



# **EFFECT OF HYDROGEN PEROXIDE BLEACHING ON FIBER CHARGE OF SOFTWOOD KRAFT PULPS**

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## Introduction

- Fiber charge influences the WRV, the wet fiber flexibility, the fiber-fiber bonding, and the physical properties of resultant paper sheet
- Carboxylic group is the only acid groups providing charged site during papermaking process
- Kraft cooking changes the chemical structure of wood compositions
- $\text{H}_2\text{O}_2$  bleaching is mainly used to degrade chromophoric components in pulps



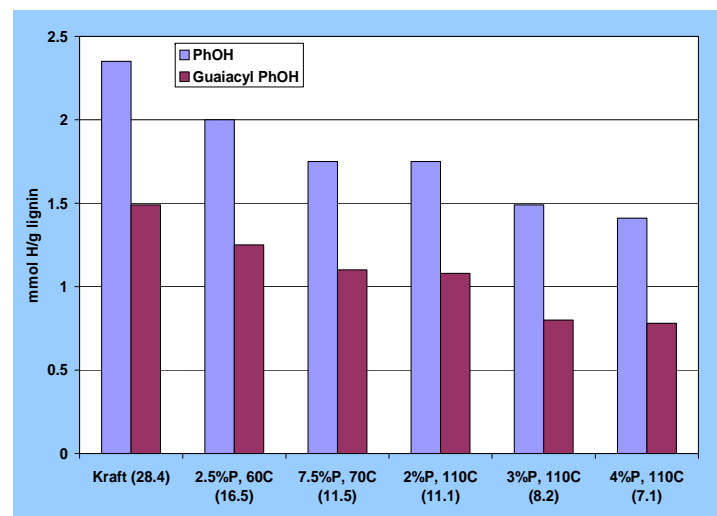
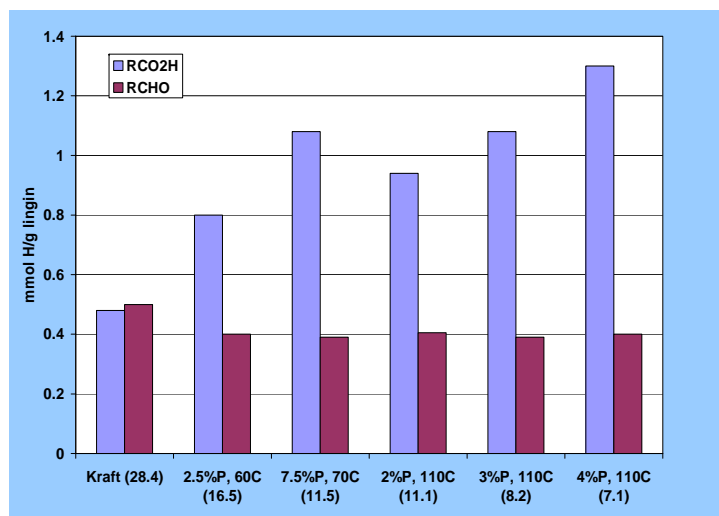
## n Objectives

- Explore the bleaching chemistry of hydrogen peroxide
- Develop a comprehensive kinetic study including kappa number, intrinsic viscosity, and carboxylic acid content on fibers during peroxide bleaching
- Develop a process of  $\text{ClO}_2$  bleaching followed by peroxide bleaching which leads to the best results regarding final kappa number, final intrinsic viscosity, and fiber charge
- Develop the relationship between the carboxylic acid content and physical strength properties of the paper sheet
- Investigate the effect of kraft cooking conditions on the following peroxide bleaching



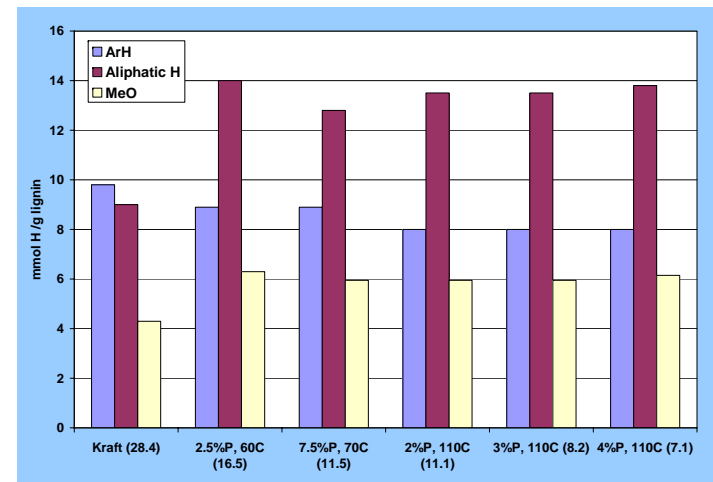
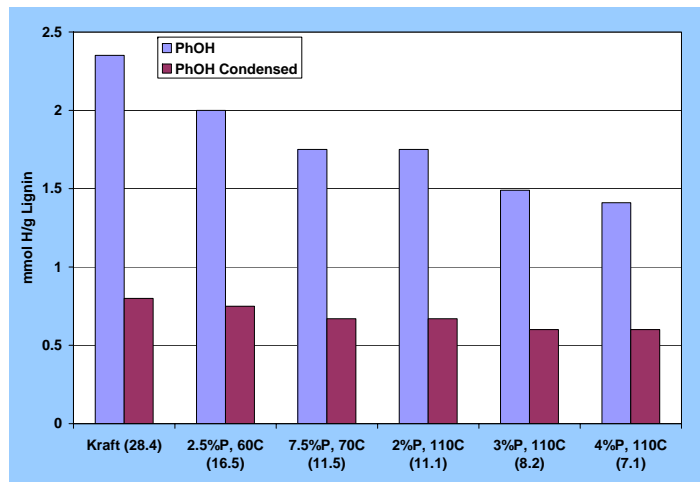
## – Bleaching chemistry (continued)

- $^1\text{H}$  NMR results of residual lignins isolated from brown stock and peroxide bleached pulps
  - Formyl (RCHO) and acid content (RCO<sub>2</sub>H) of residual lignins
  - Total phenoxy content (PhOH) and guaiacyl content of residual lignins



## – Bleaching chemistry (continued)

- $^1\text{H}$  NMR results of residual lignins isolated from brown stock and peroxide bleached pulps (continued)
  - Phenoxy content (PhOH) and condensed phenolic content of residual lignins
  - Aromatic, aliphatic, and methoxy group of residual lignins





– Preliminary tests of peroxide bleaching on fully bleached ECF kraft pulp

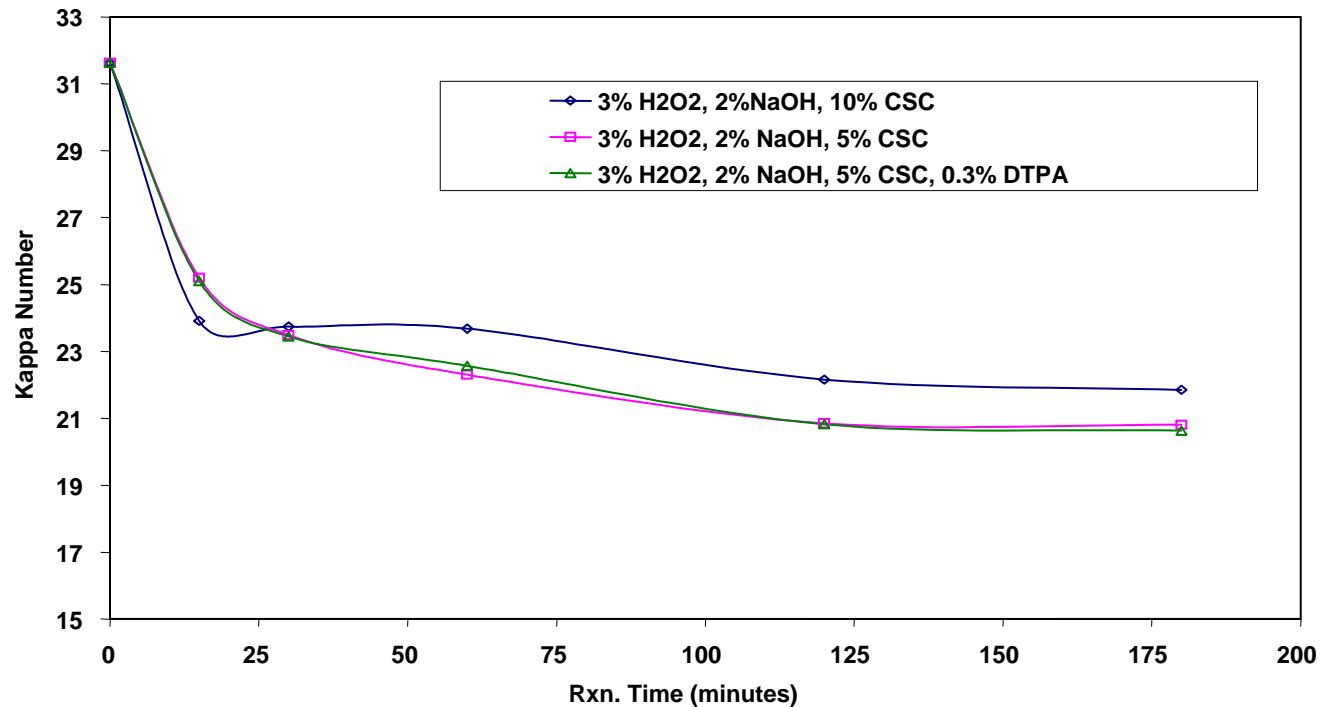
- Condition: 1% H<sub>2</sub>O<sub>2</sub>, 2% NaOH, 80°C, 1 hr, and 10% consistency

Conditions of H <sub>2</sub> O <sub>2</sub> Bleaching	Carboxylic Acid Content (meq./100g O.D. pulp)	Consumed H <sub>2</sub> O <sub>2</sub> (%)	Freeness (mL)	Tensile Index (Nm/g)	Tear Index (mNm <sup>2</sup> /g)
Original (fully bleached pulp)	3.70	~	694	15.0	11.6
H <sub>2</sub> O <sub>2</sub> bleaching without MgSO <sub>4</sub>	4.54	99.5	689	16.2	13.0
H <sub>2</sub> O <sub>2</sub> bleaching with 0.5% MgSO <sub>4</sub>	4.60	98.7	684	16.5	13.5

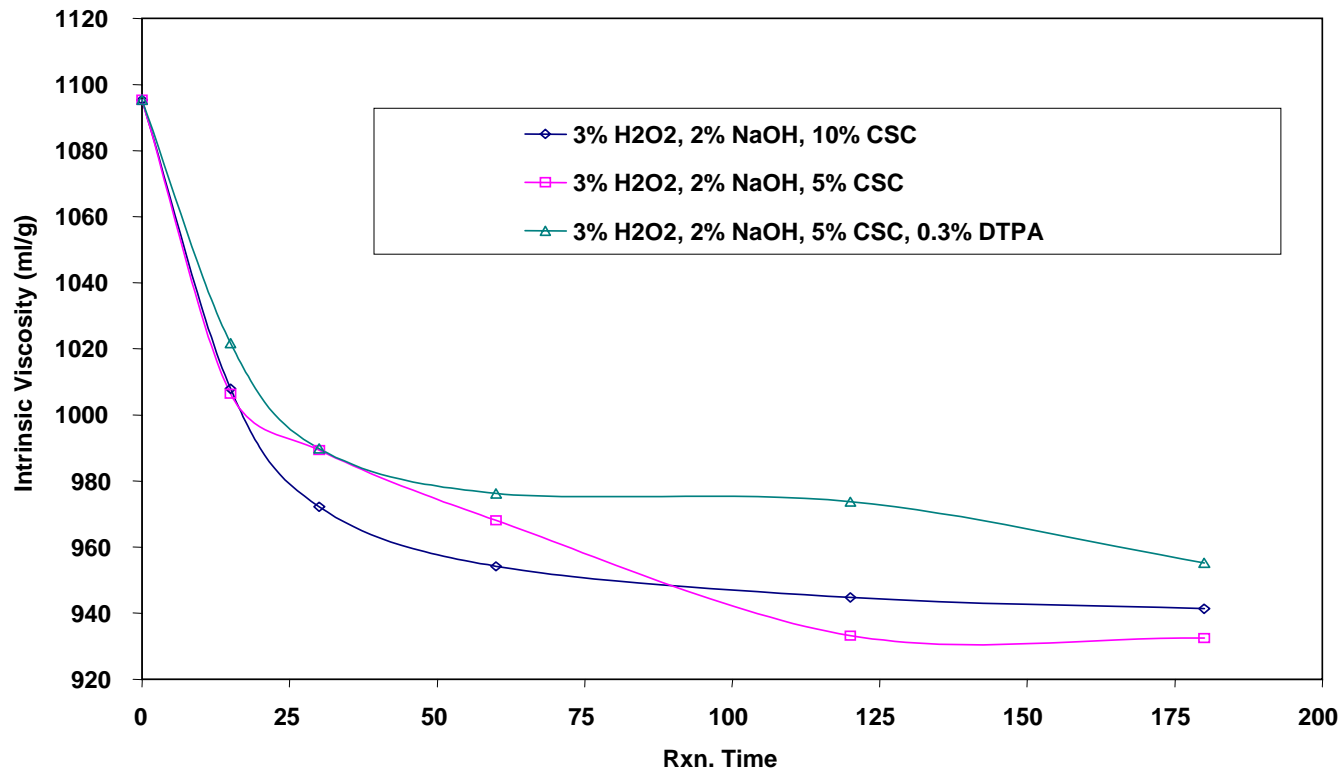


– Kinetics study of peroxide bleaching on softwood kraft pulp

- Kappa number variation during peroxide bleaching on brown stock (initial kappa number 31.26 )

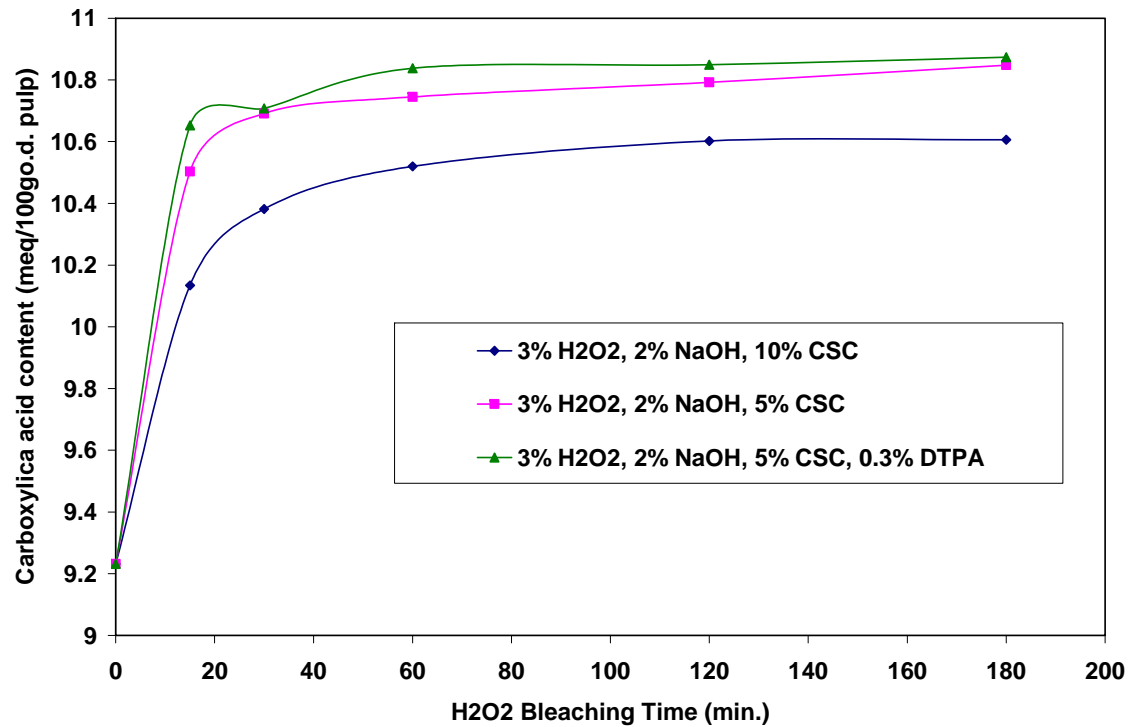


- Kinetics study of peroxide bleaching on softwood kraft pulp (continued)
  - Intrinsic viscosity variation during peroxide bleaching on brown stock (Initial intrinsic viscosity 1095.34 mL/g)



– Kinetics study of peroxide bleaching on softwood kraft pulp (continued)

- Carboxylic acid group content variation during peroxide bleaching on brown stock (Initial RCOOH 9.232 meq/100 g o.d. pulp)



## – Experimental matrix of peroxide bleaching

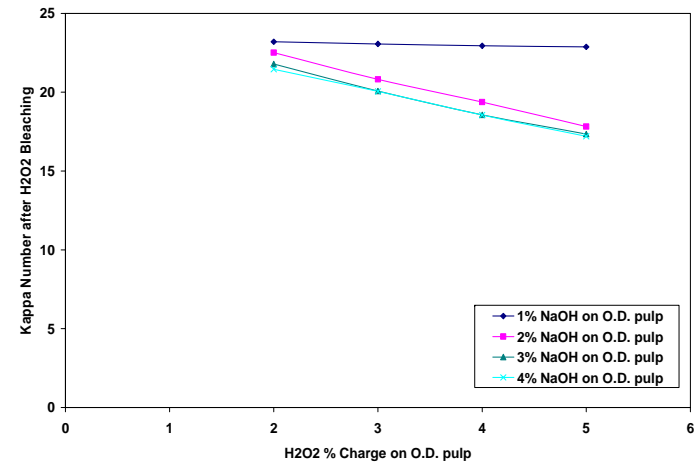
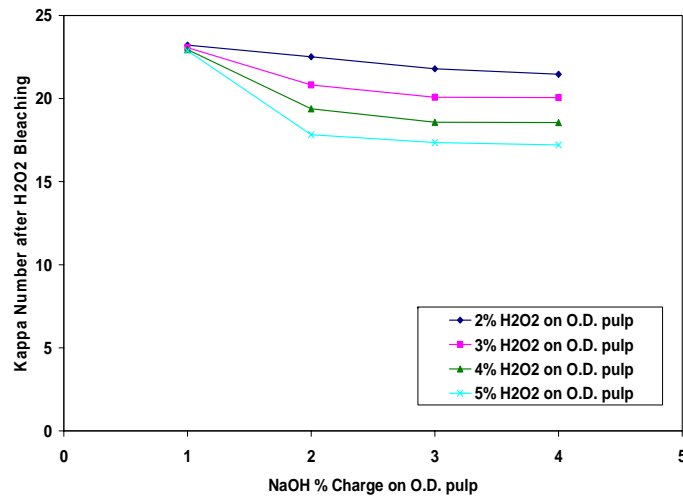
Condition :

H<sub>2</sub>O<sub>2</sub> charge 2%, 3%, 4%, and 5%

NaOH charge 1%, 2%, 3%, and 4%

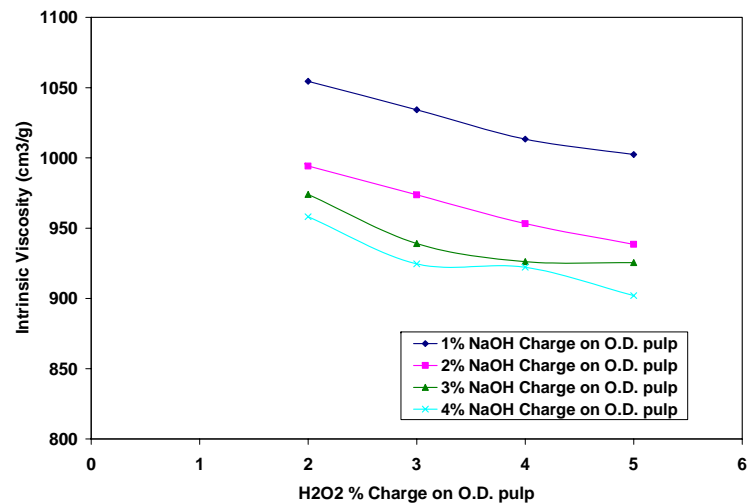
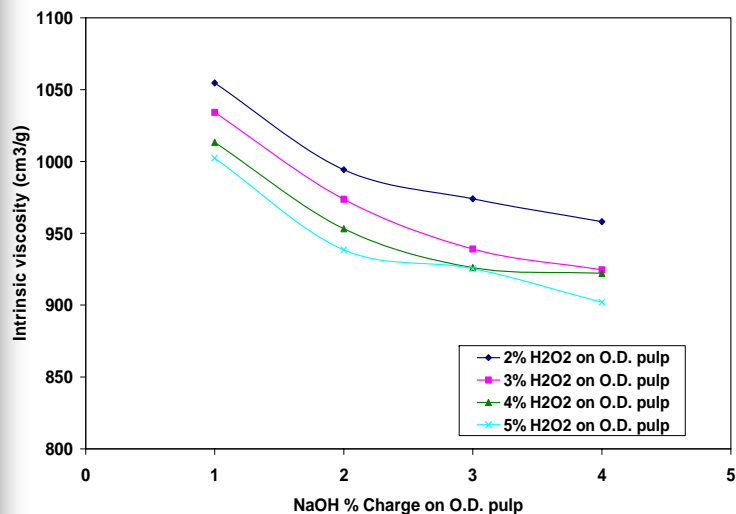
120 min, 60°C, 0.3% DTPA

- Comparison of the results for kappa number



– Experimental matrix of peroxide bleaching

- Comparison of the results for intrinsic viscosity





– Peroxide bleaching on DE pulp

- Conditions of preparing DE pulp
  - D<sub>1</sub>, 0.3% ClO<sub>2</sub>; E<sub>1</sub>, 0.4% NaOH; D<sub>2</sub>, 0.5% ClO<sub>2</sub>; E<sub>2</sub>, 0.6% NaOH
- Peroxide bleaching on DE pulp
  - 2% NaOH; 2%, 3%, 4%, 5% H<sub>2</sub>O<sub>2</sub>; 60°C, 120 min.

H <sub>2</sub> O <sub>2</sub> % on O.D. pulp	NaOH % on O.D. pulp	Kappa Number	Intrinsic Viscosity (mL/g)	Carboxylic acid content of pulp (meq./100g O.D. pulp)
2	2	13.75	1047.68	10.906
3	2	13.71	1042.52	11.105
4	2	13.68	1014.52	11.133
5	2	13.45	1011.74	11.249

## – Carbohydrate analysis by HAPEC

- Summary of results

Sample I.D.	Mass fractions of polysaccharides (%)					Kappa number	Intrinsic Viscosity (mL/g)	Carboxylic acid content of pulp (meq./100g O.D. pulp)
	Glucan	Xylan	Arabinan	Galactan	Mannan			
Brown stock	77.05%	8.65%	0.74%	0.45%	6.00%	31.62	1095.34	9.232
Peroxide bleaching <sup>1</sup> @ 15 min	80.44%	8.90%	0.75%	0.42%	6.18%	25.10	1021.71	10.653
Peroxide bleaching <sup>1</sup> @ 30 min	81.04%	8.95%	0.74%	0.42%	6.22%	23.45	989.78	10.708
Peroxide bleaching <sup>1</sup> @ 60 min	81.12%	8.97%	0.75%	0.41%	6.21%	22.57	976.22	10.838
Peroxide bleaching <sup>1</sup> @ 120 min	81.59%	8.96%	0.74%	0.40%	6.17%	20.82	973.74	10.849
Peroxide bleaching <sup>1</sup> @ 180 min	81.48%	8.96%	0.74%	0.40%	6.05%	20.63	955.20	10.874
DE <sup>2</sup> pulp	77.66%	8.60%	0.68%	0.42%	5.91%	19.44	1092.64	10.742
Peroxide bleaching <sup>3</sup> on DE pulp	79.34%	8.49%	0.67%	0.38%	6.04%	13.75	1047.68	10.906
Peroxide bleaching <sup>4</sup> on DE pulp	80.09%	8.71%	0.68%	0.38%	6.09%	13.71	1042.12	11.105
Peroxide bleaching <sup>5</sup> on DE pulp	80.97%	8.67%	0.69%	0.39%	5.99%	13.68	1014.52	11.133
Peroxide bleaching <sup>6</sup> on DE pulp	80.80%	8.64%	0.69%	0.38%	6.01%	13.45	1011.74	11.249

<sup>1</sup> 3% H<sub>2</sub>O<sub>2</sub>, 2% NaOH, 0.3% DTPA, 5% Consistency

<sup>2</sup> D1, 0.3% ClO<sub>2</sub>; E1, 0.4% NaOH; D2, 0.5% ClO<sub>2</sub>; E2, 0.6% NaOH

<sup>3</sup> 2% H<sub>2</sub>O<sub>2</sub>, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes

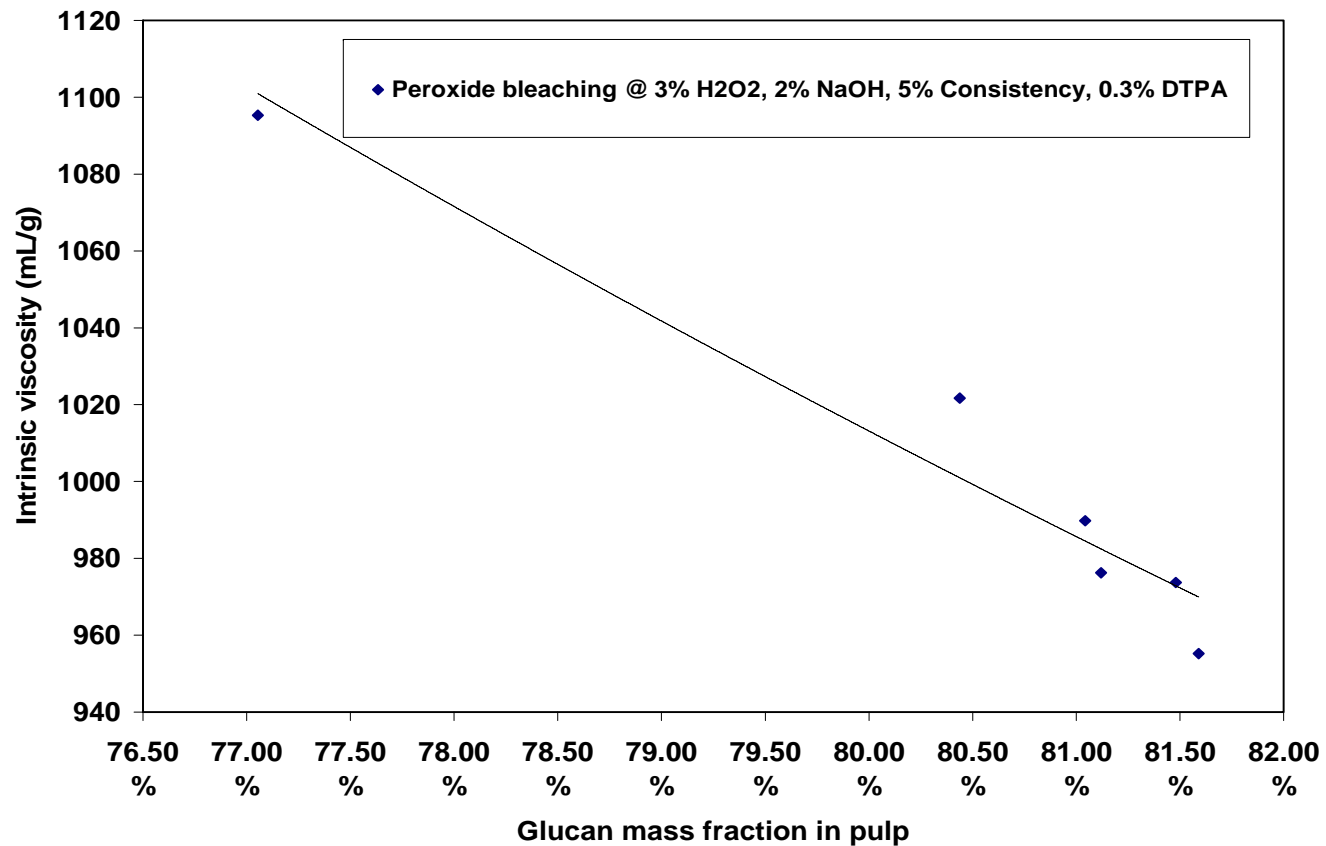
<sup>4</sup> 3% H<sub>2</sub>O<sub>2</sub>, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes

<sup>5</sup> 4% H<sub>2</sub>O<sub>2</sub>, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes

<sup>6</sup> 5% H<sub>2</sub>O<sub>2</sub>, 2% NaOH, 0.3% DTPA, 5% Consistency, 120 minutes

– Carbohydrate analysis by HAPEC (Continued)

- Intrinsic viscosity versus glucan content of pulps undergoing peroxide bleaching







## n Conclusion

- The lignin remaining after a peroxide is becoming increasingly unreactive to hydrogen peroxide.
- Peroxide bleaching has the potential of enhancing fiber-fiber bonding by enhancing carboxylic acid group on fibers.
- pH value during P-stage has a significant effect on delignification.
- Higher temperature during P-stage leads to higher delignification and higher degradation of carbohydrate
- $\text{ClO}_2$  bleaching process also increases carboxylic acid group
- Cellulose content increases during a P-stage, but changes a bit after the DE process. Also cellulose degradation occurs at a faster rate than the increase in the cellulose content



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## Future work

- Develop the relationship between the carboxylic acid content and physical strength properties of the paper sheet.
- Investigate processes of  $\text{ClO}_2$  bleaching associated with peroxide bleaching including DEP, PDEP, and Enzymatic treatment with DEP.
- Investigate the effect of kraft cooking conditions on the following peroxide bleaching.

