Pyrolysis oil treatment using Kolbe electrolysis of organic acids

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Motivation

Transitioning to low carbon economy, comodity, speciality chemicals and fuels can be sourced from crude bio liquids of biomass pyrolysis.

Electrochemical Acid decarboxylation (Kolbe/non-Kolbe) is one of the promising route to convert low value pyrolysis crude into energy dense hydrocarbons and chemicals through coupling (homo and cross) reactions. The on-spot surplus or excess energy at industrial pyrolysis facility can be utilized with integrated electrolysers for continuous up-gradation of pyrolysis oil, eliminating the need of energy intensive conventional deploymerization, hydrogenation and decarboxylation system.

Challenges for electrochemical decarboxylation

- Complexity of pyrolysis crude → Stable and cheap electrode
- Electrolyzer design → Tailoring reaction and electrode conditions for product selectivity

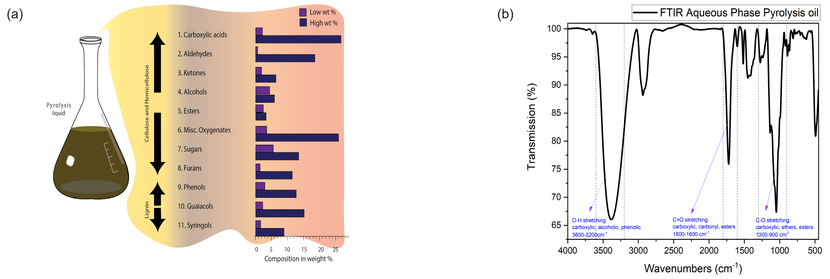


Figure 1. Complex composition of pyrolysis crude. (a) Cellulose, hemicellulose and lignin fractions functional group composition based on Ref [1]. (b) ATR-FTIR transmission spectrum of aqueous phase pyrolysis oil from BTG with carboxylic acids alcohols, hydrocarbons and esters fraction

Methodology

- Model compounds of carboxylic acids (acetic acid) was used with acetate salt as supporting electrolyte.
- pH was adjsted to near pKA of acetic acid (4.7) with variable current densities of 25-200 mA/cm².
- Tests were conducted in three electrode batch and two electrode undivided cell with Pt foil as working electrode.
- Anolyte columns were constantly purged with He to strip out gases from electrolyte solution.

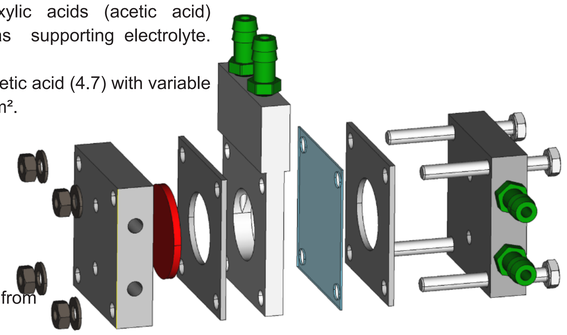


Figure 2. Schematic 3D overview of flow electrolyzer made of stainless steel and designed by Condias®.

EBIO's ultimate goal is to accelerate and widely deploy an economically viable, environmentally friendly and socially acceptable process for transport fuel production from biomass. Specifically, we target the electrochemical conversion of two representative low-valued and industrially available bio-liquids, pyrolysis oil and black liquor, into green fuels, platform chemicals and high-added value compounds

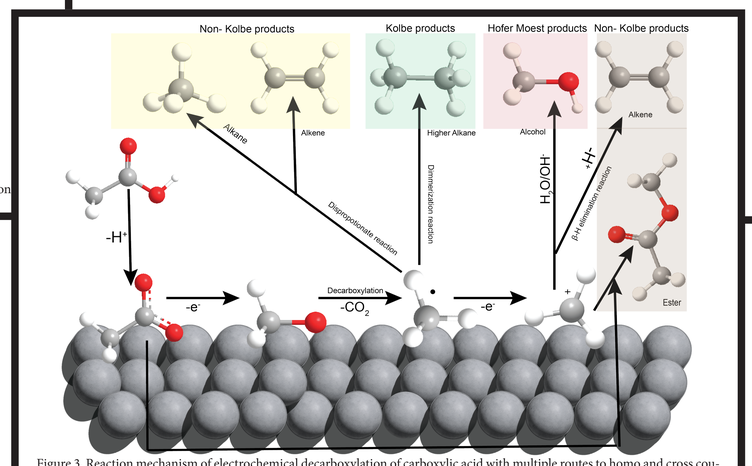


Figure 3. Reaction mechanism of electrochemical decarboxylation of carboxylic acid with multiple routes to homo and cross coupling reactions on platinum surface based on reaction mechanism proposed by Ref.[2]

- Three electrode batch cell was used for early stage of electrode development. The electrocatalyst was screed by SEM, XRD, Raman, Contact angle.
- The products analysis were carried out by inline gas chromatography with FID and TCD detector, GC with headspeace.

Results

- With platinum foil as working electrode in three electrode controlled undivided batch cell, 85-100% faradaic efficiency to ethane was achieved. The impact of cations on Kolbe electrolysis is significant with highest F.E to ethane of 99% at 25 mA/cm² and pH 5.
- In undivided batch cell, the F.E towards ethane at different current densities was achieved with highest F.E of ~75% at 100 mA/cm².
- Difference in batch and flow cell for Kolbe electrooxidation is significant and it can involve various factors such as flow conditions, flow rate, electrolyzer design, two and electorde system.

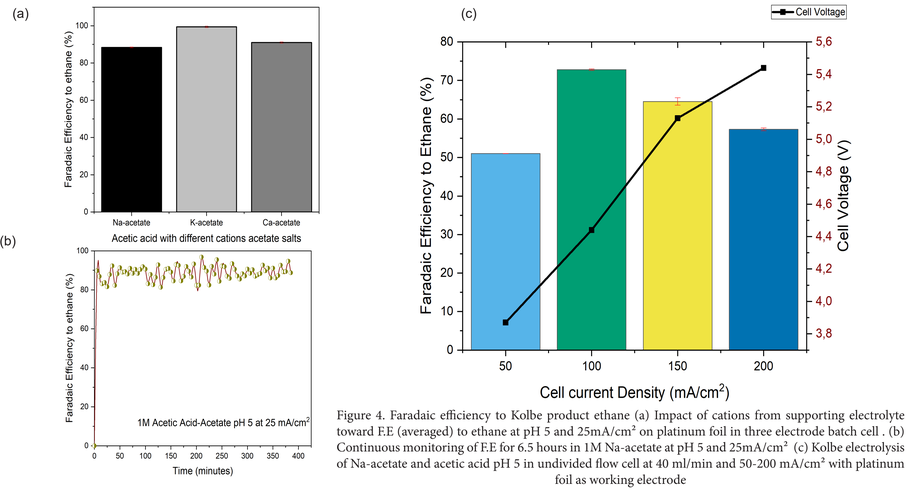


Figure 4. Faradaic efficiency to Kolbe product ethane (a) Impact of cations from supporting electrolyte toward F.E (averaged) to ethane at pH 5 and 25mA/cm² on platinum foil in three electrode batch cell . (b) Continuous monitoring of F.E for 6.5 hours in 1M Na-acetate at pH 5 and 25mA/cm² (c) Kolbe electrolysis of Na-acetate and acetic acid pH 5 in undivided flow cell at 40 ml/min and 50-200 mA/cm² with platinum foil as working electrode

- With boron doped diamond as working electrode, the Kolbe products were not observed with integrated electrochemical mass spectrometer (ECMS).
- Hofer Moest, non Kolbe and acid decarboxylation products were analyzed.
- Indirect carboxylic oxidation on BDD occurs by weakly adsorbed OH- radicals on electrode surface. Ref.[3]

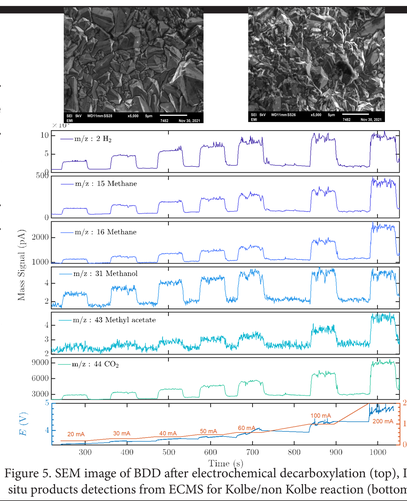
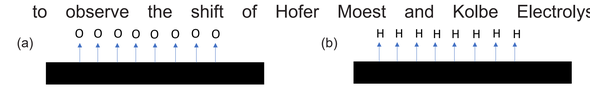


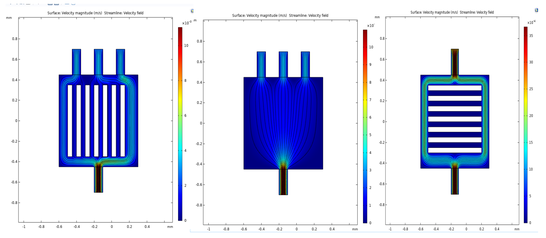
Figure 5. SEM image of BDD after electrochemical decarboxylation (top), In-situ products detections from ECMS for Kolbe/non Kolbe reaction (bottom)

Outlook

- Platinum electrode shows highest current efficiency to ethane production. BDD electrode will be optimized , functionalized and grafted to observe the shift of Hofer Moest and Kolbe Electrolysis .



- Simulation and Development of flow fields and microstructured electrodes for enhanced decarboxylation and coupling reaction.



- Electrolyzer scale up for electrodes upto 81cm² for large volume electrolysis at high current densities.

- Integration of optimized electrodes and electrolyzer into pyrolysis liquid production loop

▪ Scale up Electrode surface area from 3.14 cm² to 81 cm²

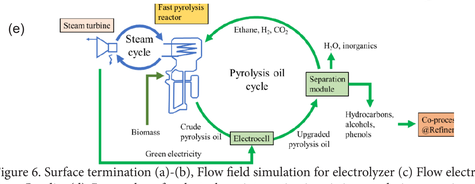


Figure 6. Surface termination (a)-(b), Flow field simulation for electrolyzer (c) Flow electrolyzer from Condias (d), Process loop for electrolyzer integration in existing pyrolysis processing unit(e)

References

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