# Pulp Properties Influencing Oxygen Delignification Bleachability

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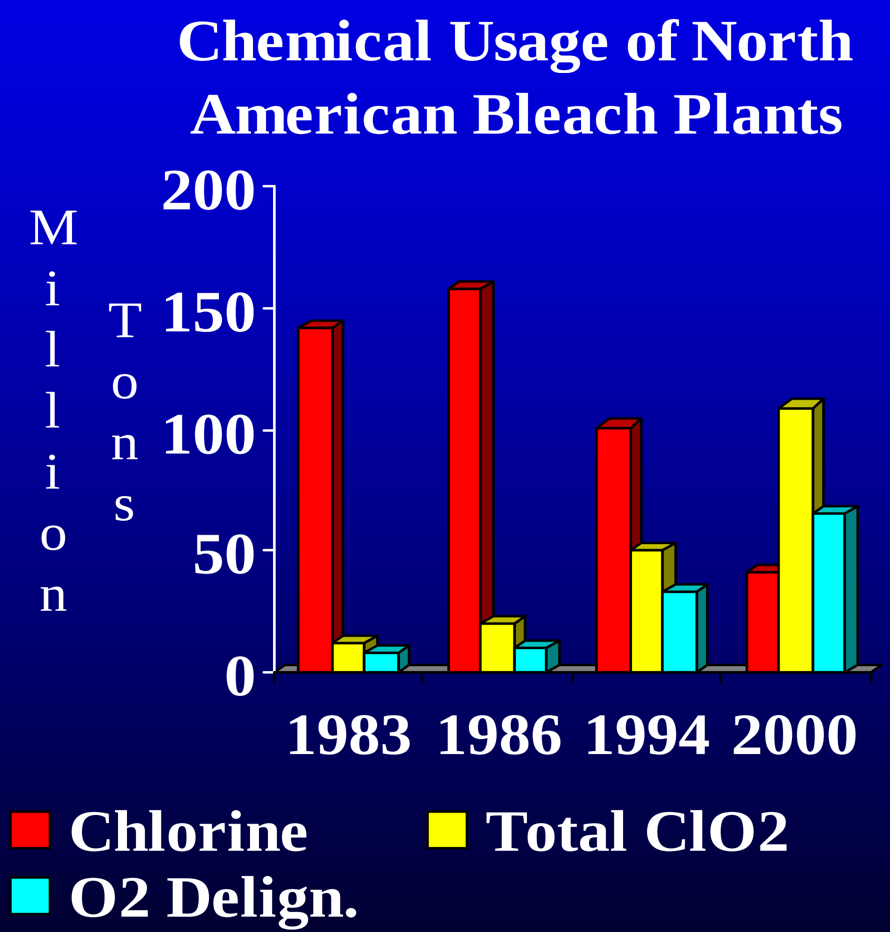
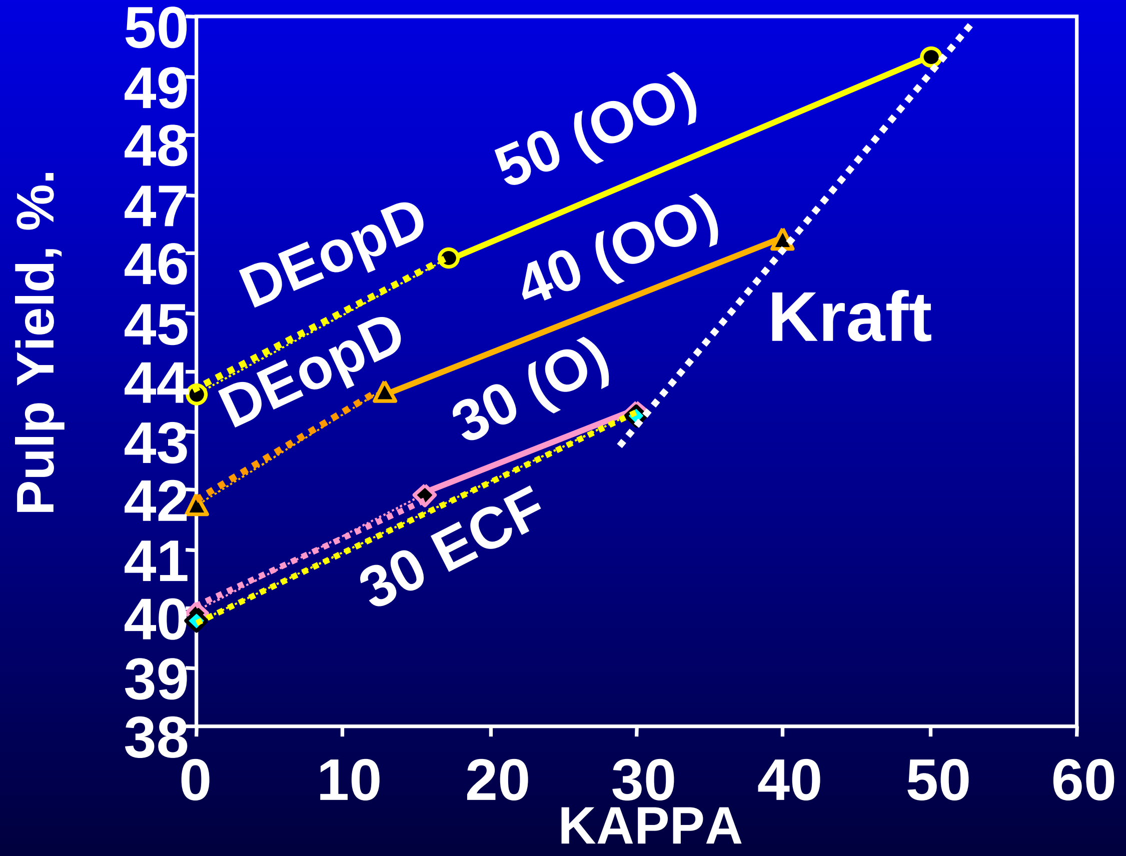
# Oxygen Delignification




Improved environmental and operating cost performance

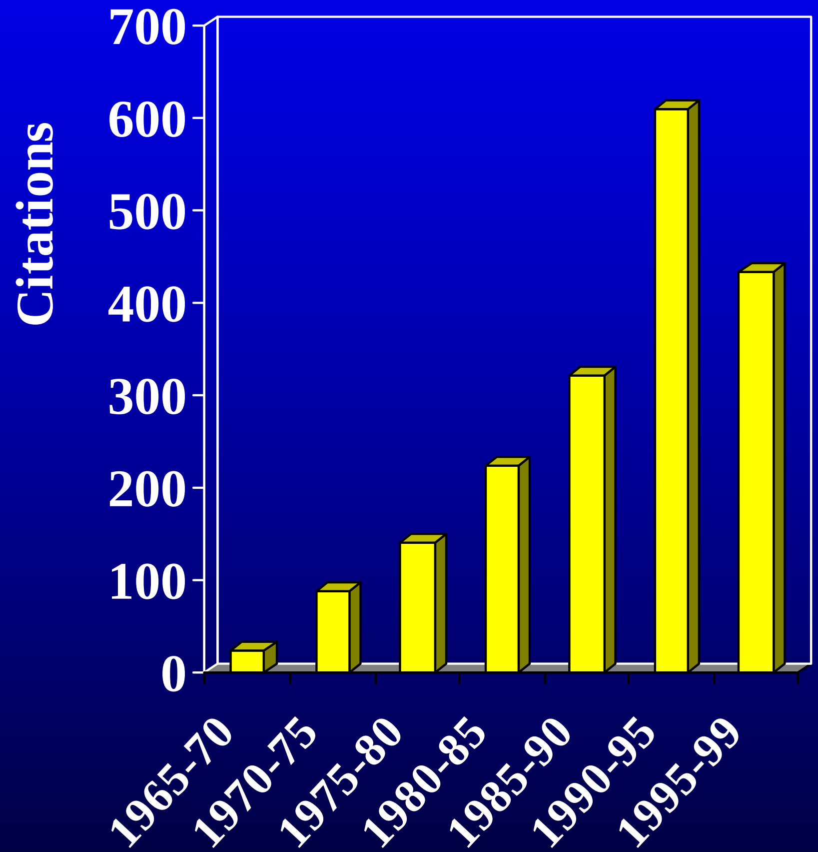
# Oxygen Delignification

- Increased interest in one and two-stage oxygen delignification




Improved environmental, operating, and capital cost performance

# Oxygen Delignification: Back ground

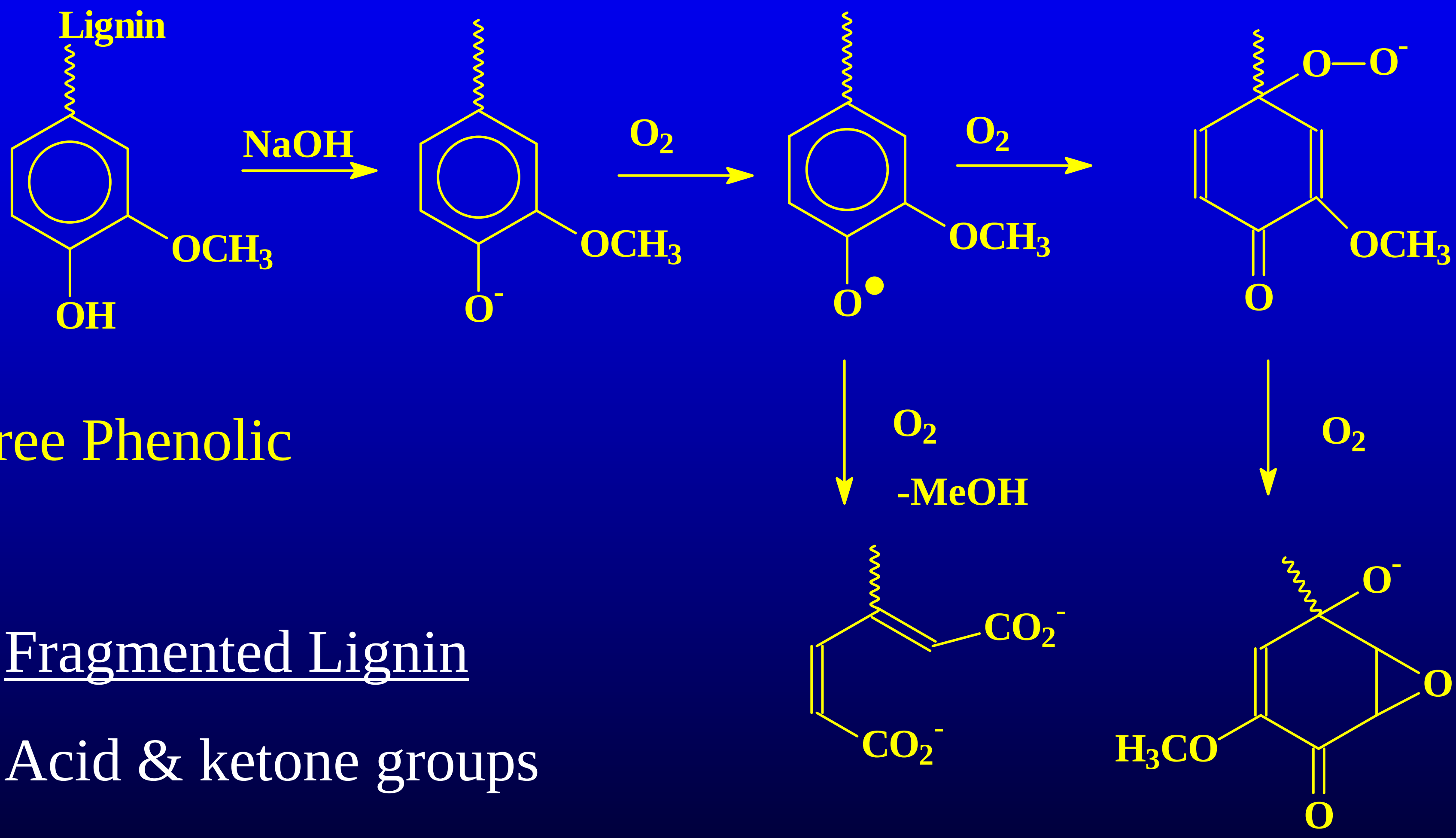



**Literature**

- 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

# Fundamentals of Oxygen Delignification

# Oxygen Delignification: Back ground

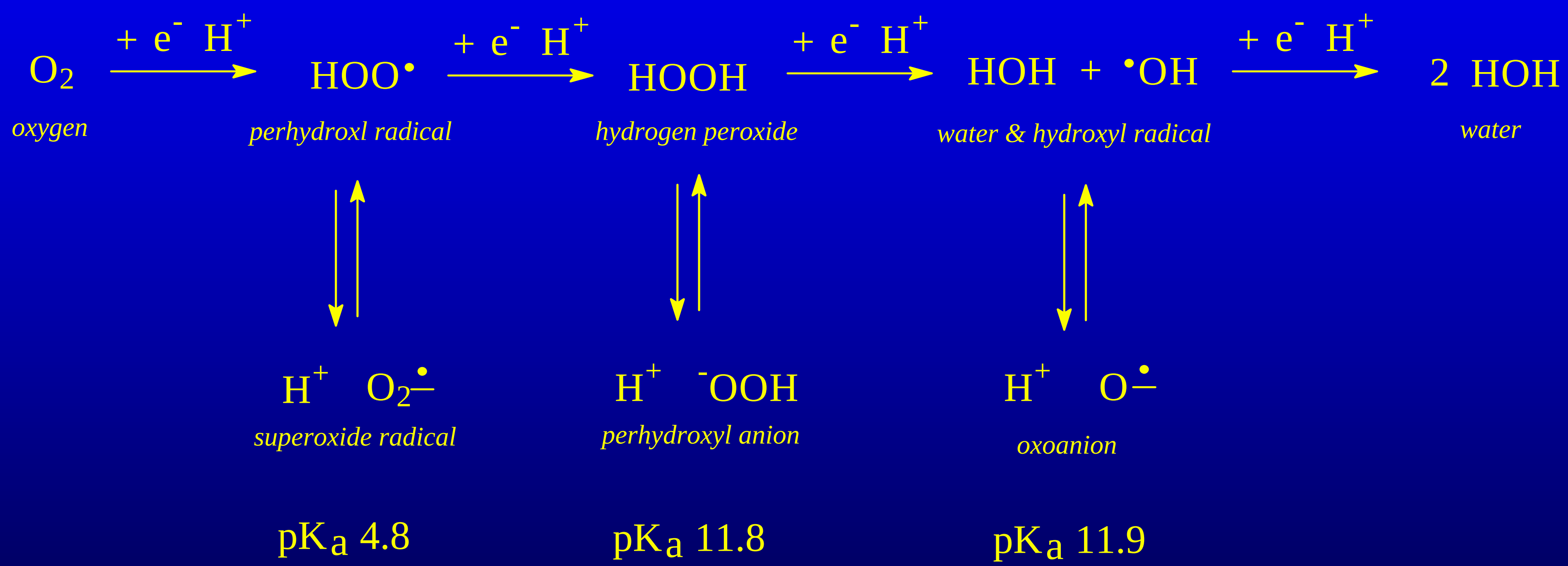



Free Phenolic

<u>Fragmented Lignin</u>

Acid & ketone groups

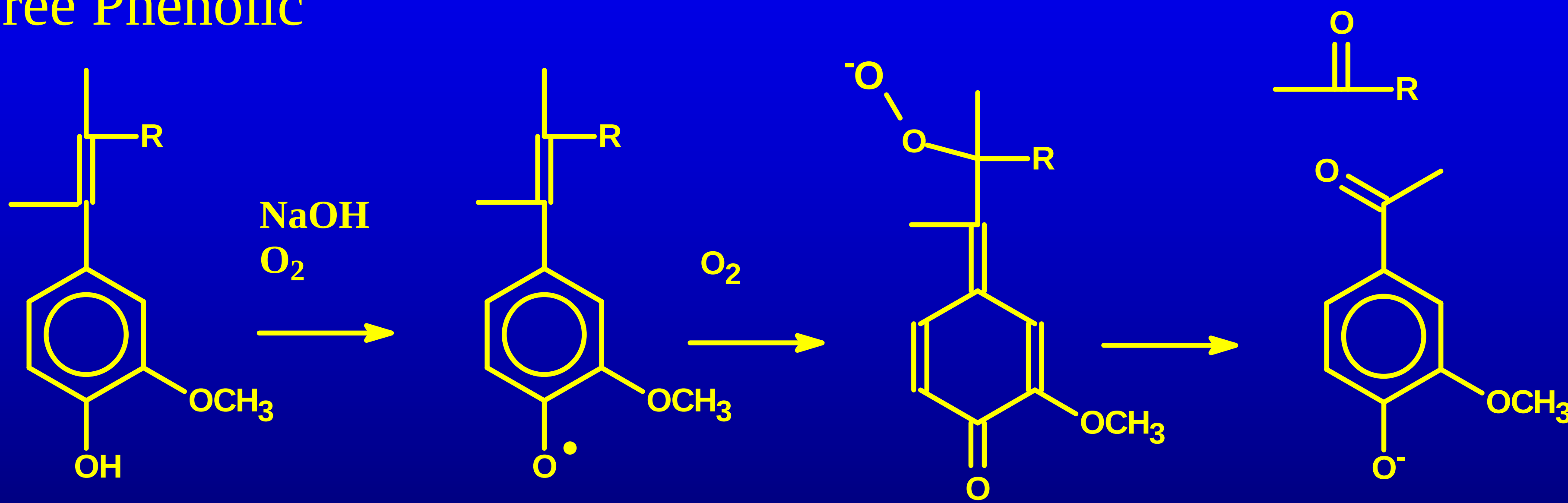
# Oxygen Delignification: Back ground




Several potential bleaching agents with varying sensitivities to reactions with transitional metals

# Oxygen Delignification:  Back ground

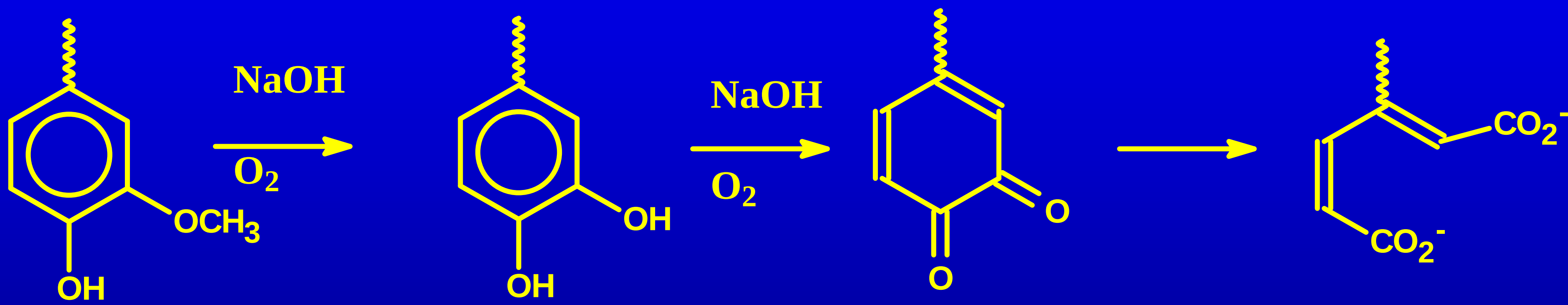
Free Phenolic




<u>Chain Fragmented Lignin</u>

Enriched with carbonyl groups

# Oxygen Delignification: Back ground




Free Phenolic

**MeOH**

**(colored)**

# O Delignification: Lignin Structure Studies

"Oxygen delignification leads to a decrease of various types of phenolic groups in residual lignin. However, condensed phenolics survived....to a large extent" Jiang & Argyropoulos, JPPS, 1999.

"Oxygen delignification does not change the residual lignin structure of kraft pulp to a large-degree" Moe & Ragauskas. Holzforschung, 1999.

"After the oxygen stage, the isolated residual lignin seems to have a somewhat more intact and less oxidized structure than the corresponding lignin from the unbleached pulp." Gellerstedt, Heuts, & Robert, JPPS, 1999.

Discrepancies exist between model compound and residual lignin studies

# O Delignification

## <u>Research Objectives - I</u>

- Examine use of standard O, Pa, and aggressive O* delignification conditions on high and low kappa pulps evaluated by:
  - % Delignification
  - Brightness
  - Viscosity
  - Fundamental lignin structures

# O Delignification: Experimental Design

## Bleaching Conditions

- 75 psig, 60 min., 6% csc
- 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
- Pa: 4% Pa, pH ≈8, 70°C
  - distilled peracetic acid

## Bleach Sequences

- High Kappa SW
  - O, O*, OO
  - PaO, PaO*, OPaO
- Low Kappa SW
  - O, O*,
  - PaO, PaO*

# O Delignification

Research Objectives-II

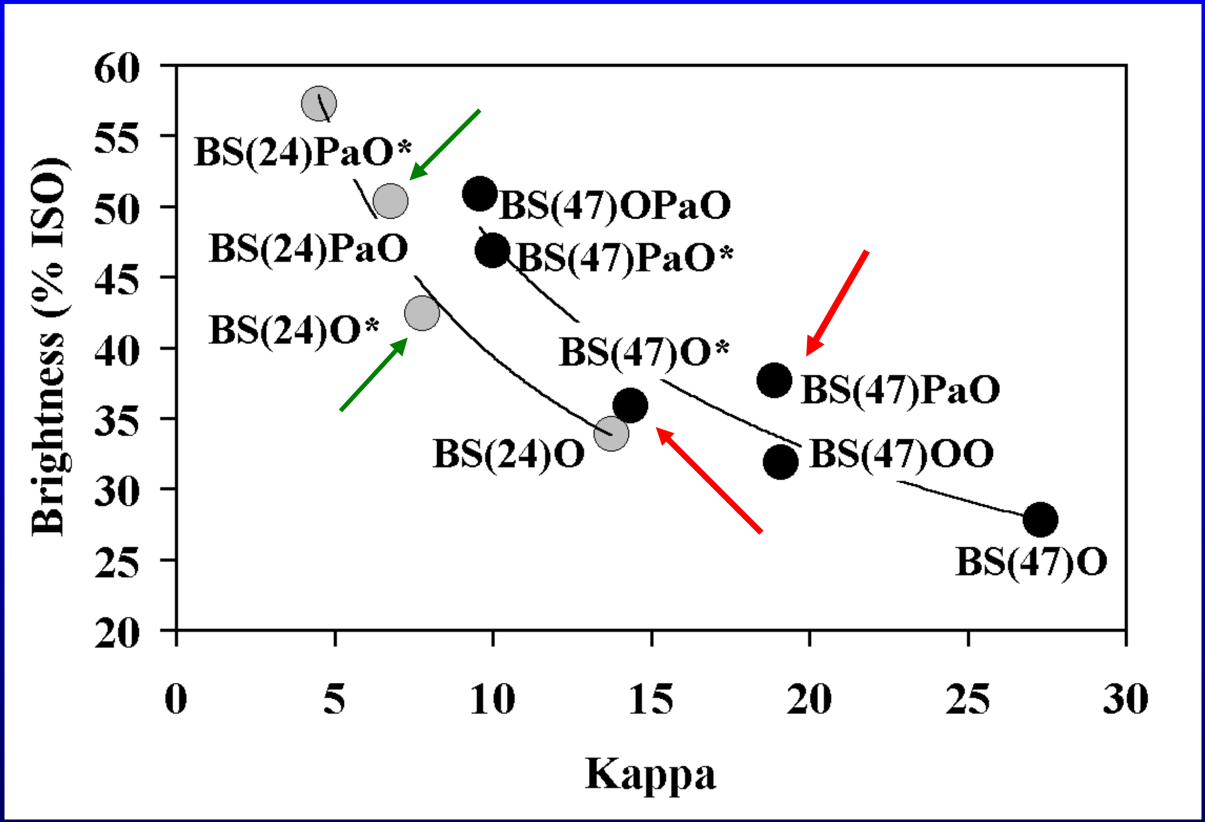
- Determine how varying O and Pa-stages influences residual lignin structure and controls bleachability

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*

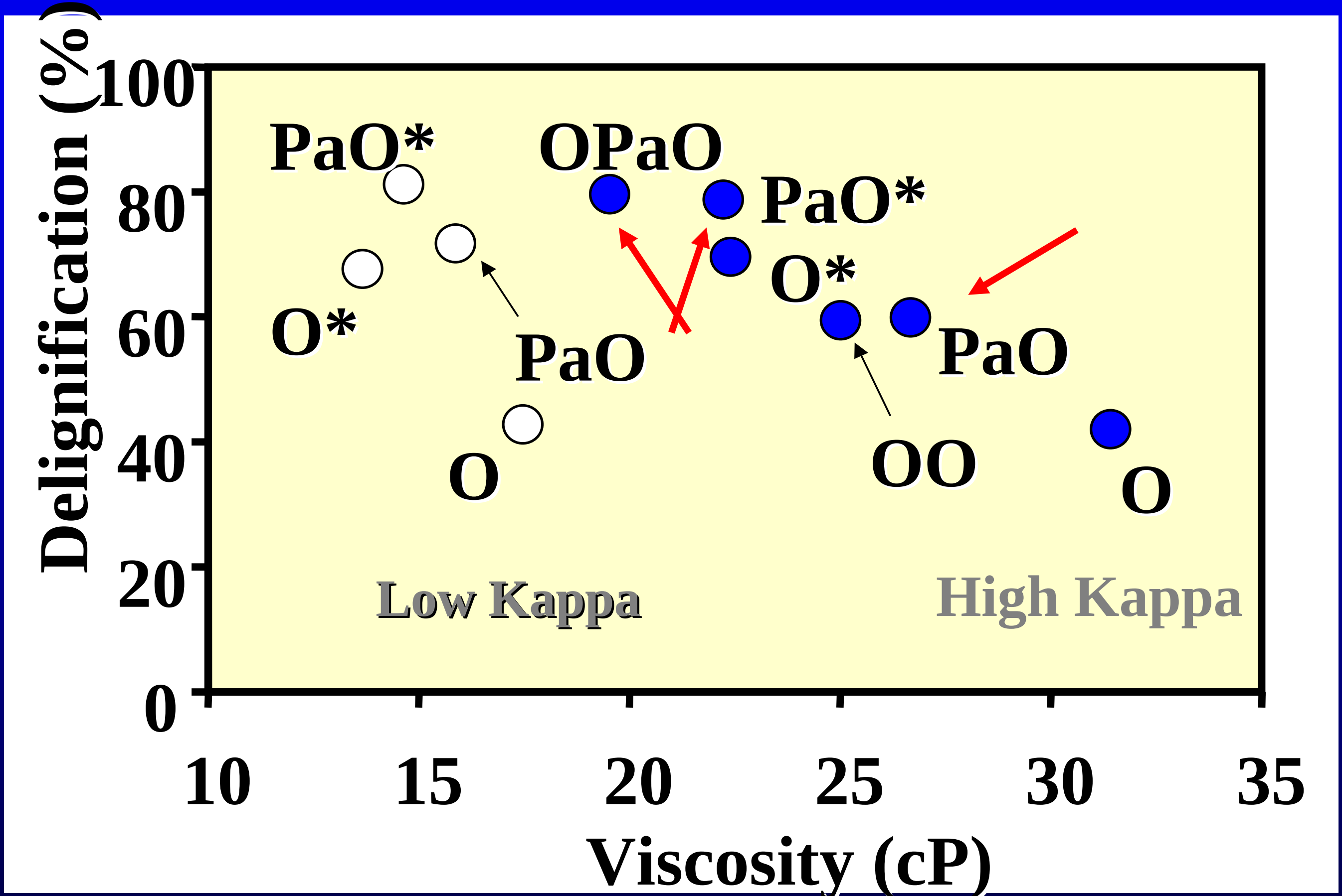
•Brightness increases as % delign. increases*

<u>Low Kappa Delignification</u>

•PaO > O*

Pa treated pulps usually exhibit a higher brightness

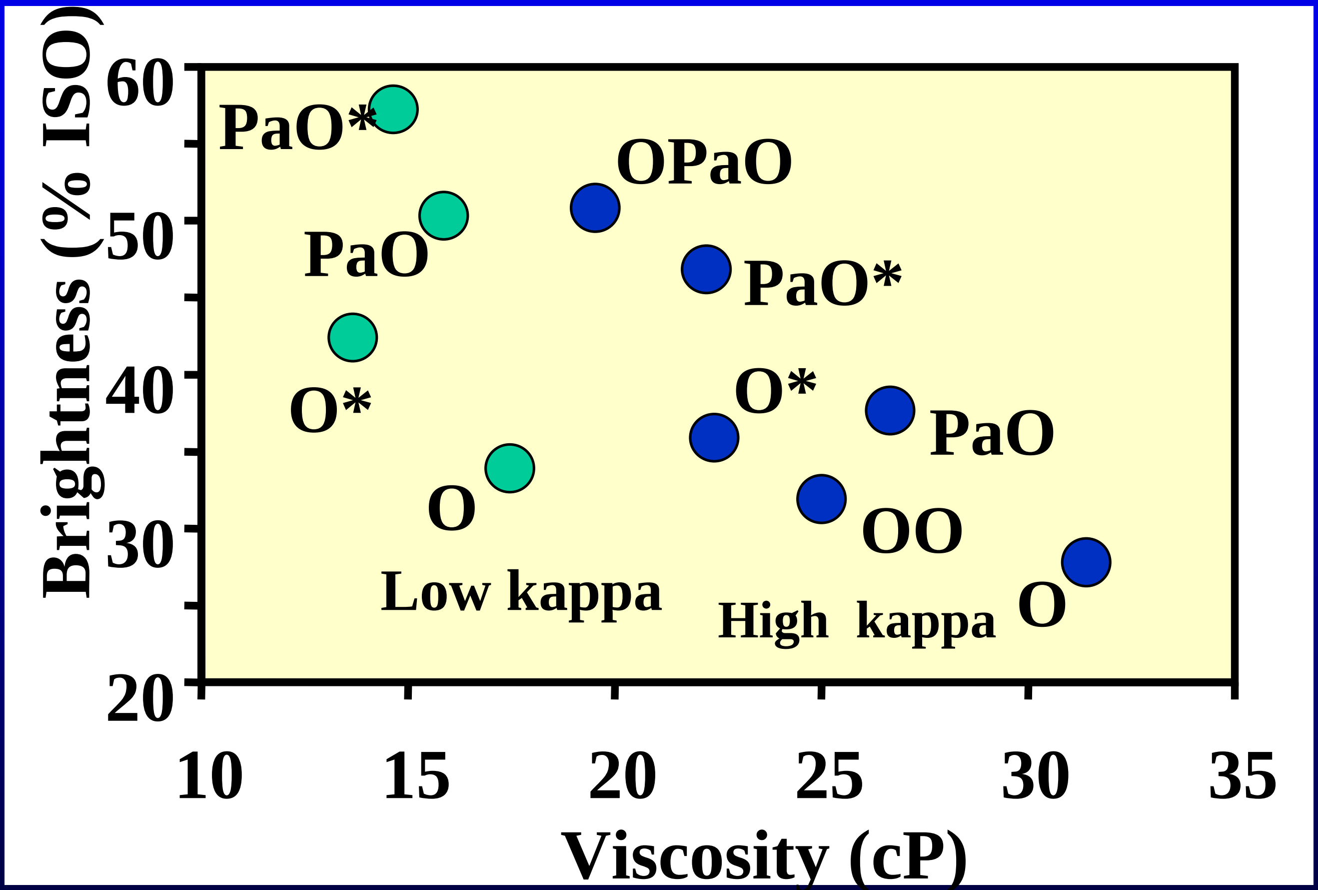
# O-Delignification: Viscosity vs. Delignification




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

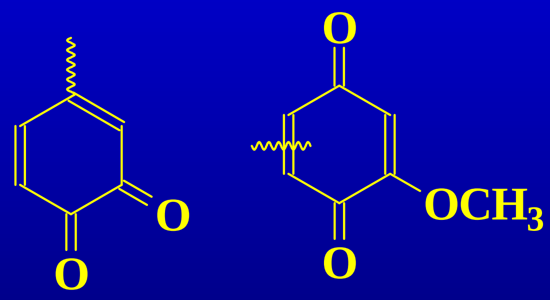
# O - Delignification: Summary

<u>Pulp Results</u>

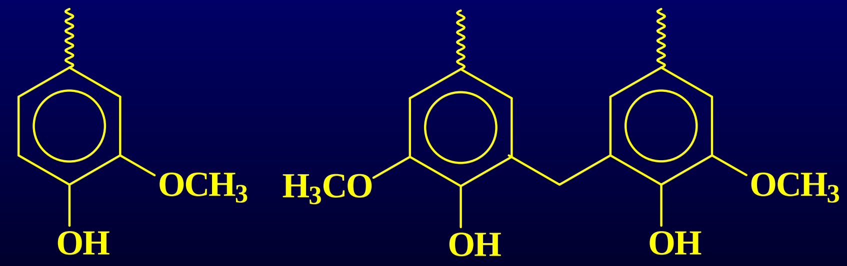
- High kappa SW pulp responded very well to all O treatments
- Pa improved O performance
- >50% O delignification is a possible target

What is the Chemistry?

Color Bodies

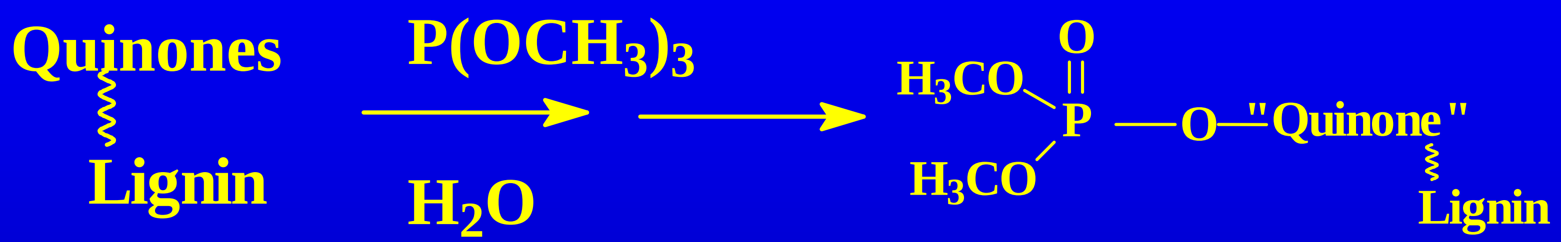


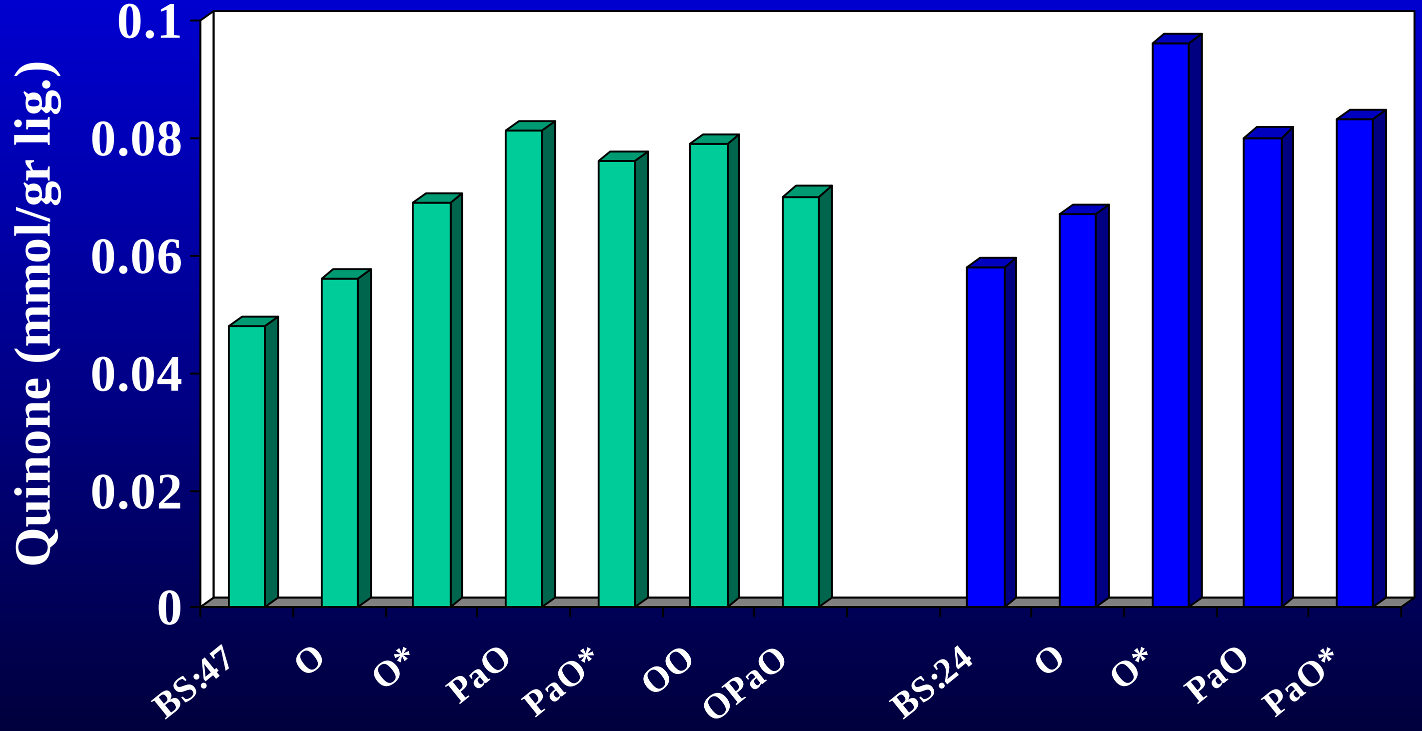

Reactive Sites



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

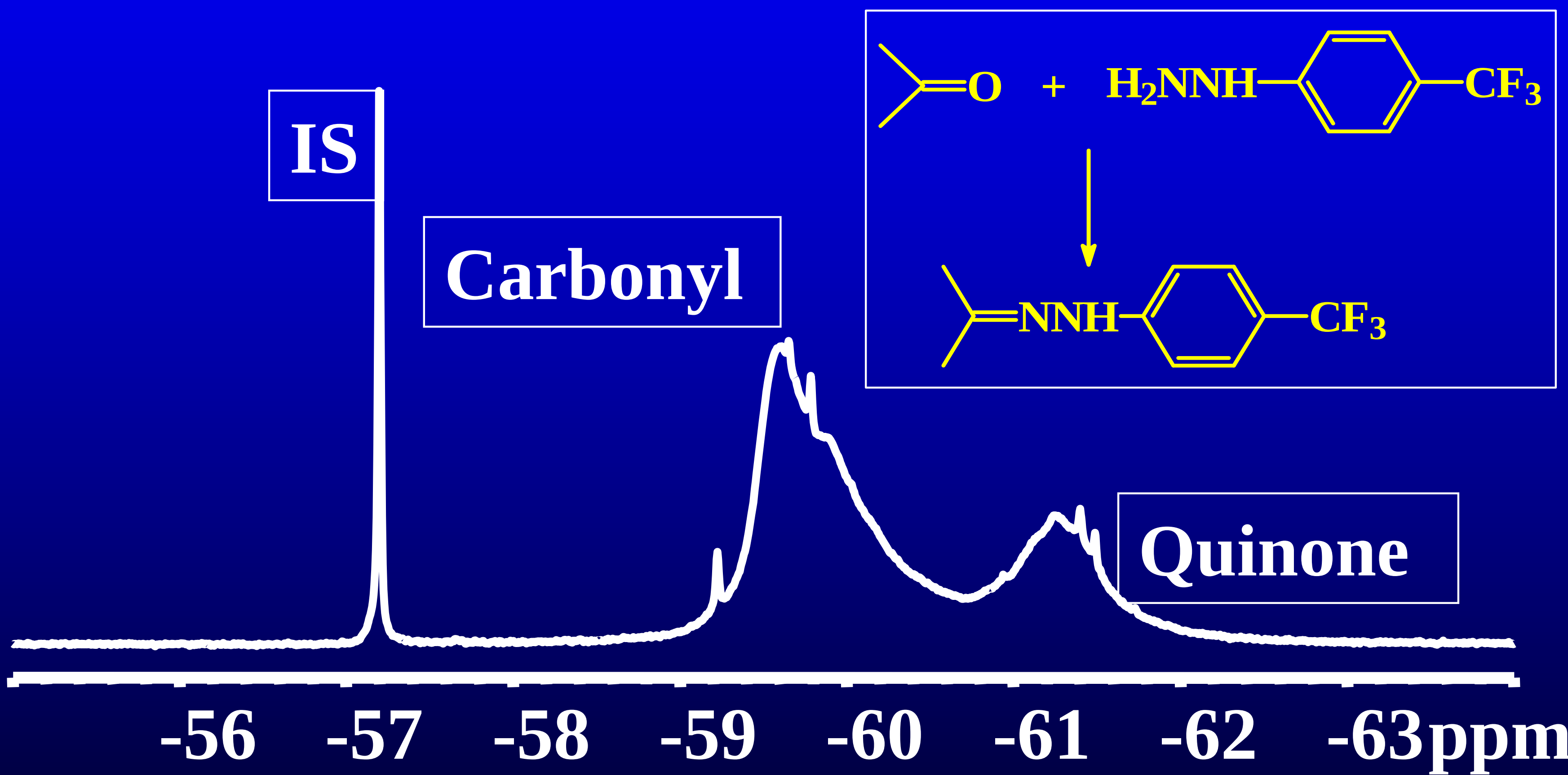
# O - Delignification: Quinones



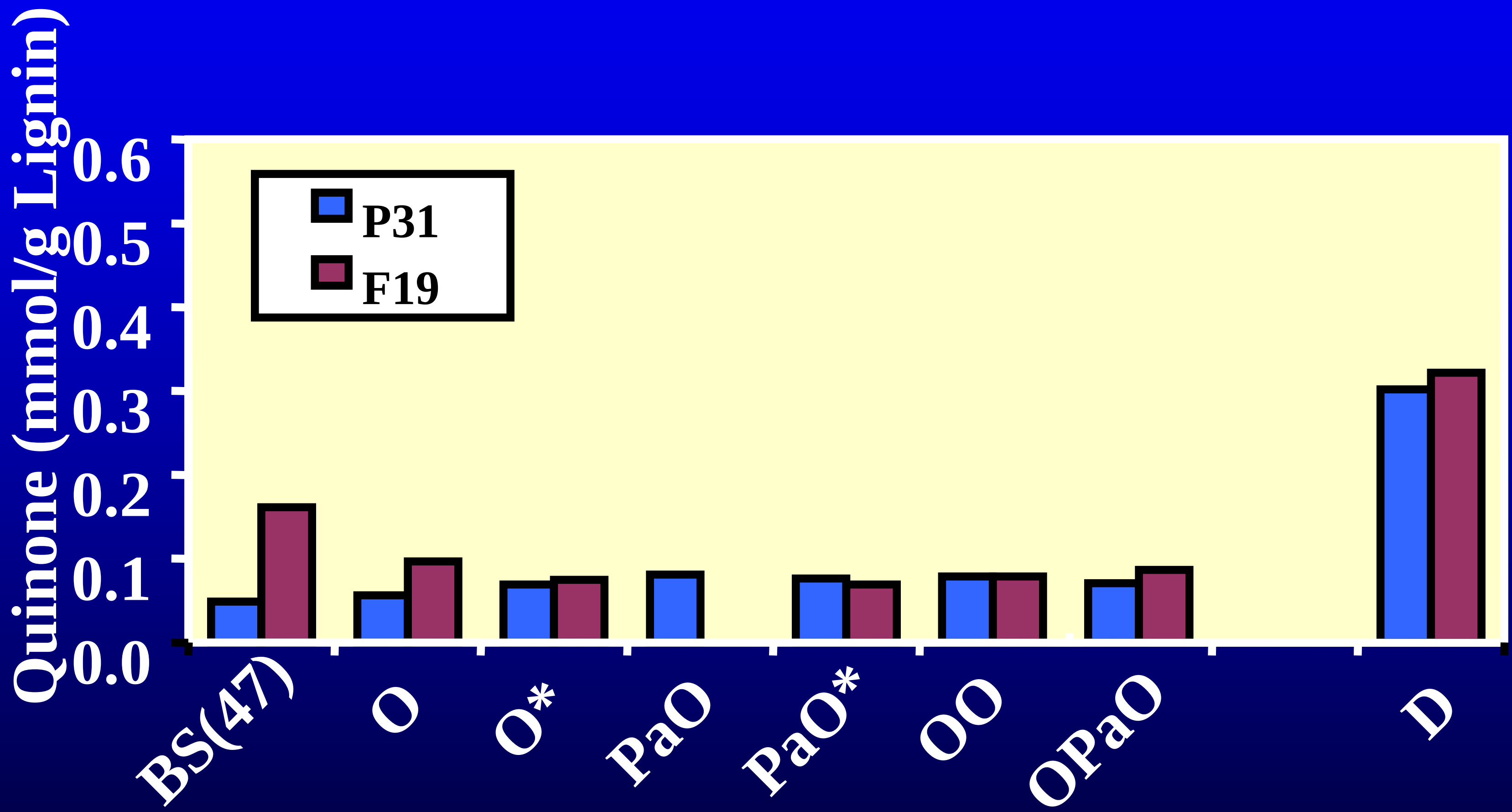



# O - Delignification: Quinones

## $^{19}$F-NMR: Lignin

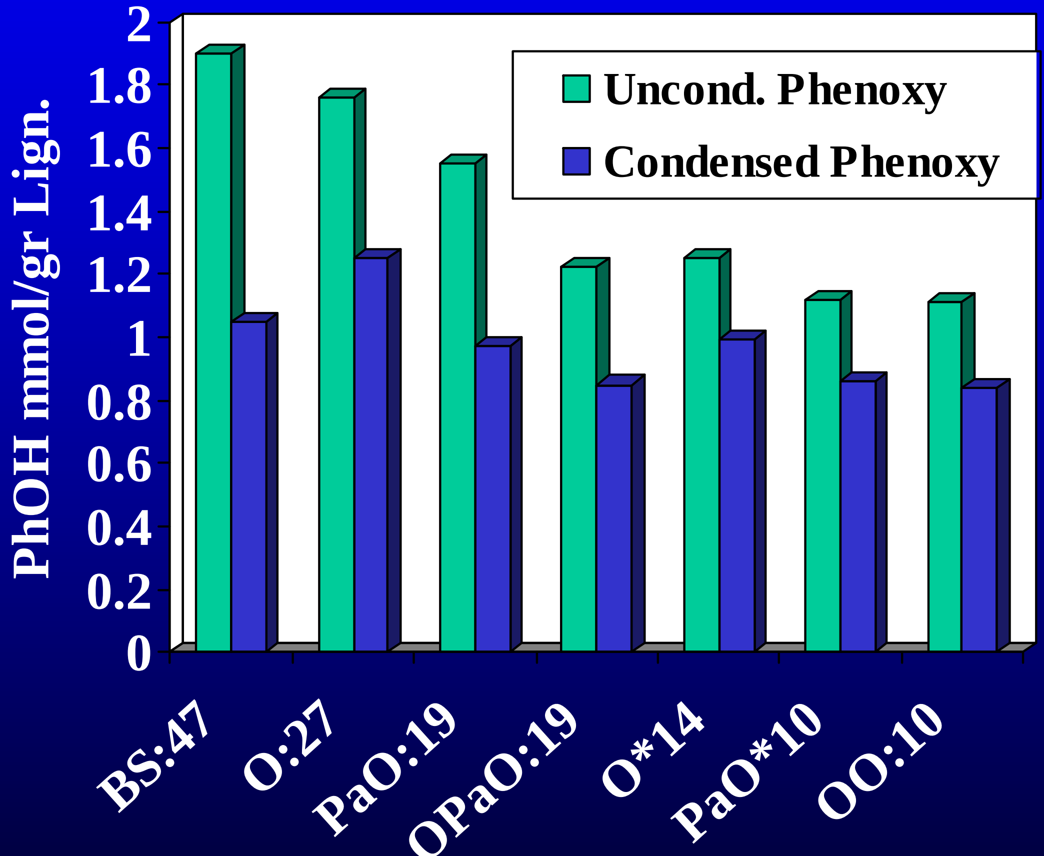


# O - Delignification: Quinones

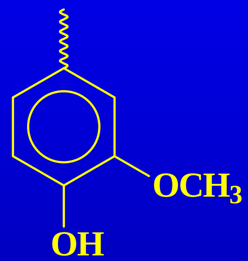



Minor increase in quinones and virtually no increase in carbonyl content of residual lignin

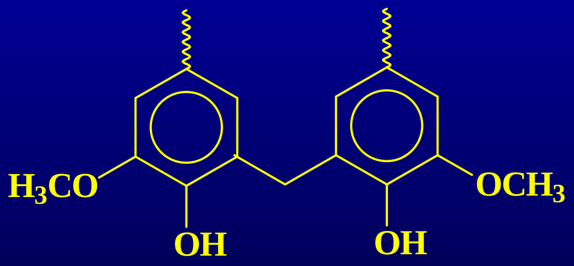
# O - Delignification: Phenoxy Groups



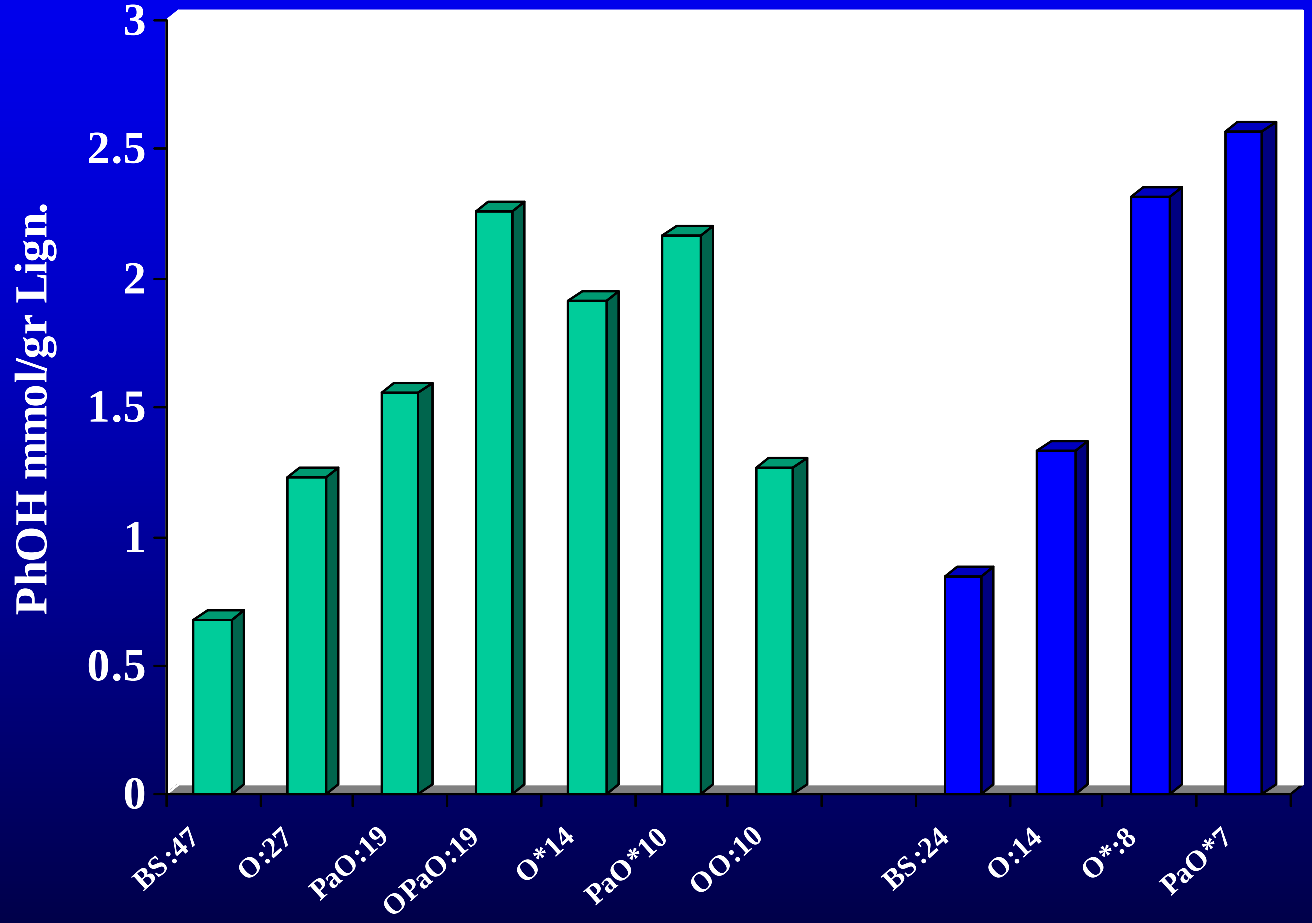

Reactive




Unreactive



# O - Delignification: Acid Groups

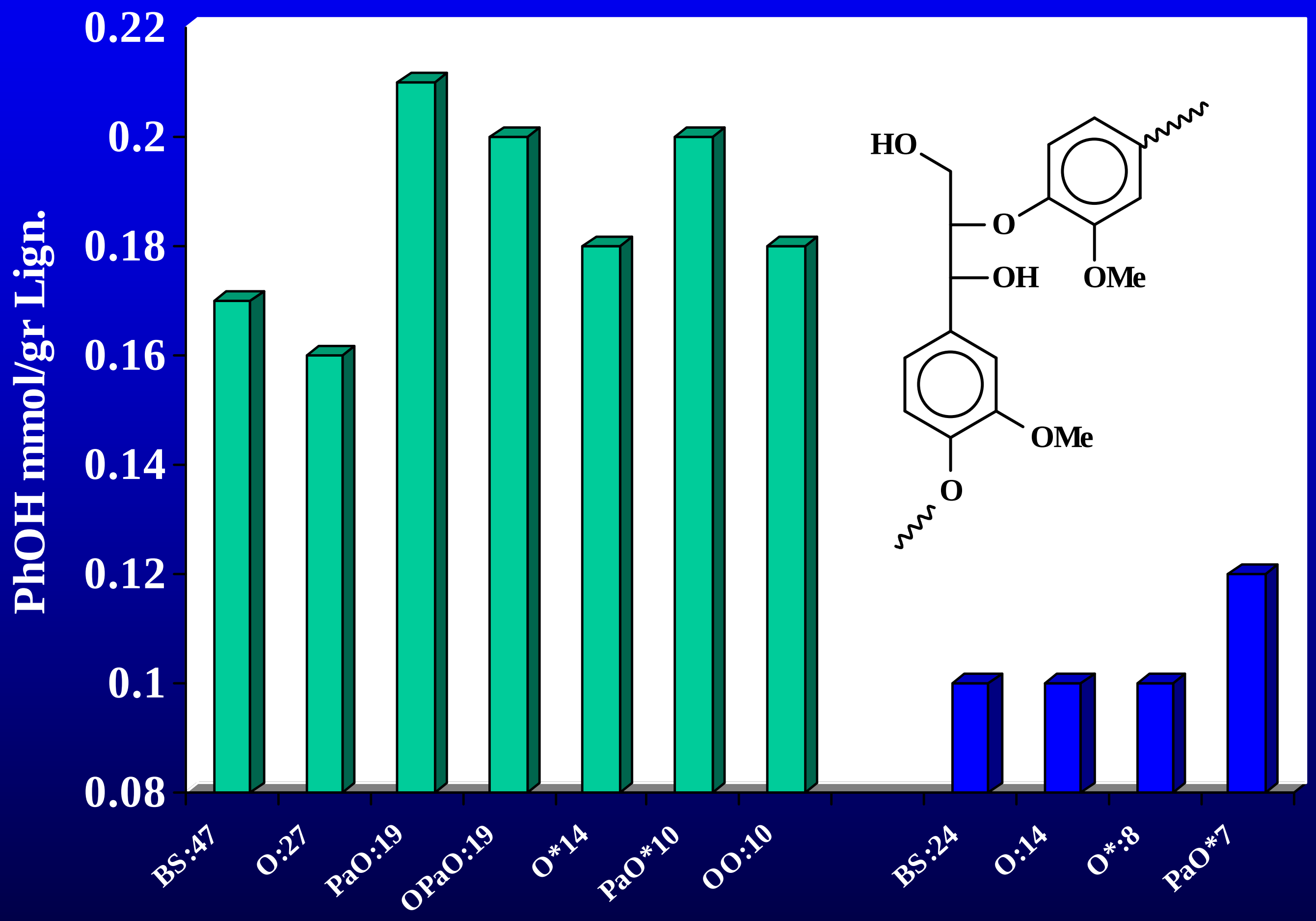



<u>Generally</u>

- 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
- Lignin structure enriched in acid groups
- Quinones/carbonyls appear not to accumulate during O-delign. hence brightness gains not due to their destruction
- PhOMe and β-O-Aryl ether unreactive

# O - Delignification: Implications

- Enhanced O-stages must activate both condensed and unsubstituted PhOHs.
- Cleavage of β-O-Aryl ether may improve O delign.
- Lignin model compounds provided limited practical guidance.
- Mass transfer limitations could explain portions of residual lignin chemistry.

# IPST Member Companies
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