial vanillin production from guaiacol is largely dependent on petroleum and the vanillin price is very sensitive to the global oil price.²⁴

In contrast, a Norwegian company, Borregaard, plays a leading role in producing vanillin from liginosulfonate oxidation using a Cu-based catalyst, as depicted in Figure 4²⁶ under about 100 °C to 185 °C.²⁷

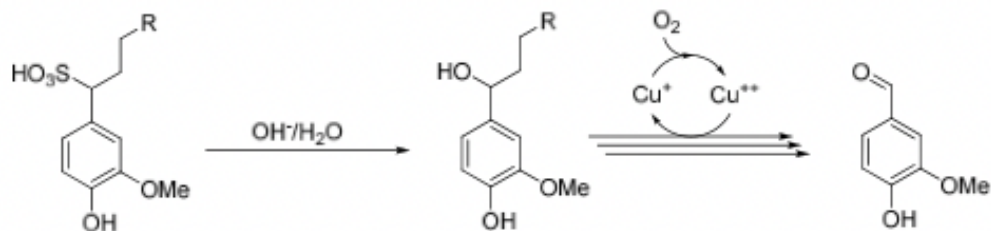


Figure 4 Borregaard's oxidation of lignosulfonate to vanillin, adapted from M.Lersch, 2009²⁶

It is also reported by previous studies that, experimental conditions such as temperature, lignin concentration, oxygen partial pressure and OH^- concentration have a relatively high influence on the vanillin yield. While oxygen partial pressure should be taken into account carefully where too much oxygen could result in vanillin over-oxidation while too little oxygen hinders the lignin degradation reaction.²⁴

In this project, vanillin, which is derived from the oxidative cleavage of the β -O-4 aryl ether linkage within the lignin polymer and electrochemically transformation of the coniferyl alcohol groups inside the lignin,²⁸ along with its oxidated form, vanillic acid, are the targeted products for this lignin oxidative valorization project. To crack the aryl ether carbon-carbon bonds and to yield the aromatic compounds, oxidative depolymerization was selected to be the valorization strategy for lignin.²³ A mechanism for lignin oxidation into vanillin was proposed by Tarabanko et al. where coniferyl alcohol acts as the intermediate product.²⁹ However, not many electrochemical catalysts have been tested on Kraft lignin for oxidation, this literature review section also draws insights from traditional thermal catalysts used in the lignin oxidation projects as electrocatalysts selection guidance.

2.3 Lignin Electrochemical Valorization Catalysts

2.3.1 Nickel-based catalysts

Nickel-based electrocatalysts have shown a good catalytic effect on the OER (oxygen evolution reaction)³⁰ as well as biomass valorization for its catalytic effects towards alcohol groups.³¹ There are many publications regarding nickel-based electrocatalysts on lignin valorization in recent years. Smith et al. tested liginosulfonate oxidation with nickel anodes under constant current density in a high pressure, high temperature, highly alkalic 3 M NaOH flow reactor system, yielding vanillin as their targeted product. They also suggested that the vanillin product could be over-oxidized into other products.³² With reaction conducted by Yan et al. under room temperature with organosolv lignin with an undivided three-electrode setup¹³ or by Zirbes et al. under high temperature with Kraft lignin⁹ using nickel foam in an undivided cell, value-added products such as vanillin and syringaldehyde were yielded, suggesting that nickel can be used as an effective catalyst in the process of electro-oxidation and depolymerization of lignin. Di Fidio et al. reported that using NiOOH electrode prepared with Ni wire in an H-cell setup also gives the possibility of yielding value-added chemicals from P1000 soda lignin such as vanillic acid, syringic acid, acetovanillone, 2,6-Dimethoxyphenol, 2,4-Dihydroxyacetophenone, and 3,5-Dimethoxy-4-hydroxyacetophenone, vanillin and syringaldehyde.³³ Stiefel et al. worked with a flow cell system testing Ni catalysts with different morphologies: Ni plates, Ni wire, Ni fleece, and Ni foam. After the reaction, the lignin solution was recirculated back into the reactor feed while the ultrafiltration captures the value-added products to prevent product over-oxidation, as depicted in Figure 5.³⁴

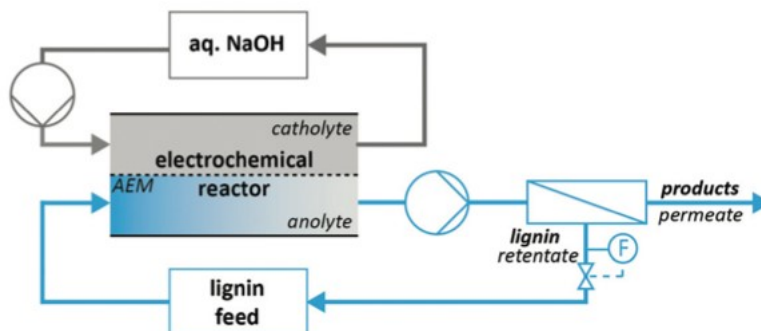


Figure 5 Scheme of the flow cell system combined with ultrafiltration unit, adapted from Stiefel et al.³⁴

On the other hand, some researchers are working on lignin valorization focusing on other targeted products besides vanillin. Di Marino et al. used Ni foam electrodes as both working and the counter electrode in a ‘Swiss-roll’ reactor producing carboxylic acids as their targeted products.³⁵

In addition to simply using pure Ni, researchers have been investigating on binary metallic electrode materials such as Ni-Co electrocatalysts for lignin upgrading. Gharemani et al. synthesized Ni-Co catalyst via electrochemical deposition and found that increasing the Co content in the electrocatalyst can lower the overpotential of the lignin electrooxidation process and that Co can also increase the active surface area by providing more roughness on the surface thus improves the electrocatalytic activity as well as slows down the deactivation of the catalyst. They also found that the increase of the Co percentage in the catalyst can lead to an increase in their targeted product vanillin.¹²

2.3.2 Lead-based catalysts

Although lead-based materials are toxic, the lead/lead oxide anode has been widely studied in the field of lignin electrochemical upgrading. Gang Li’s group has been investigating Pb/PbO₂ electrode as the anodic material on lignin degradation pairing with different types

of cathode materials as depicted in Figure 6, such as copper sheet under 40°C with bamboo lignin,¹⁶ copper sheet with Kraft lignin under ambient temperature,¹⁴ stainless steel wire mesh with aspen lignin under 30°C to 90°C,¹⁵ stainless steel plates and different steel alloys such as FeW₉Cr₄V₅ and FeW₉Cr₄V₅Co₃ on wheat straw lignin under elevated temperatures and in this project the optimized operating conditions such as current density were different for different targeted products,³⁶ Cu/Ni-Mo-Co with corn stover lignin optimized at 40 °C and constant current density at 25 mA/cm²,³⁷ and nickel plates with cornstalk lignin optimized at 30 °C with a constant current density of 30 mA/cm².¹⁹ All these mentioned tests were conducted in undivided three-electrode setups. They found that the hydroxyl radicals generated on the Pb/PbO₂ electrode contribute to the C-O and C-C bonds cleavage and lead to the formation of small molecular weight products such as BHT (butylated hydroxytoluene), vanillin, syringaldehyde, toluene, and acetovanillone. Staser's group also manufactured PbO₂ electrode on multi-walled carbon nanotubes on a rotating disk electrode (RDE) and used Pt as the counter electrode for biorefinery lignin under constant applied potential that was lower than the OER potential for 48 hours. It can be reasonably postulated that in an undivided cell, different anode and cathode pairing could lead to different aromatic products. However, across all these trials, the final optimized conditions and the lignin types were different, making it hard to draw conclusions from different publications.

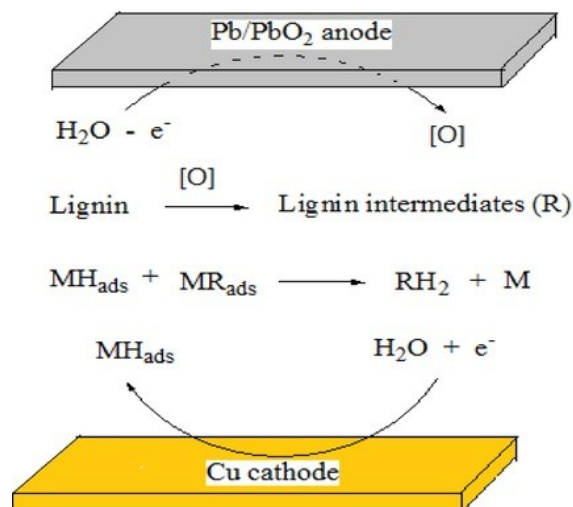


Figure 6 A schematic for lignin valorization using Pb/PbO₂ catalyst and Cu cathode, adapted from Liu et al.¹⁶

2.3.3 TiO₂-based

Aicheng Chen's group utilized TiO₂-based electrocatalysts for lignin oxidation from a wastewater treatment point of view. In 2012, they tested PbO₂ supported on TiO₂ nanotubes for lignin oxidative degradation at 60 °C with constant applied current optimized at 100 mA and they monitored the lignin concentration decrease with UV-Vis as well as the chemical oxygen demand (COD) of the lignin solution. Vanillin and vanillic acid were identified as the main two products but not much attention was given to the quantification of the two main products.³⁸ Later in 2020, Chang et al. from the same research group published their work using reduced TiO₂ nanotubes for lignin oxidation with Pt as the counter electrode in an undivided three-electrode setup. In this project, after optimization of the system, the TiO₂ grown on the Ti plate has shown great potential in lignin degradation by decreasing the lignin solution concentration after 16 hours of reaction. Besides, this publication also introduced the total organic carbon (TOC) method to monitor the organic content inside the lignin solution, through which they found that after oxidation, the total organic carbon removal

level in the lignin solution increased, which implied the degradation of lignin.³⁹ However, from a valorization point of view, the organic chemical decrease is unfavored as it is mostly because of over-oxidation of the small product molecules into gas products as CO₂ thus leaving the system.⁴⁰

2.3.4 Stainless steel and silver

Besides the ones mentioned above, stainless steel (SS304) has also been tested for wheat straw soda lignin oxidation for vanillin production⁴¹ and the system was optimized to achieve a 6% yield of vanillin after thermal treatment in a furnace at 200 °C for 2.2 hours and 7.7 hours electro-oxidation under 3.05 mA/cm².⁴²

Silver (Ag) electrode was also tested with alkali lignin in an undivided cell at 80 °C with a constant current density of 1.9 mA/cm², in which patent filed by Stecker et al. they claimed that under the same experimental condition, their silver catalyst performed better than the nickel sheet in vanillin production after 22 hours of oxidation.⁴³

2.4 Non-electrochemical metallic catalysts

As depicted in Figure 4, Borregaard used Cu catalysts to produce vanillin from lignin,²⁶ where Cu⁺/Cu²⁺ was utilized as the redox couple for electron transfer. This phenomenon could be easily extended to the field of electrochemistry where the Cu ion redox could be happening on the surface of the electrode as well as the constant electron supply from the power source.

Aluminum (Al³⁺) was found to be interactive with guaiacol through Al-O and Al-H bonds in the aforementioned guaiacol – glyoxylic acid condensation reaction in producing vanillin. As Al³⁺ helps improve the selectivity of the Mandelic Acid, which is the important

intermediate in the guaiacol condensation reaction.⁴⁴ However, it is also mentioned that the precipitated form of $\text{Al}(\text{OH})_3$ is unfavourable for the condensation reaction. It is still worth testing if the Al^{3+} on the surface of the electrocatalyst has any effects on vanillin production from an electrocatalyst point of view.

2.5 Schematic of the reaction pathway

Based on the information from the literature discussed above, a simplified mechanism for electrochemical lignin oxidation for this project could then be proposed as shown in Figure 12. The depolymerization of lignin results in the monolignols, the aforementioned G, H, and S units. The monolignols were then further oxidized into smaller molecules such as guaiacol, vanillin and syringaldehyde. Vanillin, however, could be further oxidized into vanillic acid, making the apparent yield of vanillin lower. It is also possible that the vanillic can be produced directly from the oxidation of coniferyl alcohol without passing through the intermediate aldehyde state.⁴⁵ Further discussion was conducted in section 5.1.

3 The objective of the thesis

The objective of this master's thesis project is to focus on the problem of lignin electrocatalytic oxidative valorization into vanillin and vanillic acid. To fill the knowledge gap that there is neither optimized reaction operating conditions nor unified metrics for electro-catalysts characterizations for them to be easily compared from paper to paper.⁴⁶ Different metallic catalysts were prepared via different methods, as a result, their electrochemical performances cannot be compared fairly with the interference from the various preparation methods that is resulting in different morphologies. Often in the literature, the electrochemical reaction for lignin valorization was conducted in an undivided three-electrode setup. Although it might boost the yield of certain chemicals by taking hydrogenation effects into account, the oxidative effect from the anode material cannot be isolated for analysis, making it hard for future researchers to investigate new anode materials for the oxidation-only side of the lignin depolymerization.

To address these issues, in this project, 6 metallic catalysts were prepared with the same physical vapor deposition method with identical controlled thickness. The manufactured catalysts would then be tested in a divided electrolytic H-cell reactor under ambient temperature and pressure. In addition, besides vanillin and vanillic acid, other possibilities of potential products would also be identified. However, given the low concentration in the final product solution as well as the availability of the commercial standard chemicals, only qualitative analysis would be conducted for the non-targeted products and the targeted products will be quantified with the analytical methods with standard chemicals purchased.

4 Materials and methodology

4.1 Chemicals

The Kraft lignin was obtained from Hinton Pulp, a division of West Fraser Mills. Vanillin (ReagentPlus®, 99%), Vanillic Acid (97%), Guaiacol ($\geq 98\%$), Syringaldehyde ($\geq 98\%$), and Acetovanillone standards were purchased from Sigma-Aldrich. The organic solvent used for extraction, HPLC grade Dichloromethane ($\geq 99\%$, contains 40 - 150 ppm amylene as stabilizer) was also purchased from Sigma-Aldrich. The sodium sulfate anhydrous was from Fisher Scientific.

4.2 Catalyst synthesis

In all sample preparations, YLS-T30® carbon papers from Futiantian Technology Co. were utilized as the catalyst support. Copper samples with 200 nm thickness were prepared by physical vapor deposition (PVD) method, using NexDep® platform from Angstrom Engineering. An electron beam was utilized to evaporate copper pellets (99.9999% purity provided by Angstrom Engineering) at 6×10^{-6} torr vacuum to sputter a 100 nm layer and after a 10-minute break, the next 100 nm layer was deposited. The deposition rate was set at $1.0 \text{ \AA} \times \text{s}^{-1}$ in both steps. The same procedure was developed to sputter 200 nm samples of titanium, chromium, aluminum, and nickel by BJD® platform from Angstrom Engineering. The same purity of metal targets, base pressure and deposition rates were respected. Silver samples were also prepared by the e-beam evaporation inside BJD®, but with a $2.0 \text{ \AA} \times \text{s}^{-1}$ deposition rate, mandated by the provider's recipe. Regarding the 100 nm Ni sample in the later comparison, the same procedure was followed with no need for the 10-minute break between the sputtering steps.

4.3 Reactor setup

The electrolysis was conducted in a divided 3-electrode H-type electrolytic cell (Corrtest) with a Fumasep anion exchange membrane (Fumatech) separating the cathode and anode chambers and an Ag/AgCl electrode (3 M KCl with saturated AgCl, Sigma Aldrich) as the reference electrode. On the cathode side, a 2 cm × 2 cm platinum foil (Corrtest) was used as the counter electrode for all the electrolysis experiments. All the electrochemical experiments were performed with a Metrohm Autolab PGSTAT204 potentiostat.

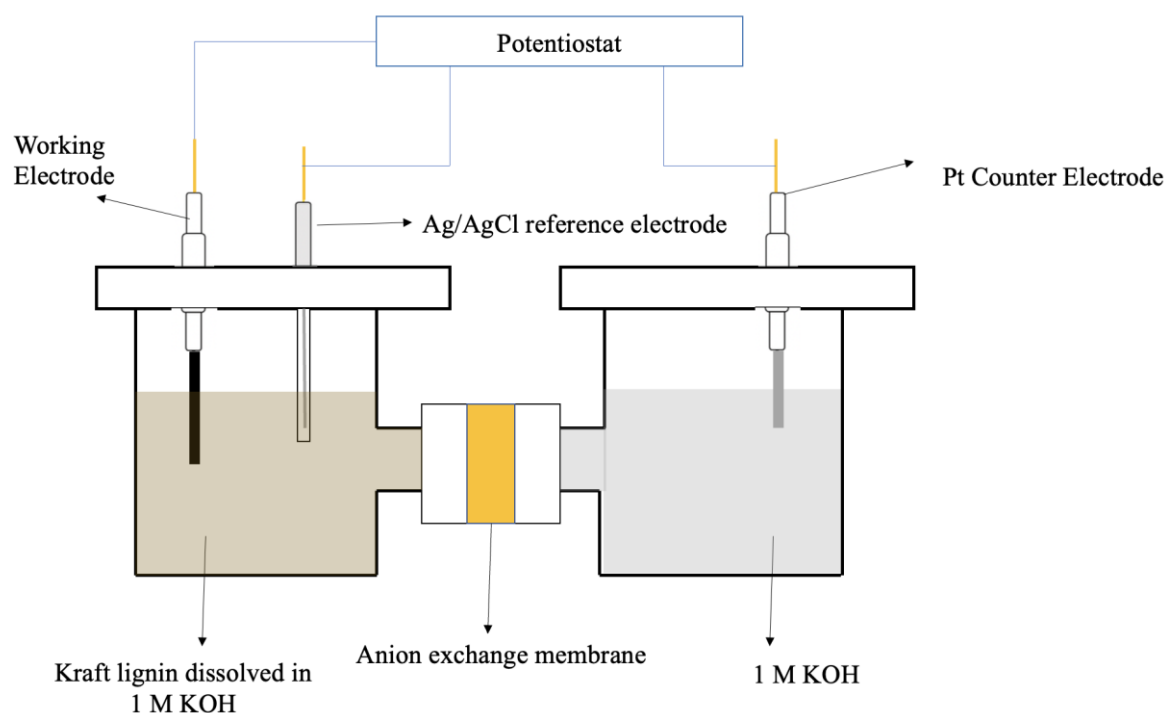


Figure 7 H-cell configuration for Kraft lignin oxidation with 1 M KOH on both sides of the cell

In one chamber of the H-cell described above in Figure 7, 0.4 g of Kraft lignin was dissolved into 40 mL of 1 M KOH, making the final lignin concentration of 10 g/L. The anode chamber

is stirred by a magnetic stir bar at a stirring rate of 400 rpm with 1 cm × 1 cm sized catalysts immersed in the lignin solution. The other cathode chamber is filled with 1 M KOH. All the electrochemical experiments and the product analysis results in the thesis were repeated at least three times and the averaged value was presented with error bars indicating the difference of the results between repetitions.

4.4 Electrochemical Characterization

4.4.1 Cyclic Voltammetry

The cyclic voltammetry method (CV) is the most common electrochemistry analytical method for measuring the electrocatalyst characteristics. A CV is a cyclic potential sweeping method between two set potential values at a certain sweeping speed. This method is mainly used to determine the catalyst activity, current-voltage relation, system onset potentials, mass, or electron transfer limits. In this work, the CV was used to determine the redox peaks for each metallic catalyst and to observe the current density of the system with and without the addition of lignin throughout the whole potential window. In contrast, linear sweep voltammetry (LSV) only scans half of the cycle and is associated with no backward scan.

4.4.2 Electrochemical Active Surface Area (ECSA)

ECSA is a common technique for benchmarking electrochemical catalysts as it measures the real active surface area of the catalyst regardless of its shape and morphology. It is usually determined via the measurement of the capacitive current associated with the double-layer capacitor effect on the surface of the catalyst by scanning cyclic voltammetry (CV) with different scan rates. The CV window is typically centered at the open-circuit potential (OCP)

of the system with a range of 0.1 V,⁴⁷ and it is in the non-Faradaic region where the macro-LSV looks like a flat curve.

4.4.3 Chronoamperometry (CA)

Chronoamperometry (CA) test is done by applying a fixed potential across either a half cell (3-electrode setup) or across the entire electrolyzer (2-electrode setup) and the resulting current and the charge supply in the electrolyzer is recorded. Over time, the behaviour of the current reveals the reaction kinetics and catalyst stability. In this project, the chronoamperometry test was performed at a potential of 1 V vs Ag/AgCl.

4.5 Product analysis

4.5.1 Liquid-Liquid Extraction and Rotary Evaporation

After the reaction, 25 mL of the lignin solution was taken from the H-cell and acidified with a 1:1 volume ratio of 1 M H₂SO₄ so that the unreacted lignin solid could be precipitated out.

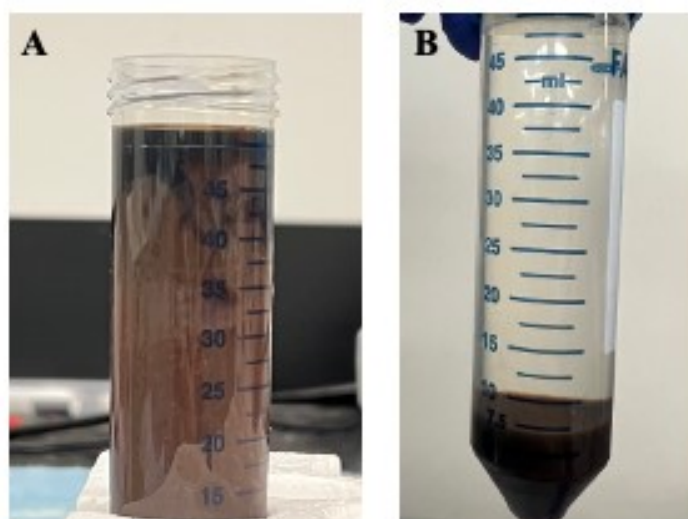


Figure 8 Lignin solution acidified with an equal volume of 1 M H₂SO₄, before (A) and after (B) centrifuge

To accelerate the solid-liquid separation, the mixture was then centrifuged with a Beckman Coulter Allegra® X-12R centrifuge at 3500 rpm and 25 °C for 15 minutes. According to the literature, the most commonly used extraction solvents are ethyl acetate,⁹ dichloromethane,⁴⁸ chloroform.^{12,17} In this project, dichloromethane was selected as the organic solvent for product extraction. After the centrifuge, 20 mL of the clear solution was transferred into a separation funnel and extracted with 20 mL HPLC-grade dichloromethane for three times (60 mL in total). The organic phase from liquid-liquid solvent extraction was collected from the bottom of the separation funnel and put through a fine filter paper filled with sodium sulfate anhydrous to remove the moisture as well as to remove the small lignin solid particle remainder from the centrifuge.

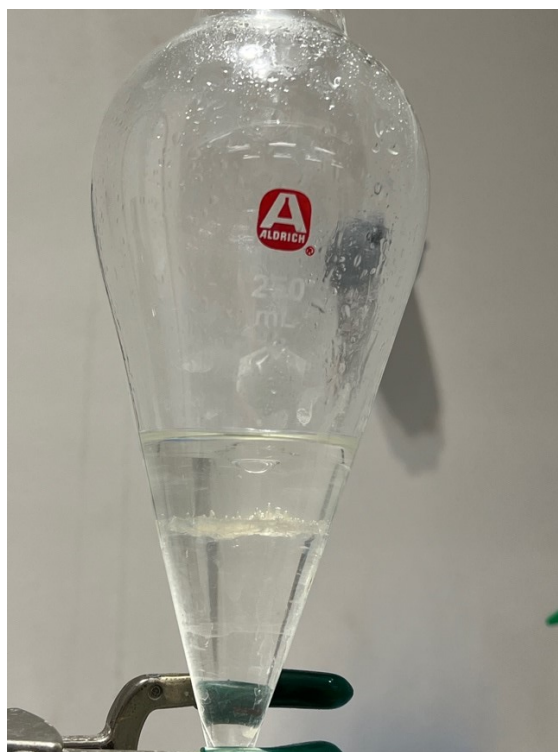


Figure 9 Separation funnel with aqueous phase (product solution from centrifuge) on top and organic phase (dichloromethane) at the bottom

The filtered organic solution was then put into a BUCHI® R-210 rotary evaporation system with a water bath at 47 °C, pressured at 773 mbar, and the coolant temperature set at 18 °C. After around 10 minutes, a dried light-brown solid was seen at the bottom of the evaporation flask. The dried solution was then re-concentrated in 3 mL of HPLC-grade dichloromethane before entering GC-MS.



Figure 10 Overview of the rotary evaporation system

4.5.2 GC-FID/GC-MS

Gas chromatography (GC) is widely utilized in the field of lignin valorization. It is a common type of chromatography used for separating and analyzing the products retained from the degraded lignin.

The GC methods that are used in this project are both GC-FID (Gas Chromatography -Flame Ionization Detector) and GC-MS (Gas Chromatography-Mass Spectrometry). GC-FID, which uses a flame ionization detector, combusts the gaseous organic compounds in a hydrogen flame and the ion generated is proportional to the concentration of the organic species in the sample. For the commercially available products, standard chemicals were purchased for calibration in a range from 0 ppm to 200 ppm and for method validation with the GC-FID for quantitative analysis. Given the low yield of the reaction, the product solution should be concentrated via evaporation described above before being put into the GC-FID. In this GC-FID method, nitrogen is used as the carrier gas and hydrogen, air and the second cylinder of nitrogen is used as the make-up gas. The column used is RXI-5MS, 30 m, 0.25 mm inner diameter. The internal standard method was used for quantification analysis to exclude the environmental influences on the sample injections. The initial temperature is 50 °C and held for 5 minutes, with a temperature ramp of 15 °C/min until the temperature reaches 250 °C and it is then held for another 5 minutes. The internal standard used in this project is 75 ppm (mass based) of 2-Fluorophenol, which is proved to be a distinctive chemical that is not present in the product lists and has a similar chemical structure with the targeted chemicals¹². The calibration curves built with the GC-FID are shown below. The peak area of each standard chemical was normalized to the peak area of the internal standard to decrease the variation between each injection.

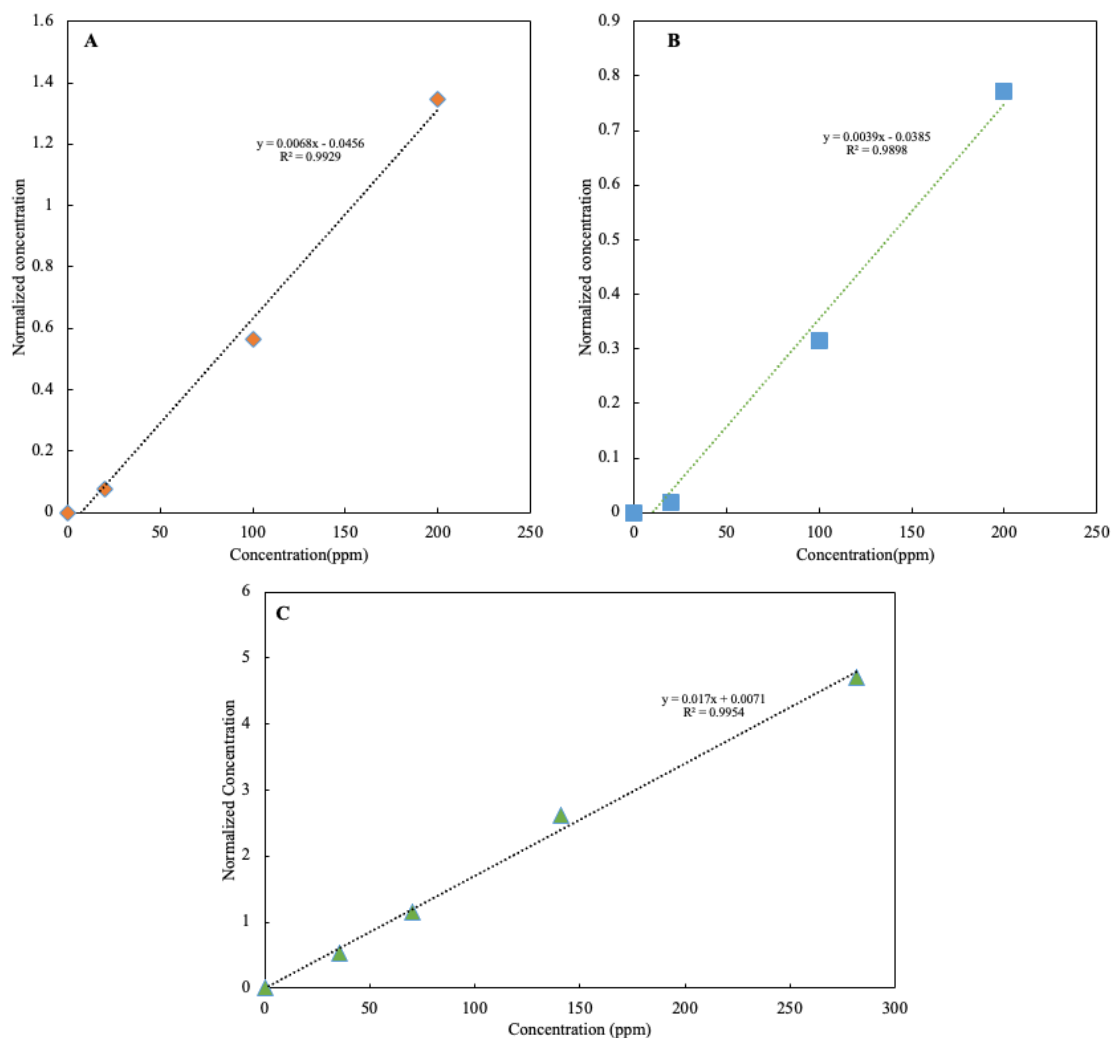


Figure 11 GC-FID Calibration A: Vanillin B: Syringaldehyde C: Guaiacol

However, as the GC-FID results were not as consistent as HPLC (high-performance liquid chromatography) in our tests, it was not selected as the final quantification method. This is because the GC machine used required more frequently maintenance and after each maintenance, the result was found varied to some extent from the old data.

GC-MS (Gas Chromatography-mass spectrometry) is also widely used in the lignin valorization field to identify the product species. The GC-MS was performed on Agilent 6890N with a Rxi-5ms column (length: 30 m, inner diameter: 0.25 mm, film, 0.25 μ m) with

an Agilent 5975B MS detector. The GC-MS test runs for 26 minutes with an initial temperature of 40 °C and the temperature increases at a rate of 15 °C/min and the temperature is maintained at 250 °C until the end of the analysis. Helium was used as the carrier gas at a flow rate of 1.5 mL/min. The ion masses were recorded in the range of 40 to 300 (m/z) in the scan mode. The detected compounds were identified according to the NIST library database. As the reaction time of 1500 s was not long enough for the system to generate enough products to significantly differentiate the products with small yields from the noises, to enlarge the absolute product yield. The electro-oxidative reaction was performed in the same H-cell described above under 1 V vs Ag/AgCl electrode for 10 hours and Ni foam was used for the GC-MS product preparation.

4.5.3 HPLC-UV

After the reaction, a 2 mL reaction solution sample was mixed with an equal volume of 1 M H₂SO₄ to fully precipitate the unreacted lignin. The mixture was then filtered with a 0.2 µL PTFE syringe filter (Sigma-Aldrich) and then analyzed by the HPLC-UV for product quantification. HPLC tests were performed on a Thermo Ultimate 3000 HPLC system using a Thermo Acclaim 300 C-18 column with a UV detector. The mobile phase was prepared according to previous studies⁴⁹ where two solutions A and B were used. Solution A is composed of water, methanol, and acetic acid at a volume ratio of 89:10:1, and solution B is prepared by mixing water, methanol, and acetic acid at 9:90:1. The HPLC method runs for 60 min. It starts with 100% A and a linear gradient of B is run to increase B from 0 to 40% in the first 30 min. After B reached 40%, the mobile phase mixture is held for another 30 min. The results are collected with a UV detector at 280 nm for phenolic compound characterization.⁴⁹

5 Results and discussion

5.1 Proposed schematic for lignin reaction

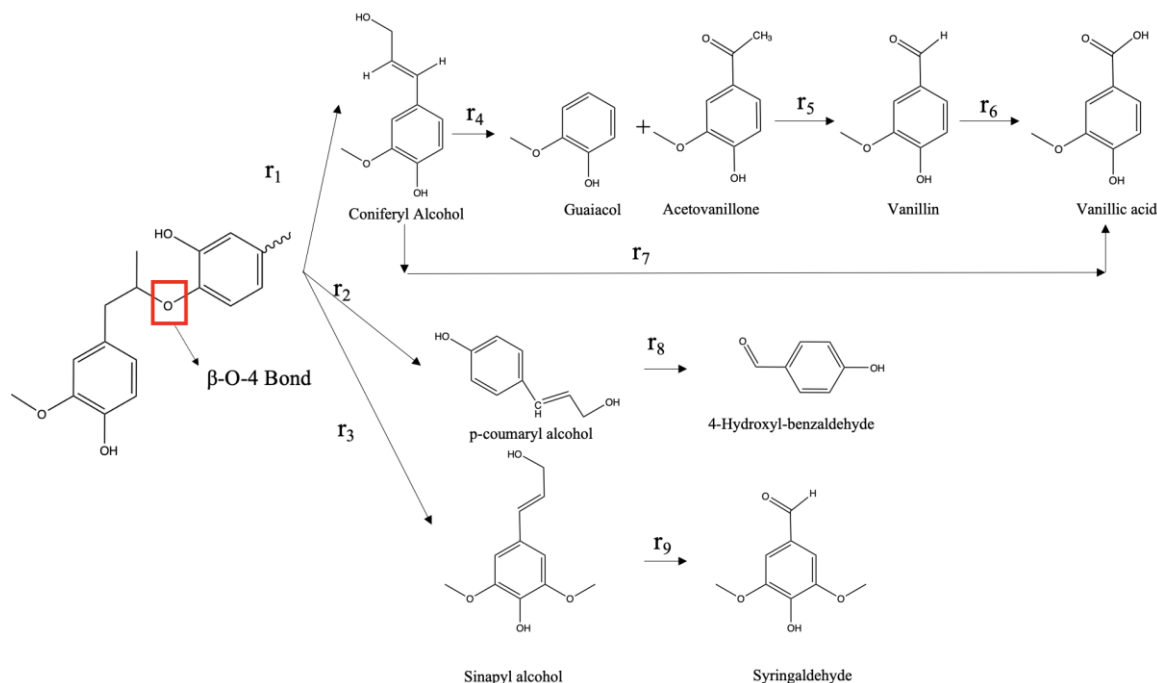


Figure 12 Proposed simplified lignin oxidative depolymerization for aromatic chemical production

Based on the information from the literatures, a simplified mechanism for electrochemical lignin oxidation for this project could then be proposed as shown in Figure 12. The depolymerization of lignin results in the monolignols, G-type, H-type, and S-type monolignols, respectively coniferyl alcohol, p-coumaryl alcohol, and sinapyl alcohol.²² And the main product from lignin depolymerization, vanillin, is derived from the oxidative cleavage of the β -O-4 aryl ether linkage within the lignin polymer and electrochemically transformation of the coniferyl alcohol groups inside the lignin.²⁸ Although syringaldehyde and guaiacol are also deemed as products, in this project however, the change between before

and after the reaction was too minor to draw useful conclusions regarding these two chemicals' yield, as a result, they were not quantified in the latter product analysis section.

In the proposed scheme of this project, the G and S monolignols were then further oxidized into smaller molecules such as guaiacol, vanillin, acetovanillone, and syringaldehyde. However, acetovanillone could also act as an intermediate and be oxidized into vanillin.⁵⁰ Vanillin could be further oxidized into vanillic acid. Besides, it is also possible that vanillic acid can be produced directly from the oxidation of coniferyl alcohol without passing through the intermediate aldehyde state.⁴⁵

5.2 Electrochemical characterization of electrode materials

Firstly, cyclic voltammetry (CV) was performed on all the sputtered materials at a scan rate of 5 mV/s from -0.5 V to 1 V vs Ag/AgCl electrode (saturated in 3 M KCl) as depicted in Figure 13A. Ag, Ni and Cu all showed a reversible pattern in the CV window from -0.5 V to 1 V. Ag showed two oxidation peaks, one at 0.3 V and the other at around 0.68 V, and two reduction peaks at 0.3 V and -0.06 V respectively, where the formation and reduction Ag₂O and AgO occurred.⁵¹ The oxidation peak for Ni was seen at 0.4 V and reduction at 0.25 V. For Cu, a small oxidation peak was seen around 0.33 V and a reduction peak around 0.56 V. In contrast, Cr and Ti only showed their oxidation peak in the first CV cycle and no oxidation nor reduction peak was seen in the later CV tests. This indicates that the electrochemical oxidation and reduction process on the surface of Cr and Ti under the prescribed experimental condition is not reversible in the tested potential window. This also reveals the 'valve properties' of Ti, where surface TiO₂ shows poor conductivity and protects the base layer of Ti.¹⁷ The surface of the catalysts remains in the oxidized form of CrO₂⁵² and TiO₂.¹⁷

For Al, as the catalyst was exposed to open air after the sputtering process, the surface of the catalyst is all oxidized into Al_2O_3 and it did not show any oxidation peak during the entire CV scans. It is acknowledged that under 1 V, the tested metals are all in their oxidated form on the catalyst surface, which aligned with the main objective of this project which is to compare these catalysts under the same applied voltage.

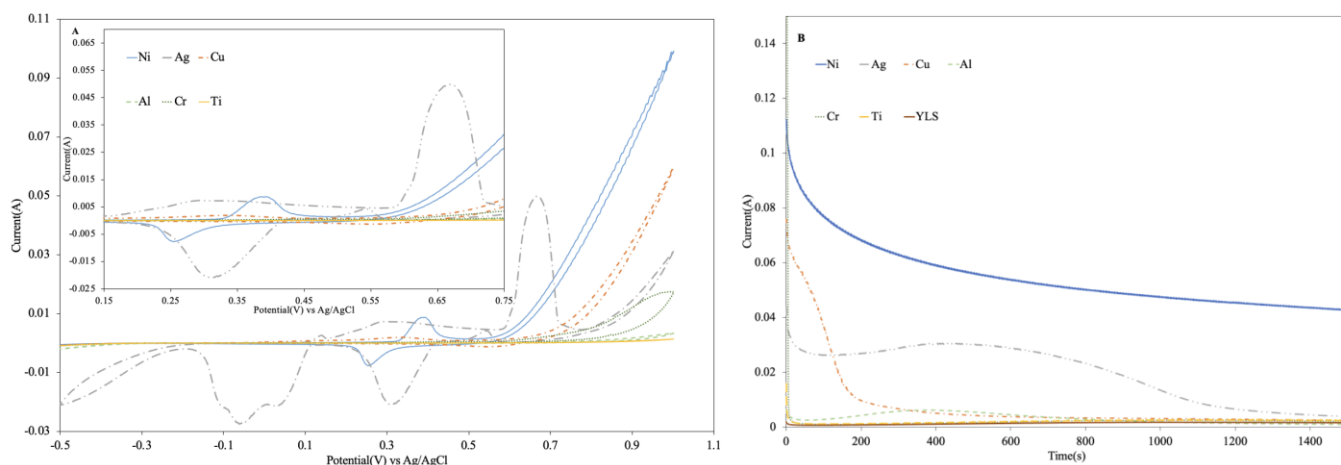


Figure 13 A: Cyclic Voltammetry of tested physical vapor deposited metallic catalysts with 200 nm thickness in 1 M KOH from -0.5 V to 1 V vs Ag/AgCl B: Chronoamperometry test for tested physical vapor deposited metallic catalysts and YLS carbon paper base with 10 g/L Kraft lignin under 1 V

Chronoamperometry (CA) test was conducted under 1 V vs Ag/AgCl for 1500 s where all the metals besides Ni almost completely lost their activity as depicted in Figure 13B. The CA test result shown in Figure 13B illustrates the current response for all the different anode materials. Among all the tested materials, 200 nm Ni showed the highest current density for the longest reaction time, making it the most active anode material for lignin oxidation in this scenario. However, all other metals besides Ag and Ni were deactivated very quickly probably due to the lack of catalytic activity for their metal oxides. It is also worth noting that Cu was more active than Ag in the first 120 seconds, but it was deactivated quickly and

lost its activity after around 600 seconds. Although Ni shows the highest activity, its current density also decreases with time. This phenomenon indicated the deactivation of the catalyst due to the phenolic radical intermediates poisoning the catalyst surface, which was reported in one of the previous studies.⁵³

5.3 Chemical species identification

Besides the targeted compounds vanillin and vanillic acid, GC-MS reveals some of the unknown peaks in the HPLC that no standard chemicals were available for quantification. Several chemicals were identified with the NIST library both increased and decreased. Although not quantified, the relative chemical amount changes were determined by comparing the integrated GC-MS peak area at the same retention time under the same GC-MS operation conditions. To increase the apparent yield for a more concentrated sample for product analysis, the GC-MS sample was prepared using a 1 cm x 1 cm Ni foam electrode under 1 V and reacted for 10 hours.

Table 1 Identified chemical species whose amount was decreased after the reaction

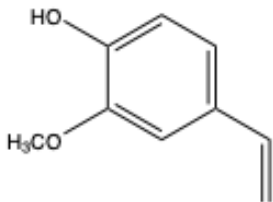
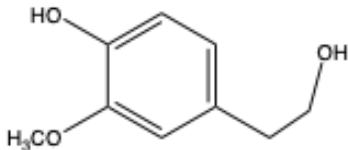
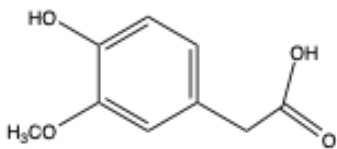
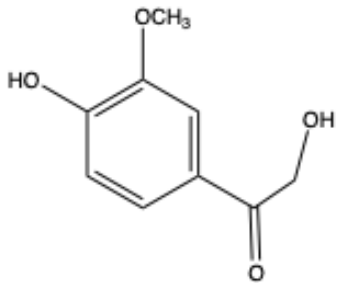
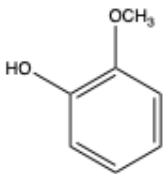
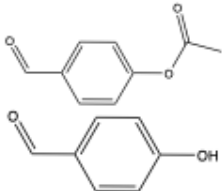
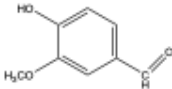
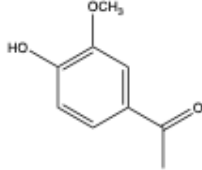
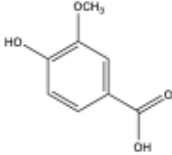
Time(min)	Name	Structure
10.20	2-Methoxy-4-vinylphenol	
12.15	Homovanillyl alcohol	
13.06	Homovanillic acid	
13.32	2,4'-Dihydroxy-3'-methoxyacetophenone	

Table 2 Chemical species whose amount was increased after the reaction

Time(min)	Name	Structure
7.883	Guaiacol	
10.55	4-Acetoxybenzaldehyde OR Benzaldehyde, 4-hydroxy-	
11	Vanillin	
11.76	Acetovanillone	
12.30	Vanillic acid	

It can be found that in our Kraft lignin, most of the identified chemicals were derived from the G unit, inferring that in the tested Kraft lignin, most of the monolignols from depolymerized lignin were coniferyl alcohol. Among the increased compounds, the chemical at the retention time of 10.55 minutes was given two possible options by the NIST library with the same probability. However, as the aromatic products are believed to be derived from

either the G, H, or S group, 4-hydroxy-benzaldehyde is more favorable to be the product as its structure is likely derived from a p-coumaryl group.

5.4 The apparent yield of the targeted chemicals

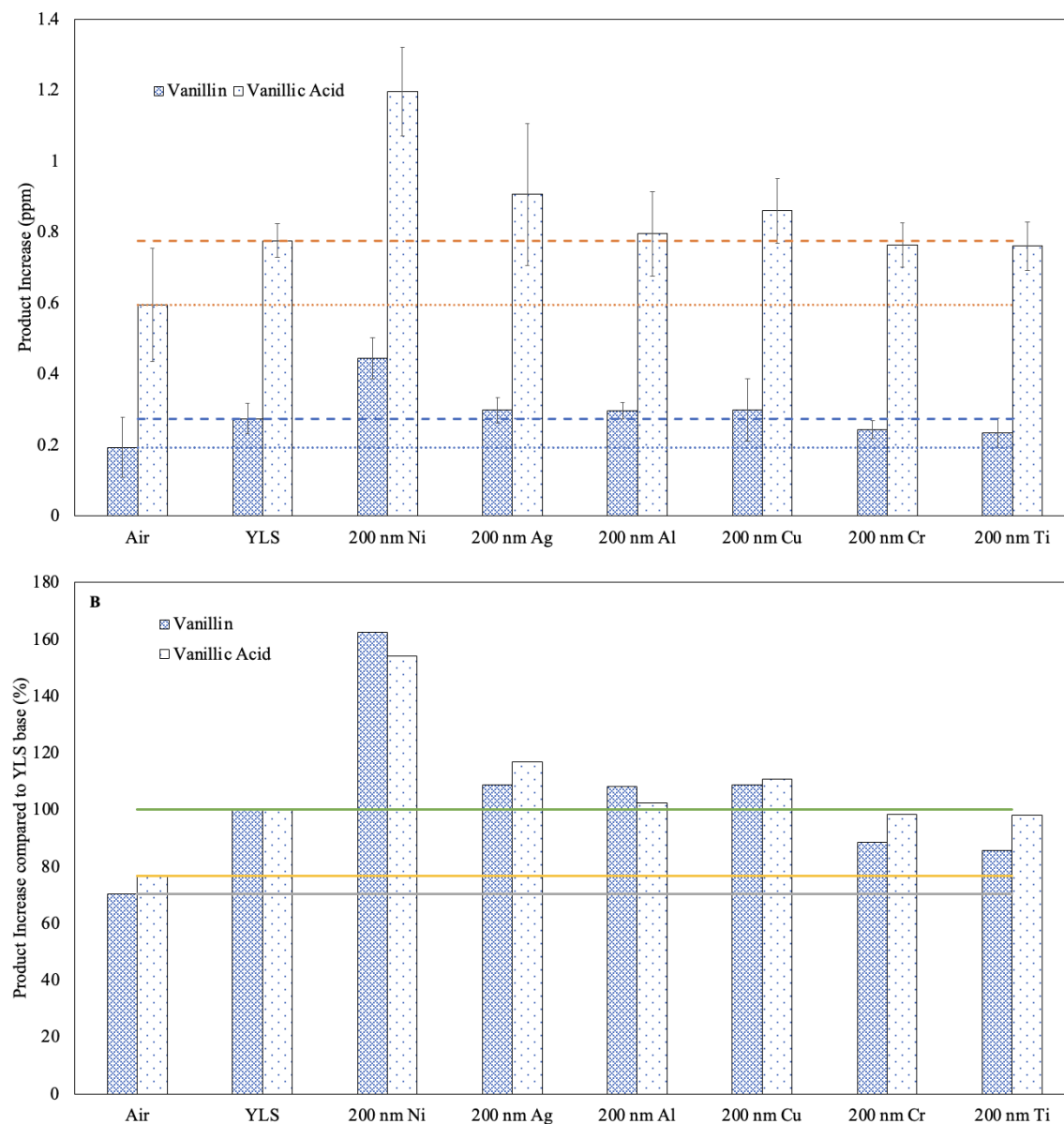


Figure 14 Vanillin and Vanillic acid increase for different anode materials. A: Original concentration in ppm B: normalized to YLS base. The lines are for better visualization for comparison for electricity effects (air) and metallic catalyst effects (YLS carbon paper).

The HPLC was calibrated with standard vanillin and vanillic acid and used to measure the quantity of vanillin and vanillic acid both before and after the reaction. The HPLC results proved the existence of vanillin and vanillic acid in the Kraft lignin solution before the reaction with a concentration of 0.196 ppm and 0.332 ppm respectively. The increase presented was found by subtracting the original amount of vanillin and vanillic acid before reaction from the HPLC measured values for samples after the electrochemical reaction, with a benchmark of stirring in the air without applying electricity to take the oxygen effect from the air into account.

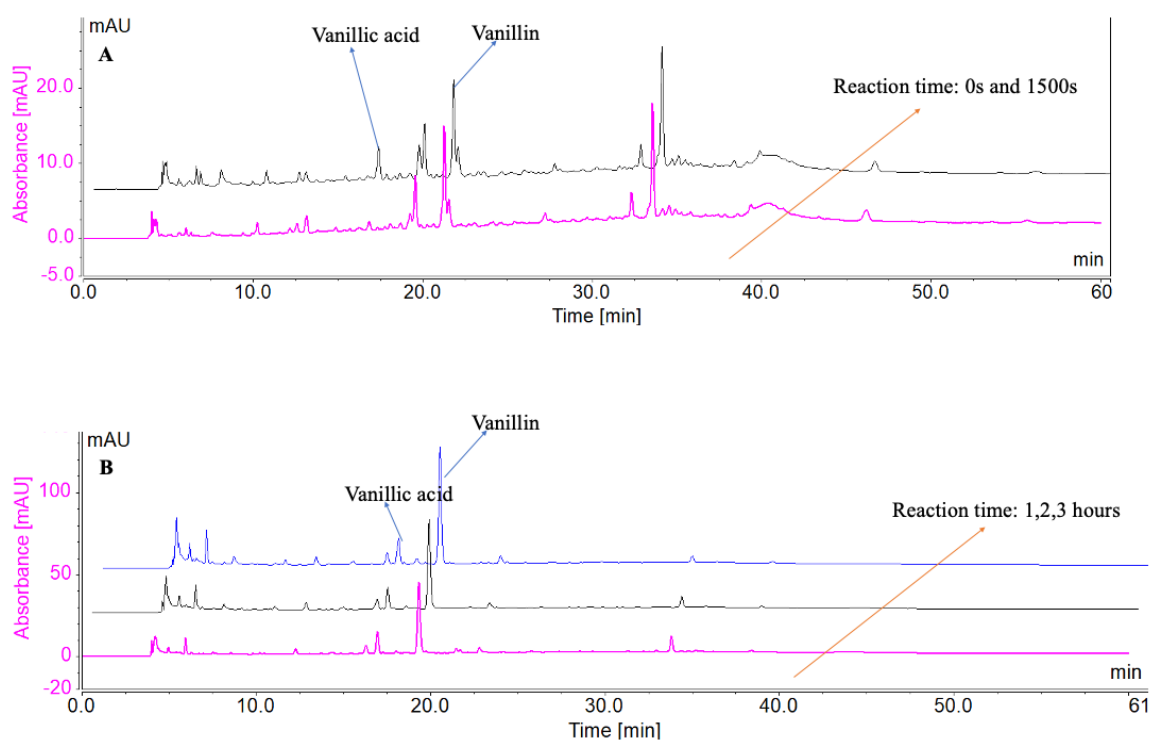


Figure 15 HPLC Chromatogram A: 200 nm Ni before reaction and after 1500 s reaction B: 1 cm x 1 cm Ni foam, after 1, 2, and 3 hours of reaction. Both with 10 g/L Kraft lignin in 1 M KOH and the reaction were under 1 V vs Ag/AgCl. Only the two targeted products were labeled in the HPLC chromatogram.

It is found that almost all electrode materials except Cr and Ti have led to the increase of either vanillin or vanillic acid due to the electrochemistry effects compared to simply stirring in the open air. Besides, when compared to the YLS carbon paper without any sputtered metal, Ni, Ag and Cu showed a relatively significant change toward targeted product generation, which is corresponding to the CA results, where Ni, Ag and Cu led to an increase in current density in lignin reaction.

The 200 nm Ni sample gave the largest yield in both vanillin and vanillic acid compared to non-metal YLS carbon paper, yielding a 62.4% increase in vanillin and a 54.1% increase in vanillic acid compared to YLS carbon paper. Ag and Cu did not show a huge catalytic effect towards vanillin increase compared to bare carbon paper. Previous studies on Ag catalysts can support the view that the AgO catalyst is less selective towards the aldehyde production. It was found in a methanol electrooxidation study that the formate is the only product from methanol.⁵⁴ It was also found in previous studies on methanol oxidation that under 300 K and high surface oxygen coverages, the Ag surface reconstructs into AgO which tends to suppress the selectivity of formaldehyde formation.⁵⁵ While maintaining a similar vanillin yield as pure carbon paper, Ag and Cu sputtered catalysts promoted the vanillic acid generation with a 16.8% and 10.8% increase compared to carbon paper samples. In contrast, Al did not show any improved catalytic effect towards either of the targeted chemicals. Cr and Ti maintained the vanillic acid yield level as the carbon paper while their vanillin yield decreased by 11.5% and 14.4% respectively, indicating the over-oxidation effects of vanillin⁹ surpassed the rate of vanillin generation. The slight decrease in vanillic acid yield for Cr and Ti can be also attributed to over-oxidation of vanillic acid. According to a previous study, the most possible aromatic product that the vanillic acid was converted to is protocatechuic

acid⁵⁶, or it was over-oxidized into gas products as CO₂.⁴⁰ However, due to the low conversion rate, the oxidation product of vanillic acid was not identified nor quantified in this work.

5.5 ECSA Normalized yield

To better compare the intrinsic property of the catalyst material and normalize the effects from surface area, shape, and morphology of the catalyst, a metric should be used to normalize the apparent yields. Thus, an electrochemical active surface area (ECSA) normalization was proposed for the lignin product analysis, where the yields for both vanillin and vanillic acid are normalized to the measured ECSA, regardless of the catalyst structure and thickness. The method of ECSA measurement through electrochemical double-layer capacitance (C_{DL}) was adapted from a previous study on the OER.⁴⁷

$$\text{ECSA} = \frac{C_{\text{DL}}}{C_s} \quad \text{Equation 1}$$

As the specific capacitance C_s was assumed the same for catalysts under the same electrolyte condition, the ECSA normalization was simply conducted by normalizing the apparent yield to the C_{DL} values.

$$\frac{\text{ECSA}_1}{\text{ECSA}_2} = \frac{C_{\text{DL1}}}{C_s} \times \frac{C_s}{C_{\text{DL2}}} = \frac{C_{\text{DL1}}}{C_{\text{DL2}}} \quad \text{Equation 2}$$

Thus, the ECSA normalized yield would be,

$$\frac{\text{Yield}_1/C_{DL1}}{\text{Yield}_2/C_{DL2}} = \frac{\text{Yield}_1 C_{DL2}}{\text{Yield}_2 C_{DL1}} \quad \text{Equation 3}$$

To assess the intrinsic characteristic of the deposited 200 nm Ni which gave the best apparent yield for both vanillin and vanillic acid among all the 200 nm samples, a 1 cm × 1 cm Ni foam, which was a widely tested material for lignin electrochemical valorization in previous studies,⁹ and a thinner layer of 100 nm Ni sample were tested for 1500 s under the same experimental condition and used as a benchmark for the deposited Ni catalyst.

Table 3 ECSA Normalization of Ni-based catalysts product yield

Catalyst	Vanillin	Vanillic Acid	C _{DL} (mF)	ECSA Normalized	ECSA Normalized
Type	Apparent	Apparent		Vanillin Yield	Vanillic Acid Yield
	Yield after	Yield after		(ppm/mF)	(ppm/mF)
	1500 s (ppm)	1500 s (ppm)			
Ni foam	4.35	3.49	0.0002	21725	17450
200 nm Ni	0.44	1.19	0.00008	5550	15240
100 nm Ni	0.43	1.28	0.00004	10713	31878

From the apparent product yields, it is observed that Ni foam has yielded 9.78 times more vanillin and 2.86 times more vanillic acid in the apparent yield than the 200 nm Ni catalyst. Based on the double layer capacitance measurement, it was found that Ni foam possesses 2.5 times more active area than 200 nm Ni, suggesting that using porous structured materials could improve the production per active surface area for both vanillin and vanillic acid.

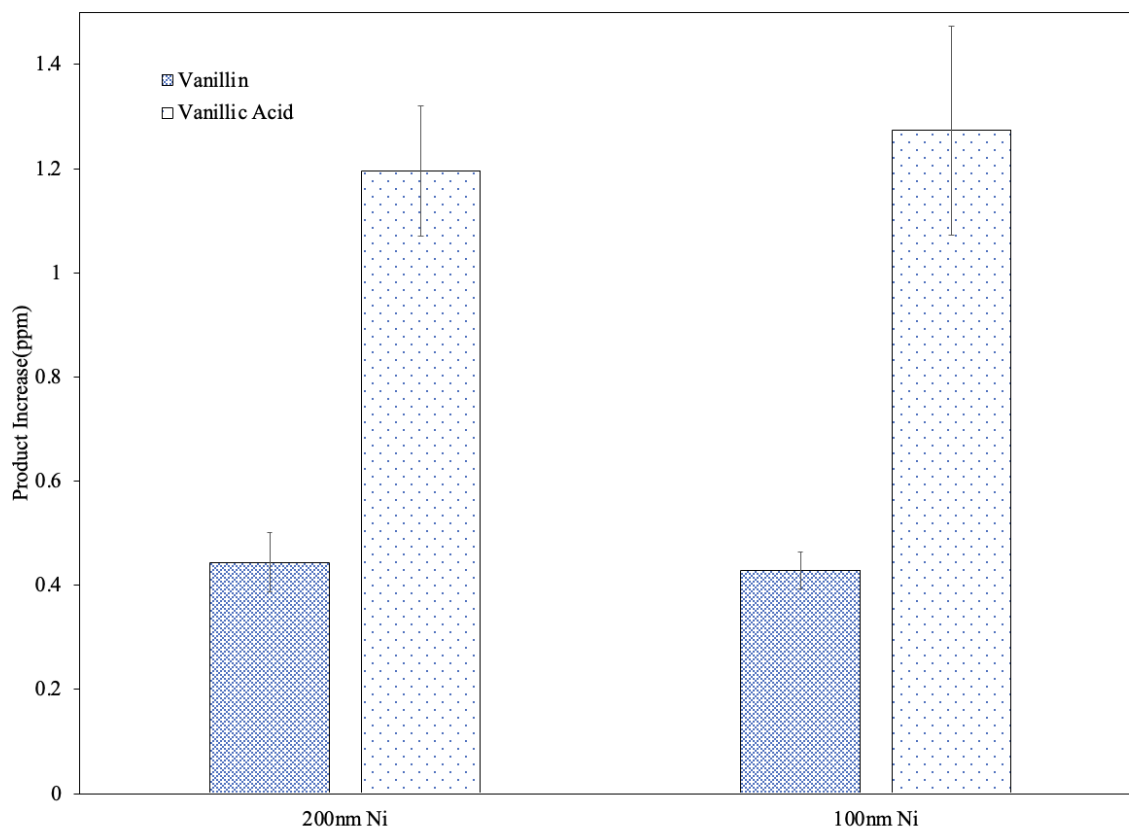


Figure 16 Vanillin and Vanillic acid yield comparison for 200nm Ni and 100nm Ni samples

When compared to the 200 nm Ni, the vanillin and vanillic acid apparent yield of the 100 nm Ni remained at a similar level as shown in Figure 16 only with half ECSA as the thicker sample. As a result, the 100 nm Ni demonstrated higher vanillin and vanillic acid yield per active surface area. Surprisingly, its normalized vanillic acid yield is even higher than that of Ni foam, indicating that thinner layer of 100 nm Ni sample prepared by physical vapor deposition could significantly make the reaction more selective towards vanillic acid.

5.6 Effects from the OER and charge efficiency

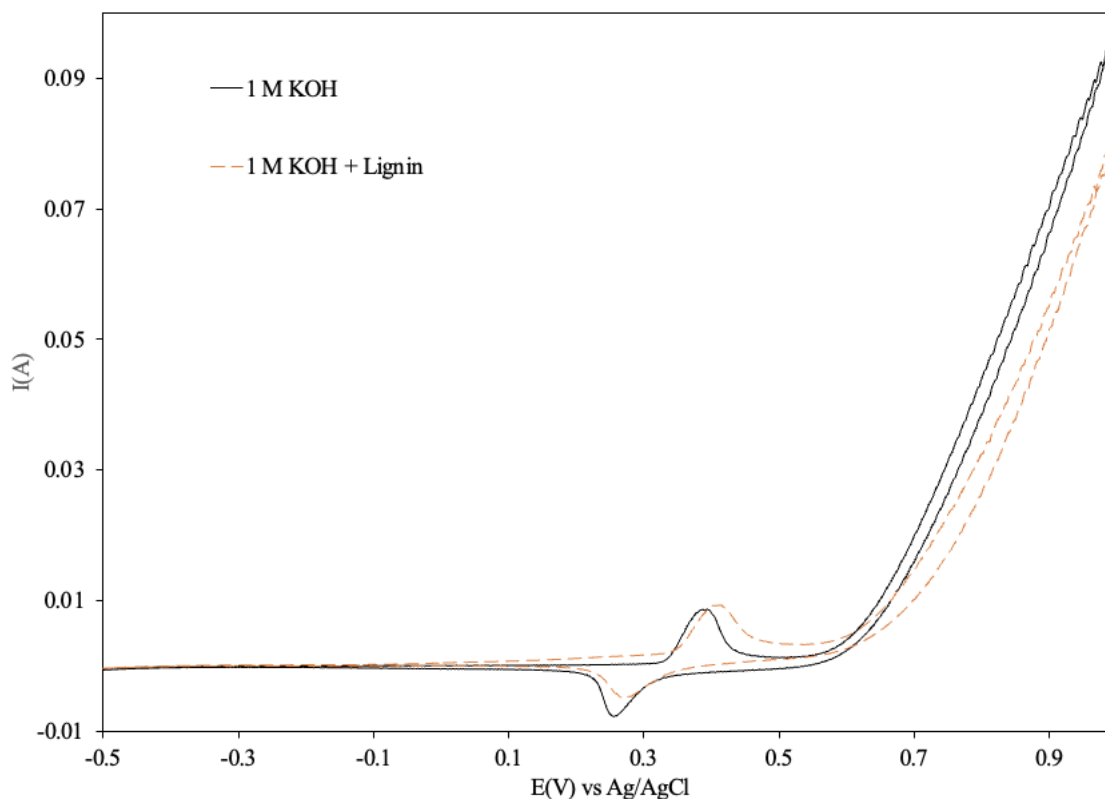


Figure 17 CV scans with 200 nm Ni with (orange) and without (black) Kraft lignin

Comparing the CV scans for 200 nm Ni sample in 1 M KOH with and without adding lignin as shown in Figure 17, it was found that the current density was higher with lignin presence and Ni^{2+} before the Ni oxidation peak at 0.4 V. After the Ni^{2+} was oxidized to Ni^{3+} , the current density difference became larger, which indicates that the Ni^{3+} in NiOOH have a higher activity towards lignin oxidation.³³ The current density was found lower with lignin present in the system in the OER region after 0.6 V, indicating that the lignin reaction suppresses the OER reaction.

It was observed that stirring at 400 rpm in the air also leads to a slight increase in vanillin and vanillic acid as shown in Figure 14, indicating that the presence of oxygen also helps the oxidation of lignin. As a result, it is reasonable to postulate that the OER might not serve only as the side reaction that is competing with the lignin-oxidation for the electron supply, but also helps the lignin oxidation to some extent.

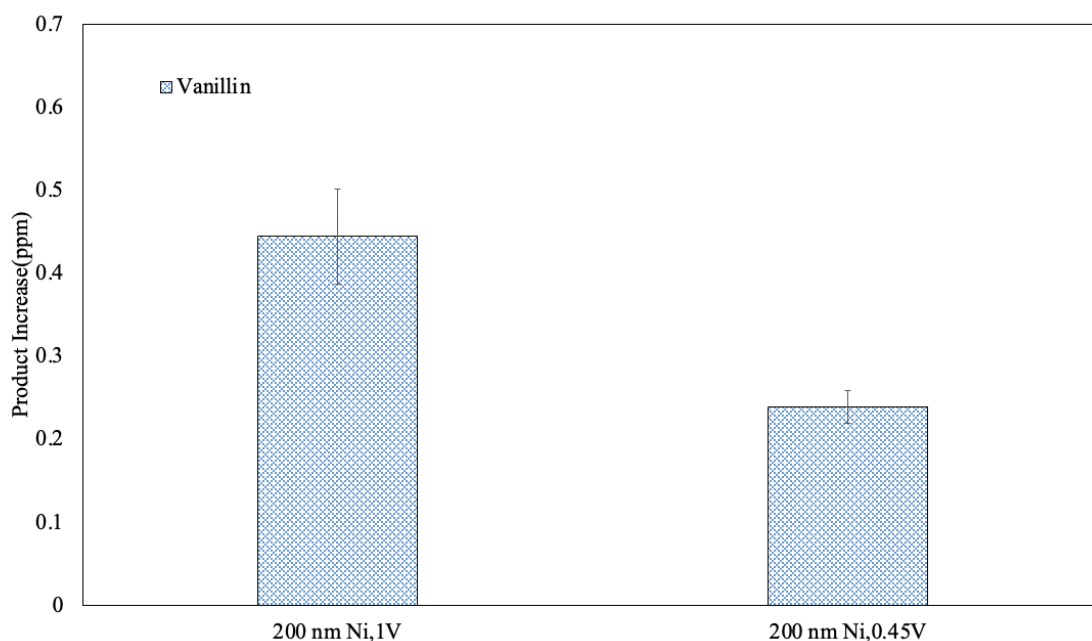


Figure 18 Vanillin yield difference due to applied potential difference

To investigate the role of OER in the lignin electro-oxidation process, 200 nm Ni was tested under 0.45 V, which is after the Ni oxidation peak where the catalyst surface is believed to be oxidized to Ni^{3+} but not high enough for OER to occur. The result showed that without the OER, the vanillin yield decreased significantly even with the presence of Ni^{3+} , indicating that higher voltage is helping the lignin oxidation process towards more vanillin yield with the presence of OER.

To exclude the effect from dissolved oxygen in the solution, N₂ was purged for 20 minutes before applying constant potential and the reaction was conducted under 1 V with the N₂ continuously being purged to decrease the oxygen level in the solution. It was found that with N₂ purging, the vanillin production decreased by 47% compared to without N₂ purging with 100 nm Ni as the catalyst.

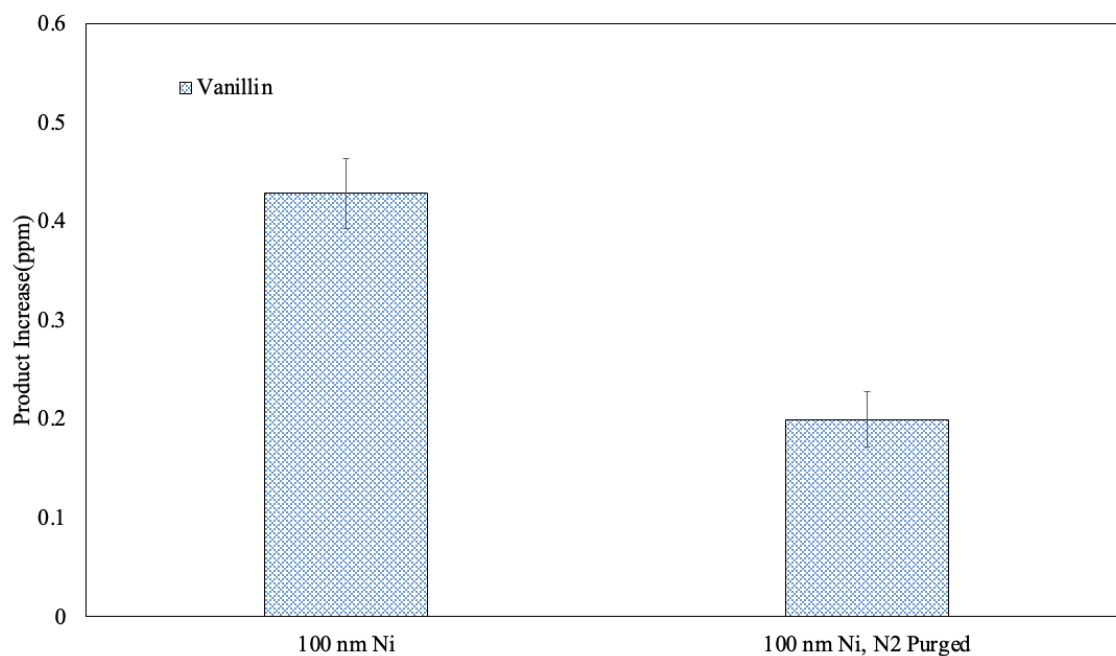


Figure 19 Vanillin production due to the purge of nitrogen gas with 100nm Ni under 1 V for 1500 s

The role of the OER thus can be treated as both a competition reaction that consumes electrons for oxygen generation and a factor that accelerates the lignin oxidation reaction for more vanillin and vanillic acid yield. To balance these two characteristics from the OER, a new metric should be proposed to quantify the electrons that go to the wasted oxygen that escaped the system versus the oxygen that helps the lignin reaction. In traditional electrochemistry, Faradaic efficiency (FE) is usually used for characterizing this

phenomenon. However, the Faradaic efficiency (FE) has not been reported in the field of lignin electro-oxidation as it is challenging to calculate FE because of the natural variety of lignin structures, with varying pathways of product generation and the number of electrons transferred for each pathway. Besides, the electron transfer cannot be monitored for those unidentified and unquantified products. Previous study has used an estimated count of 4 transferred electrons per mole of product generation,³³ however, each product might have different reaction pathways and a fixed number might not be reflective for all products. As an alternative, we propose a new metric for energy efficiency (ε) for lignin product analysis based on the total charge supply, where we treated the n (charge transfer per mol of product) as a black box parameter, neglected the Faraday constant as it is a constant and do not interfere with the relative comparison. The apparent product concentration increase (c) compared to before reaction lignin solution was used as the substitution for the molar amount for the product due to the relatively low yield rate, as shown in Equation 4 and Equation 5. Charge supply was monitored for both tests and the vanillin and vanillic acid yield was then normalized to the total charge consumed as a representative measure for their charge efficiency.

$$\text{FE (Faradaic Efficiency)} = \frac{n \times F \times \text{mol}}{C_{\text{total}}} \quad \text{Equation 4}$$

$$\varepsilon = \frac{c}{C_{\text{total}}} \quad \text{Equation 5}$$

As tested in the ECSA normalization section above, as shown in Figure 16, thinner layer of 100 nm Ni had similar level of vanillin and vanillic acid production rate as the thicker 200

nm Ni catalyst. However, from the CA tests, the charge supply for these two catalysts was different as depicted in Figure 20.

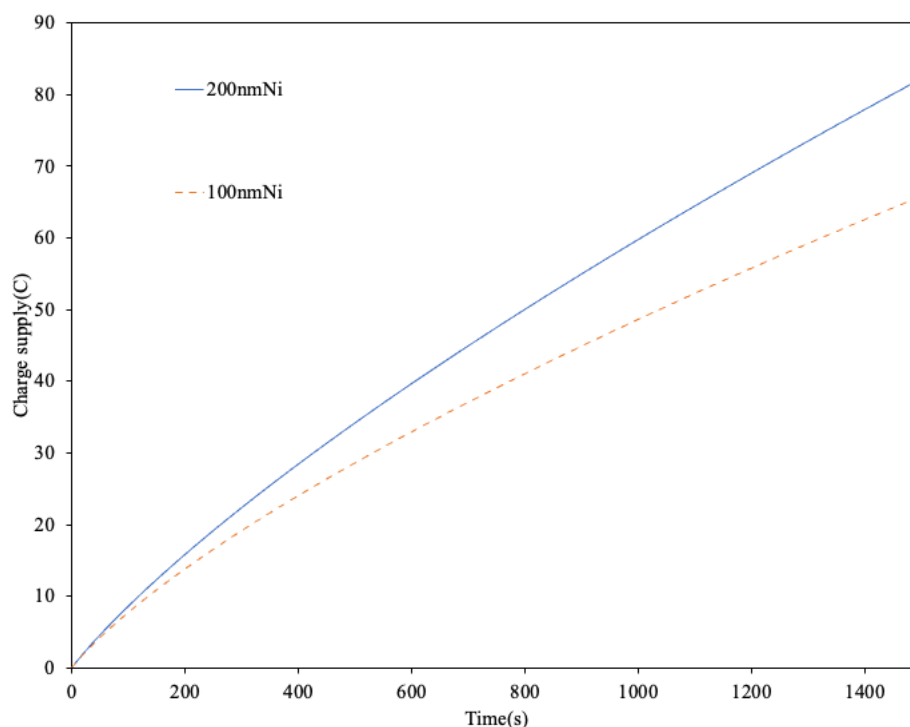


Figure 20 Total charge transfer for 200nm Ni sample and 100nm Ni sample

Throughout the whole 1500 s reaction time, 200 nm Ni consumed 82 C of charges while 100 nm Ni consumed 65 C of charges. Moreover, 100 nm Ni maintained 96.5% vanillin yield and generated 105% yield of vanillic acid compared to the 200 nm Ni sample. As a result, per Coulomb of charge supplied, thinner layer of deposited Ni catalyst is able to maintain the high vanillin and vanillic acid production while saving the supplied electricity.

Along with the OER suppression phenomenon at 1 V as shown in the cyclic voltammetry in Figure 17 as well as the results from ECSA normalization, it is reasonable to postulate that

due to the bulky polymeric molecular structure of lignin, the mass transfer is intrinsically difficult for lignin. While the OER can be generated in porous Ni layer in alkaline solution, lignin molecules cannot access the inner-layer Ni sites and be oxidized. As a result, to have higher reaction selectivity and charge selectivity toward lignin oxidation, we either need to have thinner layer of active catalyst as 100 nm Ni, or foam-like 3D material as Ni foam to allow macro molecules to go through with better flow patterns.

6 Conclusion

In this work, six different metal catalysts prepared with the vapor deposition method were tested in a H-cell setup under room temperature and pressure for Kraft lignin oxidation. From the GC-MS method, various aromatic compounds such as vanillin, vanillic acid, and guaiacol were identified. Two targeted chemicals in this project, vanillin and vanillic acid, were also quantified with HPLC and 200 nm Ni was selected for further analysis for its higher apparent yield among all the tested single metallic catalysts. To address the one of the many current challenges in this field that is the lack of specific and useful metrics to evaluate the catalysts due to the complex nature of lignin, ECSA normalization and charge efficiency were proposed as two novel metrics to consider in the field of lignin electro-oxidation. The ECSA normalization accounts for different shapes and morphology of the catalyst surface that can result in different active areas given the same geometric area. The supplied charge normalization acts as an alternative for Faradaic efficiency in this field to evaluate the charge efficiency for different catalysts. It was found that after ECSA normalization, Ni foam showed higher production rate towards vanillin per active surface area while less increase was seen for vanillic acid generation per active area. Thinner deposited Ni catalyst also showed higher vanillin and vanillic acid generation per active surface area and its ECSA normalized vanillic acid production was even higher than that of Ni foam. It was also found through the supplied charge normalization that the thinner deposited Ni layer can maintain a relatively high increase for targeted products while demanding less electric charge. These two metrics could be applied to future lignin electrocatalytic valorization projects in designing more porous while thinner layered catalysts, lending more insights towards the electrochemistry side into the field besides the overall yield of targeted compounds.

7 Limitations and Future Directions

7.1 Limitations

The author acknowledges that in the 0.45 V, 200 nm Ni test shown in Figure 18 and the N₂ purged test shown in Figure 19, the HPLC experienced unknown issues with the column used where its vanillic acid detection was malfunctioning whereas the vanillin results were correctly measured. The tests were repeated several times and confirmed that there was no human error. However, as these two tests were done in the very late part of the project for validation purposes, the vanillic acid results were non-comparable with the previous shown results as in Figure 14. As a result, only the vanillin results were reported. Also, in this thesis, no material characterization was included, to characterize the electrode surfaces, X-ray photoelectron spectroscopy (XPS) could be used to characterize the oxidation states of the catalyst surface. In addition, lignin conversion was not calculated in this project. However, after acidification for both before and after reaction lignin solution, the lignin solid can be washed and dried. By comparing the weight difference of the two lignin solids, lignin conversion can be estimated.

7.2 Reaction under elevated temperature

The tests done in this project were all conducted under ambient temperature and pressure. However, there were many tests that is reporting higher absolute product yield with an undivided cell setup under elevated reaction temperatures^{9,53} and it is reasonable to postulate that applying higher temperature with an H-cell reactor would also increase the product yield. In future works, to investigate the possible outcomes for lignin oxidative reaction in an H-cell reactor with higher temperature under 100 °C avoiding the boiling of the aqueous

electrolyte. Future work could also be designed with a customized H-cell that can endure higher temperatures and pressure while not boiling the electrolyte. Such experimental design would be interesting to investigate the oxidative effect of different catalysts on lignin.

7.3 HPLC-MS product identification

In this project, GC-MS was used for product identification and HPLC-UV was used for major product quantification. However, even the extraction-evaporation method was widely used in the field of lignin valorization by Li's, Staser's and Waldvogel's research group in their previous studies,^{9,12,19} there is inevitable product loss in the extraction process. Given the nature that the current absolute yield of lignin oxidation product is relatively low, in the product identification process, less processing should be applied in order to maintain an intact product profile after lignin oxidation. HPLC-MS was used by Di Fidio et al.³³ in one of the previous studies for P1000 soda lignin H-cell testing with Ni/NiOOH wire as their working catalyst and 14 products were identified. Through the application of HPLC-MS, the product loss during sample preparation process could be potentially reduced. It could be also combined with HPLC-UV as a HPLC-UV-MS system to integrate the product identification as well as the product quantification, making it easier for the researchers to conduct the product analysis processes.

7.4 Lignin structure and reaction kinetics characterization

One of the most challenges in the field of lignin valorization is the characterization of the lignin structure as it is a polymer mixture whose structure varies from its plant origins. Although there have been analytical techniques such as FT-IR and HSQC-NMR could be used to detect the G and S units⁵⁷ and the organic linkages⁵⁸ respectively. Additionally, GPC

could also be used for lignin depolymerization characterization by detecting its distribution of molecular masses. It still requires extra effort to come up with a systematic strategy to characterize the structure of the lignin with varying origins.

Without the exact lignin structure, it is then difficult to monitor the charge transfer between the chemicals as well as propose the exact reaction scheme based on the charge transfer and the redox pathways. As a result, it is essential for future researchers to put more effort on a systematic characterization process using different analytical chemistry techniques to characterize a lignin mixture. It would be helpful if the proposed method can be universally applied to different types of lignin. From there, a lot of deep investigation regarding the lignin depolymerization reaction schematic could be proposed. It would also open the gate for computational modeling work such as designed DFT experiments to discover suitable catalysts for lignin oxidation.

7.5 Multi-Metallic systems

In this project, the metallic catalysts tested were all single metal catalysts. However, bi-metallic catalysts such as Ni-Co have been tested on lignin valorization that could synergistically combine both the catalytic effect where higher Co content can lower the energy requirement as well as add more surface area to the Ni catalyst due to its roughness.¹² As Cu and Ag also showed a catalytic effect although with low stability, the Ni-Cu and Ni-Ag bimetallic systems or even tri-metallic systems like Ni-Co-Cu or Ni-Co-Ag with different metal ratios on the surface of the catalyst could be tested for vanillin production as well as identifying new products through Mass Spectrometry. It is also possible that different bi- or tri-metallic catalysts would result in a difference in product selectivity, where other chemicals,

such as guaiacol and syringaldehyde, might become the main product rather than vanillin which is most frequently reported in the current studies.

Besides finding the best pairing of the bi- or tri-metallic combination, it is also important to optimize the catalyst by investigating different synthesis methods and the improving morphology design of the catalyst surface. To acquire more insights, electrochemical experiments should be systematically applied to further characterize the electrocatalysts along with a deeper understanding of the lignin reaction pathway.

7.6 Apply model compound results on real lignin

With the status quo being the lignin structure unknown, it is informative to predict the reaction mechanism and study the insights of a certain reaction pathway, such as the β -O-4 linkage cleavage with external oxidants such as tert-butyl hydroperoxides,⁵⁸ mediators such as 2,2,6,6-tetramethyl-1-piperidine N-oxyl (TEMPO) and 4-Acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl (ACT)⁵⁹ and the investigation of the pathway for transformation of lignin-related aromatic chemicals, such as reduction of guaiacol and phenols.⁶⁰ All these experiments with trackable chemicals could provide insights guiding the future application on real lignin. Future studies could be on the possible adaption of the well-performing catalysts or electrochemical systems from model compounds towards real-world lignin.

7.7 Closing Remarks

This study of the electro-oxidative lignin valorization successfully established a benchmark for 6 different kinds of metals, proposed novel metrics for lignin product analysis and discussed the potential effects from the OER. Hopefully his advancement could serve as a guidance for future investigations towards lignin electro-oxidative reactions.

8 References

- 1 Dale, B. E. ‘Greening’ the chemical industry: research and development priorities for biobased industrial products. *Journal of Chemical Technology & Biotechnology* **78**, 1093-1103 (2003). <https://doi.org/10.1002/jctb.850>
- 2 Zakzeski, J., Bruijninx, P., Jongerius, A. & Weckhuysen, B. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chemical reviews* **110**, 3552-3599 (2010). <https://doi.org/10.1021/cr900354u>
- 3 Ghahremani, R., Farales, F., Bateni, F. & Staser, J. A. Simultaneous Hydrogen Evolution and Lignin Depolymerization using NiSn Electrocatalysts in a Biomass-Depolarized Electrolyzer. *Journal of The Electrochemical Society* **167** (2020). <https://doi.org/10.1149/1945-7111/ab7179>
- 4 Rinaldi, R. *et al.* Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angewandte Chemie International Edition* **55**, 8164-8215 (2016). <https://doi.org/10.1002/anie.201510351>
- 5 Chatel, G. & Rogers, R. D. Review: Oxidation of Lignin Using Ionic Liquids—An Innovative Strategy To Produce Renewable Chemicals. *ACS Sustainable Chemistry & Engineering* **2**, 322-339 (2014). <https://doi.org/10.1021/sc4004086>
- 6 Nowakowski, D. J., Bridgwater, A. V., Elliott, D. C., Meier, D. & de Wild, P. Lignin fast pyrolysis: Results from an international collaboration. *Journal of Analytical and Applied Pyrolysis* **88**, 53-72 (2010). <https://doi.org/10.1016/j.jaap.2010.02.009>
- 7 Riyadi, F. A. *et al.* Enzymatic and genetic characterization of lignin depolymerization by *Streptomyces* sp. S6 isolated from a tropical environment. *Scientific Reports* **10**, 7813 (2020). <https://doi.org/10.1038/s41598-020-64817-4>
- 8 Axelsson, L. *et al.* Jatropha cultivation in southern India: assessing farmers' experiences. *Biofuels, Bioproducts and Biorefining* **6**, 246-256 (2012). <https://doi.org/10.1002/bbb.1324>
- 9 Zirbes, M. *et al.* High-Temperature Electrolysis of Kraft Lignin for Selective Vanillin Formation. *ACS Sustainable Chemistry & Engineering* **8**, 7300-7307 (2020). <https://doi.org/10.1021/acssuschemeng.0c00162>
- 10 Zirbes, M. *et al.* Anodic Degradation of Lignin at Active Transition Metal-based Alloys and Performance-enhanced Anodes. *ChemElectroChem* **6**, 155-161 (2019). <https://doi.org/10.1002/celec.201801218>
- 11 Movil, O., Garlock, M. & Staser, J. A. Non-precious metal nanoparticle electrocatalysts for electrochemical modification of lignin for low-energy and cost-effective production of hydrogen. *International Journal of Hydrogen Energy* **40**, 4519-4530 (2015). <https://doi.org/10.1016/j.ijhydene.2015.02.023>
- 12 Ghahremani, R. & Staser, J. A. Electrochemical oxidation of lignin for the production of value-added chemicals on Ni-Co bimetallic electrocatalysts. *Holzforschung* **72**, 951-960 (2018). <https://doi.org/10.1515/hf-2018-0041>
- 13 Yan, K., Zhang, Y., Tu, M. & Sun, Y. Electrocatalytic Valorization of Organosolv Lignin Utilizing a Nickel-Based Electrocatalyst. *Energy & Fuels* **34**, 12703-12709 (2020). <https://doi.org/10.1021/acs.energyfuels.0c02284>
- 14 Zhang, Y.-m., Peng, Y., Yin, X.-l., Liu, Z.-h. & Li, G. Degradation of lignin to BHT by electrochemical catalysis on Pb/PbO₂ anode in alkaline solution. *Journal of*

- Chemical Technology & Biotechnology* **89**, 1954-1960 (2014).
<https://doi.org:10.1002/jctb.4282>
- 15 Wang, Y.-s., Yang, F., Liu, Z.-h., Yuan, L. & Li, G. Electrocatalytic degradation of aspen lignin over Pb/PbO₂ electrode in alkali solution. *Catalysis Communications* **67**, 49-53 (2015). <https://doi.org:10.1016/j.catcom.2015.03.033>
 - 16 Liu, M., Wen, Y., Qi, J., Zhang, S. & Li, G. Fine Chemicals Prepared by Bamboo Lignin Degradation through Electrocatalytic Redox between Cu Cathode and Pb/PbO₂ Anode in Alkali Solution. *ChemistrySelect* **2**, 4956-4962 (2017).
<https://doi.org:10.1002/slct.201700881>
 - 17 Jia, Y. *et al.* Electrocatalytic degradation of rice straw lignin in alkaline solution through oxidation on a Ti/SnO₂-Sb₂O₃/α-PbO₂/β-PbO₂ anode and reduction on an iron or tin doped titanium cathode. *Catalysis Science & Technology* **8**, 4665-4677 (2018). <https://doi.org:10.1039/c8cy00307f>
 - 18 Cai, P. *et al.* Electrochemical conversion of corn stover lignin to biomass-based chemicals between Cu/NiMoCo cathode and Pb/PbO₂ anode in alkali solution. *Electrochimica Acta* **264**, 128-139 (2018).
<https://doi.org:https://doi.org/10.1016/j.electacta.2018.01.111>
 - 19 Lan, C., Fan, H., Shang, Y., Shen, D. & Li, G. Electrochemically catalyzed conversion of cornstalk lignin to aromatic compounds: an integrated process of anodic oxidation of a Pb/PbO₂ electrode and hydrogenation of a nickel cathode in sodium hydroxide solution. *Sustainable Energy & Fuels* **4**, 1828-1836 (2020).
<https://doi.org:10.1039/c9se00942f>
 - 20 Bateni, F., Ghahremani, R. & Staser, J. A. Electrochemical oxidative valorization of lignin by the nanostructured PbO₂/MWNTs electrocatalyst in a low-energy depolymerization process. *Journal of Applied Electrochemistry* **51**, 65-78 (2020).
<https://doi.org:10.1007/s10800-020-01451-y>
 - 21 Calvo-Flores, F. G. & Dobado, J. A. Lignin as renewable raw material. *ChemSusChem* **3**, 1227-1235 (2010). <https://doi.org:10.1002/cssc.201000157>
 - 22 Calvo-Flores, F. G. & Dobado, J. A. Lignin as Renewable Raw Material. *ChemSusChem* **3**, 1227-1235 (2010).
<https://doi.org:https://doi.org/10.1002/cssc.201000157>
 - 23 Li, C., Zhao, X., Wang, A., Huber, G. W. & Zhang, T. Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem Rev* **115**, 11559-11624 (2015). <https://doi.org:10.1021/acs.chemrev.5b00155>
 - 24 Silva, E. A. B. d. *et al.* An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. *Chemical Engineering Research and Design* **87**, 1276-1292 (2009). <https://doi.org:https://doi.org/10.1016/j.cherd.2009.05.008>
 - 25 Esposito, L. J. *et al.* in *Kirk - Othmer Encyclopedia of Chemical Technology* (2000).
 - 26 Lersch, M. in *BIOREF-INTEG Workshop* (Solihull, UK, 2009).
 - 27 Hans Evju, S., Norway. PROCESS FOR PREPARATION OF 3-METHOXY-4-HYDROXYBENZALDEHYDE. (1979).
 - 28 Mathias, A. L. & Rodrigues, A. E. Production of Vanillin by Oxidation of Pine Kraft Lignins with Oxygen. **49**, 273-278 (1995).
<https://doi.org:doi:10.1515/hfsg.1995.49.3.273>

- 29 Tarabanko, V. & Petukhov, D. Study of mechanism and improvement of the process of oxidative cleavage of ligins into the aromatic aldehydes. *Chem. Sustainable Dev.* **11**, 655-667 (2003).
- 30 Vij, V. *et al.* Nickel-Based Electrocatalysts for Energy-Related Applications: Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution Reactions. *ACS Catalysis* **7**, 7196-7225 (2017). <https://doi.org/10.1021/acscatal.7b01800>
- 31 Grill, J. M., Ogle, J. W. & Miller, S. A. An Efficient and Practical System for the Catalytic Oxidation of Alcohols, Aldehydes, and α,β -Unsaturated Carboxylic Acids. *The Journal of Organic Chemistry* **71**, 9291-9296 (2006). <https://doi.org/10.1021/jo0612574>
- 32 Smith, C. Z., Utley, J. H. P. & Hammond, J. K. Electro-organic reactions. Part 60[1]. The electro-oxidative conversion at laboratory scale of a lignosulfonate into vanillin in an FM01 filter press flow reactor: preparative and mechanistic aspects. *Journal of Applied Electrochemistry* **41**, 363-375 (2011). <https://doi.org/10.1007/s10800-010-0245-0>
- 33 Di Fidio, N. *et al.* Electro-oxidative depolymerisation of technical lignin in water using platinum, nickel oxide hydroxide and graphite electrodes. *New Journal of Chemistry* **45**, 9647-9657 (2021). <https://doi.org/10.1039/d1nj01037a>
- 34 Stiefel, S., Schmitz, A., Peters, J., Di Marino, D. & Wessling, M. An integrated electrochemical process to convert lignin to value-added products under mild conditions. *Green Chemistry* **18**, 4999-5007 (2016). <https://doi.org/10.1039/c6gc00878j>
- 35 Di Marino, D. *et al.* Carboxylic Acids Production via Electrochemical Depolymerization of Lignin. *ChemElectroChem* **6**, 1434-1442 (2019). <https://doi.org/10.1002/celec.201801676>
- 36 Chen, A. *et al.* Electrochemical Decomposition of Wheat Straw Lignin into Guaiacyl-, Syringyl-, and Phenol-Type Compounds Using Pb/PbO₂ Anode and Alloyed Steel Cathode in Alkaline Solution. *Environmental Progress & Sustainable Energy* **38**, 13117 (2019). [https://doi.org:https://doi.org/10.1002/ep.13117](https://doi.org/https://doi.org/10.1002/ep.13117)
- 37 Cai, P. *et al.* Electrochemical conversion of corn stover lignin to biomass-based chemicals between Cu/Ni Mo Co cathode and Pb/PbO₂ anode in alkali solution. *Electrochimica Acta* **264**, 128-139 (2018). <https://doi.org/10.1016/j.electacta.2018.01.111>
- 38 Pan, K., Tian, M., Jiang, Z.-H., Kjartanson, B. & Chen, A. Electrochemical oxidation of lignin at lead dioxide nanoparticles photoelectrodeposited on TiO₂ nanotube arrays. *Electrochimica Acta* **60**, 147-153 (2012). [https://doi.org:https://doi.org/10.1016/j.electacta.2011.11.025](https://doi.org/https://doi.org/10.1016/j.electacta.2011.11.025)
- 39 Chang, X., van der Zalm, J., Thind, S. S. & Chen, A. C. Reprint of "Electrochemical oxidation of lignin at electrochemically reduced TiO₂ nanotubes". *Journal of Electroanalytical Chemistry* **872**, 114528 (2020). <https://doi.org/ARTN11452810.1016/j.jelechem.2020.114528>
- 40 Stiefel, S., Lölsberg, J., Kipshagen, L., Möller-Gulland, R. & Wessling, M. Controlled depolymerization of lignin in an electrochemical membrane reactor. *Electrochemistry Communications* **61**, 49-52 (2015). [https://doi.org:https://doi.org/10.1016/j.elecom.2015.09.028](https://doi.org/https://doi.org/10.1016/j.elecom.2015.09.028)

- 41 Singh, S. & Ghatak, H. R. Vanillin Formation by Electrooxidation of Lignin on Stainless Steel Anode: Kinetics and By-Products. *Journal of Wood Chemistry and Technology* **37**, 407-422 (2017). <https://doi.org/10.1080/02773813.2017.1310899>
- 42 Singh, S. & Ghatak, H. R. Process optimization of lignin conversion into value added chemicals by thermochemical pretreatment and electrooxidation on a stainless steel anode. **72**, 187-199 (2018). <https://doi.org/doi:10.1515/hf-2017-0108>
- 43 Florian Stecker, I. M. M., Andreas Fischer, Siegfried R. Waldvogel, Carolin Regenbrecht, US patent number: US008808781B2. METHOD FOR PRODUCING ANILLIN BY ELECTROCHEMICAL OXIDATION OF AQUEOUS LIGNIN SOLUTIONS OR SUSPENSIONS,. US008808781B2 (2014).
- 44 Mao, H. *et al.* Effect and Mechanism of Aluminum(III) for Guaiacol–Glyoxylic Acid Condensation Reaction in Vanillin Production. *ACS Omega* **5**, 24526-24536 (2020). <https://doi.org/10.1021/acsomega.0c03003>
- 45 Valeriy Cherepakhin, T. J. W. Direct Oxidation of Primary Alcohols to Carboxylic Acids. *Synthesis* **53(06)**, 1023-1034 (2020). <https://doi.org/10.1055/s-0040-1706102>
- 46 Garedew, M. *et al.* Greener Routes to Biomass Waste Valorization: Lignin Transformation Through Electrocatalysis for Renewable Chemicals and Fuels Production. *ChemSusChem* **13**, 4214-4237 (2020). <https://doi.org/10.1002/cssc.202000987>
- 47 McCrory, C. C. L., Jung, S., Peters, J. C. & Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *Journal of the American Chemical Society* **135**, 16977-16987 (2013). <https://doi.org/10.1021/ja407115p>
- 48 Schmitt, D., Regenbrecht, C., Schubert, M., Schollmeyer, D. & Waldvogel, S. R. in *Holzforschung* Vol. 71 35-41 (2017).
- 49 Li, M.-F., Sun, S.-N., Xu, F. & Sun, R.-C. Ultrasound-enhanced extraction of lignin from bamboo (*Neosinocalamus affinis*): Characterization of the ethanol-soluble fractions. *Ultrasonics Sonochemistry* **19**, 243-249 (2012). <https://doi.org/https://doi.org/10.1016/j.ultsonch.2011.06.018>
- 50 Alunga, K. R., Ye, Y.-Y., Li, S.-R., Wang, D. & Liu, Y.-Q. Catalytic oxidation of lignin–acetoderivatives: a potential new recovery route for value-added aromatic aldehydes from acetoderivatives. *Catalysis Science & Technology* **5**, 3746-3753 (2015). <https://doi.org/10.1039/C5CY00419E>
- 51 Innocenti, M. *et al.* Electroactivation of Microparticles of Silver on Glassy Carbon for Oxygen Reduction and Oxidation Reactions. *Journal of The Electrochemical Society* **161**, D3018 (2014). <https://doi.org/10.1149/2.003407jes>
- 52 Wyantuti, S., Hartati, Y. W., Panatarani, C. & Tjokronegoro, R. Cyclic Voltammetric Study of Chromium (VI) and Chromium (III) on the Gold Nanoparticles-Modified Glassy Carbon Electrode. *Procedia Chemistry* **17**, 170-176 (2015). <https://doi.org/https://doi.org/10.1016/j.proche.2015.12.109>
- 53 Beliaeva, K. *et al.* New insights into lignin electrolysis on nickel-based electrocatalysts: Electrochemical performances before and after oxygen evolution. *International Journal of Hydrogen Energy* **46**, 35752-35764 (2021). <https://doi.org/10.1016/j.ijhydene.2021.01.224>

- 54 Orozco, G., Pérez, M. C., Rincón, A. & Gutiérrez, C. Electrooxidation of methanol on silver in alkaline medium. *Journal of Electroanalytical Chemistry* **495**, 71-78 (2000). [https://doi.org/10.1016/S0022-0728\(00\)00396-X](https://doi.org/10.1016/S0022-0728(00)00396-X)
- 55 Karatok, M. *et al.* Formaldehyde Selectivity in Methanol Partial Oxidation on Silver: Effect of Reactive Oxygen Species, Surface Reconstruction, and Stability of Intermediates. *ACS Catalysis* **11**, 6200-6209 (2021). <https://doi.org/10.1021/acscatal.1c00344>
- 56 Rekik, R., Hamza, M., Jaziri, M. & Abdelhedi, R. Electrochemical oxidation of vanillic acid by electro-Fenton process: Toward a novel route of protocatechuic acid electrosynthesis. *Arabian Journal of Chemistry* **13**, 357-365 (2020). <https://doi.org/10.1016/j.arabjc.2017.05.001>
- 57 Deng, Z., Fan, H., Lan, C., Zhang, S. & Li, G. Simultaneous electro-transfer of vanadium slag and electrocatalytic degradation of lignin in sulfuric acid solution. *Journal of Industrial and Engineering Chemistry* (2022). <https://doi.org/10.1016/j.jiec.2021.12.034>
- 58 Ma, L., Zhou, H., Kong, X., Li, Z. & Duan, H. An Electrocatalytic Strategy for C–C Bond Cleavage in Lignin Model Compounds and Lignin under Ambient Conditions. *ACS Sustainable Chemistry & Engineering* **9**, 1932-1940 (2021). <https://doi.org/10.1021/acssuschemeng.0c08612>
- 59 Rafiee, M., Alherech, M., Karlen, S. D. & Stahl, S. S. Electrochemical Aminoxyl-Mediated Oxidation of Primary Alcohols in Lignin to Carboxylic Acids: Polymer Modification and Depolymerization. *J Am Chem Soc* **141**, 15266-15276 (2019). <https://doi.org/10.1021/jacs.9b07243>
- 60 Wijaya, Y. P., Smith, K. J., Kim, C. S. & Gyenge, E. L. Synergistic effects between electrocatalyst and electrolyte in the electrocatalytic reduction of lignin model compounds in a stirred slurry reactor. *Journal of Applied Electrochemistry* **51**, 51-63 (2020). <https://doi.org/10.1007/s10800-020-01429-w>

9 Appendix

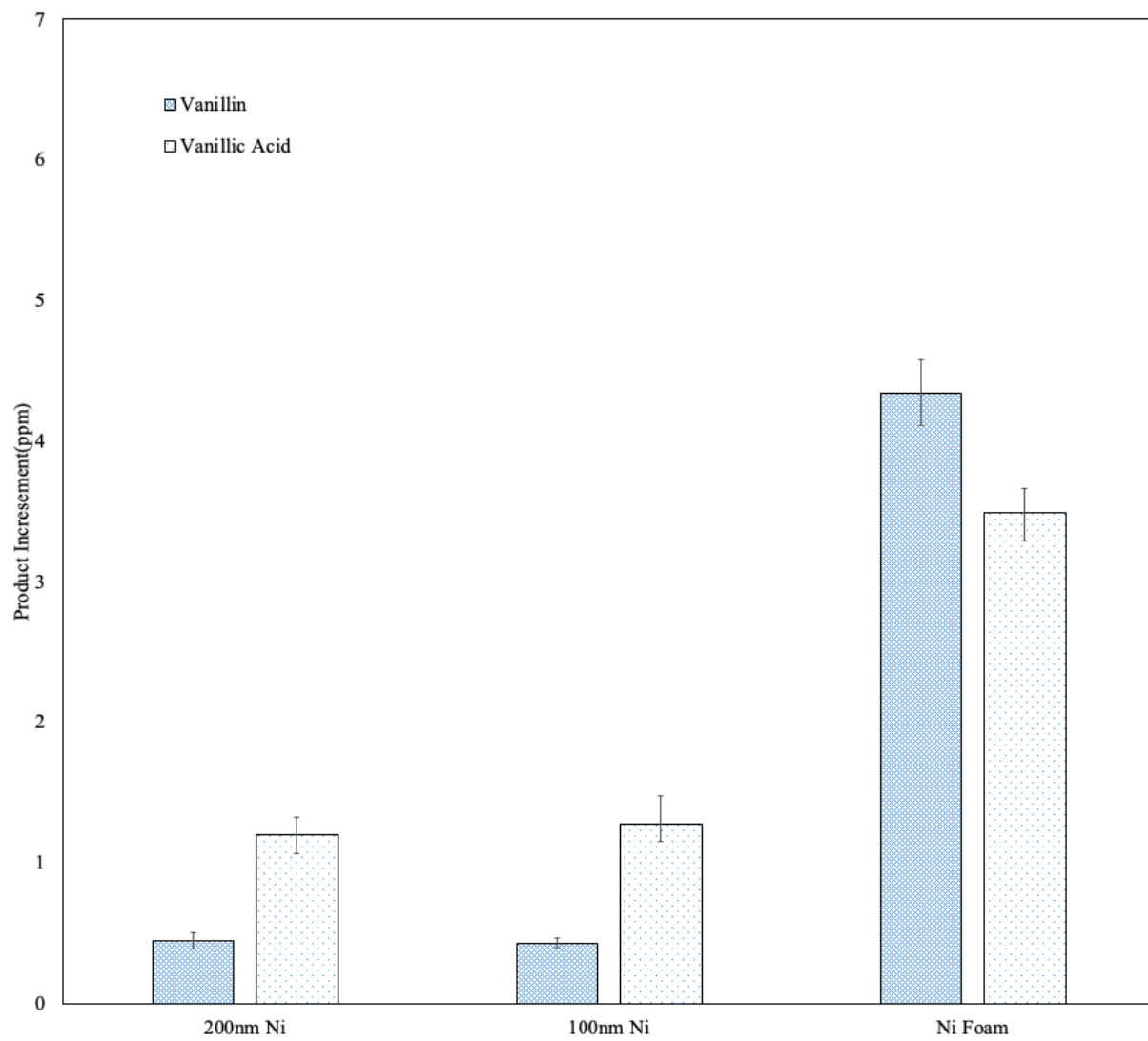


Figure 21 Vanillin and vanillic acid increase after 1500s reaction under 1V

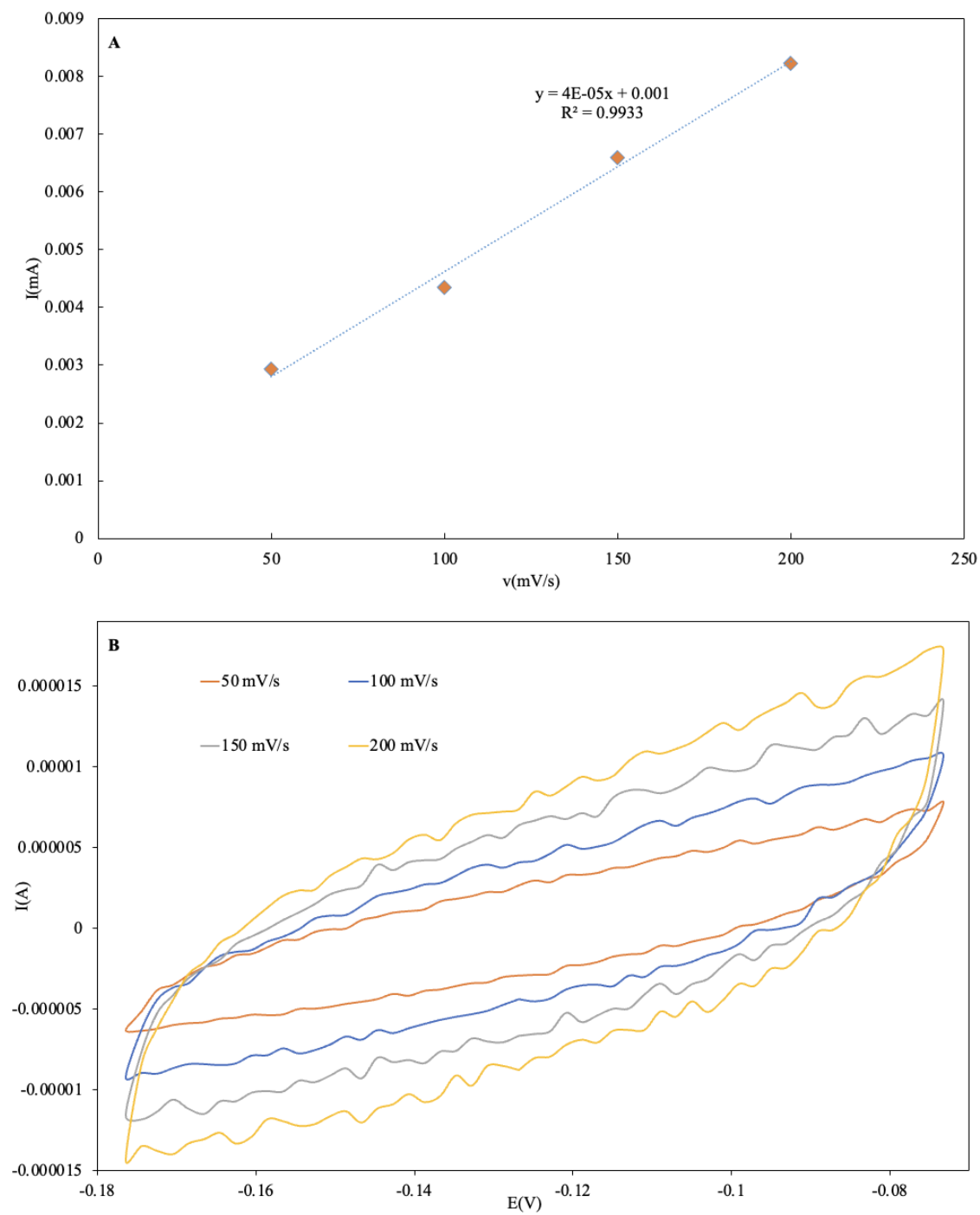


Figure 22 A: Double-layer capacitance plot for 100 nm Ni B: ECSA scans for 100 nm Ni

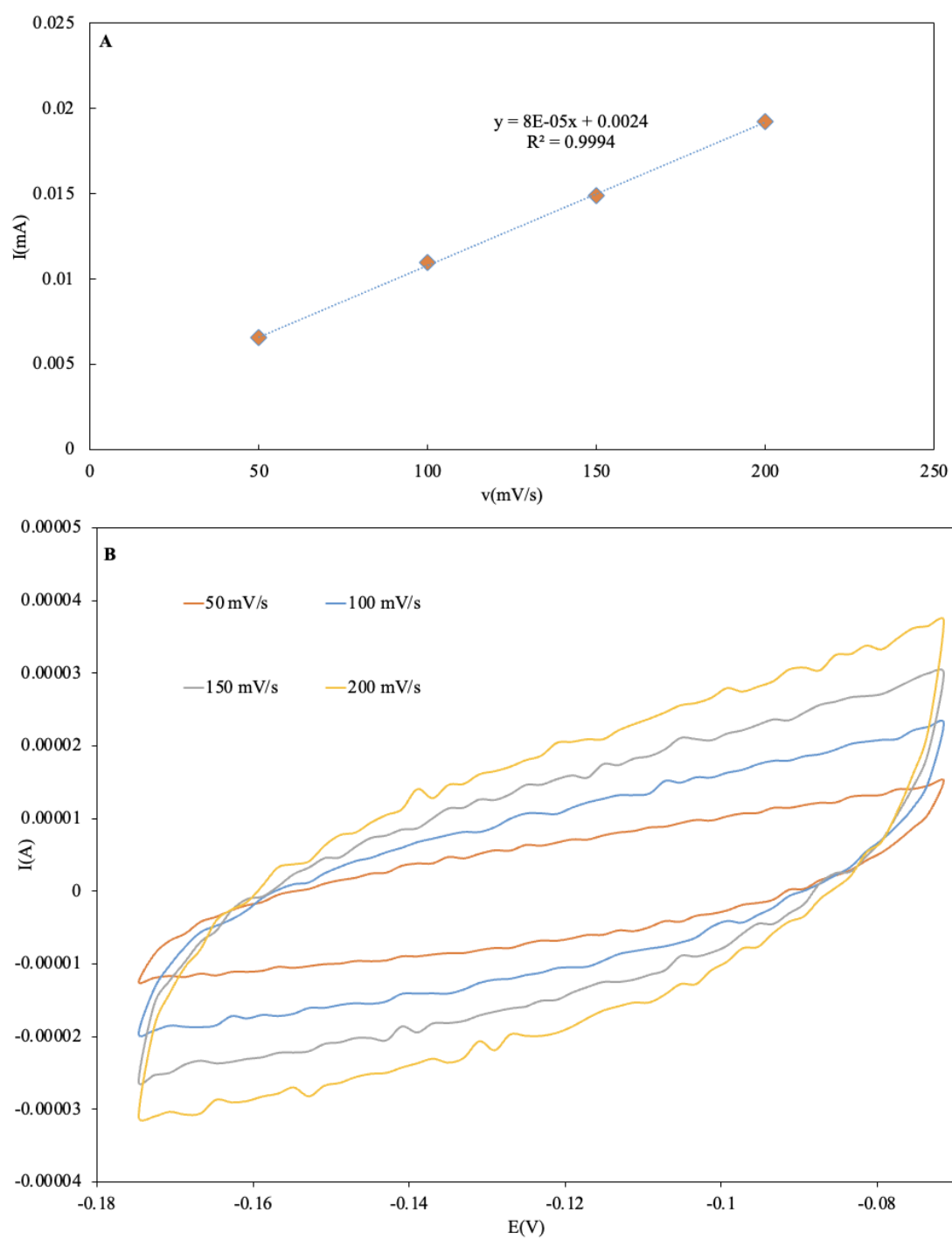


Figure 23 A: Double-layer capacitance plot for 200 nm Ni B: ECSA scans for 200 nm Ni

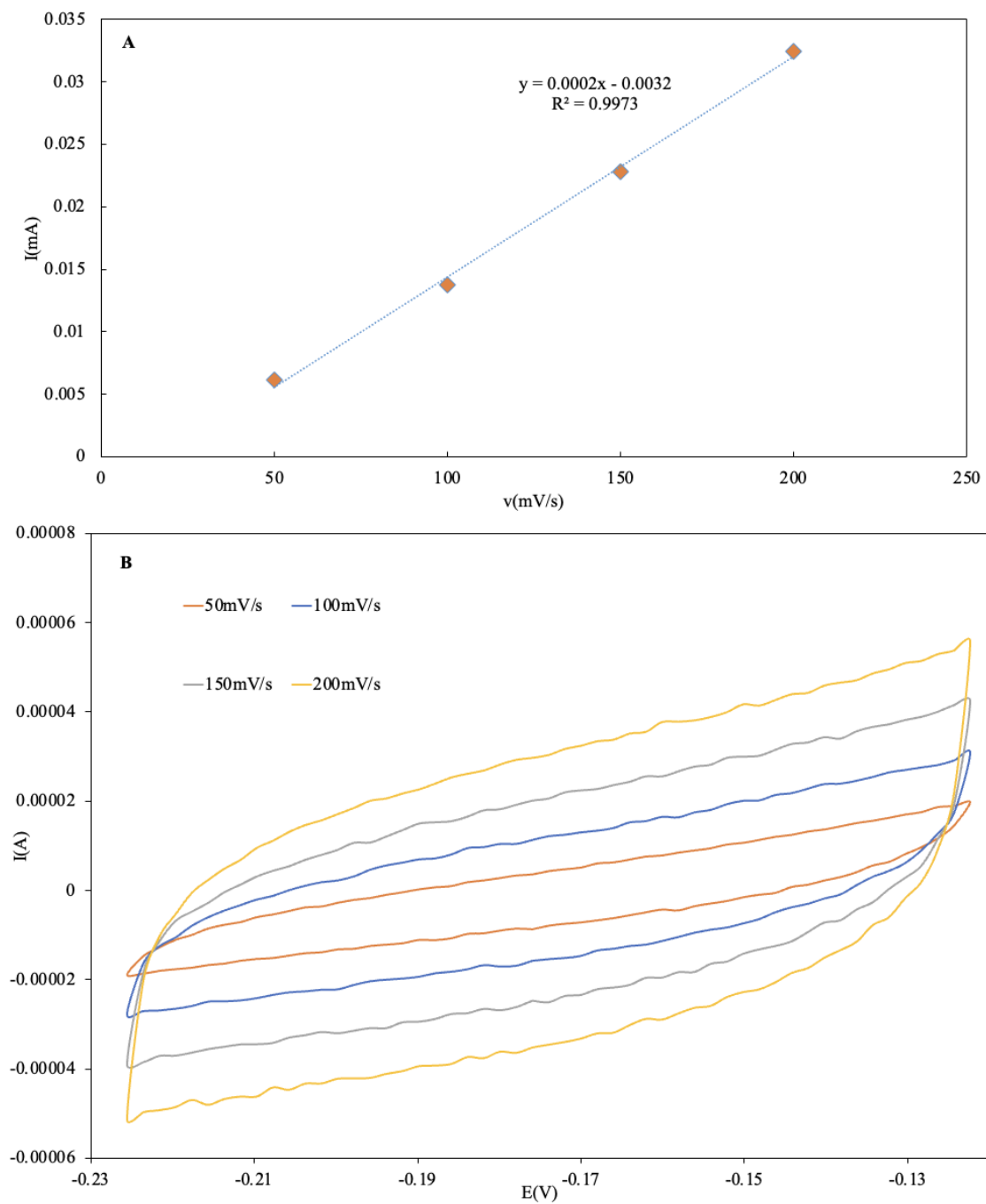


Figure 24 A: Double-layer capacitance plot for Ni foam B: ECSA scans for Ni foam

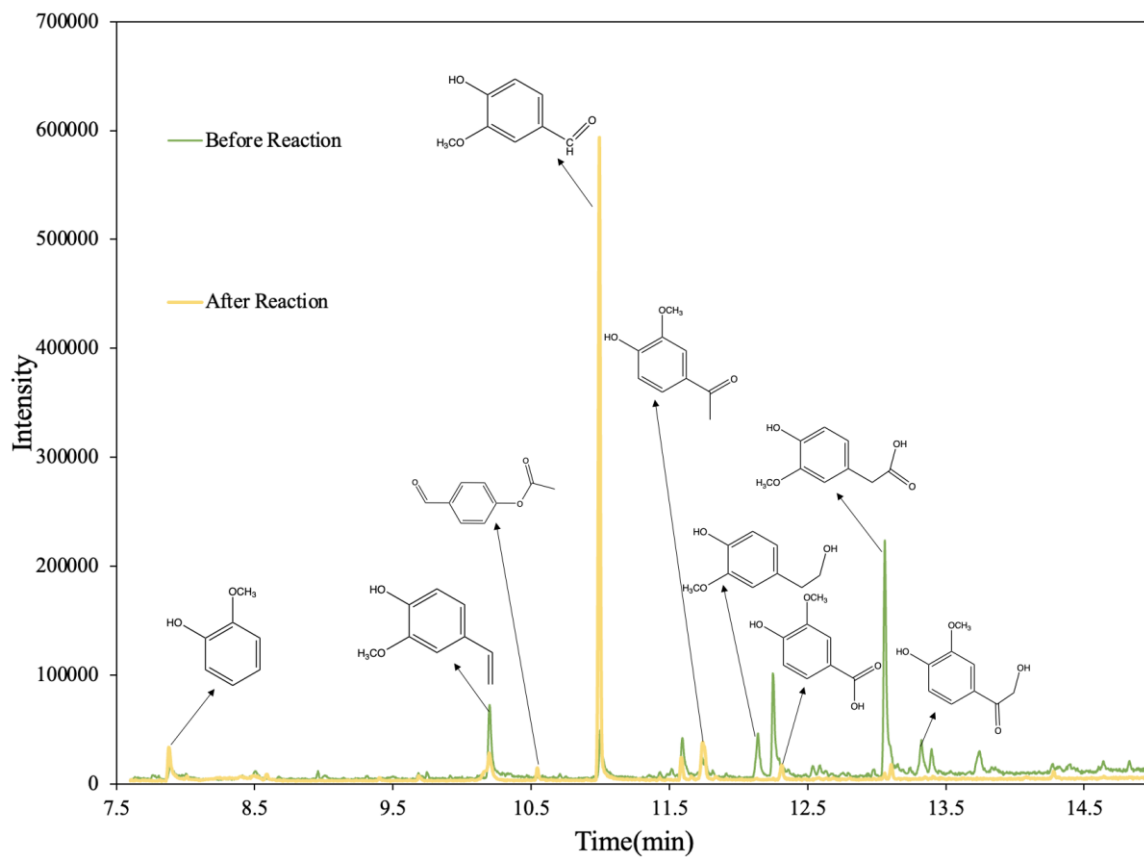


Figure 25 GC-MS Chromatogram for Kraft Lignin before and after reaction under 1V for 10 hours with 1cm x 1cm Ni foam

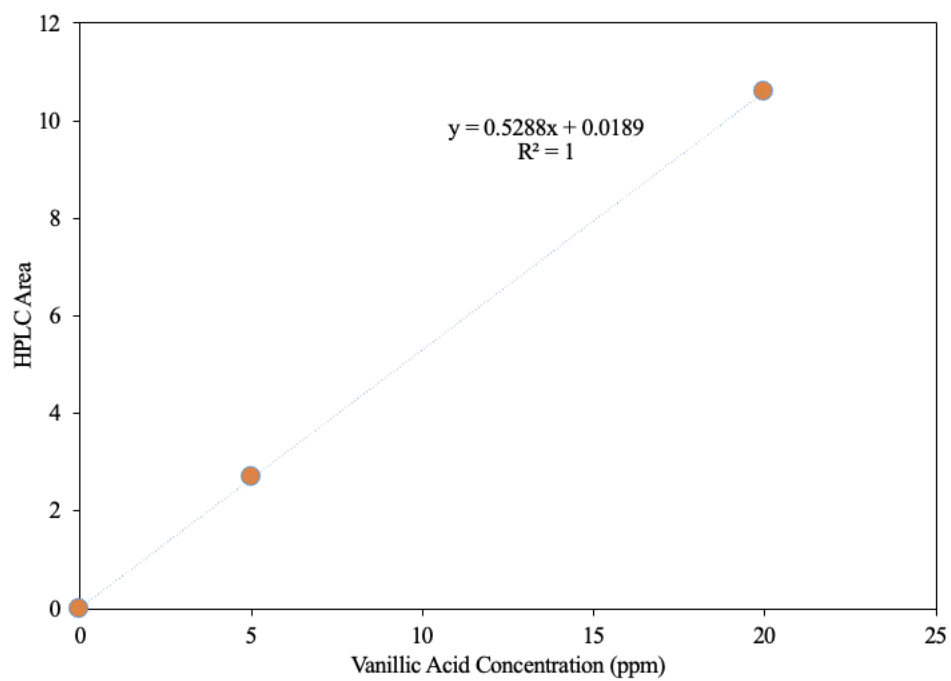
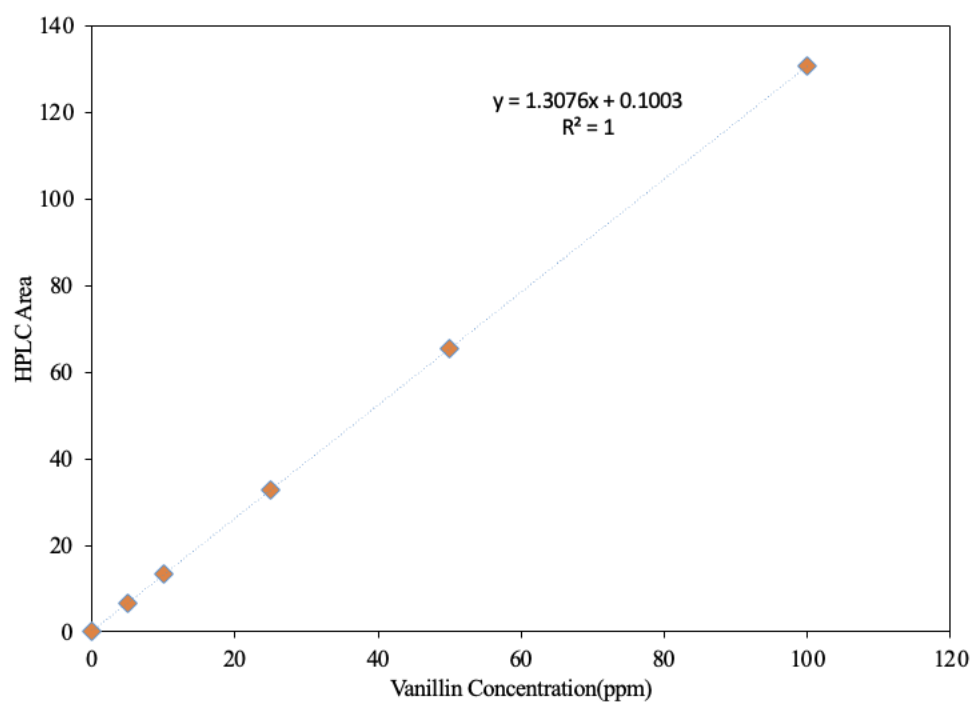


Figure 26 HPLC calibration curve for vanillin and vanillic acid