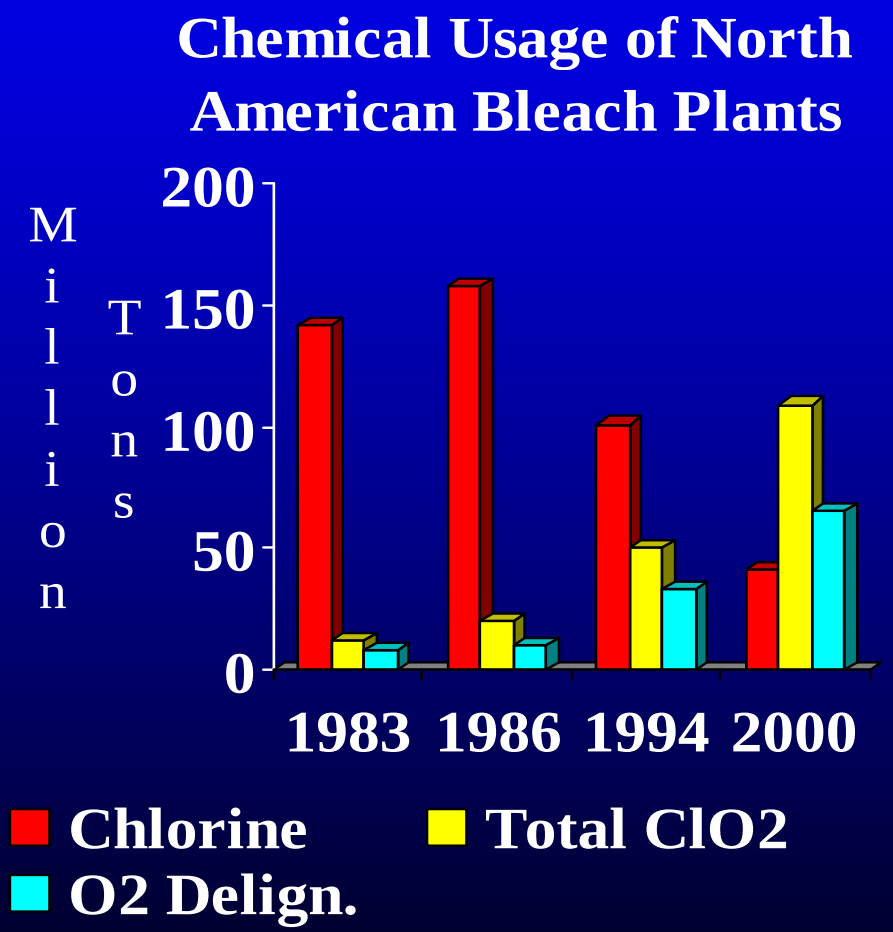
Pulp Properties Influencing Pa & Oxygen Delignification Bleachability

A.J. Ragauskas

Institute of Paper Science and Technology

arthur.ragauskas@ipst.edu

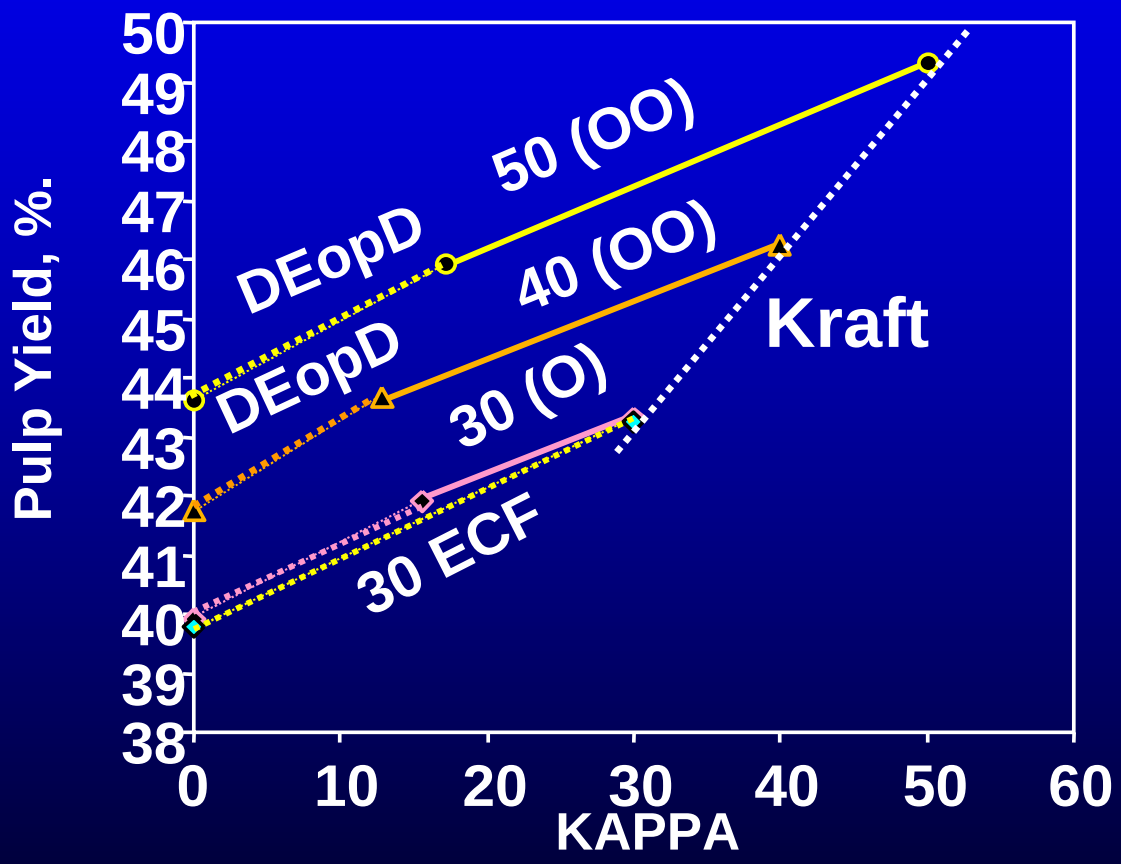
Oxygen Delignification



Improved environmental and operating cost performance

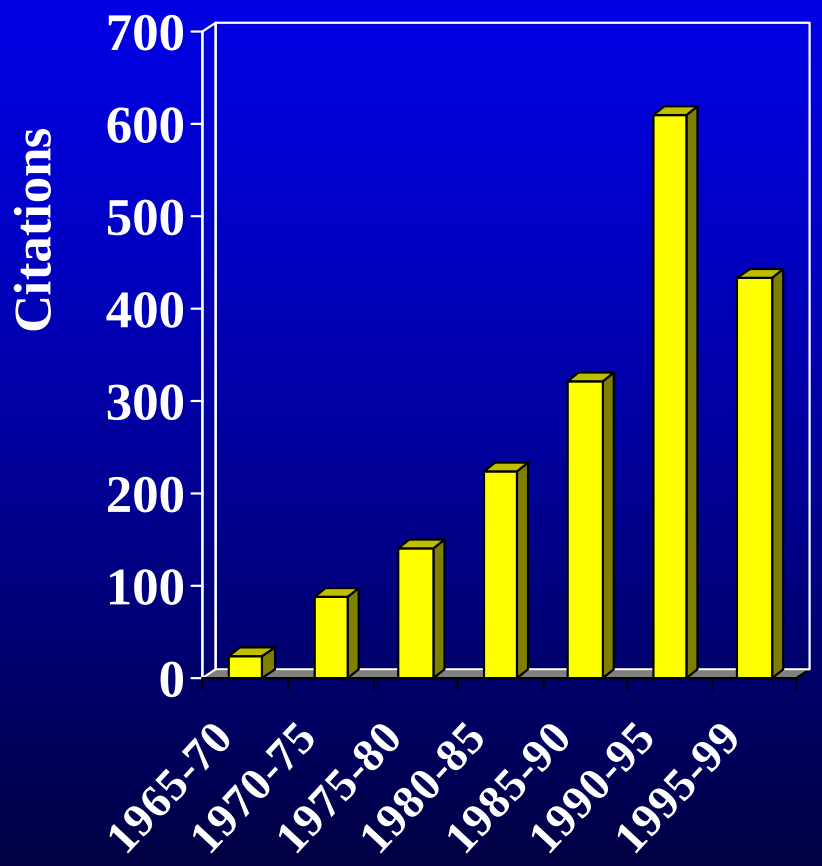
Oxygen Delignification

- Increased interest in one and two-stage oxygen delignification



Improved environmental, operating, and capital cost performance

Oxygen Delignification: Back ground



Literature

- 1960/70s
  - basic engineering & chemistry
- 1980/early 90s
  - process parameters, energy, environmental, pretreatments, fundamental chemistry, pulp properties
- Late 1990's
  - yield, selectivity, process parameters, lignin/carbohydrate chemistry, catalysts

O Delignification

Research Objectives

- Examine use of standard O and aggressive O* delignification conditions on high and low kappa pulps
- High Kappa SW kraft (47)
  - O: 2% NaOH, 90°C
  - O*: 4% NaOH, 105°C
- Low Kappa SW kraft (24)
  - O: 1% NaOH, 90°C
  - O*: 2% NaOH, 105°C
- Effect of Peracetic Acid Treatment

Bleach Sequences

- High Kappa SW
  - O, O*, OO
  - PaO, PaO*, OPaO
- Low Kappa SW
  - O, O*,
  - PaO, PaO*
- Pa: 4% Pa, pH ≈8, 70°C

O Delignification

Research Objectives-II

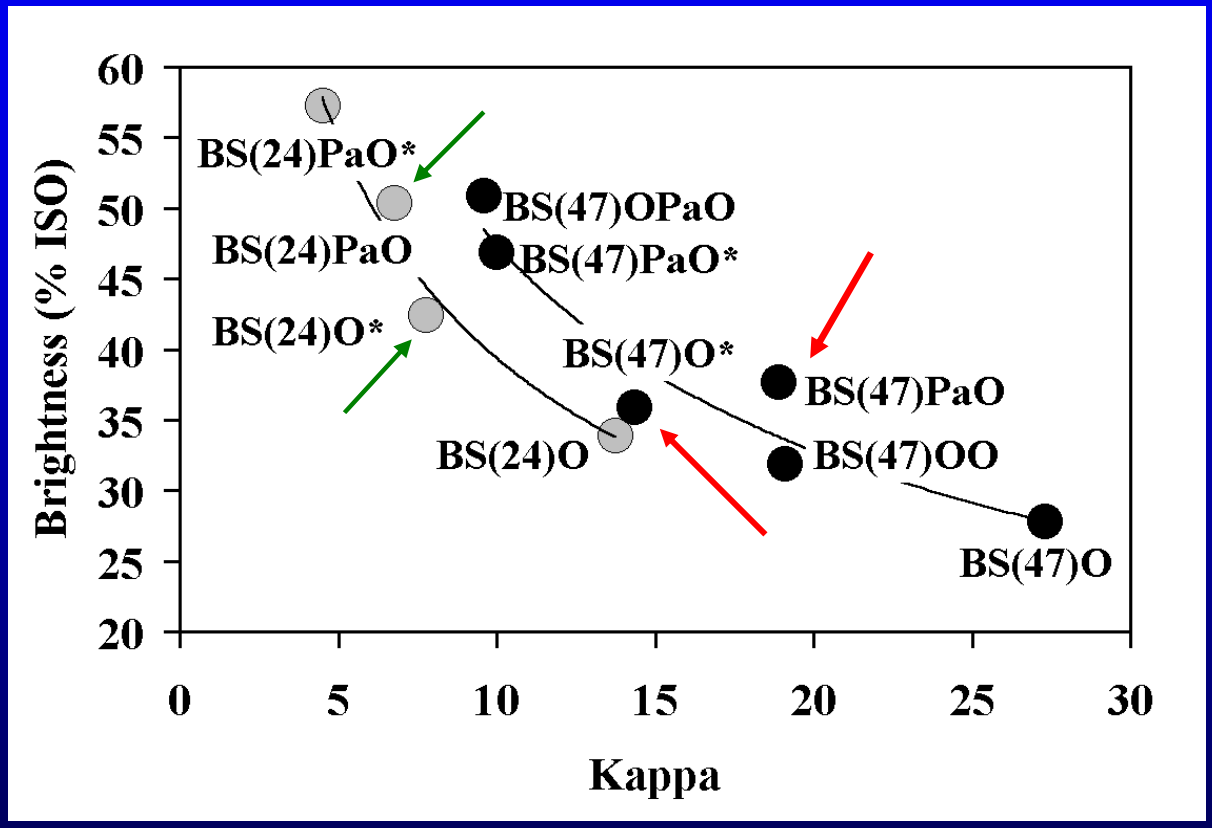
- Determine how varying O and Pa-stages influences residual lignin structure and controls bleachability

Lignin Analysis Techniques

- Isolate residual lignin
- Analyze residual lignin functional groups:
  - **uncondensed phenoxy**
  - **free phenoxy**
  - **acid groups**
  - **quinones**
  - **carbonyl groups--ketones**

O, O*, and Pa Delignification Results

O-Delignification



<u>High Kappa Delignification</u>

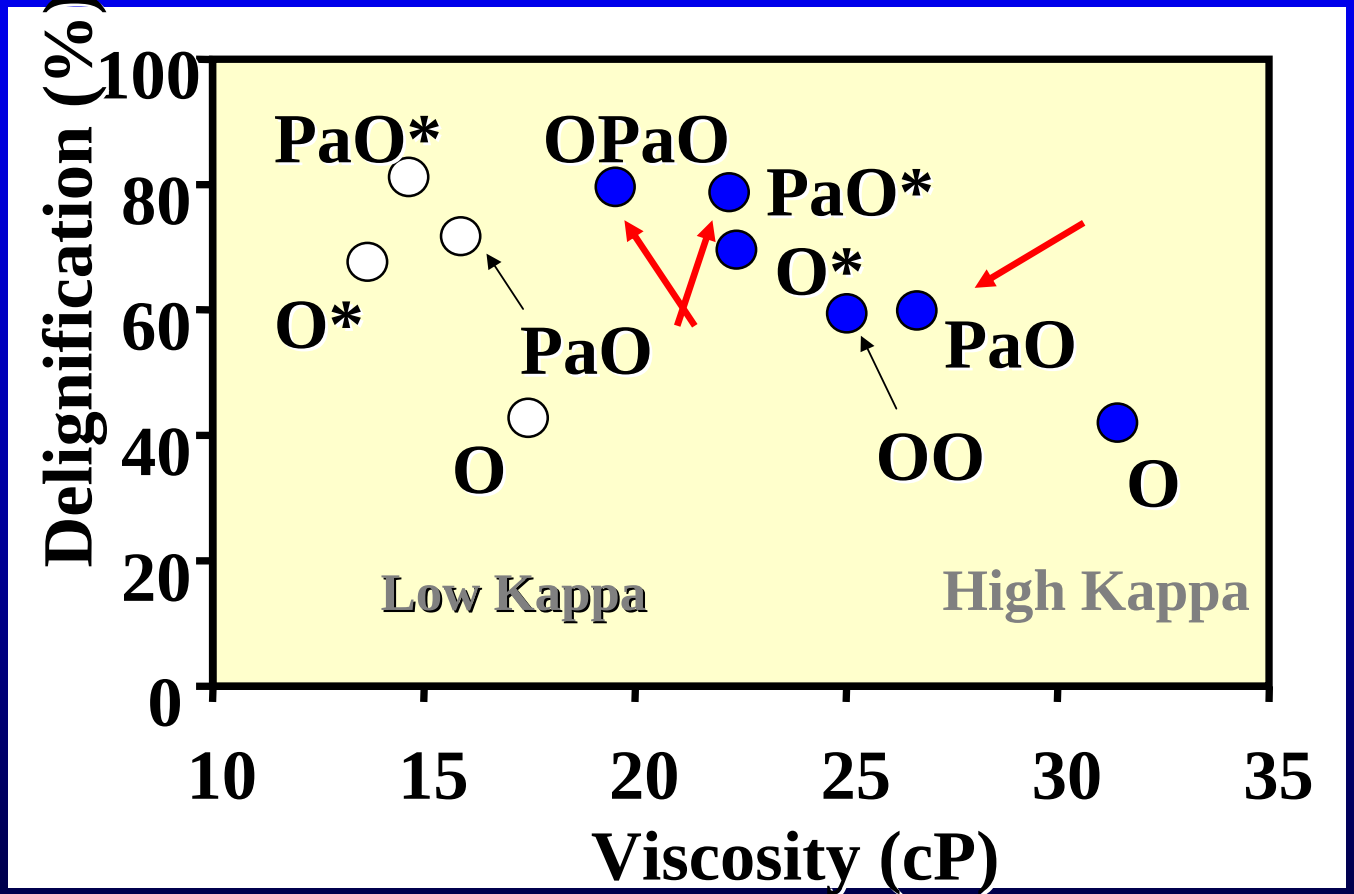
- PaO equivalent to OO
- O* >> PaO or OO
- PaO* >> O*
- Brightness increases as % delign. increases*

<u>Low Kappa Delignification</u>

- PaO > O*

Pa treated pulps usually exhibit a higher brightness

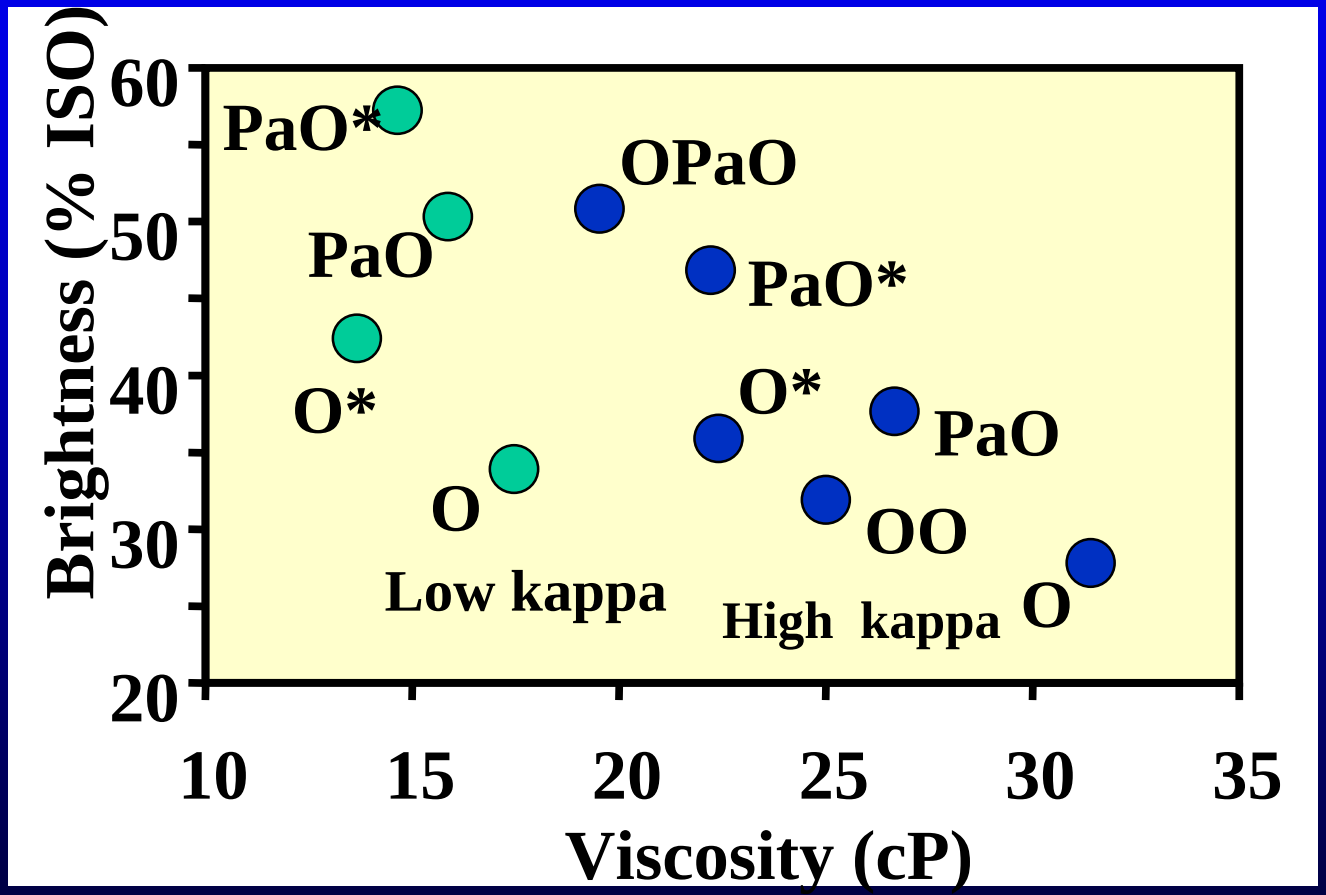
O-Delignification: Viscosity Vs Delignification



Greater delignification incurs greater loss in viscosity

Higher kappa pulps yield higher post O viscosity

O-Delignification: Viscosity vs. Brightness



Higher kappa pulp yields higher brightness at a given brightness

O - Delignification: Summary

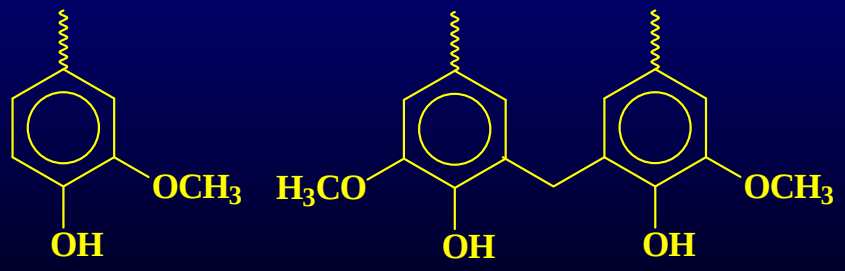
<u>Pulp Results</u>

- High kappa SW pulp yield responded very well to all O treatments
- Pa improved O performance
- >50% O delignification is a possible target

What is the Chemistry?

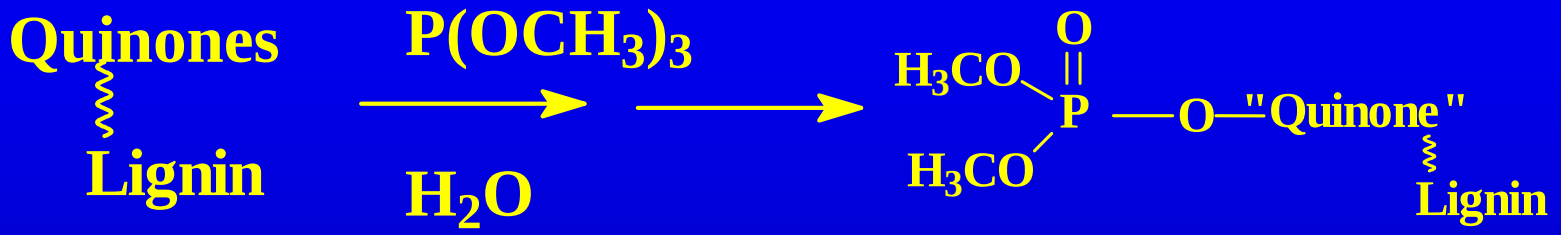
Color Bodies

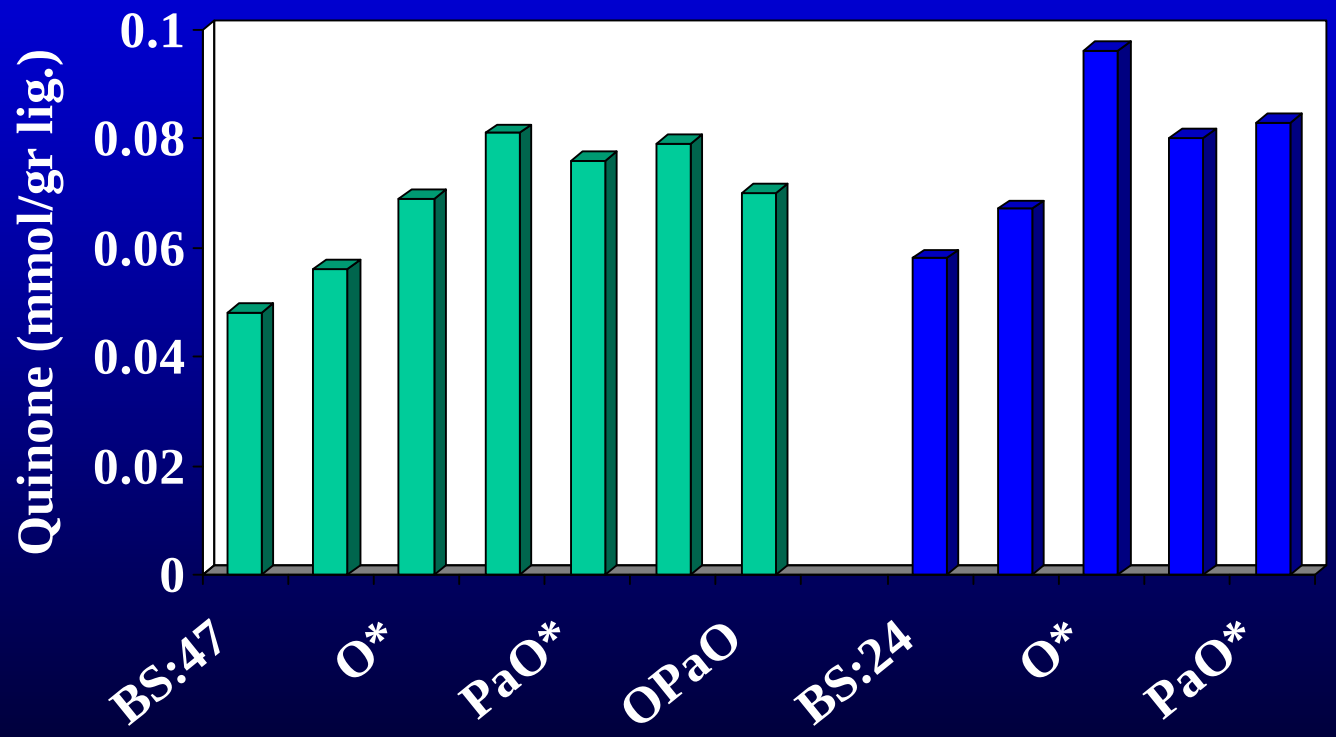
Reactive Sites



Fate of Quinones and Carbonyl Groups After O, O*, & Pa

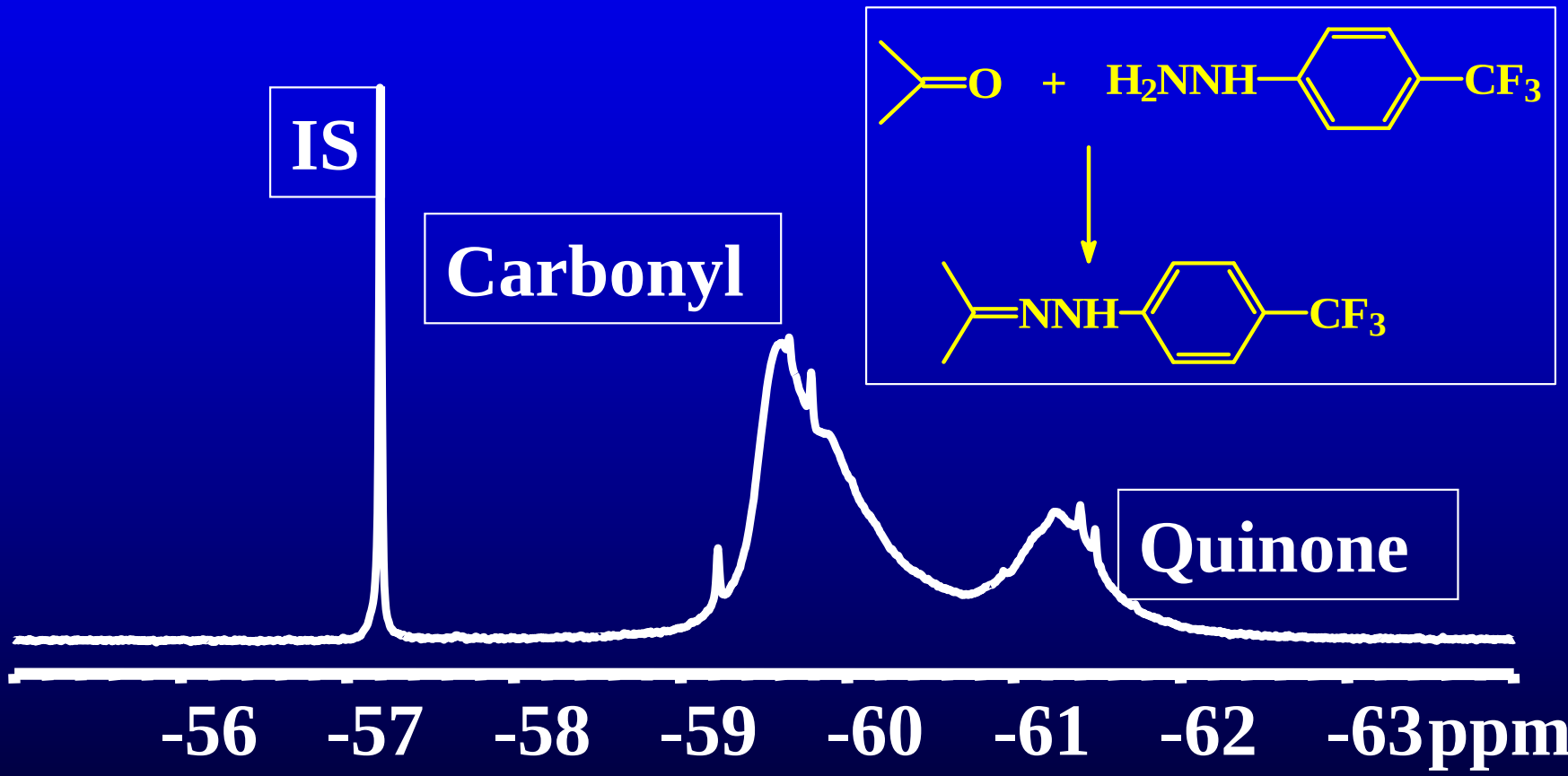
O - Delignification: Quinones



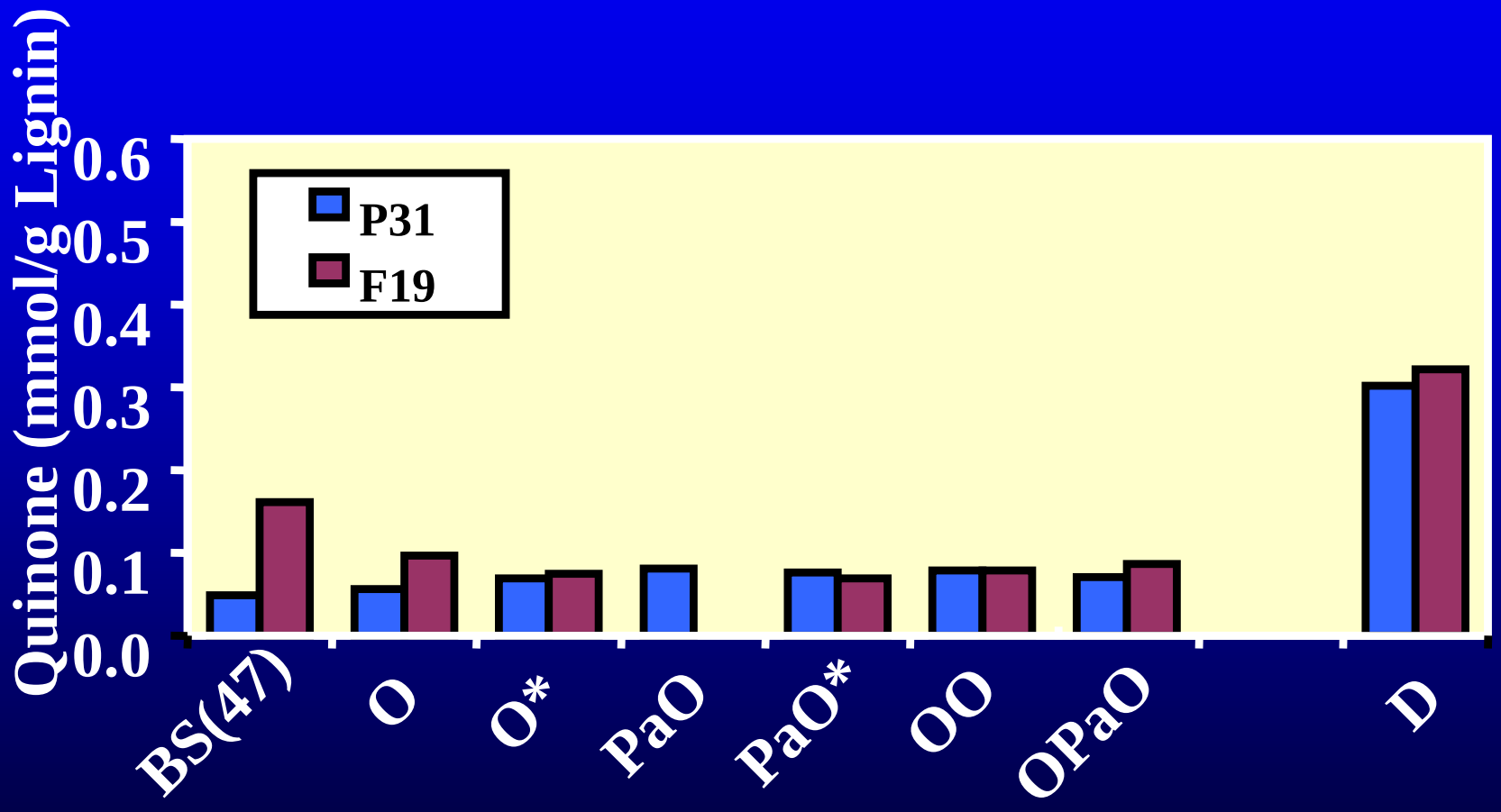


O - Delignification: Quinones

^{19}F-NMR: Lignin

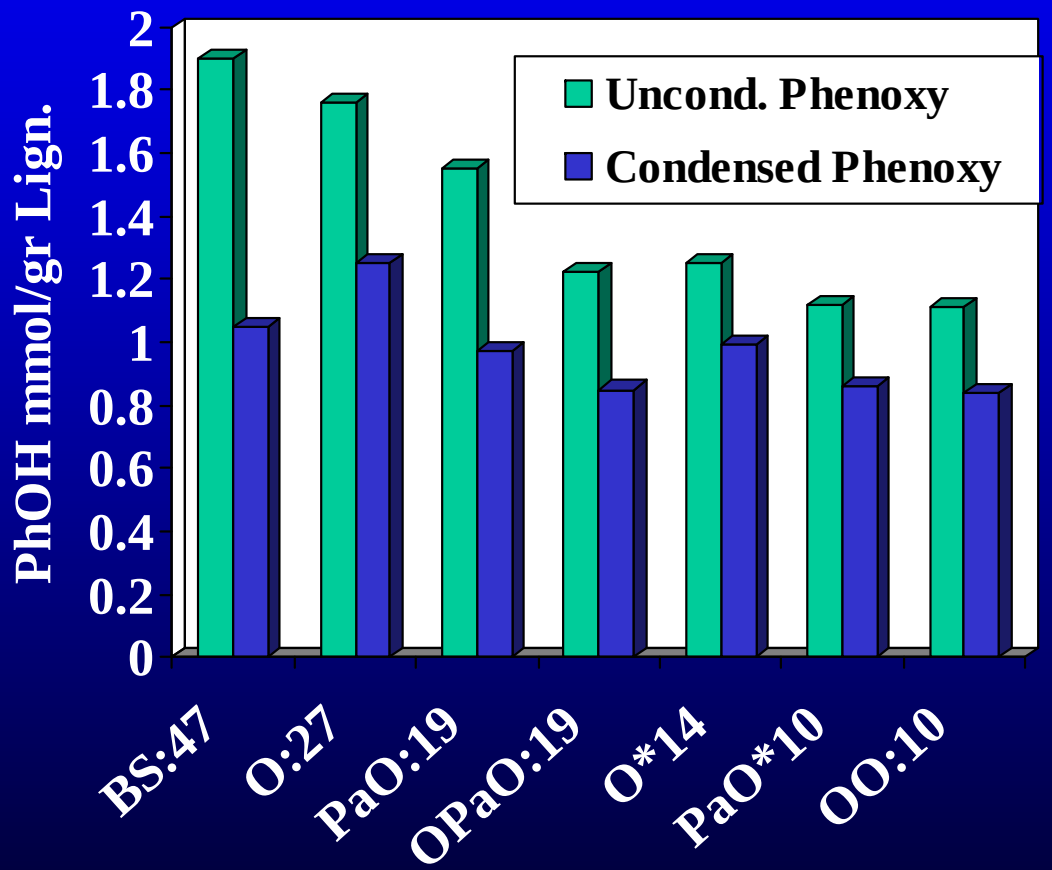


O - Delignification: Quinones

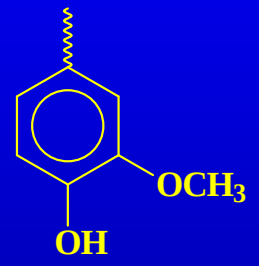


Minor increase in quinones and virtually no increase in carbonyl content of residual lignin

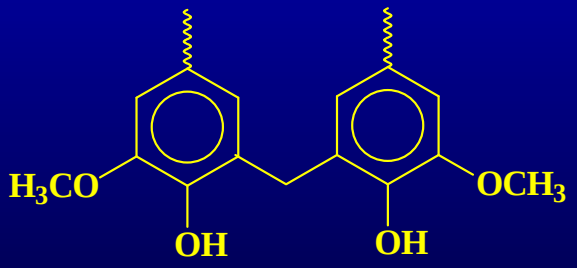
O - Delignification: Phenoxy Groups



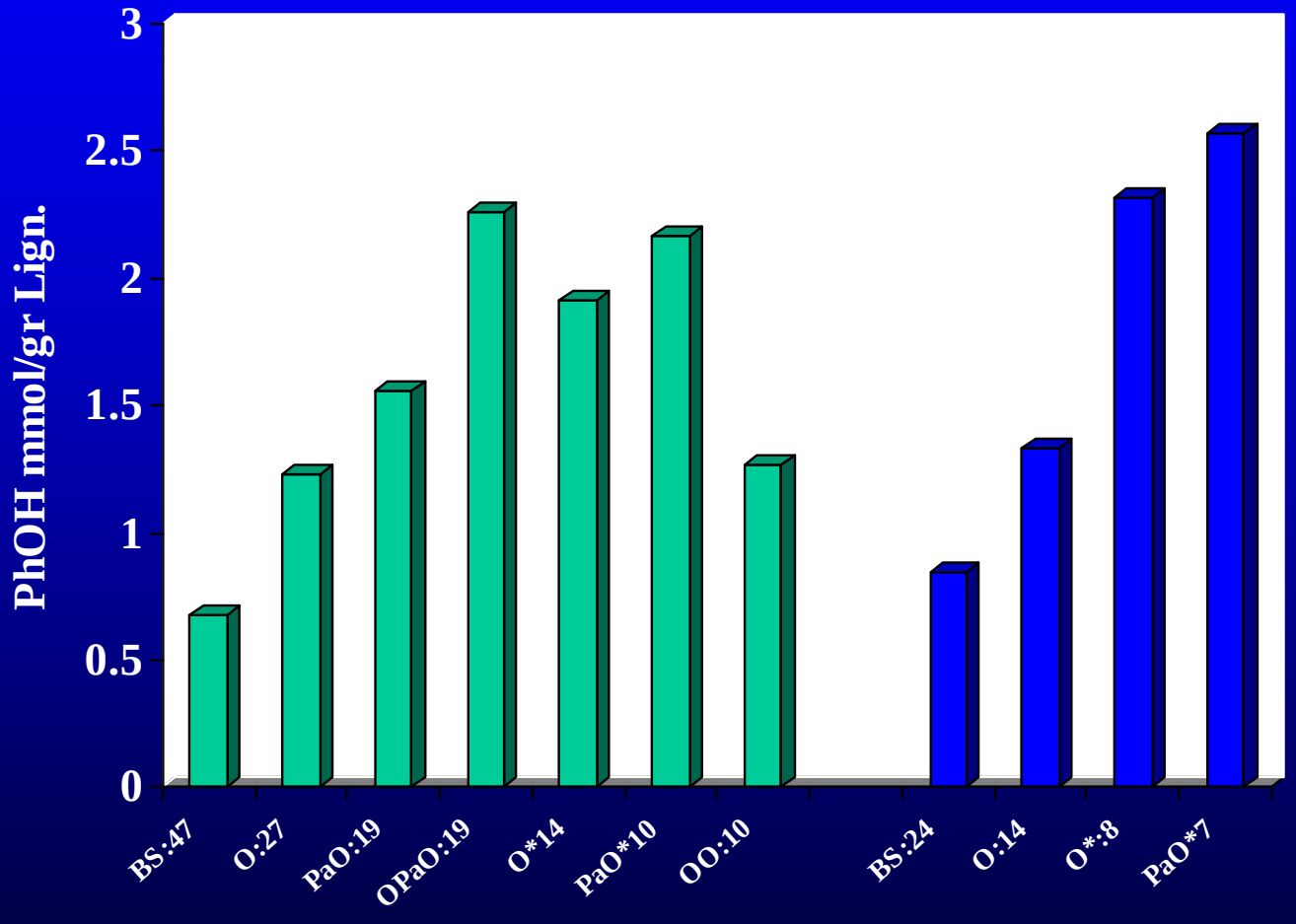
Reactive



Unreactive



O - Delignification: Acid Groups

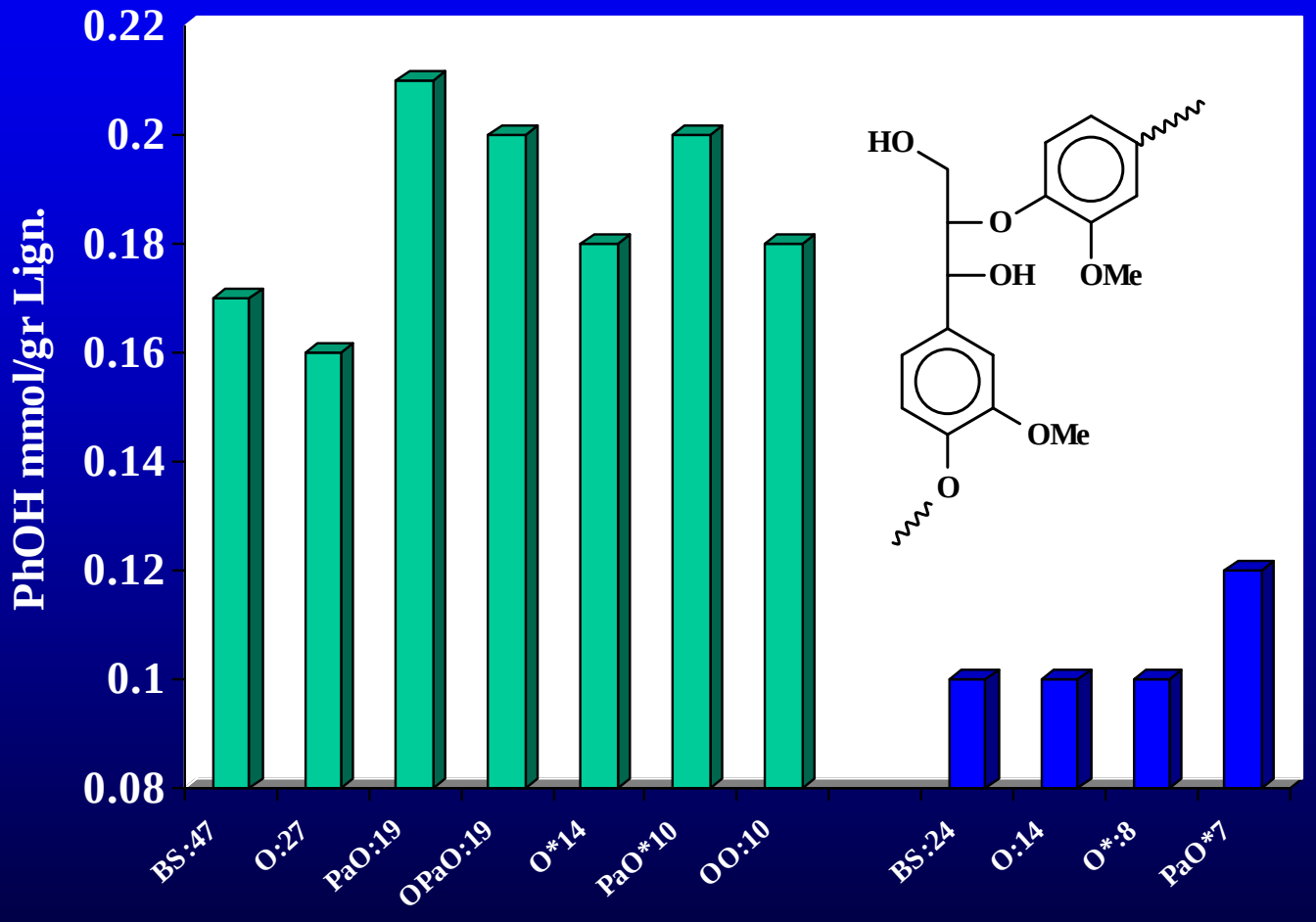


Generally

- Acid groups ∝ % delign.
- Pa introduces more acid groups

Note: despite increased lignin ‘solubility’ resistant to extraction

O - Delignification: β-O-Aryl Ether Groups



Important linkage in pulping & D

Not in O

Note: PhOMe does not change

O - Delignification: Residual Lignin Results

- Primary site of oxidation is unsubstituted phenolics
- Substituted phenols resistant to oxidation
- Quinones/carbonyls appear not to accumulate during O
- Lignin structure enriched in acid groups
- PhOMe and β-O-Aryl Ether unreactive

O - Delignification: Implications

- Enhanced O-stages must activate both condensed and unsubstituted PhOHs
- Mass transfer
- Lignin model compounds provided limited practical guidance

ragauskas@hotmail.com