Hydrothermal liquefaction of solvent-fractionated lignin for aromatic monomer production

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Lignin

- Lignin represents 15-30% of biomass
- Categorized as "waste" with a predicted annual production of nearly 62 M dry tons/year
- Lignin’s chemical structure makes it a potential renewable source of organic compounds, especially those containing electron rich aromatic rings
- Primarily consists of methoxylated phenylpropanoid (guaiacyl and syringyl) subunits.
  - This structure gives lignin an energy density 30% greater than that of polysaccharide polymers

**Lignin-derived monomers = precursors for renewable aromatics and drop-in fuels**
Co-solvent Enhance Lignocellulosic Fractionation: CELF Process

- THF is used to weaken the bonds between lignin and holocellulose
- CELF Lignin: low molecular weight, few phenolic hydroxyl groups, low content of aryl ether bonds, and strong grindability

<table>
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<tr>
<th>Biomass</th>
<th>CELF Conditions</th>
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<tbody>
<tr>
<td>Agricultural Feedstock</td>
<td>Pine, Corn Stover, Bagasse 150°C, 25 min, 0.5% acid, 1:1 THF:Water</td>
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<tr>
<td>Wood</td>
<td>Poplar, Maple 160°C, 15 min, 0.5% acid, 1:1 THF:Water</td>
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Fig. CELF Pretreatment and lignin extraction process
Carbohydrate peaks at 65-95 ppm almost disappeared in all CELF Lignin samples
• “No” (<2%) polysaccharides left

Aromatic C-O peak (155 ppm) and COO peak (172 ppm) reduced
• Signifies cleavage of linkers between aromatic rings and OCH₃ bond

**Table.** NMR-based quantification of lignin monomers in wood

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<tr>
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<tr>
<td>Bagasse</td>
<td>0.41</td>
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<tr>
<td>Poplar</td>
<td>0.72</td>
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<tr>
<td>Maple</td>
<td>0.80</td>
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Hydrothermal Liquefaction (HTL)

- From CELF process, a warm and wet lignin-rich precipitate is generated from a continuous flow system
  - HTL (a wet-based thermochemical conversion technique): convert lignin to aromatic hydrocarbon-rich biofuels or phenolic monomer chemicals, without cooling and drying feedstock

- In a HTL process, subcritical water in the form of OH\(^-\) and H\(^+\) ions can dissolve and catalyze lignin fragments into phenolic products

**Reaction Conditions:**
- Temperature: 300 °C
- Reaction time: 60 min
- Pressure: 15 MPa
- Solid loading: 10 wt%
- Purge gas: Helium

Why 300°C?
- Typical for HTL
- Gets most acc. to TGA
- Less efficient the hotter you go

**Fig.** Schematic of Hydrothermal Liquefaction of Lignin, including phase separation, and solvent extraction
Observe yield of biocrude for CELF lignin
- PW and MW CELF Lignin produced the greatest yield of biocrude oil after HTL (approximately 52 wt%)

β-O-4 linkages
- Alkyl-aryl-ether linkage
- Most common linkage in lignin – major site for lignin depolymerization

Recombination possible during reactor cooling

Fig. Mass Distribution from HTL of Kraft and CELF Lignin samples. The operating condition was 300°C and 60 min w/ 10% solid loading. Error bars represent standard deviation of two repeated tests.
Volatile monomers in biocrude: GC-MS Spectra

Qualitative identification of compounds/monomers in biocrude
- Mostly phenolic monomers observed
- Lignin is 3D crosslinked phenolic polymer

Kraft (Norway spruce) and Pine are guaiacol rich sources
- Shows highest abundance of guaiacyl units

3-ethylphenol and creosol peaks are only observed in Bagasse and Corn Stover CELF lignin biocrude

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Fig. GC-MS Spectra for biocrude of Kraft and CELF Lignin samples depicting aromatic monomers present in volatile component of biocrude

- Maple
- Poplar
- Bagasse
- Corn Stover
- Pine
Monomer yield: Quantified using GC-FID

- Two major monomers still left to quantify
  - 3-ethylphenol and creosol

- Kraft lignin is dominated by monomers containing guaiacol subunit
  - Pine also shows similar trend

- All other CELF lignin except pine have similar total monomer yield with variations in quantities of each subunit

Fig. Yield of monomers in HTL biocrude per gram of lignin. Calibrated and quantified using GC-FID.
Conclusion

- A clean lignin byproduct is obtained from the CELF process; open for valorization in the form of renewable aromatic chemicals and drop-in fuels

- CELF produces a clean lignin byproduct with almost complete removal of polysaccharides
  - 13C NMR and Cai’s NREL analysis

- Biocrude oil yield of hardwood sources higher: facilitated by more S units
  - Higher S units and feed source could facilitate mass yield by enhancing depolymerization and preventing condensation reactions

- Monomers obtained mostly comprise of phenolic aromatics containing guaiacol and syringol subunits