



**ADVANCES IN UNDERSTANDING
THE BASICS OF THE FIRST
ALKALINE EXTRACTION STAGE
IN BLEACHING**

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Topics Covered

- | Project Objectives
 - | Main Reactions of Alkaline Extraction
 - | Initial Observation
 - | Study on E reactions on isolated D lignin
 - | Study on E reactions on pulp
 - | Study on various D conditions
 - | Conclusions
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Project Objectives

- | Explore the fundamental chemistry of reactions occurring during the alkaline extraction stage
 - | Focus on the E1 stage after a D delignification stage
 - | Look at various oxidant reinforcements
 - (E+Ar), E, (E+O), (E+O+P)
 - | Use NMR spectroscopy to measure functional group changes.
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Alkaline Extraction Chemistry

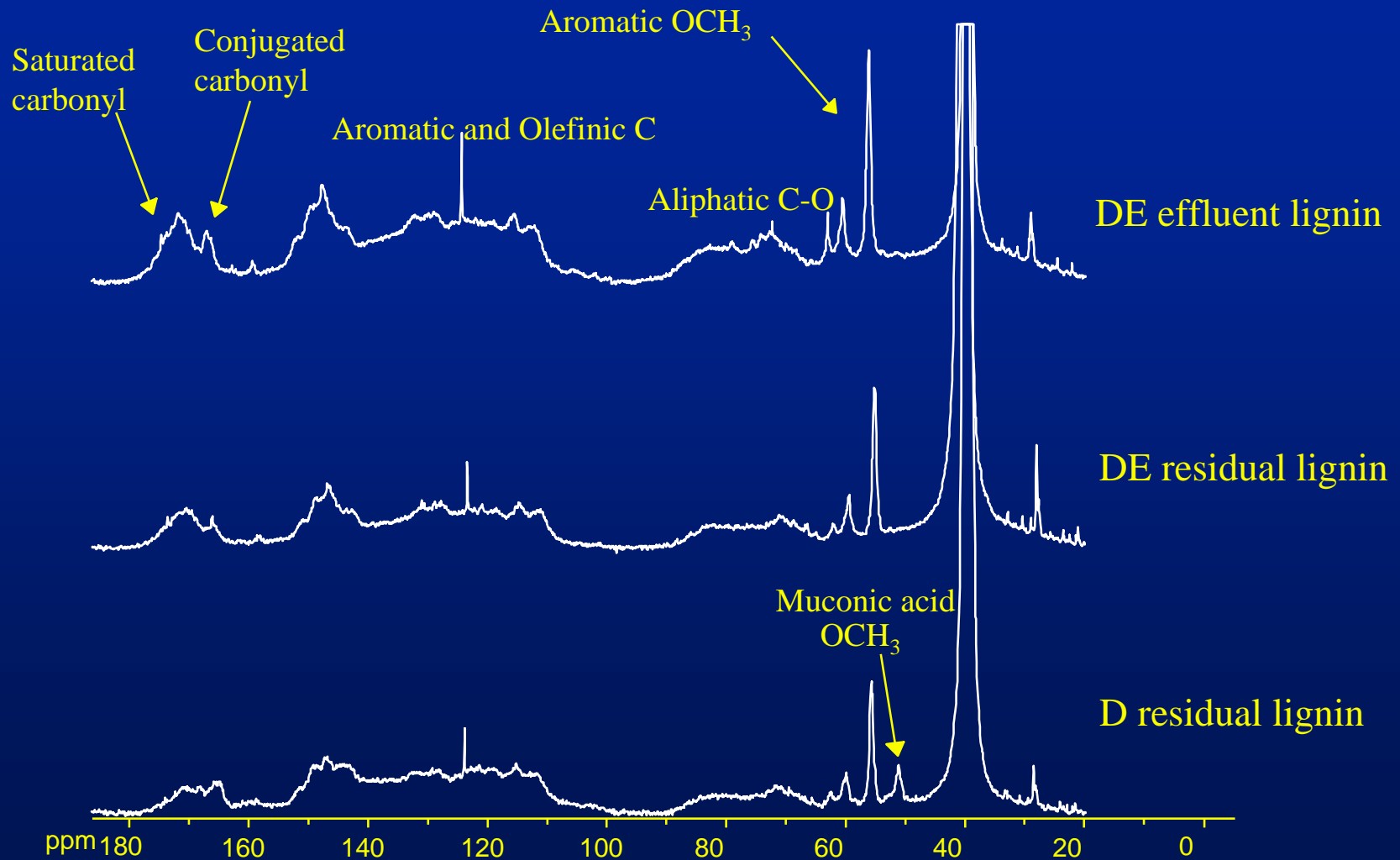
- | Main reactions (from Literature)
 - Neutralization of acidic groups in lignin from earlier oxidation stage
 - Base catalyzed hydrolysis of organically bound chlorine
- | NaOH is both a strong base and relatively good nucleophile, other reactions may be important

Start of Investigation - Initial Observation

- | ^{13}C NMR spectroscopy of lignin around an alkaline extraction (E) stage
 - Aliphatic carbonyl region increased while aromatic carbonyl decreased
 - Muconic acid methyl ester signal in D residual lignin was eliminated in E residual and effluent lignin



¹³C NMR Spectra around the E stage



Initial Investigation

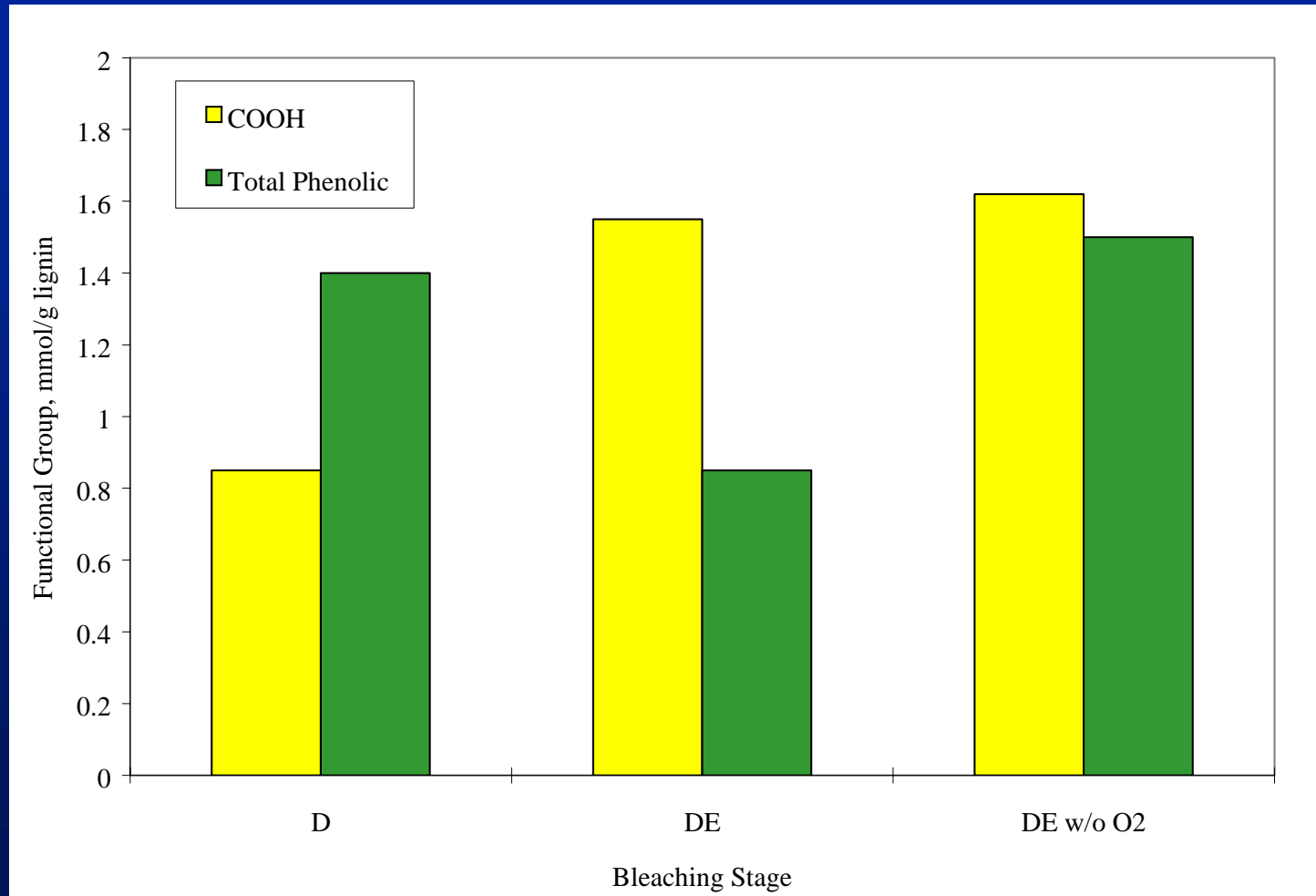
- | Reacted Isolated D stage lignin with NaOH
 - Lignin from a 28 kappa SW conventional BS pulp
 - D stage at 10% solids, 0.20 KF, 45 °C, 45 minutes, and an initial pH of 4.5
 - Lignin was reacted in suspension of 9:1 dioxane to water
- | Reaction conditions
 - E without oxygen (designated E+Ar) at a 50% TAC charge at 70 °C for 60 minutes
 - E under atmospheric oxygen (normal E) at a 50% TAC charge at 70 °C for 60 minutes

Initial Investigation - cont.

- | Reacted lignins were isolated
 - removed p-dioxane by evaporation under reduced pressure
 - lignins were acid precipitated and washed with water
- | Lignin functional group measured with ^1H NMR spectroscopy



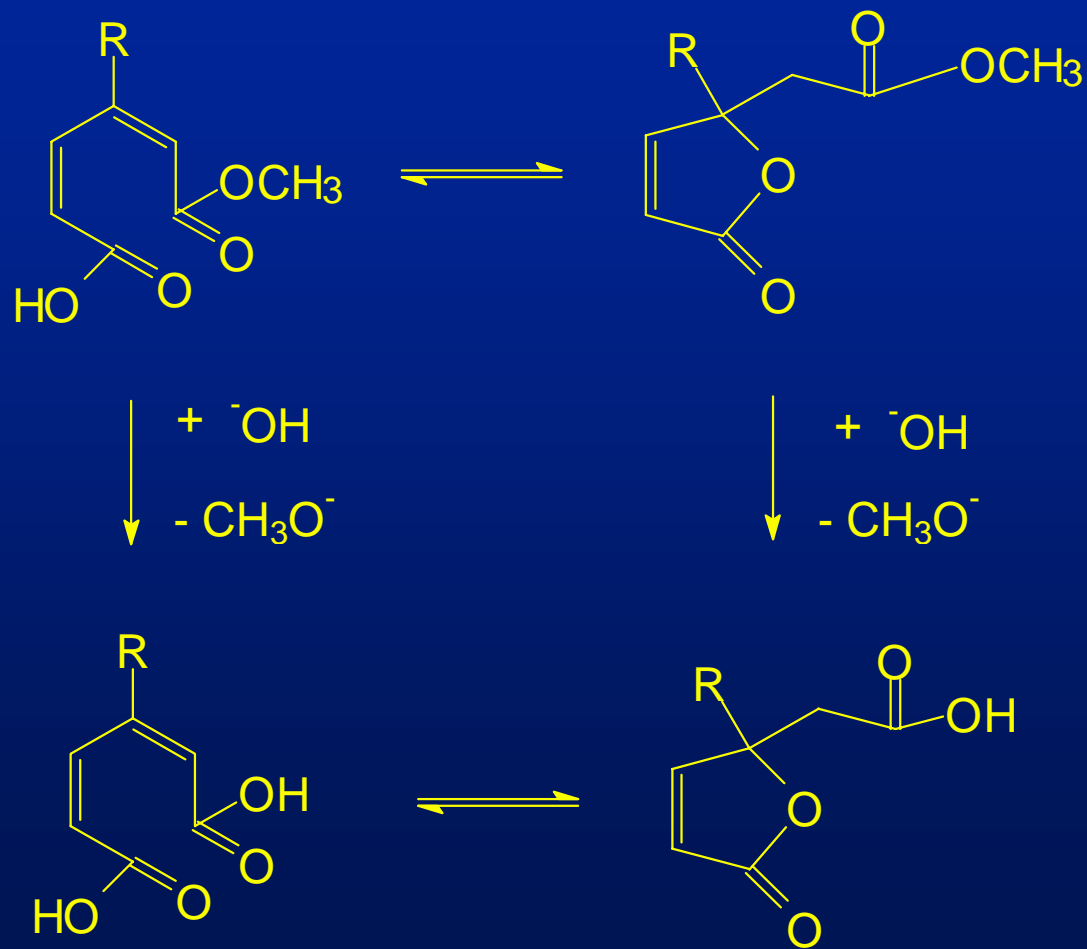
Phenolic & COOH Functional Group changes



Initial Investigation Results

- | COOH groups increase to approximately same level regardless if oxygen is present
- | Phenolic groups decrease only when oxygen is present
- | Implications:
 - COOH groups generation is predominantly by a NaOH reaction
 - Oxygen reactions with phenolic groups does not generate significant amounts of COOH groups

Saponification of the methyl ester group in muconic acid methyl ester



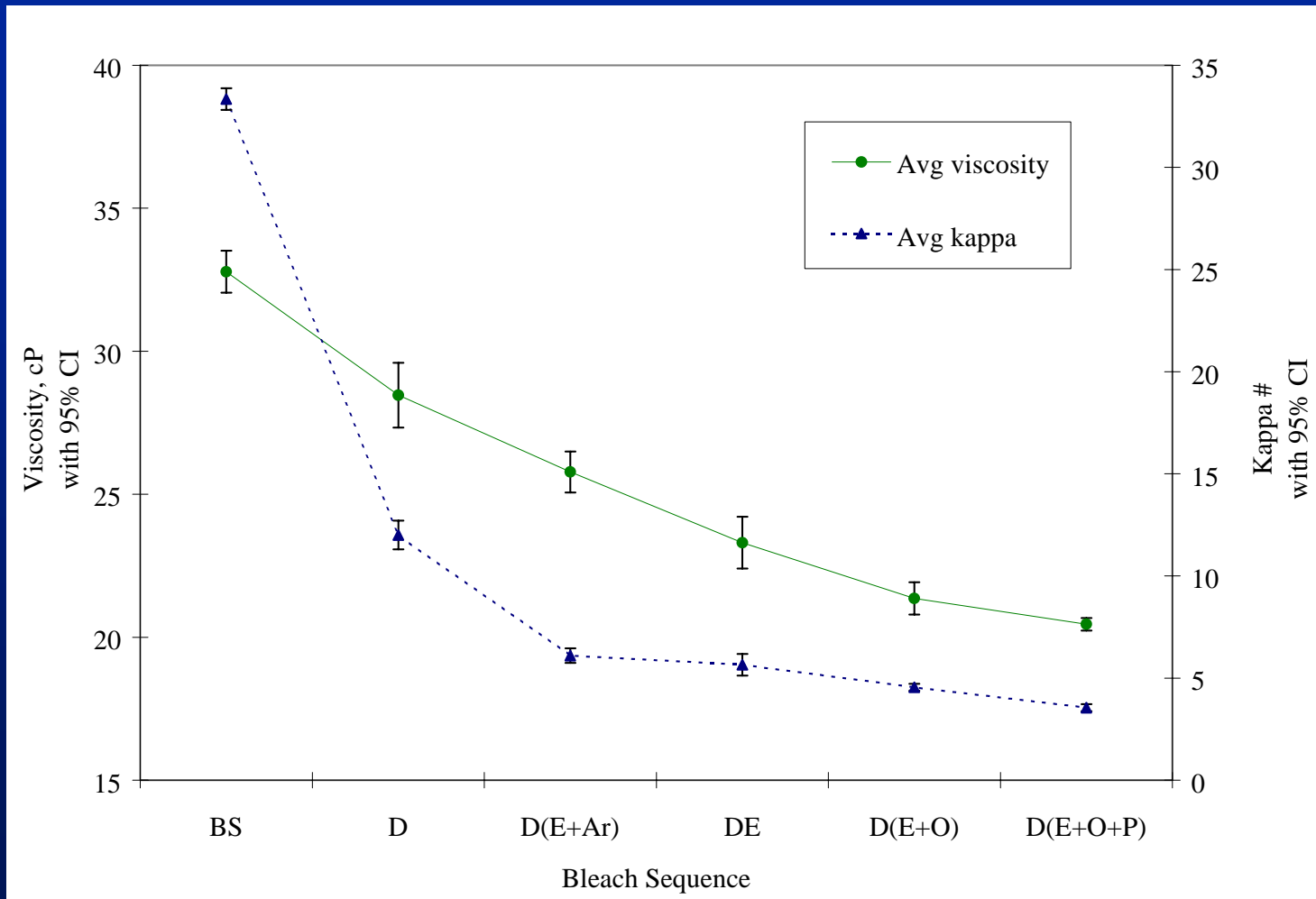
Repeat Study using Pulp

- | Study was repeated using pulp instead of isolated lignin
- | Perform bleach sequences, isolated lignin using acid hydrolysis procedure
- | D stage on 30 kappa SW pulp from a conventional cook.
- | D stage
 - Lignin from a 28 kappa SW conventional BS pulp
 - D stage at 10% solids, 0.20 KF, 45 °C, 45 minutes, and an initial pH of 2.5

Repeated Study - cont.


- | E stages done at 70 °C for 60 minutes with 45% TAC NaOH charge
 - E+Ar - frozen/thawed done under Ar
 - E
 - E+O
 - » Oxygen at 60 psi (-10 psi/5 min.)
 - » Extra 0.5% NaOH charge
 - E+O+P
 - » oxygen at 60 psi (-10 psi/5 min.)
 - » hydrogen peroxide at 0.5%
 - » Extra 0.5% NaOH charge

Pulp Kappa # and Viscosities

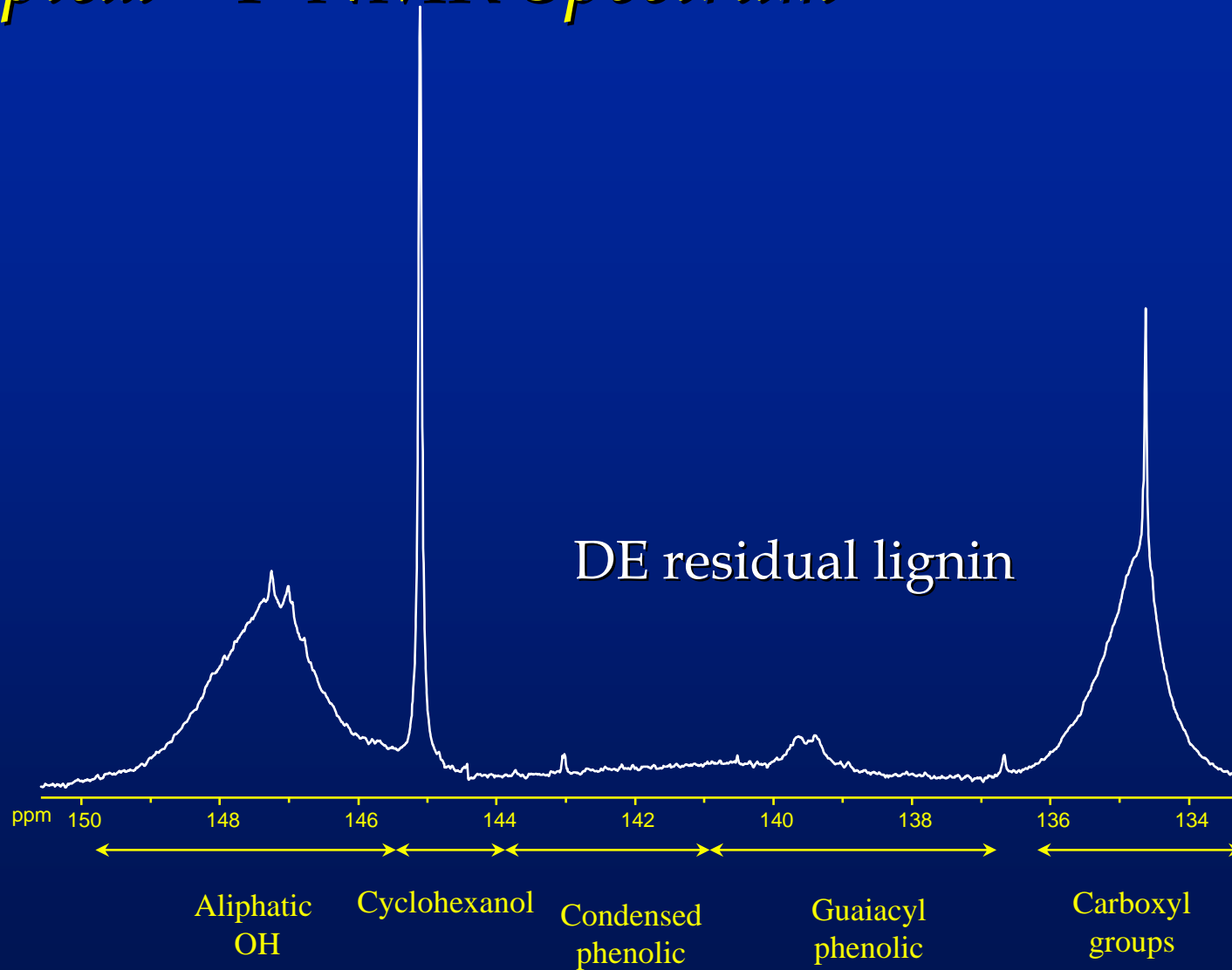




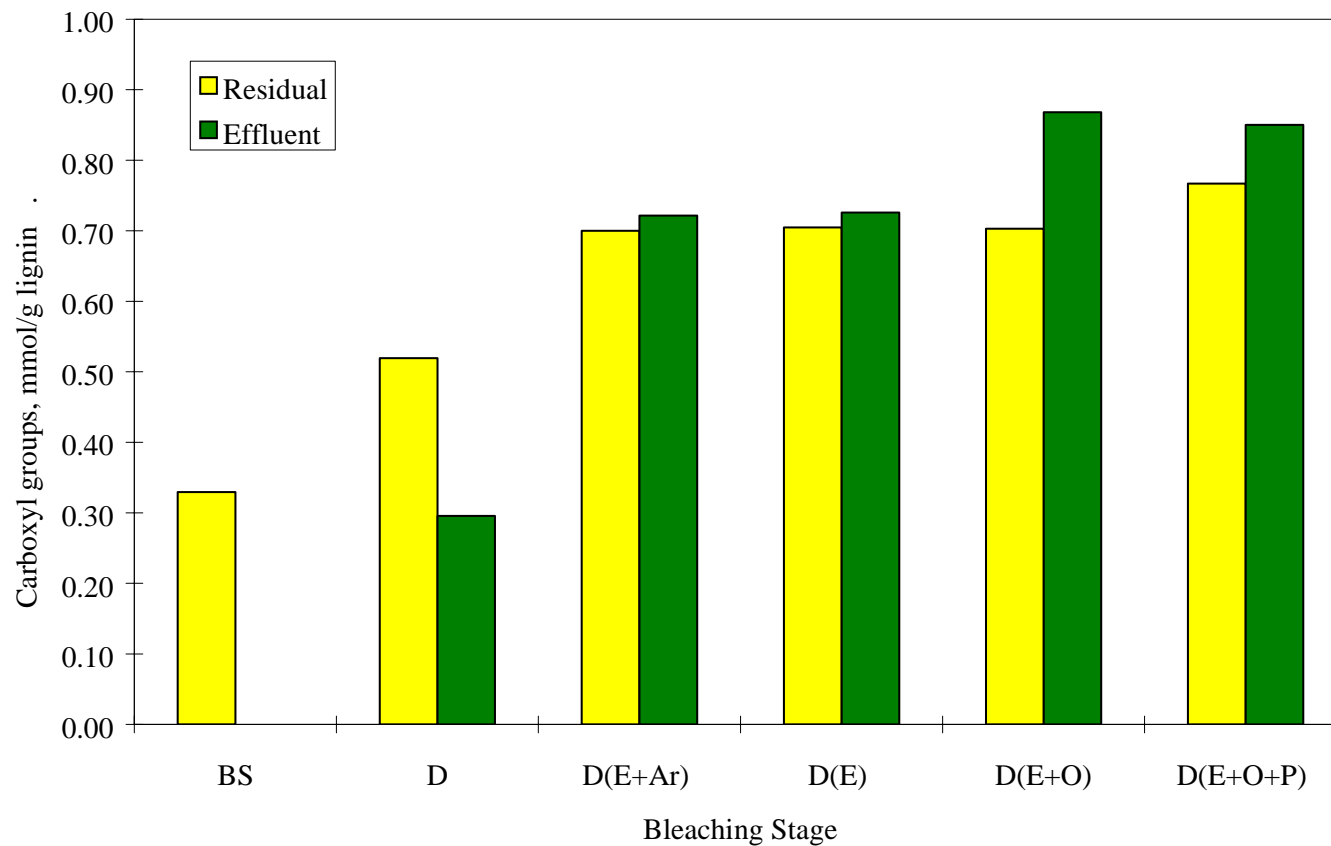
Functional Group Analysis

- | Residual lignins were isolated using acid hydrolysis procedure
 - | Effluent lignins were dialyzed, concentrated, submitted to a mild acid hydrolysis, and freeze dried.
 - | ^{31}P NMR analysis was performed on lignins
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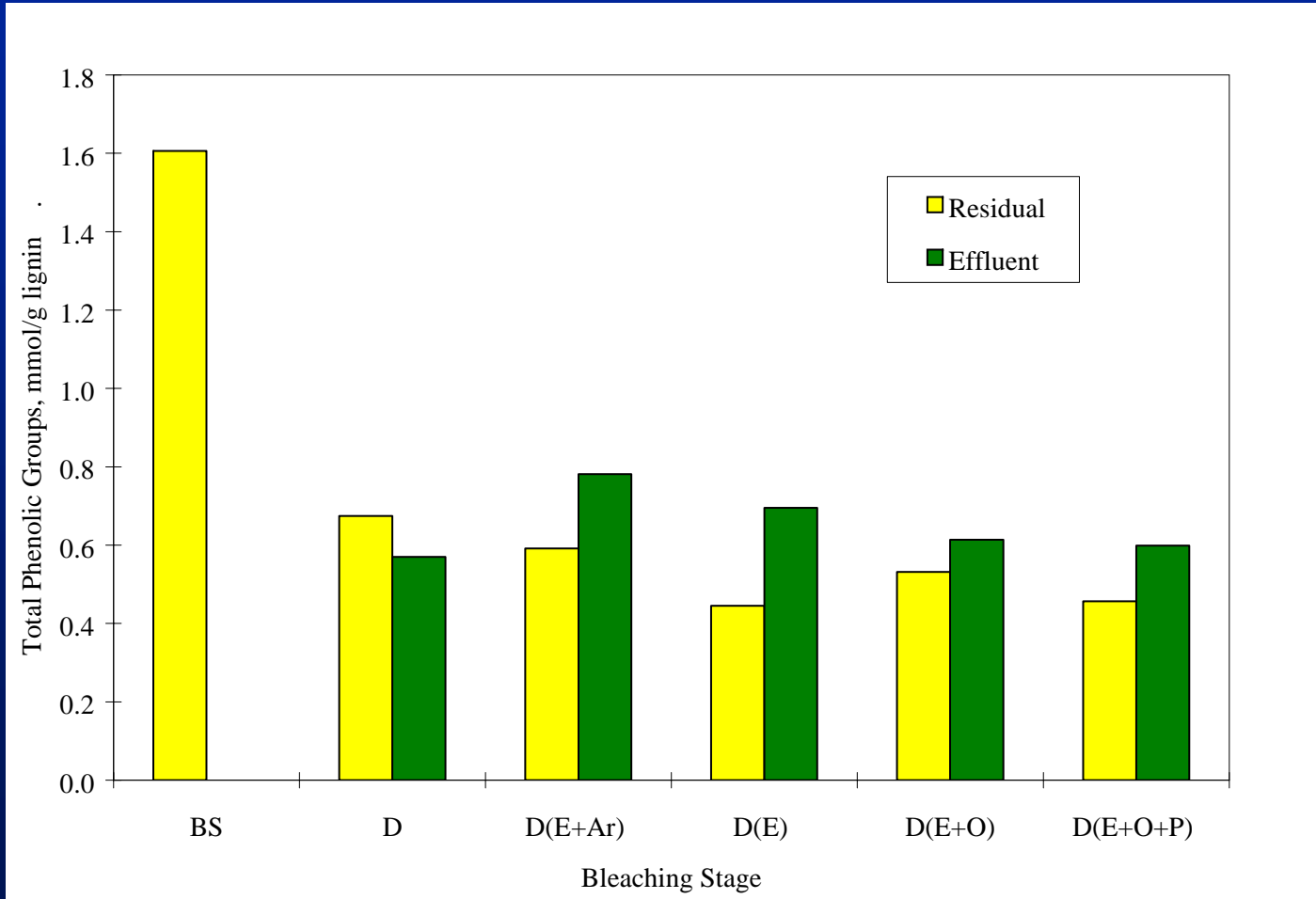
Typical ^{31}P NMR Spectrum




COOH Groups of Residual and Effluent Lignin



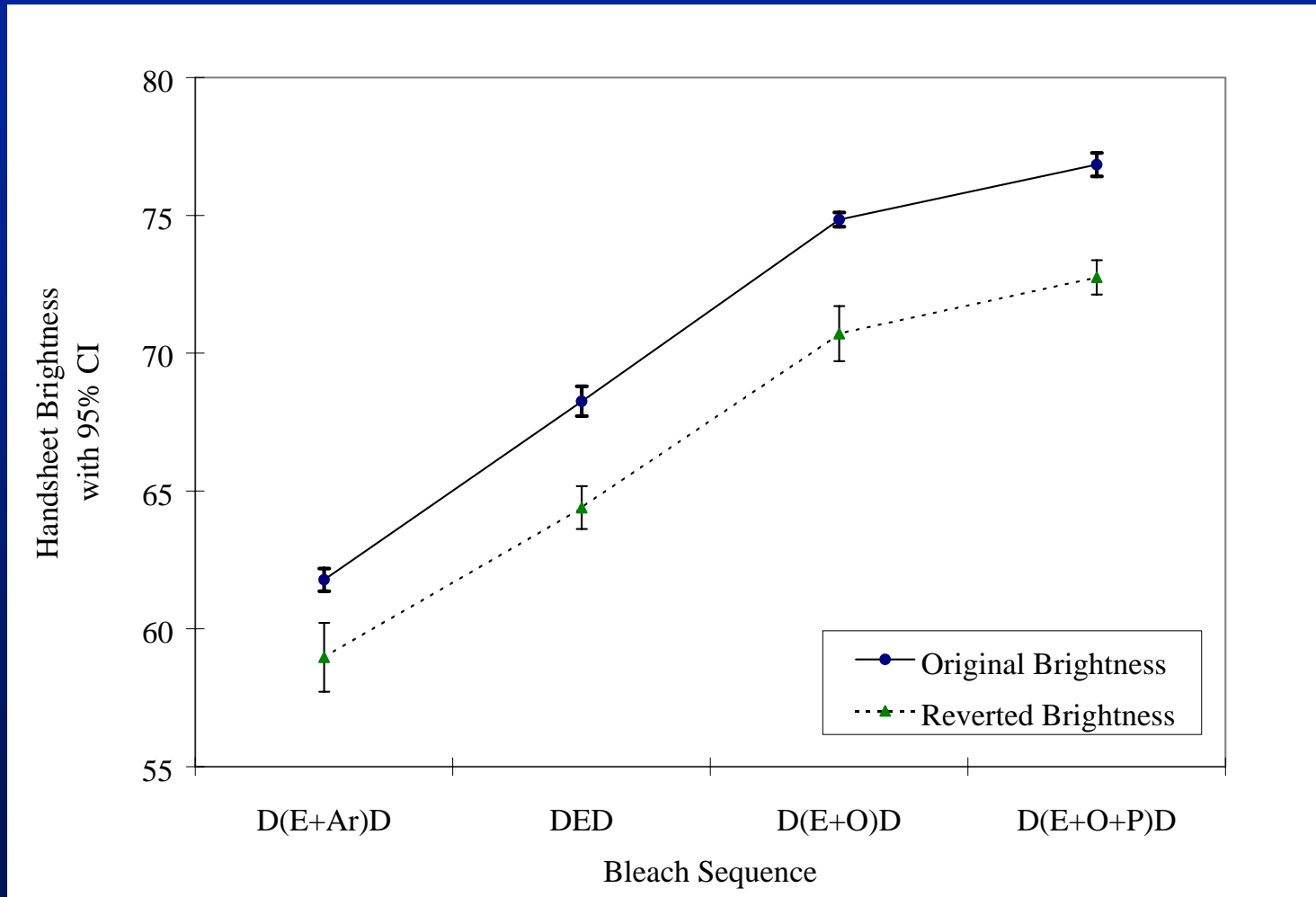
Total Phenolic Groups of Residual and Effluent Lignin



Results from 2nd Study

- | COOH groups saw similar increases as initial study
 - | Extra oxidant did give a modest increase in COOH groups
 - | Phenolic groups decreased but not to the same extent
 - | Oxidant reinforcement gave on a slight decrease in phenolic groups
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Pulp Handsheet ISO Brightness




Investigate various D stage conditions

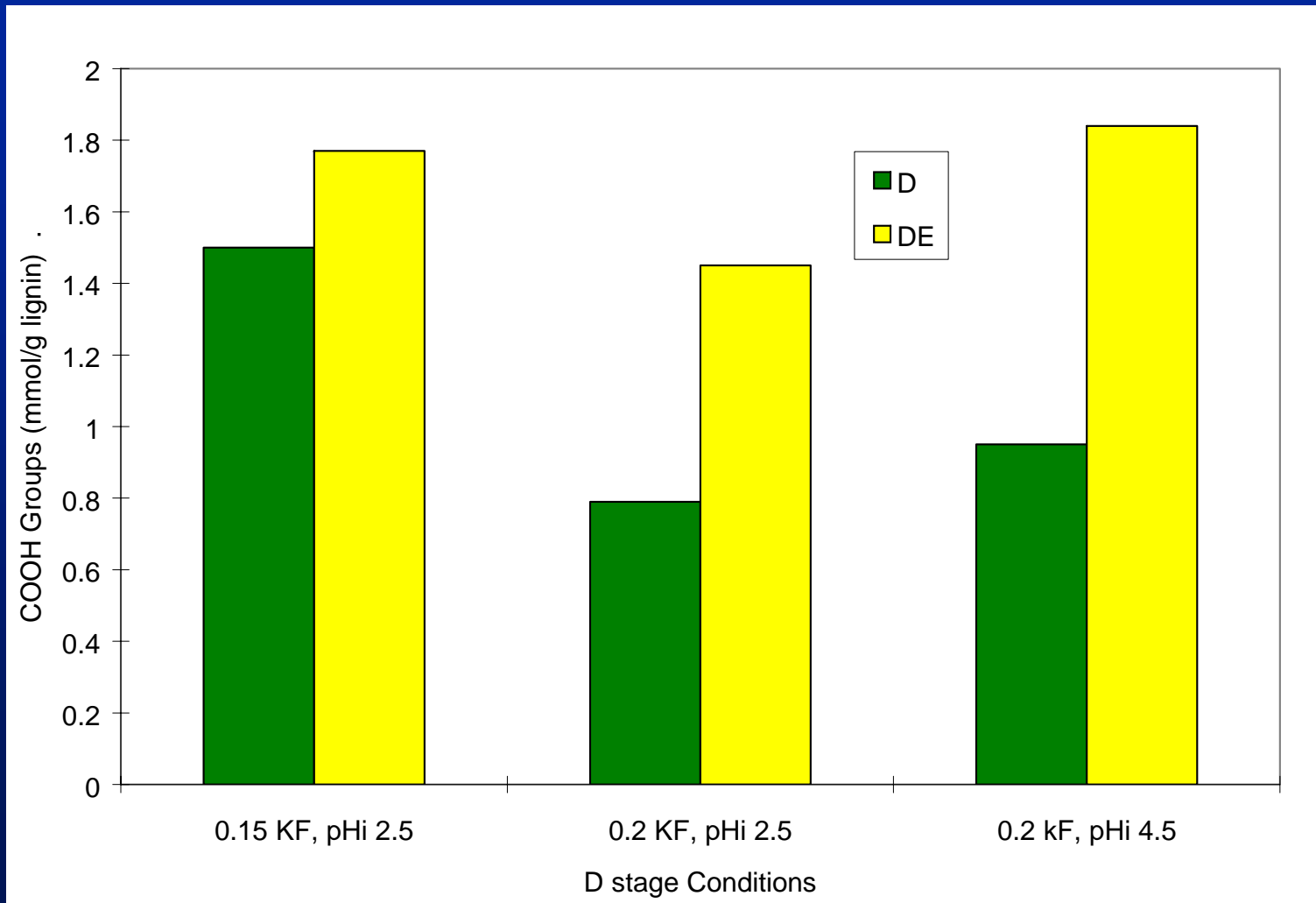
- | The difference in phenolic group consumption in the E stage between the two studies was hypothesized to be due to vary severities in the initial D stage
- | Second study D stage's lignin had a lower phenolic content
- | Invesitgate with 3 various D conditions
 - pH initial 4.5, KF of 0.20
 - pH initial 4.5, KF of 0.20
 - pH initial 4.5, KF of 0.20



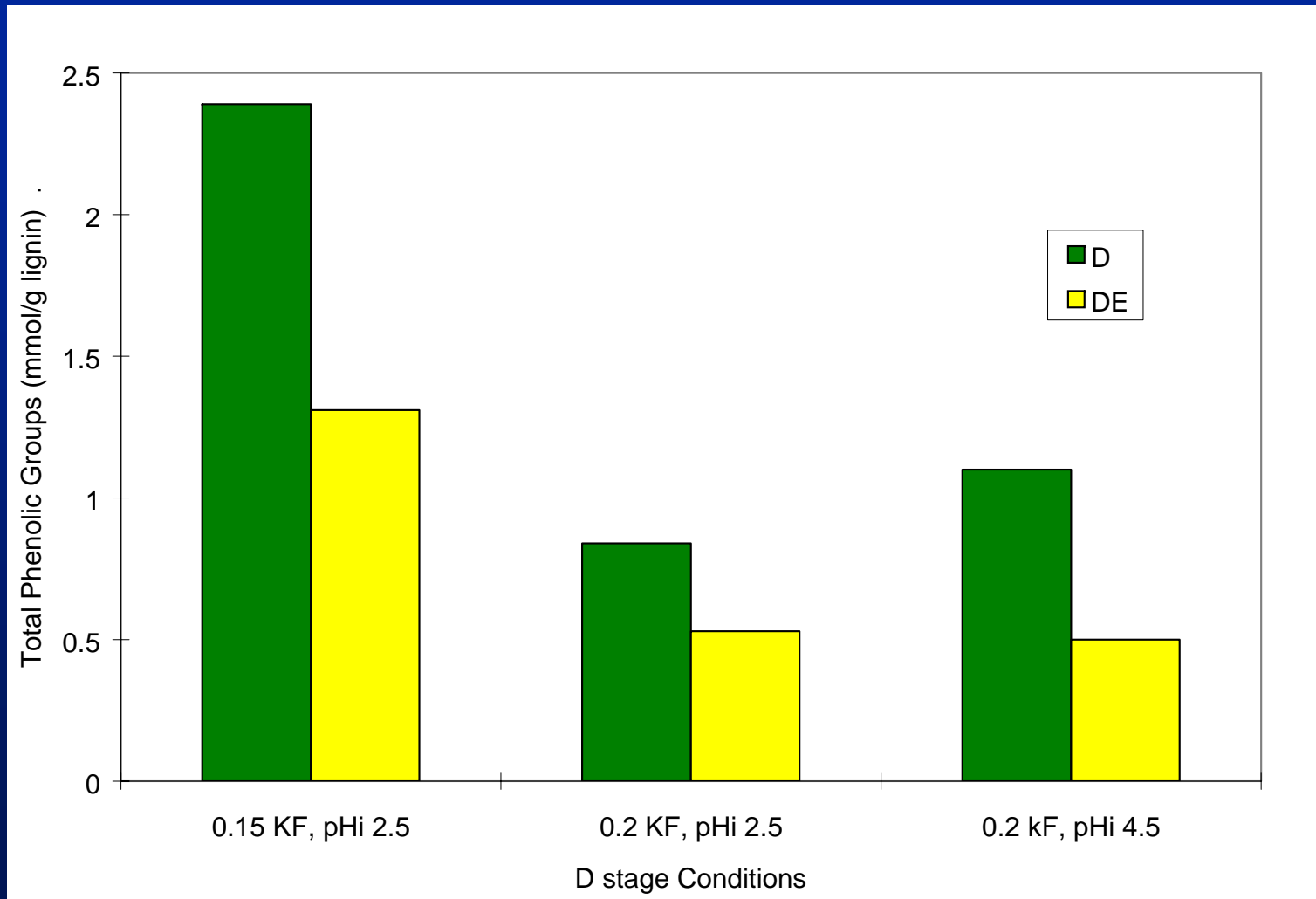
D condition study conditions

- | D stages were performed at 45 °C for 45 minutes
 - | E stage were performed at 45% TAC at 70 °C for 75 minutes
 - | Residual lignins were isolated using acid hydrolysis
 - | ¹H NMR was used to measure COOH and phenolic groups
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D stage Effect on COOH Groups




D Stage Conditions Effect on Phenolic Groups





D condition study results

- | Kappa factor decrease (0.20 to 0.15)
 - Increased COOH group primarily by increasing the amount left in the D residual
 - Significantly increased D stage phenolic allowing for a greater decrease in the subsequent E stage
 - | Initial pH decrease (4.5 to 2.5)
 - Increased COOH group in D and E stage
 - Increased phenolic in D stage resulting in a greater decrease in following E stage
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Conclusions

- | Base saponification of muconic acid methyl ester structures generated in the D stage is a significant E stage reaction
- | Significant depletion of phenolic groups can occur with atmospheric oxygen pressure
- | E stage oxidants reinforcement reactions with residual D stage lignin phenolic groups appears to be dependent on the amount left.

