

# Comparisons of Oxidant Reinforcements in Alkaline Extraction of ClO<sub>2</sub> Delignified Pulp

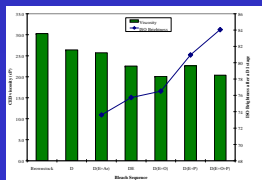
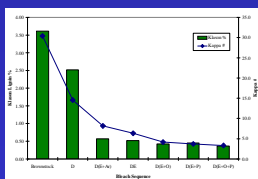
## Bleaching Response



- 30 Kappa Softwood pulp was delignified with a 0.20 kappa factor D stage.
- Alkaline Extractions were performed at 45% of total available chlorine in the D stage.
  - E+Ar - frozen/thawed done under Ar.
  - E
  - E+O
    - Oxygen at 60 psi (-10 psi/5 min.).
    - Extra 0.5% NaOH charge.
- E+P
  - Hydrogen peroxide at 0.5%.
  - 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.



- Kappa # and Klason lignin determinations were performed to measure the amount of residual lignin left.
- Results show a decrease in the residual lignin through use of oxidant reinforcement.



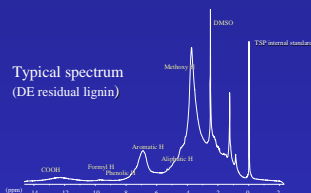
- Viscosity measurements show a slight decrease with added oxidant (especially oxygen).
- Brightness measurements were taken after a D<sub>1</sub> brightening stage (at a 0.75% charge).
- Brightness increased with added oxidants. Hydrogen peroxide increased brightness more than oxygen.



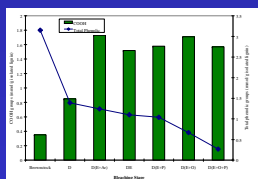
## NMR Results



- A Bruker Avance DMX 400 MHz machine was used
- <sup>1</sup>H NMR spectra were obtained on undervitized lignin

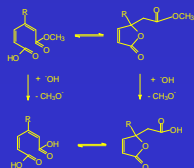


Typical spectrum (DE residual lignin)



- Phenolics were depleted in the alkaline extraction stage only when oxygen was present (atmospheric or pressurized).
- Carboxylic acid groups increased to approximately the same level regardless of the presence of an oxidant.

### Saponification of the methyl ester group in muonic acid methyl ester

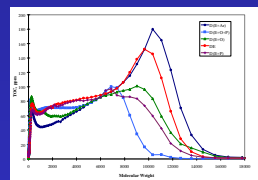


- Hypothesized conclusions
  - The increase in carboxylic acid groups is due primarily to the saponification of muonic acid methyl ester created in the previous D stage.
  - Oxygen and hydrogen peroxide oxidation reactions do not create significant amounts of carboxylic acid structures.

## Effluent MW Distribution

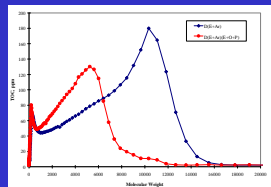
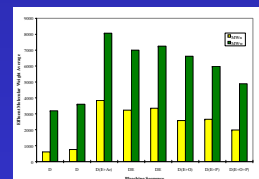


- Uses 2 sephadex packed LC columns and 0.1 N LiCl as eluent.
- 5 ml of prepared effluent travel through column according to size.
- Column exit stream is measured by a total organic carbon (TOC) detector.
- Molecular weights (MW) calculated from calibration standards of PEG and methanol.



- The TOC of various alkaline extraction effluents was plotted (as an indicator of amount of lignin) against calculated MW to create a MW profile.
- The profiles show increased oxidant in the alkaline extraction shifts the profile to lower molecular weights.

- The MW profiles were used to calculate a number average (MW<sub>n</sub>) and a weighted average (MW<sub>w</sub>). The plotted averages demonstrate the a significant decrease in MW occurs with oxidant reinforcement.
- It was hypothesized that the extra oxidant was reacting with lignin already free of the fiber.

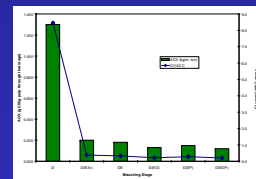


- It was desired to test if it was possible to degrade lignin that was already extracted with NaOH.
- Effluent from the E+Ar stage was reacted with oxygen and peroxide in NaOH in amounts equal to an E+O+P stage. The MW distribution shows a clear decrease strengthening the initial hypothesis.

## Environmental Impact

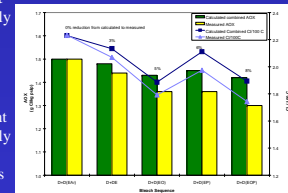


- Adsorbable Organic Halide (AOX) was used to compare advantages of oxidant reinforcement in relation to environmental impact.
- AOX measurements were normalized using a Total Organic Carbon (TOC) measurement. The normalized measurement was expressed as Cl atoms/100 C atoms.



- Effluent samples were collected immediately after the bleaching stage and acidified to pH 2.0 with nitric acid.
- D and E stage effluent samples were also combined based on an equal pulp weight basis and acidified.
- The samples were stored frozen until AOX and TOC measurements were performed.

- AOX and Cl/100 C measurements show slight decreases in the organically bound chlorine in the effluent from the oxidant reinforcement.
- The combined stages demonstrated further slight decreases in the organically bound chlorine when oxidant reinforcement was used.



- The calculated combined AOX or Cl/100 C is based on the sum of the two stages. The difference between the calculated and measured value shows any further degradation due to the combination of the stages.
- Further AOX decrease can be expected if a lower ClO<sub>2</sub> charge is used in the first stage to offset the amount of delignification done by the oxygen or hydrogen peroxide reinforcement.

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