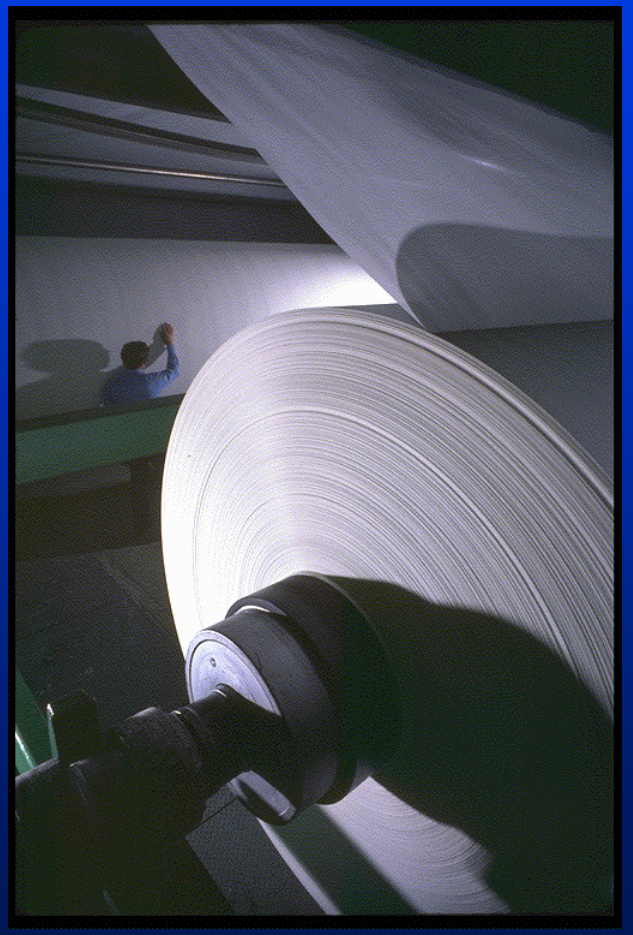
Hydrogen Peroxide Bleaching Highlights

State of the Art and
Research Direction

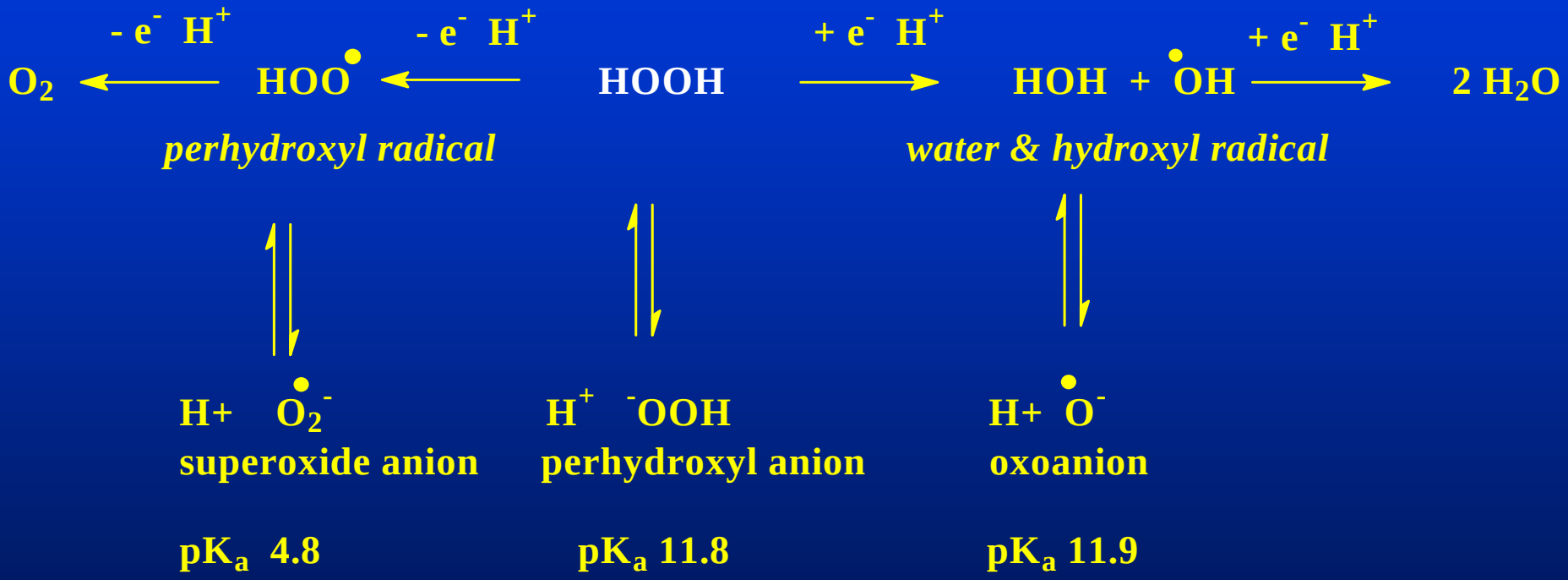
Art J. Ragauskas

Hydrogen Peroxide Bleaching

- Background
- Mill Applications
- Research Directions



Peroxide Bleaching: Background



-active bleaching species is HOO^- and derivatives

Peroxide Bleaching: Background

$H_2O_2 + M \rightarrow HO\cdot + HO^- + M^+$

$H_2O_2 + HO^- \rightarrow HO_2^- + H_2O$

$HO_2^- + M^+ \rightarrow HO_2\cdot + M$

$HO_2\cdot + HO^- \rightarrow O_2^{-\cdot} + H_2O$

$O_2^{-\cdot} + M+ \rightarrow O_2 + M$

$O_2^{-\cdot} + HO\cdot \rightarrow O_2 + HO^-$

$2O_2^{-\cdot} + H_2O \rightarrow O_2 + HO_2^- + HO^-$

$HO\cdot + HO_2^- \rightarrow H_2O + O_2^{-\cdot}$

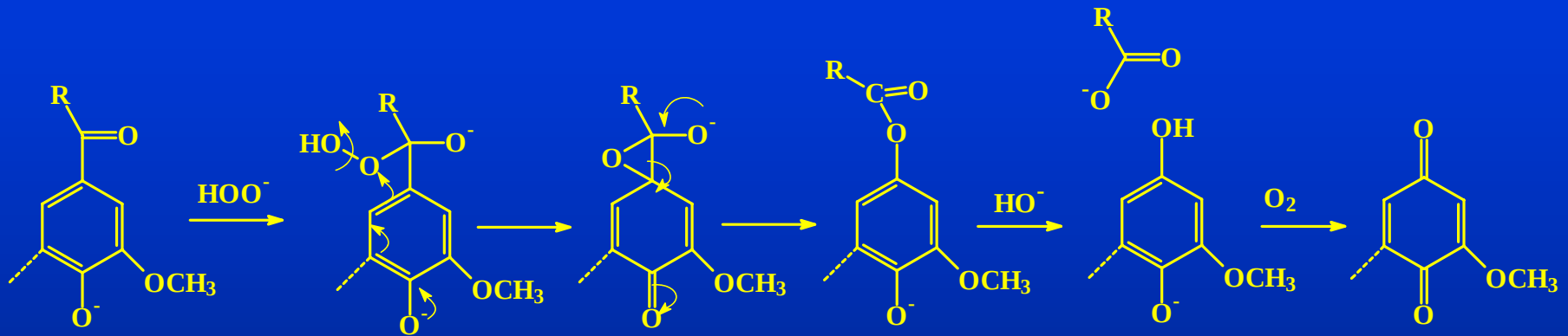
$HO\cdot + M \rightarrow HO^- + M^+$

$HO\cdot + HO\cdot \rightarrow H_2O_2$

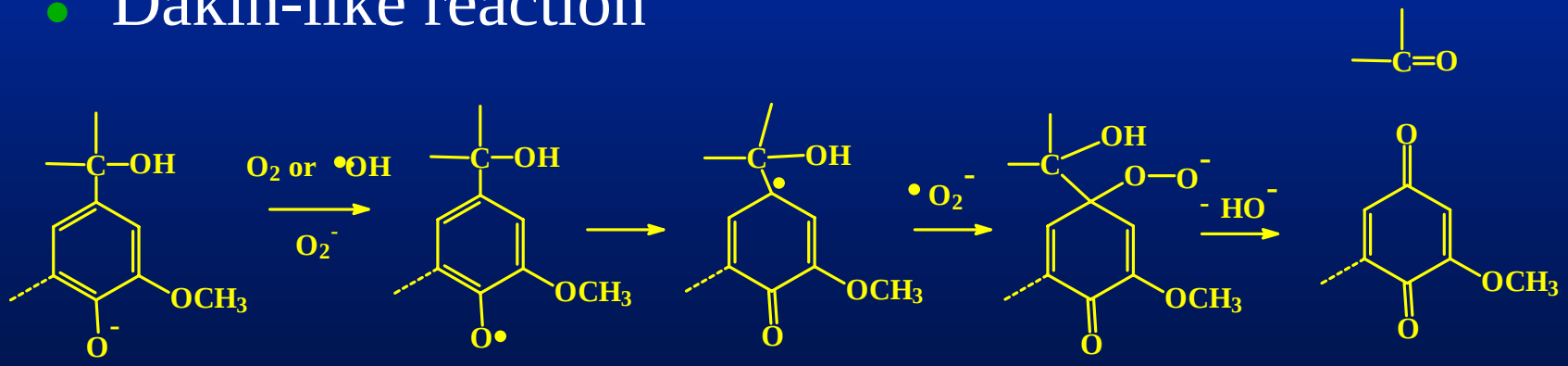
Peroxide chemistry strongly influenced by metals

Peroxide Bleaching: Background

- Dakin reaction



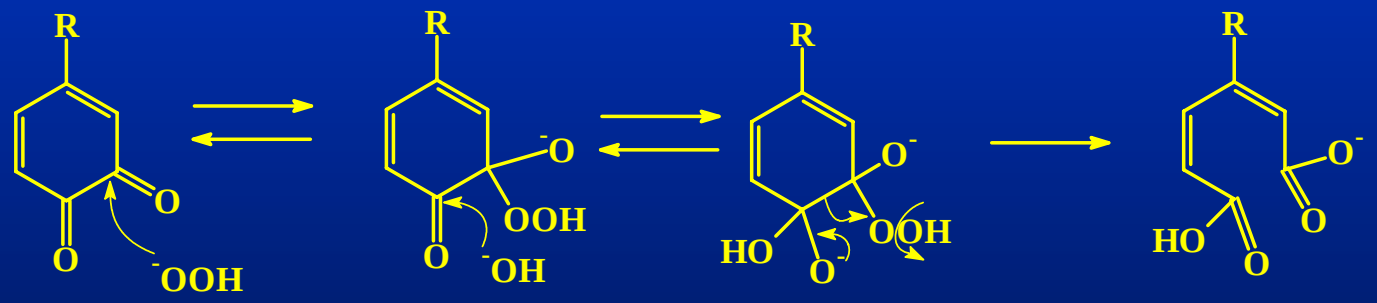
- Dakin-like reaction



Lignin fragmentation reactions

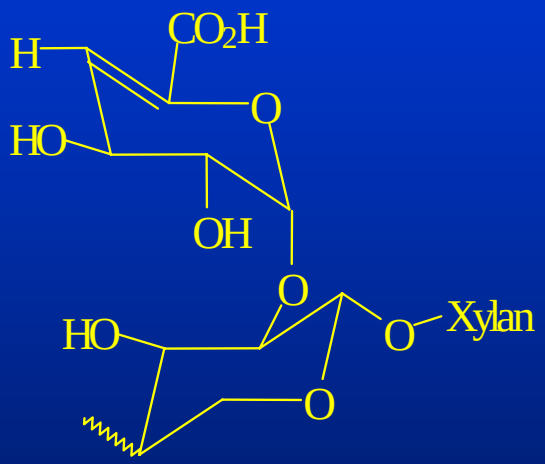
Peroxide Bleaching: Background

- Addition to quinone structures



Destruction of color bodies

Peroxide Bleaching: Background



$H_2O_2/NaOH$ → **NR**

Formed during pulping

- 30 -50% of Southern HW Kappa #
- 10 - 20% of Southern SW Kappa #

Peroxide: Mill Applications

Eop

- Peroxide 0.1 - 0.5%
- Temp.: 55 - 85^{o}C
- Time: 50 - 134 min
- O_2: 0.5 - 0.7%$_{consumed}$
- first extraction stage
- P is largely brightening chemistry

- Ep
  - Peroxide: 0.1 - 0.2%
  - Temp. 65- 85^{o}C
  - Time: 45 - 120 min.
  - second extraction stage
  - Brightening chemistry
- *P*
  - *Peroxide: 0.5 - 1.5%*
  - *Temp. 65- 85^{o}C*
  - *Time: 45 - 120 min.*

Peroxide: Mill Applications

- PO
  - Requires pre Q-stage
  - Peroxide: 0.5 - 3.0%
  - Temp: 100 - 110^{o}C
  - Time: 60 - 120 min
  - O_2: 75 - 120 psi
  - Stabilizer
  - Brightening & delignifying
- P_{HT}
  - Pre Q stage preferred
  - Peroxide 0.5 - 3.0%
  - Temp.
    - 105 - 110^{o}C for 5-15 min
    - 90 - 98^{o}C for 180 - 240 min
  - O_2: 70 - 120 psi
  - Stabilizer
  - Brightening & delignifying

Peroxide: Mill Applications

- North America
  - Primarily ECF
    - D(Eop)DED
    - D(Eop)DEpD,
    - OD(Eop)D or OD(Eop)DEpD
    - D(Ep)DED

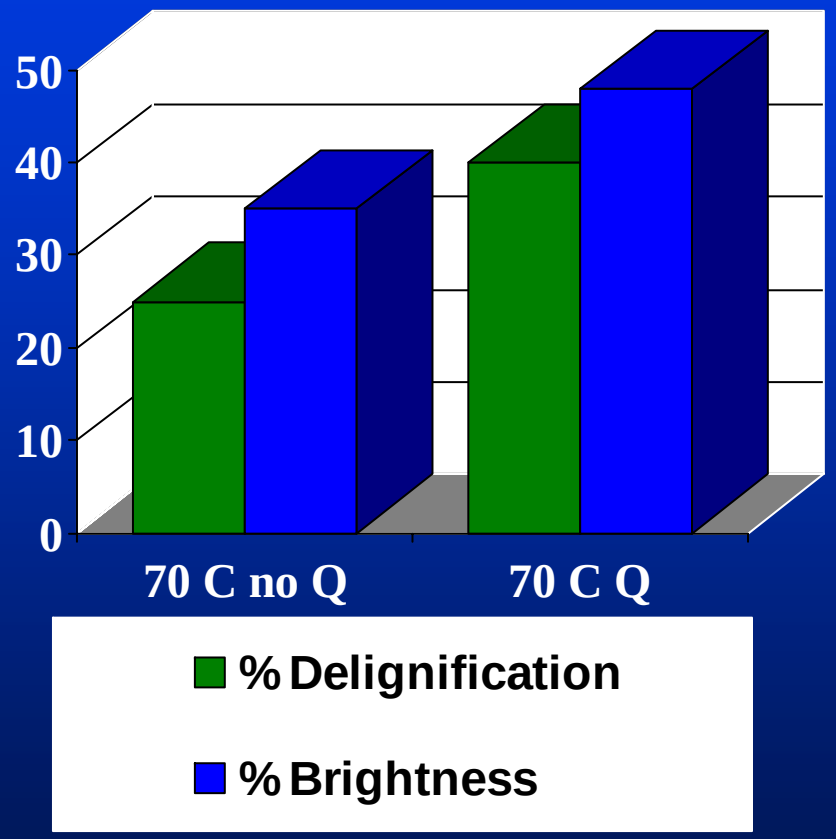
    - HD storage (0.1 - 0.2% P, pH approx. 9)

P-Stage Mill Applications

- Europe
  - Greater bleaching sequence diversity in ECF & TCF
    - OD(Eop)DED
    - O/OD(Eop)DP
    - OQ(Op)PaaQ(PO)
    - ODQ(PO)
    - OAZQ(Eop)(PO)
    - OQPZP

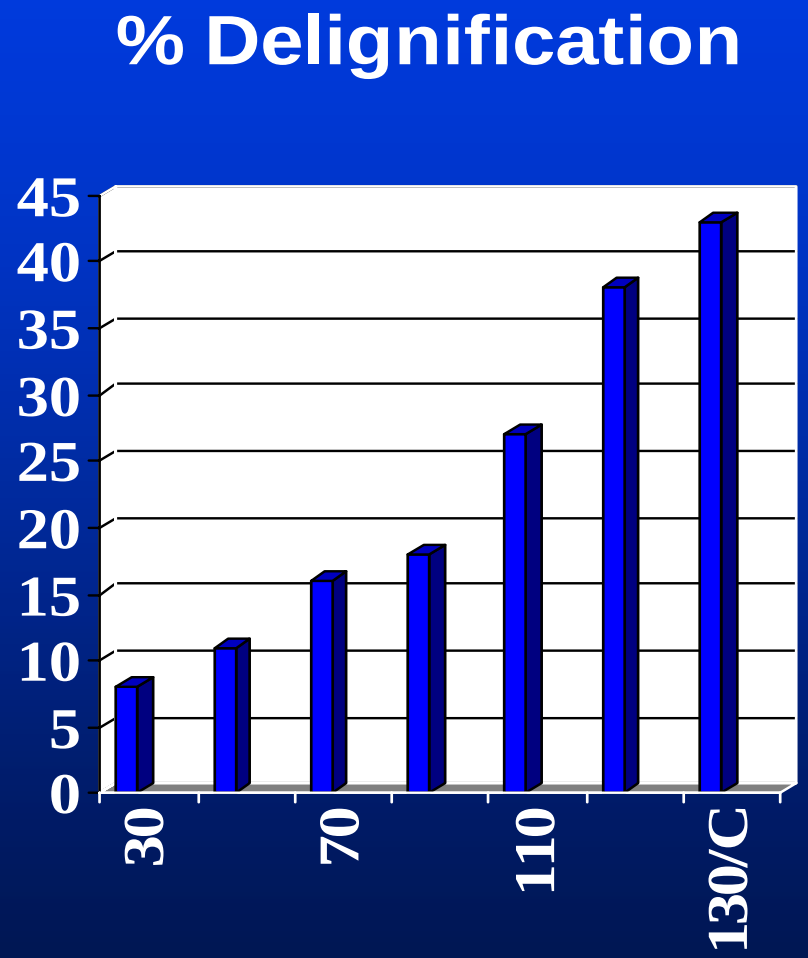
Peroxide Bleaching: Role of metals
2.5% P, Q vs. no Q for SW Kraft Pulp

- P-delignification requires metal management via Q-stage
- Favorable M: Mg^{2+}
- Harmful: Fe, Cr, Ni
  - Mn favorable/harmful
- Note: C/D or D not M sensitive



Peroxide Bleaching: Role of Temperature
2.5% P Q HW Kraft Pulp

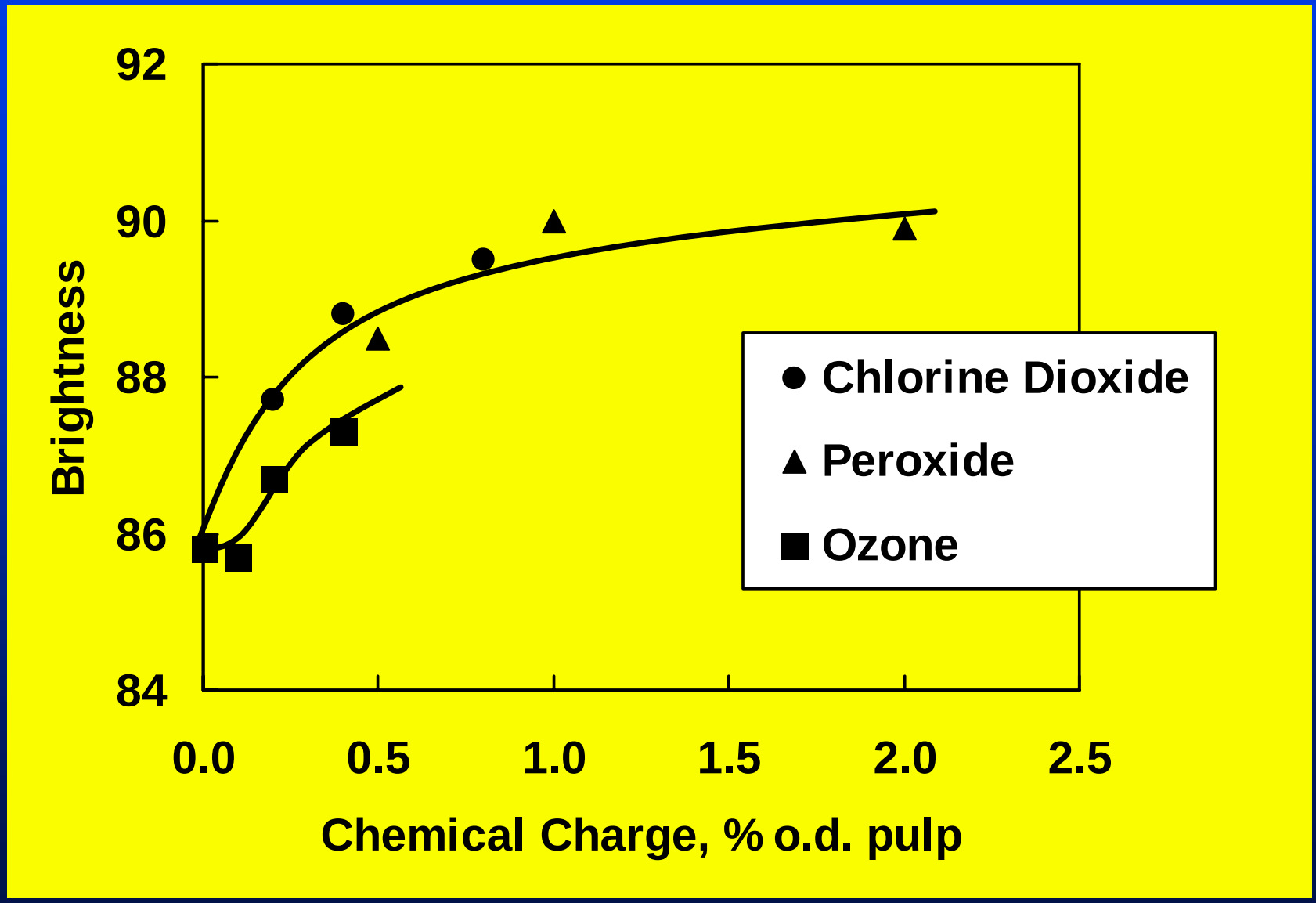
- **P* significantly improves peroxide**
- **P* not just increase in rates**
- **Capital intensive**
- **Sensitive to M^+**
  - **Q stage**
  - **yield**



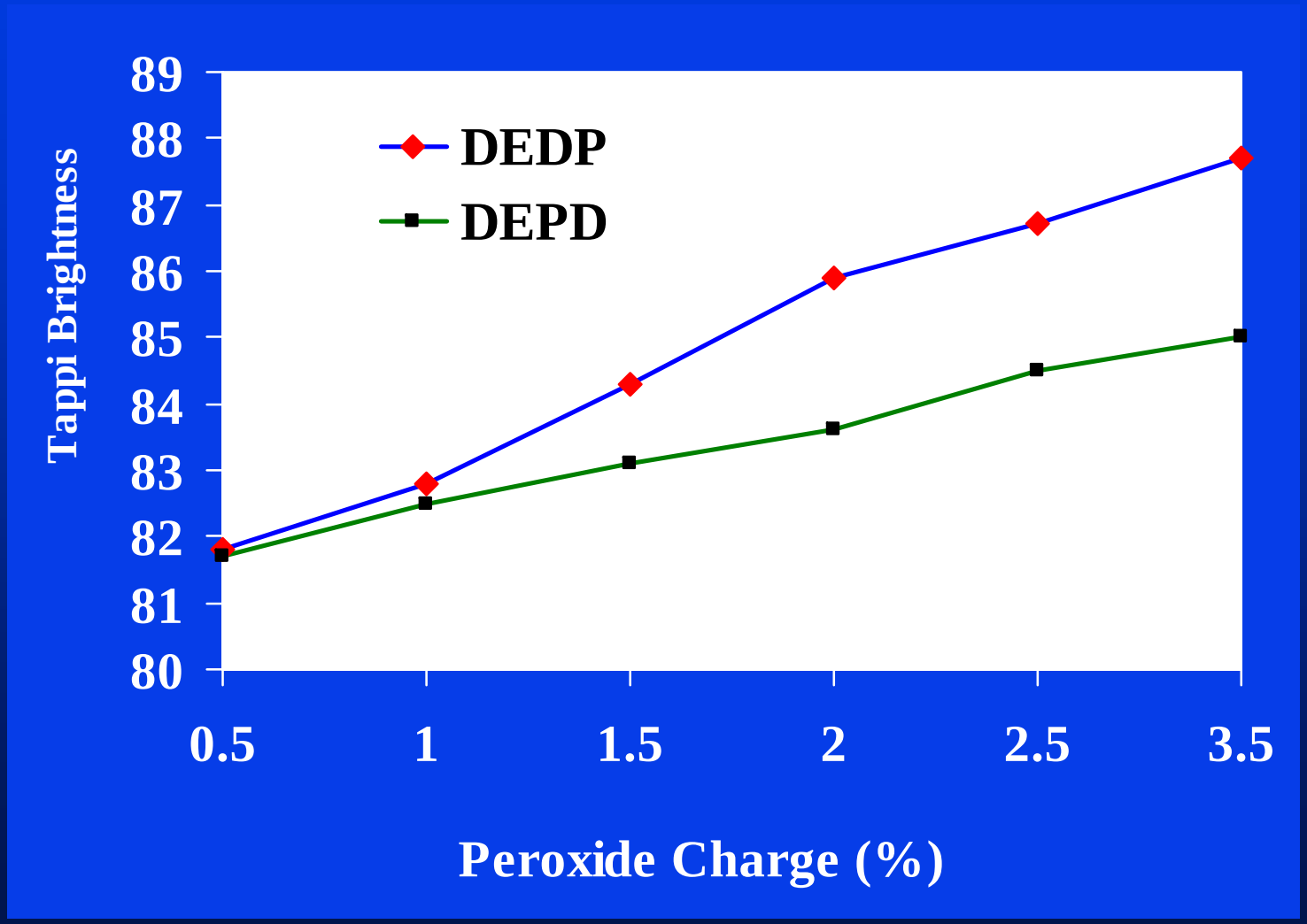
P-Stage Future Research Directions

- Peroxide Efficiency
  - Improved Conditions
  - Catalysis
  - Modification of fibers

Brightening After OD(EPO)D Kraft HW



Peroxide Brightening Effects



- D-stage generates active lignin structures for P-stage

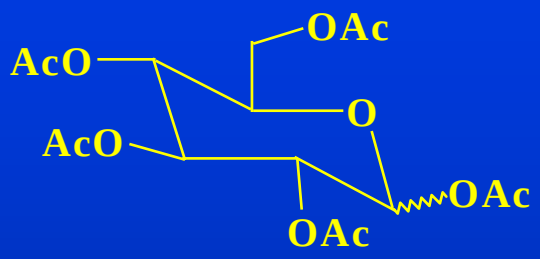
Peroxide Activation - Catalyst

Peroxide Bleaching: Research

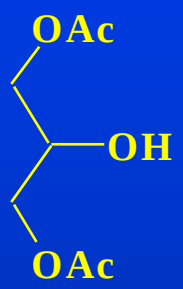
- Bleaching properties of P_{HT} and PO suggest that a catalyst could improve delignification and/or brightening

- First generation
  - HO_3SOOH, CH_3CO_3H

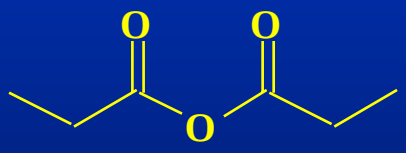
Peroxide Bleaching: Research P-activators



Pentacetyl Glucose



Diacetin



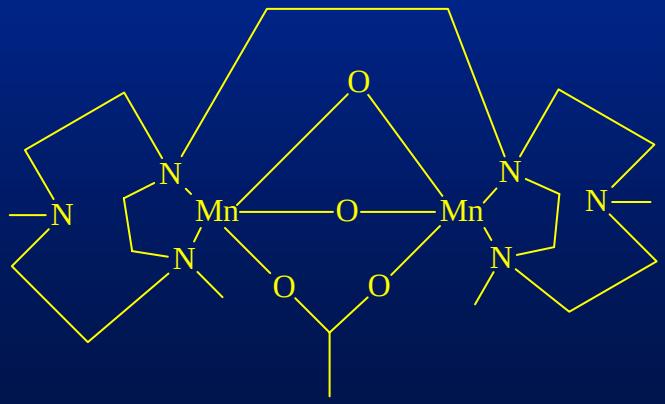
Diethyl Pyrocarbonate

DAED

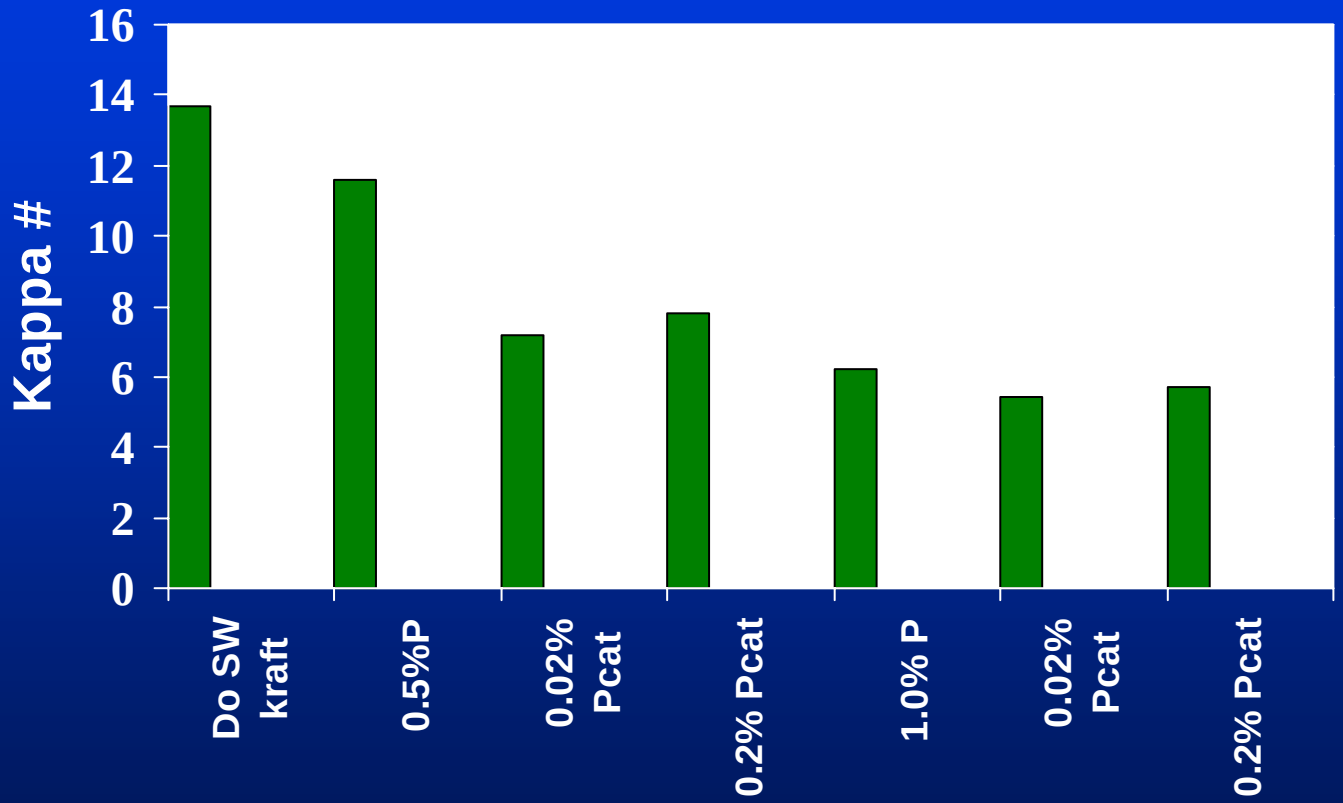
TAED

All improve a P-stage by 15 - 40% >>stoichiometrically

Peroxide Bleaching: Research P-catalyst



Peroxide Bleaching: Research P-catalyst



Catalytic Peroxide Activation: Use of Mn-catalyst to improve alkaline peroxide bleaching of Do SW kraft.

Peroxide Fiber Modification

Strength Effects of O and (PO) on (OZE) SW Kraft

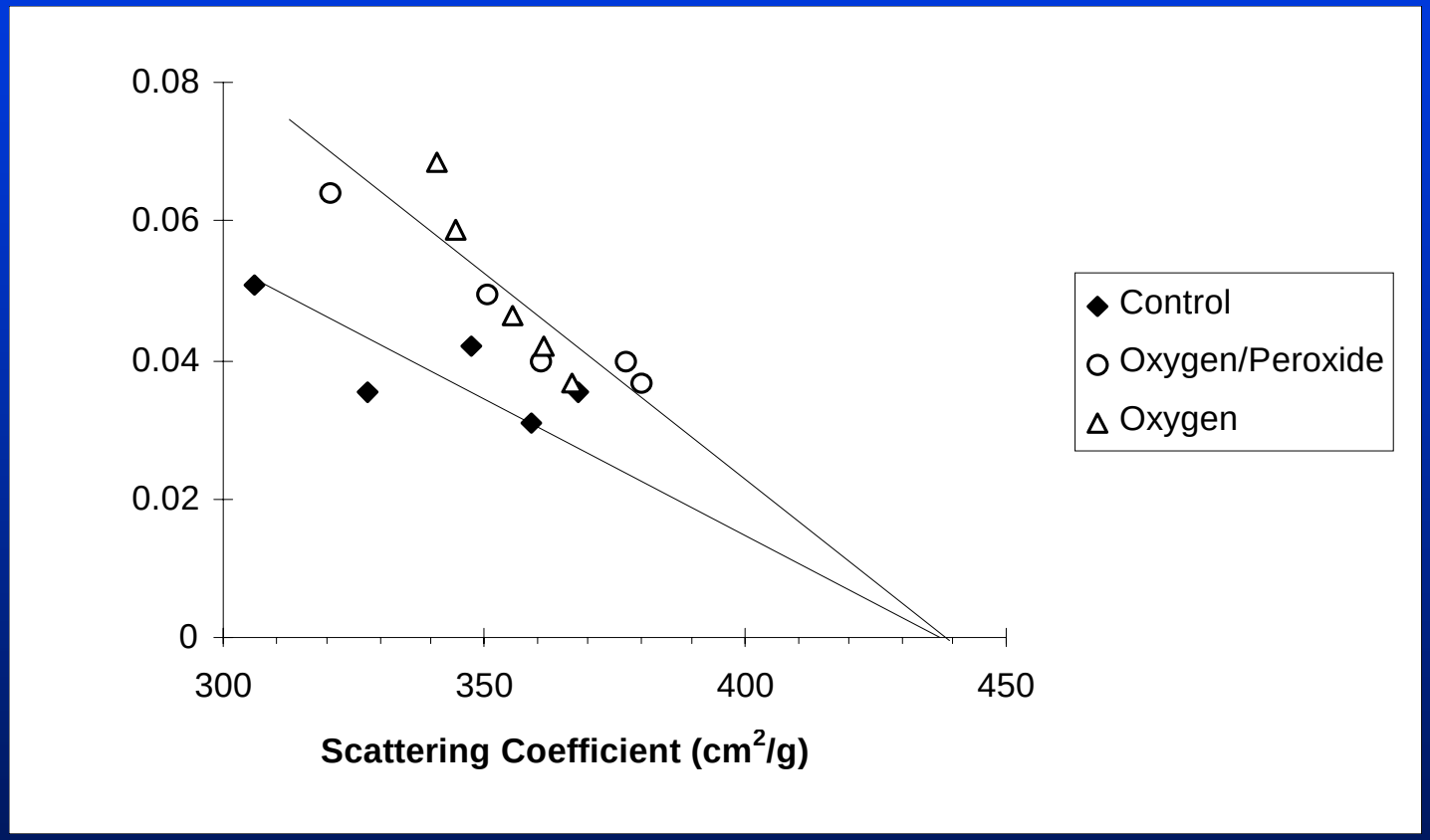
Use an OZE pulp and apply O or (PO)

Bleaching stage enriched acid groups content of pulp fibers

(PO) increased acid groups by 65%

(O) increased acid groups by 37%

Practical Application - Bleaching



CONCLUSIONS

- Additional acid groups on or near fiber surfaces increased specific bond strength.
- Strength benefit mechanism is not known, but could be intermolecular diffusion.
- The possibility exists to produce stronger, bulkier sheets than by conventional processes.

Peroxide Summary

- Current peroxide bleaching chemistry has dramatically advanced.
- P-stage delignifies but destroys color bodies more effectively.
- Environmentally compatible.
- Sensitive to certain metals.
- Peroxide research is directed at reducing capital requirements.
- Improved peroxide delignification will be achieved.
- New research opportunities in fiber modification.

Acknowledgments

Member Companies IPST