IOWA STATE UNIVERSITY
Mechanical Engineering

TCBiomass
April 19-21, 2022, Denver, Colorado

Efficient Biomass Conversion based on Plasma Electrolysis in Aprotic Solvents

Lusi A, Harish Radhakrishnan, Xianglan Bai

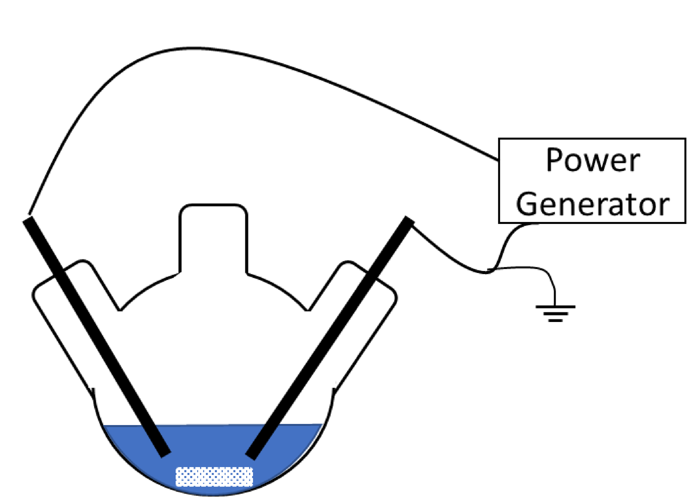
Introduction

- Major challenges for enabling economic bio-based chemicals include low chemical selectivity, high energy input, complex process, and low-quality lignin byproducts.
- One-pot conversion of biomass to chemicals and lignin was investigated in this work by employing a novel plasma electrolysis approach.
- Plasma is a partially ionized gas containing electrons, ions, radicals, molecules and atoms, which is generated by applying electric field.
- Non-thermal plasma can create chemically reactive environment using mild temperatures and low-energy inputs.
- By generating plasma in organic solvents, unique reactions that otherwise impossible for conventional thermochemical conversions can be achieved.

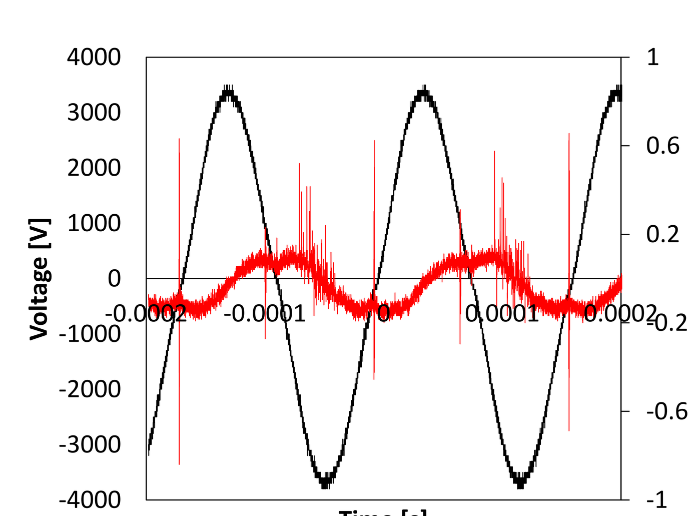
Experimental

- ***Feedstock:*** Red oak or cellulose
- ***Plasma electrolysis:*** Altering current (AC) electricity is applied in an atmospheric-pressure reactor containing γ-Valerolactone (GVL), 1 to 4wt% biomass, and 7 to 14 mM H_2SO_4
- ***Thermally-based solvolysis:*** Biomass, solvent and acid are converted in a heated reactor.
- ***Recovery of lignin:*** Water is added to post-reaction liquids to recover solid lignin products
- ***Pyrolysis of lignin:*** Lignin was pyrolyzed using micropyrolyzer with online GC/MS-FID.

< Plasma electrolysis reactor>

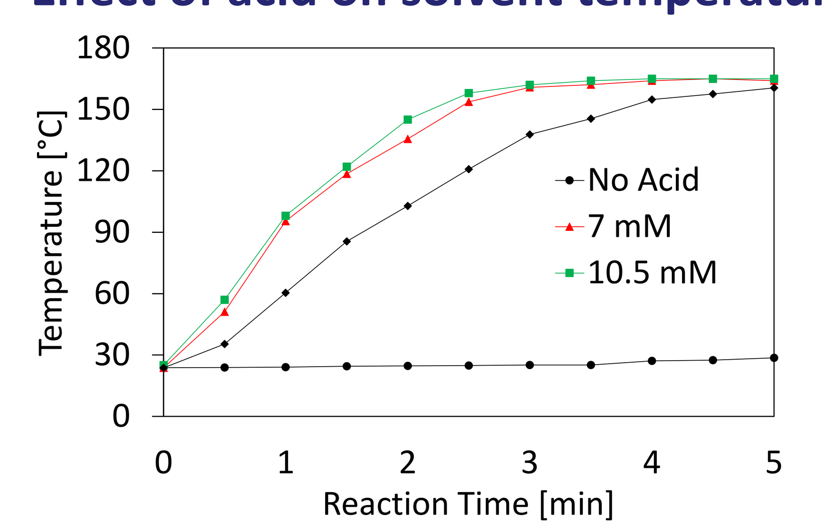


< Voltage-current diagram: Plasma formation in liquid >



Results & Discussion

Effect of acid on solvent temperature

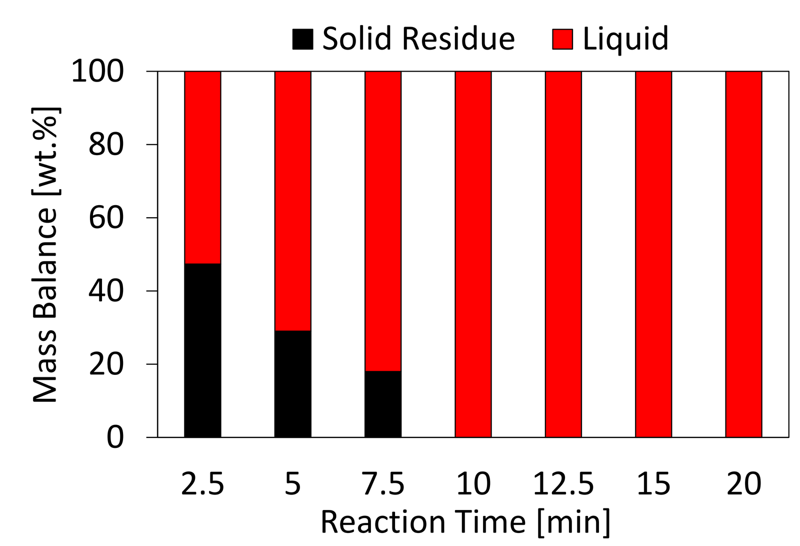


(V = 6 kV and f = 6 kHz)

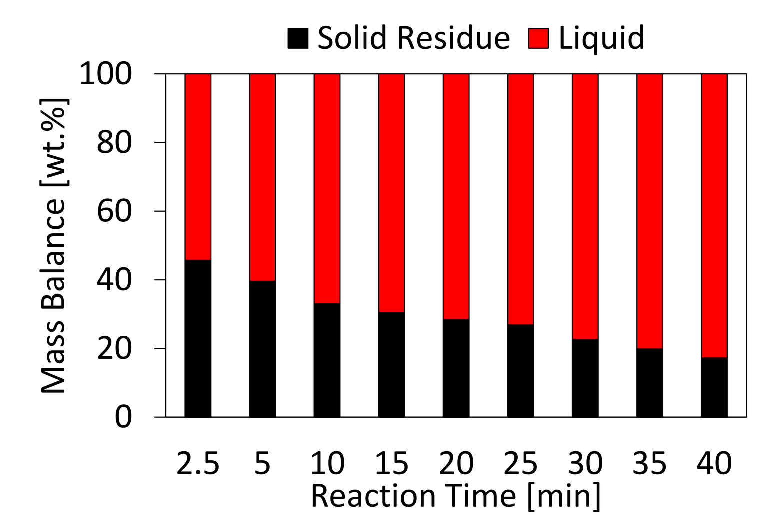
- During plasma electrolysis, solvent temperature remained near room temperatures when acid was absent.
- Solvent temperature rapidly increased to about 165 °C in the presence of acid.
- Presence of acid induced Joule heating and facilitated plasma formation.

Mass balance of red oak

Plasma electrolysis:
(10.5 mM acid, V = 7 kV and f = 6 kHz)



Conventional solvolysis:
(10.5 mM acid, 165 °C)



- Rapid liquefaction of red oak occurred during plasma electrolysis.

Product yields of red oak

Reaction condition	Reaction time [min]	Yield [mol%] FF	LGO	LA	DGP	LG
Conventional solvolysis						
165 °C, 10.5 mM	2.5	2.5	0.5	0.1	0.7	0.0
165 °C, 10.5 mM	10	65.1	4.0	1.3	5.0	2.2
165 °C, 10.5 mM	35	84.7	12.5	2.5	0.0	0.0
Plasma electrolysis						
7 kV, 6 kHz, 10.5 mM	2.5	48.0	3.3	0.0	0.5	0.0
7 kV, 6 kHz, 10.5 mM	5	98.0	15.3	1.2	8.7	0.0
7 kV, 6 kHz, 10.5 mM	10	79.0	28.0	7.6	7.9	0.0

Plasma electrolysis using red oak or cellulose as feedstock

Reaction condition	Reaction time [min]	Yield [mol%] FF	LGO	LA	DGP
Red oak	5	98.0	15.3	1.2	8.7
	7.5	85.6	39.5	6.0	5.1
	10	79.0	28.0	7.6	7.9
Cellulose	5	3.2	32.3	2.9	13.7
	7.5	4.5	40.6	4.7	10.3
	10	5.2	33.5	4.3	7.0

- Using red oak or cellulose as feedstock resulted in comparable product yields, suggesting there is no need to separate cellulose by biomass pretreatment.

2D-NMR results of plasma electrolysis-derived lignin (PEL)

	MWL	PEL 10 min	PEL 15 min	PEL 20 min
β-O-4 [%]	61.90	0.00	0.00	0.00
β-β [%]	14.43	12.71	10.62	10.32
β-5 [%]	2.66	0.00	0.00	0.00
$X2_\beta$ [%]	0.48	16.93	25.17	34.03
FA_β [%]	0.00	2.73	4.82	8.16
HKγ [%]	1.63	13.01	20.86	39.09
S/G	1.78	1.66	1.55	1.09
S'/S	0.14	0.24	0.35	0.41
G'/G	0.09	0.64	0.75	0.85

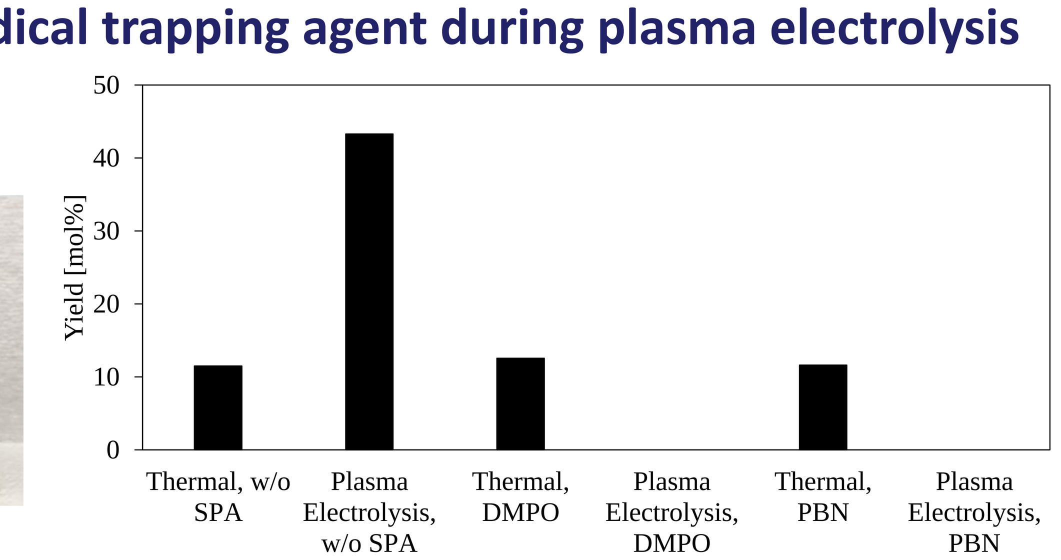
- Plasma electrolysis-derived lignin is a selectively oxidized lignin.

Phenolic monomers produced from lignin pyrolysis

Monomer yield	MWL	PEL 10 min	PEL 15 min	PEL 20 min	Thermally-based Lignin
[wt%]	8.61	16.92	20.86	20.91	6.96

- Plasma electrolysis-derived lignin produced significantly higher amounts of aromatic monomers than MWL or thermally-based lignin.

Effect of adding radical trapping agent during plasma electrolysis



- Adding radical trapping agents nearly terminated biomass conversion during plasma electrolysis, but it had no effect on conventional biomass conversion.
- Plasma electrolysis of biomass proceeds via novel radical-based mechanisms.

Conclusions

- Plasma electrolysis rapidly liquefies biomass to produce high yields of levoglucosenone (LGO) and furfural (FF), as well as oxidized lignin in one pot using a single step process.
- Using red oak or cellulose as the feedstock produced comparably high yield of LGO, suggesting biomass pretreatment can be eliminated.
- Plasma electrolysis-based lignin can be upgraded to aromatic monomers in high yields.
- Novel radical-based reaction mechanisms were identified.

Results published in
- A, L., Radhakrishnan, H., Hu, Ha., Hu, Hu., Bai, X (2020), Plasma Electrolysis of Cellulose in Polar Aprotic Solvents for Production of Levoglucosenone, *Green Chemistry*, 22, 7871-7883
- A, L., Radhakrishnan, D. Vincent Sahayaraj, J. Tessonnier, H., Hu, H., Bai, X (2021) One-pot production of oxygenated monomers and selectively oxidized lignin from biomass based on plasma electrolysis, *Green Chemistry* 23 (22), 9109-9125