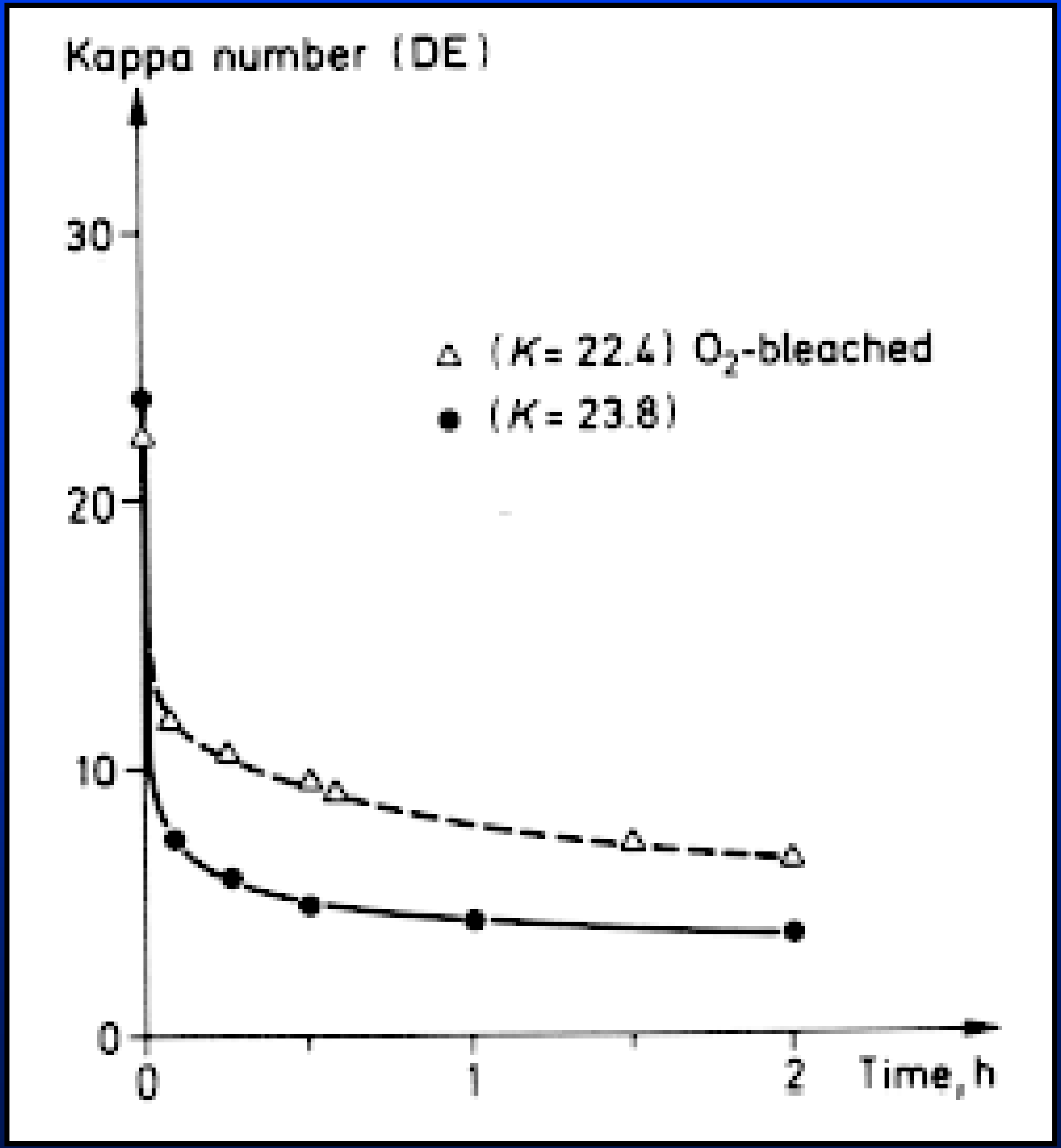
Relationship between Residual Lignin Structure and Reactivity to ClO2 Pulp Bleachability

Background

- Influence of residual lignin structure on ClO_2 reactivity
  - Residual lignin structure is influenced by pulping conditions and the extent of delignification
  - Residual lignin's structure will influence its reactivity towards ClO_2



Germgard (1982)

Objectives

- Determine how the extent of delignification and pulping process variables influence bleachability in a D(EO) delignification sequence
- Relate the unbleached residual lignin structure and residual lignin reactivity towards ClO_2 to bleachability

Experimental Approach

- Bleach pulps in a D(EO) sequence and define a bleachability parameter (TAC/Δ Kappa #)
- React isolated residual lignins with ClO_2 and monitor functional group changes in these lignins

Pulps Investigated

Loblolly Pine Chips

- **Conventional kraft**
  - C28
  - C18
- **Simulated EMCC**
  - E29
  - E18
  - E14

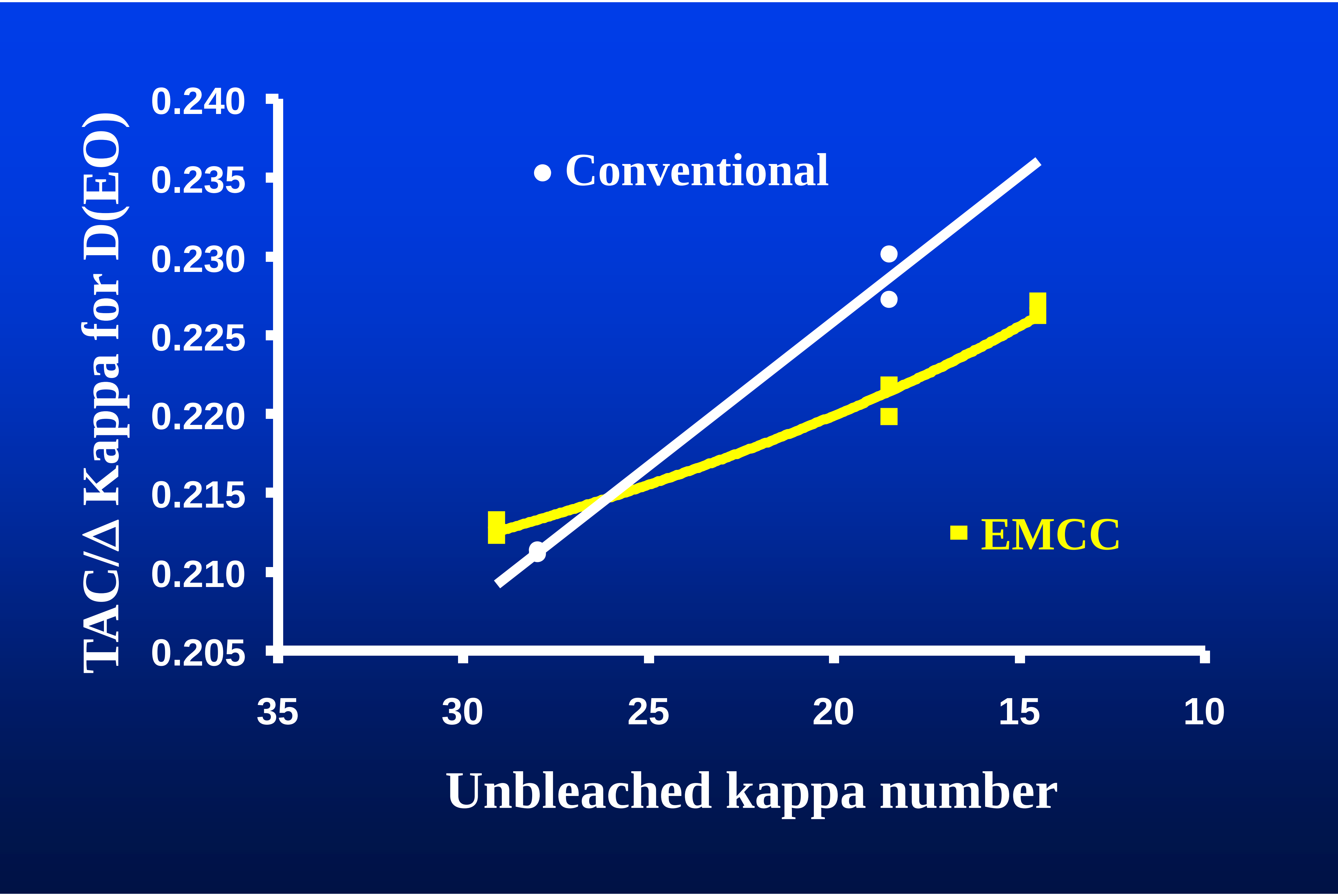
Bleaching conditions in the D(EO) partial sequence

D Stage		EO stage	
KF	0.187±0.005	% NaOH	50% TAC
Time	30 min	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)
		Mixer	Peg

Bleachability parameters for CK and EK pulps.

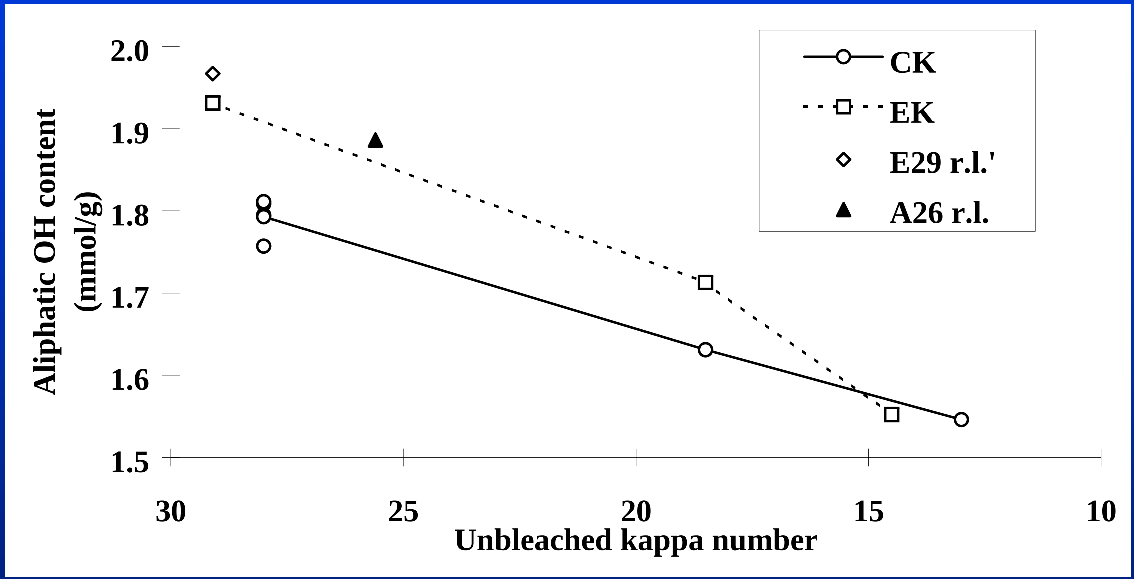
Parameter	CK		EK		
Unbleached Kappa No.	28.0	18.5	29.1	18.5	14.5
Kappa No. after D	11.0	9.2	11.0	7.5	6.0
TAC[1]/ΔKappa	0.30	0.37	0.30	0.31	0.33
Kappa No. after (EO)	3.8	3.5	3.3	3.0	2.3
TAC[1]/ΔKappa	0.21	0.23	0.21	0.22	0.23
Brightness after (EO)	47.4	49.9	49.8	50.2	53.5

[1]TAC-percent total active chlorine consumed



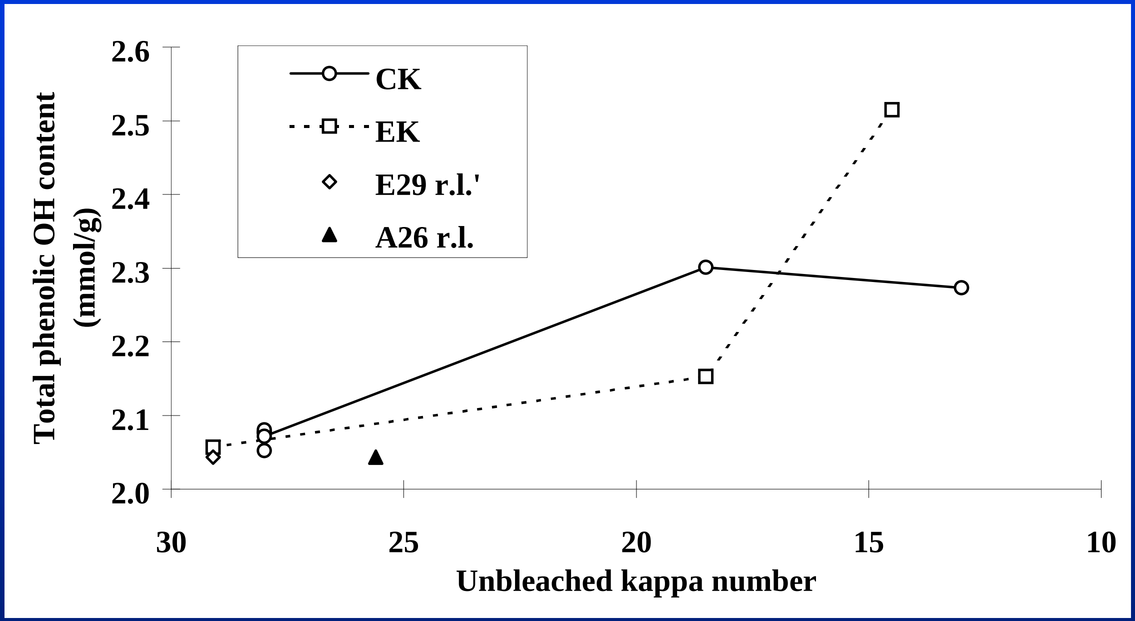
TAC/Δ Kappa for D(EO)
0.240
0.235
0.230
0.225
0.220
0.215
0.210
0.205
Conventional
EMCC
35
30
25
20
15
10
Unbleached kappa number

Structure Of Residual Kraft Lignin



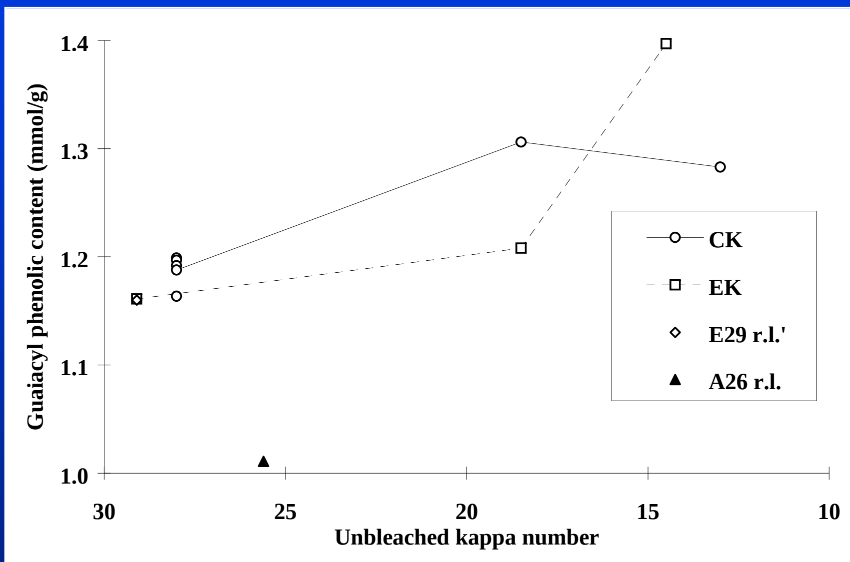
Aliphatic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.' and four replicates of C28 r.l.

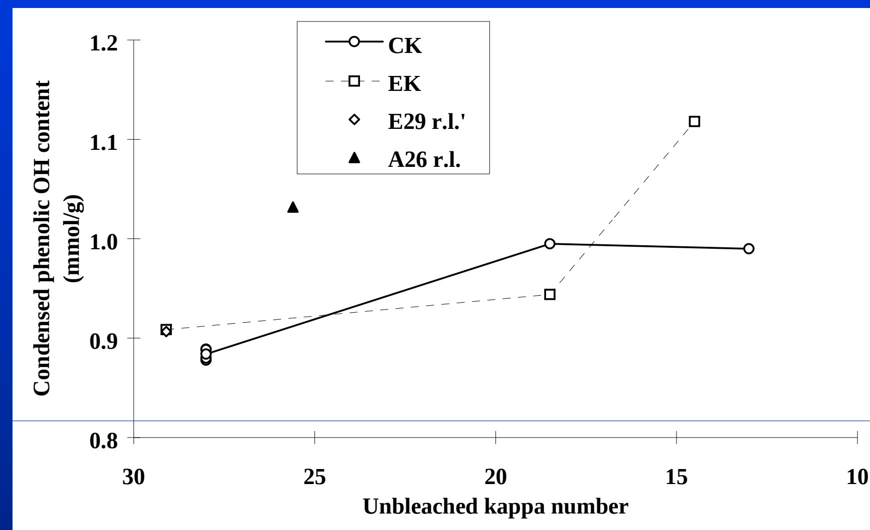
Structure Of Residual Kraft Lignin



Total phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR.

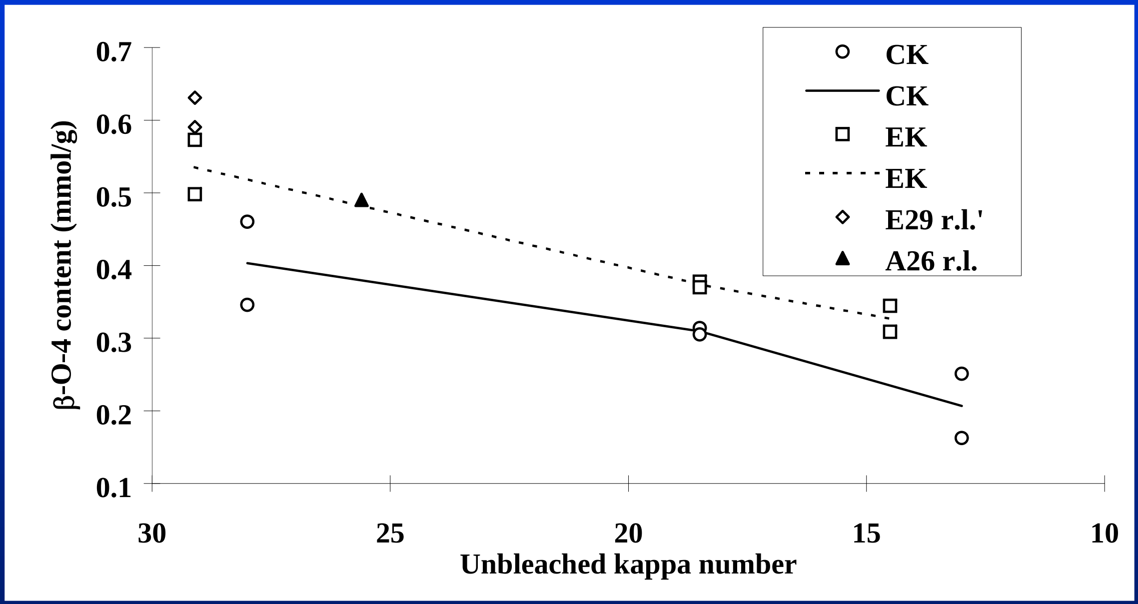
Structure Of Kraft Residual Lignin





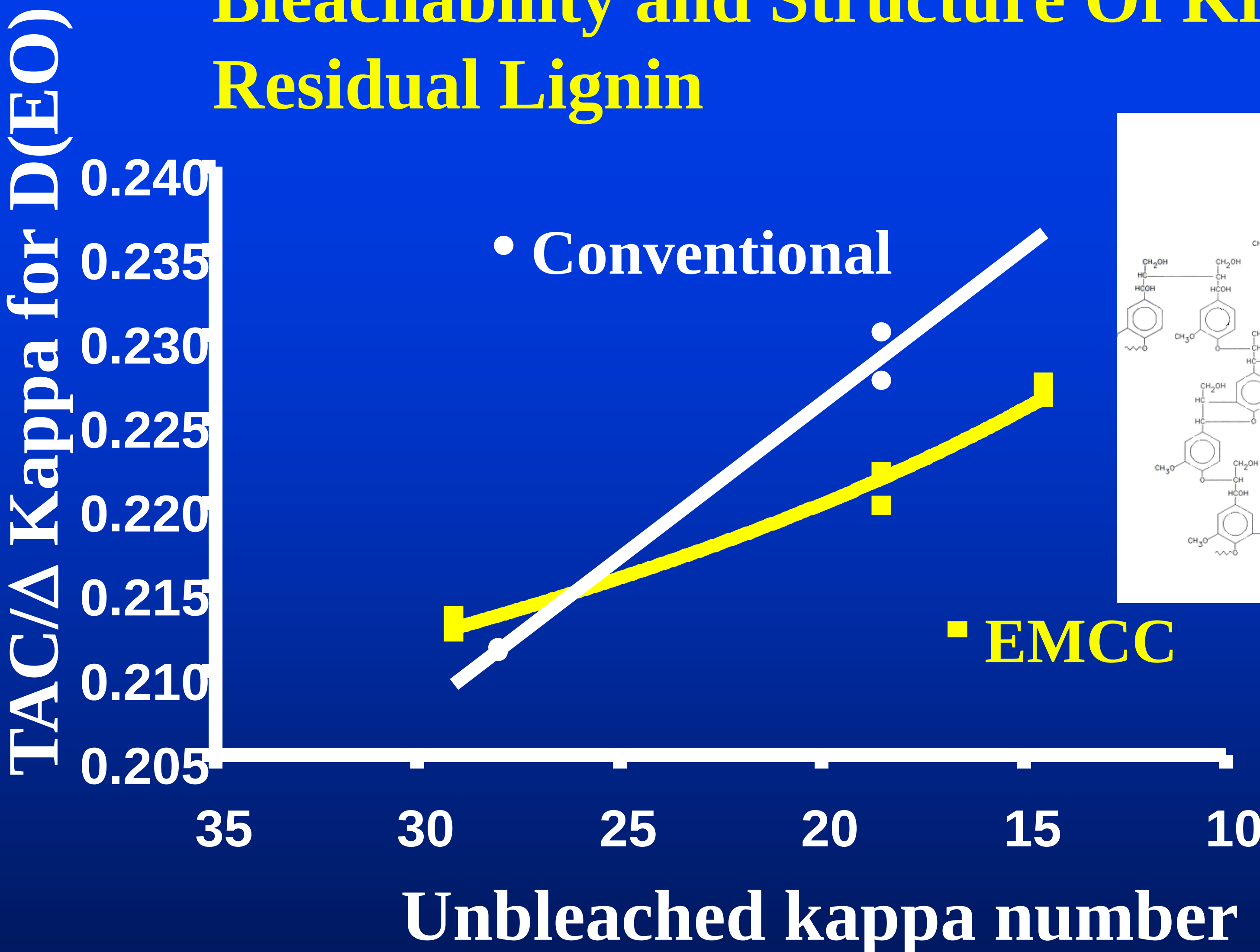
Guaiacyl phenolic and C5 Condensed hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR.

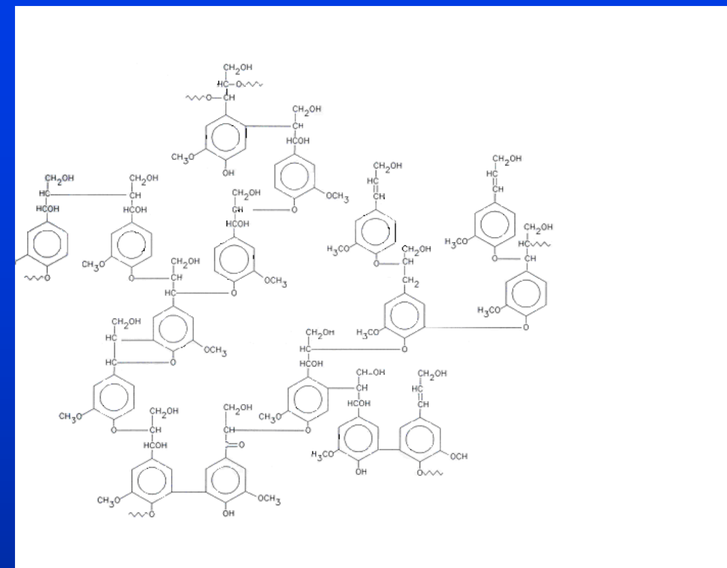
Structure Of Kraft Residual Lignin



β-O-4 content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of lignin acetates.

Bleachability and Structure Of Kraft Residual Lignin





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

Reactivity of residual lignin toward ClO_2

- Reacted the isolated residual lignins with ClO_2
- Measured reactivity by quantifying changes in functional groups

Experimental

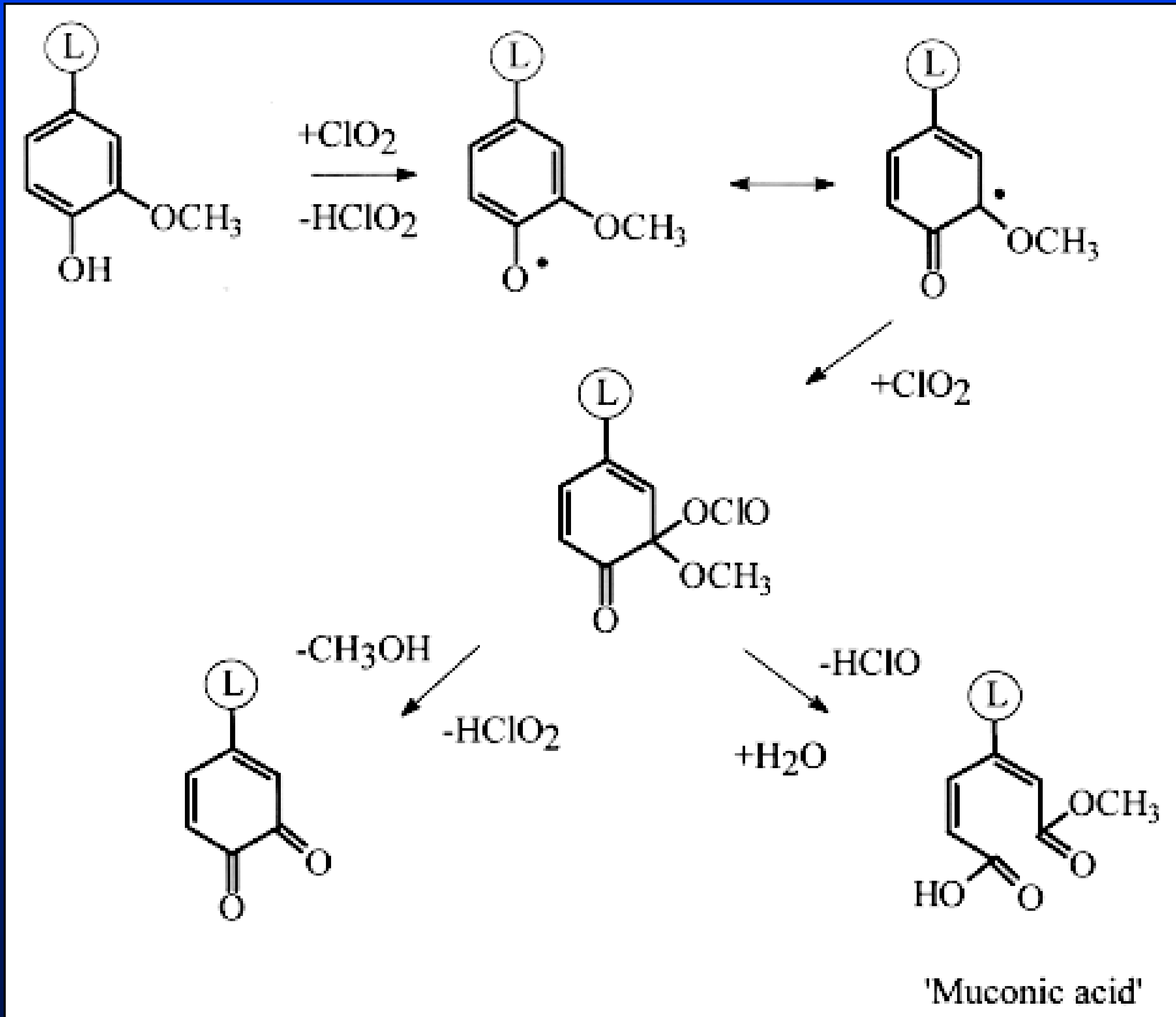
Isolated residual lignins in 9:1 dioxane:water

ClO_2 Treatment
0.05 / 0.10 / 0.20 KF

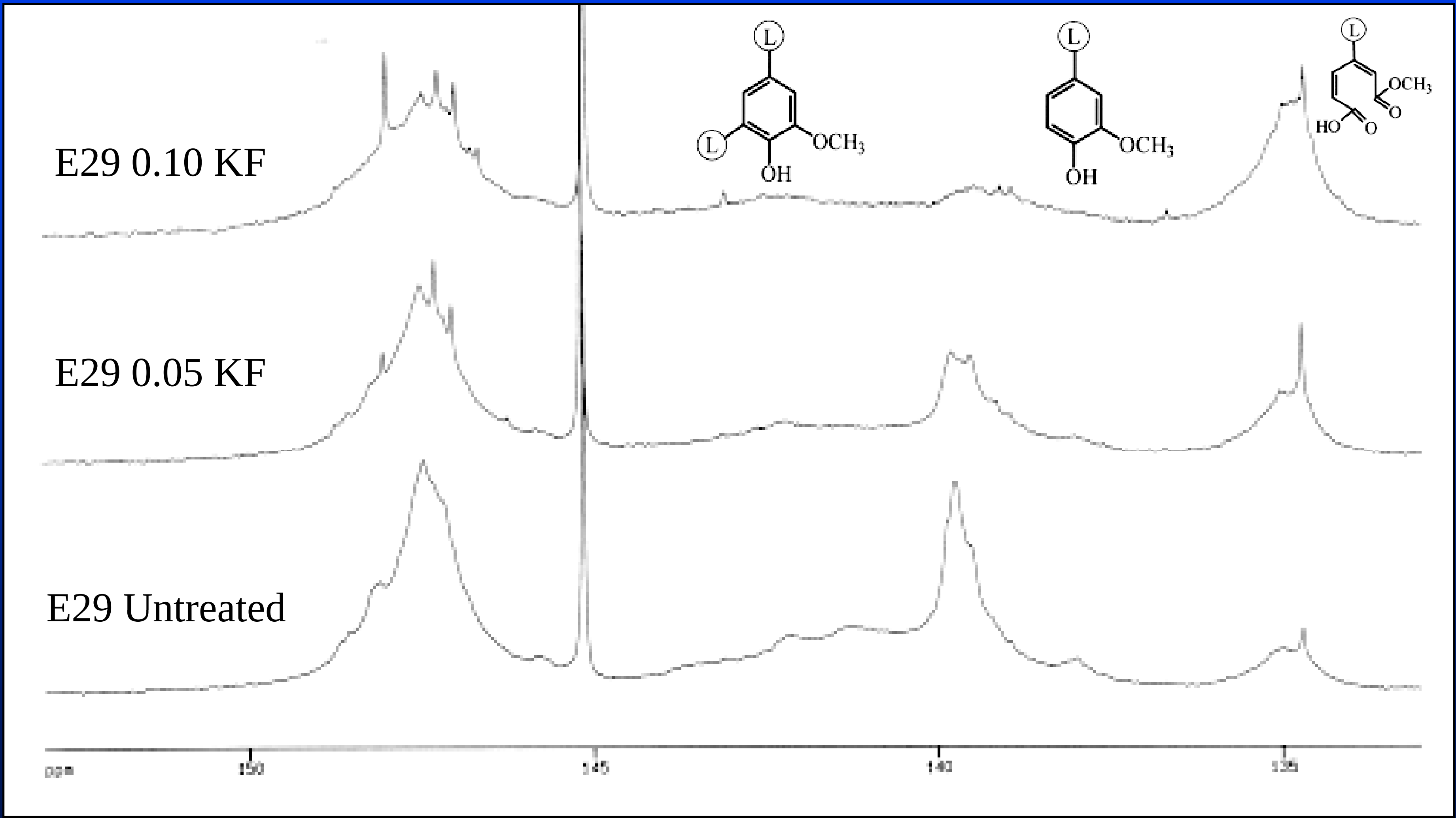
ClO_2 reacted lignins

^{31}P-NMR analysis

Monitor:
Guaiacyl/Condensed phenols
COOH groups

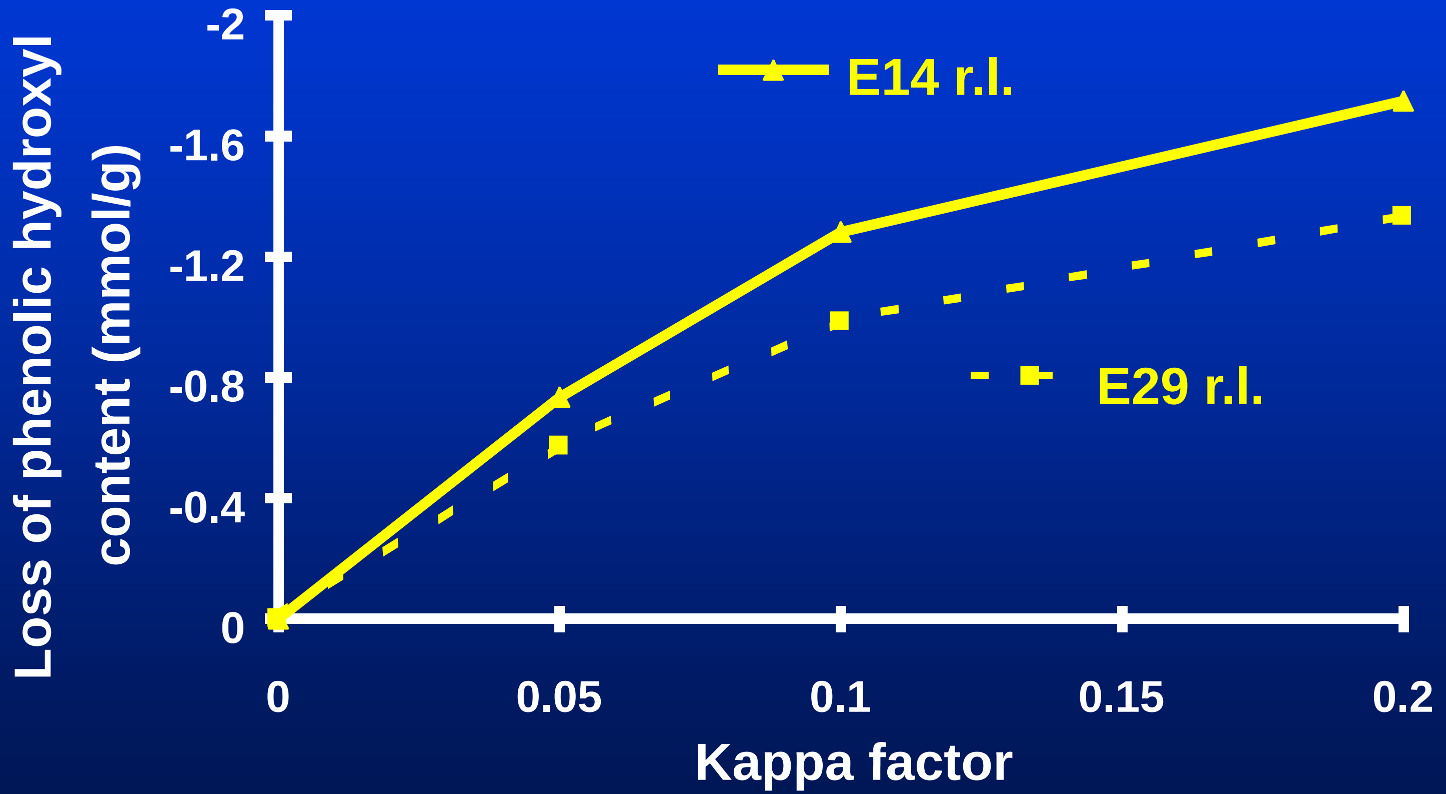

L
OCH3
OH
+ClO2
-HClO2
O•
+ClO2
OClO
-CH3OH
-HClO2
-HClO
+H2O
O
HO
'Muconic acid'

^{31}P-NMR spectra of residual lignin treated with ClO_2



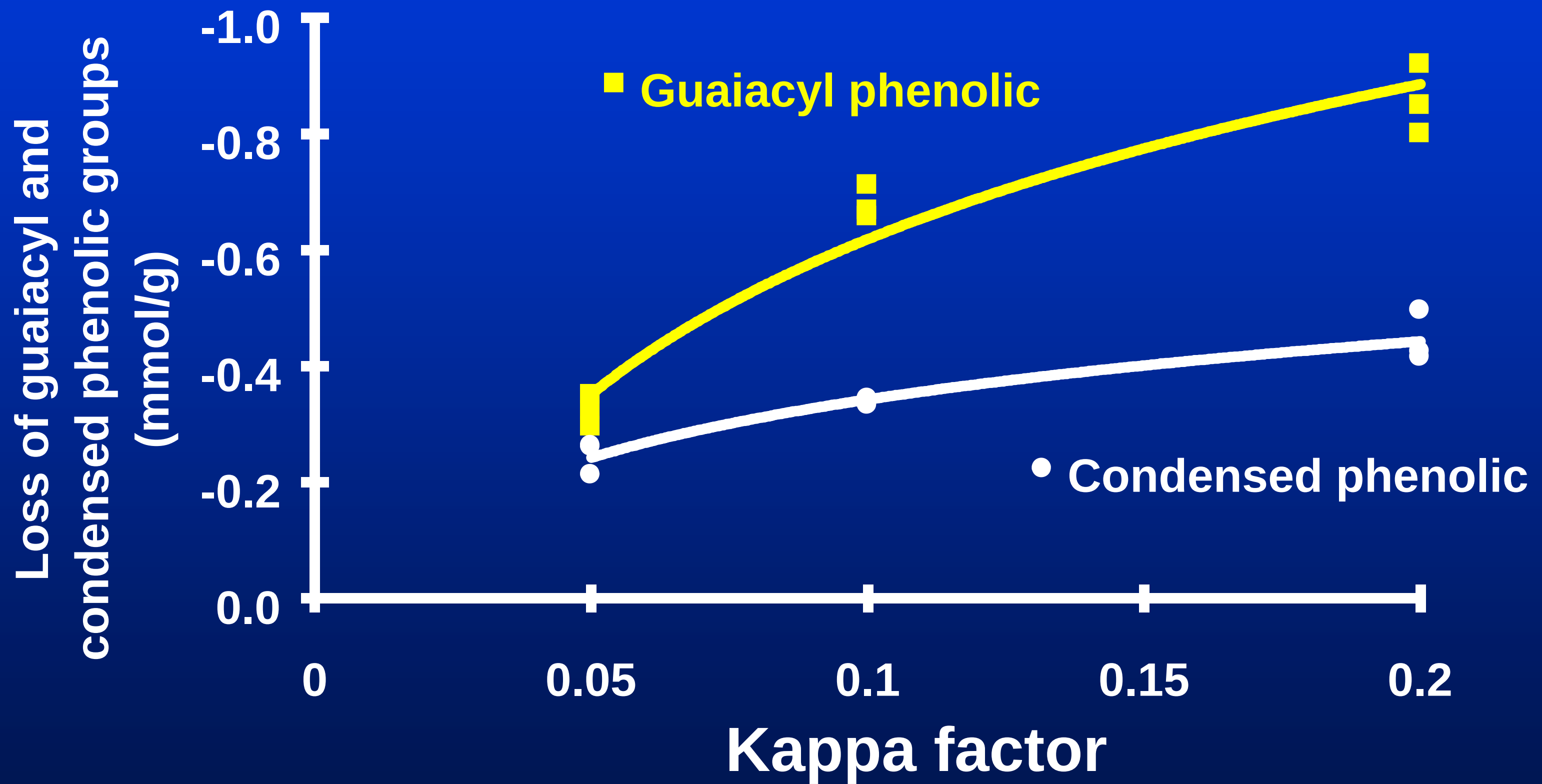
Loss of phenolic hydroxyl groups

EMCC residual lignins-reactions with ClO_2



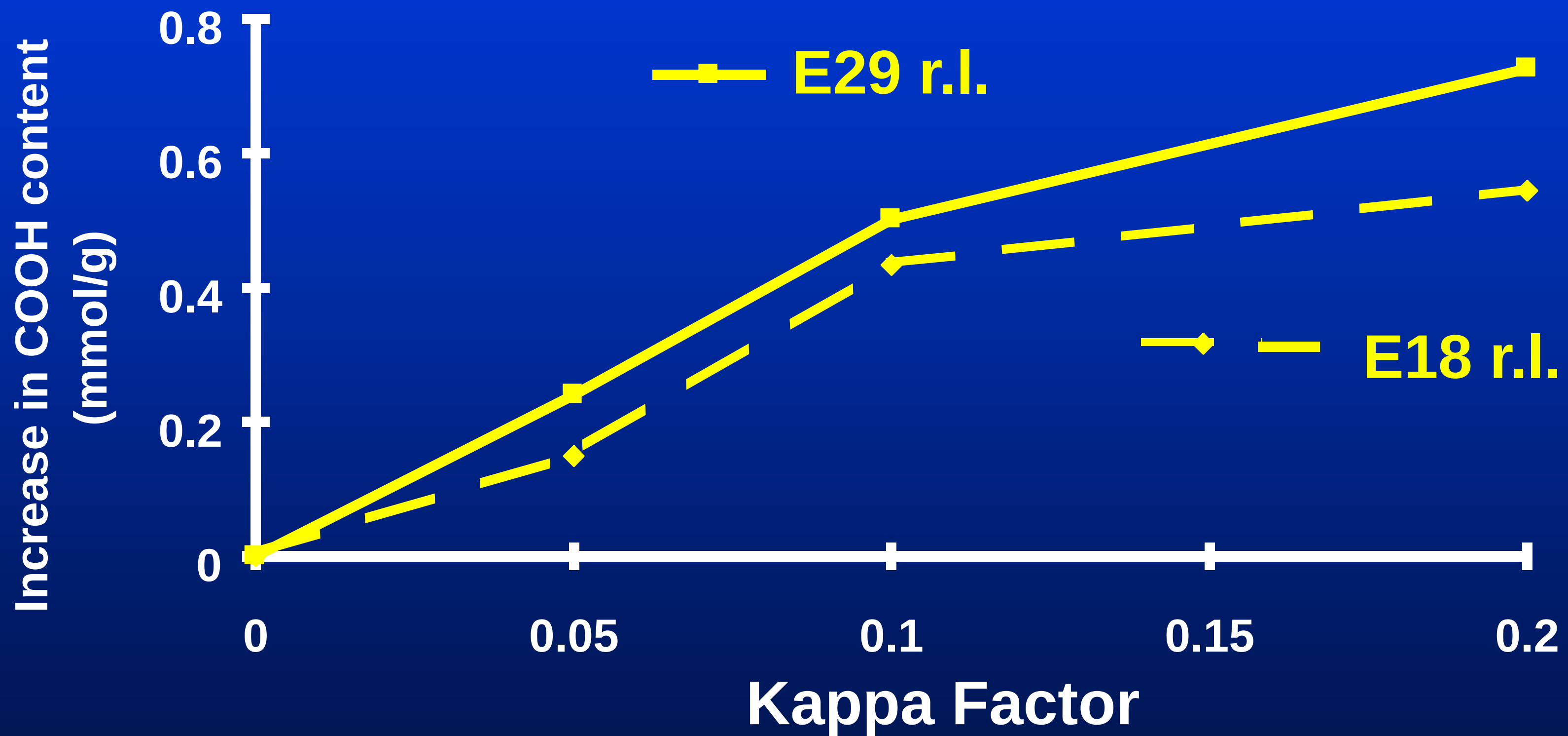
Loss of phenolic hydroxyl groups

Various residual lignins-reactions with ClO_2



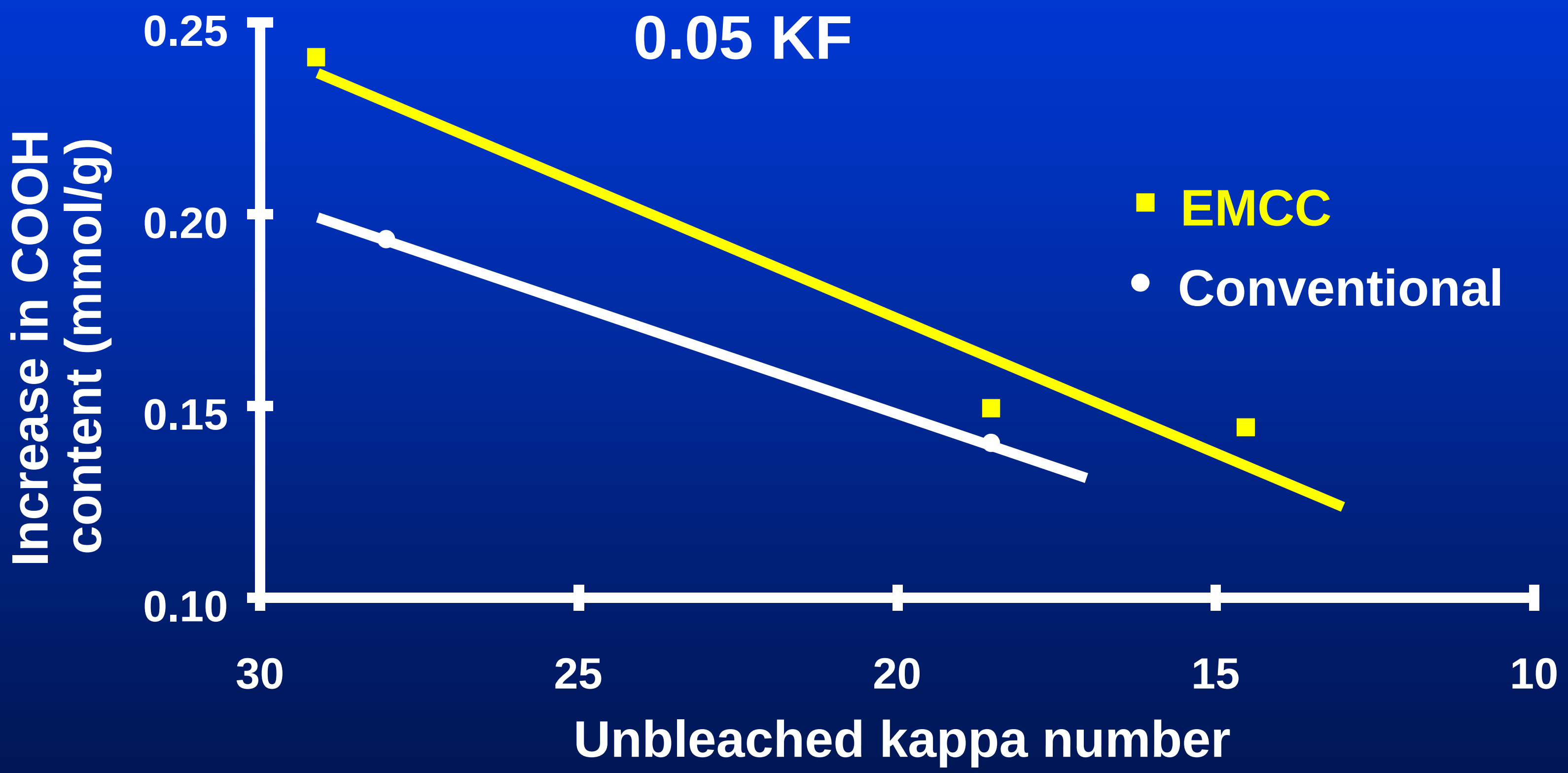
Increase in carboxylic acid groups

EMCC residual lignins-reactions with ClO_2



Increase in carboxylic acid groups

Various residual lignins-reactions with ClO_2



Conclusions

- Residual lignin structure and reactivity toward ClO_2 will influence bleaching in a D(EO) sequence
  - Condensed phenolics not as reactive
  - B-O-aryl ethers
- Pulping conditions influence residual lignin structure and suggests that these conditions can be optimized to enhance and improve ECF bleachability