GREAT LAKES BIOENERGY RESEARCH CENTER

# Strategies for Clean Lignin Streams and Subsequent Depolymerization


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U.S. DEPARTMENT OF ENERGY

DOE Bioenergy Research Centers

MiFBI, October 11-12, 2017

# Cu-catalyzed Alkaline Hydrogen Peroxide Pretreatment (Cu-AHP)

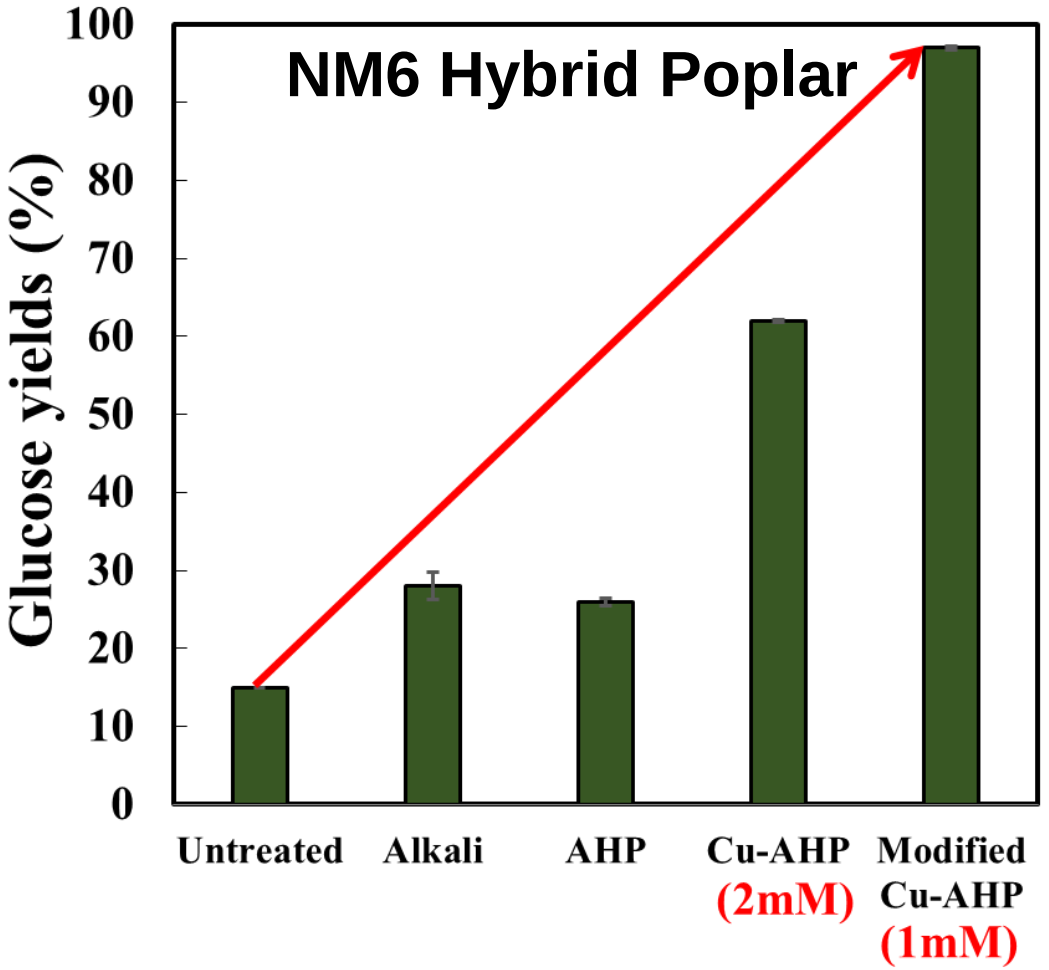
Raw Biomass

**Stage 1**
Alkaline Extraction → (30 °C)

Extracted Biomass

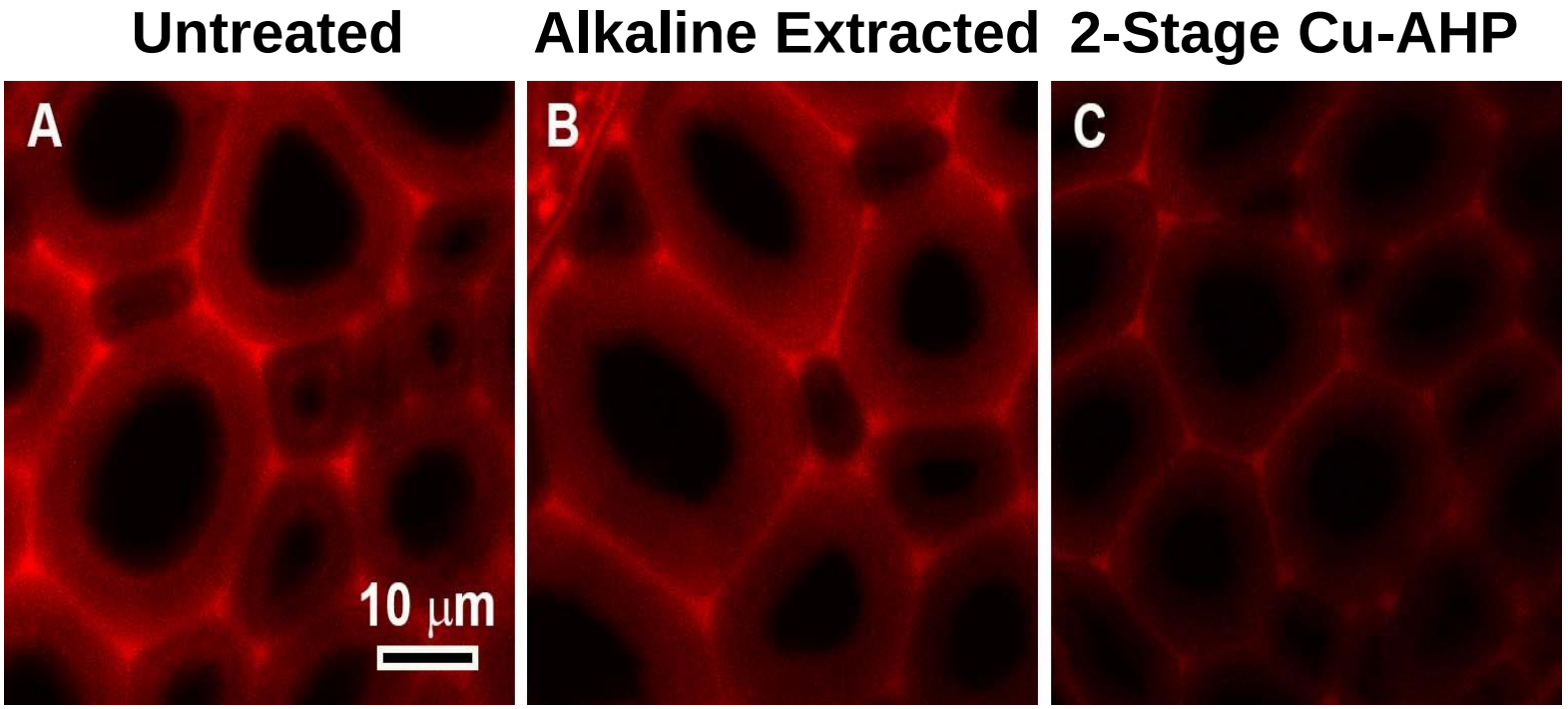
**Stage 2**
1. NaOH
2. Cu(bpy)
3. $H_2O_2$ → (30 °C)

Cu-AHP Biomass




- *Biotechnol. Biofuels* **2016**, *9*, e34

# Confocal Microscopy Reveals Changes in Lignin Content

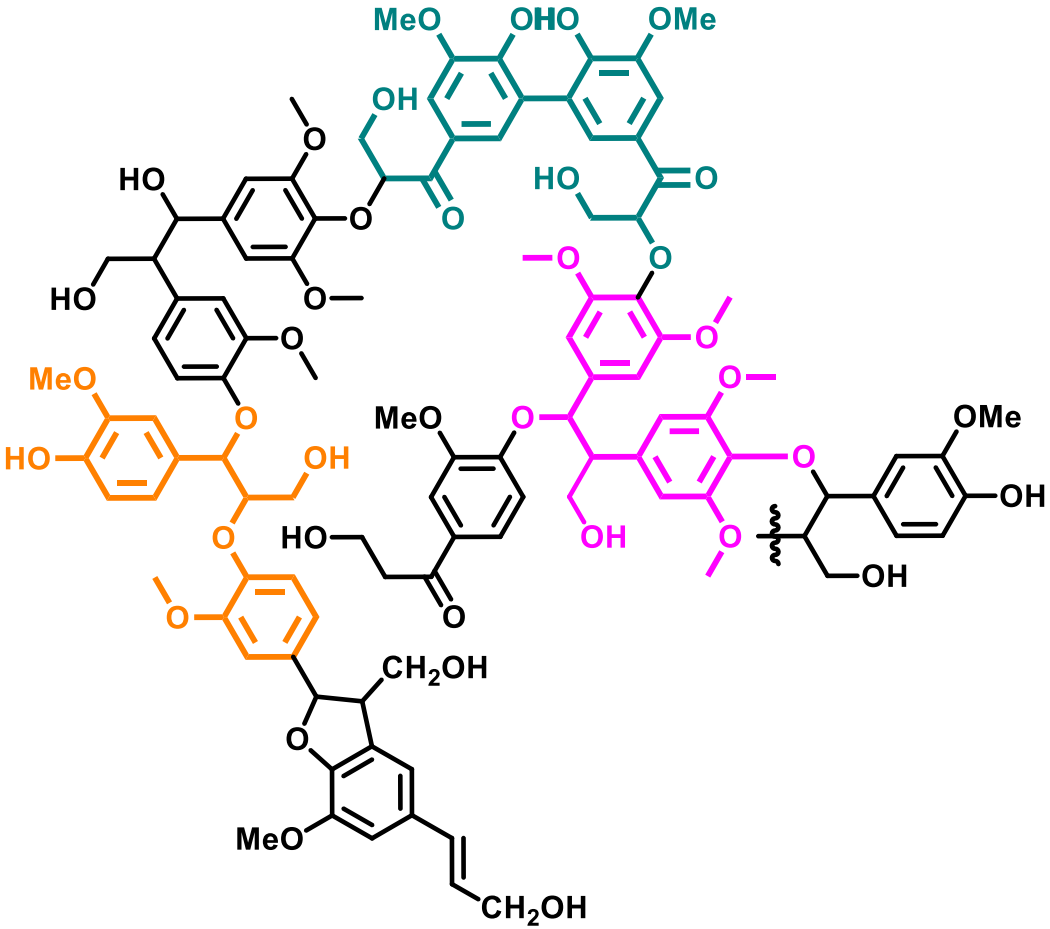


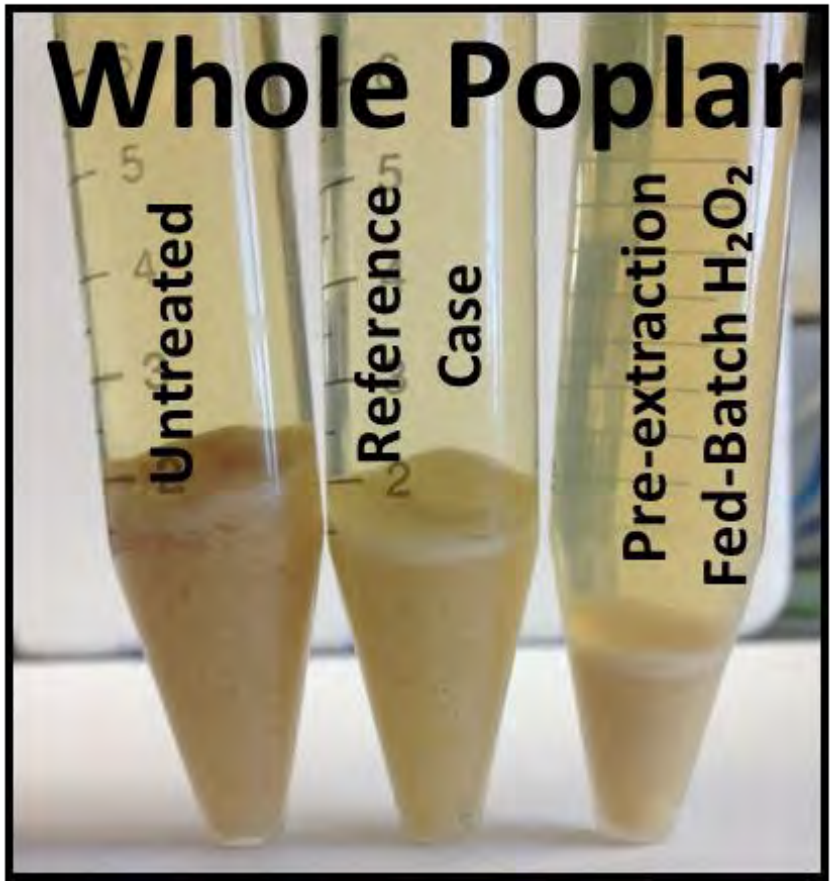

- *In collaboration with Shi-You Ding (MSU)*

**Cu-AHP pretreatment releases lignin**

# Lignin: An Underutilized Product

- Cu-AHP released 40% or more of the lignin from poplar



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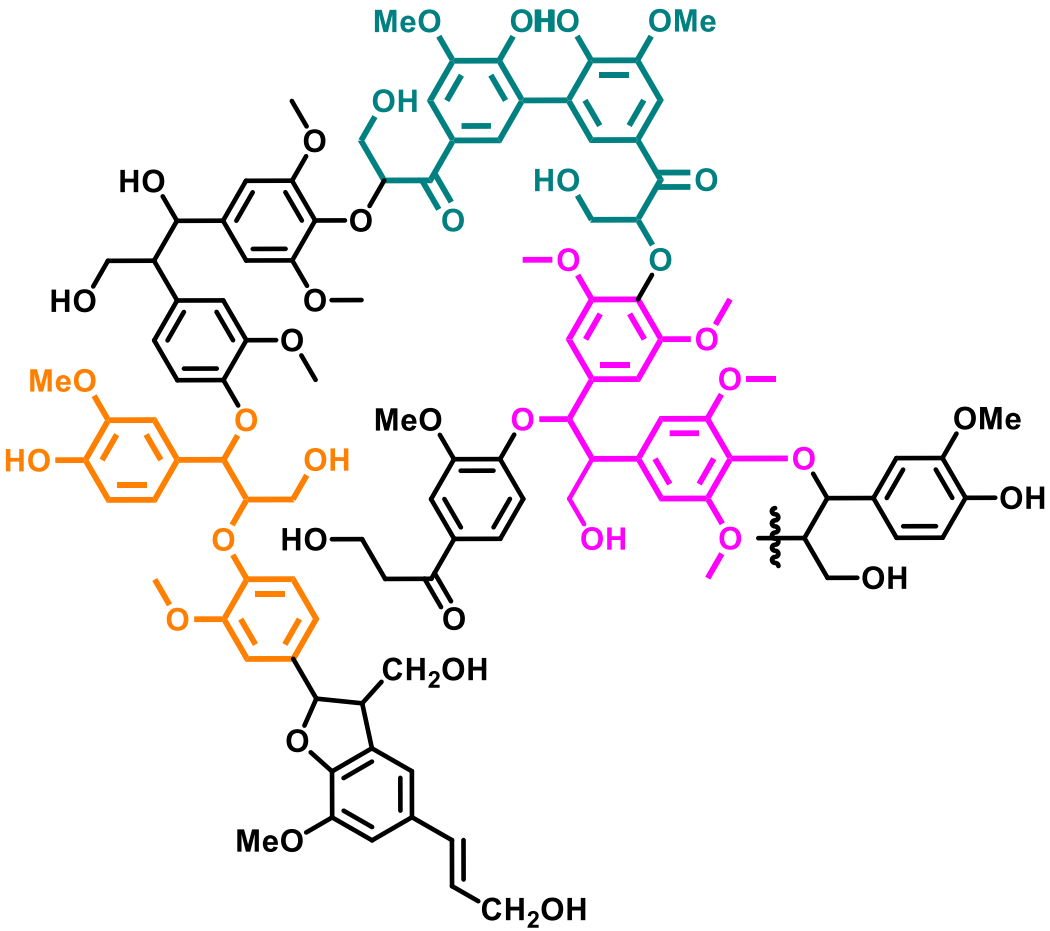
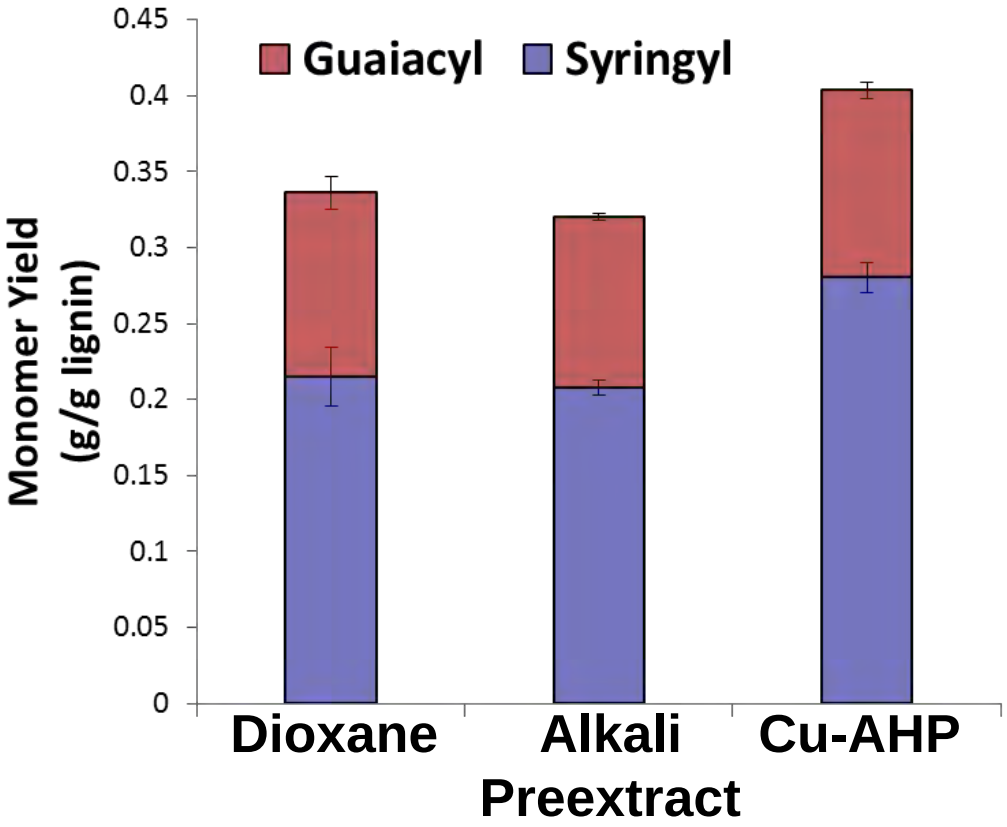



# Analysis of the Lignin Fraction

## Thioacidolysis

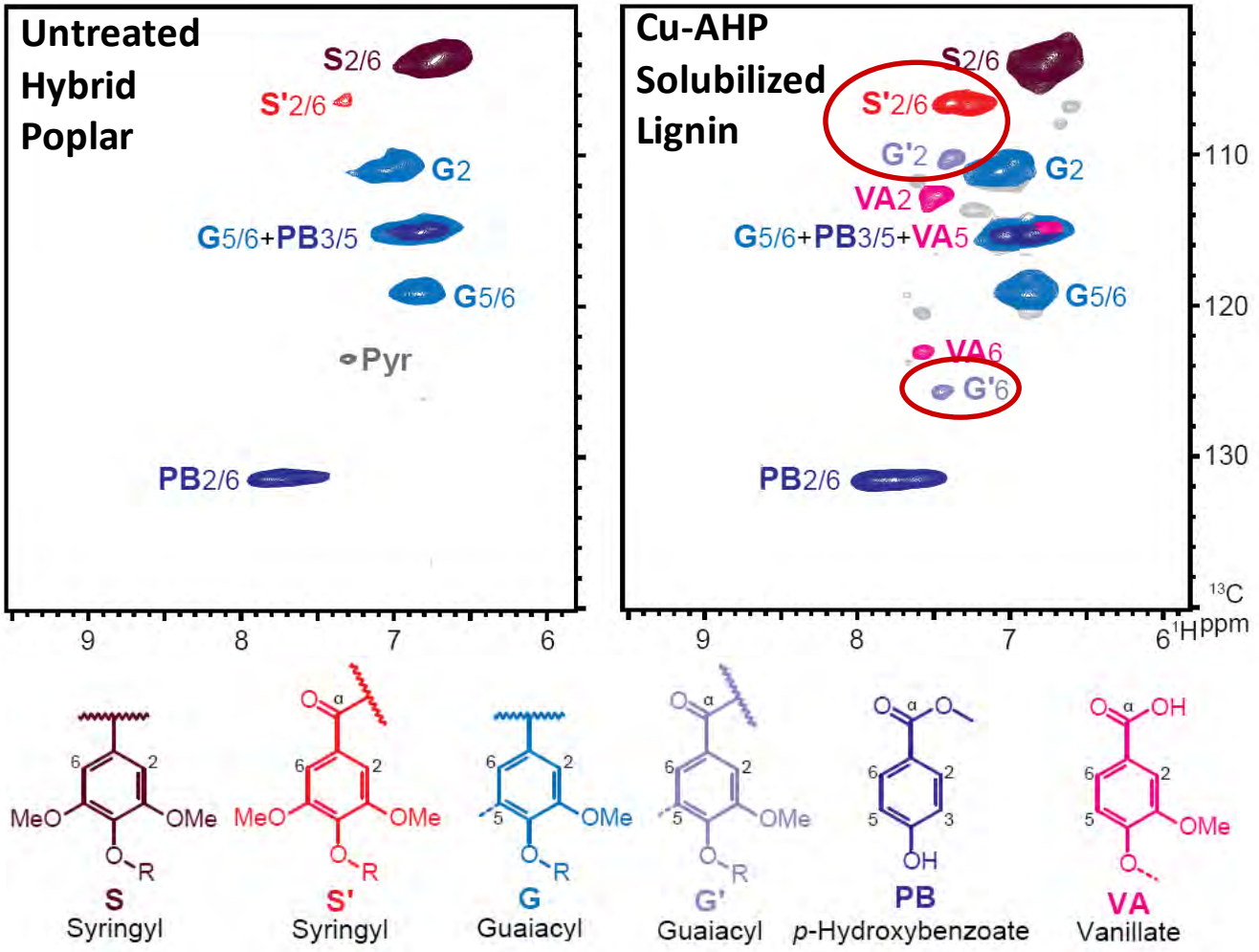



## Gel Permeation Chromatography

| Lignin | $M_n$ | $M_w$ | PDI |
|---|---|---|---|
| Cu-AHP (1st stage) | 5,800 | 13,000 | 2.2 |
| Cu-AHP (2nd stage) | 16,800 | 43,200 | 2.6 |
| Native lignin | 15,100 | 48,400 | 3.2 |

- Cu-AHP lignin stream is largely unmodified and maintains the β-O-4 linkages.

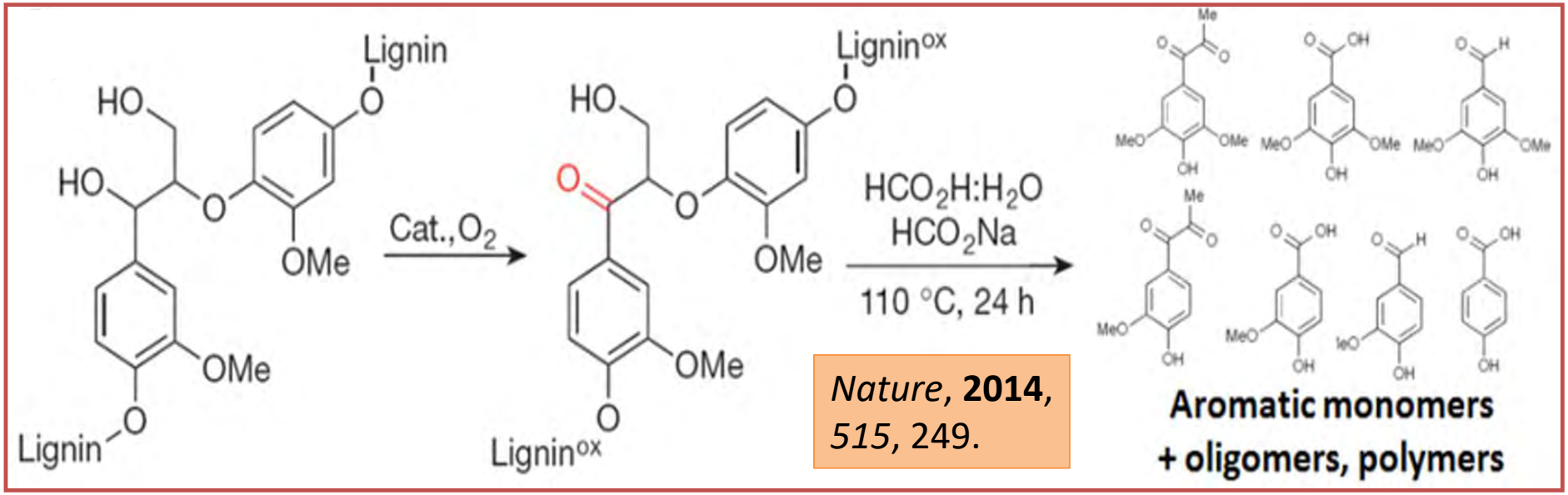
# Lignin Stream Is Slightly Oxidized



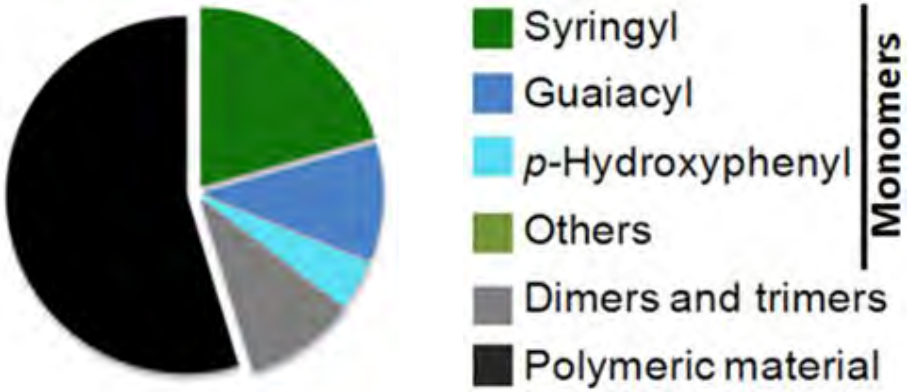

- *In collaboration with John Ralph and Ali Azarpira (UW-Madison)*

# Oxidative Depolymerization

- Stahl process: (1) partial oxidation of β-O-4 bonds
  (2) depolymerization with formic acid

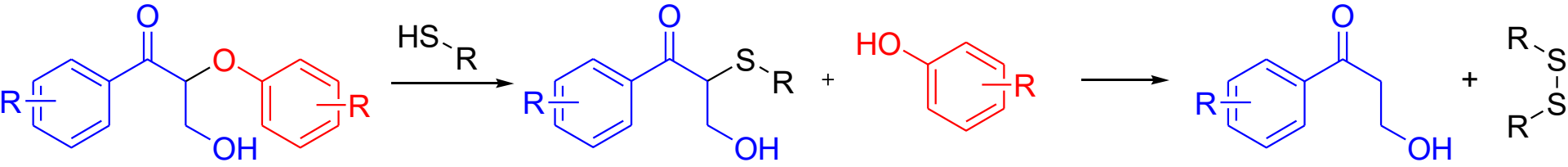



- Cu-AHP lignin stream is uniquely susceptible to depolymerization by this process

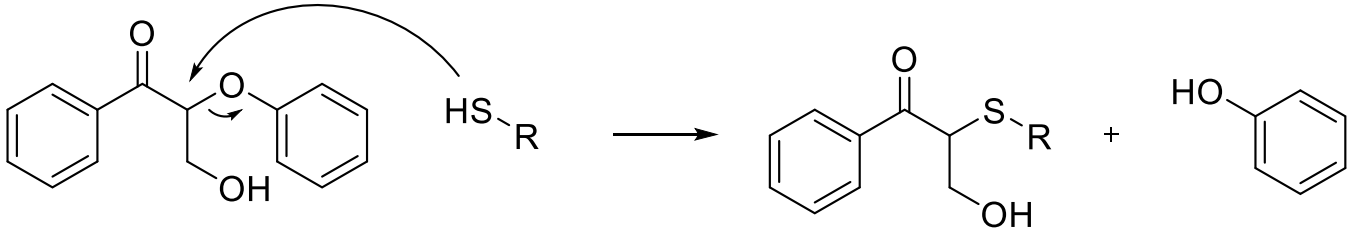


# Reductive Depolymerization

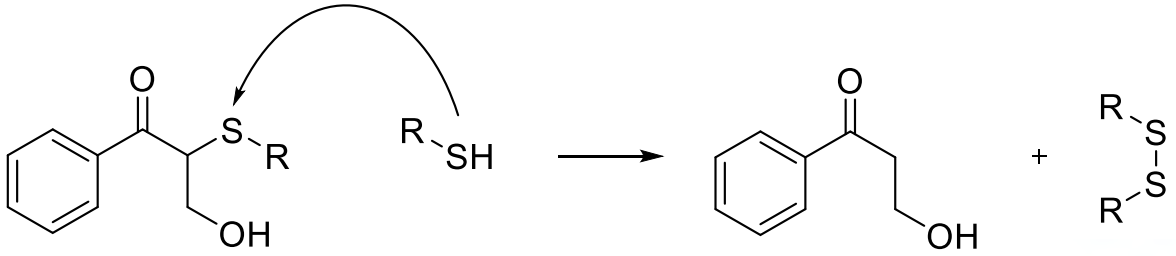
1. Use a small molecular thiol to mimic natural pathway
2. Use electrochemistry to reduce disulfide and make process catalytic




Step 1:




Step 2:



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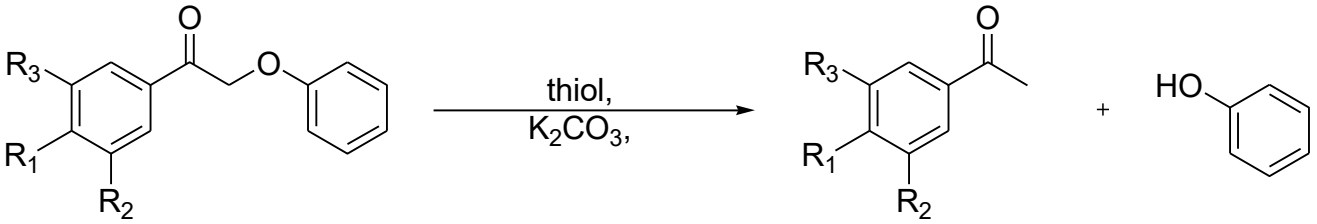
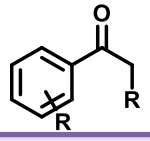
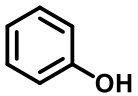
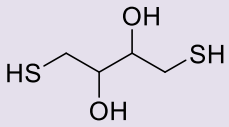
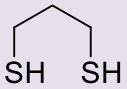



| thiol | Solvent | Mole Ratio | Temp |  |  | % Conv. |
|---|---|---|---|---|---|---|
|  | MeCN | 1:1 | Refluxing | 5.86 | 12.59 | 18.45 |
| | | 1:2 | | 46.67 | 52.81 | 69.10 |
| | | 1:10 | | 25.06 | 33.75 | 55.35 |
| | | 1:100 | | 28.66 | 30.69 | 34.22 |
|  | MeCN | 1:1 | Refluxing | 2.17 | 6.80 | 8.07 |
| | | 1:2 | | 4.37 | 9.61 | 12.24 |
| | | 1:10 | | 17.74 | 19.12 | 32.92 |
| | | 1:100 | | 87.89 | 88.87 | 99.64 |

# Improving the Separation of Sugar and Lignin Streams

- TEA and LCA will help us simultaneously optimize:
  - Input costs
  - Sugar and lignin yield
  - Lignin properties
- Subject of a new DOE BETO grant