Electrocatalytic hydrogenation of guaiacol in diverse electrolytes using a slurry reactor

Yanuar Philip Wijaya, Kevin J. Smith, Chang Soo Kim, Elöd L. Gyenge

*Chemical and Biological Engineering
The University of British Columbia
Vancouver, Canada*

ECS 236th Atlanta (October 16, 2019)

Outline

► **Introduction:**

- ❖ *Research background and motivation*
- ❖ *Literature review - State of the art*
- ❖ *Research objectives*

► **Experimental Results and Discussion:**

- ❖ *ECH of guaiacol in different catholyte-anolyte pairs*
- ❖ *Parametric study under galvanostatic control*
- ❖ *Process mechanisms and catalyst reusability tests*

► **Summary and Key Findings**

THE VERSATILITY OF BIOMASS-DERIVED PRODUCTS

TRANSPORTATION FUELS

Gasoline, diesel, jet fuel

***Biomass-derived products
for daily life applications***

FINE CHEMICALS

*Perfume,
Food flavors,
Solvent*

POLYMERIC MATERIALS

Nylon, plastics

TRANSFORMATION OF LIGNOCELLULOSIC BIOMASS INTO BIO-PRODUCTS

Fractionation + Upgrading

Biomass deconstruction

Energy densification, Carbon retention

BIOMASS

- Low energy density
- High functionality

FUELS

*Oxygen removal
(Deoxygenation)*

- High energy density
- Low functionality

GOAL:

Concerns:
C-H bonds
C-C bonds

Biological

- Enzymatic hydrolysis

Thermo
chemical

- Acid hydrolysis
- Fast pyrolysis

Biological

- Fermentation (anaerobic)

Thermo
chemical

- Hydrodeoxygenation
- Hydrogenation, etc.

Electro
chemical

- Hydrogenation
- Hydrogenolysis, etc.

Research
Focus

ELECTROCHEMICAL VS. THERMOCHEMICAL APPROACHES

	ECH	TCH
Operating conditions	Mild (low T < 60 °C, P ≈ 1 atm)	Harsh (high T > 200 °C and P > 100 bar)
Hydrogen source	Proton/water reduction (<i>in situ</i>)	External supply: H ₂ gas/organic solvents
Carbon recovery	High (> 80%)	Moderate to low (< 80%)
Selectivity control	Cell potential/current density, temperature, and/or electrolyte pH	Temperature and pressure control, catalyst functionalities
Challenges	Low organic solubility in aqueous solution	Substantial coke formation (catalyst deactivation)
Attractiveness	Integration with renewable electricity (wind, solar)	Adaptable technology with petroleum infrastructures

Source: Key World Energy Statistics 2017

- Potentials:**
- Electricity costs tend to be more economical with the supply from renewable sources
 - Energy storage (in chemical form) via electrolysis supplied with renewable electricity becomes economically attractive

Note: ECH = electrocatalytic hydrogenation-hydrogenolysis; TCH = thermocatalytic hydrogenation-hydrogenolysis

SCOPE OF WORK: ECH OF GUAIACOL IN DIVERSE ELECTROLYTES

Plausible reaction pathways for ECH of guaiacol

Targeted products:
cyclohexanone, cyclohexanol
(precursor chemicals for Nylon)

Challenges:

- Low current efficiency
- Carbon diffusive loss
- Practical feasibility

Research objectives:

- ❖ Electrolyte pair effects (potentiostatic/galvanostatic)
- ❖ ECH performance and efficiency in a slurry reactor

ELECTROCATALYST CONFIGURATION: STATE OF THE ART

Electrodeposition

[Zhao et al., 2014.
Electrochemical Society
of Japan]

Impregnation, Spray Deposition

[Li et al., 2012. Green
Chemistry]

Slurry reactor

[Song et al., 2016.
Applied Catalysis B]

Novelty: *In this work, we used stirred slurry reactor (SSR) with different pairs of electrolytes. This configuration offers some benefits, such as: recoverability and high current efficiency*

ECH OF GUAIACOL IN A STIRRED SLURRY REACTOR

Catalyst: 5 wt.-%-Pt/C
R/M ratio $\approx$ 315

Acid-acid and neutral-acid pairs are the two most effective for ECH applications

Acidic anolyte is preferred for an effective ECH

*Constant potential
Chronocoulometry*

Acid: H_2SO_4 (0.2 M)
Neutral: NaCl (0.5M)
Base: NaOH (0.2 M)

Acid-acid

Neutral-acid

GALVANOSTATIC ELECTROLYSIS: CATHOLYTE-ANOLYTE PAIR EFFECTS

Conditions:

Reactant: Guaiacol (0.1 M)

Acid: H_2SO_4 (0.2 M)

Neutral: NaCl (0.2 M)

$j = -109 \text{ mA cm}^{-2}$

$T = 50^\circ\text{C}$

Catalyst: 5 wt%-Pt/C

Reaction pathway was affected by pH

Protons for ECH were mostly supplied from the anode

F.E. was higher in neutral-acid case at the observed conditions

Different HER mechanism:

Proton reduction (Acid)

Tafel: $(\text{H})\cdot\text{M} + (\text{H})\cdot\text{M} \rightarrow \text{H}_2 + 2\text{M}$

Heyrovsky: $(\text{H})\cdot\text{M} + (\text{H}^+)_{\text{aq}} + e^- \rightarrow \text{H}_2 + \text{M}$

Water reduction (Base)

$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$

GALVANOSTATIC ELECTROLYSIS: OPERATING CONDITION EFFECTS

(a) Acid concentration effect
(b) Current density effect
(c) Temperature effect

Conditions:
(a) $j = -182 \text{ mA cm}^{-2}$, $T = 50 \text{ }^{\circ}\text{C}$
(b) $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, $T = 50 \text{ }^{\circ}\text{C}$
(c) $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, $j = -182 \text{ mA cm}^{-2}$

	X	F.E.	S.C.
Acid conc.	+	+	×
Current	+	-	×
Temp.	+	+	✓

X = guaiacol conversion; F.E. = Faradaic efficiency;
S.C. = selectivity changes

TIME-DEPENDENT PROFILES FOR SELECTED EXPERIMENTS

F.E. decreased over time with the conversion of the organics

Conditions:

	$[\text{H}_2\text{SO}_4]$ (M)	j (mA cm ⁻²)	T (°C)
(d)	1.0	-182	50
(e)	0.5	-255	50
(f)	0.5	-182	60

- Cyclohexanone selectivity increased at 60 °C
- Temperature and cathode potential/current density affected H coverages

POTENTIOSTATIC ECH: COMPLEMENTARY TESTS

(a) The effect of initial guaiacol concentration

Faradaic efficiency (F.E.) and conversion rates increased with the initial guaiacol concentration

Increasing cathode potential increased guaiacol conversion and cyclohexanol yield at the expense of F.E.

(b) The effect of cathode potential

Conditions: (a) H_2SO_4 (0.2 M), $E = -1.25$ V, $I = -218$ mA cm^{-2} , $T \approx 39$ $^{\circ}\text{C}$, $t = 4$ h, (b) H_2SO_4 (0.2 M), $t = 4$ h. Catalyst: 5 wt.-%-Pt/C

POTENTIOSTATIC ECH: CATALYST REUSABILITY TESTS

Conditions:

Acid-acid: HClO₄ (0.5 M)–HClO₄ (0.5 M), *E* = -1.0 V, *j* = -218 mA cm⁻², *T* ≈ 34°C, *t* = 4 h
 Neutral-acid: NaCl (0.5 M)–H₂SO₄ (0.2 M), *E* = -2.5 V, *I* = -175 mA cm⁻², *T* ≈ 39°C
 Catalyst: 5 wt.-%-Pt/C

Catalyst characterizations

Catalyst	<i>S</i> _{BET} ^a (m ² /g)	<i>V</i> _{pore} ^b (cm ³ /g)	<i>D</i> _{pore} ^c (nm)	ϕ (%)	<i>S</i> _{metal} (m ² /g)	<i>d</i> _p (nm)
Pt/C (fresh)	1487	1.43	4.35	28.95	71.50	3.91
Pt/C (spent-A)	1025	1.07	4.37	11.49	28.38	9.86
Pt/C (spent-B)	1128	1.16	4.43	6.73	16.61	16.84

(a) Original/fresh, (b) Spent A – used in acid, (c-d) Spent B – used in alkaline

Pt/C remains active despite the morphology changes, suggesting its reusability

SUMMARY AND KEY FINDINGS

- ECH of guaiacol (and phenol) can be efficiently performed in acid or neutral solutions paired with acidic anolyte with the low loading of slurry Pt/C catalyst at low temperatures and high superficial current densities.
- Chronocoulometry is a suitable technique to comparatively investigate the electron transfer rates in different pairs of electrolyte.
- Reaction pathways and product distributions were affected by synergistic effects between proton concentration, temperature, and cathode potential, influencing the surface coverage of adsorbed hydrogen
- The advantages of stirred slurry reactor configuration are attributed to the enhanced Faradaic efficiency and reusability of the catalyst.

REFERENCES AND ACKNOWLEDGMENTS

- Song, Y., Gutiérrez, O. Y., Herranz, J. & Lercher, J. A. Aqueous phase electrocatalysis and thermal catalysis for the hydrogenation of phenol at mild conditions. *Appl. Catal. B Environ.* **2016**, 182, 236–246.
- Li, Z., Garedew, M., Lam, C. H., Jackson, J. E., Miller, D. J., Saffron, C. M. Mild electrocatalytic hydrogenation and hydrodeoxygenation of bio-oil derived phenolic compounds using ruthenium supported on activated carbon cloth. *Green Chem.* **2012**, 14, 2540.
- Garedew, M., Young-Farhat, D., Jackson, J. E. & Saffron, C. M. Electrocatalytic Upgrading of Phenolic Compounds Observed after Lignin Pyrolysis. *ACS Sustain. Chem. Eng.* **2019**, 7, 8375–8386.
- etc.

- This work is supported by:

THE UNIVERSITY OF BRITISH COLUMBIA

THANK YOU FOR YOUR ATTENTION

THE UNIVERSITY OF BRITISH