

State of Knowledge of Oxygen Delignification

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Outline

- Background (history, technology, benefits)
- Chemistry of oxygen delignification
- Reactivity of residual lignin
- Delignification/cellulose degradation selectivity
- Increasing delignification while maintaining good pulp properties
- How to improve industrial oxygen delignification

Background of Oxygen Delignification

- **History**

- First described by Nikitin (1956)
- MgSO_4 reduces cellulose degradation (Robert, 1964)
- First mill installation in 1970 in South Africa

- **Technology**

- O_2 ~1 MPa, ~ 2% on pulp, NaOH ~ 2% on pulp, T 90-95°C
- Kappa reduction about 45-50% for one stage process (softwood)
- Kappa reduction about 35% for one stage process (Eucalyptus)
- Higher temperature for Eucalyptus O_2 delig. at 105 °C

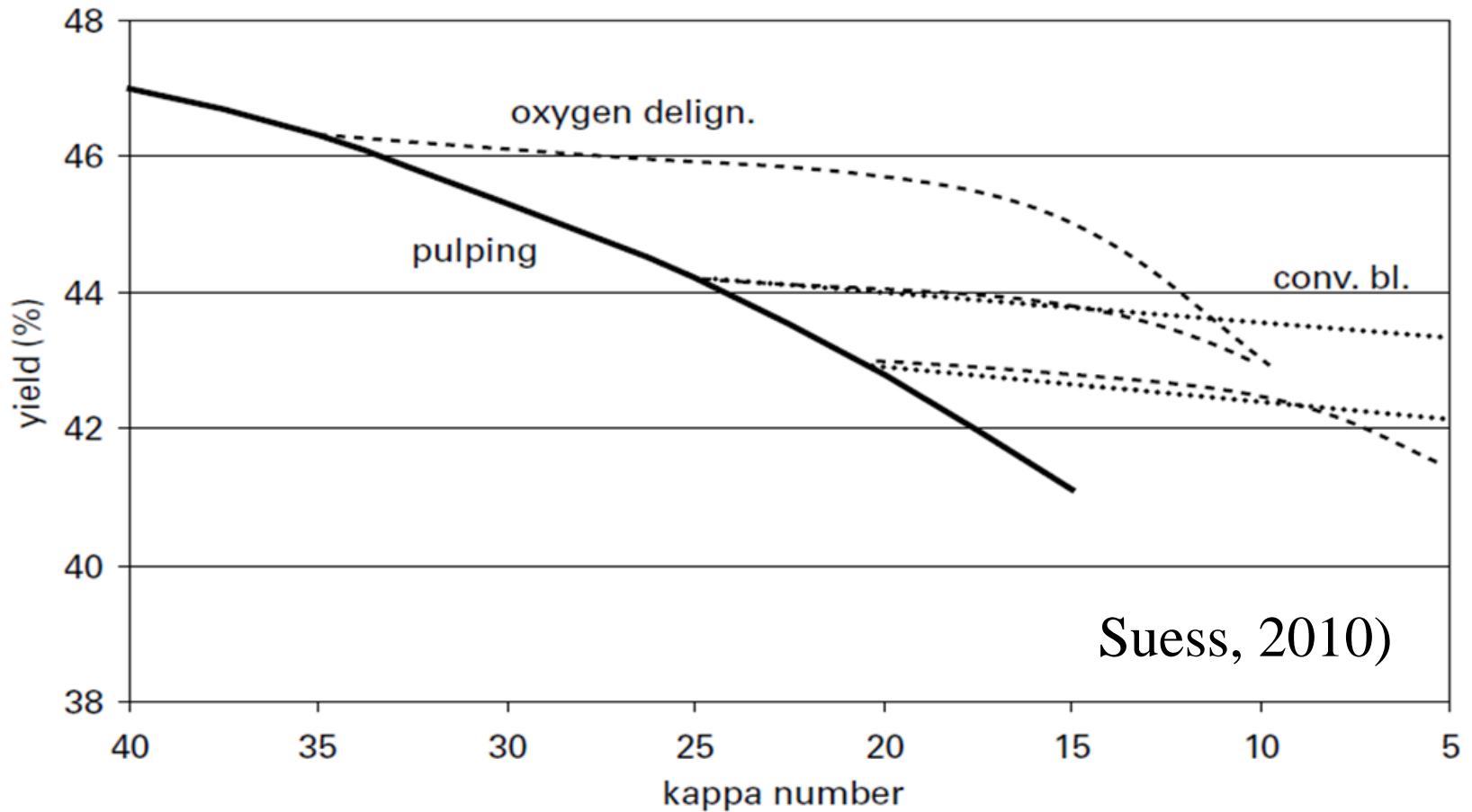
- **Benefits**

- Decreases consumption of bleaching chemicals
- Decreases dissolved organics in mill effluent

Delignification Limited by Mass Transfer of Oxygen

- In oxygen mixer less than 1% of charged O₂ dissolves
- Mixer purpose is to evenly distribute O₂ as small bubbles to avoid fast bubble rise and maximize bubble surface area
- Average bubble diameter of 60 μm in a softwood Kraft pulp suspension before tower (Mutikainen, 2014)
- Mass transfer analysis of industrial reactor system predicts 20% (relative) lower delignification than in laboratory (Rewatkar & Bennington, 2004; van Heiningen et al., 2003)

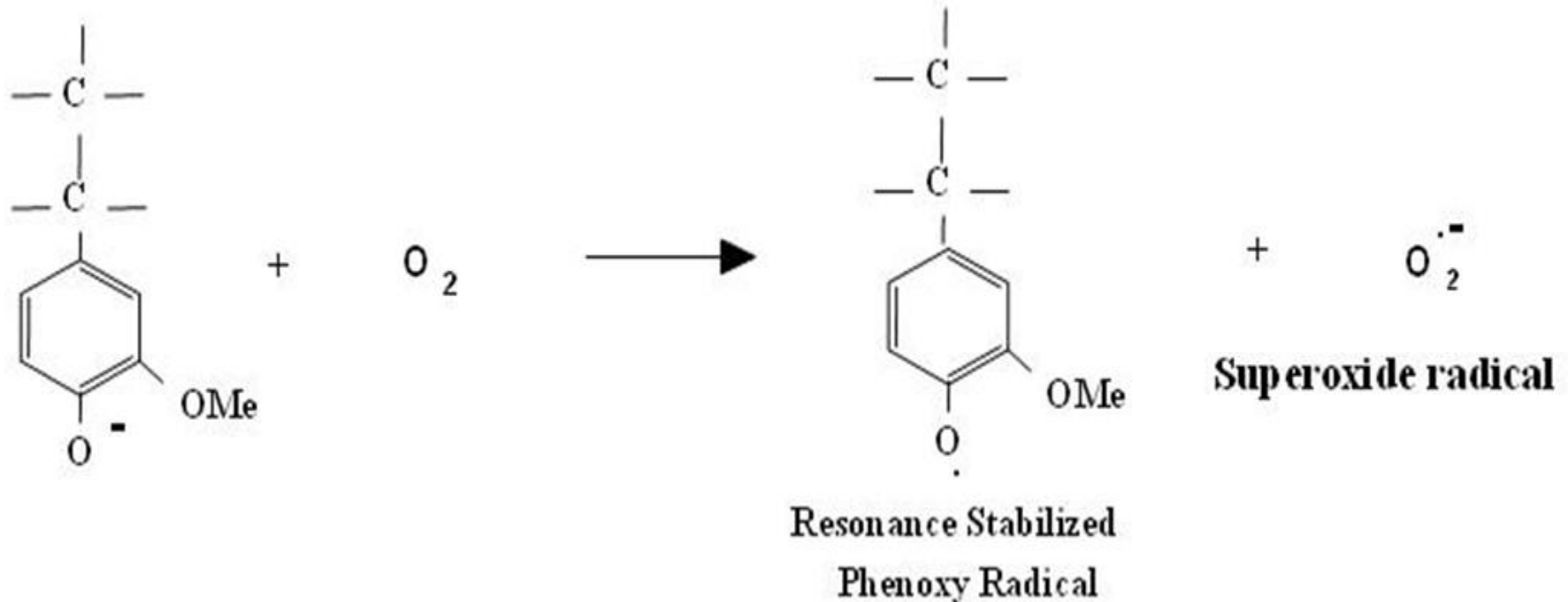
Softwood Pulp Yield Development



- Yield development same for O₂ delign. and ClO₂ bleaching
- Higher yield when starting at higher Kraft kappa number

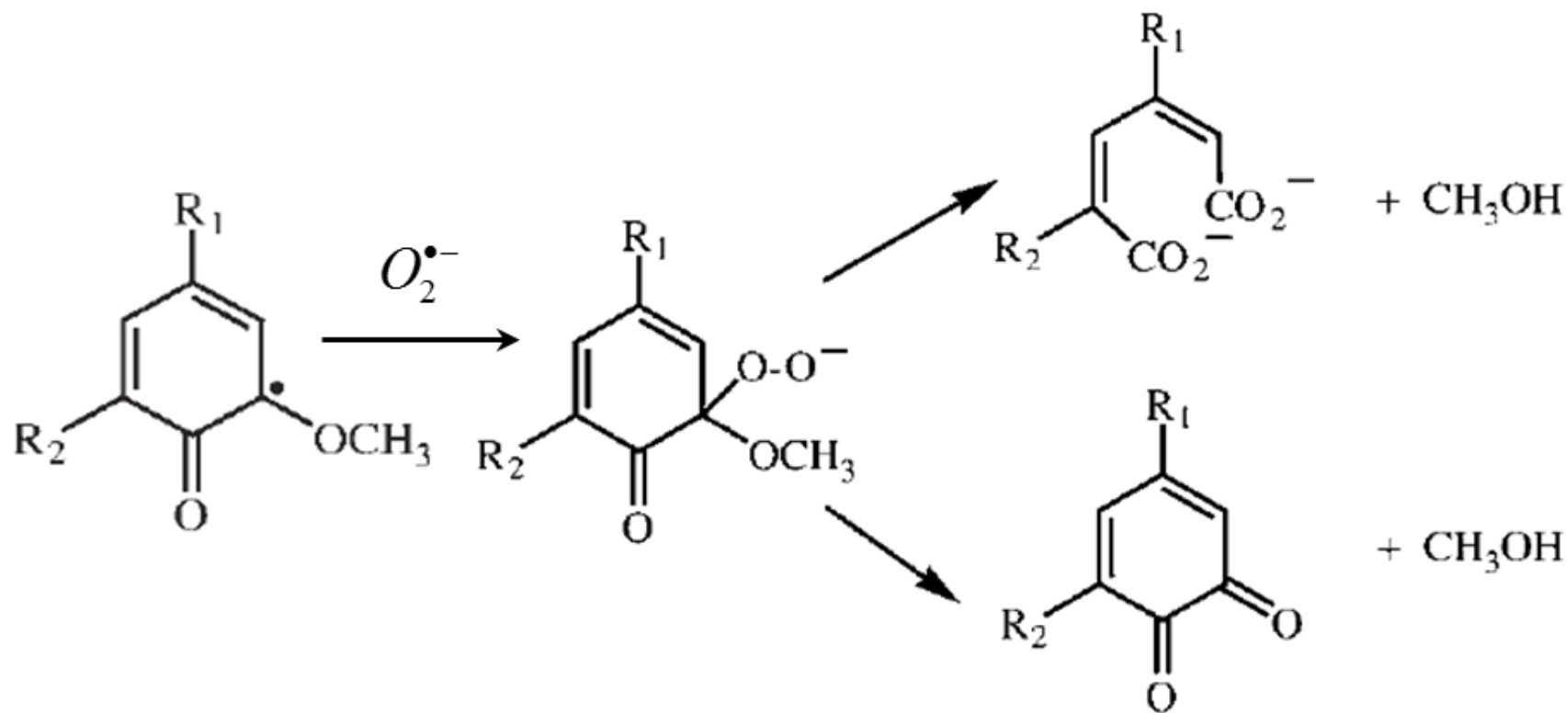
Chemistry of Oxygen Delignification

Initial Reaction of O₂ Delignification



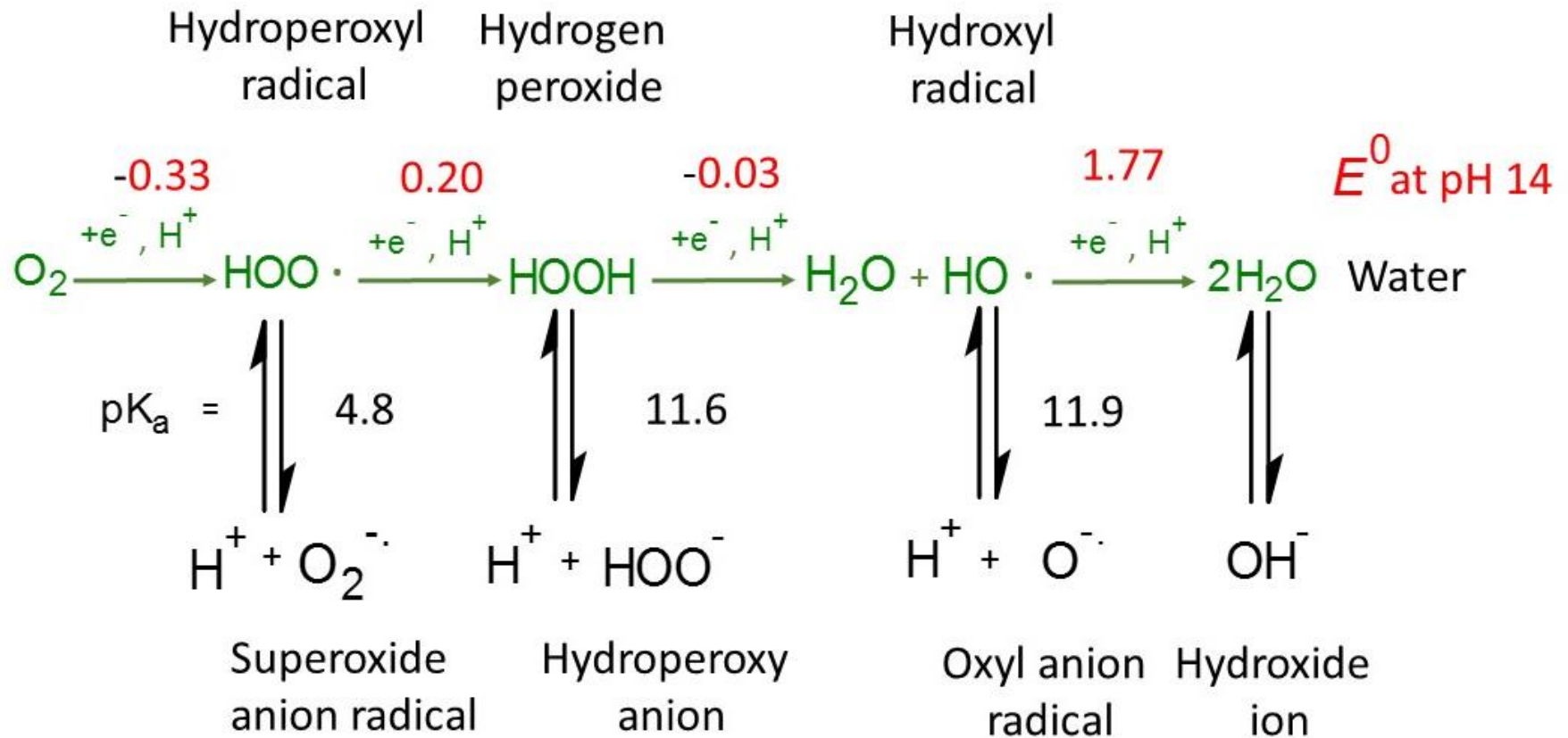
**Formation of phenoxy and superoxide radical
from dissociated phenolic lignin**

Formation of Quinone and Muconic Acid Structures from Hydroperoxide Intermediate



Ji (2009) and Kuitunen (2011)

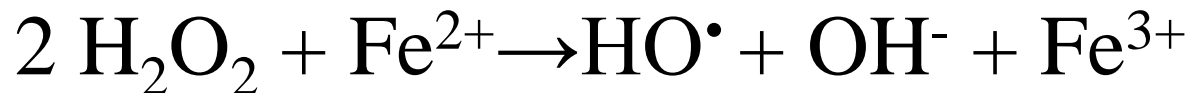
Stepwise Reduction of Oxygen to Water



H₂O₂ Conversion into Radicals by Transition Metals (Fenton Reaction)

Fe catalyzed redox reaction sequence:

Oxidation of Fe²⁺ to Fe³⁺



Reduction of Fe³⁺ to Fe²⁺



Cellulose Protection by MgSO_4

- 0.05-0.1% Mg^{2+} on pulp improves pulp viscosity
- Two, not mutually exclusive mechanisms proposed for reduced cellulose degradation
 1. Encapsulation of Mn^{2+} and Fe^{2+} ions within $\text{Mg}(\text{OH})_2$ precipitates to minimize Fenton reaction (Liden, 1997; Wiklund, 2001)
 2. Mg^{2+} ions form stable metal-carbohydrate complexes with carbonyl groups thereby reducing cellulose cleavage by β elimination at alkaline conditions (Bouchard, 2011). Coprecipitation of multivalent ions creates more sites available Mg complexation

Selectivity of Hydroxyl Radicals

HO•	Lignin Model Compounds	K_1	Veratrylglycol	$1.5 \cdot 10^{10}$
			Veratrylglycerol- β -guaiacyl ether	$1.7 \cdot 10^{10}$
	Carbohydrate Model Compounds	K_c	Me β -D-glucopyranoside	$3.2 \cdot 10^9$
			Me β -D-xylopyranoside	$2.6 \cdot 10^9$
				Rate Constant $M^{-1}s^{-1}$
Selectivity of HO• : $K_1 / K_c = 5 \sim 6$				

Therefore, the selectivity of $\cdot OH$ is rather low

Reactivity of Oxyl Radical, $O^{\cdot-}$

- Formed from OH^{\cdot} at $pH > 11.5$
- Strong nucleophile
- Abstracts hydrogen from carbohydrates as fast as it adds to aromatics
- Even more unselective as OH^{\cdot}
- Keep $pH < 12$ to avoid maximize selectivity

Reactivity of Superoxide Radical ($\text{O}_2^{\bullet-}$)

- Does not react with carbohydrates!
- Combines with lignin phenoxy radicals, which leads to ring opening and lignin solubilization
- Can diffuse some small distance before reaction
- However, superoxide may be converted into hydroxyl radical

Summary of Chemistry

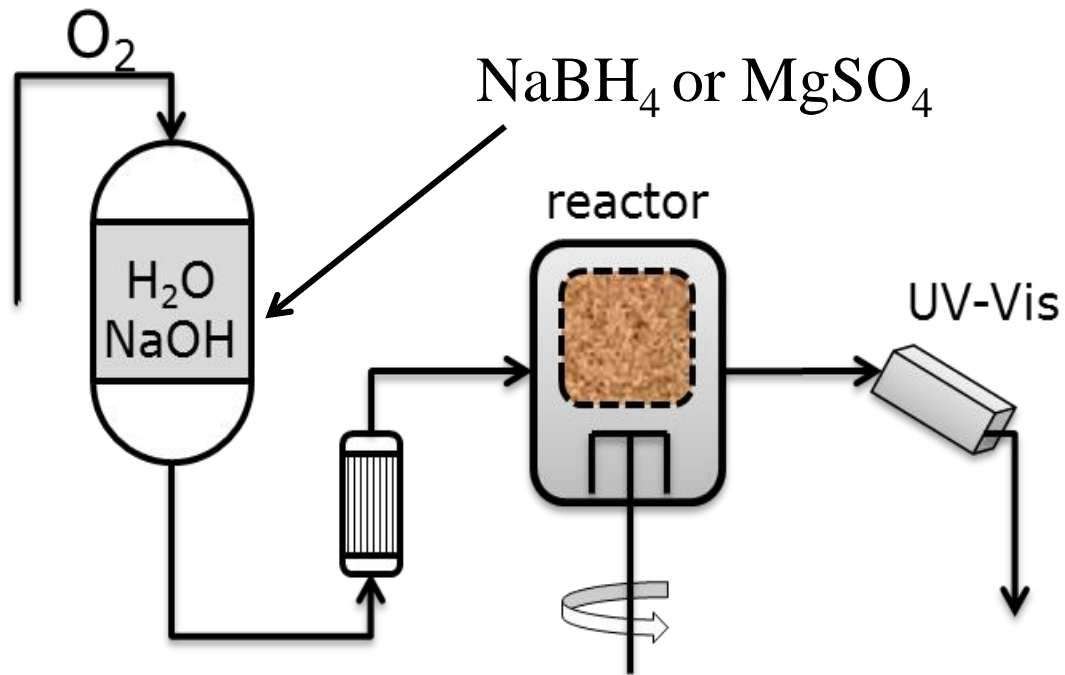
- Oxygen reacts with phenolate lignin anion; $\text{pH} > 10.5$
- Superoxide radical opens aromatic ring in lignin
- Superoxide radical do not react with cellulose
- Superoxide may be converted into hydroxyl radical and forms organic peroxides
- Hydroxyl radical cleaves cellulose but also β -O-4 linkages, creating phenolic lignin (Ohmura, 2012)
- Hydroxyl radicals react where they are created, whereas superoxide radicals are diffusible
- Oxyl radical is most unselective; $\text{pH} < 12$

Reactivity of Residual Lignin and Delignification Kinetics

Why low Reactivity of Residual Lignin at High Degree of O₂ Delignification?

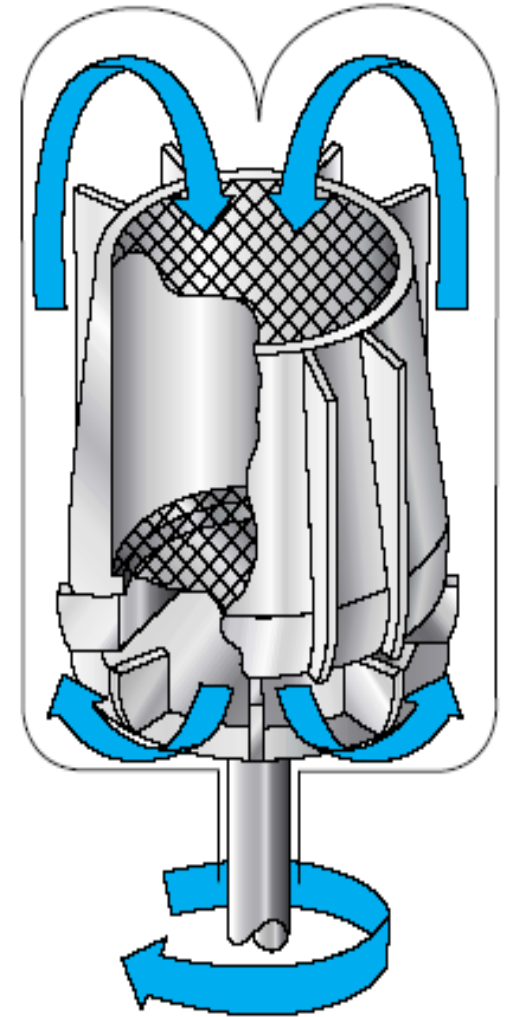
- Low reactivity not due to phenolic group depletion
- Phenolic fraction of 24.4 Kappa Southern Pine pulp decreases from 0.4 to 0.27 at 1 hr. to 0.22 after 3 hrs. (Ji., 2009)
- Accumulation of low reactivity phenolic lignin such as p-hydroxyphenyl and condensed phenolics (5,5 biphenyls and diphenyl methane) (Akim, 2001; Lai, 1994; Argyropoulos, 2003, Fu, 2003)

Measuring delignification Kinetics in Berty Flow-Through Reactor (CSTR)

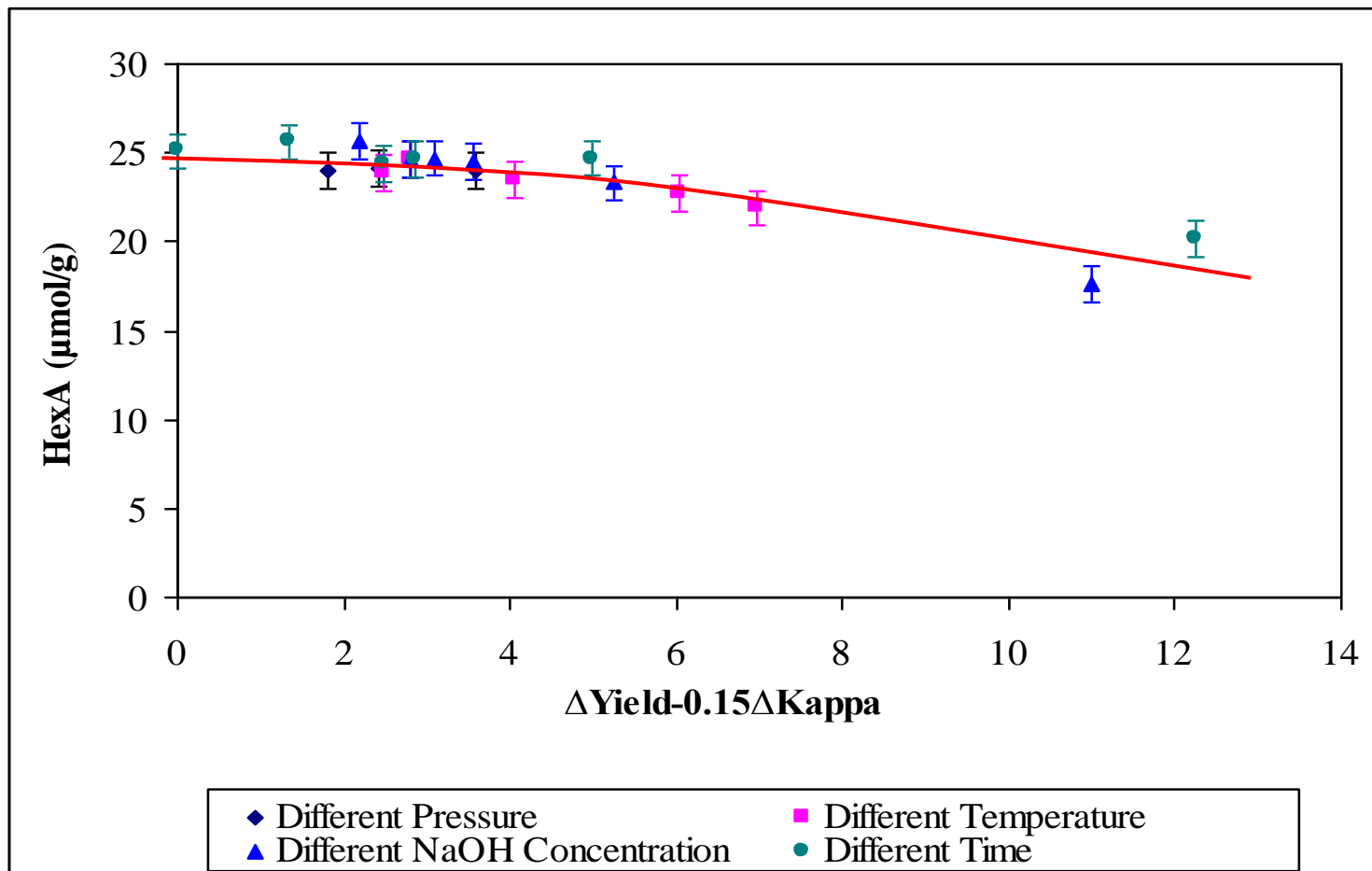


Berty Stationary Basket Reactor

- Basket: 2-inch diameter and height, volume 100 mL
- Reactor volume of 280 mL filled with well-mixed oxygenated NaOH solution circulating through pulp
- Berty reactor is CSTR with which one can measure delignification rate at each time

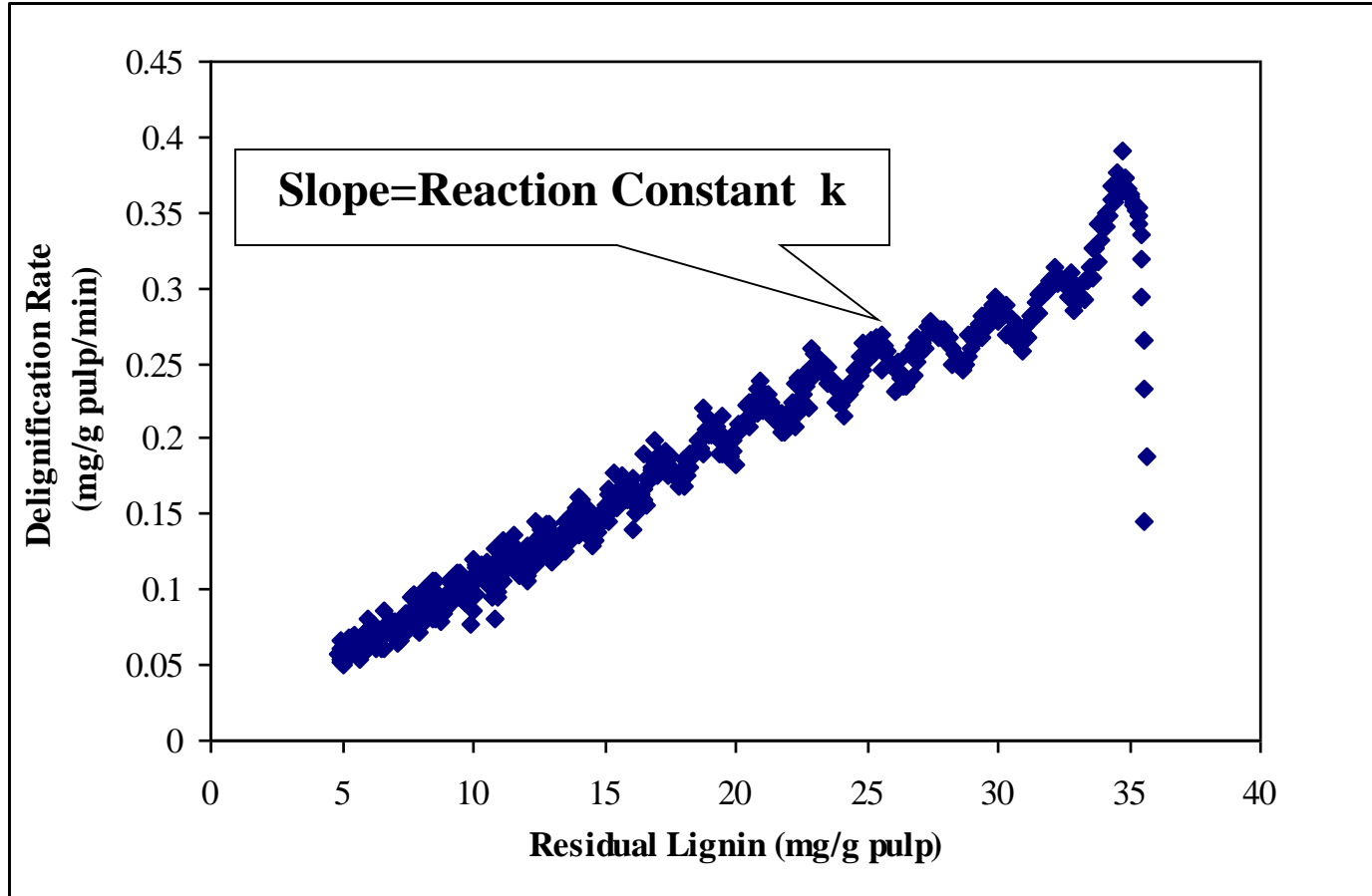


[HexA] vs. Carbohydrate Yield



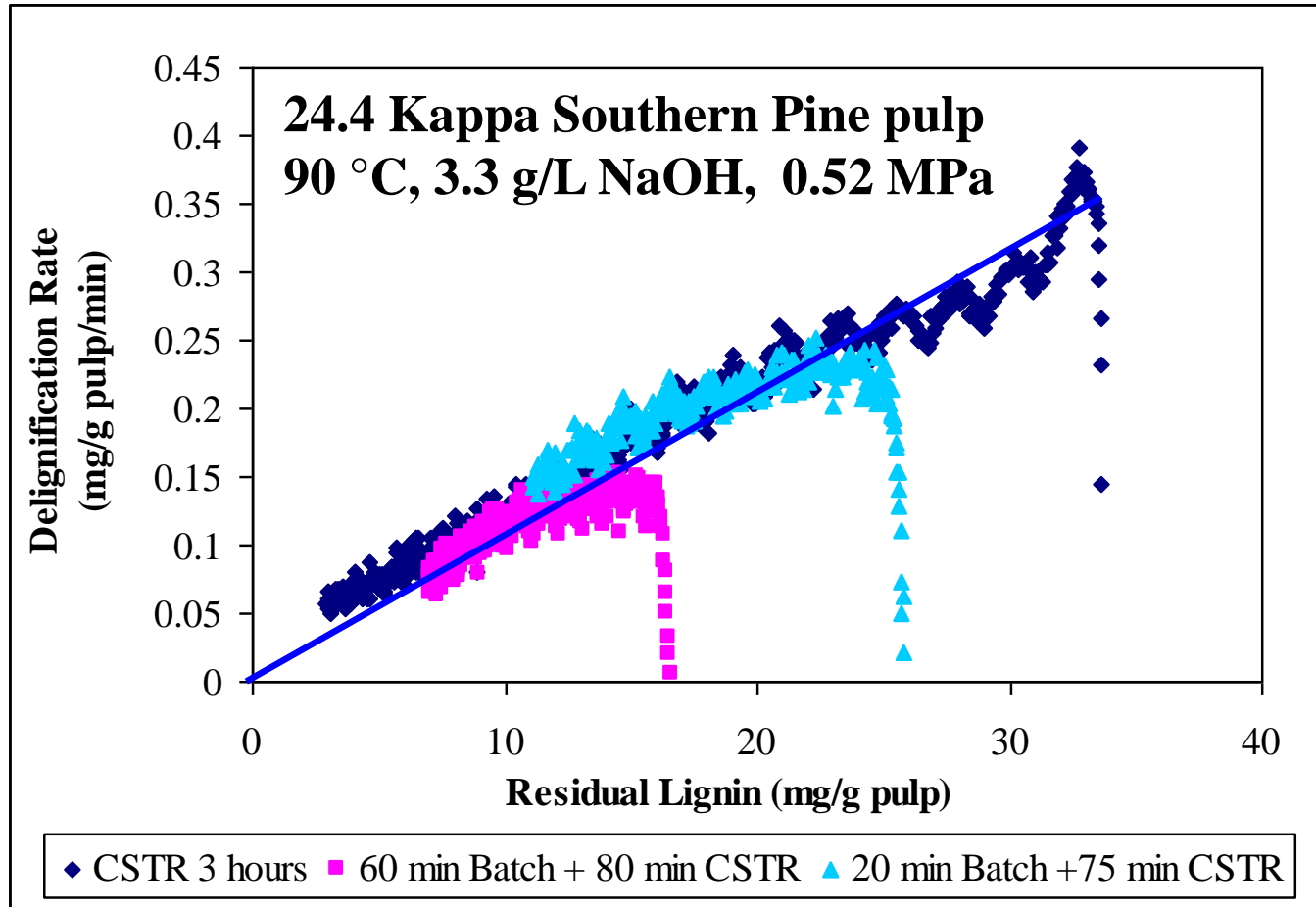
HexA is unreactive during O₂ delignification

Delignification Rate vs. Residual Lignin



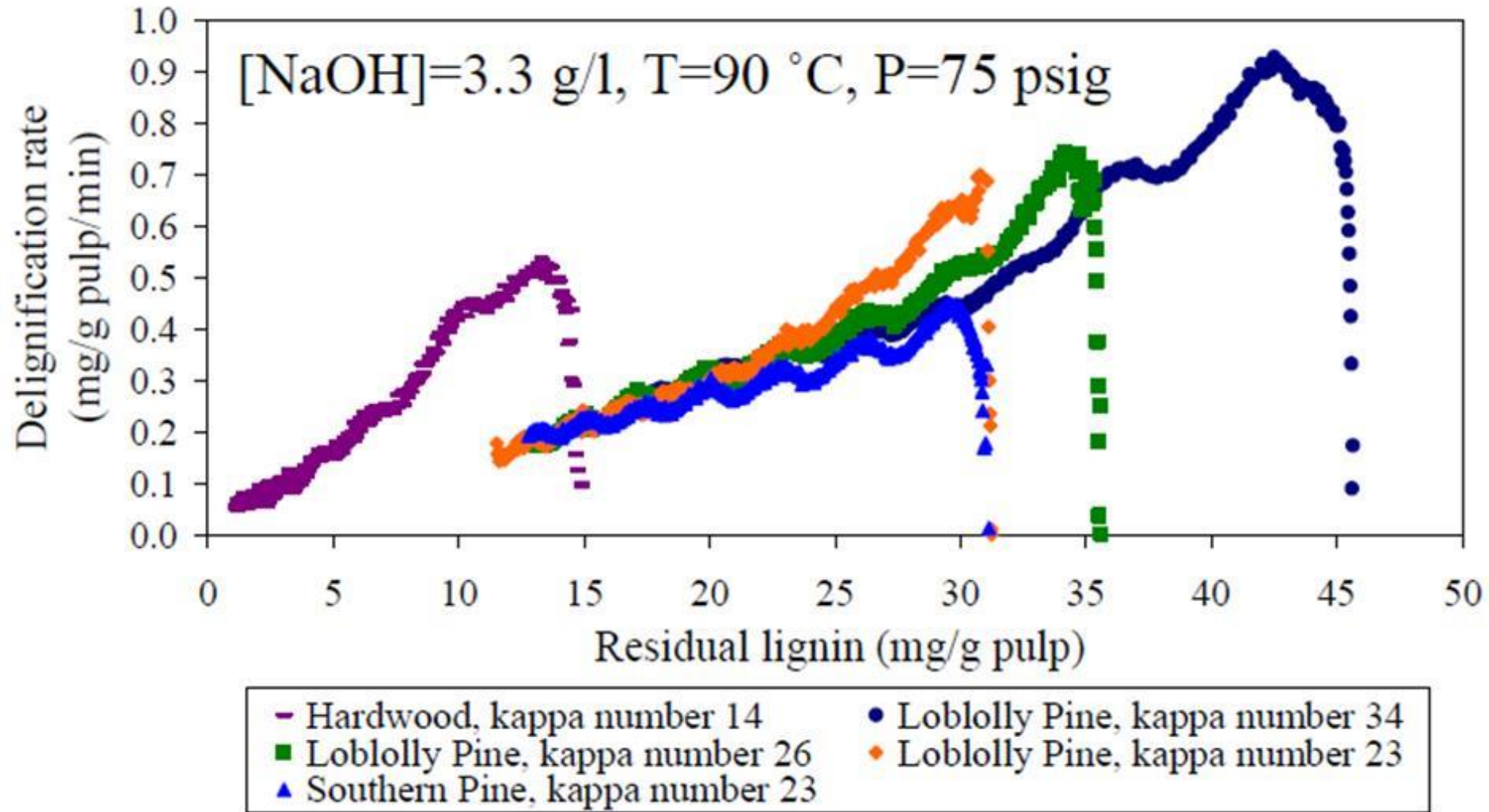
$$L_c = \left(Kappa - \frac{HexA}{10} \right) \times 1.5 \quad \left(\frac{\text{mg lignin}}{\text{g pulp}} \right) \bullet \text{ First order in lignin when initial phase is ignored.}$$

Effect of Initial Lignin Content



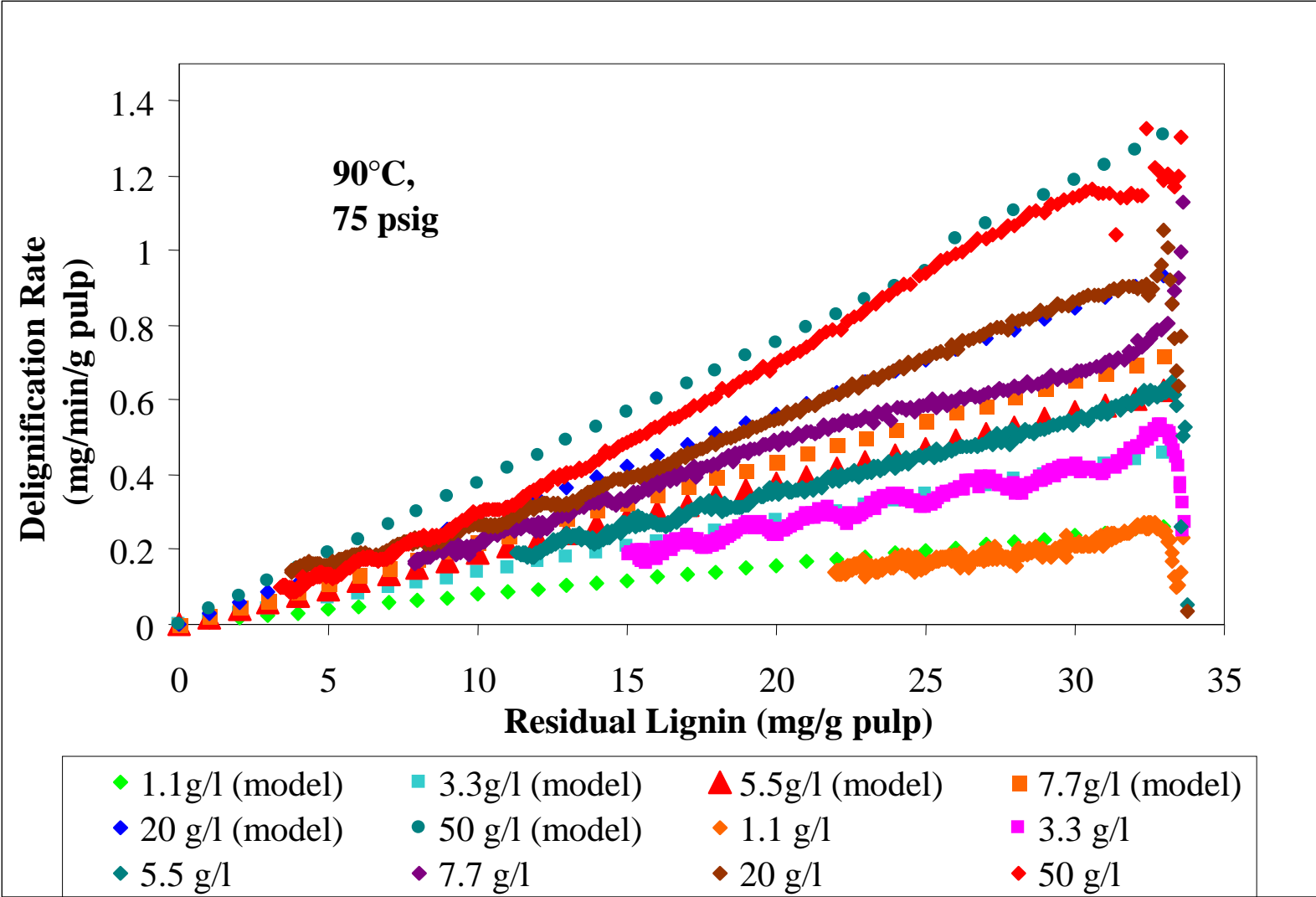
- Confirms first order reaction in HexA-free lignin
- Initial faster rate disappears after batch O₂ delig. because initial “peeling delignification” is eliminated

Initial Kappa and Softwood/Hardwood

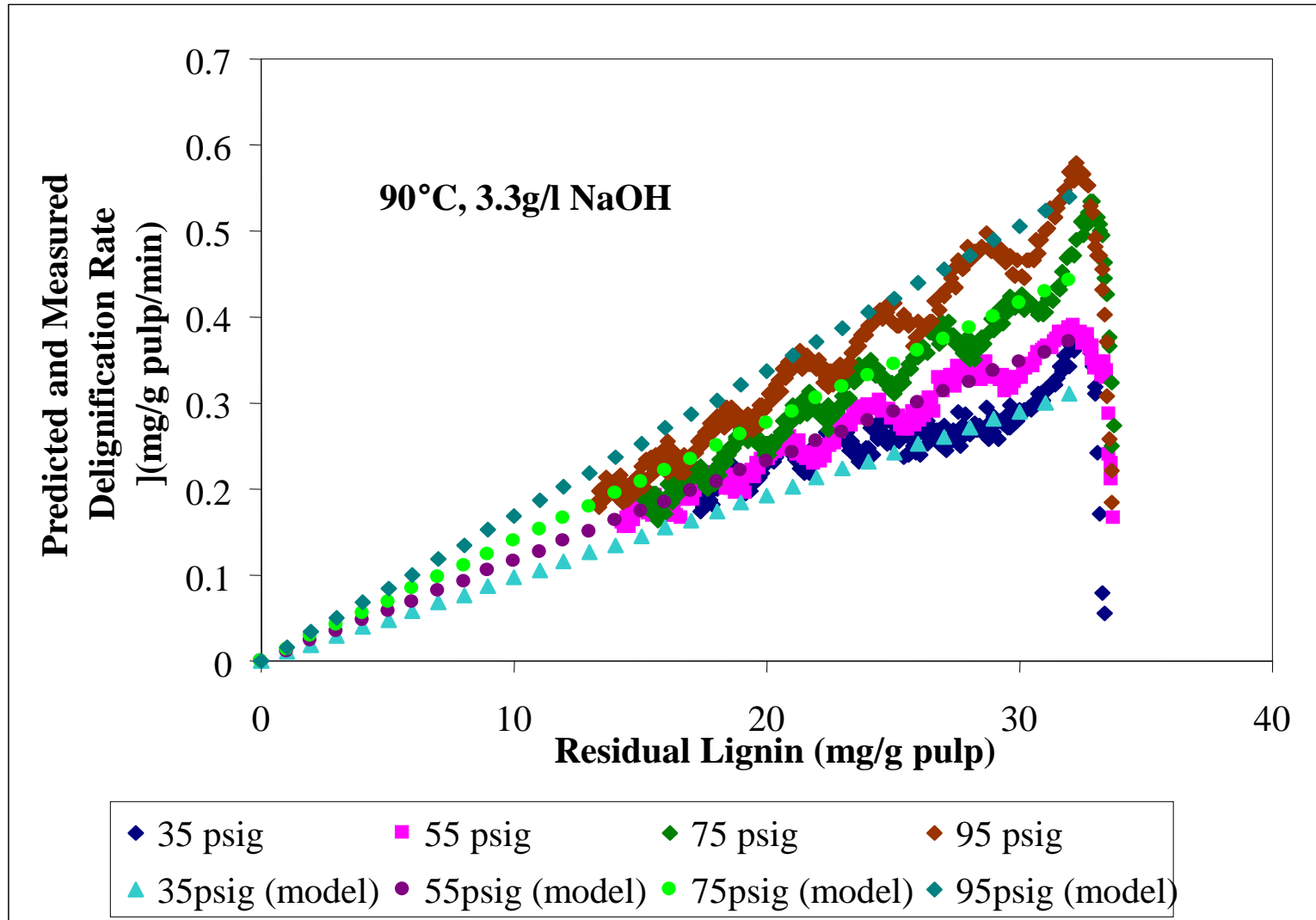


- Rates of softwood pulps merge at lignin ≤ 20 mg/g.
- Hardwood kraft pulp has higher delignification rate

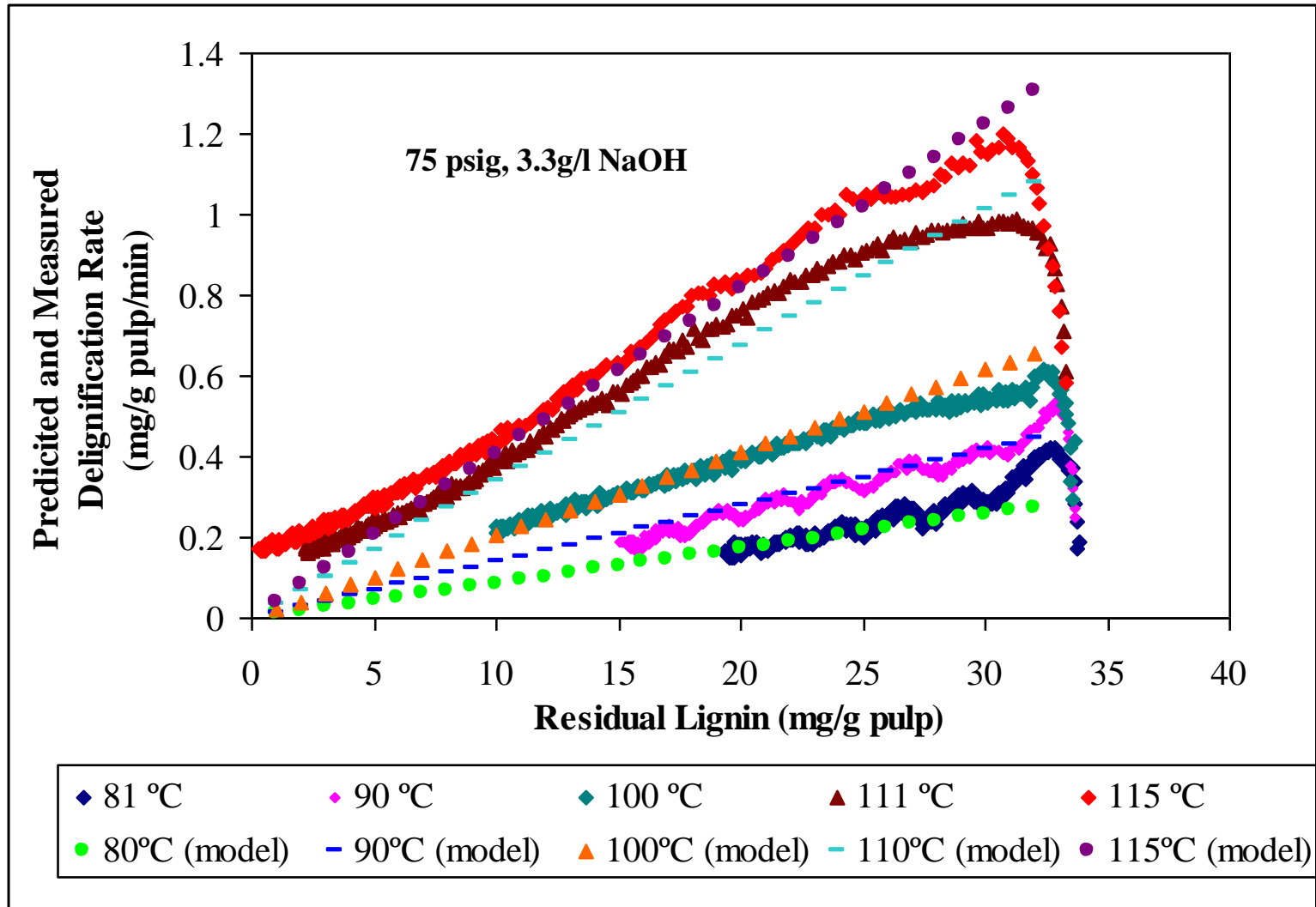
Influence of NaOH Concentration



Influence of Oxygen Pressure



Influence of Temperature



Delignification Kinetic Equation

$$r = 5 \times 10^4 e^{-\frac{5.31 \times 10^4}{RT}} [OH^-]^{0.42} [P_{O_2}]^{0.44} L_c$$

where r	delignification rate (mg/g pulp/min)
T	reaction temperature (K)
$[OH^-]$	sodium hydroxide concentration (g/l)
$[P_{O_2}]$	oxygen pressure (psia)
L_c	residual lignin corrected for HexA (mg/g pulp)

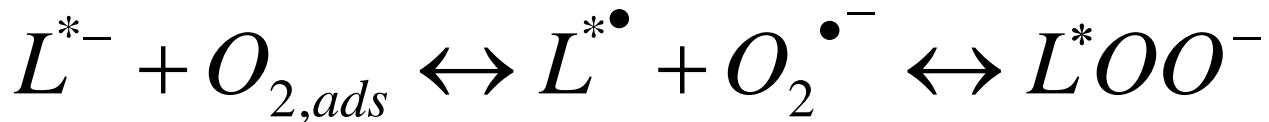
Activation energy of 53 kJ/mol in agreement with reaction controlled process

Summary of Evidence

- Delignification is first order in residual lignin content.
- This implies that active lignin sites are uniformly distributed throughout lignin, and of same reactivity
- First order in lignin despite reduction in phenolic fraction of lignin (initial 0.41; 0.22 after 3 hours @ 90 °C, 75 psig)
- Methanol formation proportional to delignification

Active lignin site for rate determining step is not phenolic group, but another acidic site uniformly distributed in lignin

Mechanistic Kinetic Equation



**Rate
Determining
Step**

$$-\frac{dL_C}{dt} = k_1 [L^*OO^-] = delig \text{ rate}$$

where HL^* is active lignin site

$O_{2,ads}$ is oxygen adsorbed on reactive lignin site

$O_2^{\bullet-}$ is superoxide anion radical

L^*OO^- is lignin peroxide anion

$[L^{*-}]$ is reactive lignin site concentration

$[O_2]_{ads}$ is adsorbed oxygen concentration on reactive lignin site

Mechanistic Kinetic Equation

Effect of $[OH^-]$

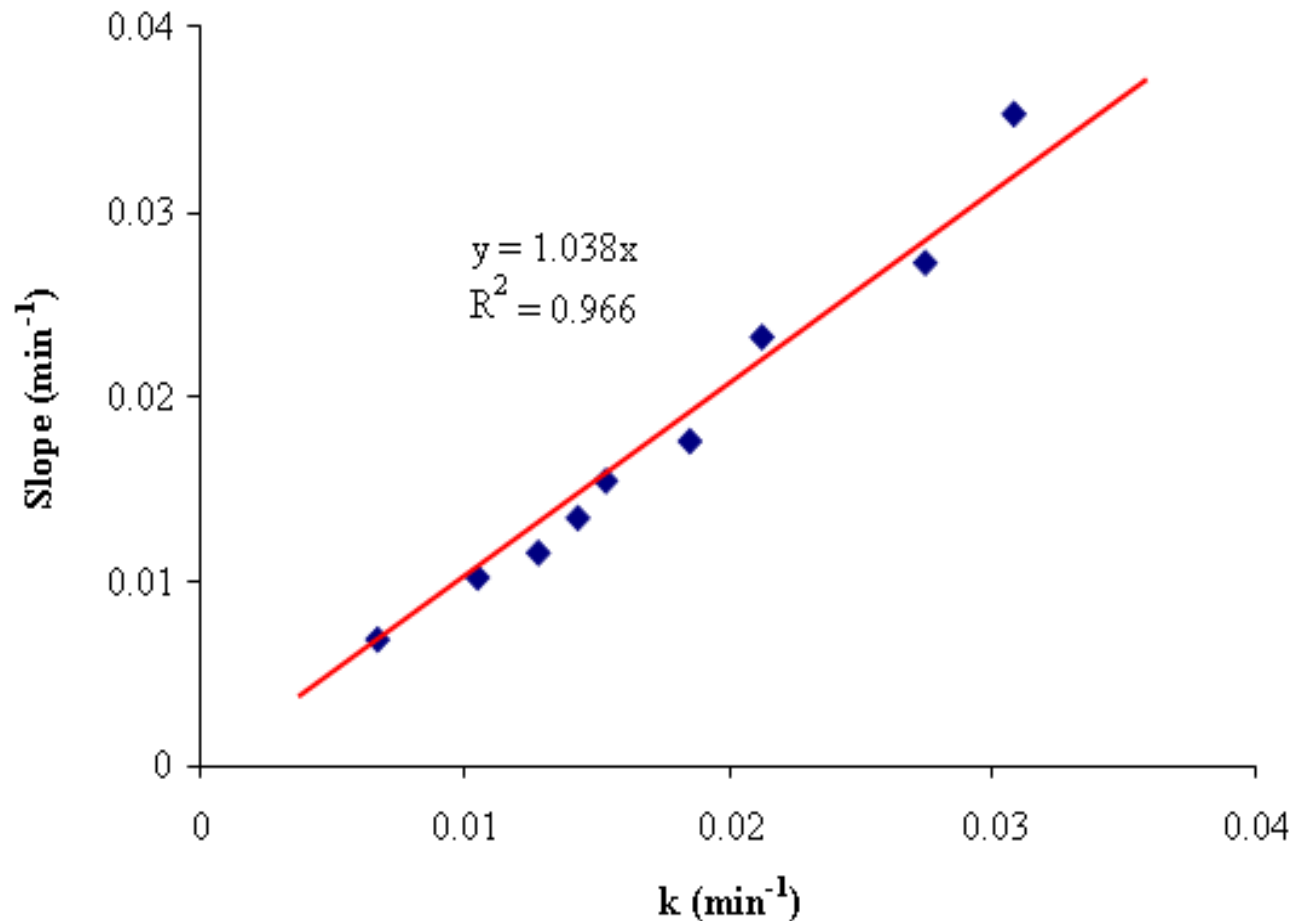
$$K_{L^*OOH} = \frac{[L^*OO^-][H^+]}{[L^*OOH_{total}] - [L^*OO^-]} \rightarrow [L^*OO^-] = \frac{K_{L^*OOH} [L^*OOH_{total}]}{[H^+] + K_{L^*OOH}}$$

$$[L^*OO^-] = \frac{K_{L^*OOH} [L^*OOH_{total}]}{\frac{K_{water}}{[OH^-]} + K_{L^*OOH}} = \frac{K_{L^*OOH} [L^*OOH_{total}] [OH^-]}{K_{water} + K_{L^*OOH} [OH^-]}$$

$$[L^*OOH]_{total} = K \cdot L_C \cdot [O_2]_{adsorbed}$$

$$-\frac{dL_C}{dt} = K_C \frac{[OH^-][O_2]_{ads}}{K_{water} + K_{HL^*}[OH^-]} L_C$$

Measured vs. Predicted Rate Constant



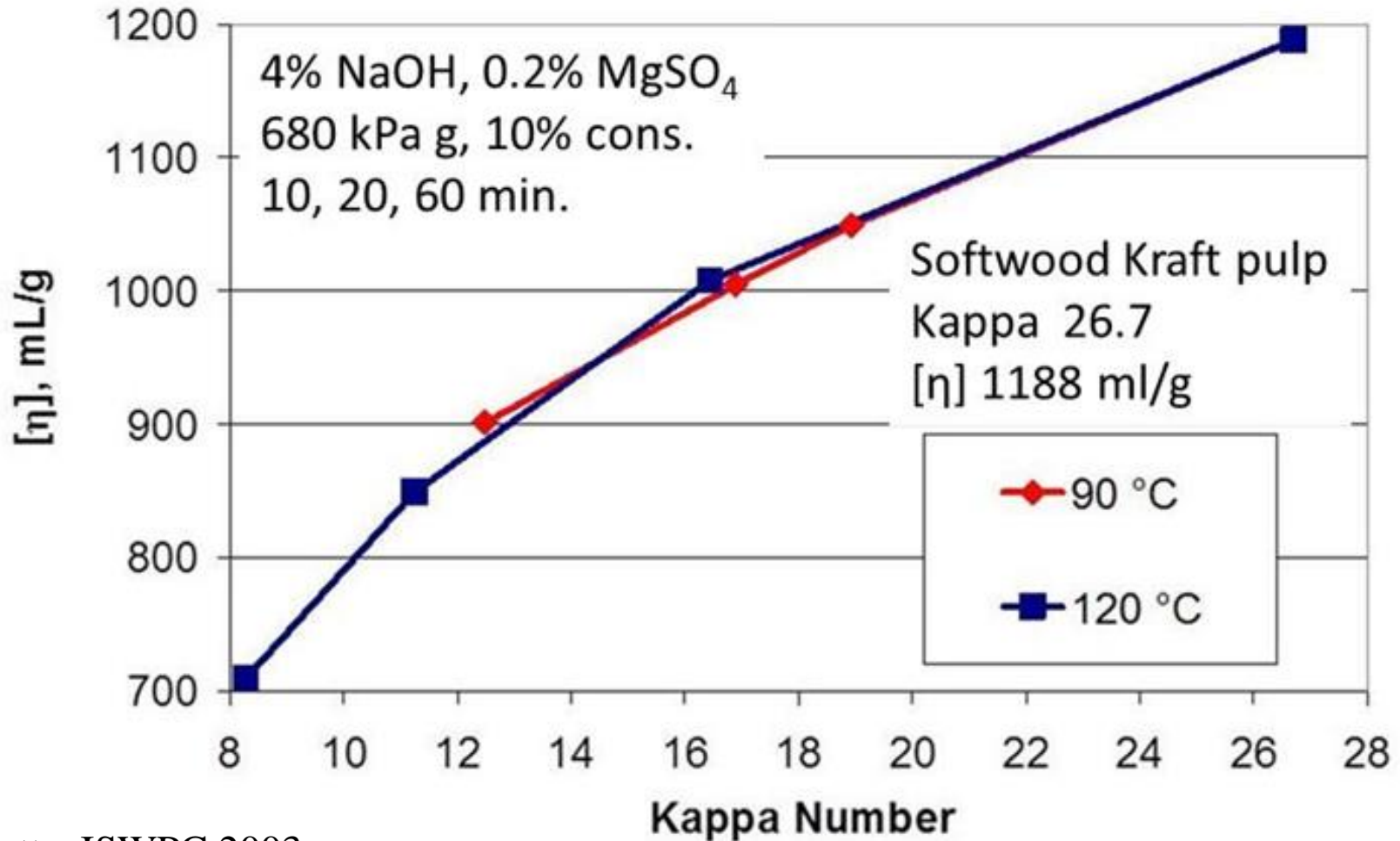
$$k = 0.175 \frac{[OH^-]}{0.1111 + [OH^-]} \cdot \frac{P_{O_2}}{1 + 3.39P_{O_2}}$$

Summary on Lignin Reactivity

- Rate of delignification is first order in HexA-free residual “lignin” content
- Hardwood lignin is more reactive than softwood
- Rate determining step of delignification is unimolecular decomposition of hydroperoxide anion at 3 carbon. Formation of the anion requires NaOH
- New kinetic equation explains broken orders in $[\text{NaOH}]$ and P_{O_2} and first order in HexA-free kappa

Delignification/Cellulose Degradation Selectivity

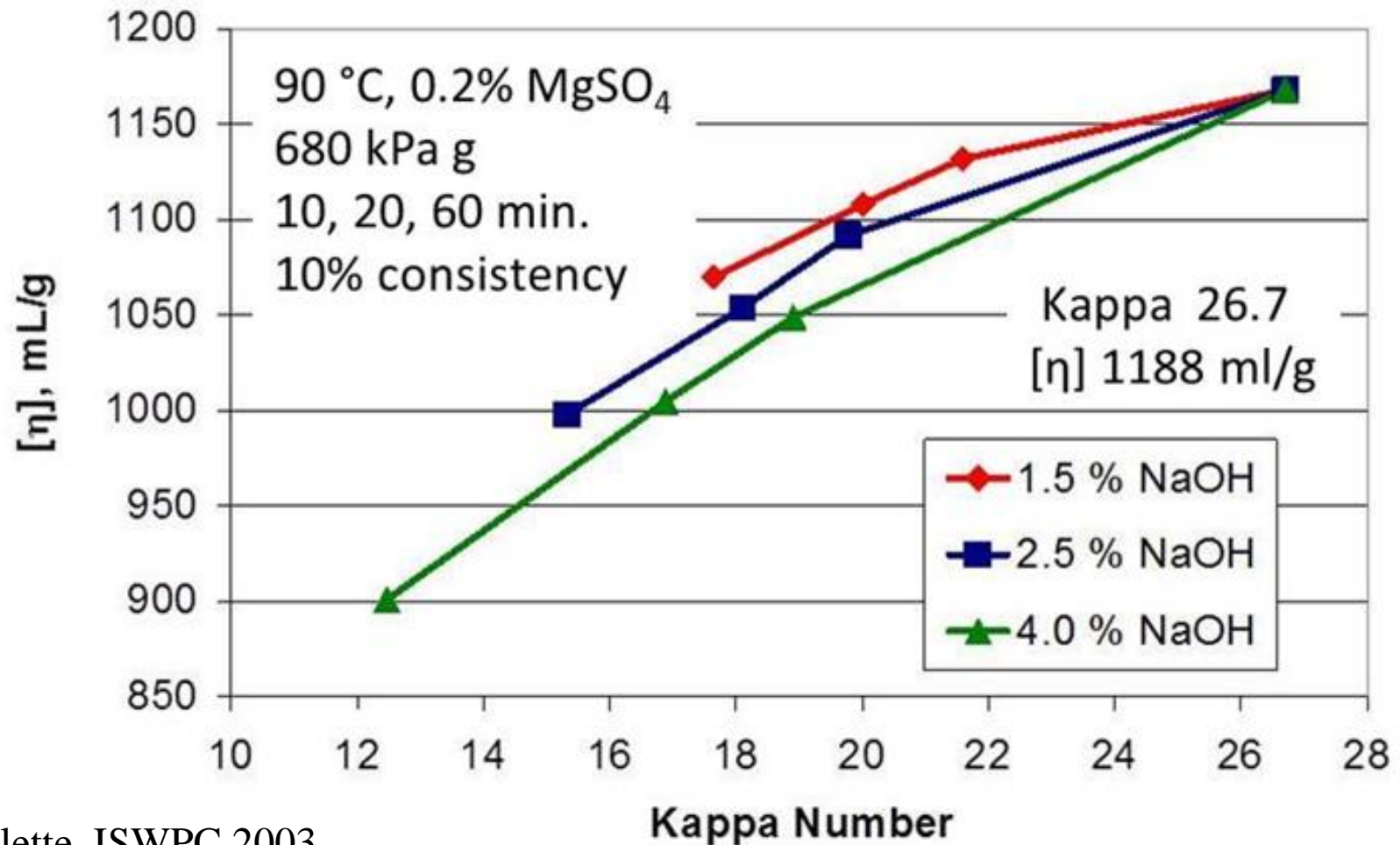
Effect of Temperature on Selectivity



S.Violette, ISWPC 2003

Selectivity unchanged by temperature but viscosity too low at longer time and high temperature

Effect of Alkali Charge on Selectivity



S.Violette, ISWPC 2003

Selectivity increases but degree of delignification decreases with decreasing [NaOH]

Oxygen Delignification Selectivity, S_{LC}

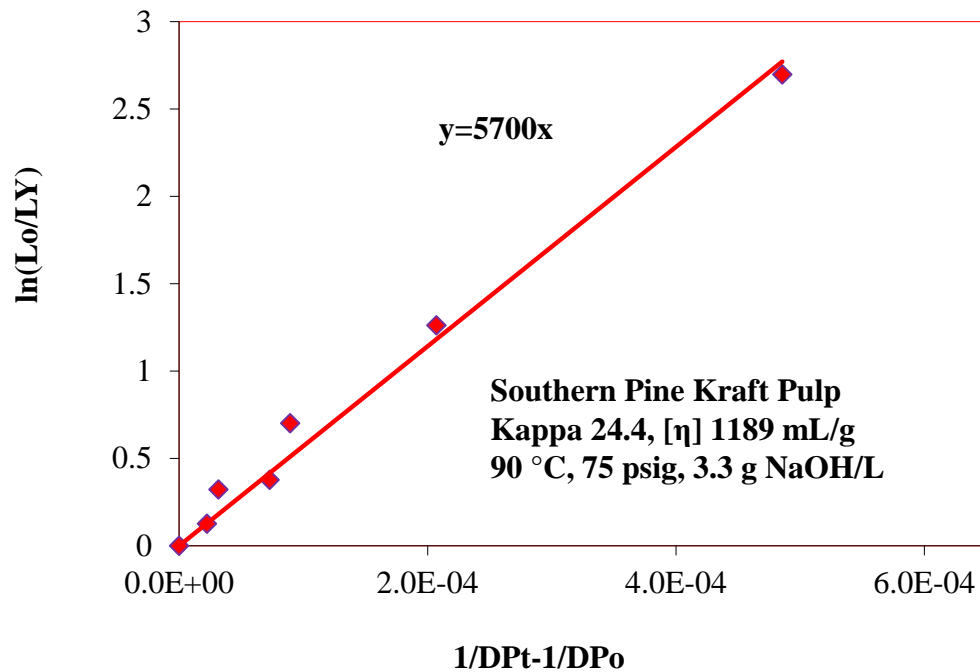
- Catalytic metals such as iron are mostly complexed by lignin
- So radicals are created near lignin, and then mostly react with lignin
- At lower lignin content a larger fraction of radicals attack cellulose
- **Assume rate of cellulose attack inversely proportional to lignin content based on original pulp weight, LY**
- **Rate of radical generation is proportional to rate of phenolic delignification**

$$\frac{d \frac{1}{DP}}{dt} = - \frac{1}{S_{LC} LY} \frac{dLY}{dt} \quad \text{Integration gives} \quad S_{LC} = \frac{\ln \frac{L_0}{LY}}{\frac{1}{DP} - \frac{1}{DP_0}}$$

where LY is Klason lignin based on original pulp weight

DP and DP_0 are cellulose DP at $t=0$ and t respectively

L_0 is initial Klason lignin content of pulp

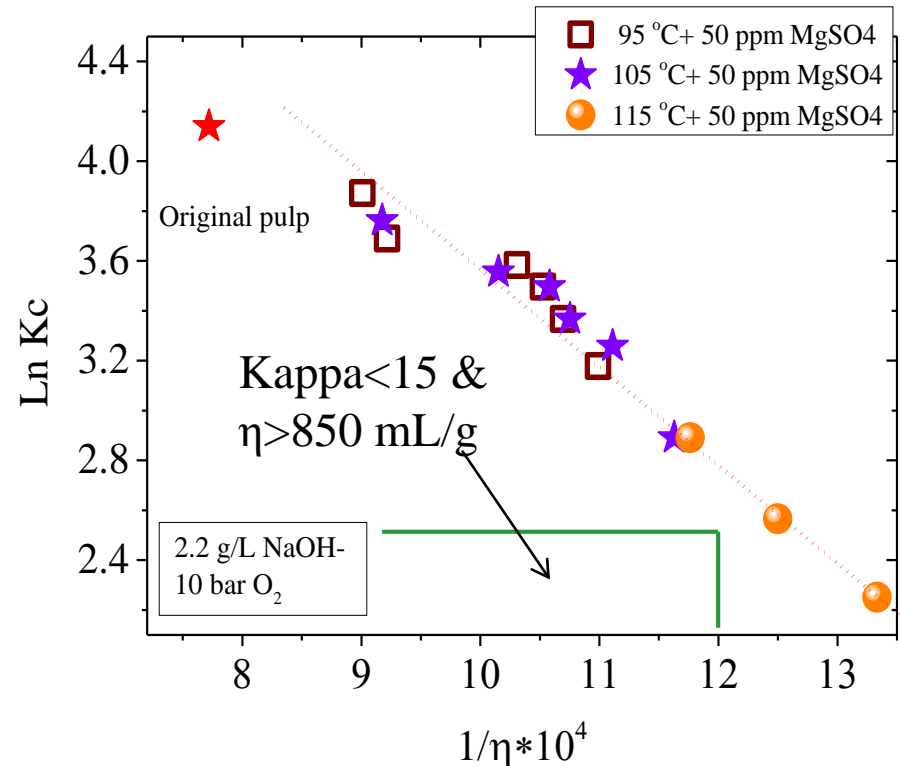
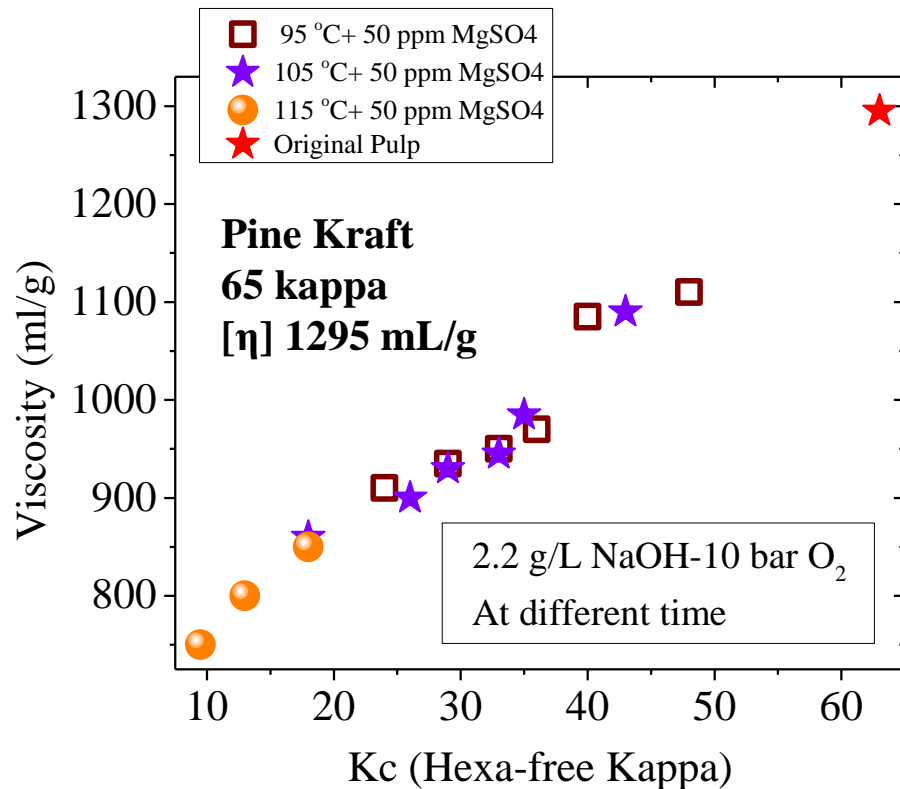


**Selectivity, S_{LC}
= slope of plot**

Time (min)	Kappa	Klason Lignin (%)	Acid Soluble Lignin (%)	Pulp Yield (%)	Intrinsic Viscosity η (ml/g)	Hemi Content H	Cellulose Content G	DP	HexA Content (μ Mol/g)
0	24.4	3.89	0.36	100	1189	0.142	0.714	6556	25.1
10	20.1	3.50	0.36	98	1079	0.139	0.732	5721	25.6
20	18.5	2.92	0.38	96.5	1033	0.142	0.734	5430	25.1
40	14.3	2.78	0.39	96.0	877	0.140	0.746	4439	24.4
60	12.7	2.02	0.39	95.4	828	0.138	0.750	4137	24.6
180	7.6	1.19	0.42	92.5	592	0.135	0.763	2782	24.7
360	3.7	0.31	0.34	84.5	380	0.126	0.815	1567	20.2

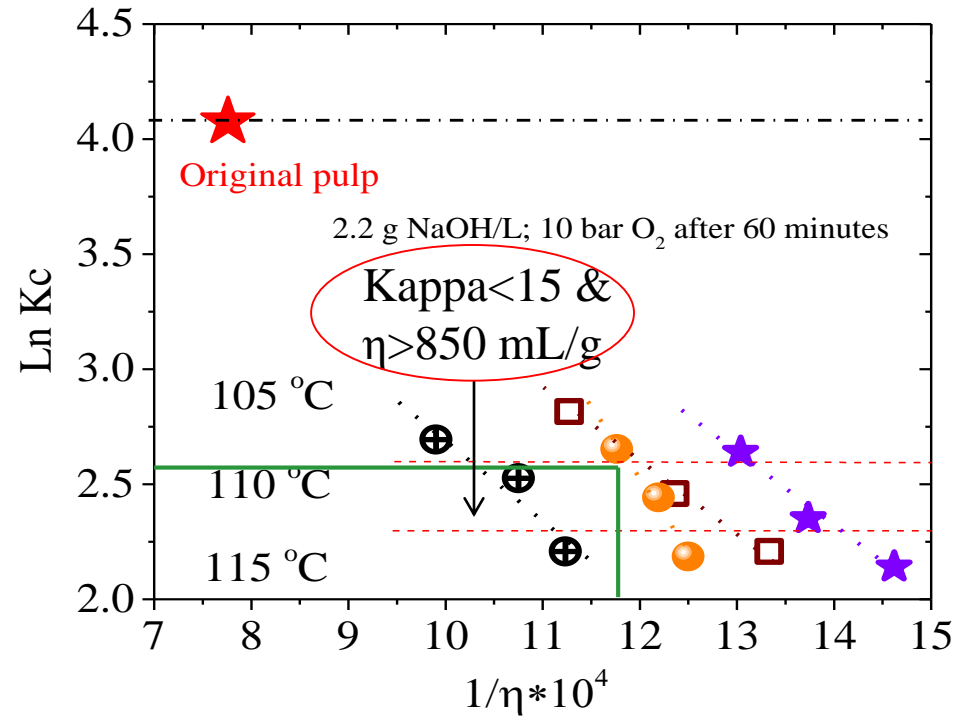
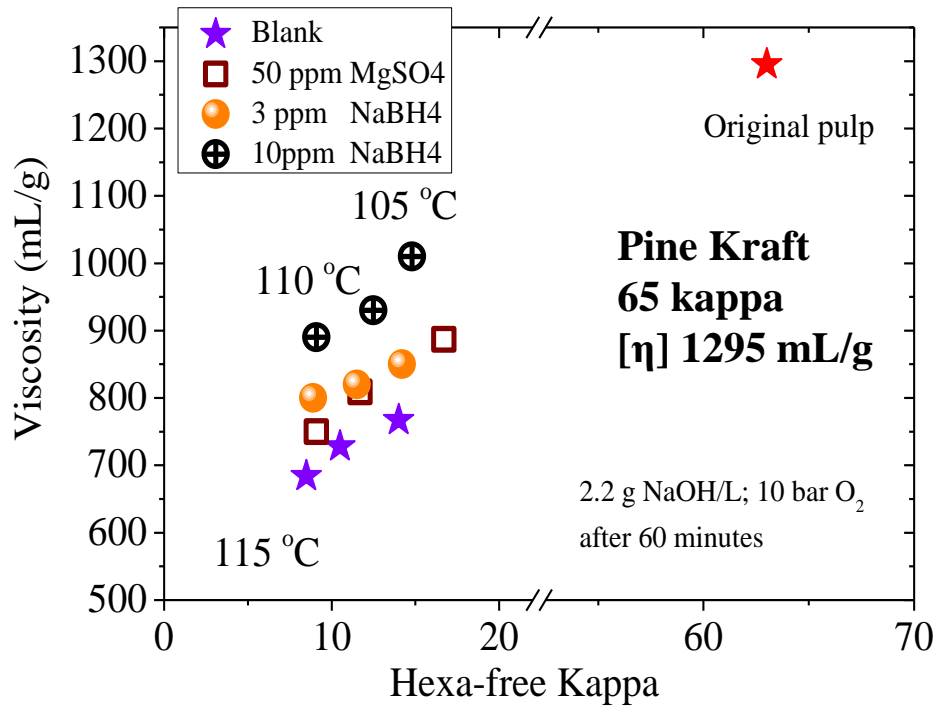
Selectivity for High Kappa (65)

Softwood Pulp with MgSO₄ Present



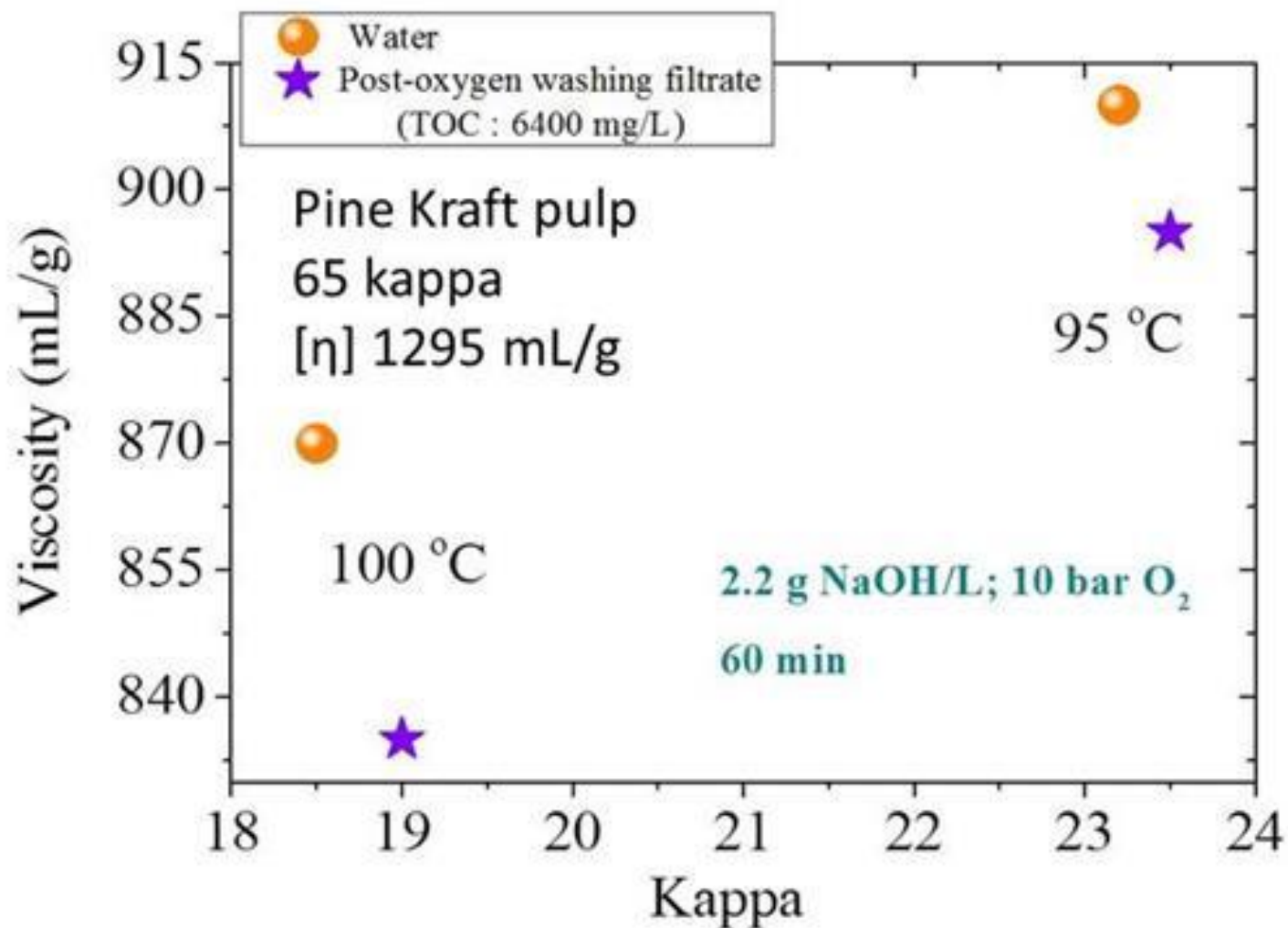
- Selectivity not affected by temperature with MgSO₄
- Delignification increases strongly with temperature

Effect of T and Additives on Selectivity



- 10 ppm NaBH₄ & 115 °C gives 10.5 kappa and [η] of 890 mL/g, i.e. bleachable grade pulp at 83% delignification
- NaBH₄ reduces cellulose carbonyls in original pulp
- NaBH₄ reduces metal ions which catalyze H₂O₂ decomp.
- Mg forms stable complexes with cellulose carbonyls

Effect of Dissolved Organics on Selectivity

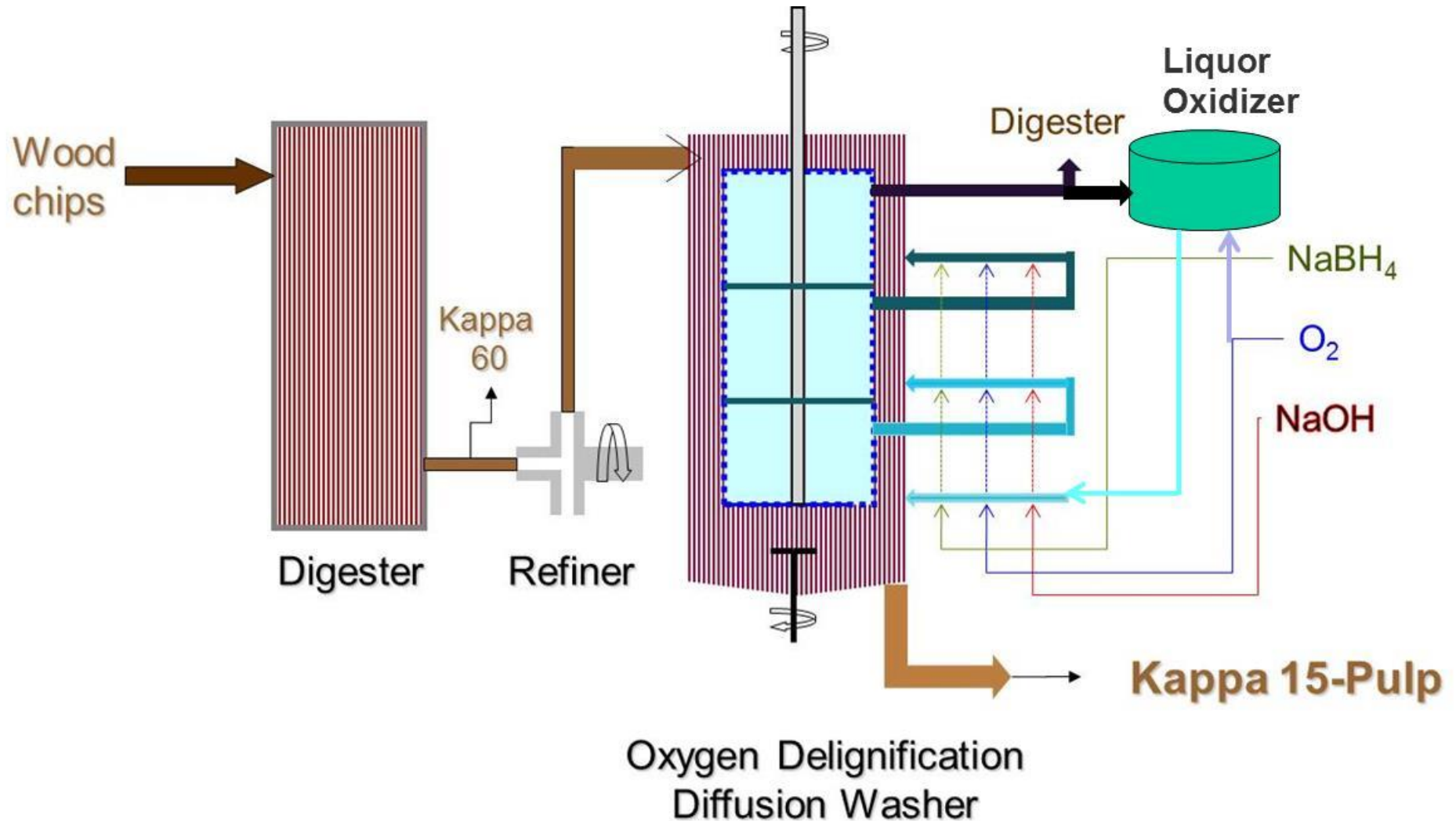


Increasing Delignification while Maintaining Good Pulp Properties

How to Increase % Delignification while Maintaining Good Pulp Properties?

- Use higher temperature to increase lignin reactivity
- Improve delignification/cellulose degradation selectivity by
 - Keeping [NaOH] at constant and low level
 - Continual replenishment of consumed NaOH
 - Oxidizing dissolved organics without pulp present
 - Use of additives (MgSO_4 , NaBH_4)
 - Use of radical scavengers (MeOH, etc.)
 - Increasing hemicellulose content

Practical Implementation of Concept?



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