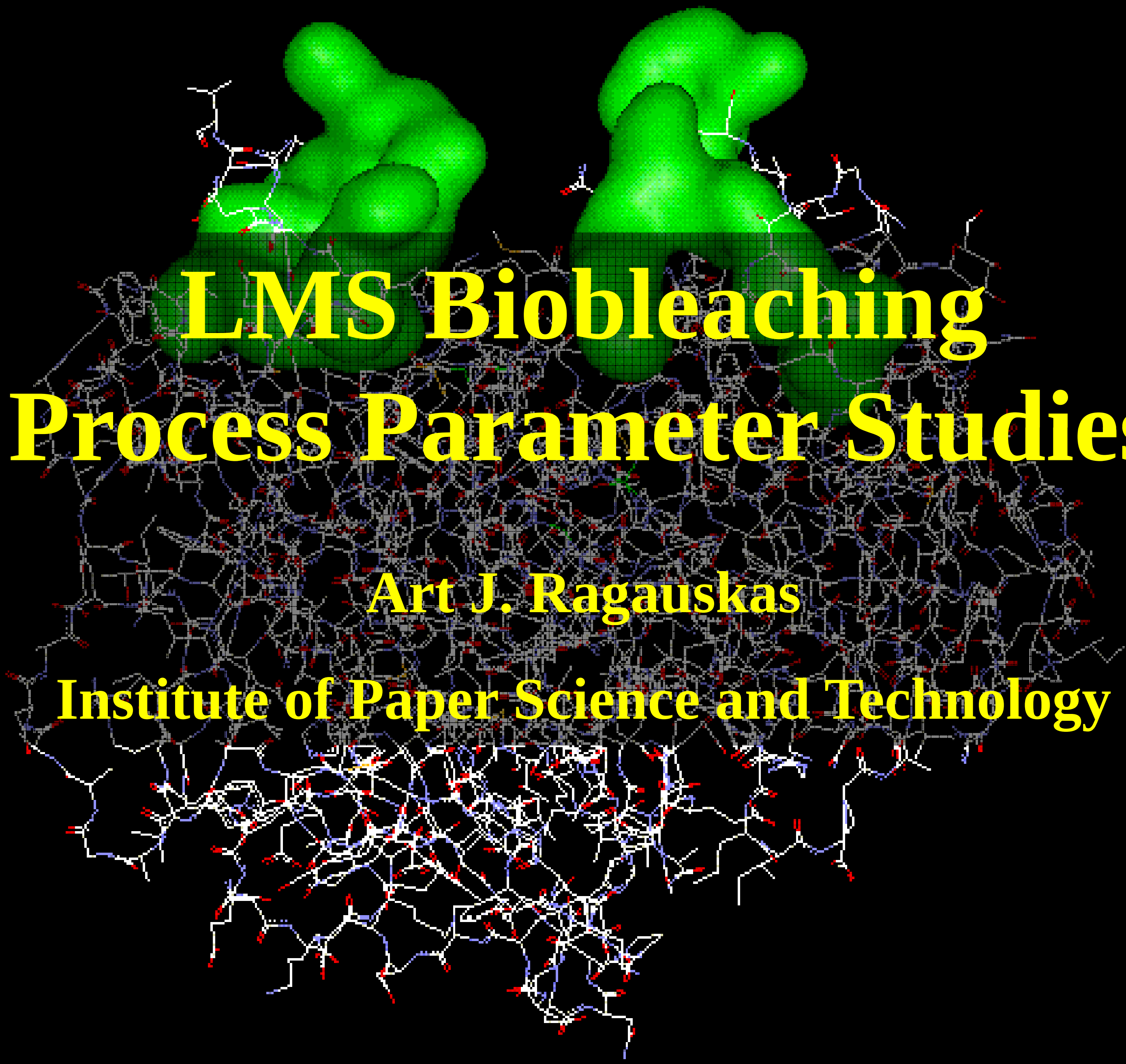


LMS Biobleaching
Process Parameter Studies

Art J. Ragauskas

Institute of Paper Science and Technology

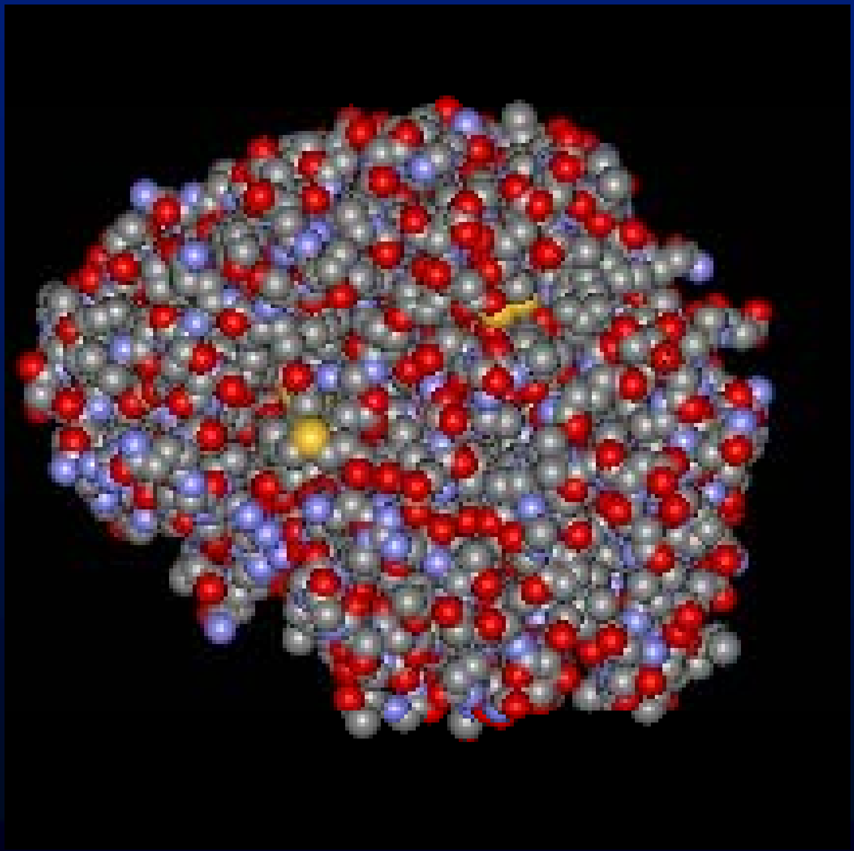
Pulp Bleaching

- Purpose of bleaching is 2-fold:
  - to remove the residual lignin
  - to brighten the pulp

- Current bleaching technologies consist of:
  - O_2, ClO_2, H_2O_2, & O_3
  - Capital intensive
  - Limited selectivity
  - D has environmental limitations

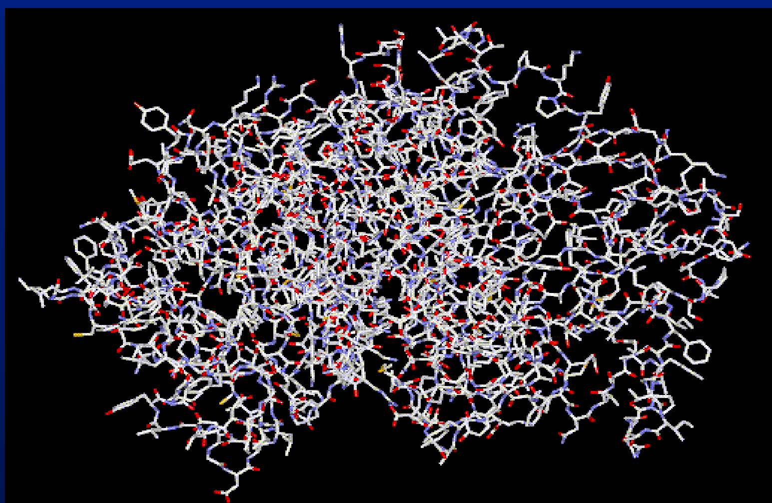
  - New bleaching agents needed!

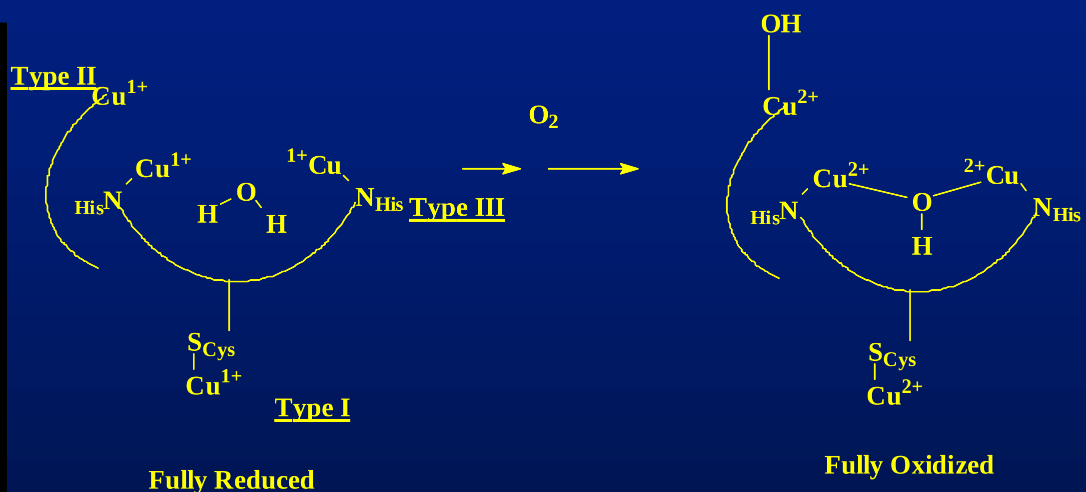
LACCASE-MEDIATED BIOBLEACHING



Laccase: Overview

Laccase





Oxidoreductase enzyme

E.I. Solomon et al

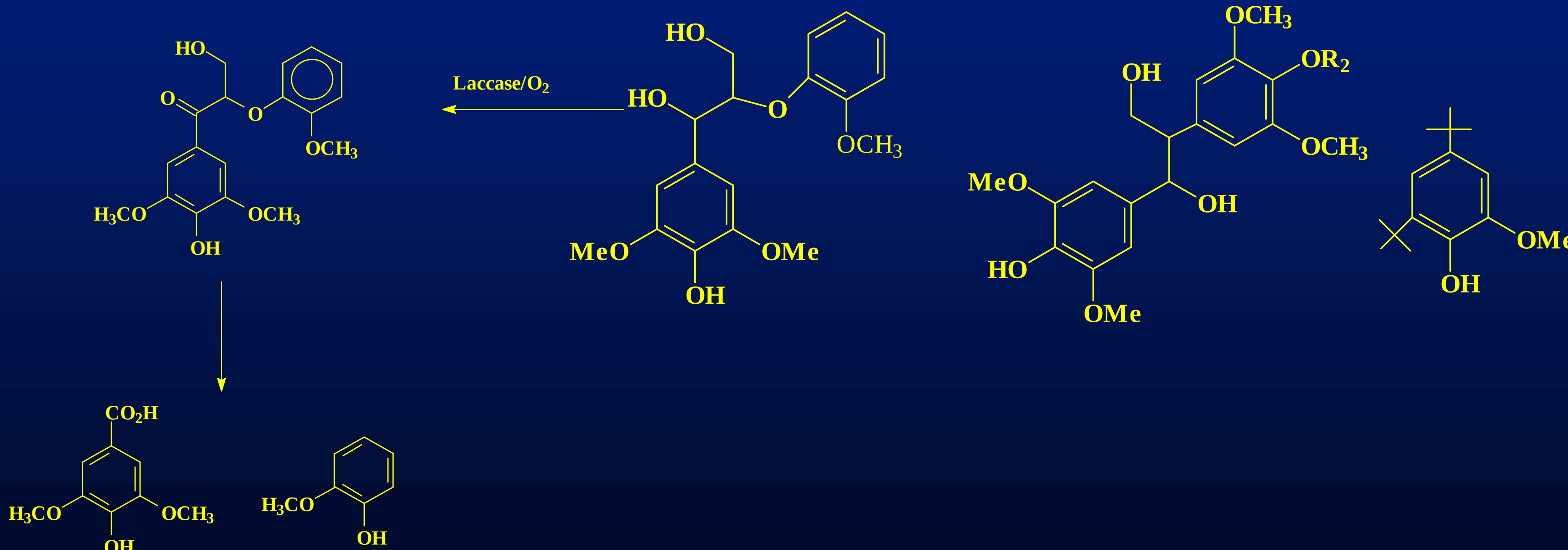
- Reduces O_2 to H_2O concomitantly oxidizes
- MW varies 65,000-140,000.
- Carbohydrate content ~10-45 (% wt).

Active sites on surface

- Catalysis occurs due to 4 copper atoms/active site
- Active sites near surface

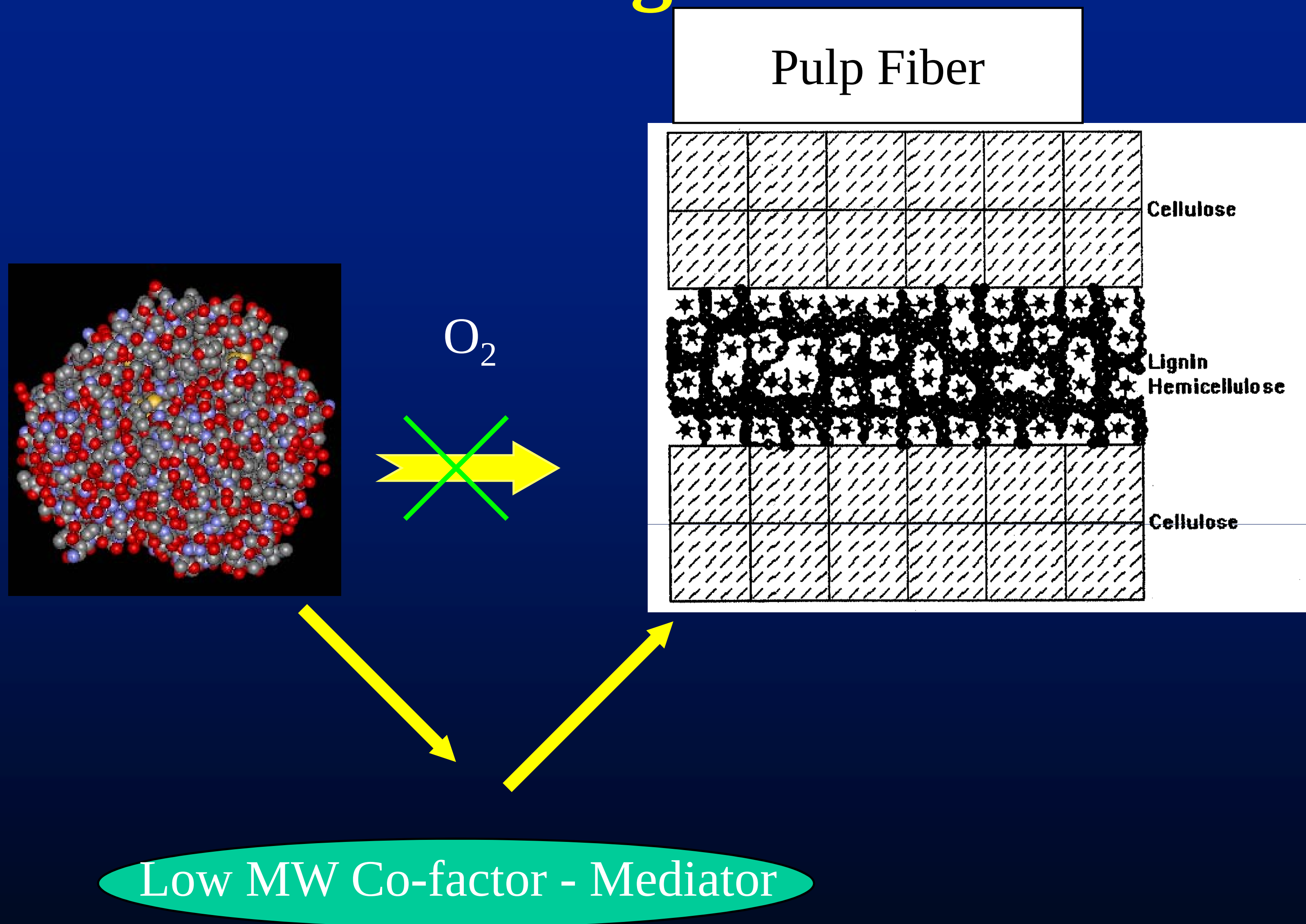
Laccase: Overview

- Proposed to be involved in lignin biosynthesis
- Oxidize a wide array of phenolic substrates



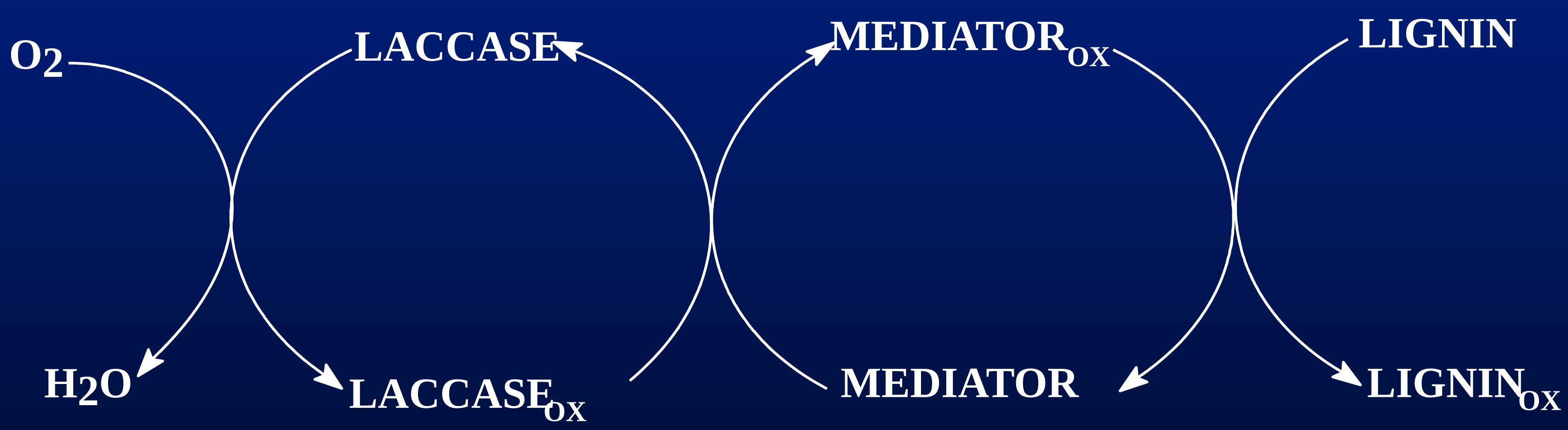
Higuchi, Wood Sci. Techn., 24, 22(1990)

Laccase Biobleaching

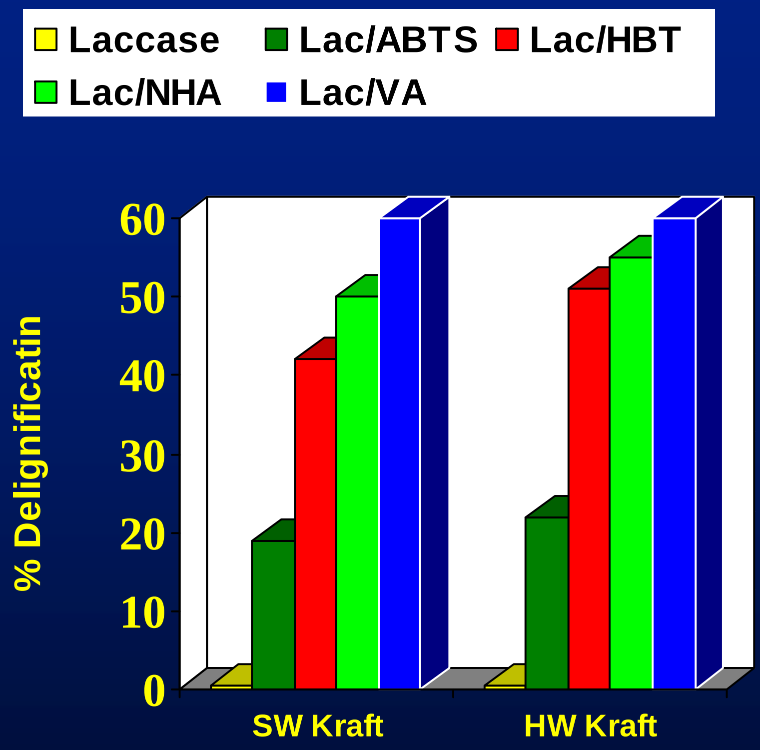


Laccase Biobleaching

LMS-Process

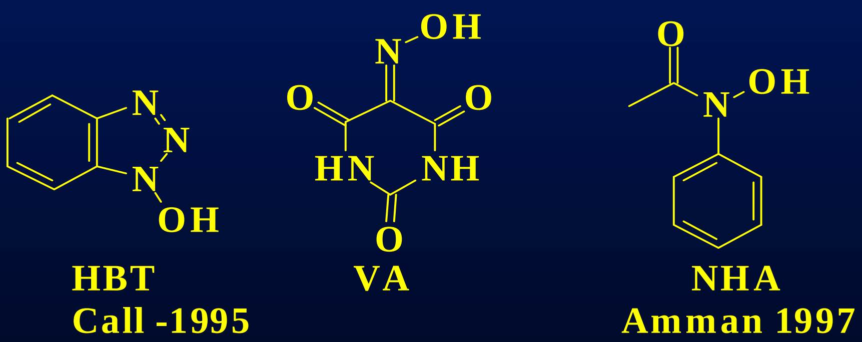


Laccase Biobleaching



Conditions LMS(E)

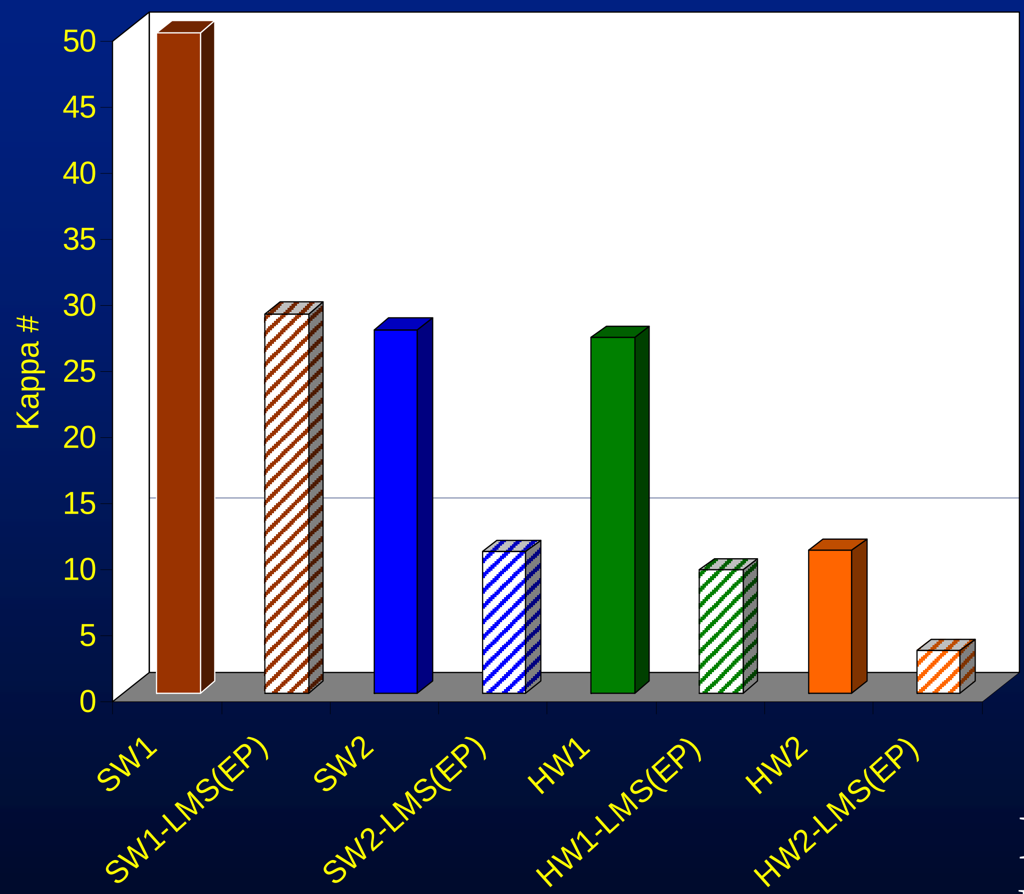
- LMS: 45ºC, 1-2 h, 5-20% csc, pH 4 - 6, 1-4% mediator, +40 psi
- E: 70ºC, 1-3 h, 1-2% NaOH



Highly selective for lignin, little degradation of pulp carbohydrates

Ragauskas et al: Enzyme and Micro. Technol., 23, 422 (1998), TAPPI J., 83(9), 66(2000); J. Wood Chem. Technol., 20(2), 169(2000)

LMSVA Biobleaching High/Low Kappa Kraft Pulps



Conditions

LMS

5.4 x 10^5 U laccase/gr od pulp

45°C, 2h, 120 psi O_2, 9% csc, med.= VA

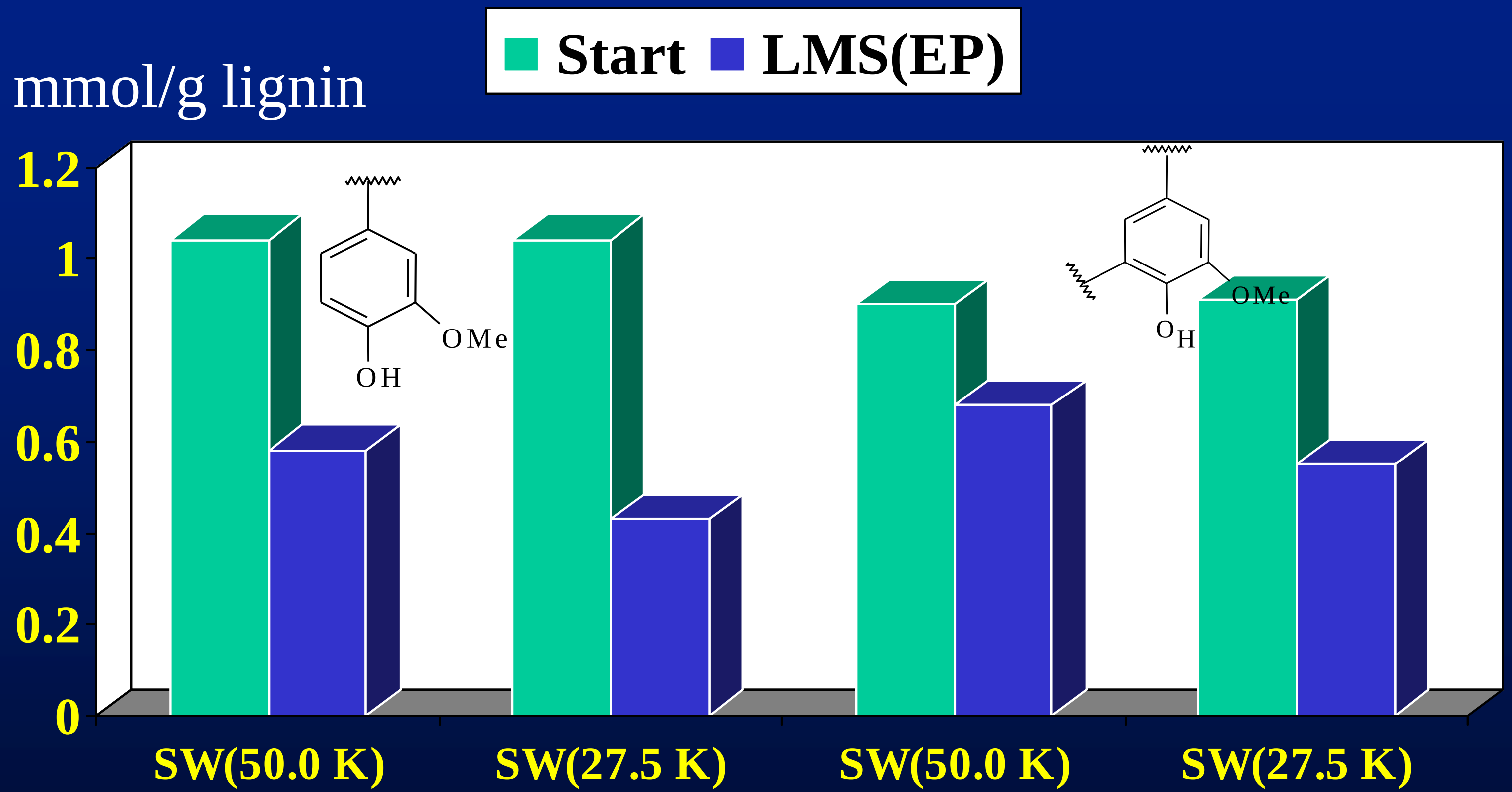
EP

80°C, 1.5 h, 0.5% H_2O_2,

10% csc

LMS applicable to low and high kappa kraft pulps

LMS$_{VA}$ Biobleaching: Lignin Reactivity



LMS reactivity primarily via phenolics, especially C5 noncondensed in SW

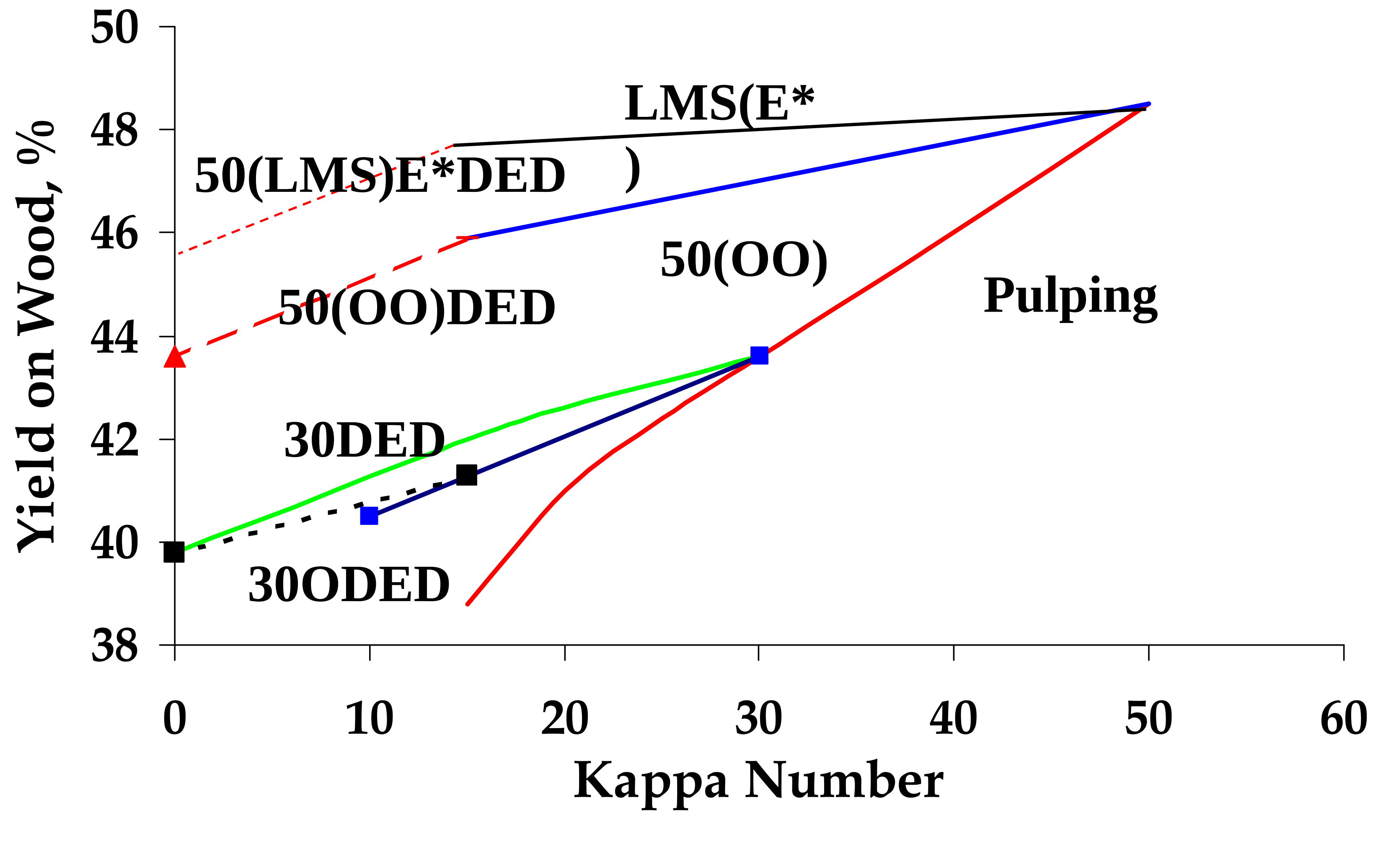
Delving into the Fundamental LMS Delignification of High-Kappa Pulps. Biotechnology in the Pulp and Paper Industry, 151-164 (2002).

Biobleaching High and Low Kappa Pulps

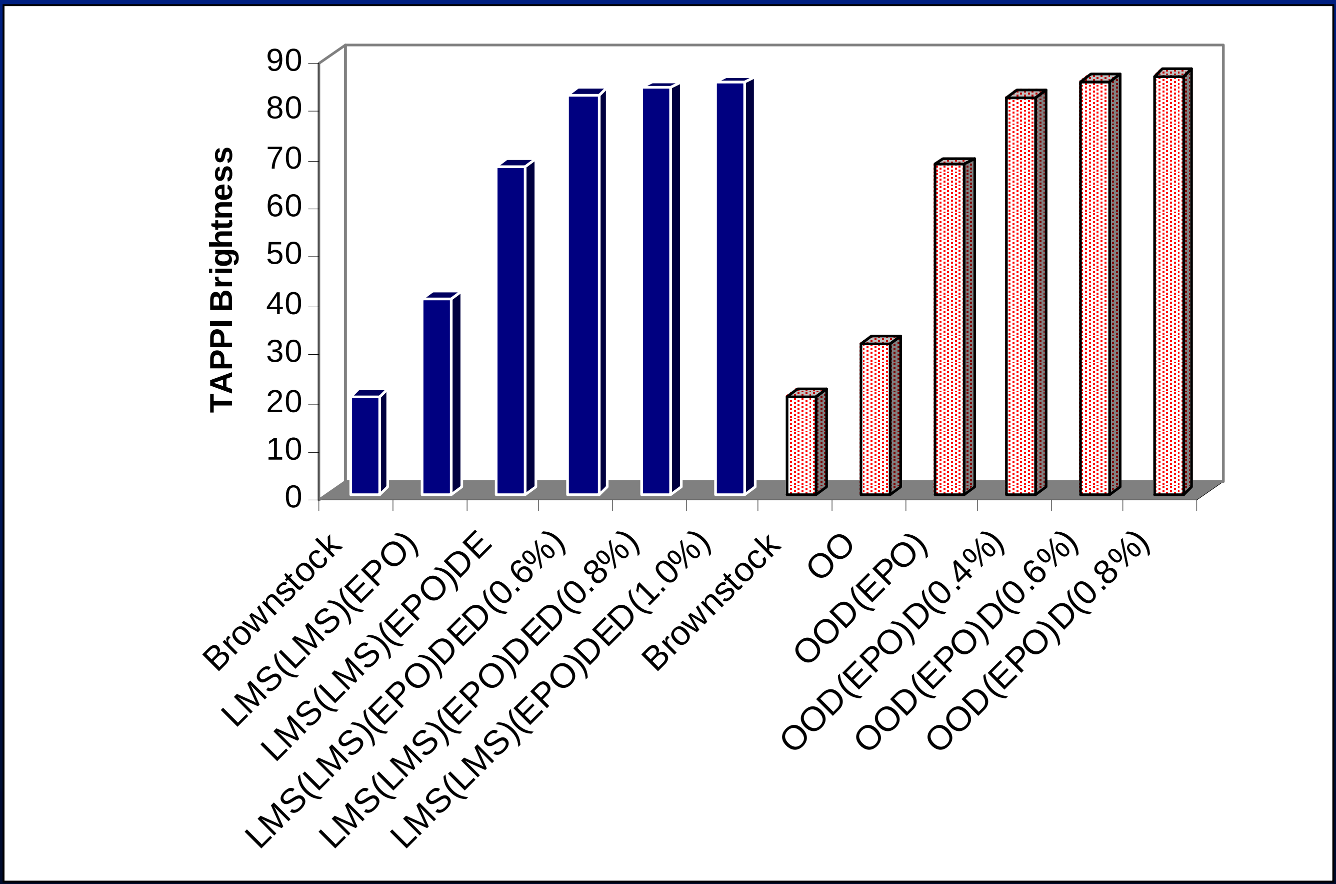
Pulp	% Delign.	% Yield
SW kappa 50	43	99.9
SW kappa 28	62	100.0
HW kappa 27	65[a]	98.6
HW kappa 11	70[a]	99.1

[a]kappa primarily hexenuronic acids

Yield Kappa Relationships



LMS_{VA} Bleaching Sequence Studies



- LMS based sequences equal to ECF in final brightness properties
- LMS yield gains occur from higher selectivity for high kappa pulps
- What is not yet established:
  - NPE effects
  - Mixing effects
  - Carryover effects

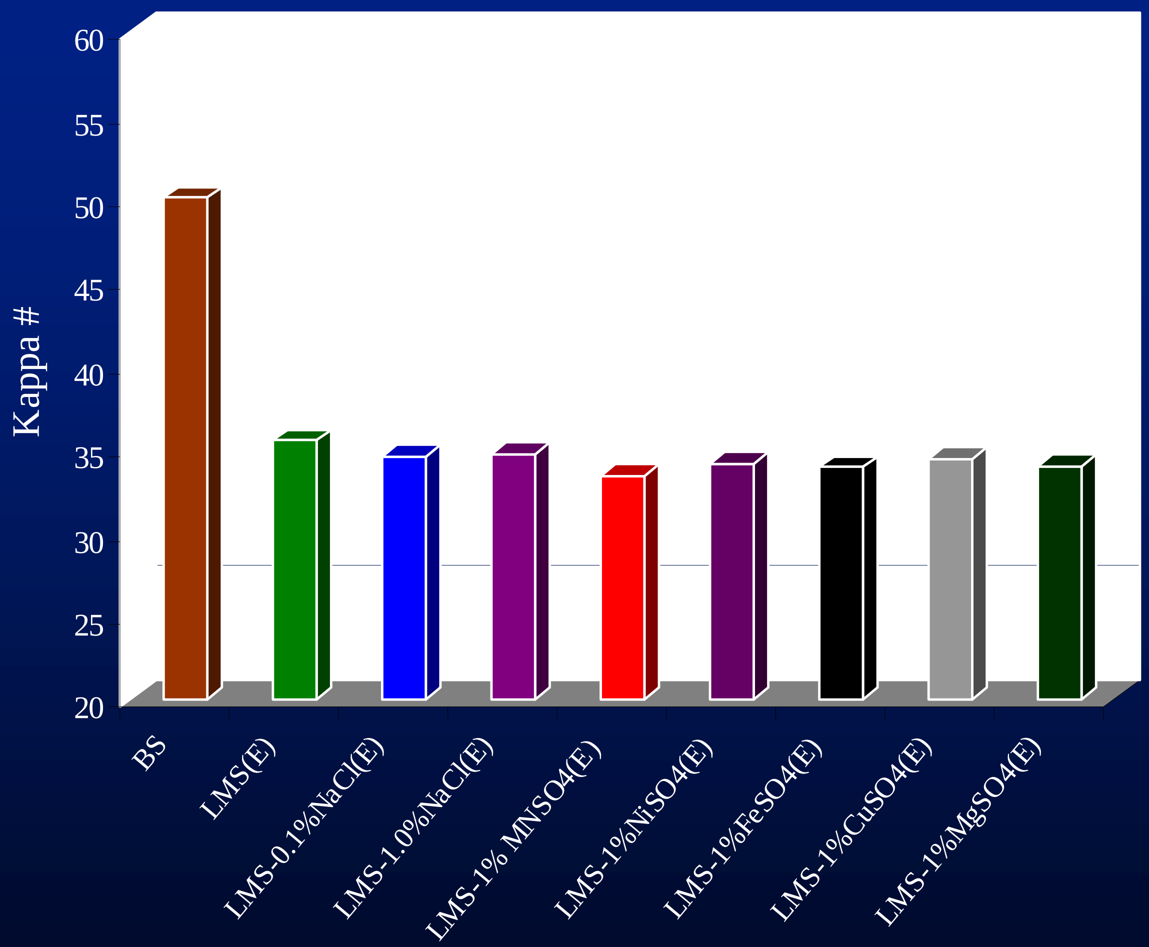
NPE’s on LMS

- Most LMS studies have been preformed using ‘clean systems’
- All kraft pulps and process streams have nonprocesss elements present (Ca, Mg, Fe, Mn, Cu, Ni, etc)

Exp. Design

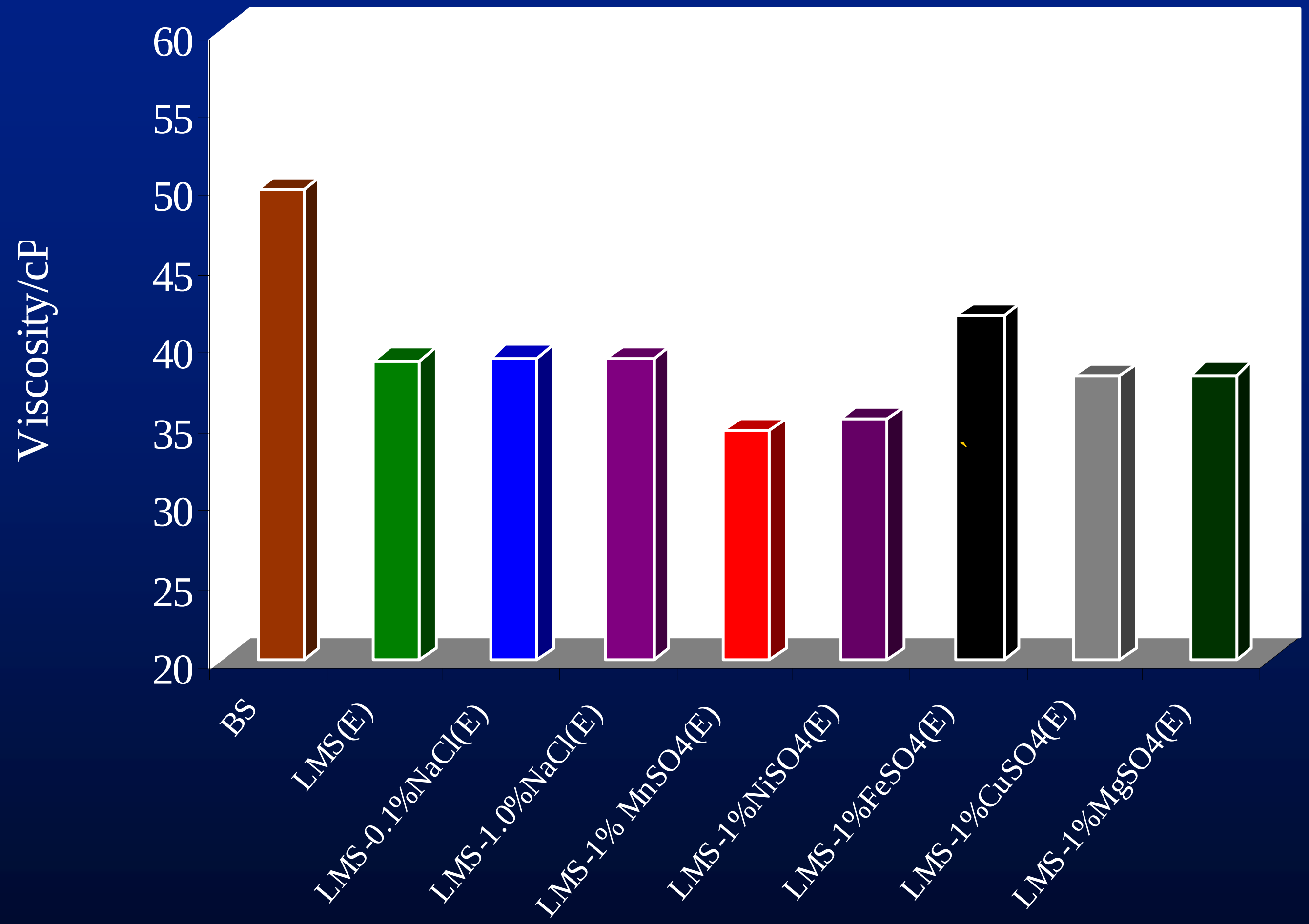
- Perform LMS(E) and repeat with NPEs
- Compare delignification and viscosity properties of biobleached pulps

LMS$_{VA}$ Bleaching: Effects of NPEs



>> no observed NPE impact on delignification

LMS$_{VA}$ Bleaching: Effects of NPEs



>> slight NPE impact on pulp viscosity

LMS_{VA} Bleaching: Effect of Mixing

Objective

Assess the impact of mixing on an LMS stage

Experimental Procedure

Biobleaching Sequence LMS(EPO)

-LMS:Lac: 1.4 x 10^7 U/10 gr pulp, 45 min., 4.5 pH, 4% VA, 120 psi O_2

Quantum reactor, 10% csc, 55^{o}C,

-(E+P+O): 70^{o}C, 1 h, 10% csc, 60 psi, 0.5% H_2O_2, 2.5% NaOH

LMS_{VA} Bleaching: Effect of Mixing

LMS Mixing Conditions: Quantum

A. 600 rpm for 10 sec every 2 min.

B. 1200 rpm for 5 sec every 2 min.

C. 2400 rpm for 2.5 sec every 2 min. [constant refining energy]

Pulp	Kappa #	Viscosity/cP	TAPPI Brightness
Brownstock	33.3	30.4	25.9
A(E+P+O)	14.6	23.6	34.2
B(E+P+O)	14.4	23.2	34.2
C(E+P+O)	14.3	23.1	33.3

LMS_{VA} Bleaching: Effect of Mixing

LMS Mixing Conditions:

D. 600 rpm for 10 sec every 2 min.

E. 3600 rpm for 10 sec every 2 min. [variable mixing energy]

Pulp	Kappa #	Viscosity/cP	TAPPI Brightness
Brownstock	33.3	30.4	25.9
D(E+P+O)	14.2	23.8	32.9
E(E+P+O)	14.0	22.7	32.6

LMS_{VA} Bleaching: Effect of Mixing

LMS Mixing Conditions:

F. 600 rpm for 10 sec every 2 min. – 20% csc (Quantum)

G. 2400 rpm for 10 sec every 2 min. – 20% csc (Quantum)

H. ≈48 rpm- constant – 10% csc (Parr reactor, paddle mixer)

Pulp	Kappa #	Viscosity/cP
Brownstock	33.3	30.4
F(E+P+O)	14.2	22.9
G(E+P+O)	14.1	23.6
H(E+P+O)	16.3	--

Provide efficient mixing is occurring in a LMS-stage, detrimental shear effects were not observed

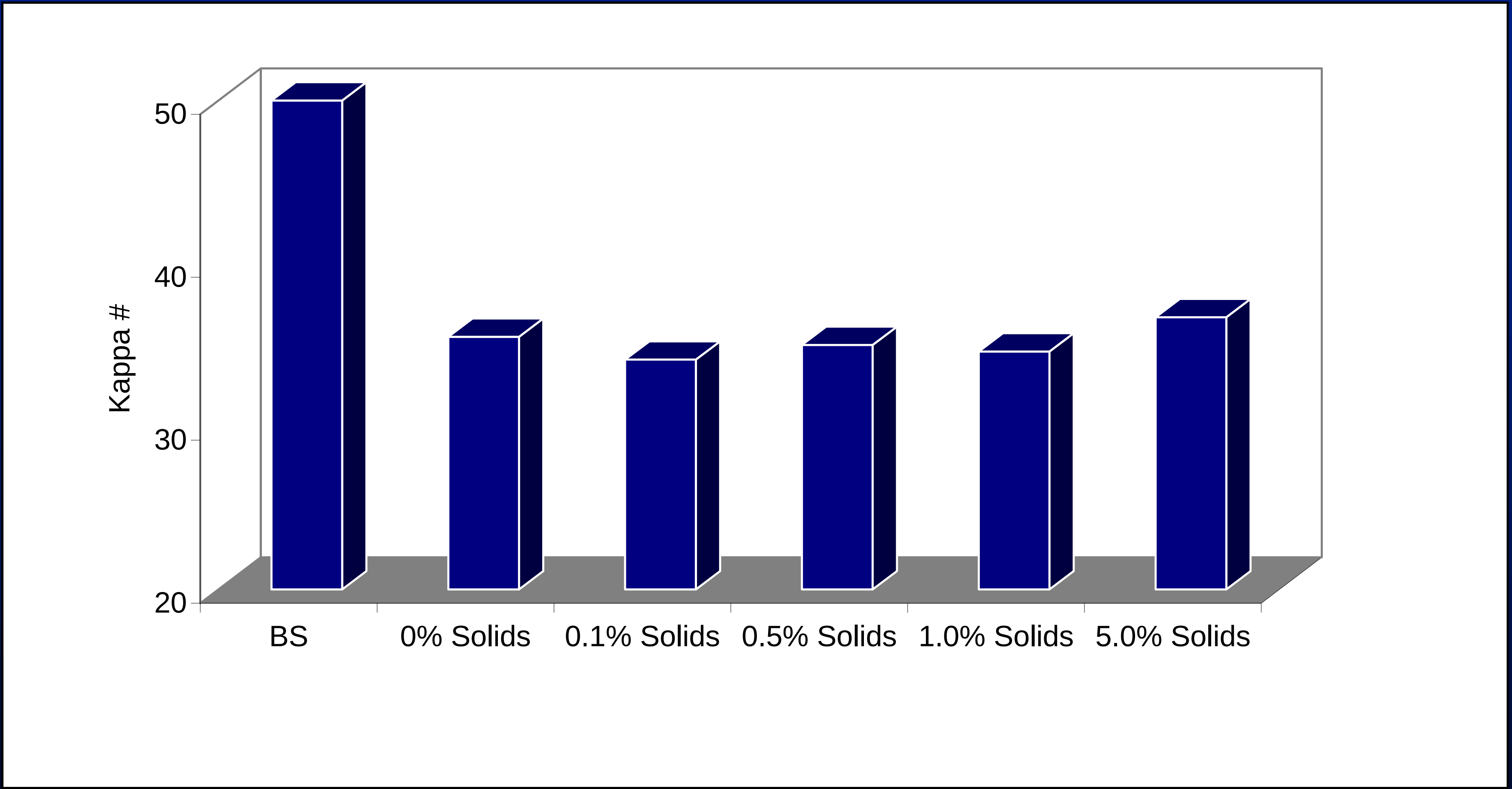
Black Liquor Carryover on LMS

- Most LMS studies have been preformed using ‘clean systems’
- All kraft pulps are delignified in the presence of black liquor carryover and this is know to influence O, D and P.
- Effect on LMS is unknown

Exp. Design

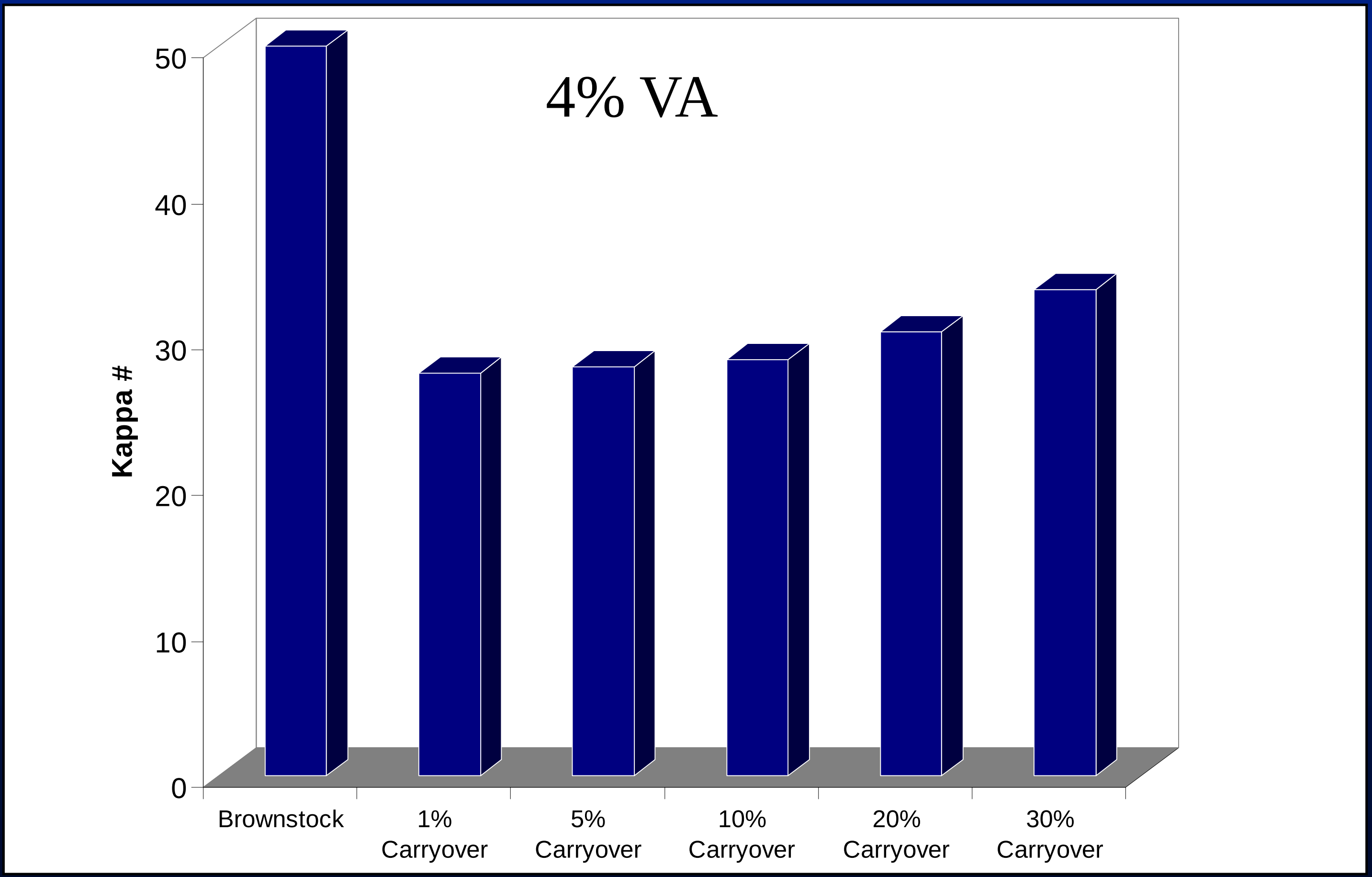
- Perform LMS(E) with and without Black liquor carryover
- Compare delignification and viscosity properties of biobleached pulps

LMS_{VA} Bleaching: Effect of Carryover



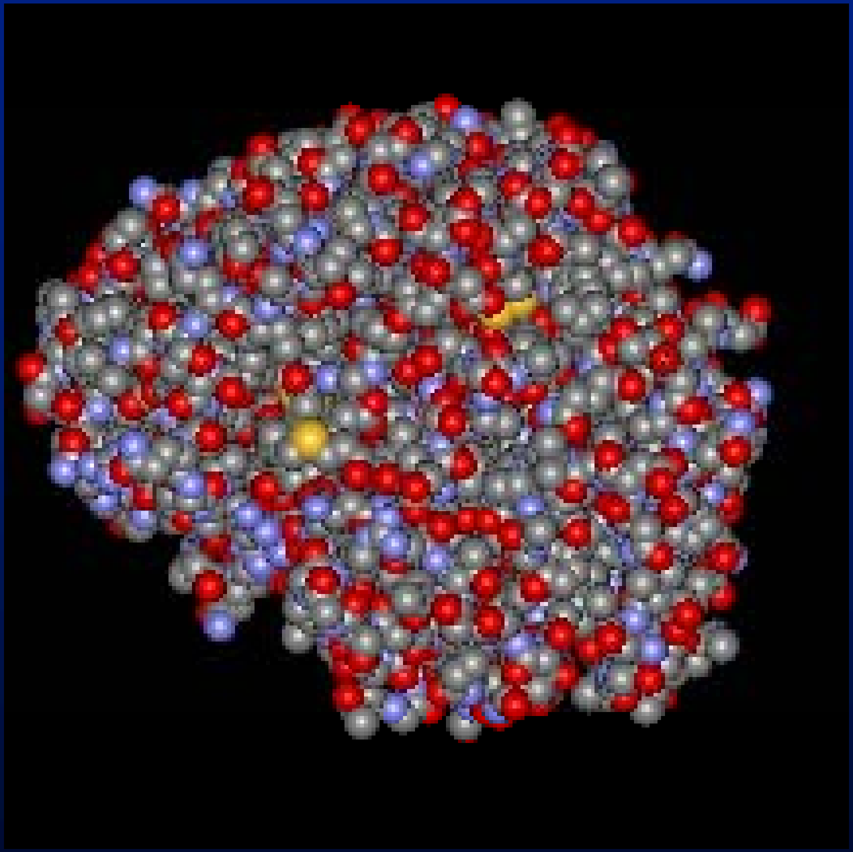
2% charge of VA in LMS_{VA}

LMS_{VA} Bleaching: Effect of Carryover



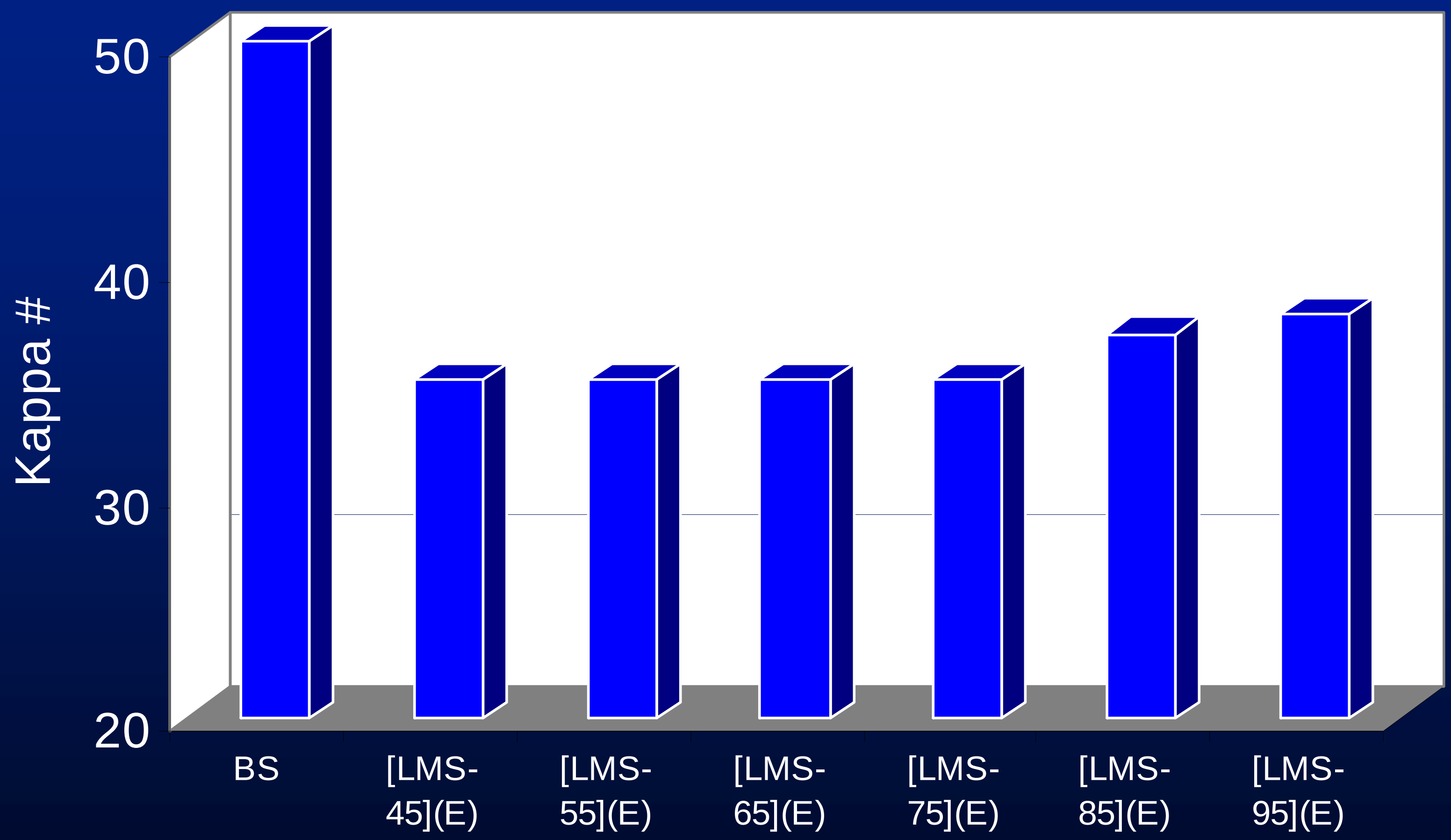
Carryover levels of 10% black liquor solids are not detrimental towards an LMS stage

LMS - BIOBLEACHING



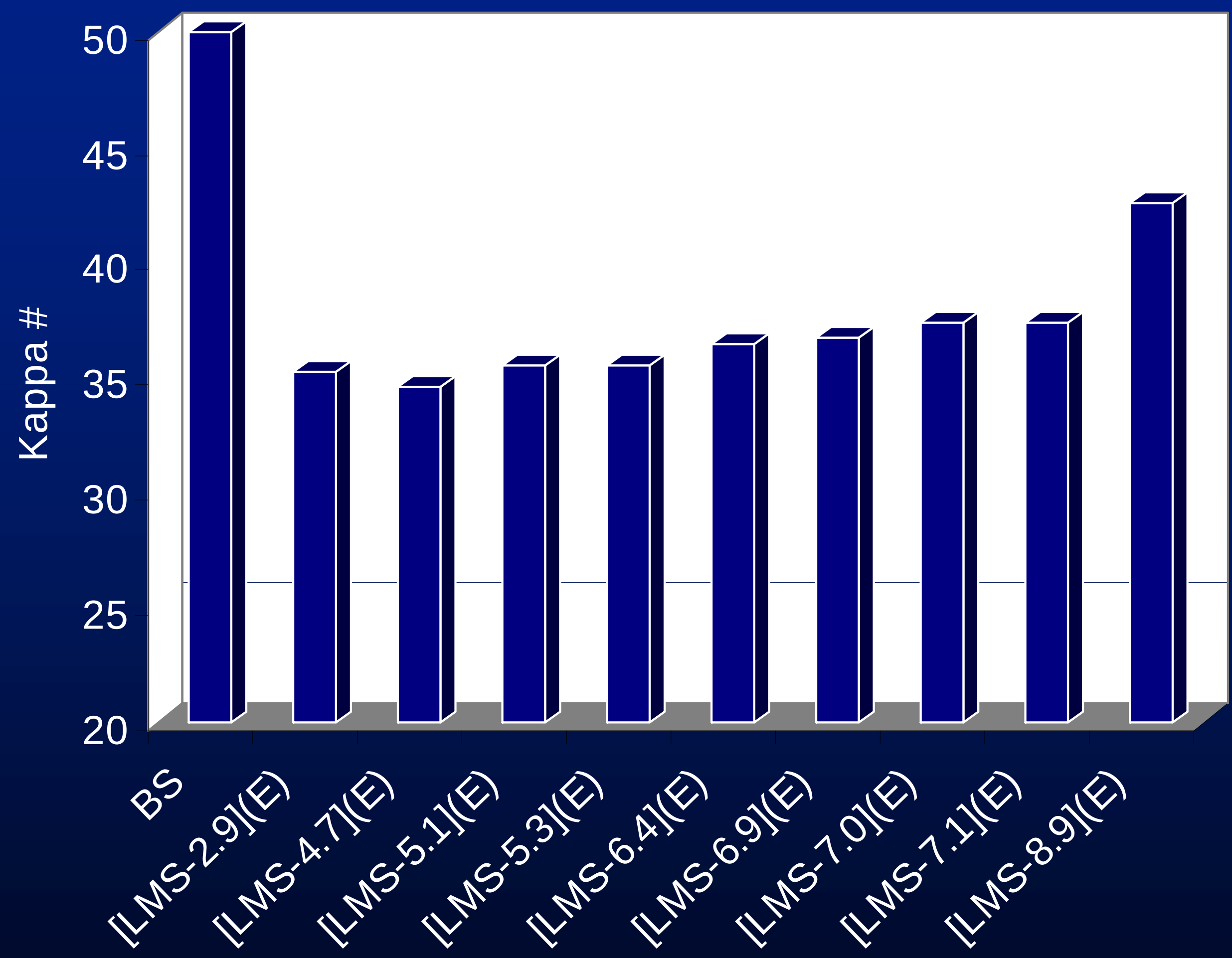
Effect of Temperature – pH on LMS

LMS_{VA} Bleaching: Effect of Temperature



Temperature limitations of laccase employed limited LMS stage to ~20–75^{o}C

LMS$_{VA}$ Bleaching: Effect of pH



pH limitations of laccase employed limit LMS stage to ~ 3 - 5

Laccase Biobleaching: Conclusions/Future

- LMS biodelignification of high kappa pulps is possible and provides distinct yield benefits
- LMS delignified pulps can be bleached to high brightness values
- NPEs have minimal impact on LMS stage
- LMS is not sensitive to shear effects
- LMS is not detrimentally impacted by moderate levels of black liquor carryover

- pH/temperature profiles of LMS need to be improved
- Cost issues surrounding LMS mediator need to be improved

Acknowledgements

U.S. Department of Energy

Member Companies of IPST