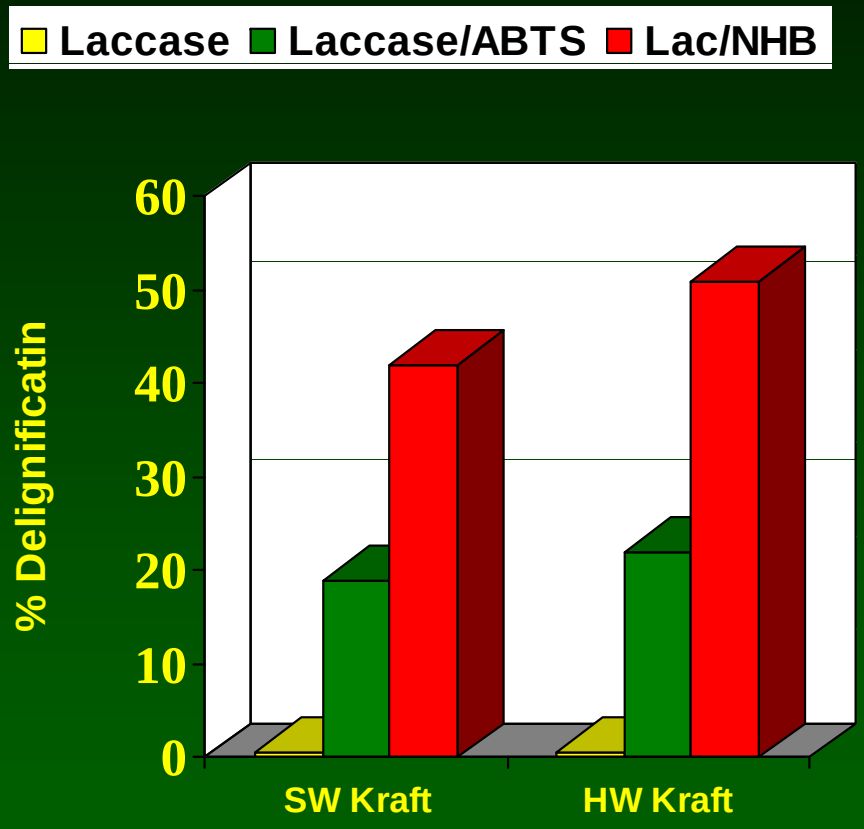
Mill Designed Laccase-Biobleaching Technologies

Project Objectives

The overall objective of this proposal is to develop a selective, catalytic laccase-mediator system (LMS) that will be used to:

1. Delignify high kappa pulps providing distinct yield improvements for bleached kraft grades;
2. Bleach pulps with improved physical properties;
3. Minimize fresh water usage and facilitate overall AOX/COD reductions in bleach effluents.
4. Develop new low operating and capital cost systems to remove lignin.

Project Background

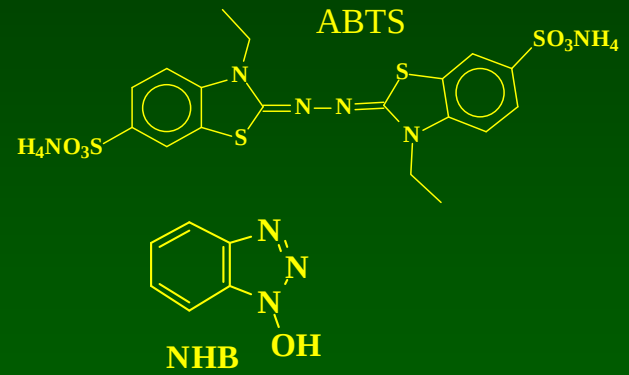


SW kraft: kappa 35 - 15

HW kraft: kappa 18 - 8

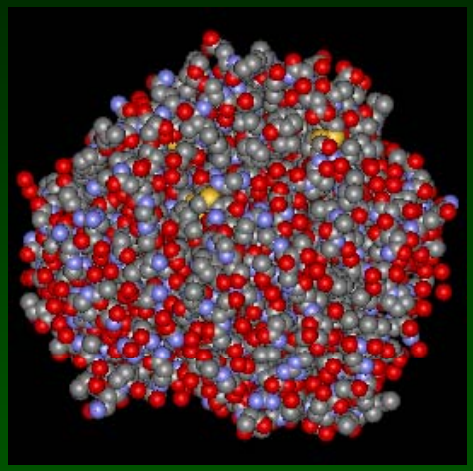
Conditions LMS(E)

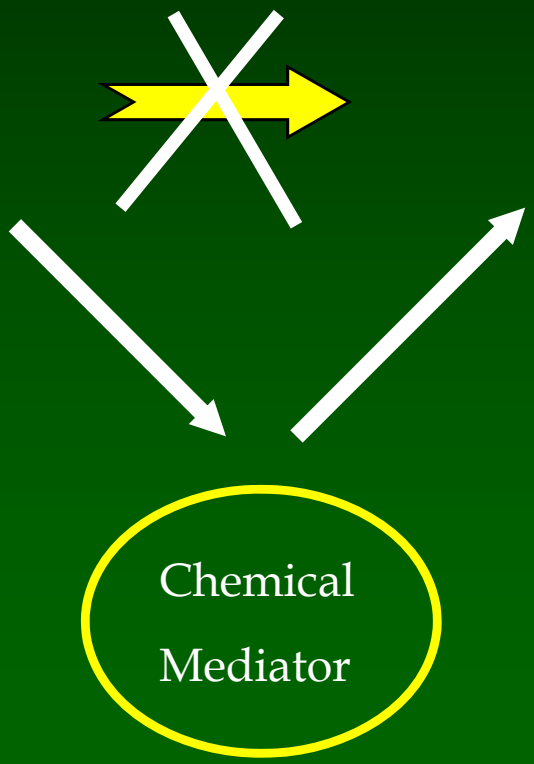
LMS: 45°C, 1-2 h, 5-20% csc, pH 4 - 6, 1-4% mediator

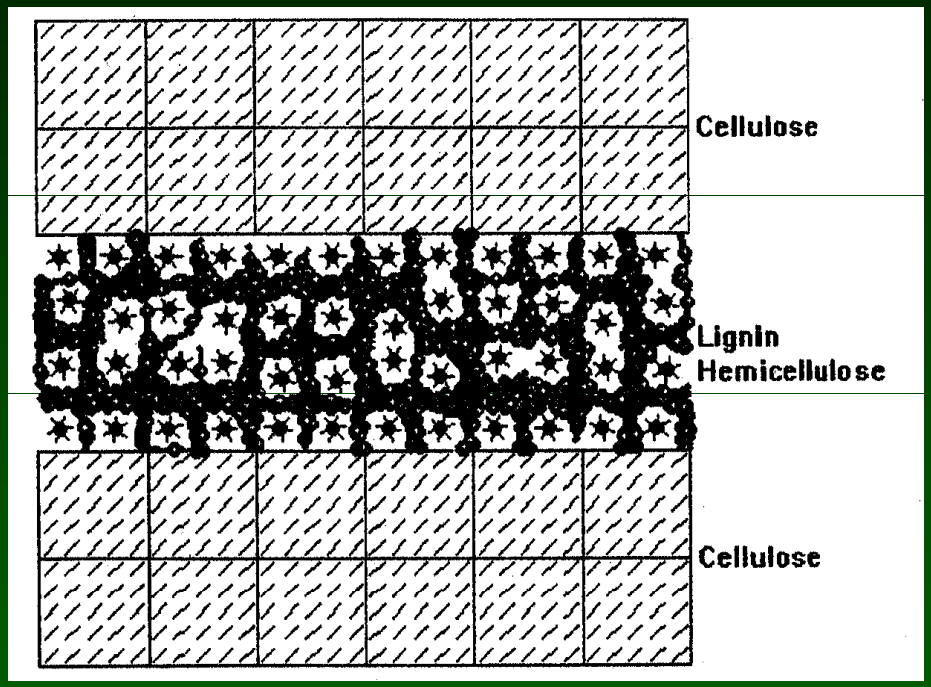


E: 70°C, 1-3 h, 1-2% NaOH

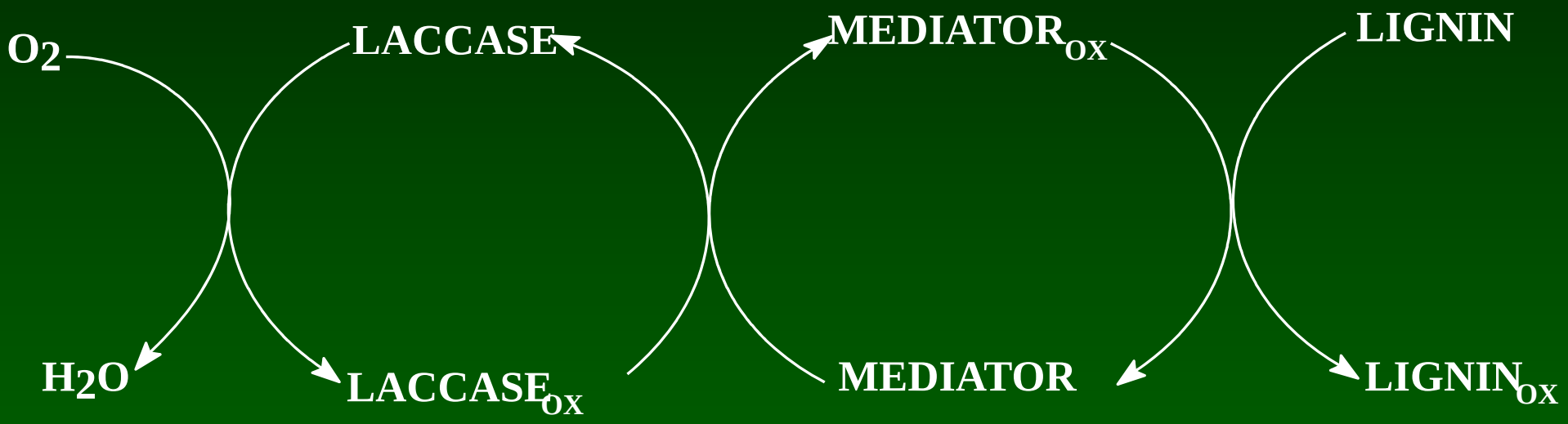
Laccase-Mediator-System







LMS-Process


O2
LACCASE
MEDIATOR ox
LIGNIN
H2O
LACCASE ox
MEDIATOR
LIGNIN ox

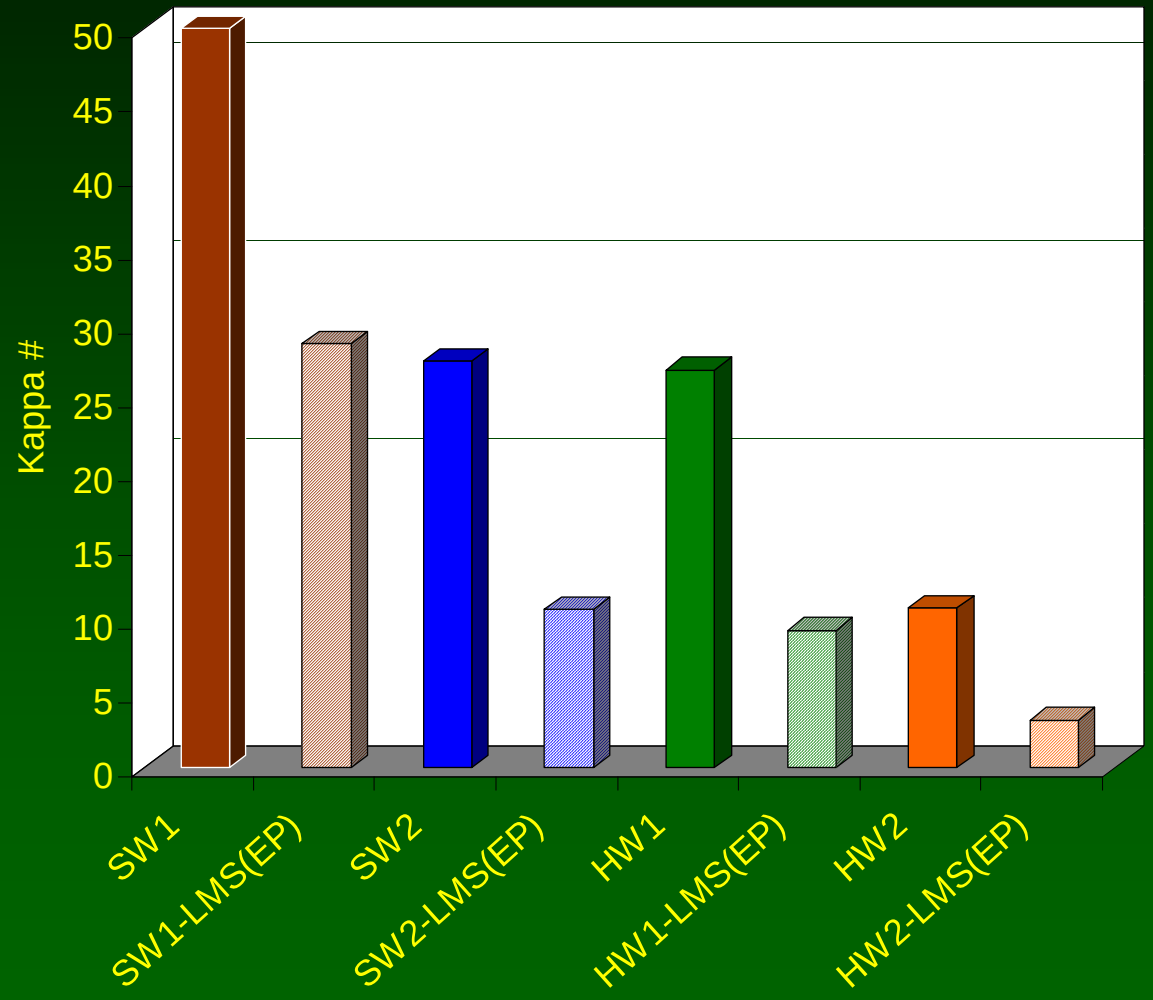
Project Objectives

- CAD-design of new catalytic mediators
  - -organic mediators
  - -inorganic mediators:
- Biobleaching with SW/HW kraft pulps
  - Conventional pulps ≈ 30 for SW; 14 for HW
  - High kappa pulps ≈ 40 for SW; 20 for HW
    - Pulp characterization; yield measurements;
    - Residual lignin structure
- Investigations into iron and manganese based mediators for LMS

Research Focus

- Model laccase/mediator delignification system
- Model mixed mediator systems
- LMS delignification of high and conventional SW kraft pulps with mixed mediator systems
- Examine optimized LMS system under closed-mill operating conditions
- Perform series of controlled bleaching studies using OOD(E+O+P)D & D(E+O+P)DED
- Bleach LMS delignified pulps to high brightness with ClO_2, examine brightness values, strength, AOX/COD of effluents with (LMS)OD(E+O+P)D, (LMS)(LMS)D(E+O+P)D and (LMS)(E+O+P)DED
- Preliminary economic assessment of new LMS system<<

Biobleaching High and Low Kappa 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

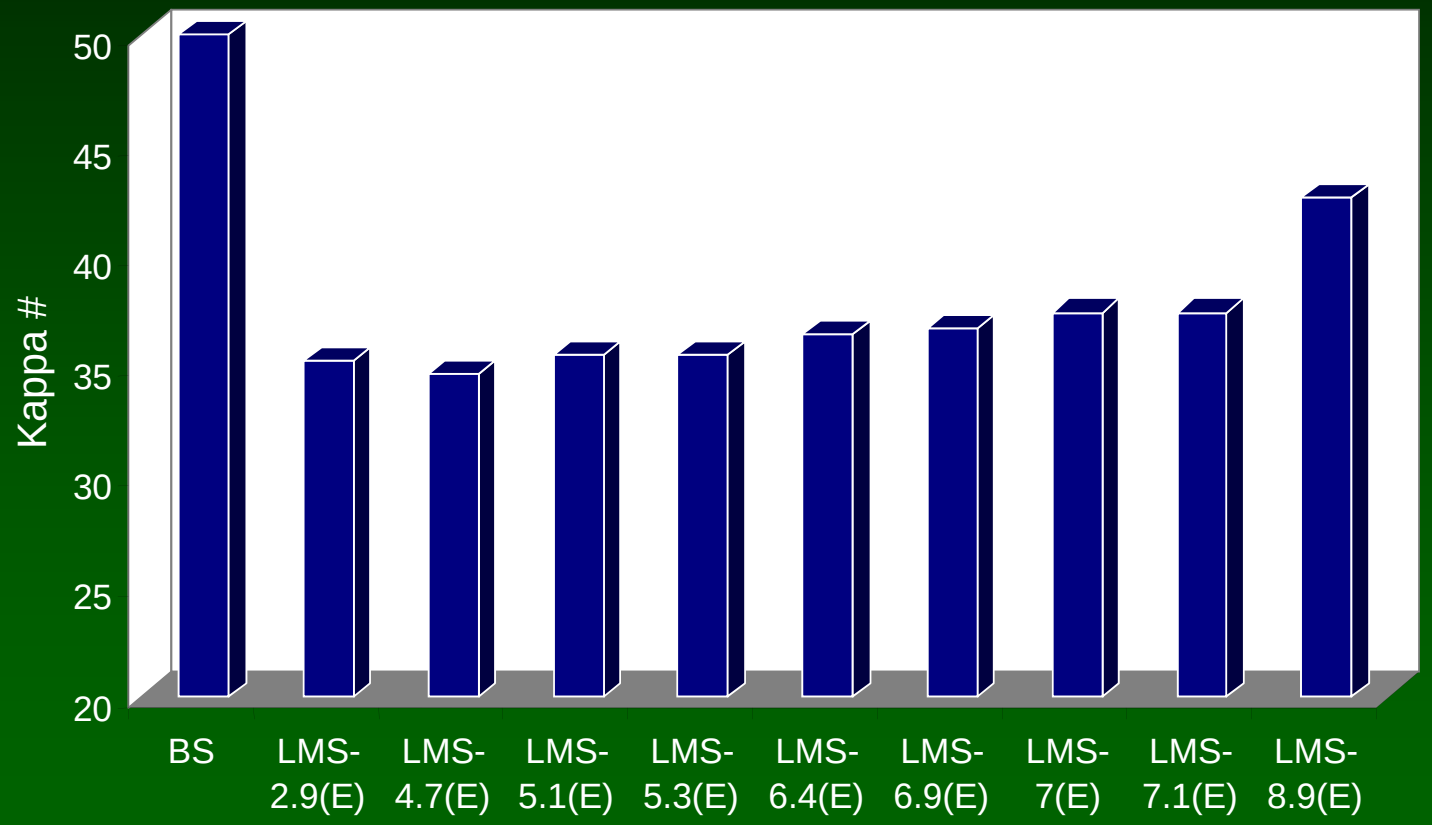
Biobleaching High and Low Kappa Pulps

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

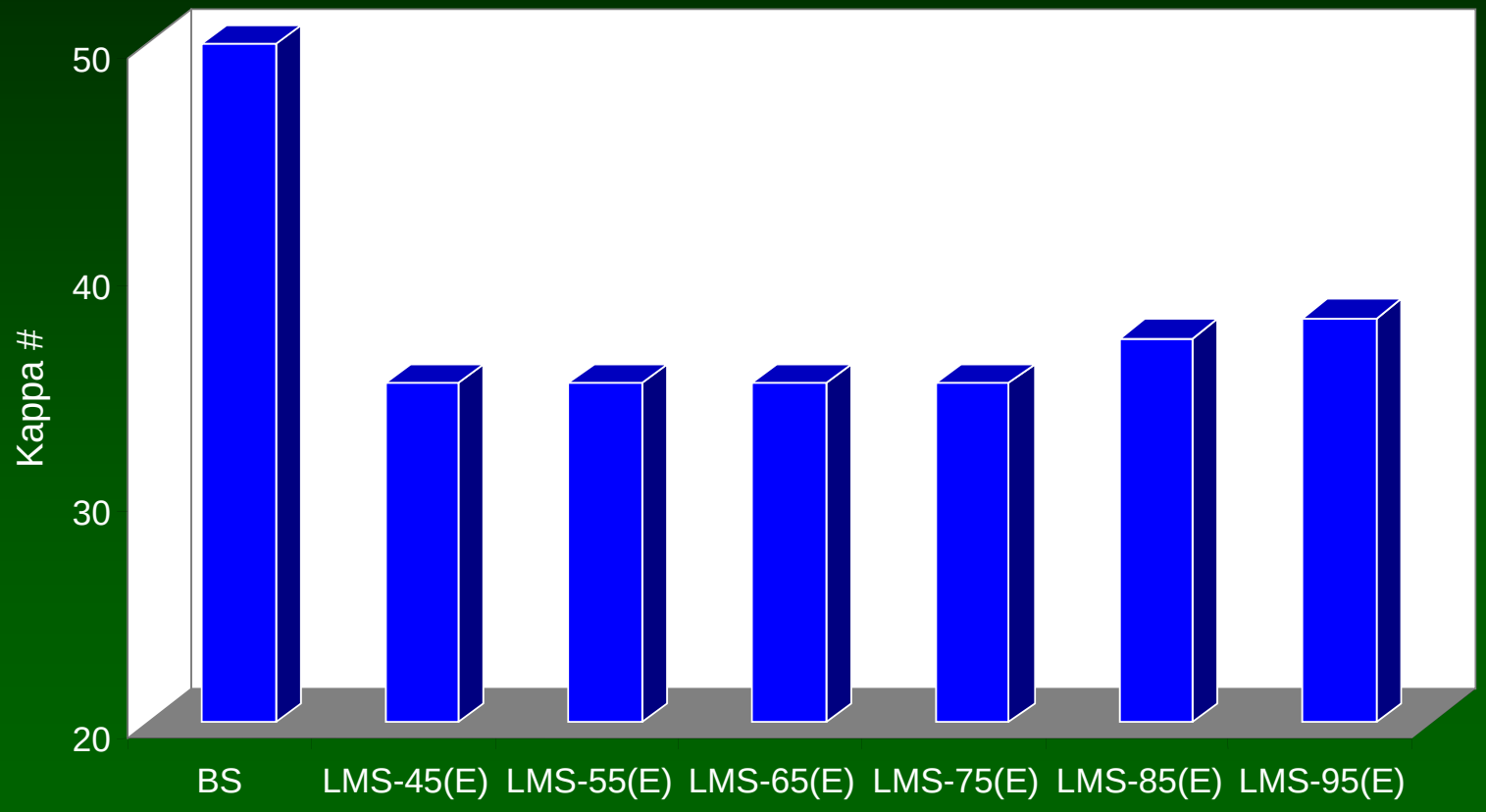
NB: LMS with fully bleached pulp leads to no change in viscosity

[a]kappa primarily hexenuronic acids

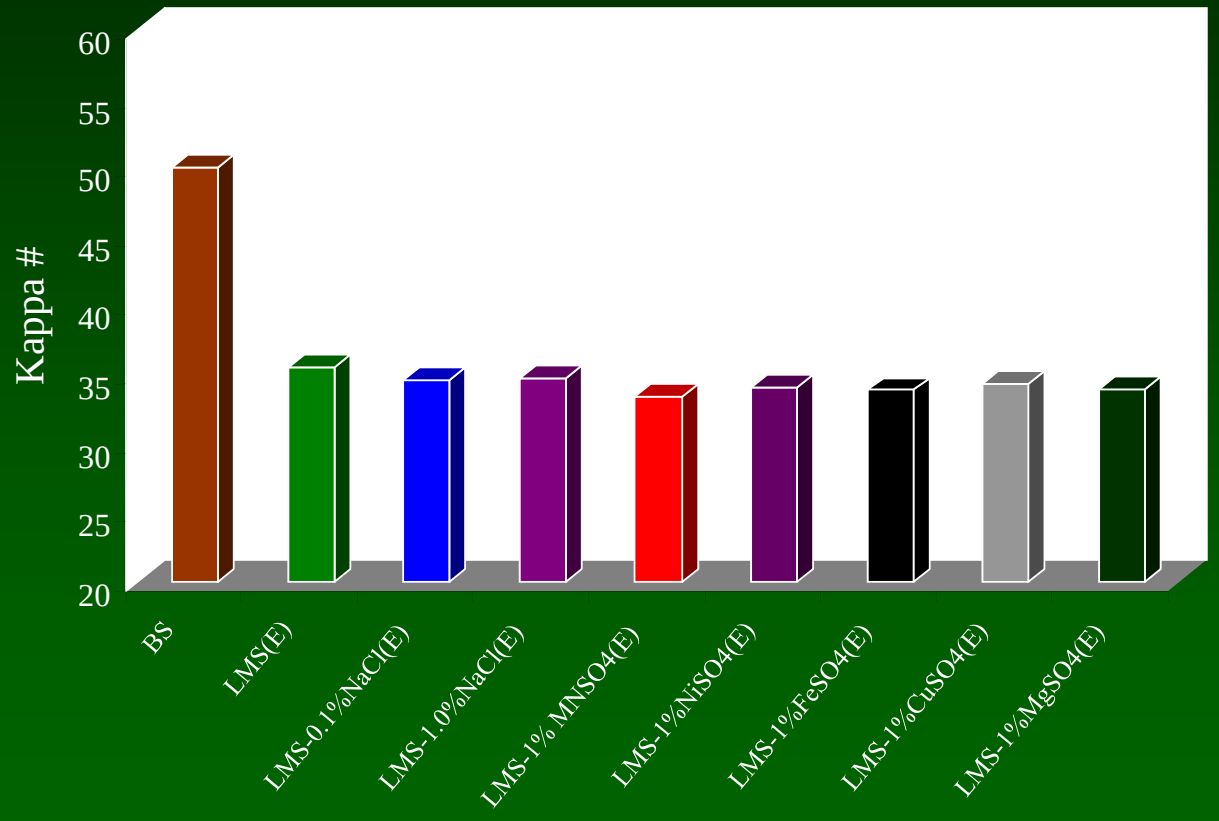
LMS Delignification: Influence of pH



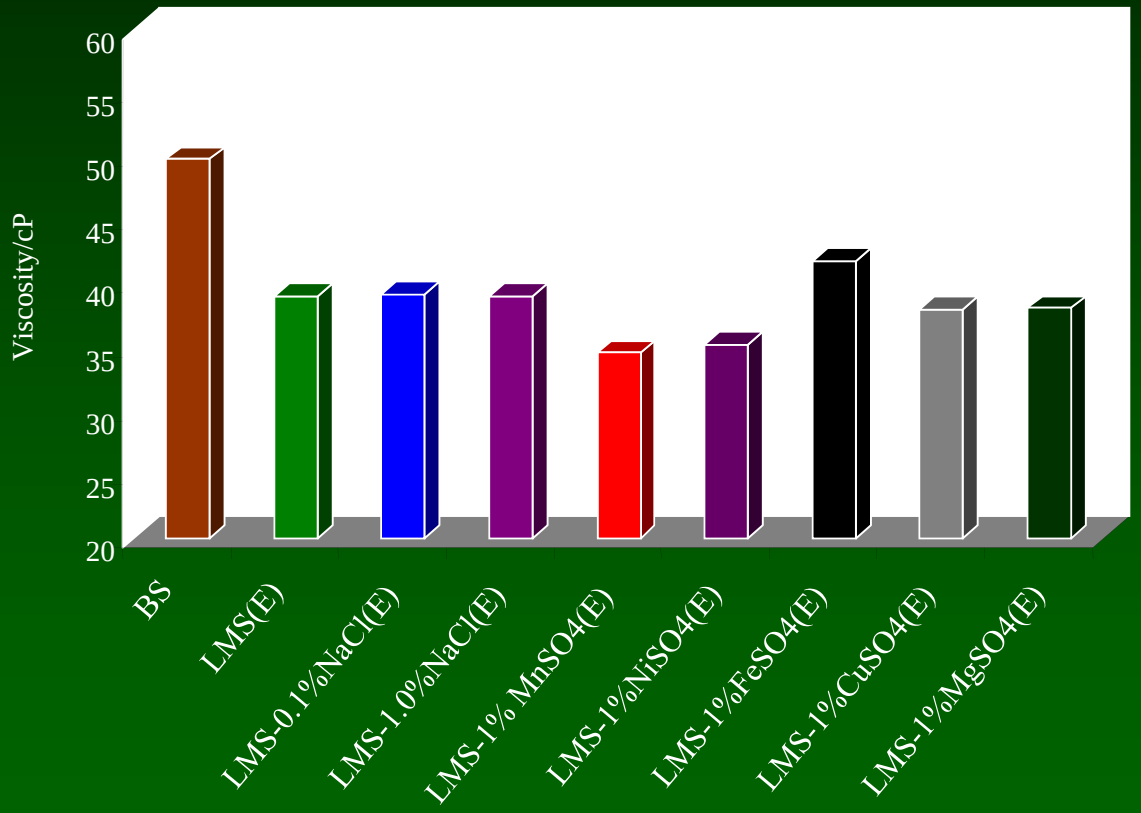
LMS Delignification: Influence of Temperature



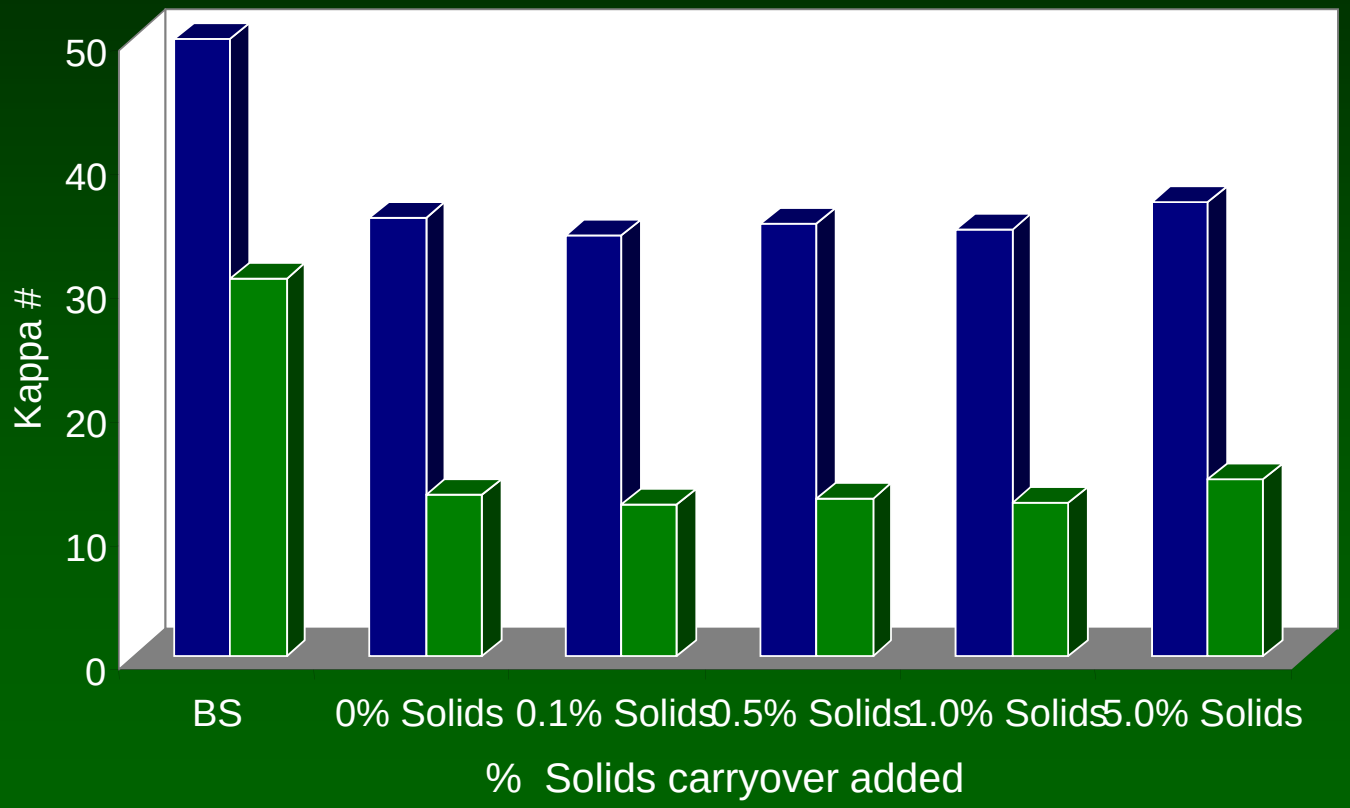
LMS Delignification: Role of NPE



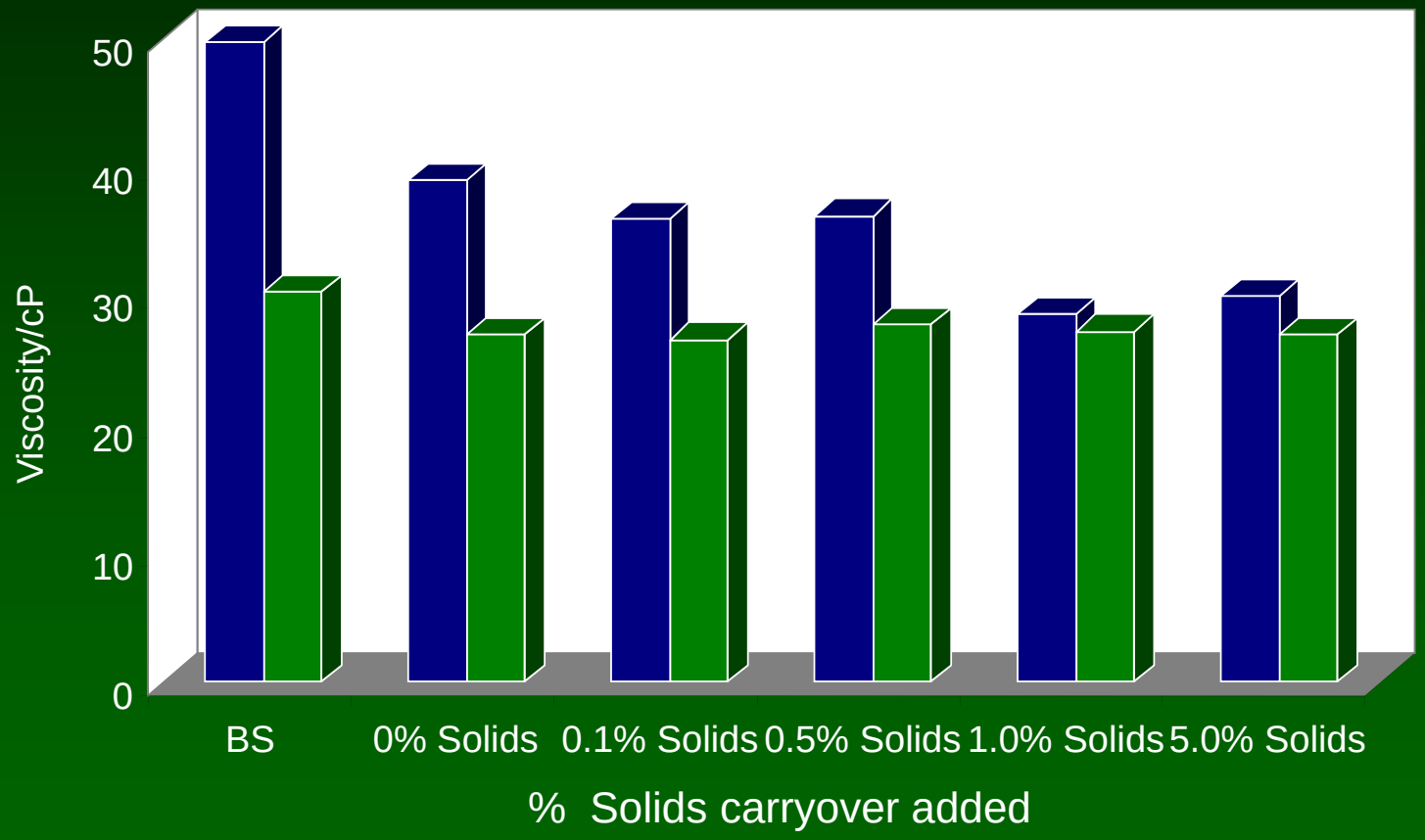
LMS Delignification: Role of NPE



LMS Delignification: Role of Carryover



LMS Delignification: Role of Carryover

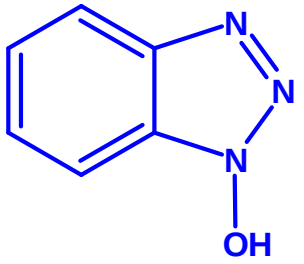


Computational Chemistry on Laccase Mediators

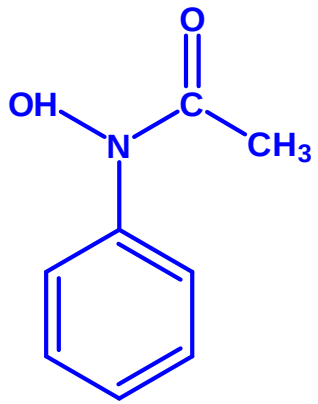
- Among these mediators, violuric acid has been found to the be most effective at delignification of pulps
- Efficacy is not well predicted by a single term
  - Oxidation potential
  - Km/Kcat
- Calculations have been performed to evaluate the electronic and energetic differences that might account for mediator behavior

Computational Chemistry on Laccase Mediators

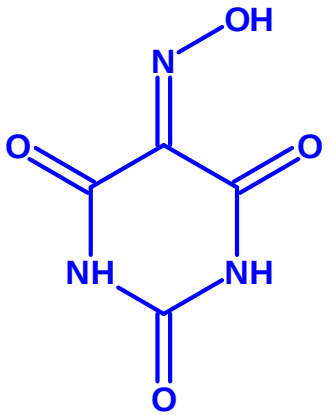
- Newest generation mediators have been examined experimentally
  - Hydroxybenzotriazole
  - NHA
  - Violuric Acid



HBT



NHA

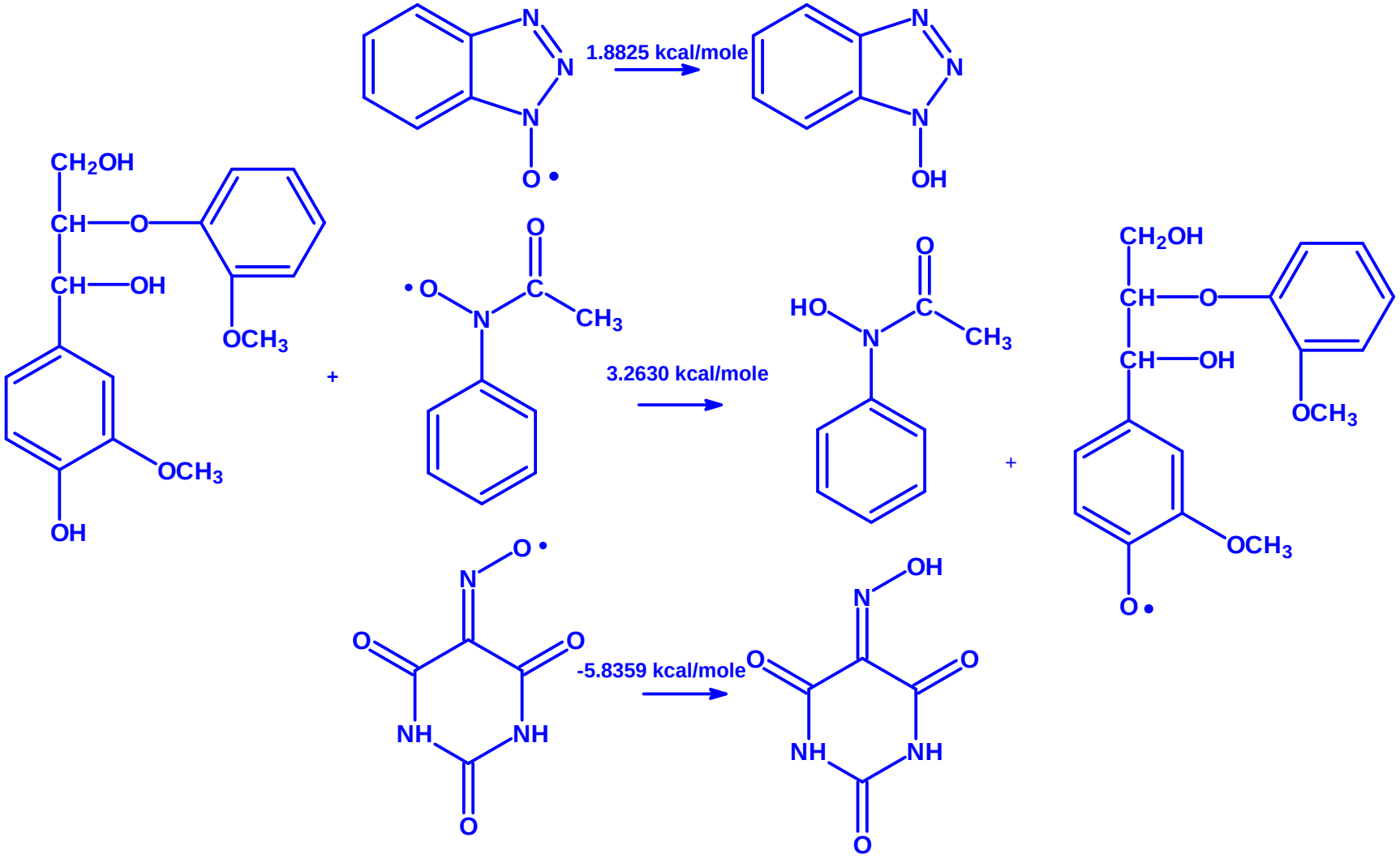


violuric acid

Computational Chemistry on Laccase Mediators

- Computational methods
  - Reactions of mediator radicals with β-O-4 lignin model compound
  - 3-21G* ab initio calculations
  - Geometry optimizations
  - UHF (unrestricted Hartee-Fock) calculations for radicals
  - Gaussian 98

Computational Chemistry on Laccase Mediators



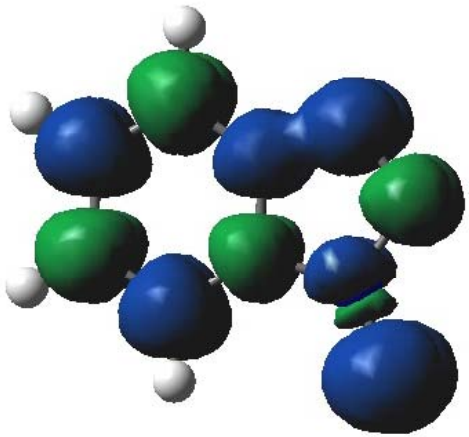
Computational Chemistry on Laccase Mediators

- The reduction of violuric acid is exothermic
- The reductions of HBT and NHA are endothermic

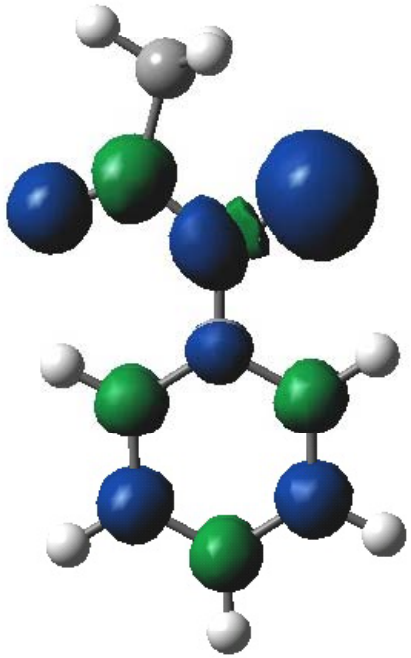
Computational Chemistry on Laccase Mediators

Spin density

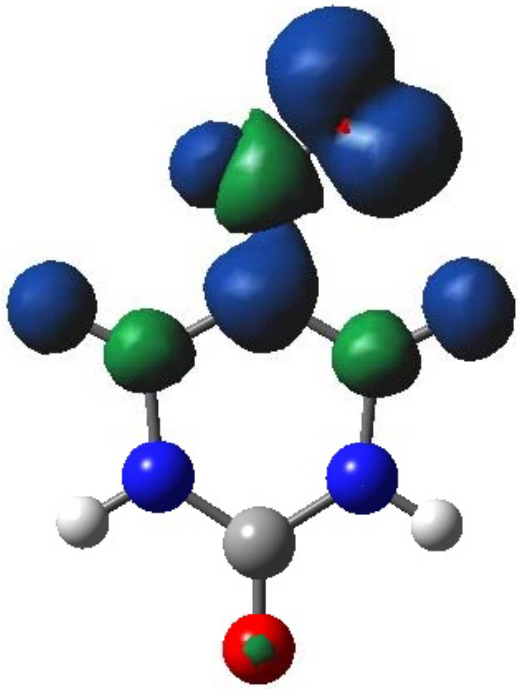
HBT



NHA



Violuric acid



Computational Chemistry on Laccase Mediators

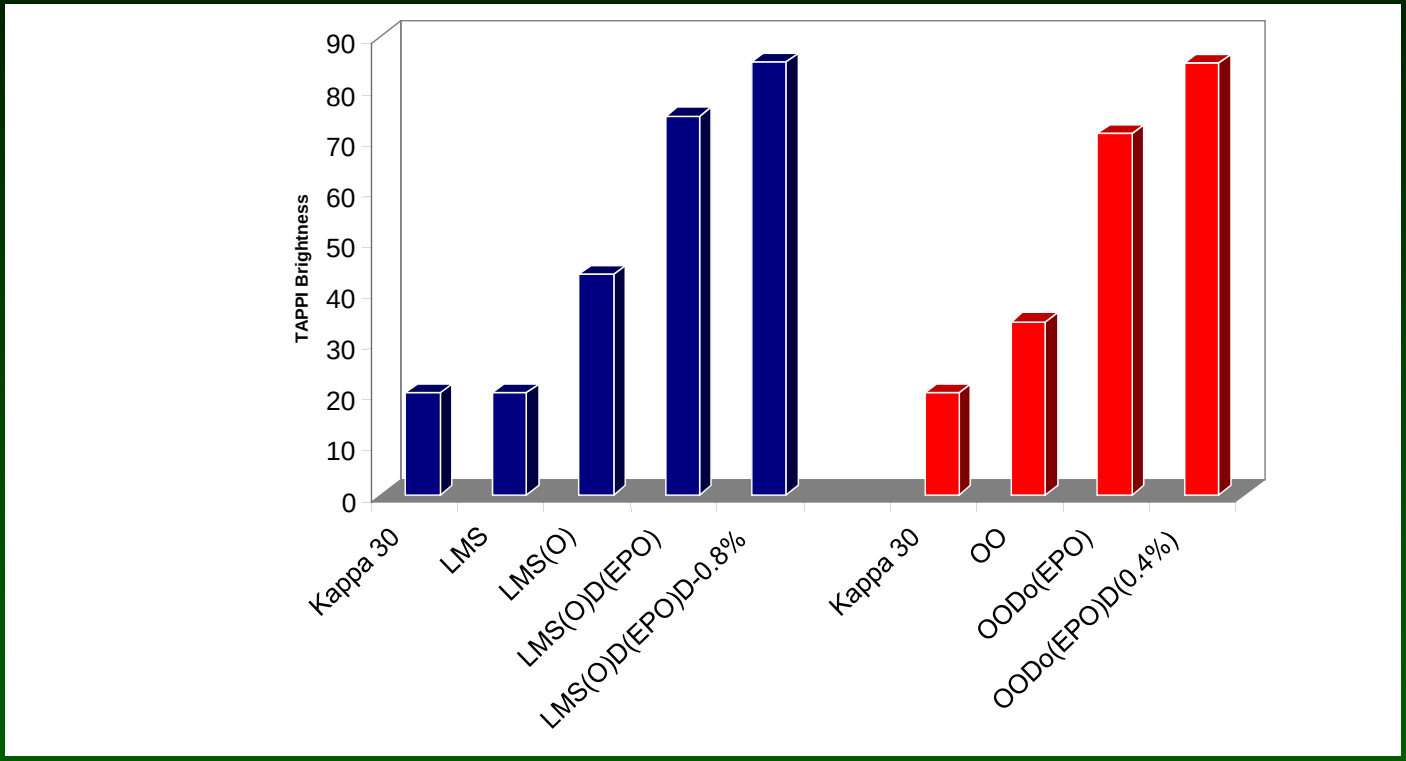
- Spin density (unpaired electron density) is greatest on the oxygen of violuric acid (0.98), followed by NHA (0.92) and HBT (0.91)
- This trend is consistent with the reduction in kappa numbers
- Mulliken charges at oxygen
  - Violuric acid=-0.097
  - HBT=-0.146
  - NHA=-0.158
  - The violuric acid may be less repellant toward the addition of an electron than the others

Computational Chemistry on Laccase Mediators

Accomplishments

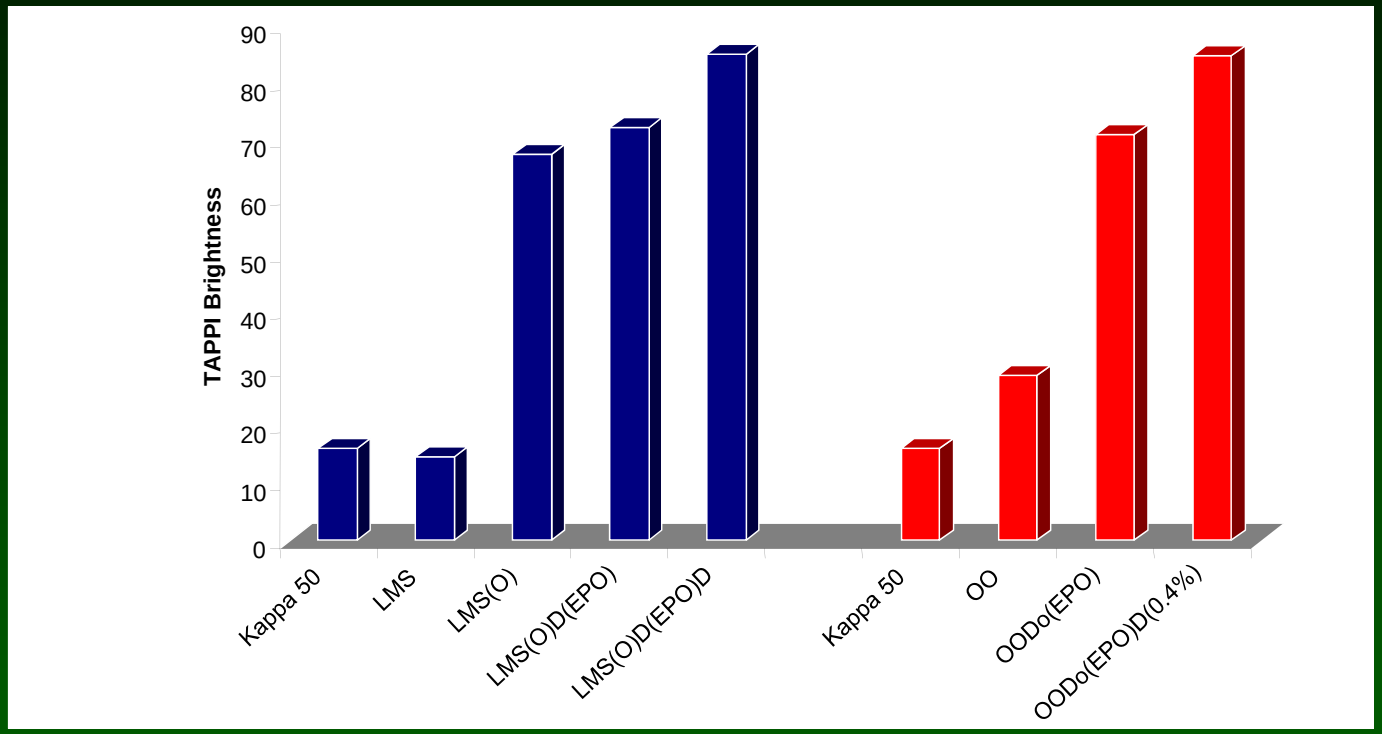
- Identified fundamental properties that may contribute to the improved performance of VA
    - Spin density
    - Mulliken charges
    - Electrostatic repulsion
- Insight provides new opportunities

LMS Bleaching Sequence Studies



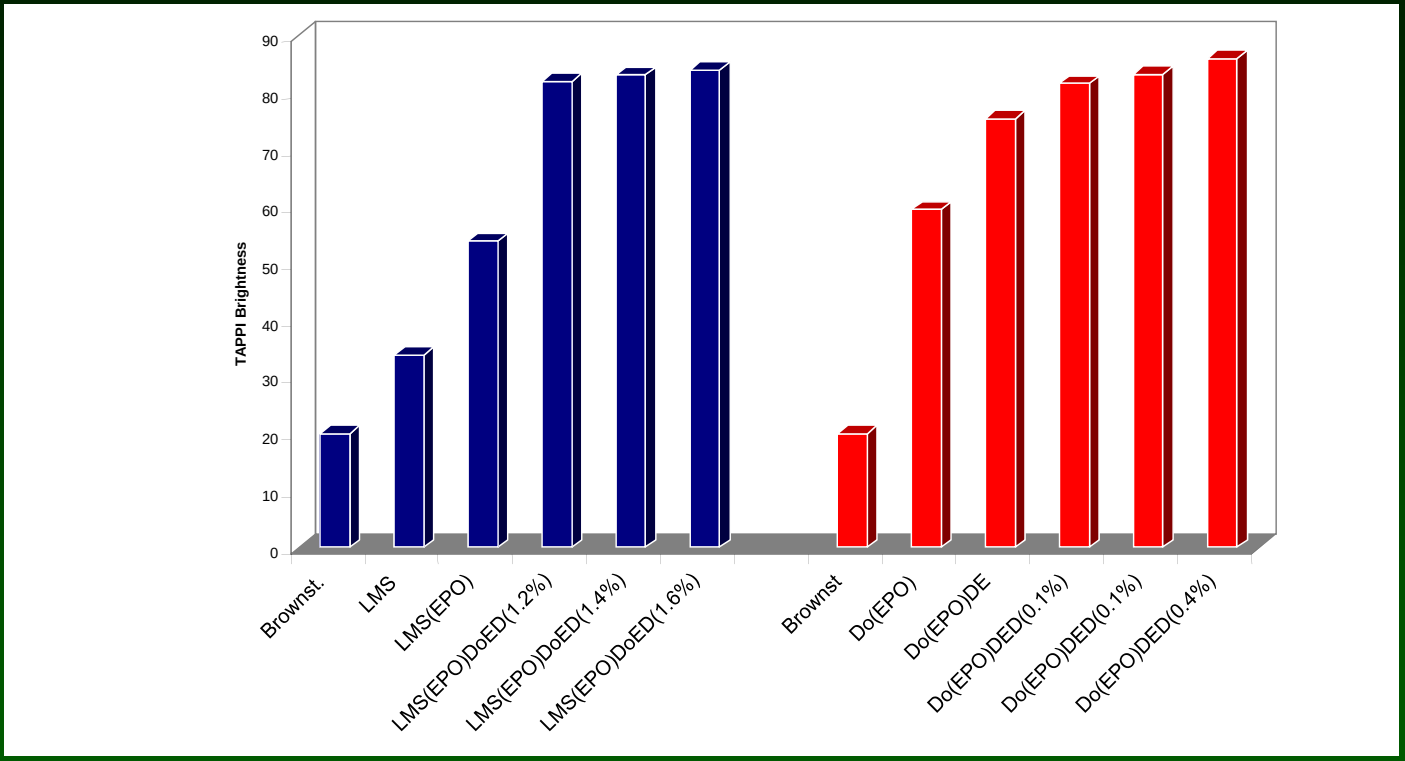
Bl. Pulp	PFI(revs)	Index:	Tensile	Tear	Burst
OO	0/2000/4000		23.9/80.3/87.9	15.2/12.2/11.0	1.6/6.3/6.8
LMS(O)	0/2000/4000		24.4/80.4/87.2	16.6/12.8/10.5	1.5/6.2/6.8

LMS Bleaching Sequence Studies



Seq.	PFI(revs)	Index:	Tensile	Tear	Burst
OO	0/2000/4000		41.1/98.5/104.4	19.1/13.4/11.4	3.3/8.5/9.4
LMSOD(EPO)D	0/2000/4000		45.2/98.8/103.5	20.0/12.7/11.5	3.2/8.0/9.0

LMS Bleaching Sequence Studies



Seq.	PFI(revs)	Index:	Tensile	Tear	Burst
ECF	0/2000/4000		15.7/69.4/75.4	12.4/18.4/15.8	0.8/6.0/6.7
LMS	0/2000/4000		22.8/77.6/87.6	13.9/14.5/11.5	1.4/6.2/6.8

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