Fundamental Aspects of Rapid ClO_2 Delignification of Conventional and Lo-Solids Kraft Pulps

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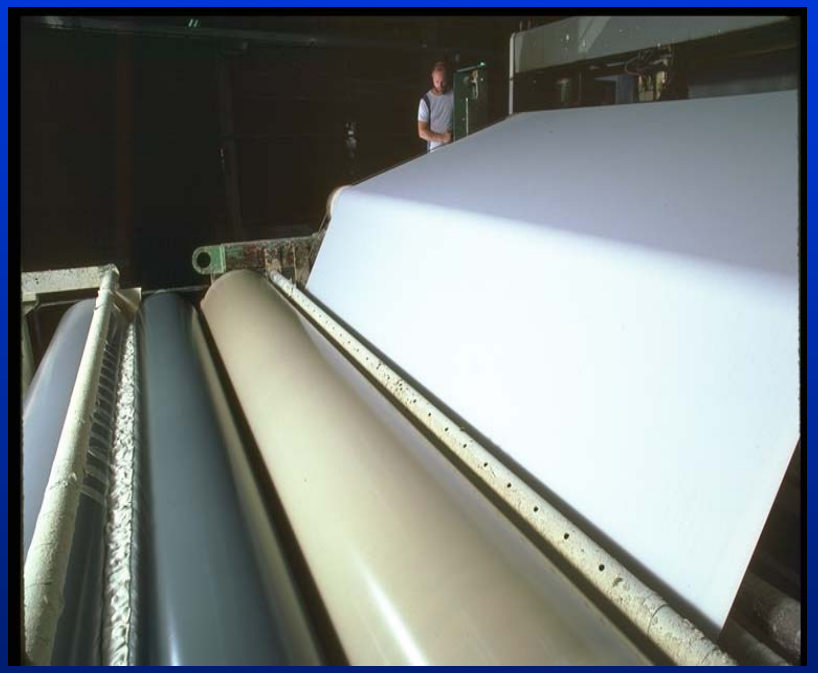
Project Drivers

- **Kraft Pulping & Bleaching Evolution**
  - **Environmentally driven**
  - **Lower kappa #**
  - **Improved selectivity & physical properties**
  - **Improved cost**

Research Goal: Improved ClO_2 Bleaching.

- Determine bleaching mechan. of advanced ClO_2 delignifi-cation technologies - gas phase and Rapid Do;
- Identify residual lignin fragments resistant to ClO_2 and modify Do or pulping process to enhance lignin reactivity;
- Develop next generation of ClO_2 delignification techn.

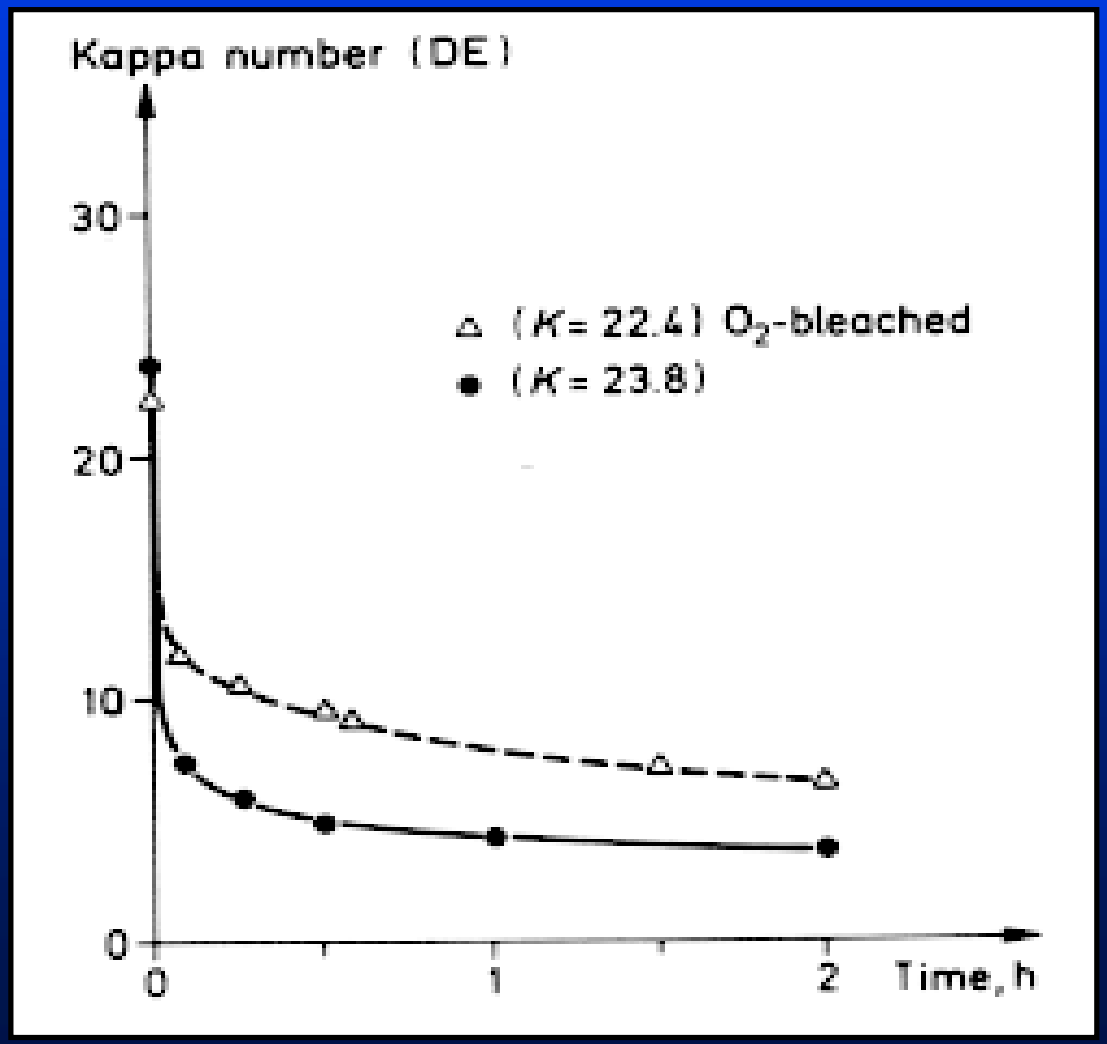


Background

- Kraft residual lignin structure
  - Residual lignin structure is influenced by pulping conditions and the extent of delignification

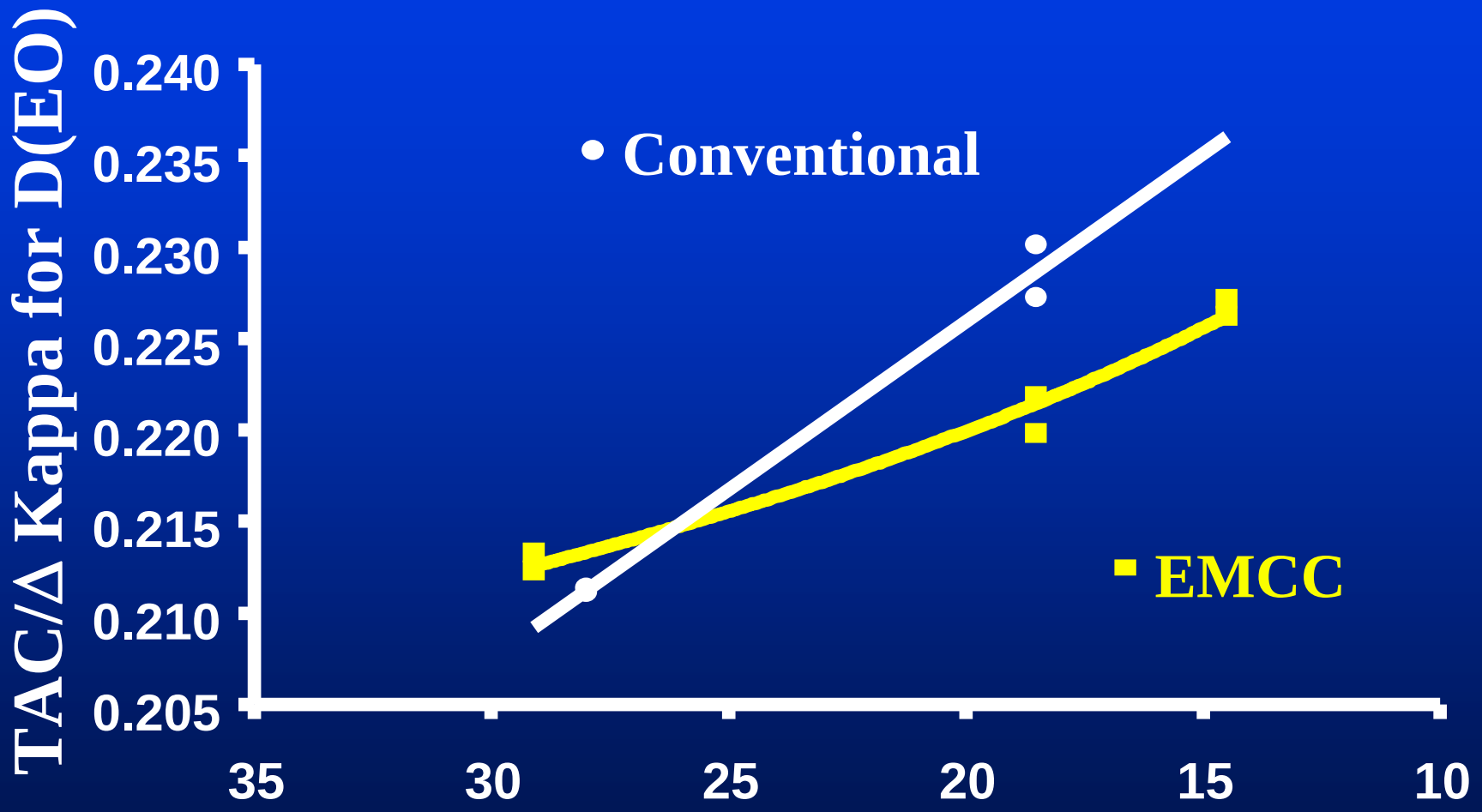
- ClO_2 is a selective bleaching agent
  - Residual lignin's structure will influence its reactivity towards ClO_2

Can Residual Lignin Structure Impact Bleachability?



Germgard (1982)

Can Kraft Pulping Impact Bleachability?



Froass et al. (1996)

Objectives

- Determine how the extent of delignification and pulping process variables influence bleachability in a D(EO) delignification sequence employing a modified Do-stage

- Relate the unbleached residual lignin structure and residual lignin reactivity towards ClO_2 to bleachability

Experimental Approach

- Bleach pulps in a Rapid Do(EO) sequence and study bleachability parameter (TAC/Δ Kappa #)
- Characterize residual lignin before and after ^{R}D(EO) stage
- Relate changes in residual to important bleachability parameters

Pulps Investigated

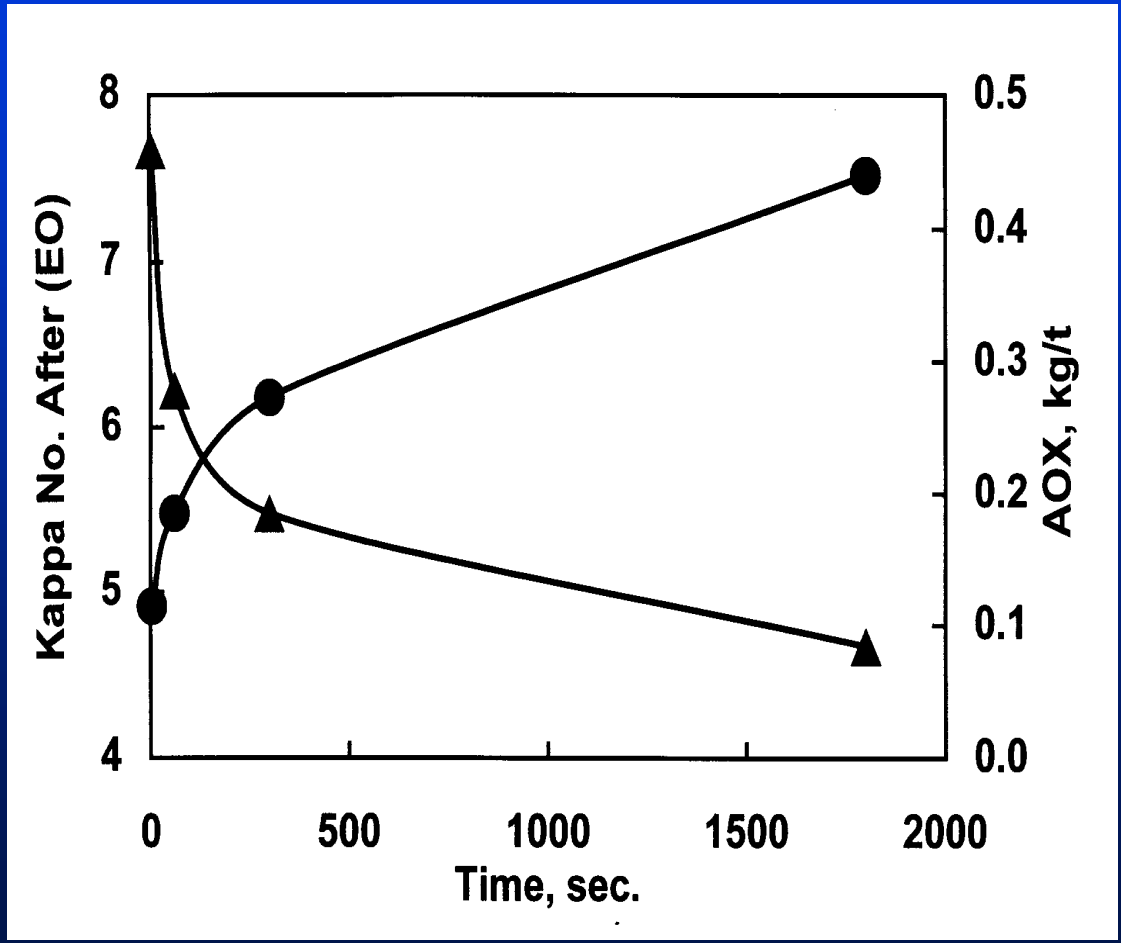
- **Conventional kraft**
  - CK 33.0 (32.6 mPa)
  - CK 21.3 (22.6)
  - CK 14.7 (13.3)
- **Extended Modified***
  - EK 29.3 (43.4)
  - EK 19.1 (25.5)
  - EK 16.0 (19.2)

*Lo-Solids

Rapid Do Bleaching Protocol

General Principles

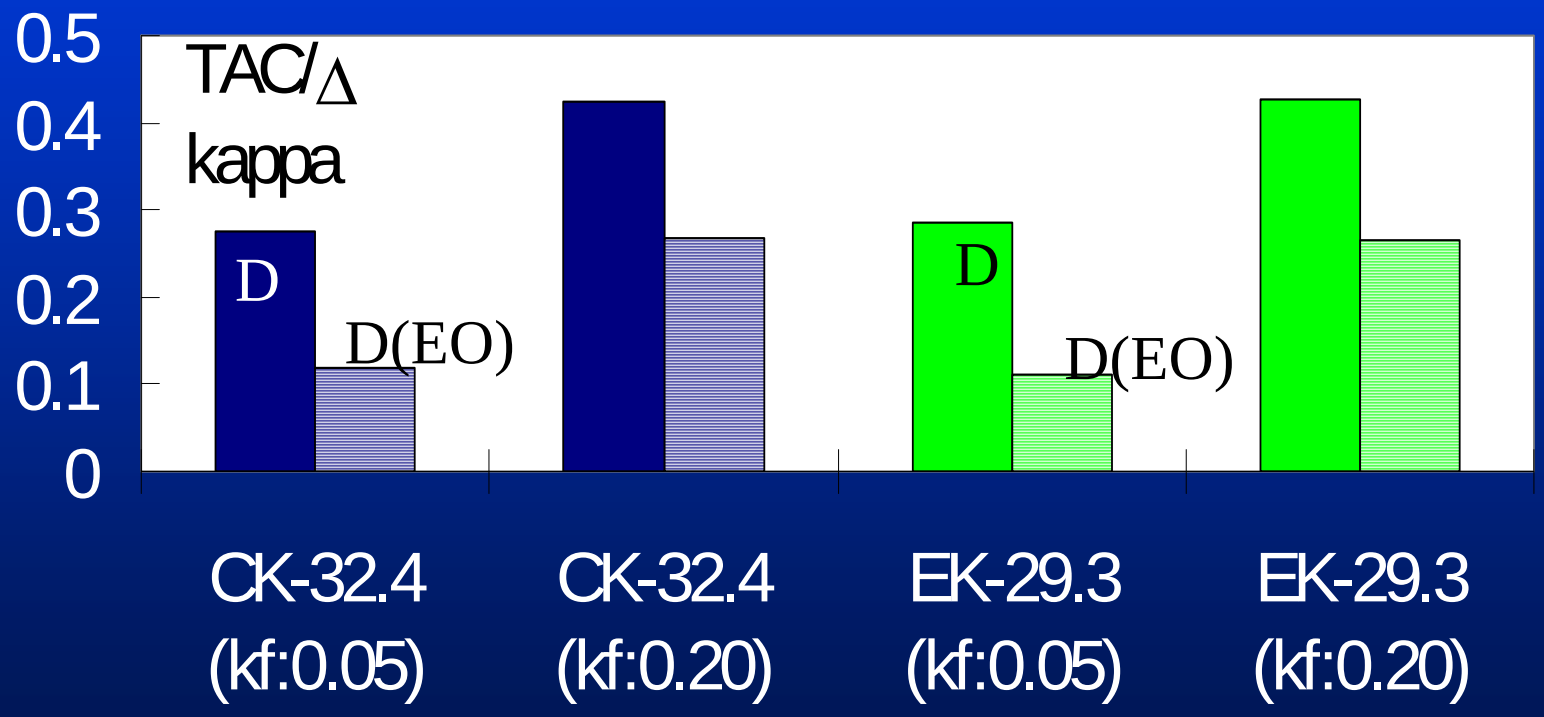
- With Good Mixing the bulk of Do delignification occurrs 1st 3 minutes
- Bulk of AOX formation occurs after 3 min.
- Rapid Do delignification kinetics offers opportunity to simplify bleaching equipment
  - use of high shear mixer and U-tube



Bleaching Conditions in the ^{R}D(EO) Partial Sequence

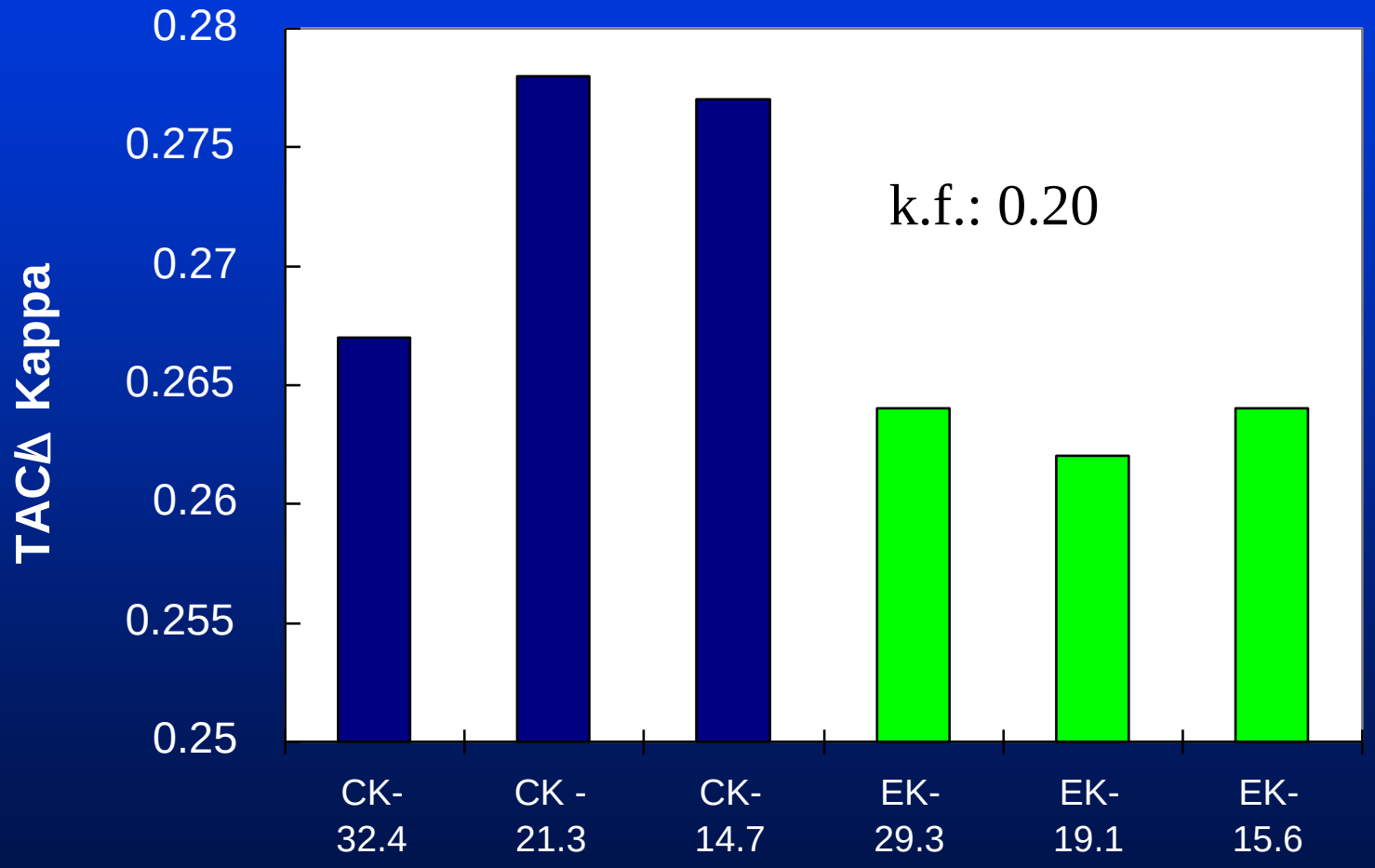
D Stage		EO stage	
KF	0.20, 0.05	% NaOH	pHoff: 11.1 $\pm$0.4
Stirring - Time	15 Hz - 30 s static - 30 s	Time	60 min
Temp.	45°C	Temp.	70°C
Consy.	10%	Consy	10%
Mixer	Quantum	O_2 Press.	60 psig (dec 12psi every 5 min)
Quench	mass Na_2SO_3 added=mass applied ClO_2 x 4.67	Mixer	Peg

Bleachability of CK & EK Pulps After $^{R}D_{0}$ & $^{R}D_{0}$(EO) k.f.: 0.05 and 0.20



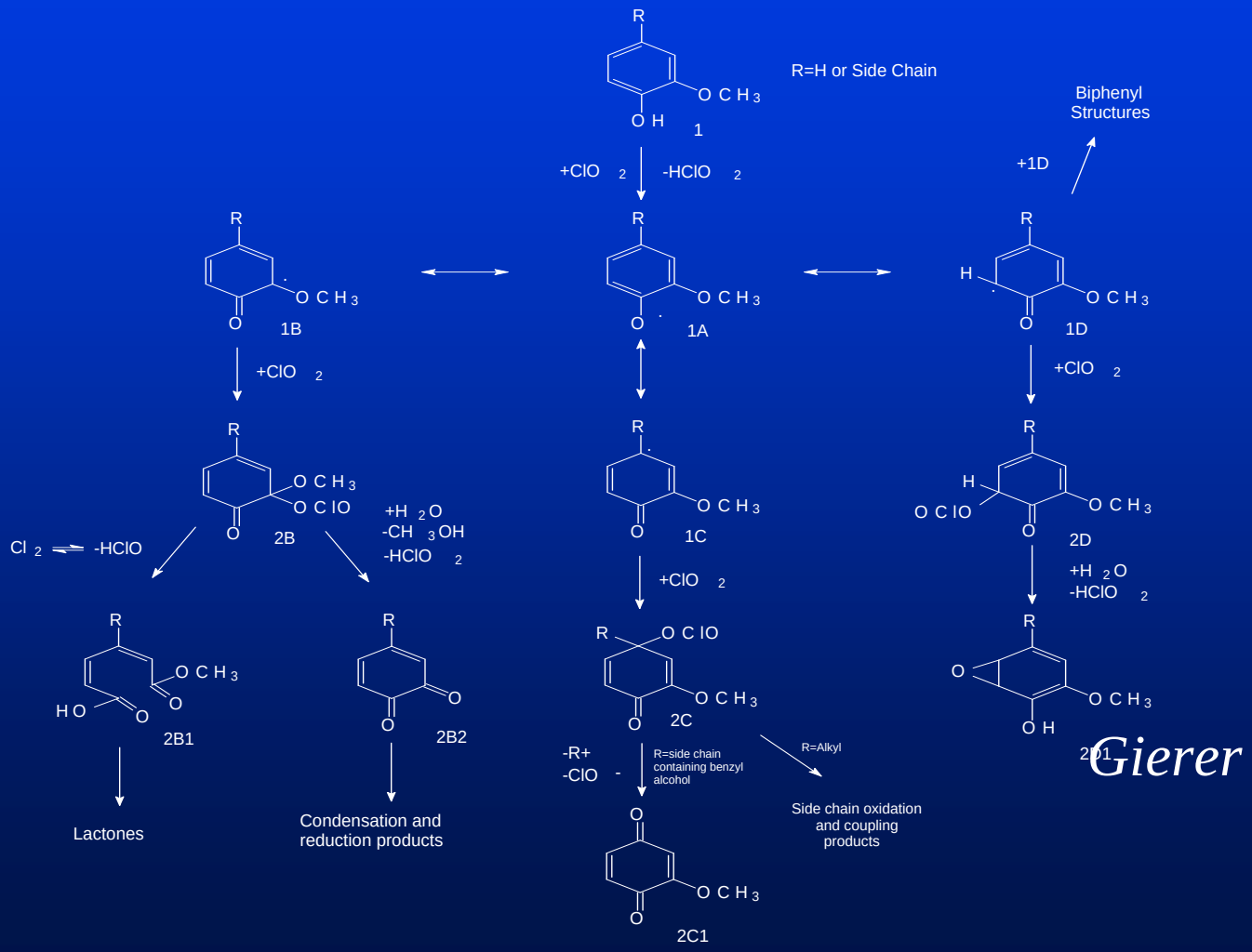
EK exhibits improved bleach.

Bleachability of CK & EK Pulps $^{R}D_{o}$ (EO)



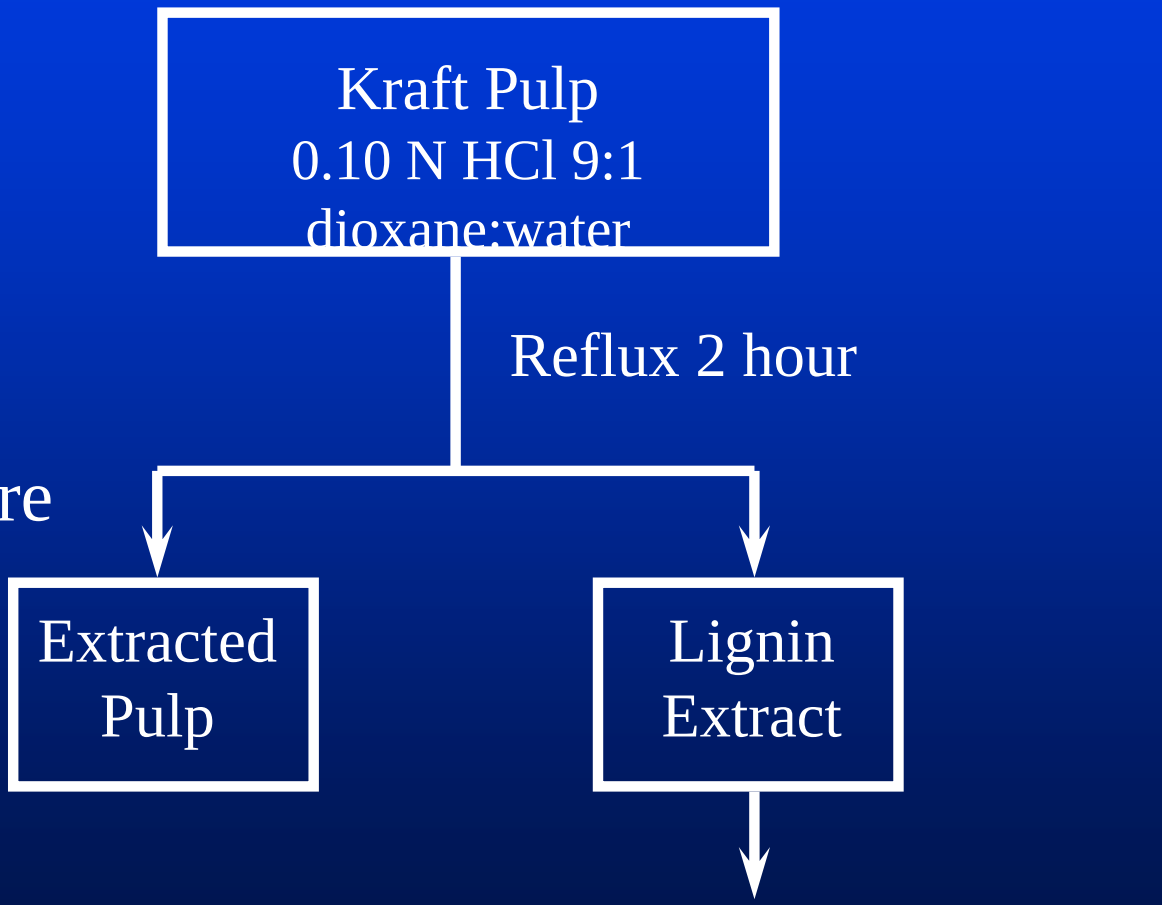
-Consistent & reproducible improved bleachability for EK pulps

Chemistry of ClO_2 Delignification



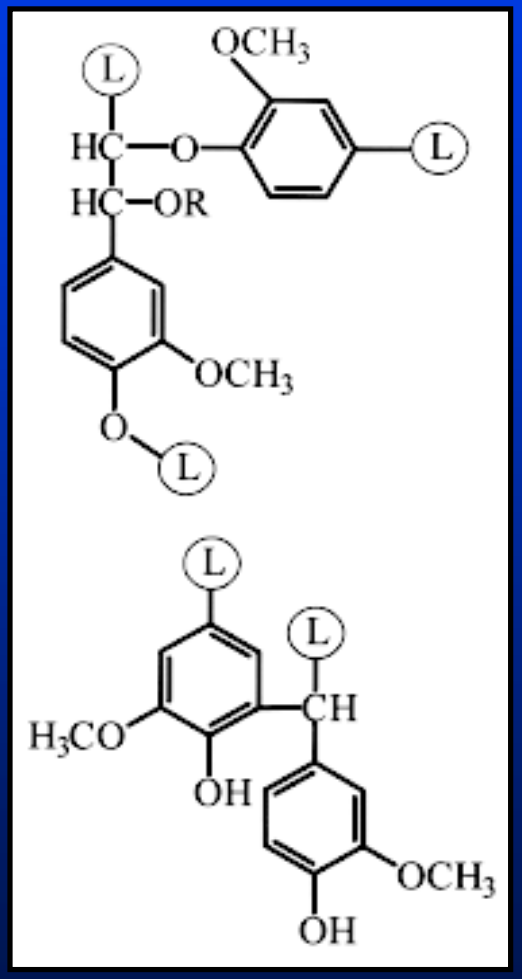
Relationship Between Bleachability and Residual Lignin Structure

- Isolate lignin before and after ^{R}Do and ^{R}Do(EO)
- Characterize Structure

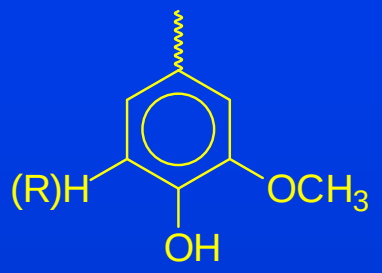


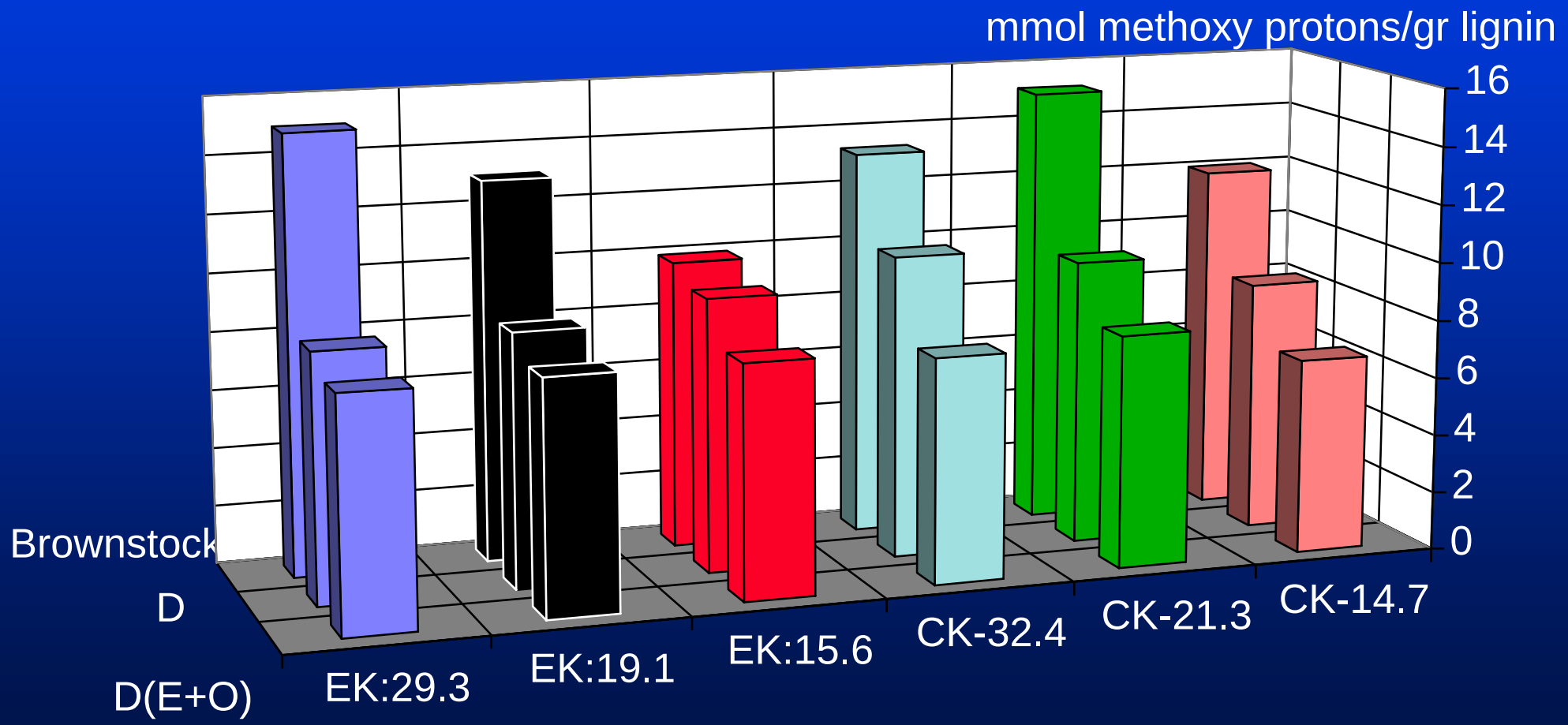
^{1}H-NMR spectroscopy

- Powerful technique to characterize lignin structure
- Structural features discernible
  - Acids
  - Phenols
    - condensed & non-condensed
  - Condensed aromatic structures
  - Methoxy
  - Aliphatic

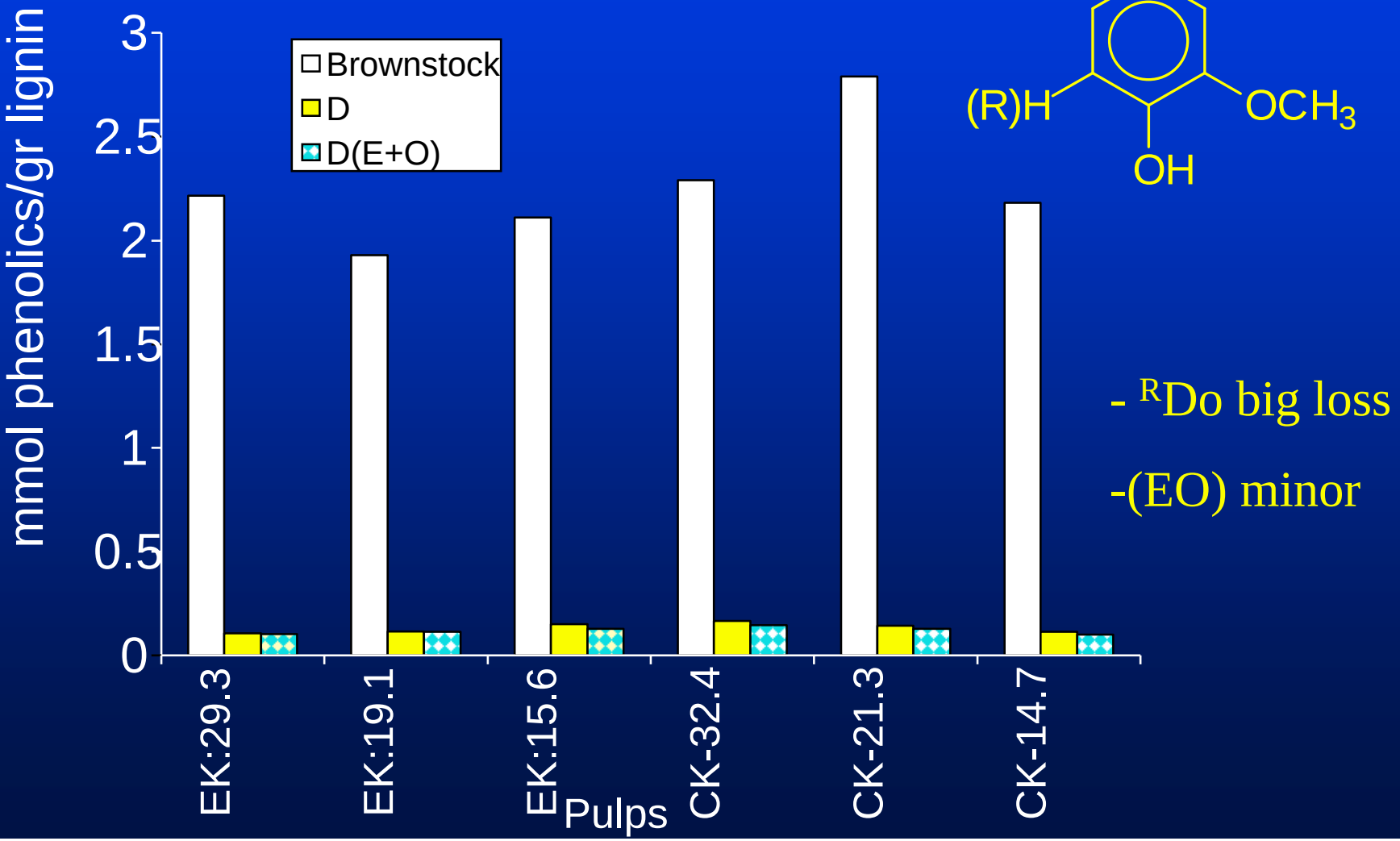


Methoxy Proton Content for Brownstock, ^{R}Do and ^{R}Do(EO).





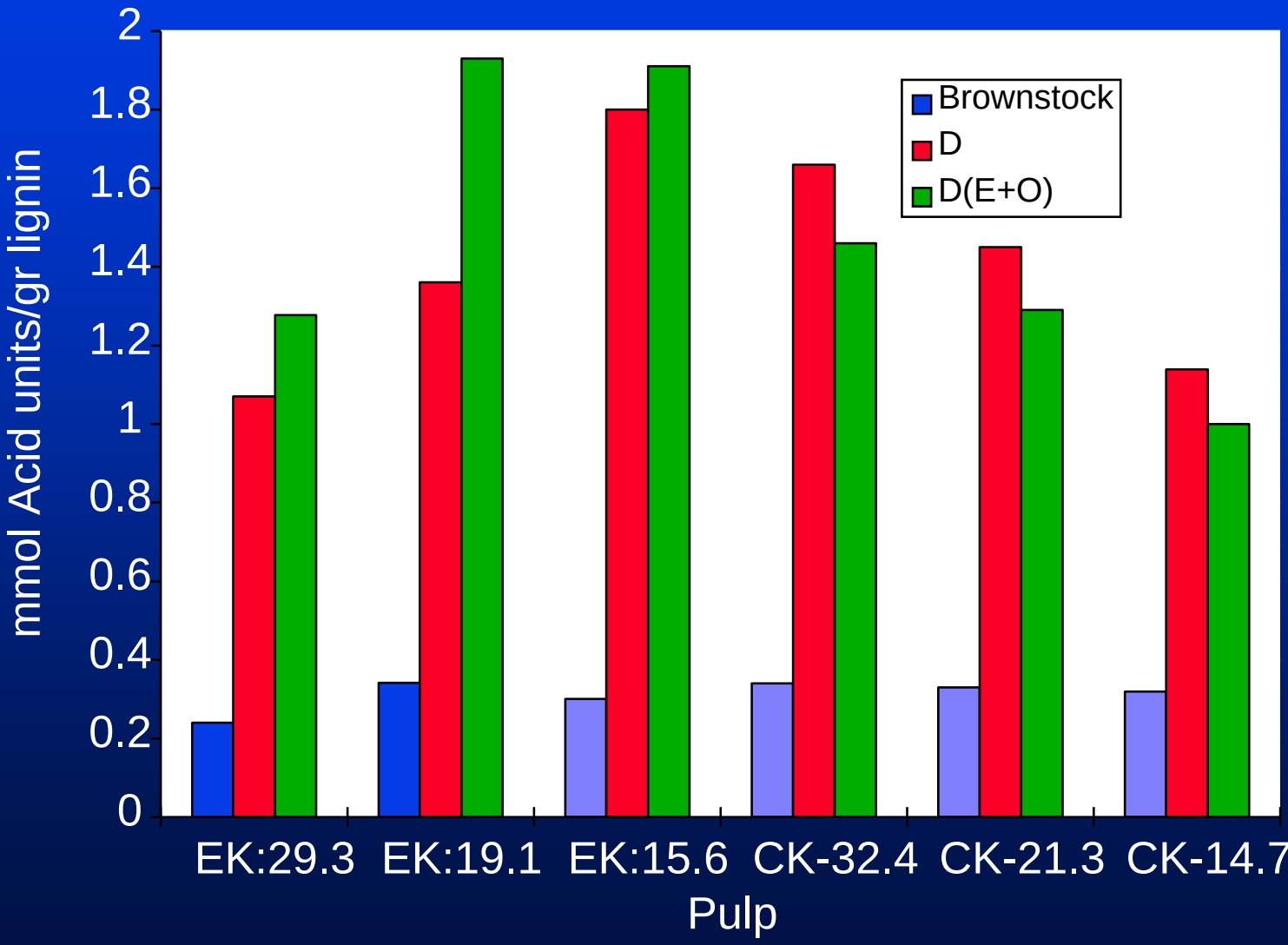
Phenolic Content of Brownstock, ^{R}Do and ^{R}Do(EO)



- ^{R}Do big loss

-(EO) minor

Acid Content of Brownstock, ^{R}Do & ^{R}Do(EO)



- D-stage large increase

Summary of ^{R}D(EO) Studies

- Biggest differences in bleachability for ^{R}D and ^{R}Do(EO) are with low k.f.
- EK pulps continue to demonstrate improved bleachability at lower kappa number
- CK & EK exhibit differences in residual lignin structure that impact bleachability
- For ^{R}D and ^{R}Do(EO) bleaching of CK and EK both HexA and lignin structure may influence bleachability

Influence of Brownstock PhOH Lignin on TAC/Δ Kappa

- Typically PhOH increases as kappa # decreases for CK (30 ➡ 20) and PhOH is higher than EK

- Extended pulp yield better bleachability

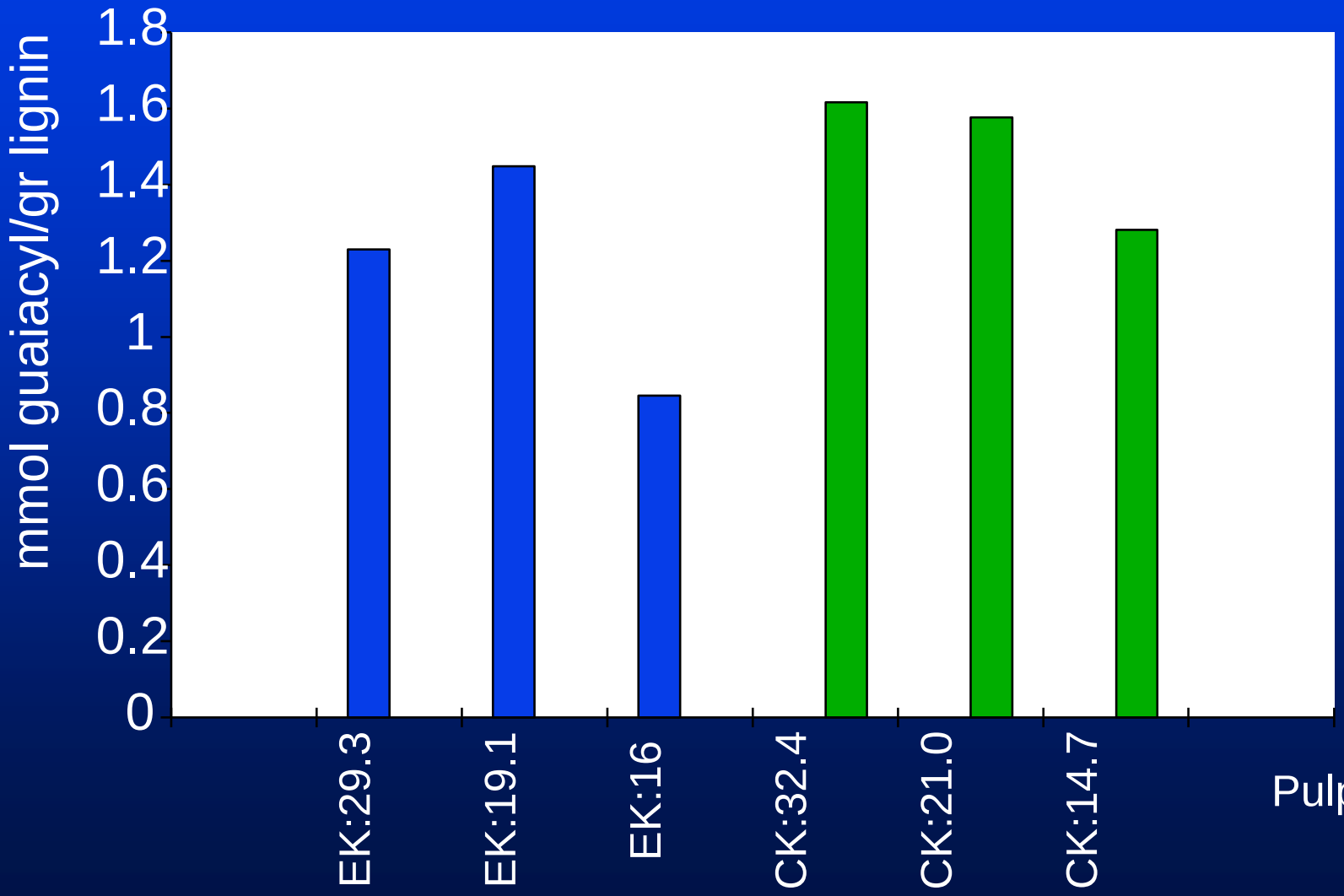
Pulp	TAC[1]/Δ Kappa	Condensed. PhOH[2]
CK-28	0.21	0.89
CK-18	0.23	0.99
EK-29	0.21	0.91
EK-18	0.22	0.94

[1] 0.20 k.f. calculated after Do(EO)

[2] mmol/gr lignin

-Froass et al. IPBC 1996

Condensed Phenolics in Brownstock Kraft Pulps Determined by ^{1}H and ^{31}P NMR



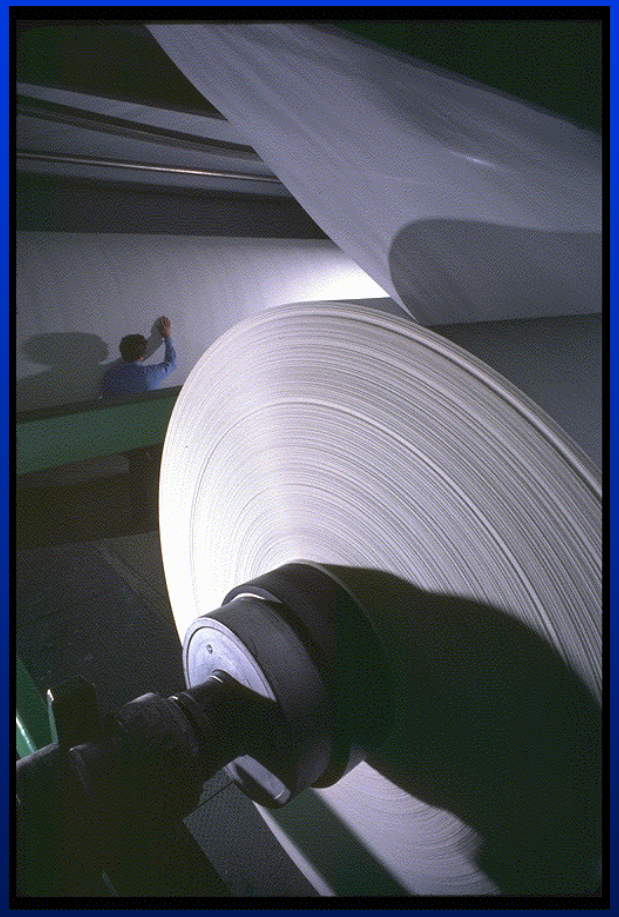
Note: lesss condensed phenolics in EK pulp vs CK pulp

Relationship between residual lignin structure and pulp bleachability

- Lower kappa number pulps are richer in phenolic content yet harder to bleach
- Bleachability seems to be related to the content of condensed structures and aryl ether linkages

Conclusions

- Residual lignin structure will influence bleaching in a D(EO) sequence
- Pulping conditions influence residual lignin structure and suggests that these conditions can be optimized to enhance and improve ECF bleachability



Acknowledgments

Member Companies IPST
Ahlstrom Machinery Corp.
DOE