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
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.
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
$^{13}$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
$^{13}$C NMR Spectra around the E stage

- Saturated carbonyl
- Conjugated carbonyl
- Aromatic OCH$_3$
- Aromatic and Olefinic C
- Aliphatic C-O
- Muconic acid
- OCH$_3$
- DE effluent lignin
- DE residual lignin
- D residual lignin
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
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 $^1$H NMR spectroscopy
Phenolic & COOH Functional Group changes

![Graph showing changes in COOH and Total Phenolic functional groups across bleaching stages (D, DE, DE w/o O2).]
**Initial Investigation Results**

- COOH groups increase to approximately the 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 do 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

![Graph showing the relationship between bleach sequence and viscosity/kappa number. The graph displays the average viscosity and kappa number with 95% confidence intervals. The x-axis represents the bleach sequence, and the y-axis shows viscosity and kappa number.]
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.
Typical $^{31}$P NMR Spectrum

DE residual lignin

- Aliphatic OH
- Cyclohexanol
- Condensed phenolic
- Guaiacyl phenolic
- Carboxyl groups
COOH Groups of Residual and Effluent Lignin

Carboxyl groups, mmol/g lignin

Bleaching Stage

- BS
- D
- D(E+Ar)
- D(E)
- D(E+O)
- D(E+O+P)

Residual
Effluent
Total Phenolic Groups of Residual and Effluent Lignin

![Graph showing total phenolic groups at various bleaching stages](image)
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
Pulp Handsheet ISO Brightness

Handsheet Brightness with 95% CI

D(E+Ar)D  DED  D(E+O)D  D(E+O+P)D

Bleach Sequence

Original Brightness

Reverted 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
- Investigate 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 conditions 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
- $^1$H NMR was used to measure COOH and phenolic groups
D stage Effect on COOH Groups

![Bar chart showing the effect of different D stage conditions on COOH groups. The x-axis represents D stage Conditions, and the y-axis represents COOH Groups (mmol/g lignin). The conditions are 0.15 KF, pH 2.5, 0.2 KF, pH 2.5, and 0.2 KF, pH 4.5. The chart uses green and yellow bars to represent different data sets.](chart.png)
D Stage Conditions Effect on Phenolic Groups

![Graph showing the effect of D stage conditions on total phenolic groups (mmol/g lignin). The x-axis represents different D stage conditions: 0.15 KF, pH 2.5; 0.2 KF, pH 2.5; 0.2 KF, pH 4.5. The y-axis represents the total phenolic groups in mmol/g lignin. The graph shows that the highest total phenolic groups are in 0.15 KF, pH 2.5, followed by 0.2 KF, pH 2.5, and the lowest in 0.2 KF, pH 4.5.]

- 0.15 KF, pH 2.5: Green bar represents D groups, Yellow bar represents DE groups.
- 0.2 KF, pH 2.5: Green bar represents D groups, Yellow bar represents DE groups.
- 0.2 KF, pH 4.5: Green bar represents D groups, Yellow bar represents DE 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
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.