

# CHEMISTRY OF AN OXIDATIVE ALKALINE EXTRACTION BETWEEN CHLORINE DIOXIDE STAGES

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# Topics Covered

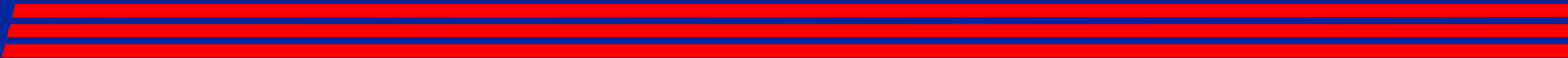
- Introduction
    - Project Objectives
    - Review of Alkaline Extraction and Oxidant Reinforcement Chemistry
  - Results and Discussion
    - Pulp Characterization
    - UV/VIS
    - Molecular Weight
    - NMR
  - Conclusions/Future Research
- 
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# Why Study Oxidative Extraction Chemistry?

- Increased ECF bleaching sequences
  - Compliance with “Cluster Rules” legislation
  - >50% of bleached chemical market pulp
  - Popular ECF sequences
    - » D(E\*)DED                      E\* = oxidant reinforcement
    - » OD(E\*)D                        of O<sub>2</sub> and/or H<sub>2</sub>O<sub>2</sub>
  - D<sub>0</sub> stage has received the bulk of research attention
  - Opportunities also exist understanding oxidative E<sub>1</sub> stage chemistry



# Ph.D. Project Objectives

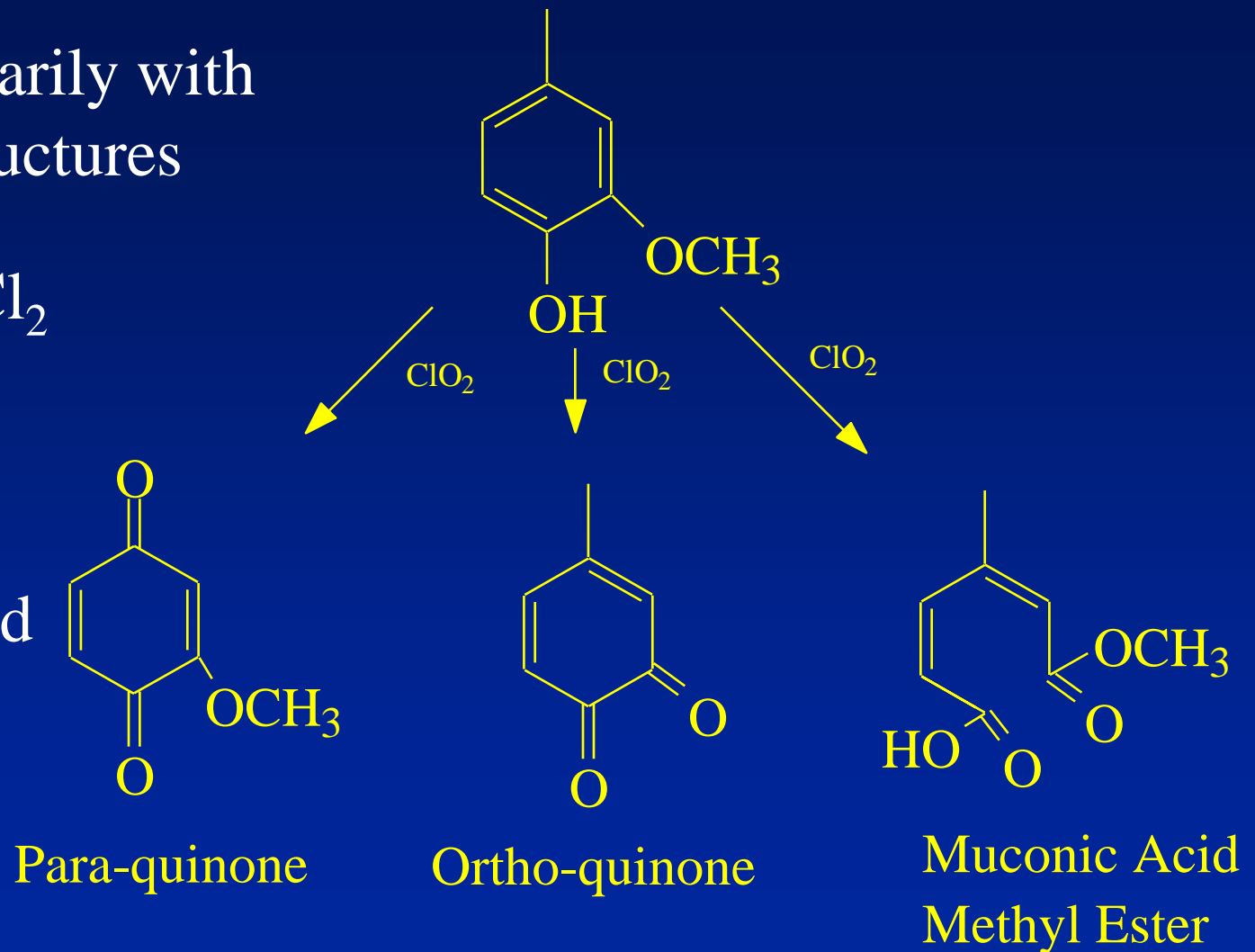
- Explore the fundamental chemistry of reactions occurring during the alkaline extraction stage
  - Focus on the E<sub>1</sub> stage after a D<sub>0</sub> delignification stage
  - Look at various oxidant reinforcements
    - (EAr), E, (EO), (EP), (EPO)
  - Use NMR spectroscopy to measure functional group changes and GPC to measure MW distribution changes
  - Measure and correlate bleachability to lignin structural changes
- 

# Brief Bleaching Chemistry Review

- Reaction schemes based primarily on model compound studies from the literature
- Briefly cover main reactions of
  - $\text{ClO}_2$
  - $\text{NaOH}$
  - $\text{O}_2$
  - $\text{H}_2\text{O}_2$

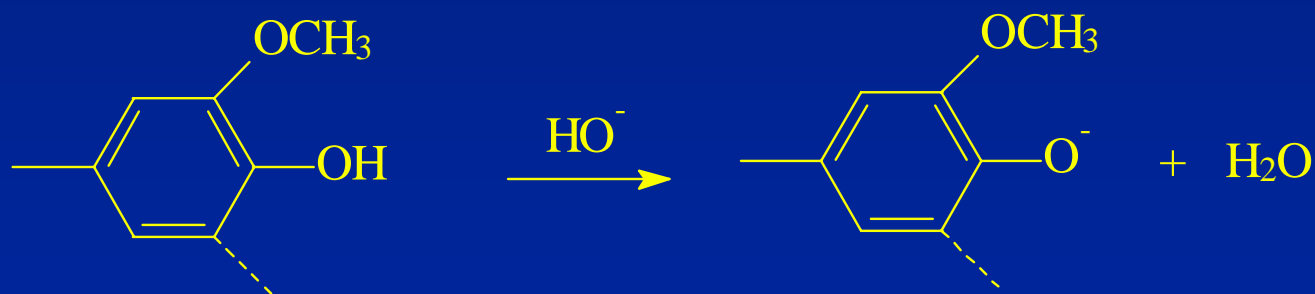
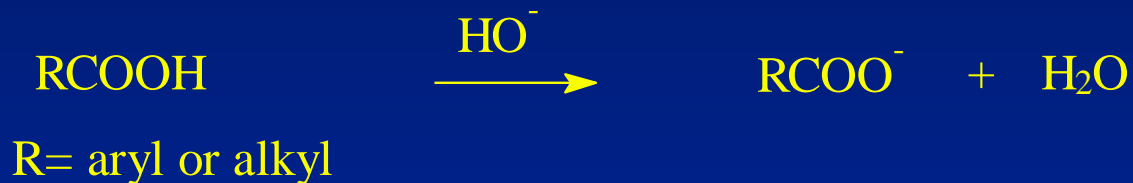
# ClO<sub>2</sub> Delignification Chemistry

- Reacts primarily with phenolic structures
- Generates Cl<sub>2</sub> and HOCl species that further delignify and form AOX



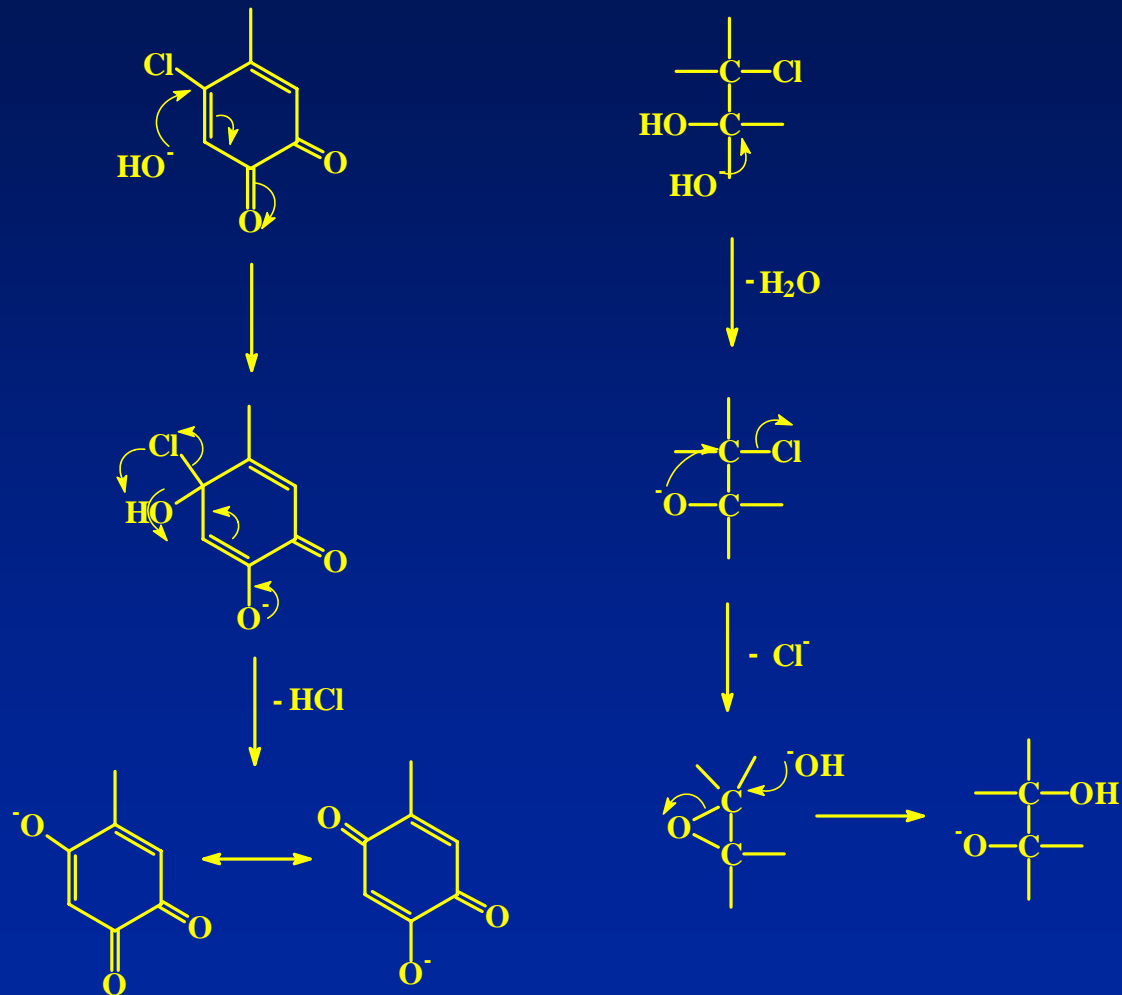
# NaOH Chemistry - Neutralization

- Ionizes acidic groups - increases solubility
- Disassociates lignin complexes allowing greater diffusion out of the fiber cell wall



# NaOH Chemistry - Chlorine Elimination

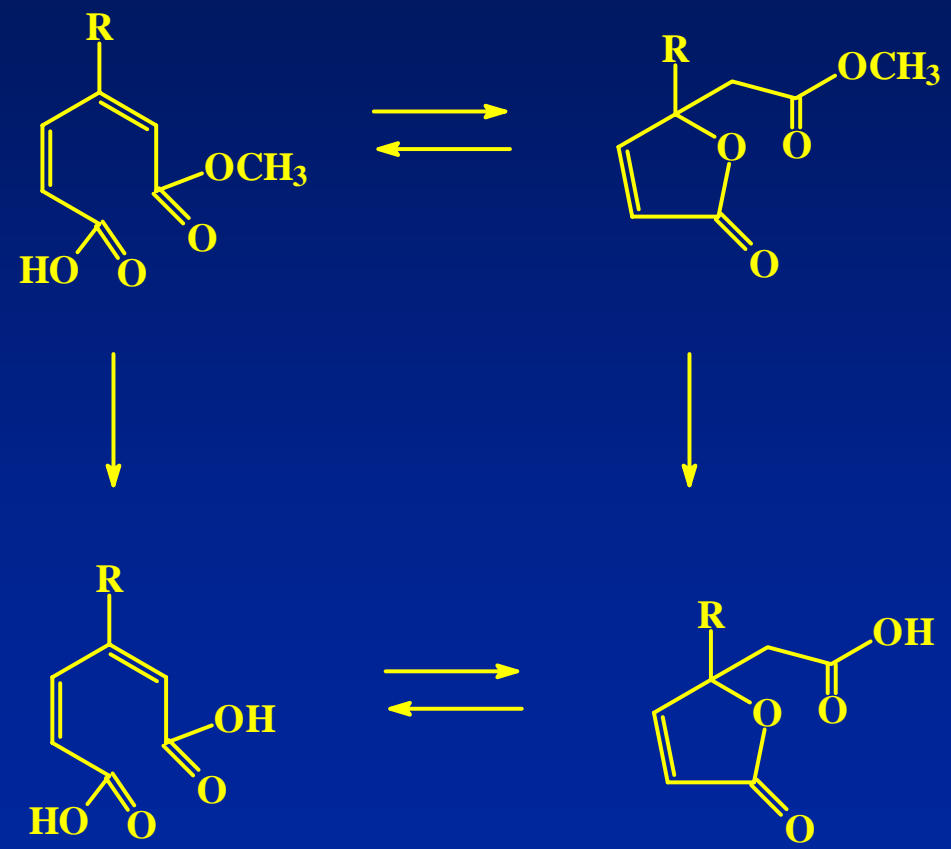
- Elimination of organically bound Cl
  - Reduces AOX
  - Increases lignin solubility
  - Increases reactivity of lignin aromatic group





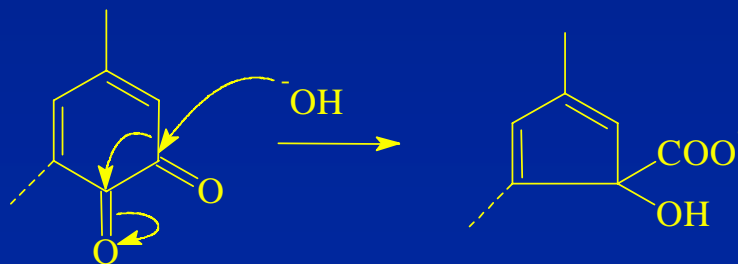
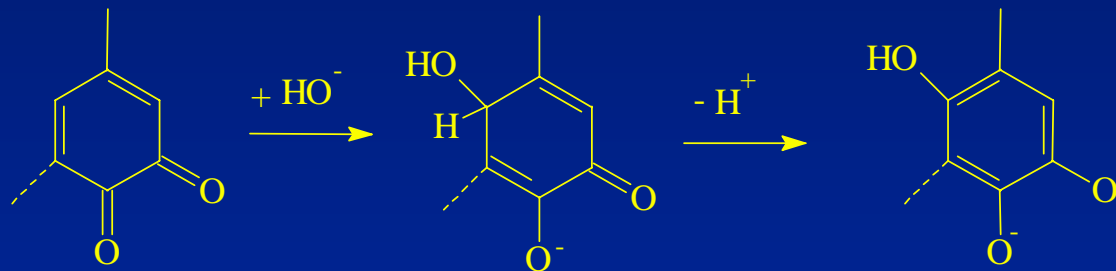
# Alkaline Saponification of Methyl Ester Group in Muconic Acid Methyl Ester

- Recent Hypothesis
  - McKague, Froass, and Evtguin et al.
- Saponification of Methyl Ester
  - MAME formed in  $D_0$  stage
  - Increases solubility



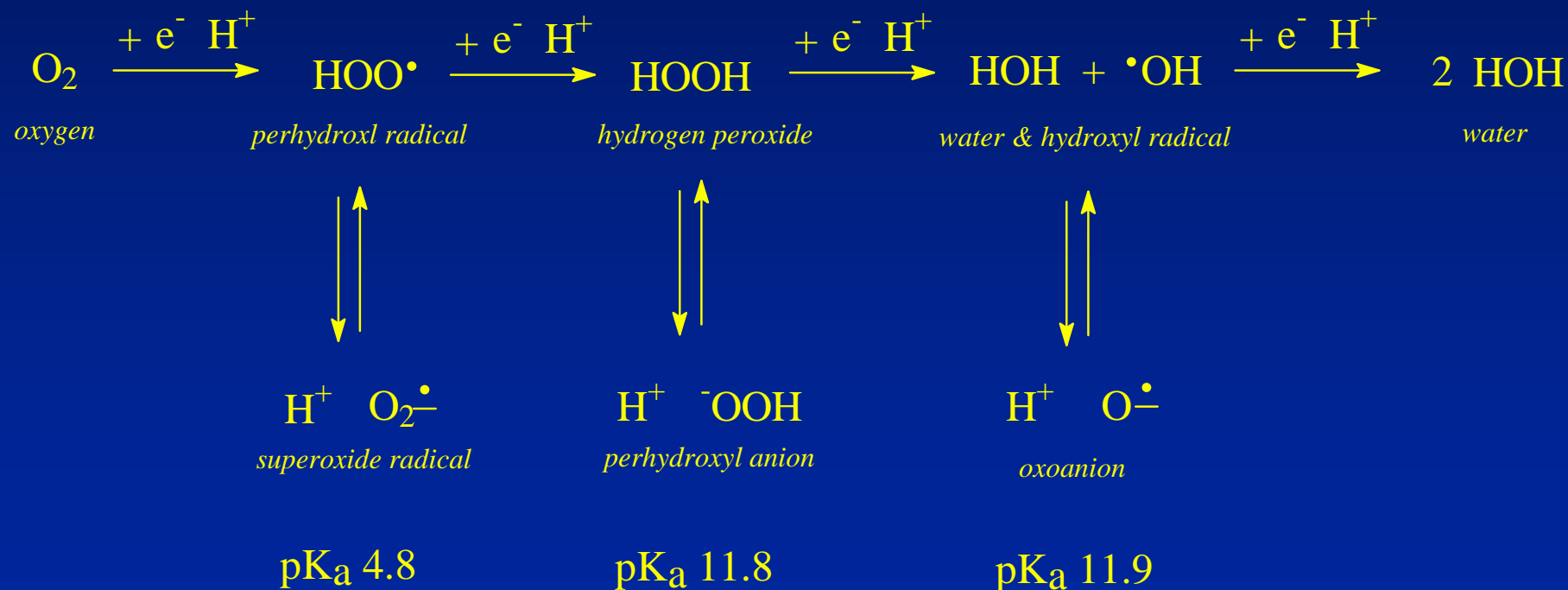
# Hydroxide Addition to Quinones

- Hydroxide addition to quinones
  - Increases lignin solubility
  - Considered minor reaction
- Alkali environment can also cause quinone radicals to form and couple



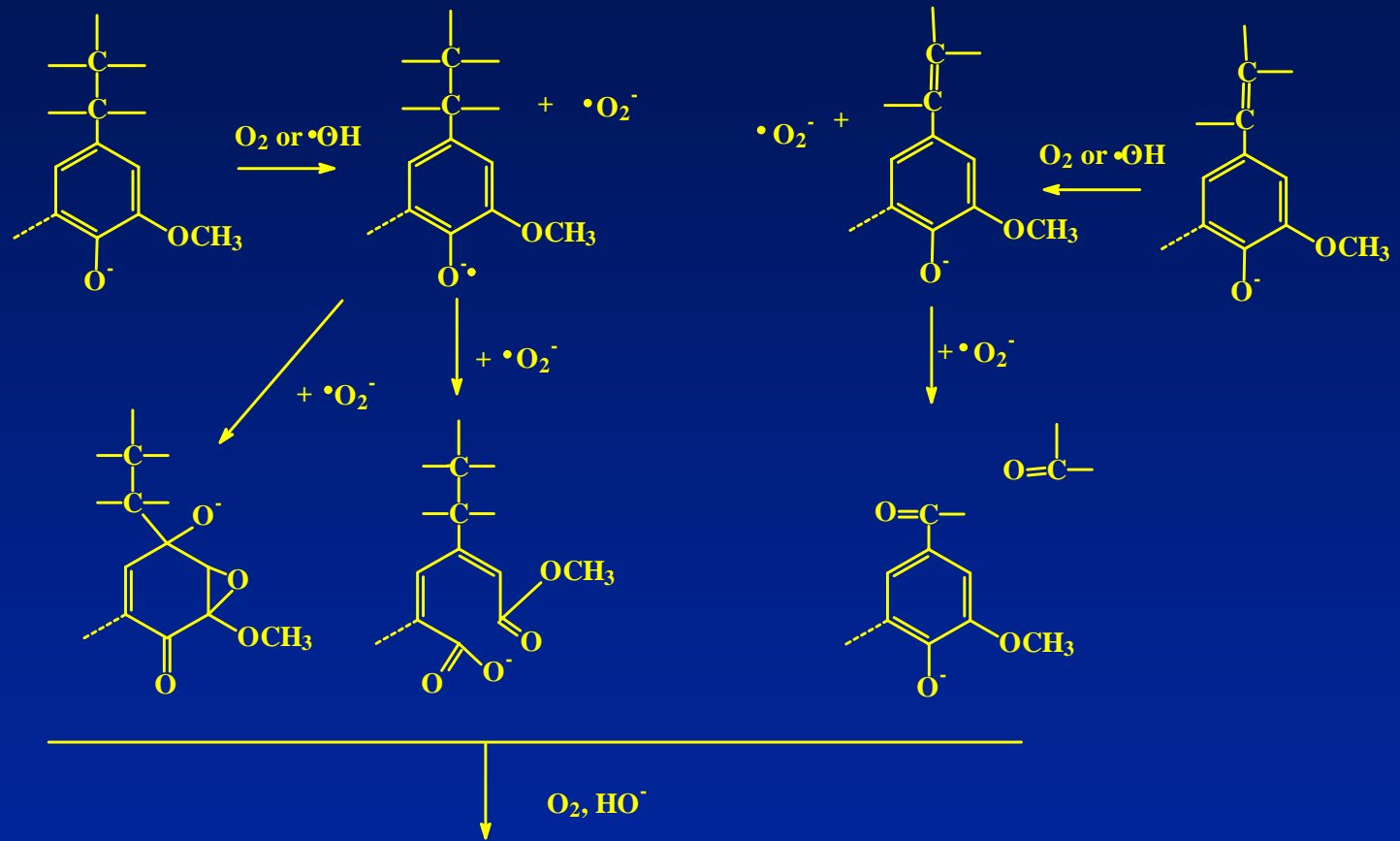
# O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> Species

- O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> form similar reactive species



# Oxygen Chemistry - Autoxidation

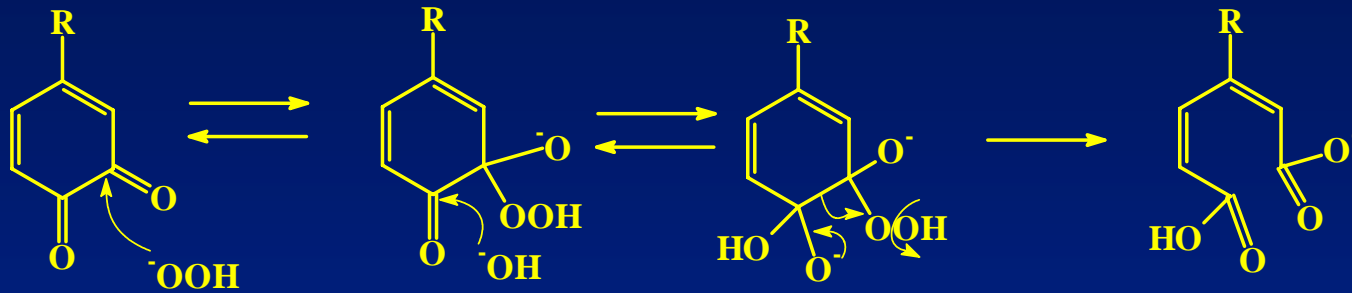
- $O_2$  reacts primarily with phenolic structures



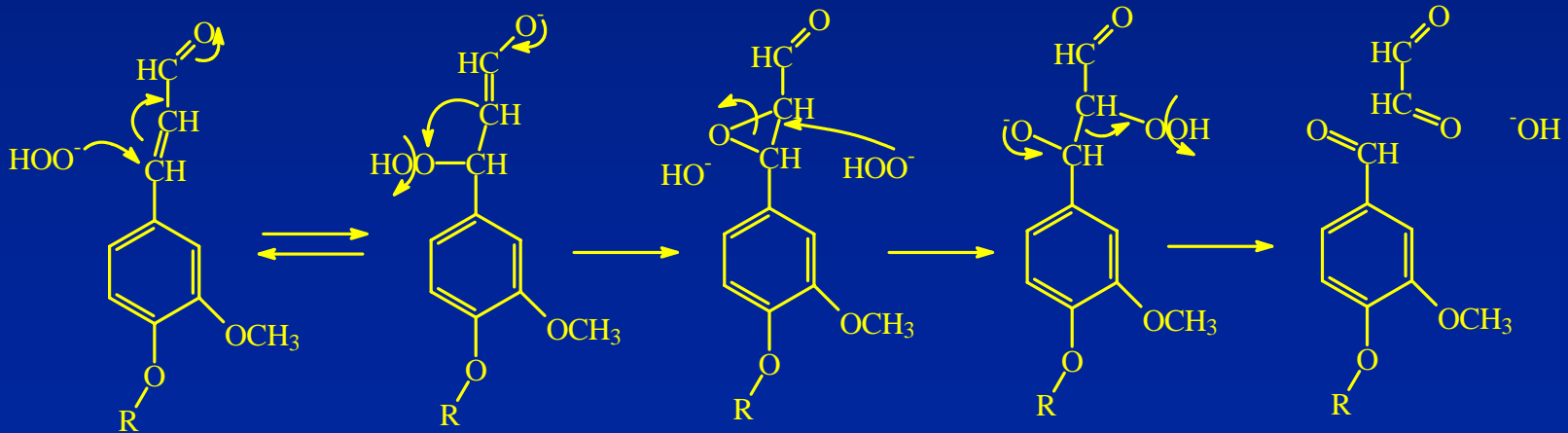
Aliphatic degradation products including methanol and carboxylic acids

# Hydrogen Peroxide Chemistry - Addition Reactions

- Addition to quinone structures

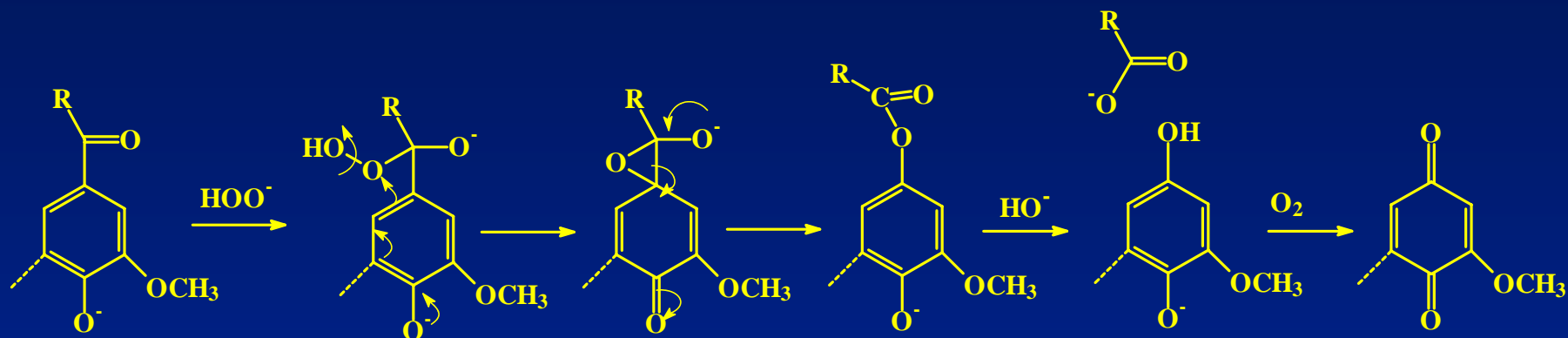


- Michael addition to conjugated carbonyl structures

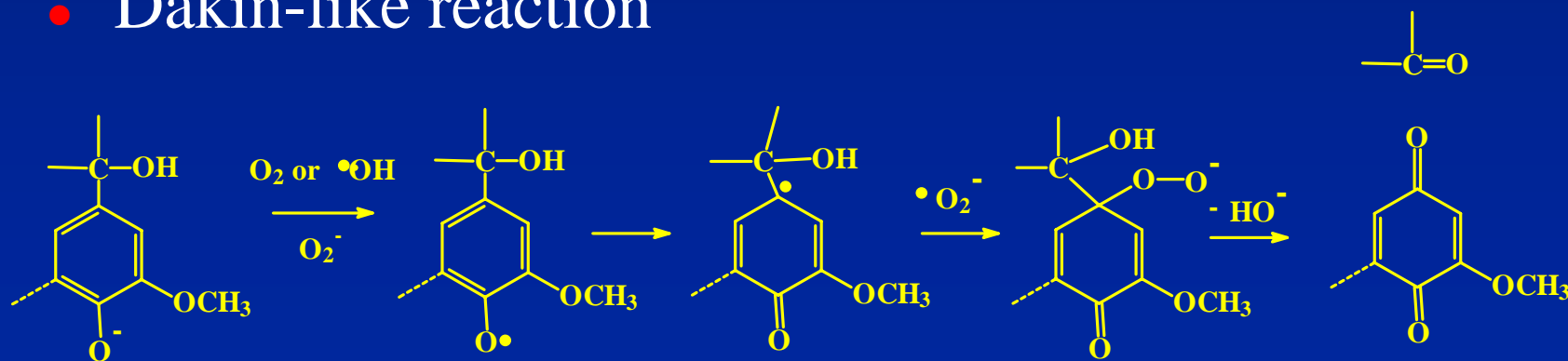


# H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> Reactions that Create Quinones

- Dakin reaction



- Dakin-like reaction



# Bleaching Conditions

- $D_0$  - 0.20 KF (2.3% charge of  $ClO_2$ )
  - 10% solids, 45 min.,  $45^\circ C$ ,  $pH_i = 2.5$
- $E_1$  stages



Bleaching Stage	Bleaching Conditions Employed
E	2.0% NaOH; atmospheric pressure.
(EO)	2.5% NaOH; 60 psig $O_2$ initially, -12 psig/5 minutes
(EP)	2.5% NaOH; 0.5% hydrogen peroxide
(EPO)	2.5% NaO; 0.5% hydrogen peroxide; 60 psig $O_2$ initially, -12 psig/5 minutes
(EAr)	All $O_2$ was removed from the pulp and chemicals. 2.0% NaOH ; slight Ar pressure

## Bleaching Conditions - continued

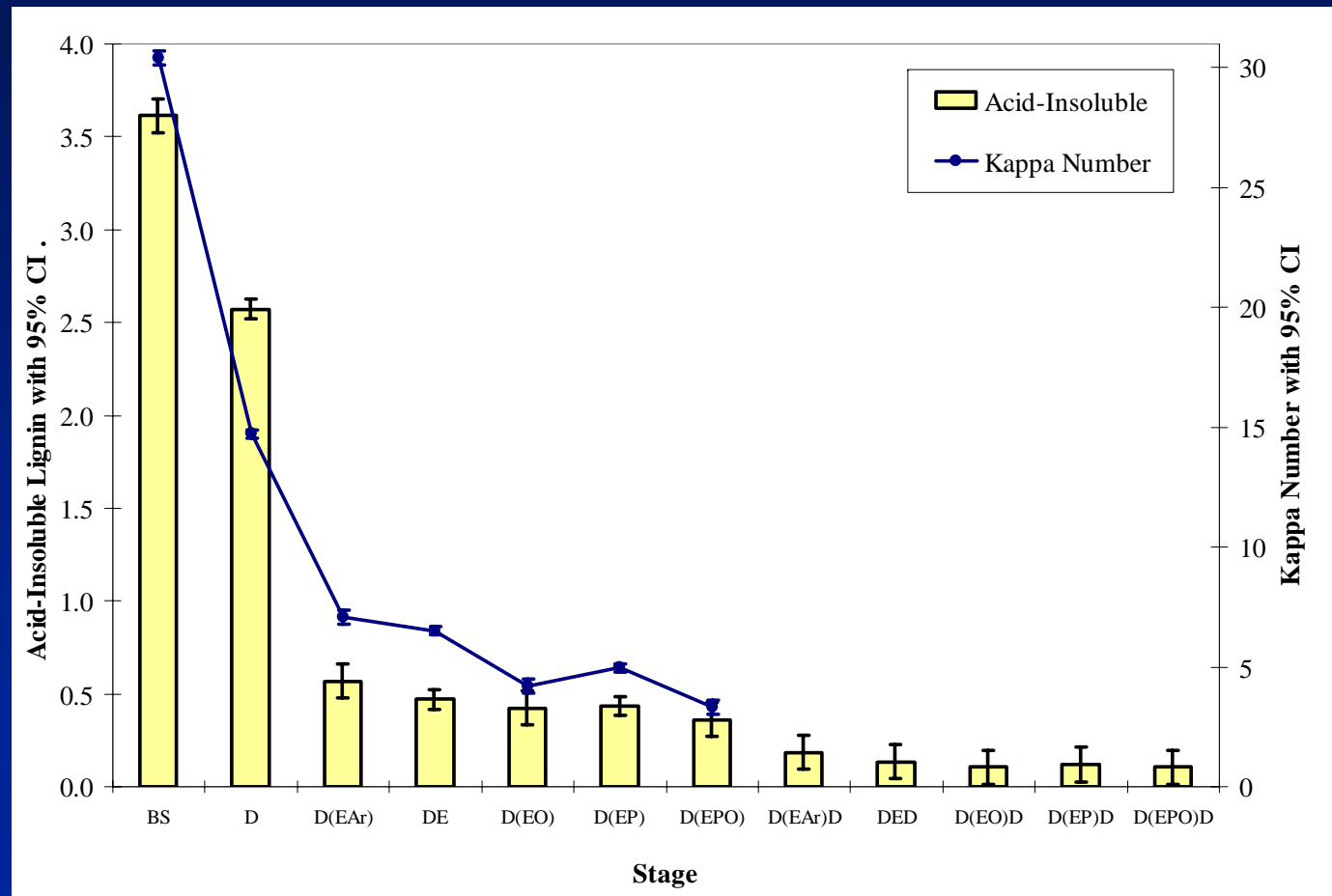
- D<sub>1</sub> - 0.75% ClO<sub>2</sub>, 0.2% NaOH
  - 10% solids, 3 hours, 70°C, pH<sub>f</sub> ~ 4.0
- E<sub>2</sub> stages - 1.0% NaOH
  - 10% solids, 75 min., 70°C
- D<sub>2</sub> - varying ClO<sub>2</sub> charge
  - NaOH charge = 20% of ClO<sub>2</sub> charge
  - 10% solids, 3 hours, 70°C, pH<sub>f</sub> ~ 4.0





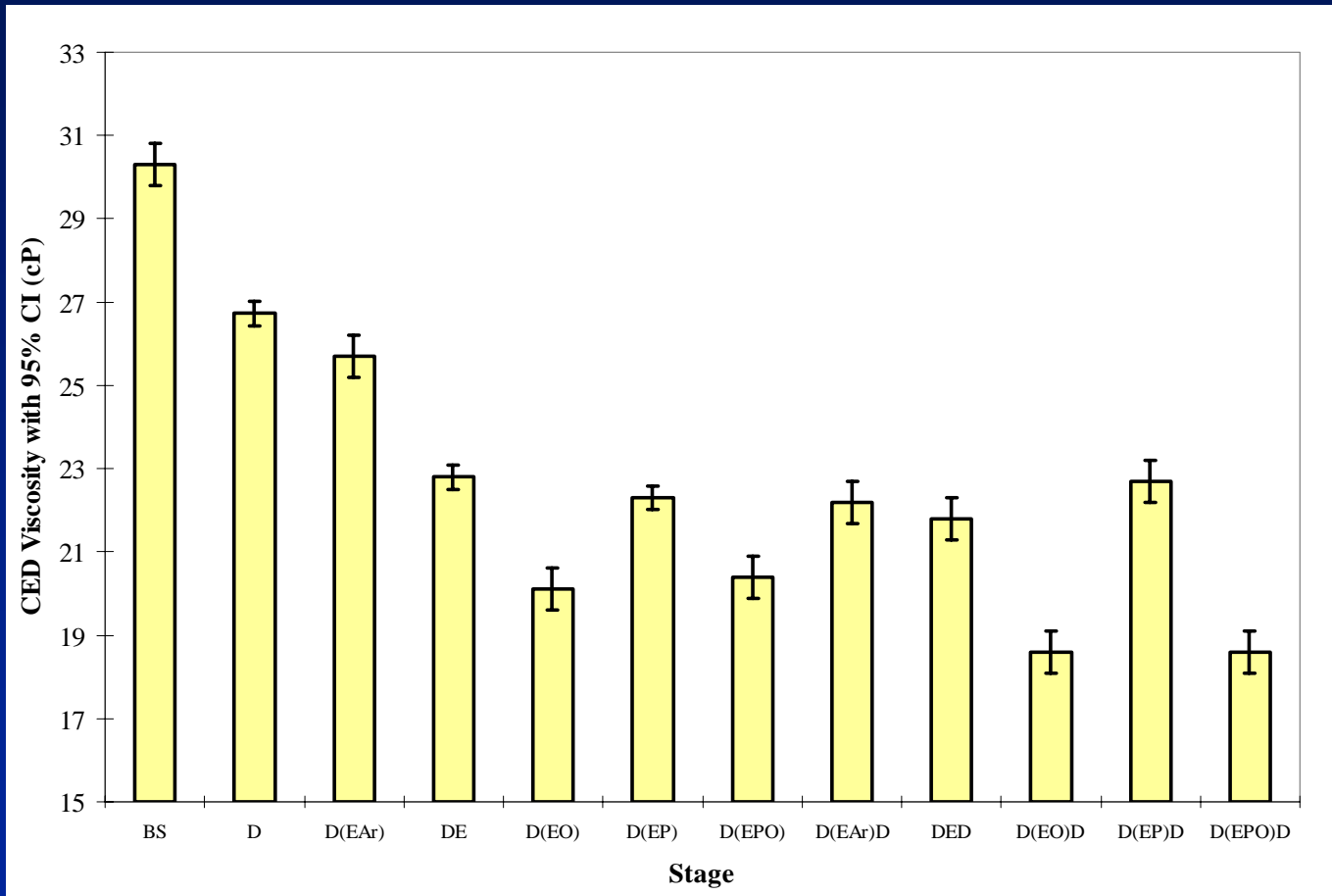
# Bleached Pulps - Lignin Content

- Oxidant reinforcement increased delignification for  $E_1^*$  stage
- $O_2$  increased delignification more than  $H_2O_2$
- Kappa more sensitive than acid insoluble lignin



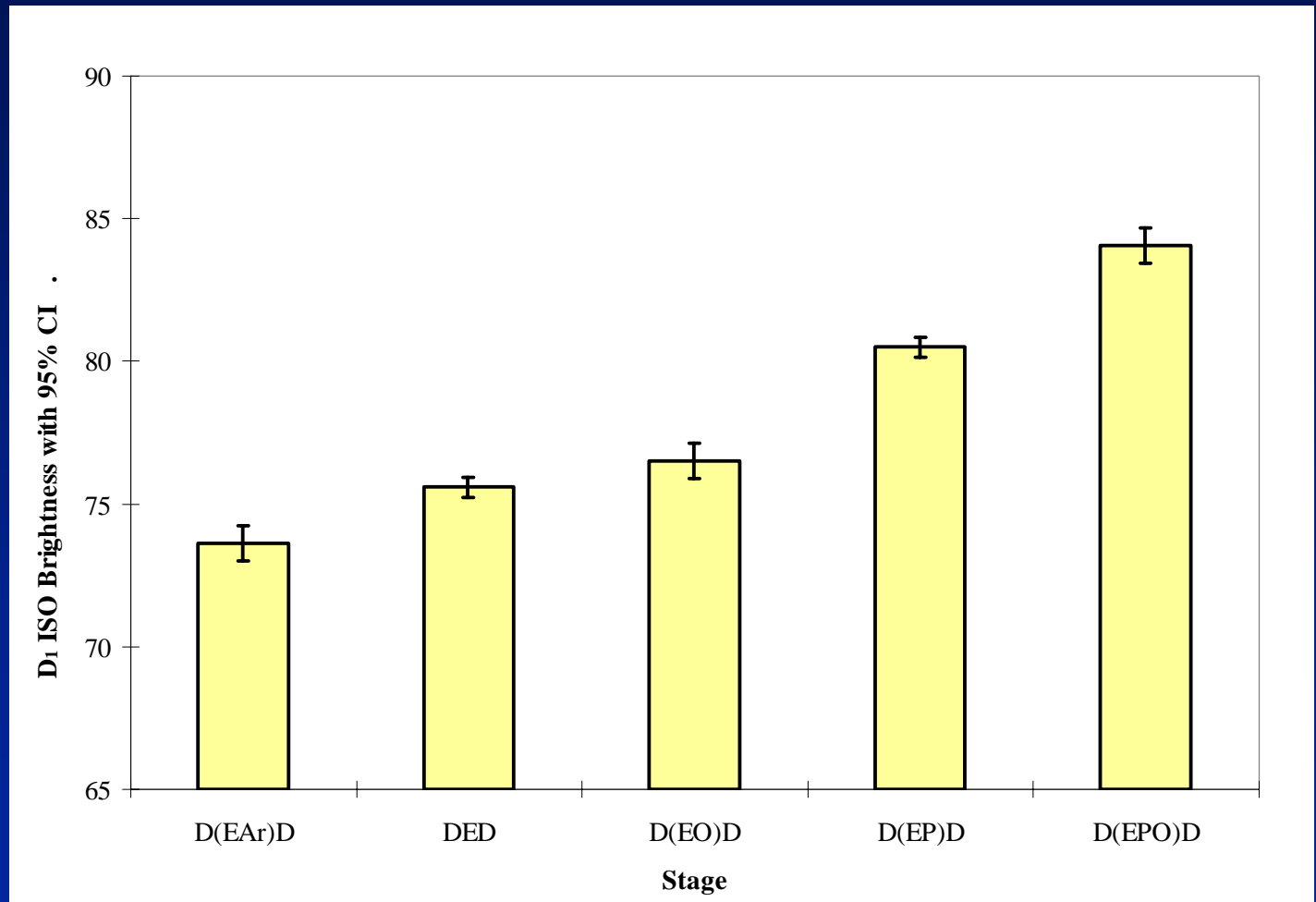
# Bleached Pulps - CED Viscosity

- Viscosity is a measure of carbohydrate degradation
- Loss from  $D_0$  - acid hydrolysis
- Loss from oxidative E
- $O_2$  cause more damage than  $H_2O_2$



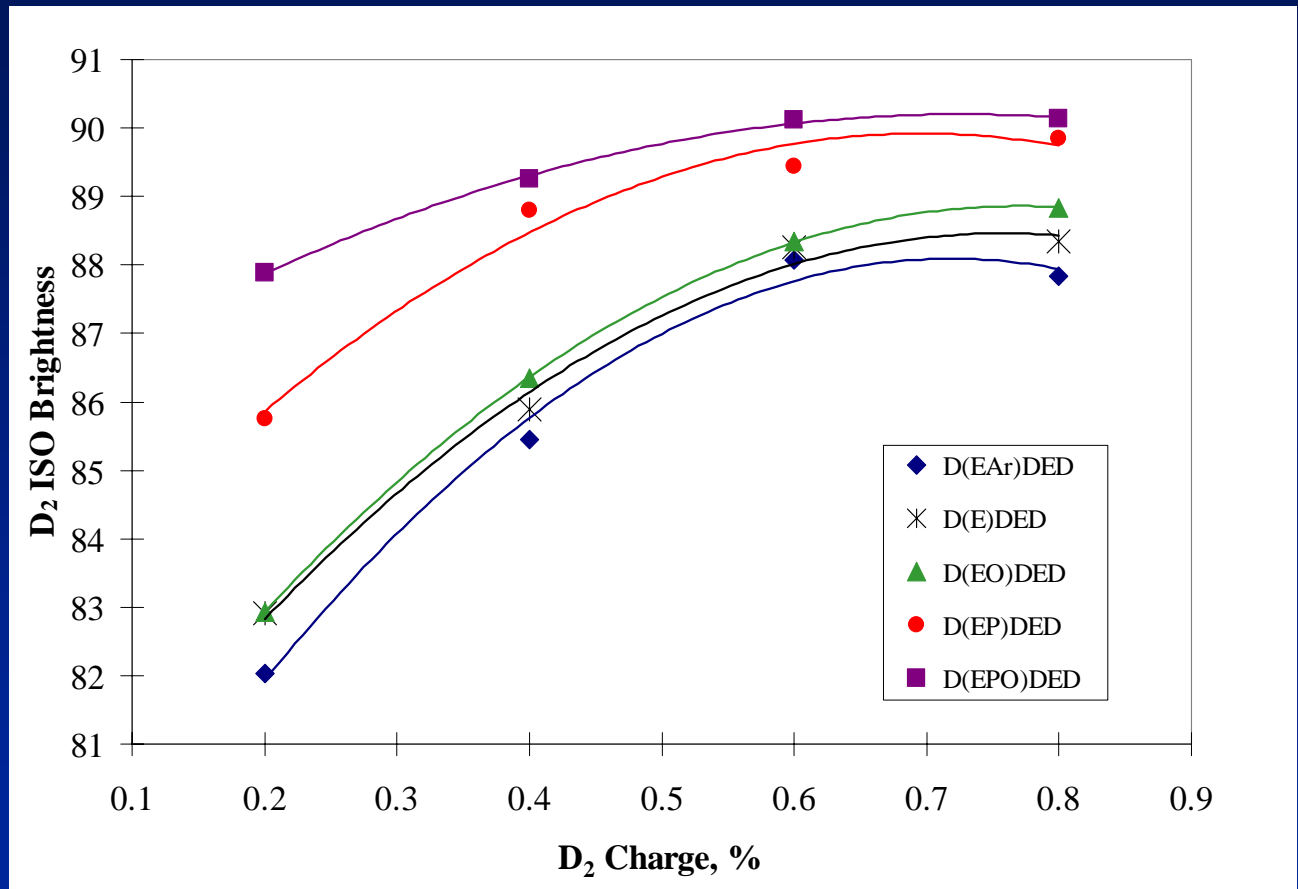
# Bleached Pulps - D<sub>1</sub> ISO Brightness

- Increased D<sub>1</sub> brightness with oxidant reinforcement
- H<sub>2</sub>O<sub>2</sub> > O<sub>2</sub>
- Affected by lignin and chromophore amount



# Bleached Pulps - D<sub>2</sub> Brightness Ceiling

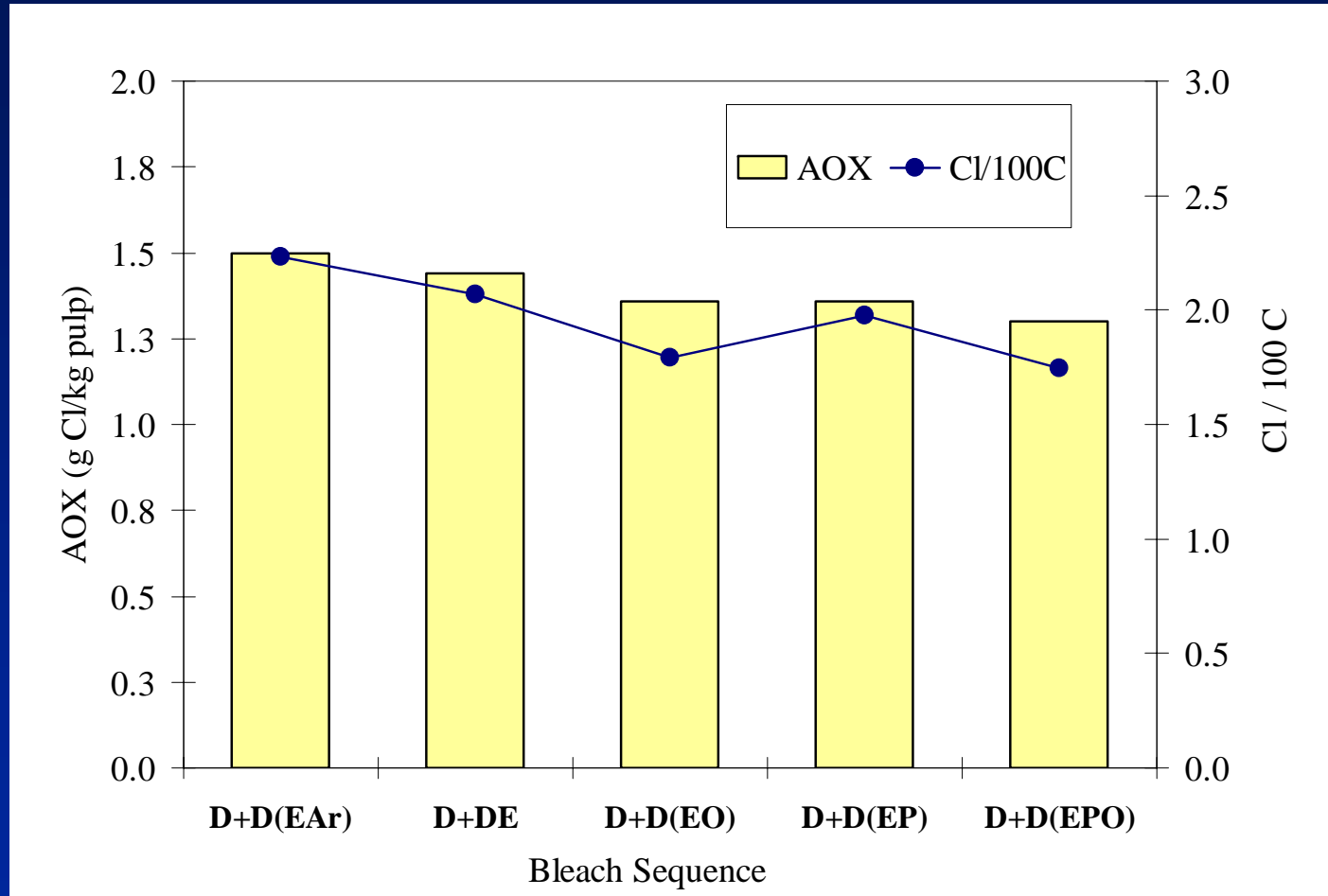
- Used various ClO<sub>2</sub> charges to generate a D<sub>2</sub> brightness ceiling
- (EAr), E, and (EO) statistically similar
- (EP) and (EPO) significantly better
- Attributed to quinone destruction



95% LSD value = 1.0 to 1.3

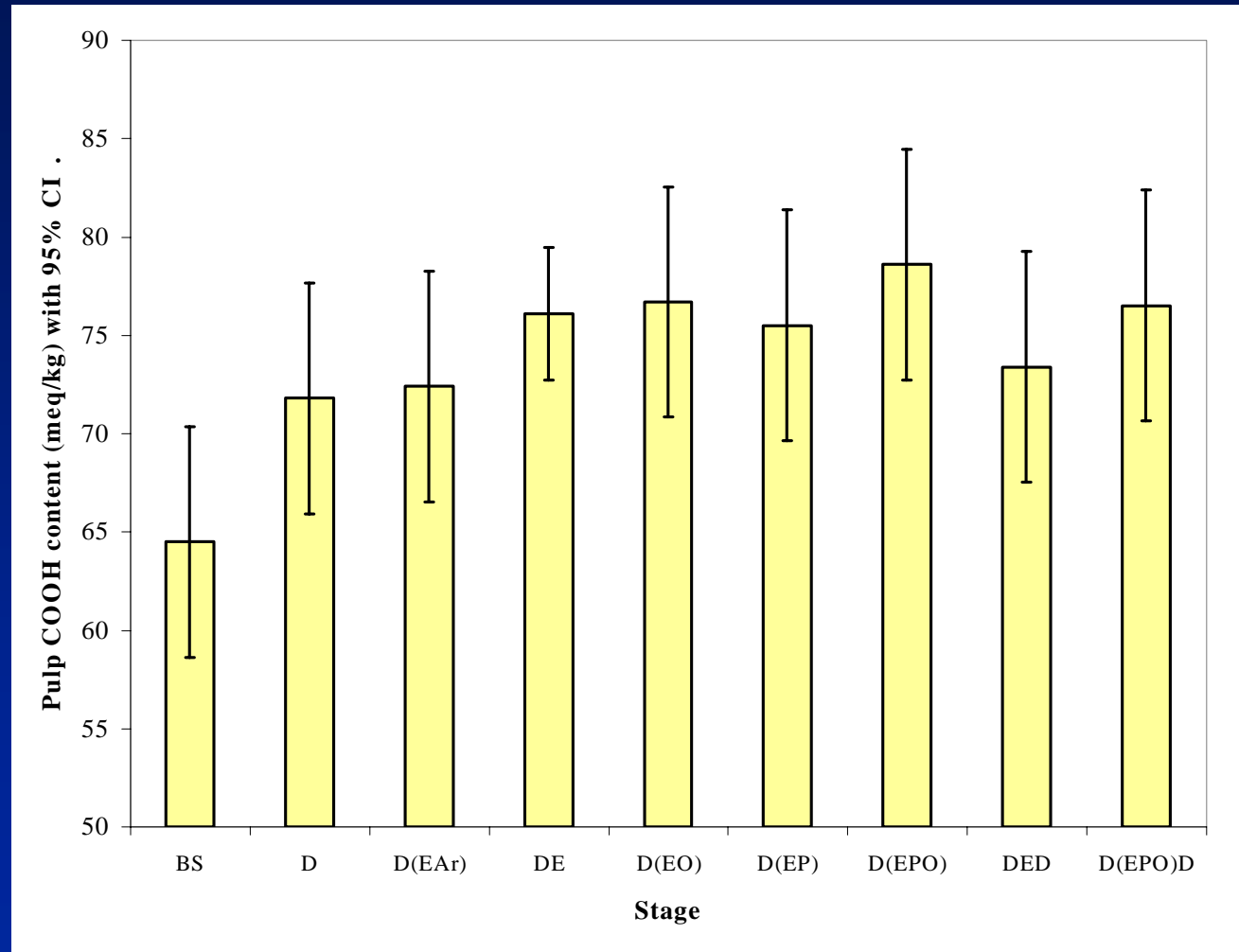
# AOX and Cl / 100 C atoms of Bleach Effluents

- Trend of decreased AOX content with increased oxidant
- Mineralization phenomena - literature
- Amount of decrease is not significant



# Bleached Pulps - Carboxyl Content

- COOH groups can control physical paper properties
- Conductometric titration
- Trend of increased COOH groups with oxidant but not significant



# Bleachability Fundamentals

- To obtain fundamental understanding of changes in delignification and bleachability
  - understand changes to lignin structure
    - Lignin color
    - Lignin size
    - Lignin functional groups



# Lignin Isolation

- Characterized pulps and effluents were used to isolate lignin
  - Residual lignin - Acid Hydrolysis
    - » 0.1 M HCl in 9:1 dioxane:H<sub>2</sub>O solution
    - » Remove dioxane & acid precipitate
    - » Wash repeatedly & freeze-dry
  - Effluent lignin - Precipitate
    - » Alkaline stages only
    - » Acid precipitate
    - » Wash repeatedly & freeze-dry



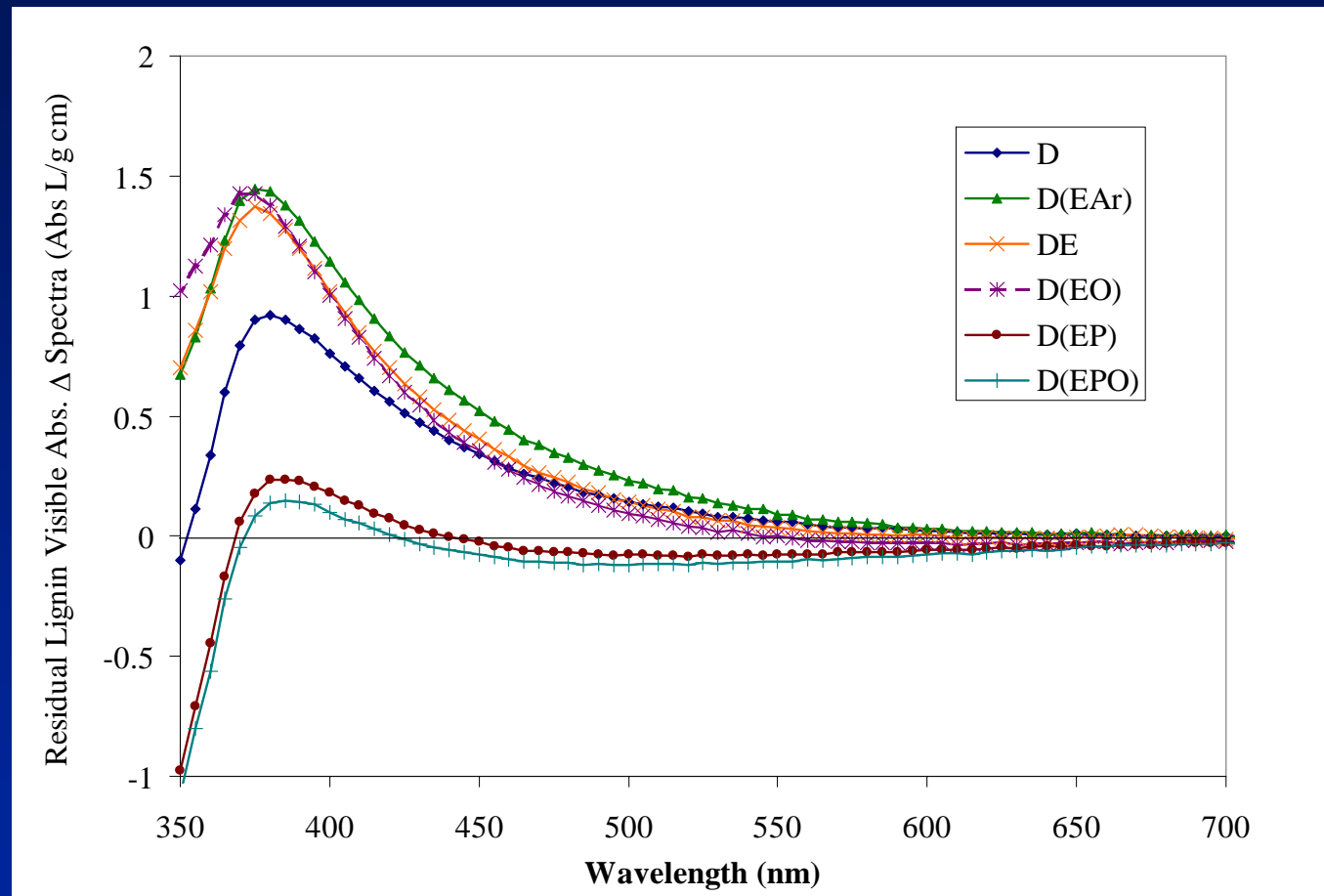
# Bleachability Fundamentals

- To obtain fundamental understanding of changes in delignification and bleachability
  - understand changes to lignin structure
    - **Lignin color**
    - Lignin size
    - Lignin functional groups



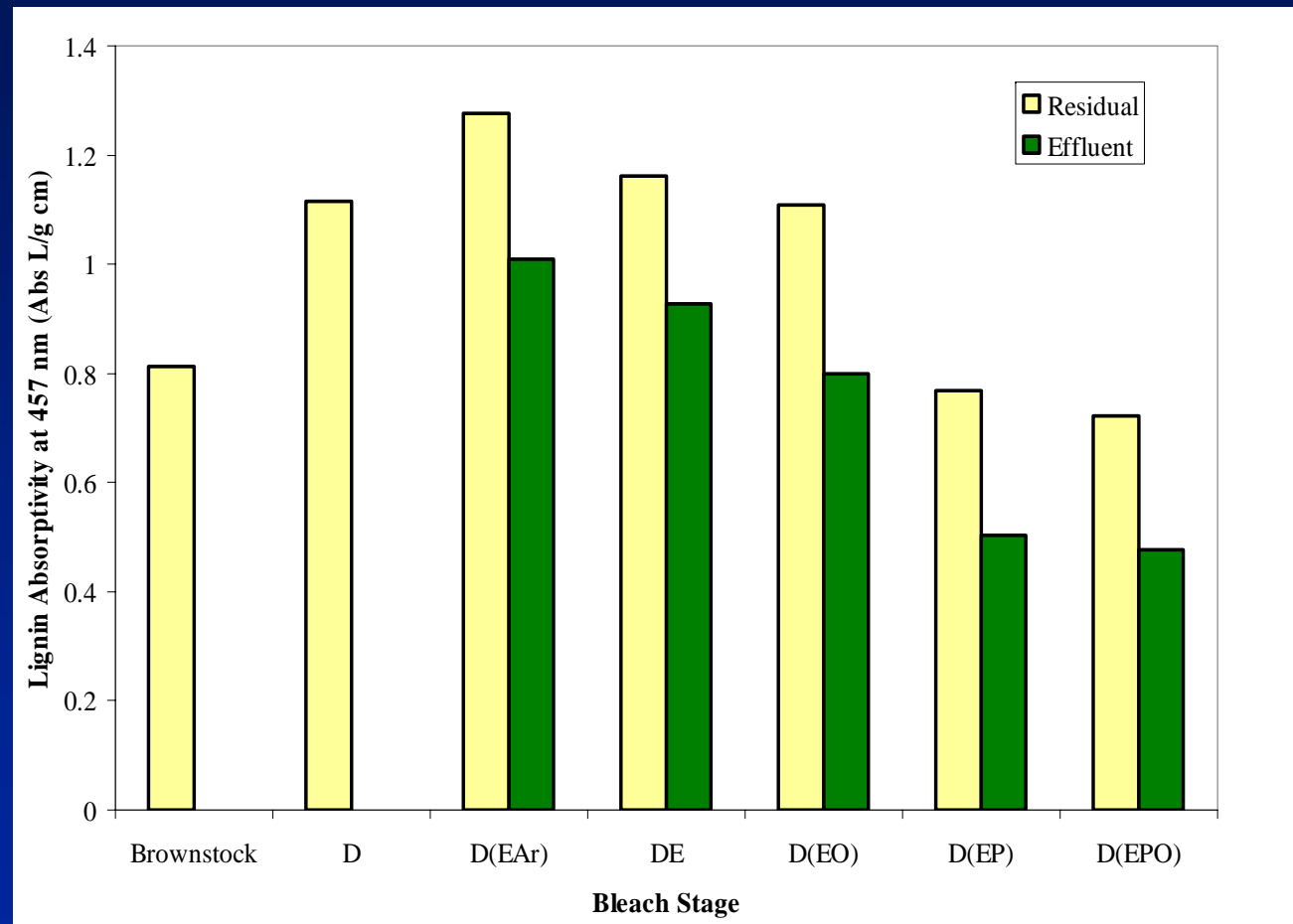
# VIS Absorbance - Residual Lignins

- Measured in 1:1 (v/v) dioxane:water
- Acidic solutions to remove ionization effects
- Greatest change in 360 to 420 nm region



# Lignin Absorptivity at 457 nm

- $D_0$  darker in color than Brownstock
- EAr, E, and EO darker in color than D
- EP and EPO lighter in color than Brownstock
- Effluent lighter in color than residual lignin



95% LSD value = 0.0587

# Bleachability Fundamentals

- To obtain fundamental understanding of changes in delignification and bleachability
  - understand changes to lignin structure
    - Lignin color
    - **Lignin size**
    - Lignin functional groups



# Effluent Apparent MW Distribution

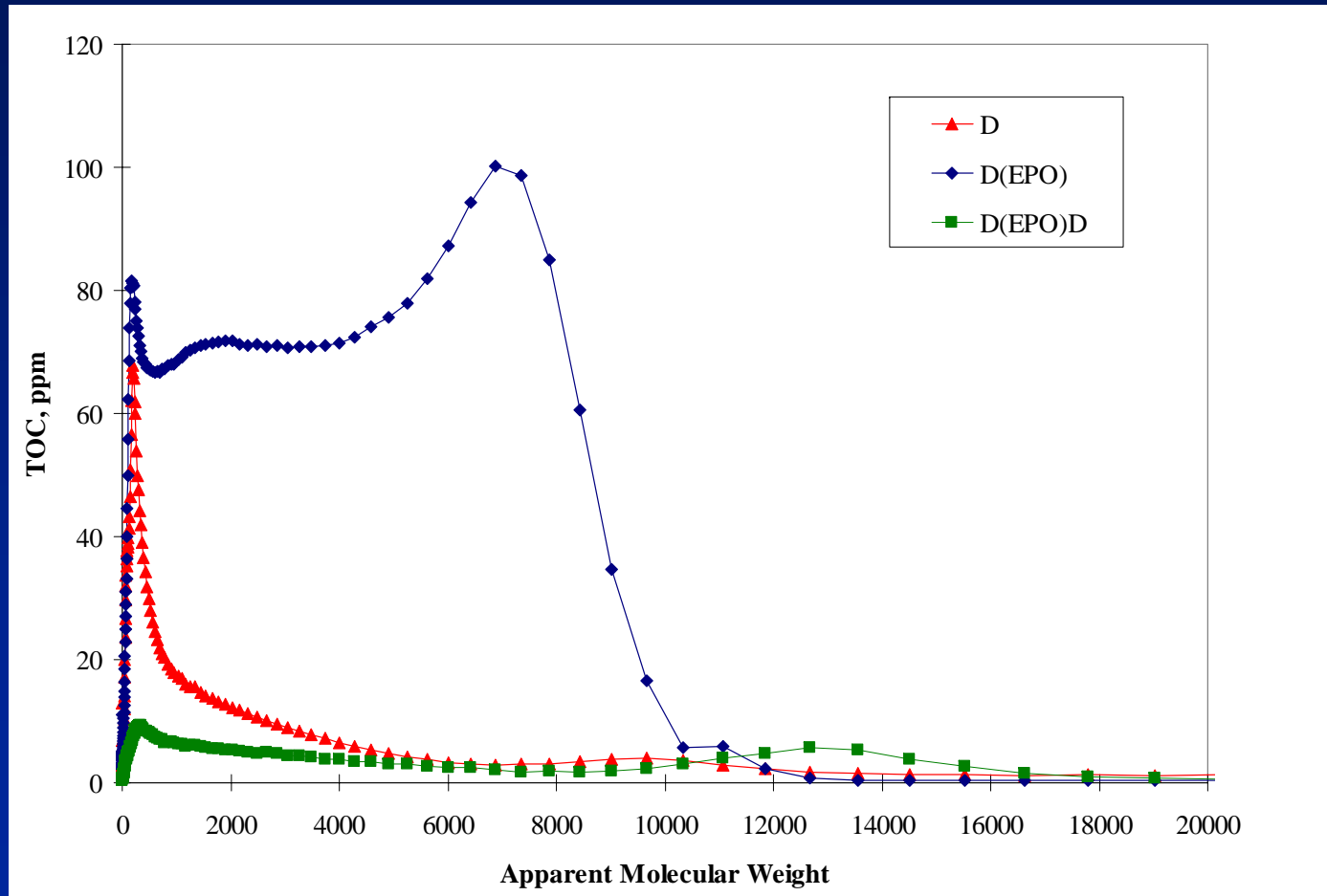
- Effluent apparent MW were performed using LC procedure



- Uses 2 Sephadex packed LC columns and 0.1 N LiCl as eluent
- 5 ml of prepared effluent travel through column according to size
- Column exit stream is measured by TOC detector
- MW calculated from calibration standards of PEG and methanol

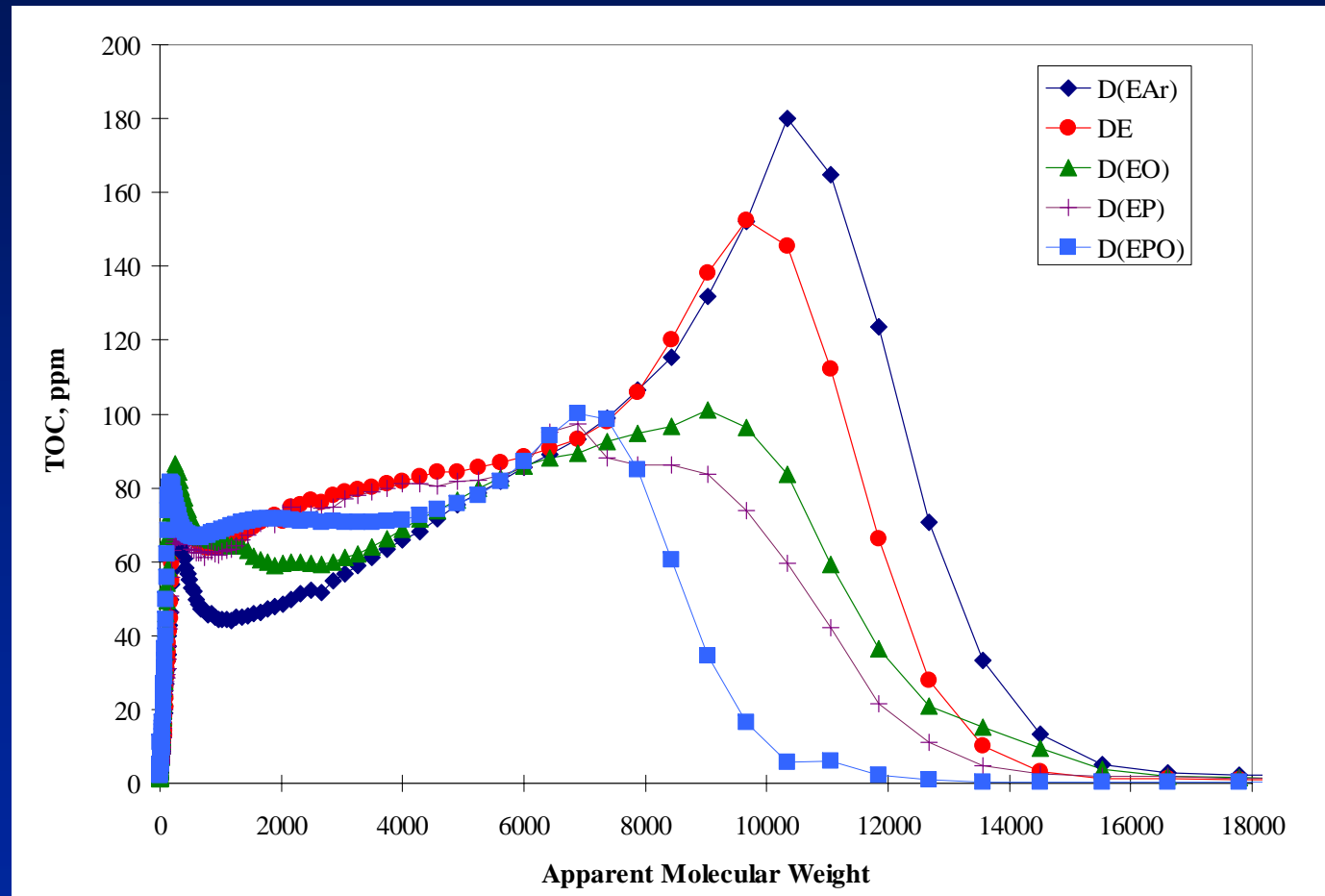
# Apparent MW Distributions of Bleach Stage Effluents

- $D_0$  - low MW fragments only
- $E_1^*$  - bimodal distribution
- $D_1$  low amount of organic matter



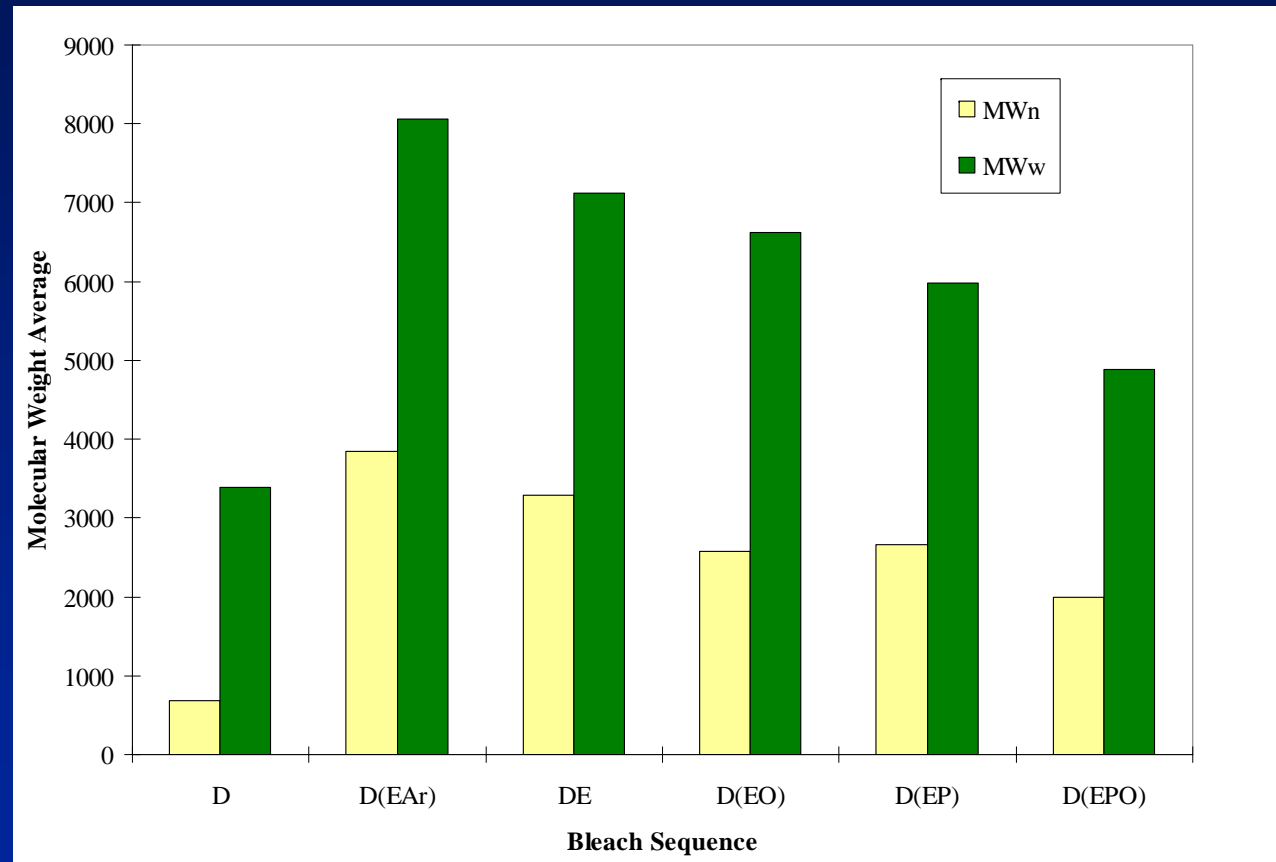
# Alkaline Extraction Oxidant Affect on E\* Stage Effluent Apparent MW Distributions

- Oxidant reinforcement decreases effluent apparent MW
- Signifies oxidant is reacting with dissolved effluent lignin



# Average Effluent Molecular Weight

- Quantify MW decrease with number and weighted average
- Decrease in  $MW_W > MW_N$  due to changes occurring mainly in higher MW fraction

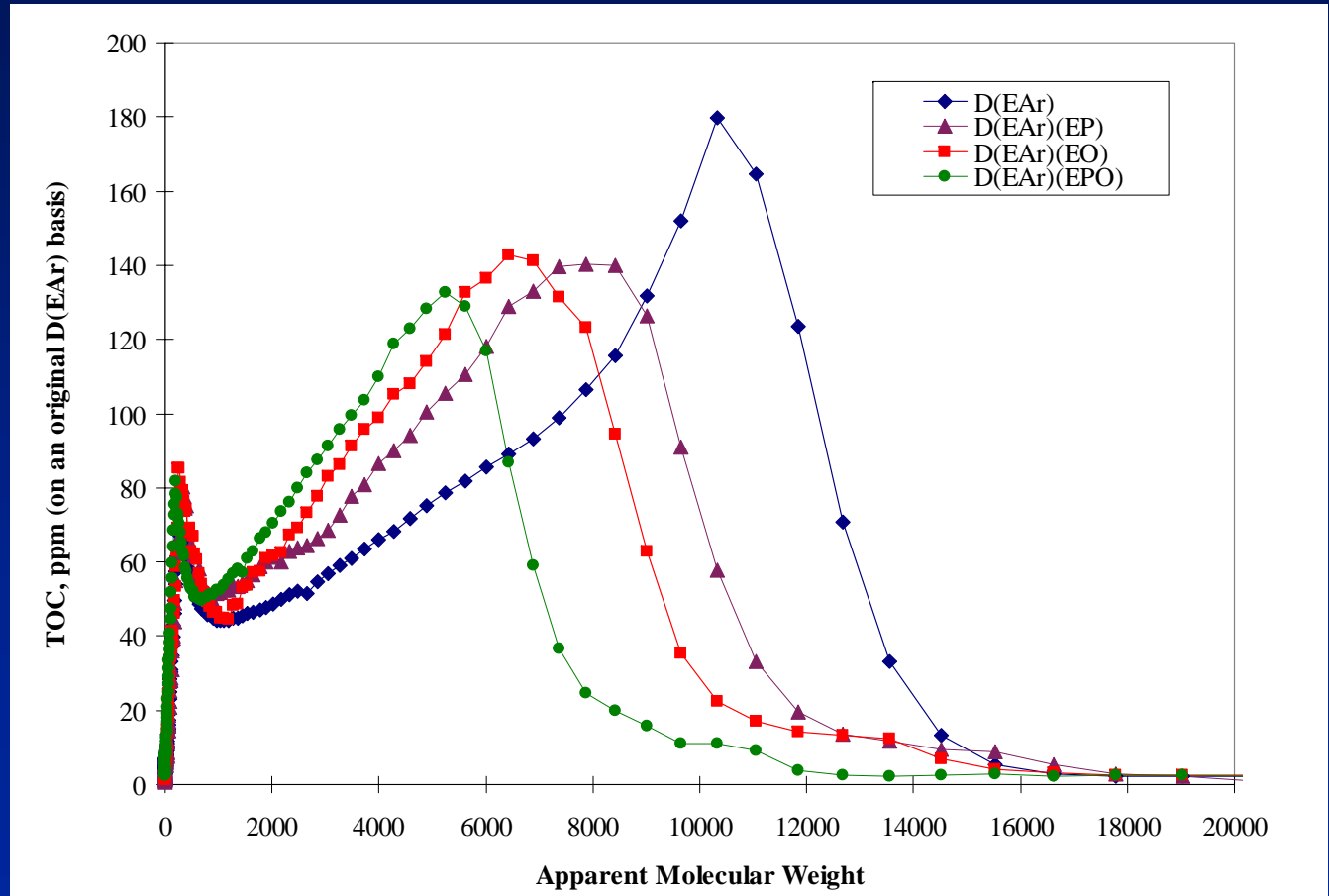


$MW_N$  95% LSD = 621;  $MW_W$  95% LSD = 718

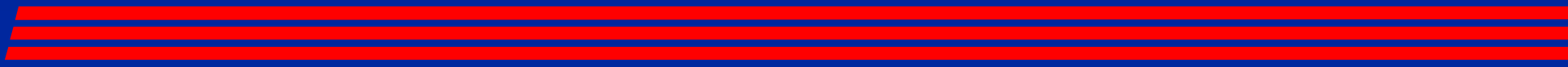


# Controlled Experiment of Oxidant Addition on Effluent Lignin Apparent MW Distribution

- D(EAr) effluent was treated to (EP), (EO), and (EPO)
- Oxidants were able to degrade effluent lignin

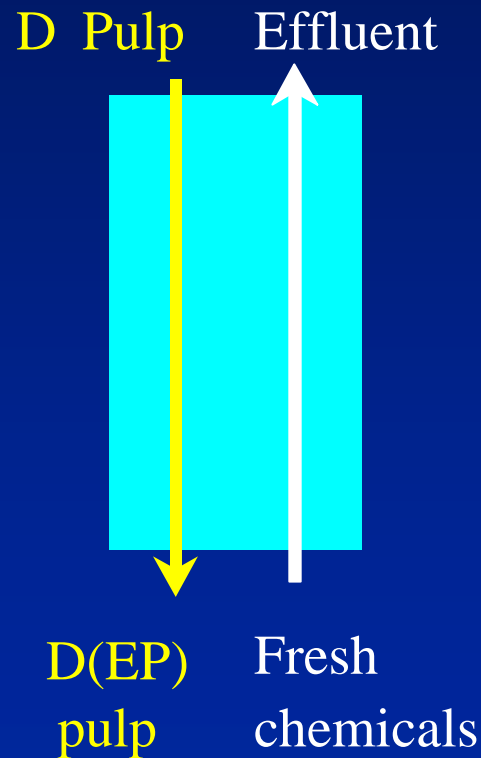


## Hypothesis - Effluent Apparent MW

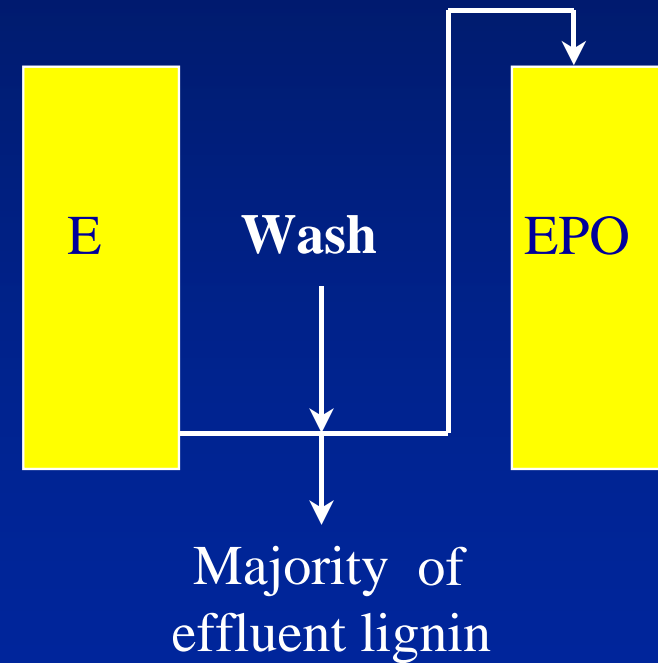
- Hypothesis: Dissolved lignin in effluent of  $E_1^*$  stage reacts with  $O_2$  and  $H_2O_2$  reinforcement - consuming chemicals
  - Test with alternative  $E_1$  stages that remove the bulk of the effluent lignin before the  $O_2$  and  $H_2O_2$  are applied
- 

# Alternative Alkaline Extraction Experiments

## Counter-current Extraction



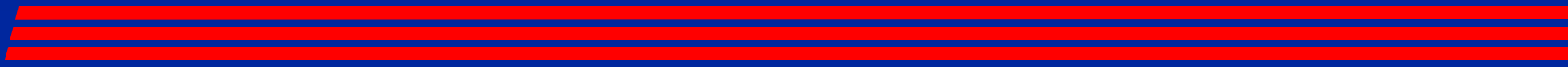
## Double Extraction



## Results of the Alternative Extraction Stages

- Removal of effluent lignin before applying oxidant reinforcement does not significantly improve delignification or brightness
- Additional experiments with increasing  $\text{H}_2\text{O}_2$  charges indicated residual lignin was reactive to further oxidant chemical
- This suggests that very little oxidant is wasted reacting with effluent lignin

# Bleachability Fundamentals

- To obtain fundamental understanding of changes bleachability - understand changes to lignin structure
    - Lignin color
    - Lignin size
    - **Lignin functional groups**
- 

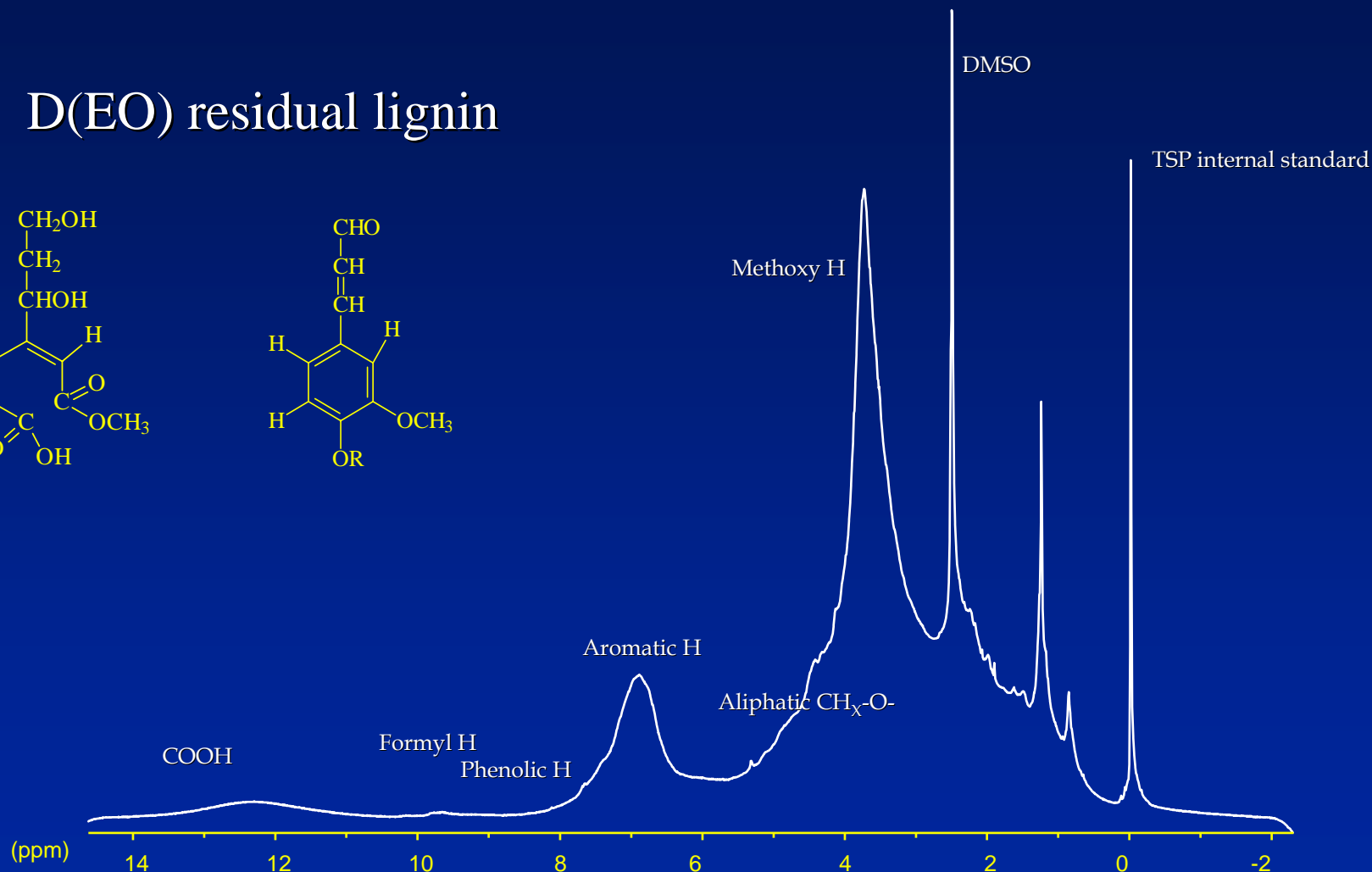
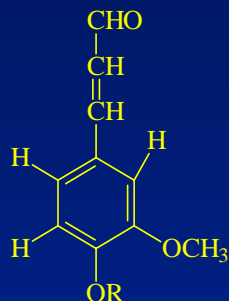
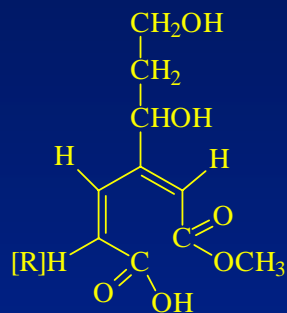
# NMR Spectroscopy on Lignin

- Bruker 400 MHz
- Experiments Performed
  - $^1\text{H}$  NMR
  - $^{13}\text{C}$  NMR
  - $^{31}\text{P}$  NMR - Hydroxyl groups
  - $^{31}\text{P}$  NMR - Quinones
  - $^2\text{H}$  NMR - Alkyl Carbonyls



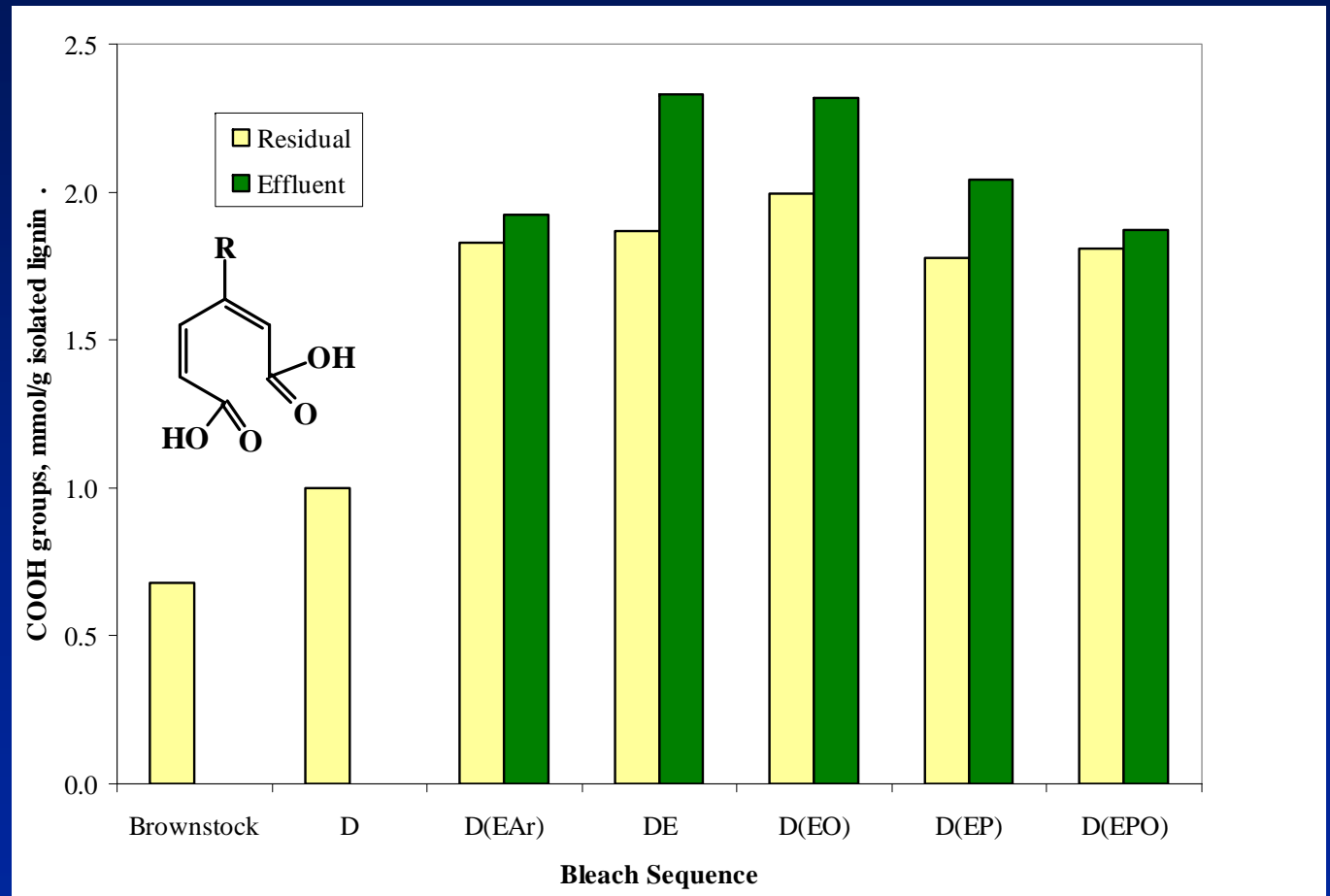
# Typical $^1\text{H}$ NMR Spectrum

D(EO) residual lignin



# <sup>1</sup>H NMR - COOH groups

- COOH increase due to alkali
- Attributed to MAME saponification
- O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> do not give appreciable increases

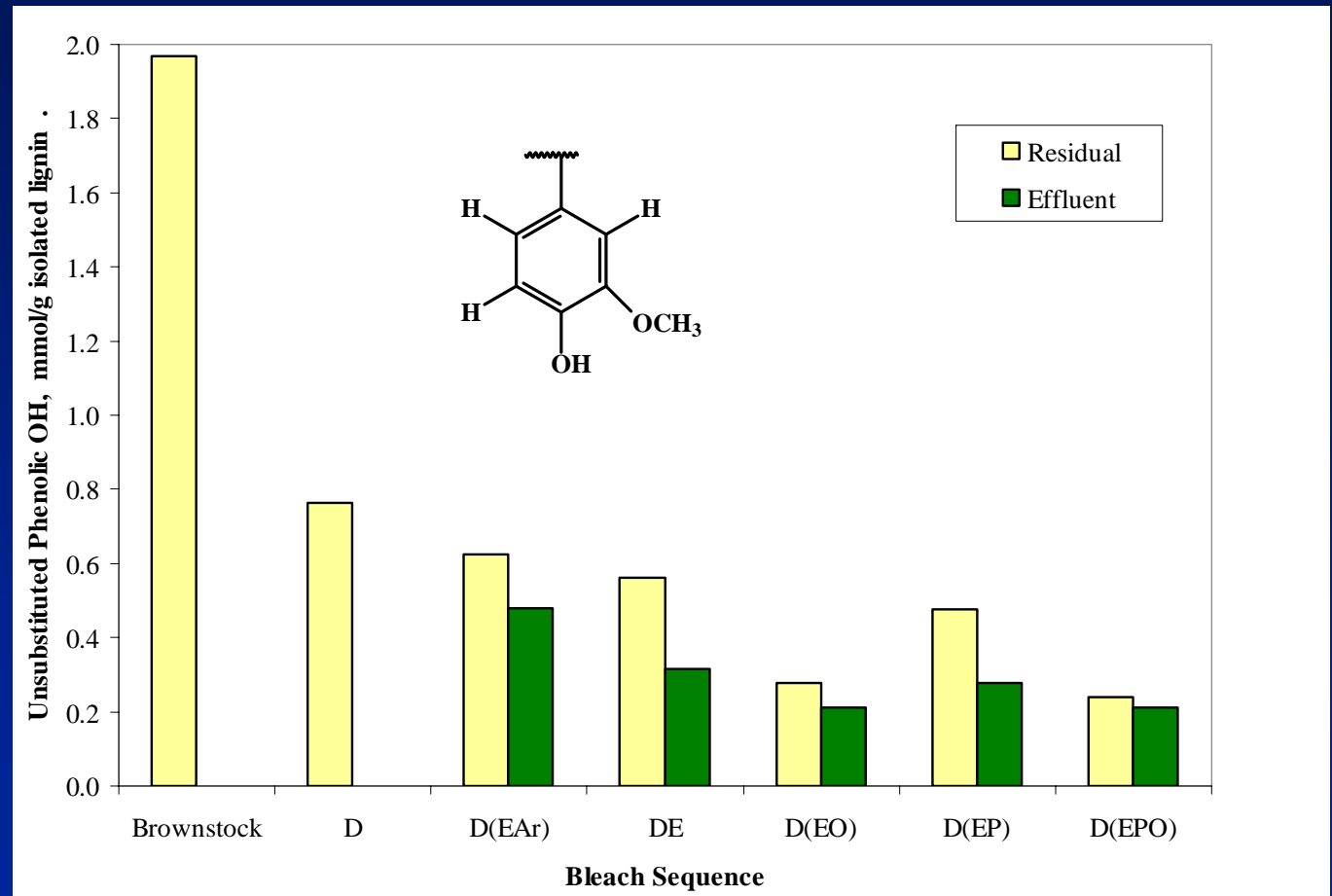


95% LSD = 0.159



# <sup>1</sup>H NMR - Unsubstituted Phenolic Groups

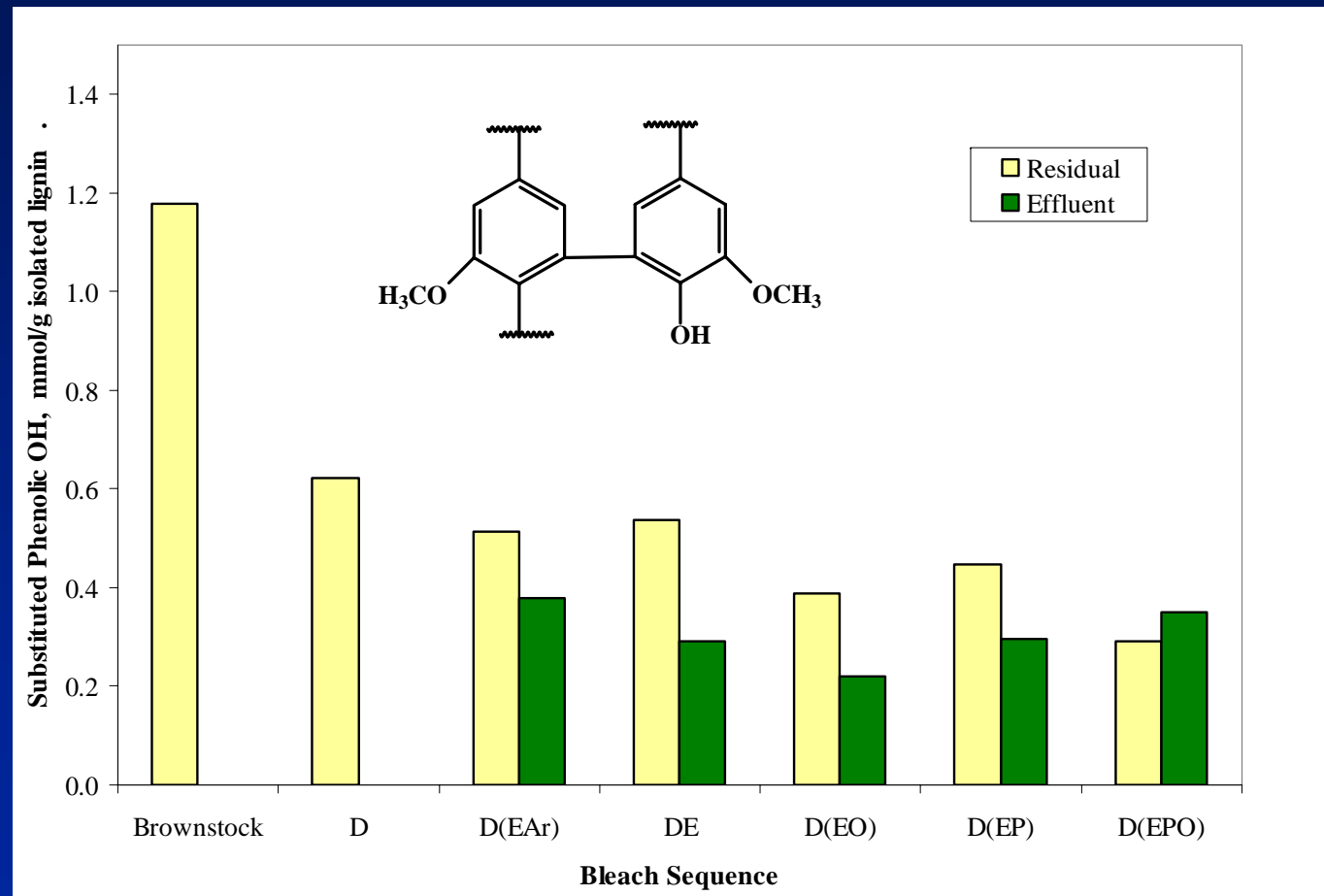
- Significant phenolic decrease in O<sub>2</sub> reinforced stages
- Attributed to autoxidation reactions



95% LSD = 0.183

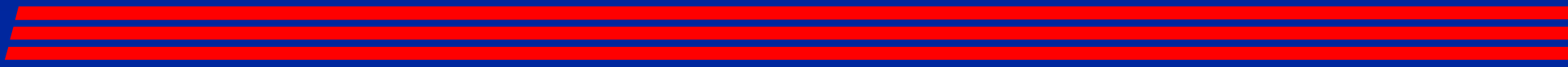
# <sup>1</sup>H NMR - Substituted Phenolic Groups

- Decrease in O<sub>2</sub> reinforced stages
- Substituted phenolic did not decrease as much as unsubstituted - indicating less reactive



95% LSD = 0.054

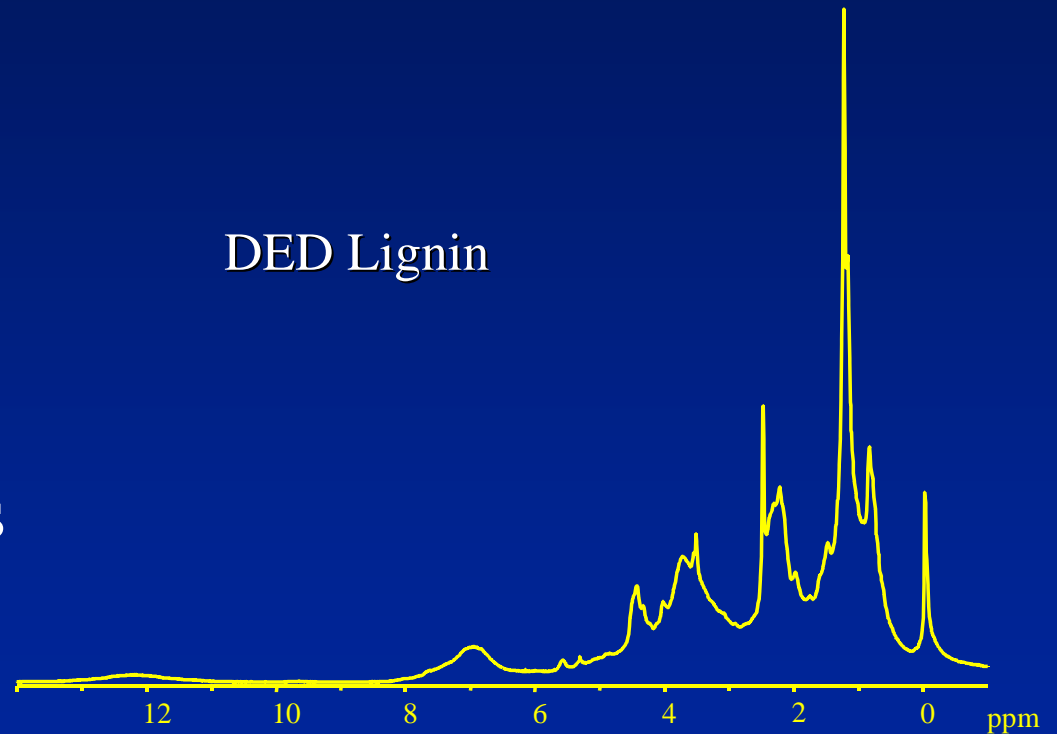
# $^1\text{H}$ NMR - Other Groups

- Formyl
    - No change during  $\text{D}_0$
    - slight decrease with  $\text{O}_2$  reinforcement
  - Aromatic
    - decrease during  $\text{D}_0$
    - No change in  $\text{E}_1^*$
  - Methoxyl and Aliphatic  $\text{CH}_x\text{-O-}$ 
    - high variability
- 

# $^1\text{H}$ NMR - D<sub>1</sub> stage

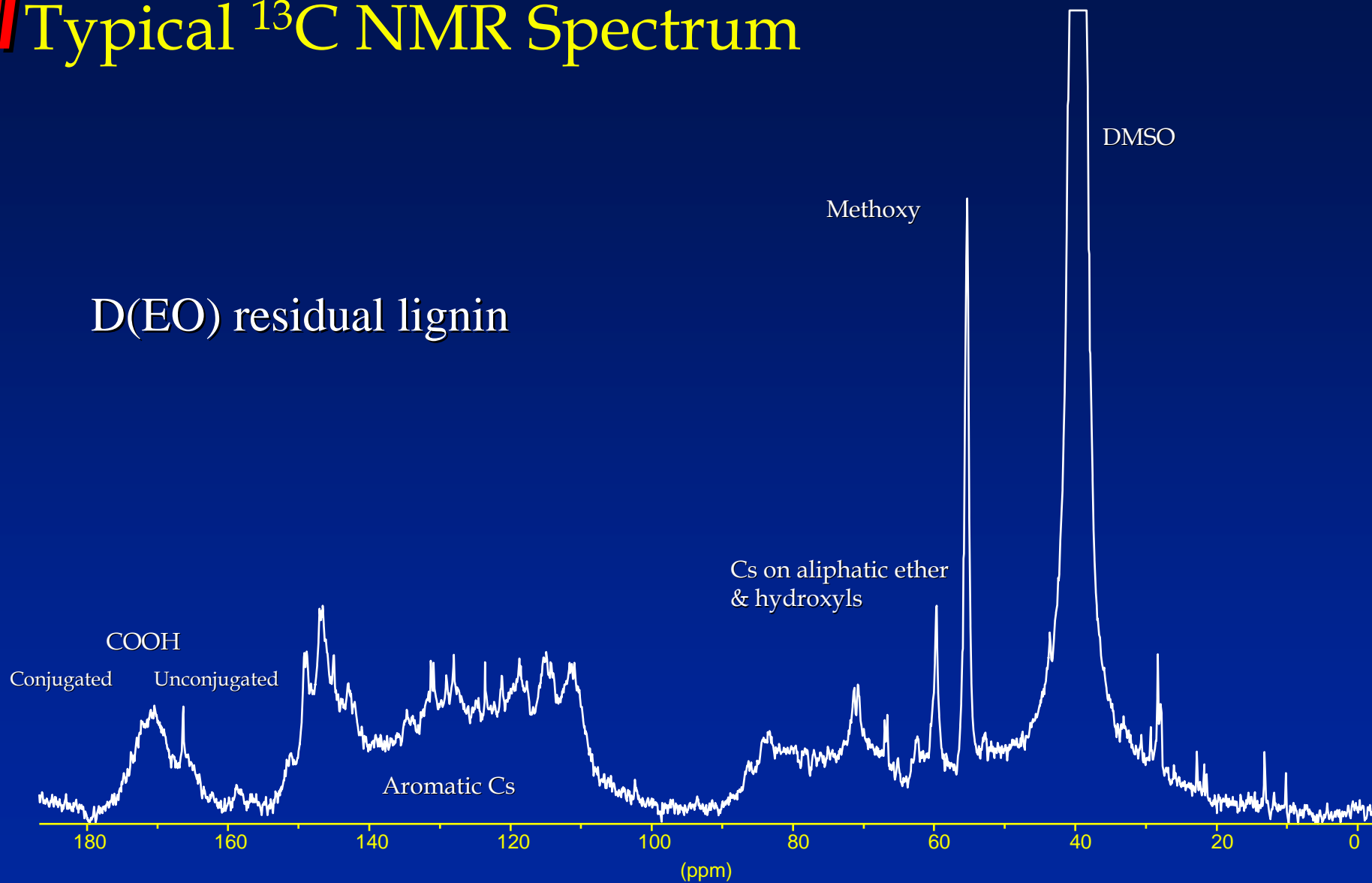
- D<sub>1</sub> Stage
  - Destroys aromatic nature of lignin
  - Leaves primarily aliphatic structures
- No differences noted between functional groups from previous E<sub>1</sub>\* stage

DED Lignin



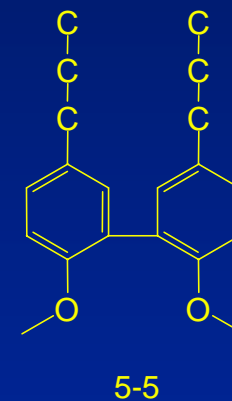
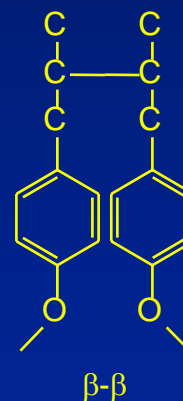
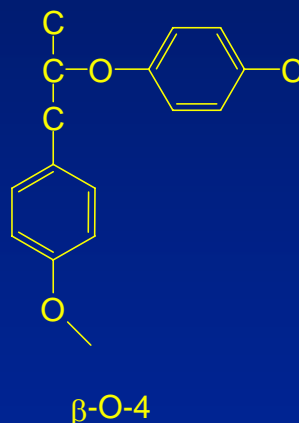
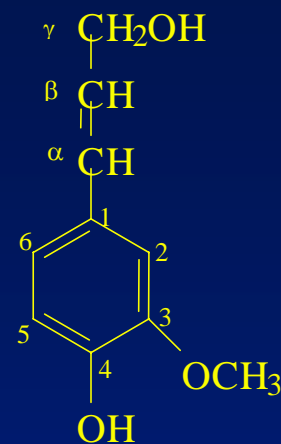
# Typical $^{13}\text{C}$ NMR Spectrum

D(EO) residual lignin



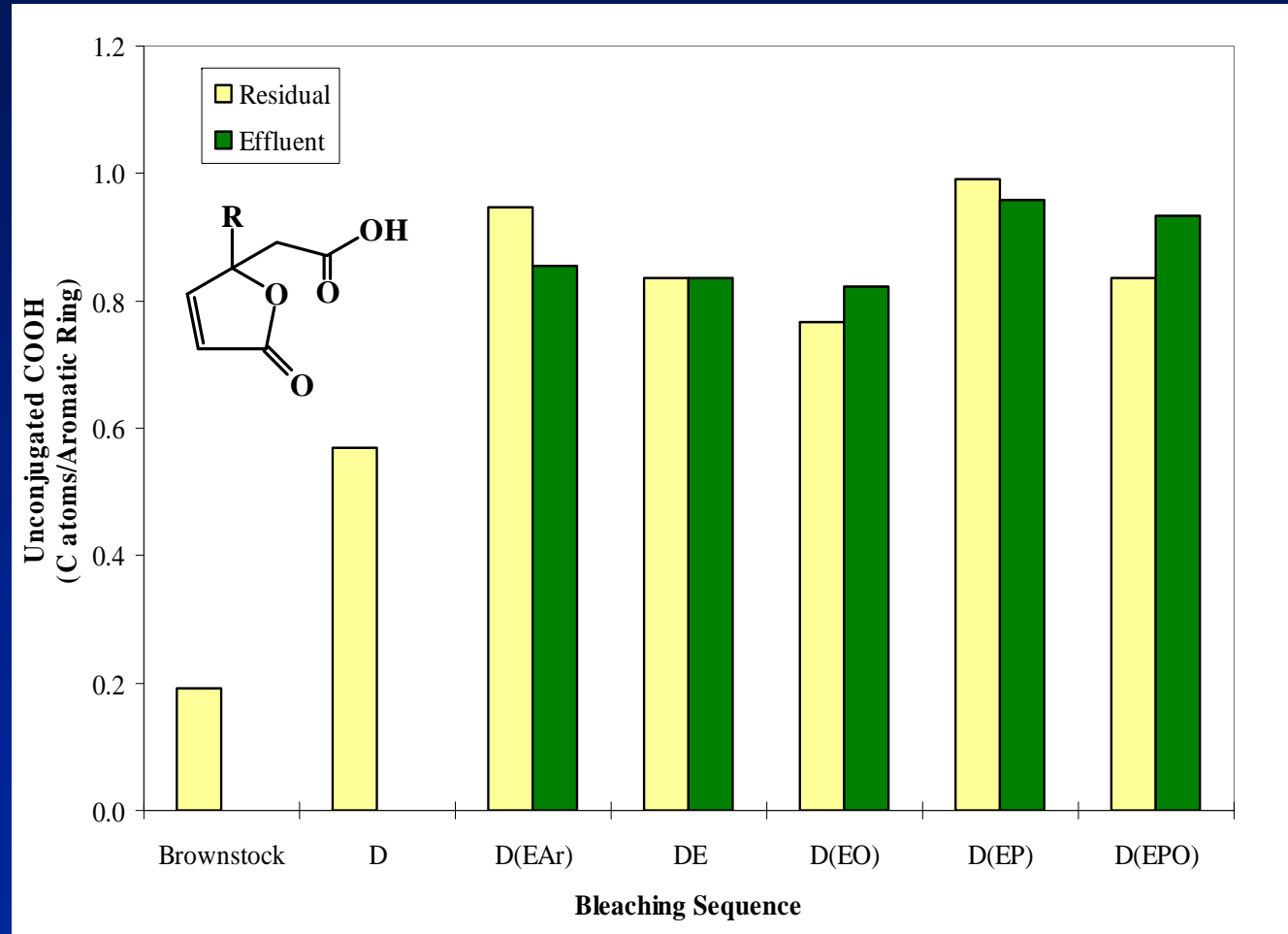
# <sup>13</sup>C NMR Structures

- Unconjugated COOH
- Conjugated COOH
- C3, C4 Aromatic ether or hydroxyl
- C1, Aromatic C-C bond
- C5, Aromatic C-C bond
- C2, Aromatic C-H bond
- C5, Aromatic C-H bond
- C6, Aromatic C-H bond
- Methoxyl OCH<sub>3</sub>
- C $\beta$  in  $\beta$ - $\beta$  and C $\beta$  in  $\beta$ -5
- Aliphatic C-O bond, C $\beta$  in  $\beta$ -O-4; C $\alpha$  in  $\beta$ -5 and  $\beta$ - $\beta$
- Aliphatic C-O bond, C $\alpha$  in  $\beta$ -O-4
- Aliphatic COR
- Aliphatic C-O C $\gamma$  in  $\beta$ -O-4



# <sup>13</sup>C NMR - Unconjugated COOH

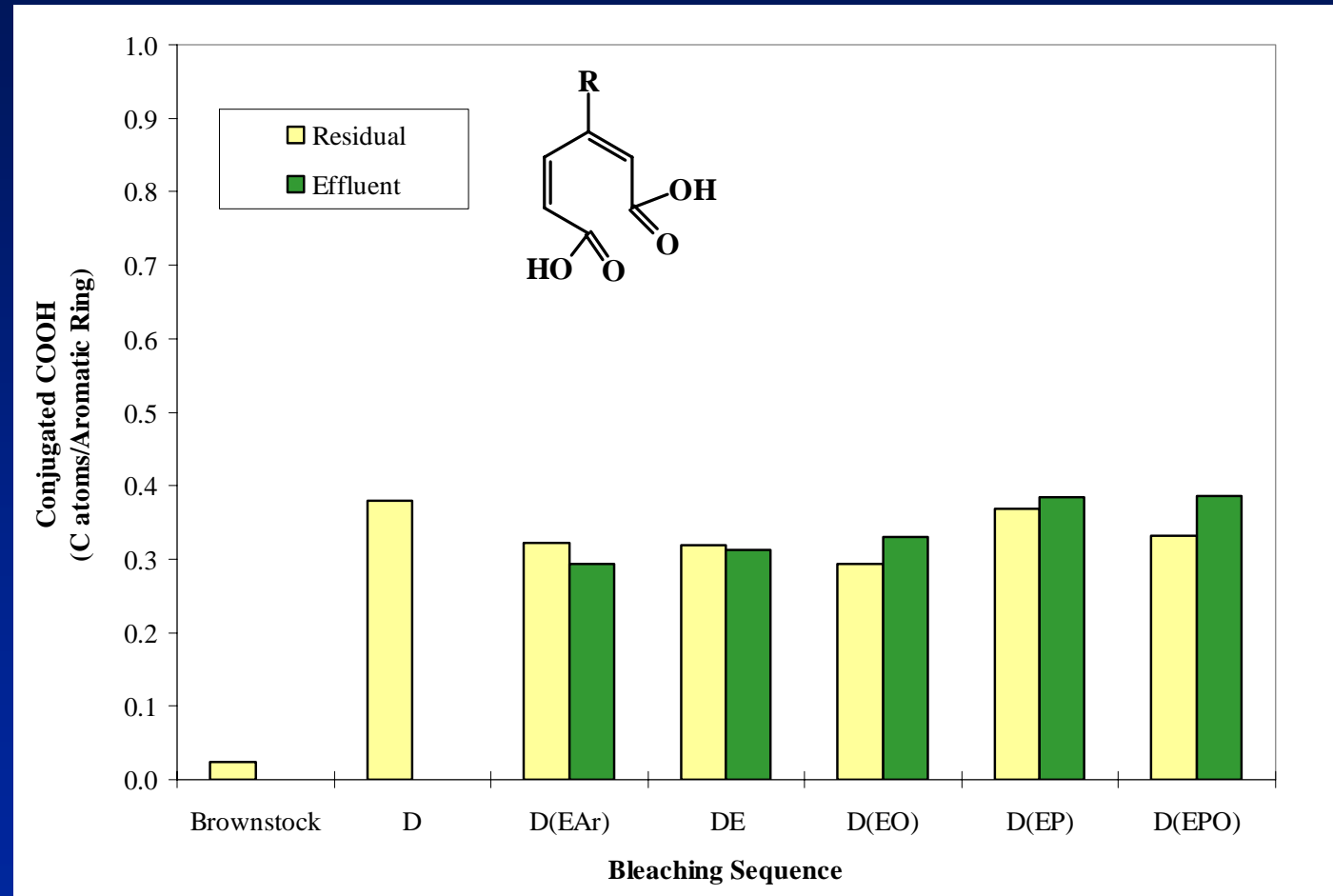
- Increase in D<sub>0</sub> stage and all E<sub>1</sub>\* stage
- Suggests an increase in COOH groups due to alkali



95% LSD = 0.095

# <sup>13</sup>C NMR - Conjugated COOH

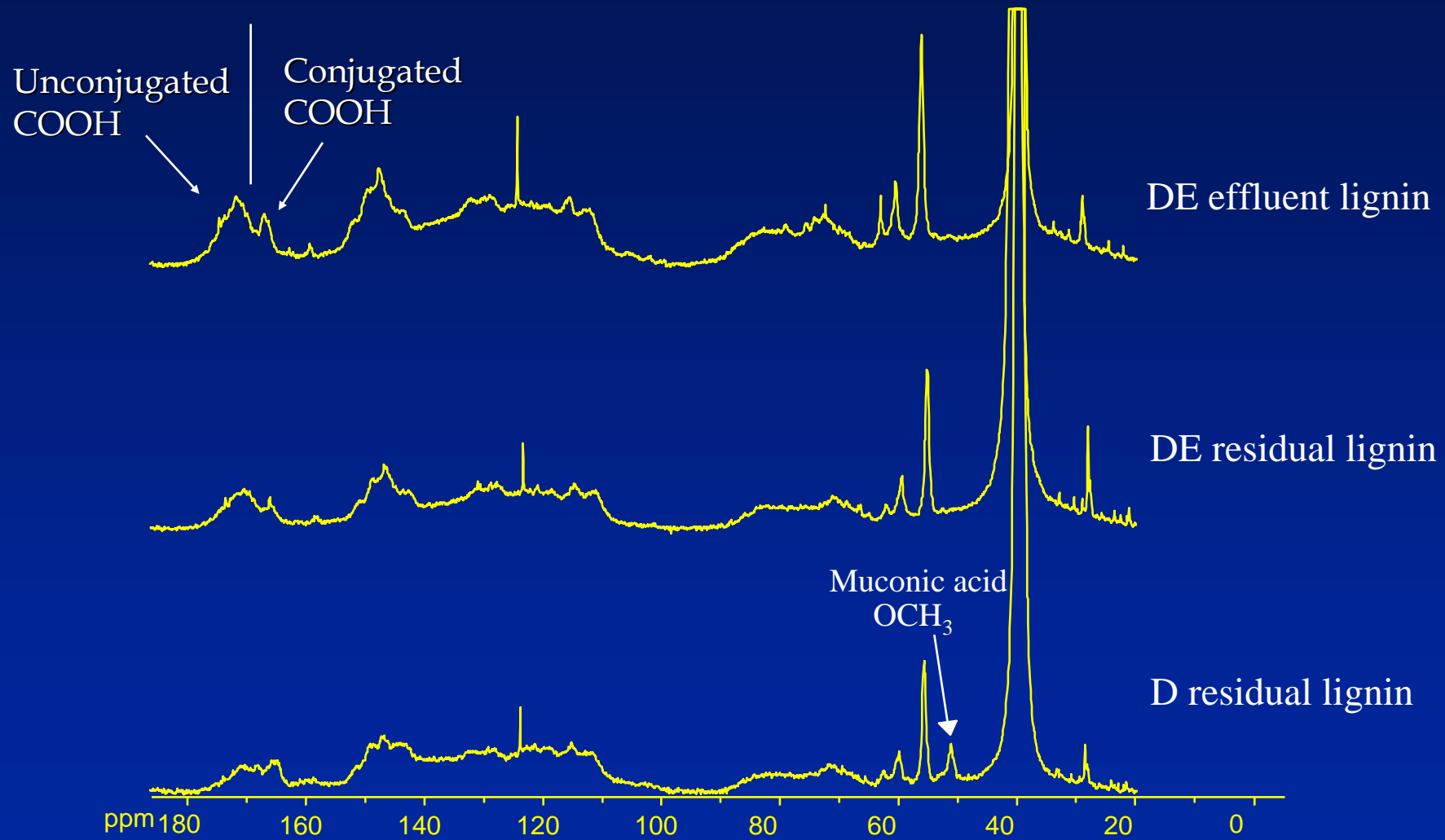
- Increase in  $D_0$
- No increase in  $E_1^*$
- Suggests the muconic acid structures are in the lactone form.



95% LSD = 0.088

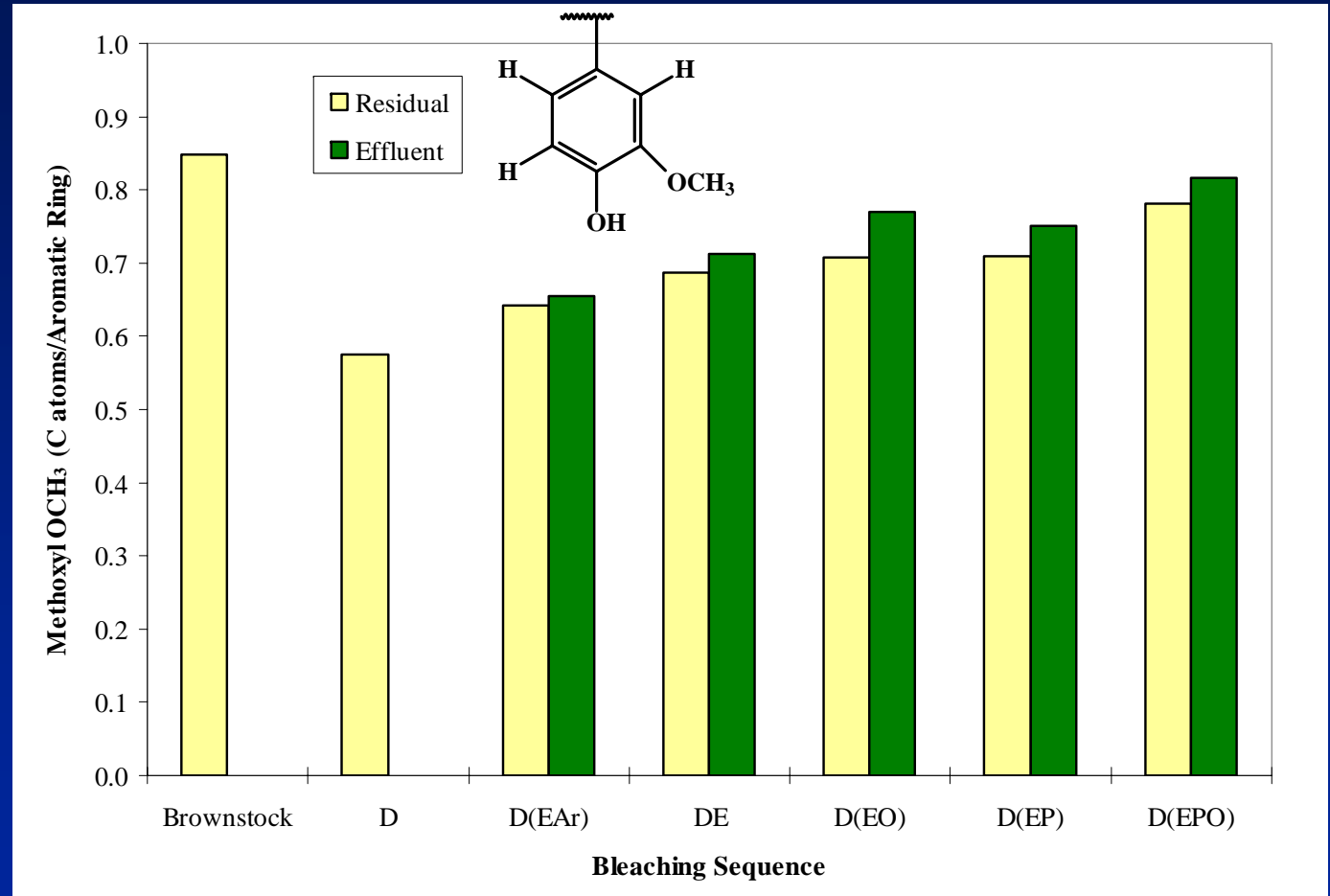


# $^{13}\text{C}$ NMR Spectra Around the E stage



# <sup>13</sup>C NMR - Methoxyl

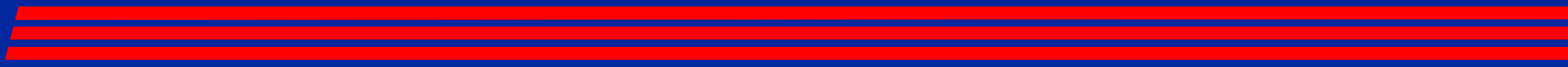
- Methoxyl enrichment relative to aromatic signal
- Not creating methoxyl groups
- Demethylation reactions create phenolic, which react via autoxidation



95% LSD = 0.097

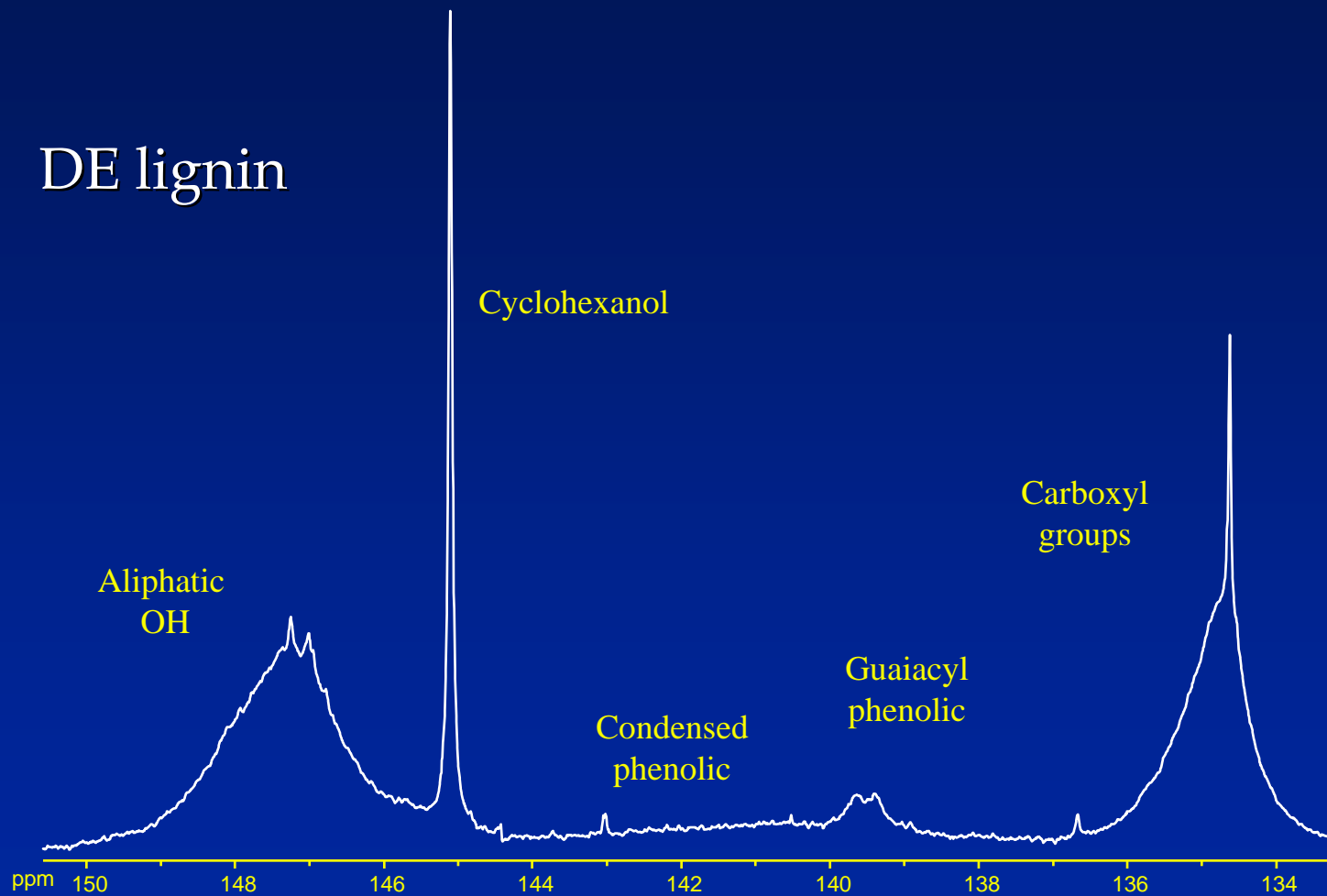


## <sup>31</sup>P NMR - Hydroxyl Groups

- 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane derivatized
  - Lignins used
    - Preliminary study - small scale
      - » 33 kappa industrial softwood pulp
    - D<sub>0</sub> residual lignin
      - » Performed E<sub>1</sub>\* stage reactions
      - » 1:1 (v/v) dioxane:water
      - » Isolated lignin
  - Similar results
- 

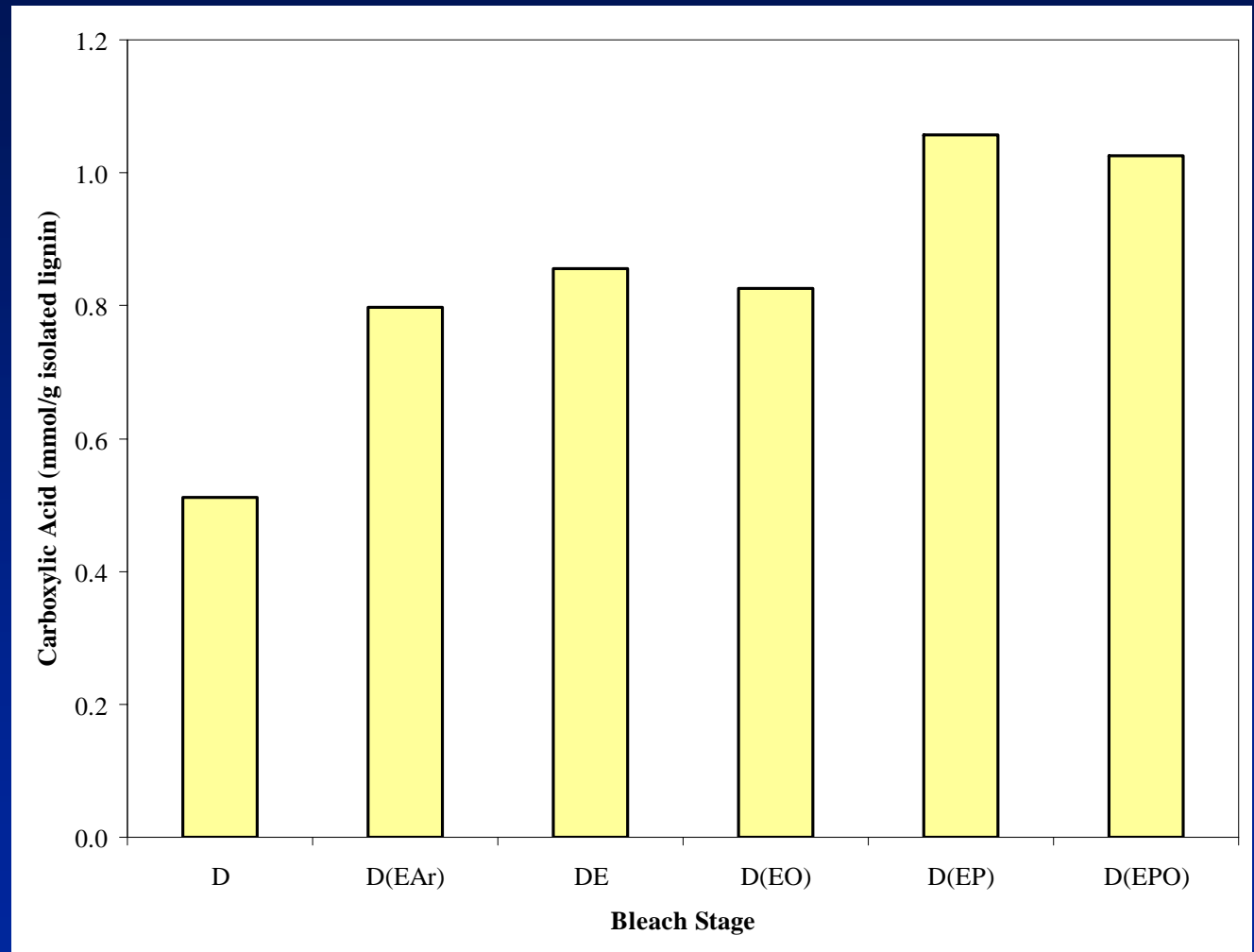
# Typical $^{31}\text{P}$ NMR Spectrum

DE lignin



# <sup>31</sup>P NMR - Carboxyl Groups

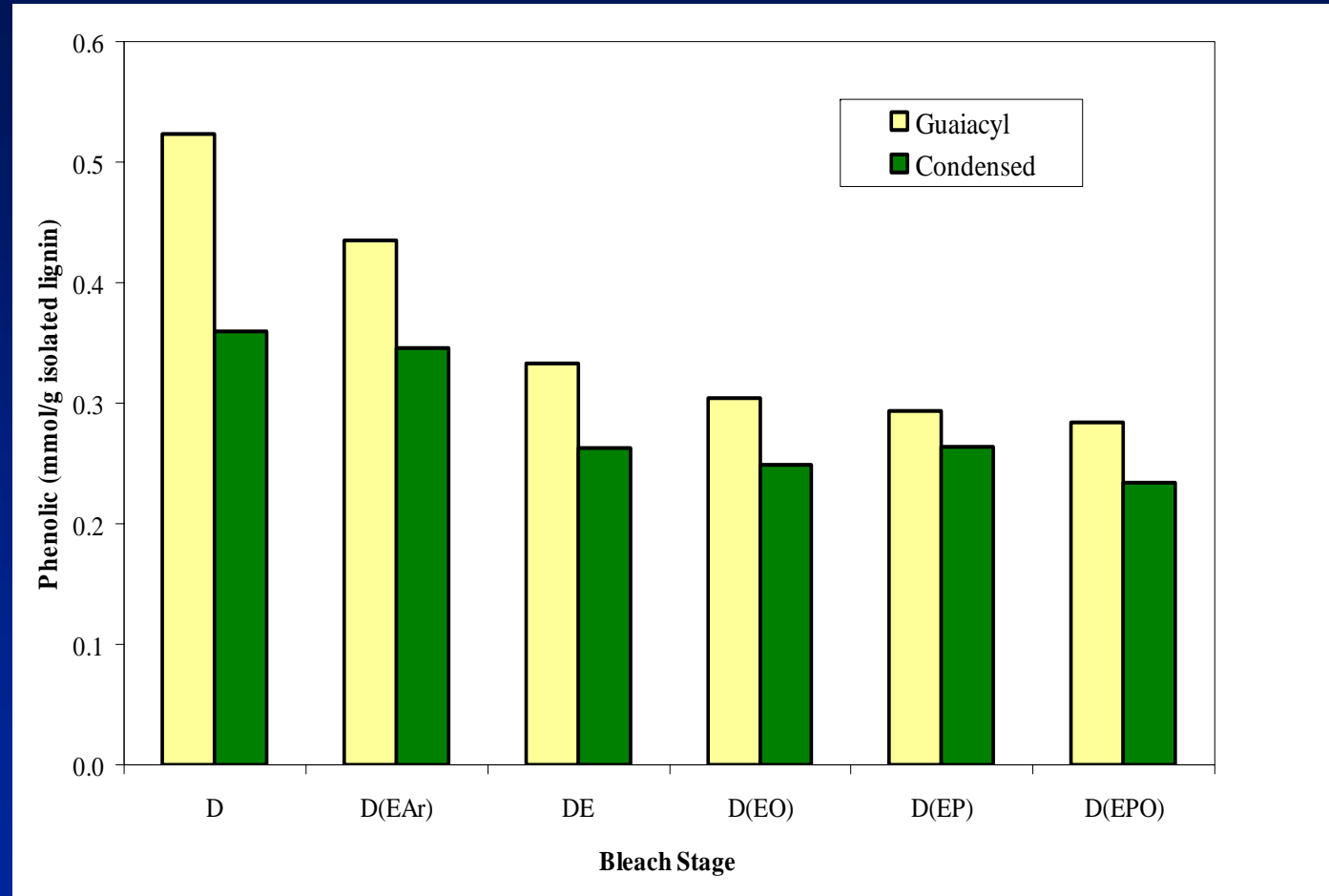
- Increase in COOH with alkali - MAME saponification
- Increase with H<sub>2</sub>O<sub>2</sub> reinforcement - perhydroxyl addition to quinone structures



95% LSD = 0.191

# <sup>31</sup>P NMR - Phenolic

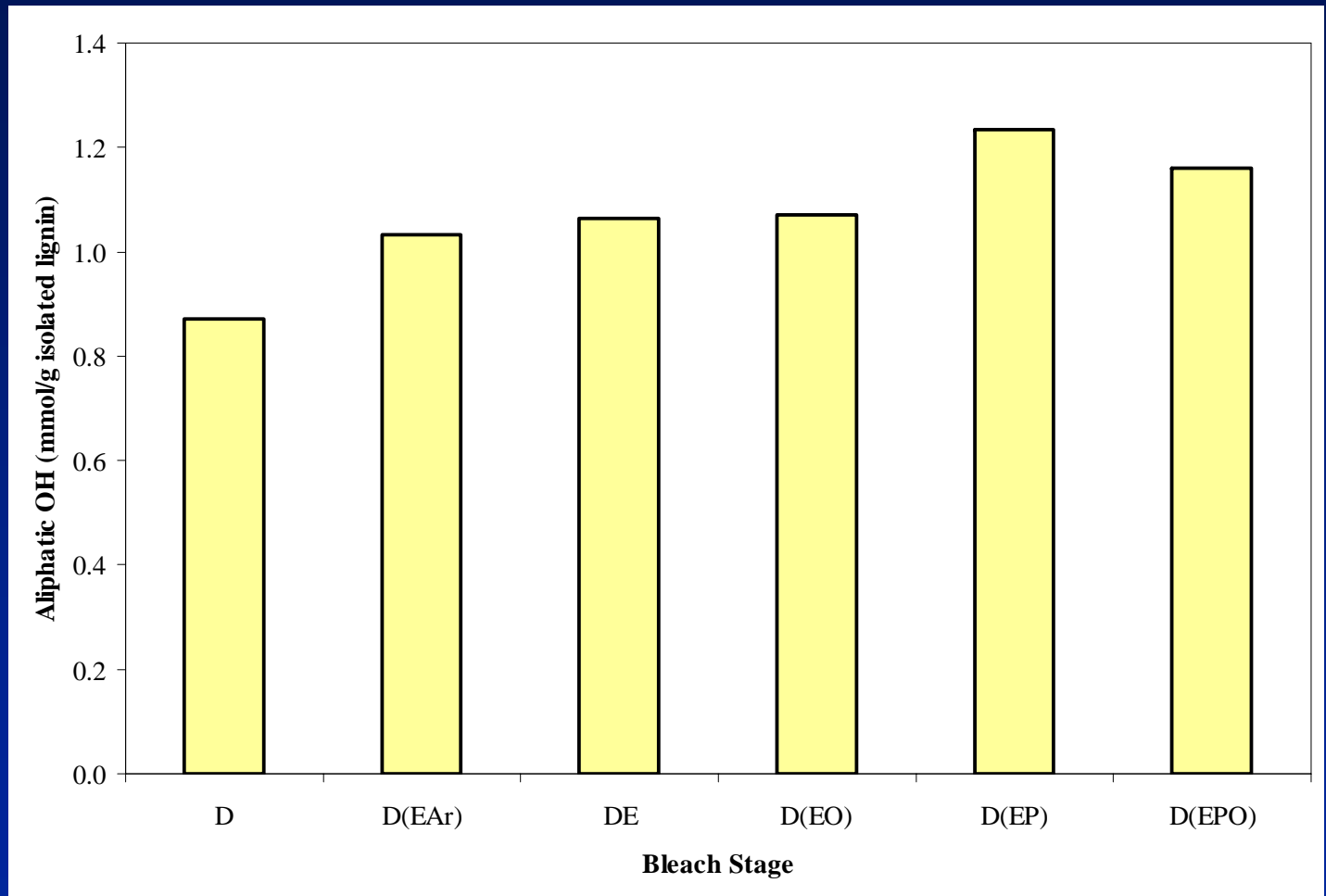
- Phenolic decrease with oxidant reinforcement - autoxidation reactions
- Condensed phenolic smaller drop indicating lower reactive than guaiacyl



Condensed phenolic 95% LSD = 0.059; Guaiacyl phenolic 95% LSD = 0.024

# <sup>31</sup>P NMR - Aliphatic Hydroxyl Groups

- Increase in aliphatic hydroxyl due to alkali
- Possibly due to chlorine elimination reactions



95% LSD = 0.150

# Existing NMR Techniques Summary

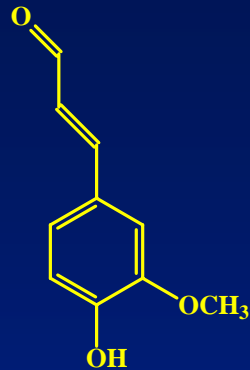
- Existing techniques are able to show some major delignification reactions
- Measured structures correlated well with delignification but not brightness
- New NMR techniques needed to measure chromophore structures



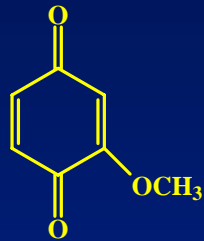
# Lignin Chromophore Structures

- Consists primarily of conjugated carbonyls

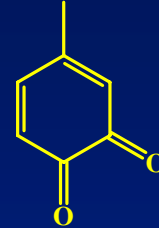
- Quinones
- Conjugated alkyl carbonyls



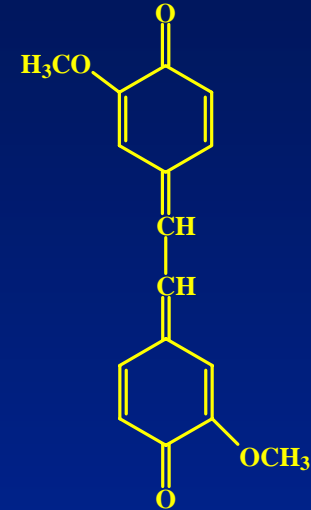
coniferaldehyde



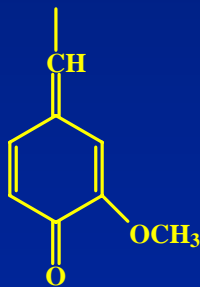
para-quinone



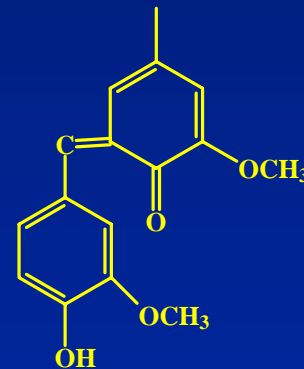
ortho-quinone



para-para-stilbene quinone



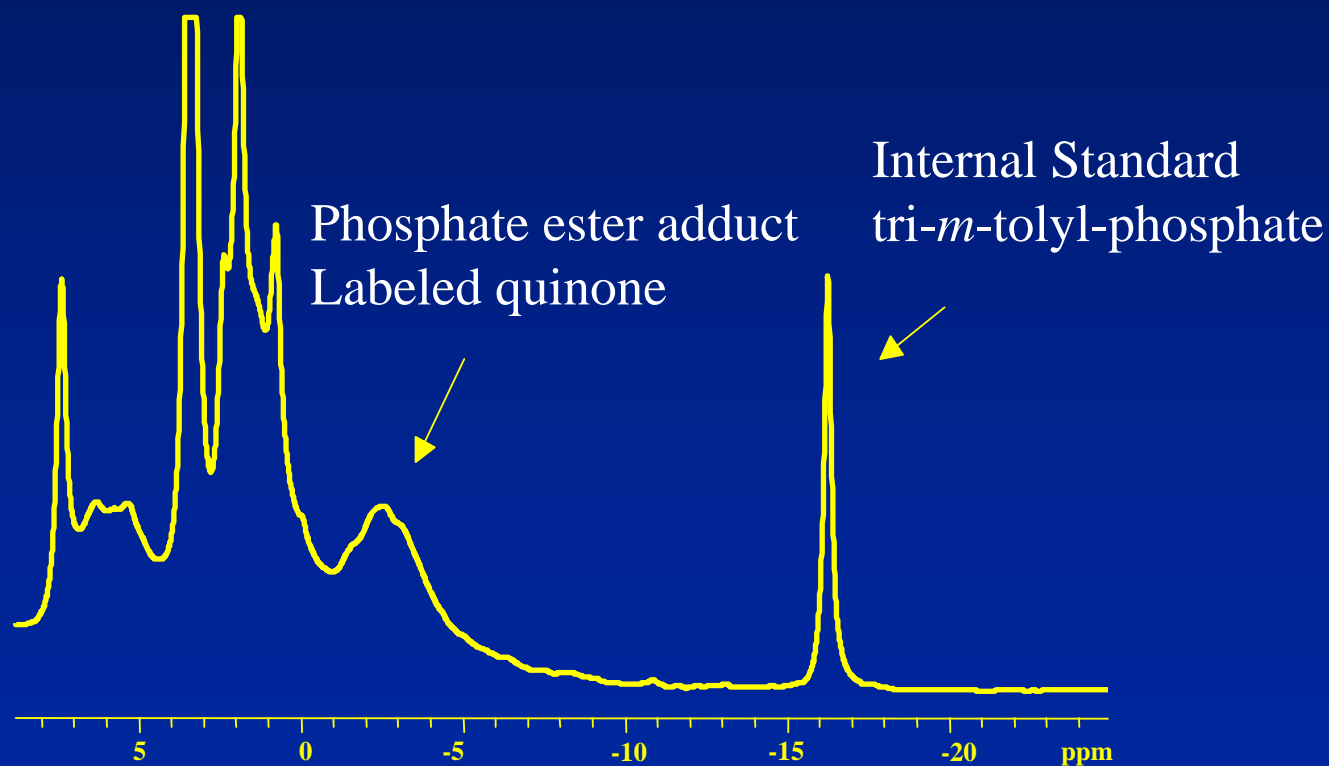
para-quinone methide



ortho-quinone methide

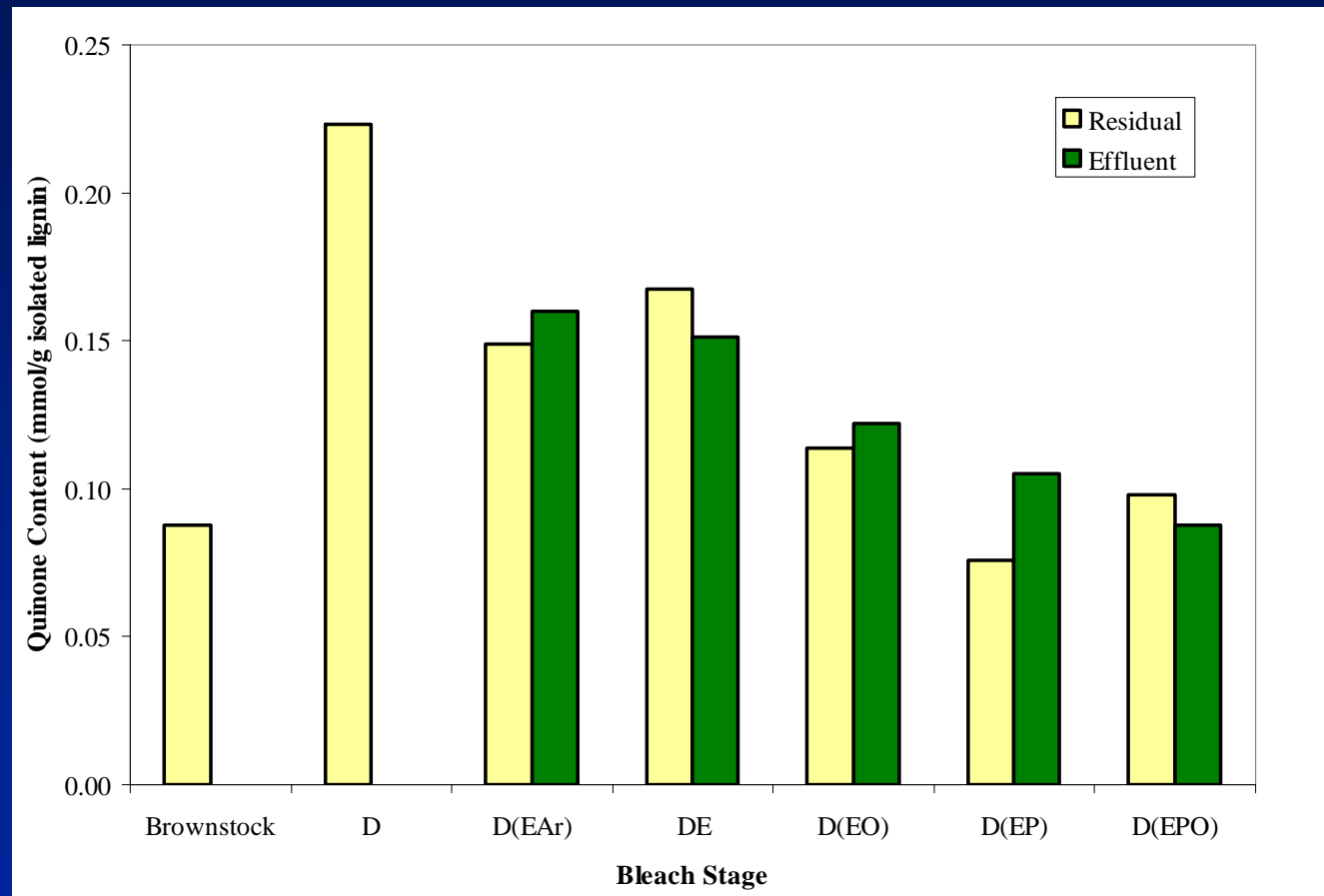
## <sup>31</sup>P NMR - Quinones

- Procedure developed by Zawadzki et al.
- Tri-methyl phosphite derivatized



# <sup>31</sup>P NMR - Quinone Content of D<sub>0</sub> and E<sub>1</sub>\*

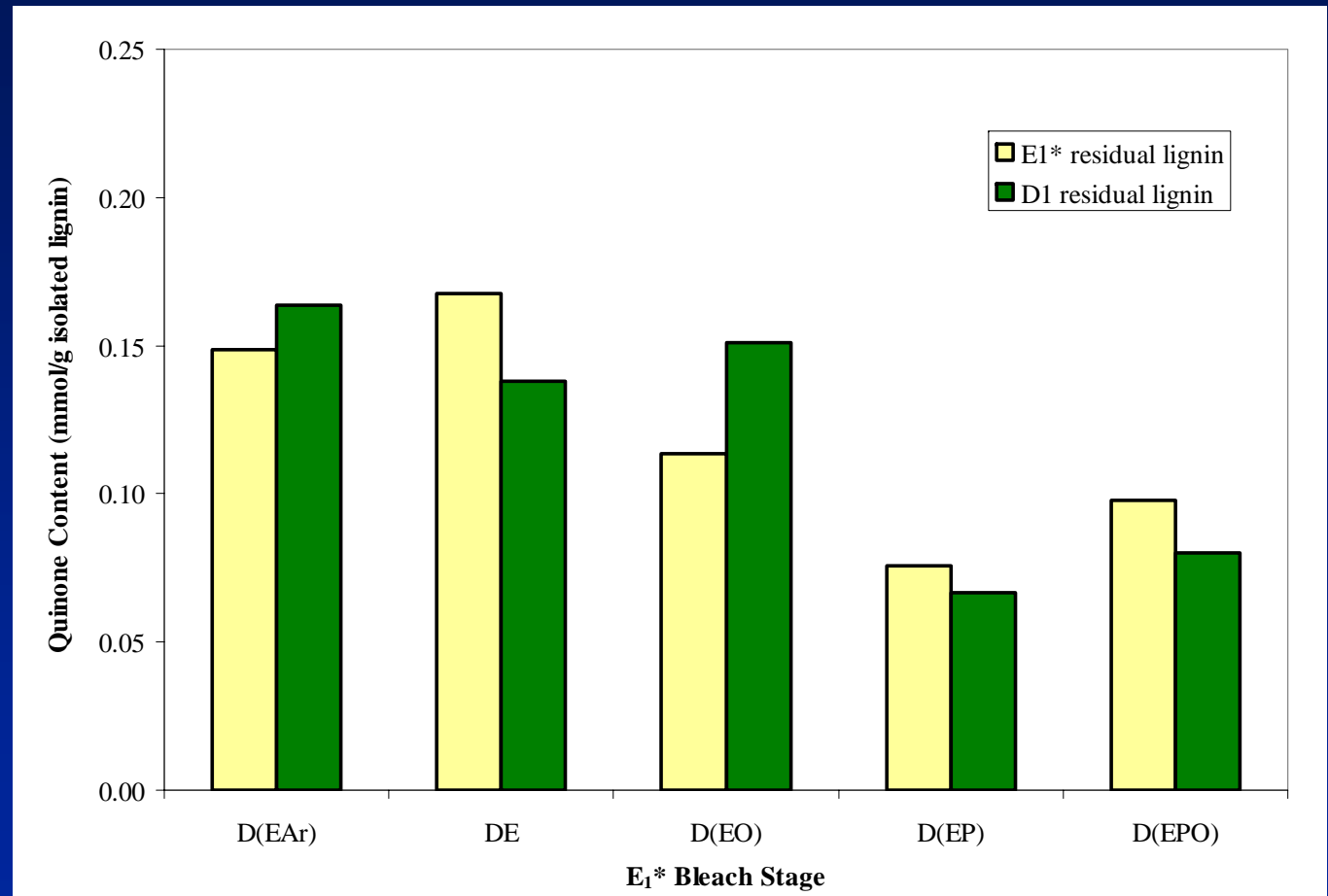
- D<sub>0</sub> stage increase quinones - phenolic reaction
- Alkali decreases quinone - hydroxide addition & BAR
- O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> decreases quinone - perhydroxyl addition



95% LSD = 0.053

# <sup>31</sup>P NMR - Quinone Content D<sub>1</sub> Stage

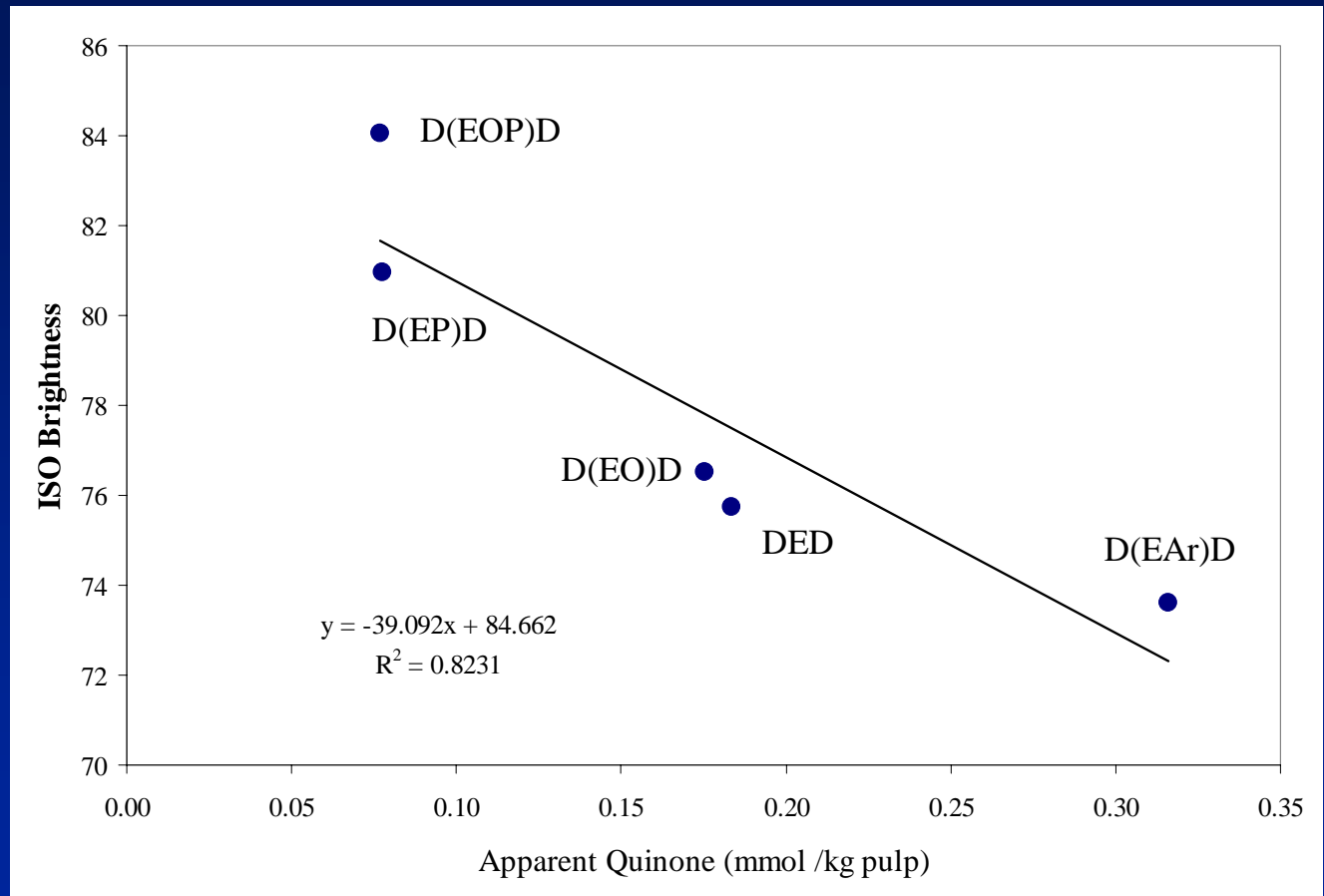
- D<sub>1</sub> stage does not affect quinone content
- Brightening of D<sub>1</sub> stage possibly from lignin removal and conjugation destruction



95% LSD = 0.053

# Apparent Quinone Content vs D<sub>1</sub> Brightness

- Apparent quinone = quinone content on pulp weight basis (acid - insoluble lignin)
- Correlates well brightness suggesting it is a major chromophore



## Conclusions

- First research to compare fundamental differences between oxidant reinforcement in an alkaline extraction stage
- Able to show delignification and brightening reactions occur in the oxidative E<sub>1</sub> stage
- Structural changes measured by existing NMR techniques of <sup>1</sup>H-, <sup>13</sup>C-, and <sup>31</sup>P-hydroxyl NMR useful in explaining delignification reactions but do not correlate to brightness

## Conclusions - continued

- Summary of main effects of each chemical
  - NaOH
    - » Dramatic increase in COOH - MAME saponification
  - O<sub>2</sub>
    - » Increases delignification - autoxidation reactions
    - » Unsubstituted phenolics more reactive than substituted
    - » Ambient O<sub>2</sub> increases delignification
  - H<sub>2</sub>O<sub>2</sub>
    - » Increases brightness - quinone addition reactions



Acknowledgments:

IPST Member Companies

IPST Wood Chemistry Group