Advanced technologies for bleached eucalyptus pulp production: from wood to product

Jorge L. Colodette, UFV

José L. Gomide, UFV

Andréia Magaton, UFV

Brazilian Pulp and Paper Industry

PULP		
Country		1,000 tons
1.	USA	49,243
2.	China	22,042
3.	Canada	18,536
4.	Brazil *	14,164
5.	Sweden	11,877
6.	Finland	10,508
7.	Japan	9,393
8.	Russia	7,421
9.	Indonesia	6,278
10.	Chile	4,114
11.	India	3,931
12.	Germany	2,762
	Other	25,313
TOTAL WORLD		185,582

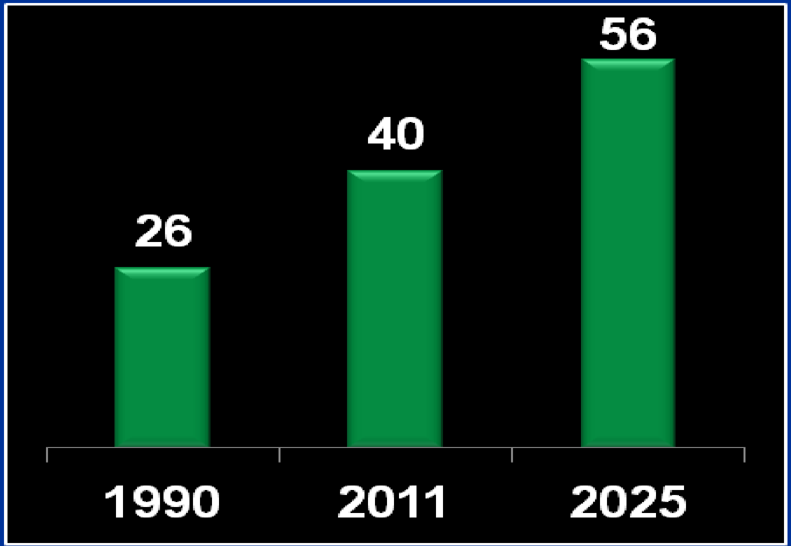
PAPER		
Country		1,000 tons
1.	China	92,599
2.	USA	75,849
3.	Japan	27,288
4.	Germany	23,122
5.	Canada	12,787
6.	Finland	11,789
7.	Sweden	11,410
8.	South Korea	11,120
9.	Indonesia	9,951
10.	Brazil *	9,844
11.	India	9,223
12.	Italy	9,146
	Other	89,771
TOTAL WORLD		393,899

New Capacity

COUNTRY	START UP	COMPANY	LOCALE	ADT/YR
Brazil	2012	ELDORADO	Três Lagoas - MS	1,400,000
Uruguay	2013	StoraEnzo/ Arauco	MdP- UY	1,300,000
Brazil	2014	Suzano	Imperatriz - MA	1,400,000
Brazil	2015	Klabin	Ortigueira - PR	1,500,000
Brazil	2015	CMPC	Guaíba - RS	1,350,000
Brazil	2016	Fibria	Três Lagoas - MS	1,400,000
Brazil	2016	StoraEnso/Fibria	Porto Seguro - BA	1,400,000
Chile	2016	Arauco	Arauco - CL	1,500,000
Brazil	2017	Suzano	Somewhere - PI	1,500,000
Brazil	2018	Cenibra	Belo Oriente - MG	1,500,000
Brazil	2018	BRAXCEL	Gurupi - TO	1,500,000
TOTAL				15,750,000

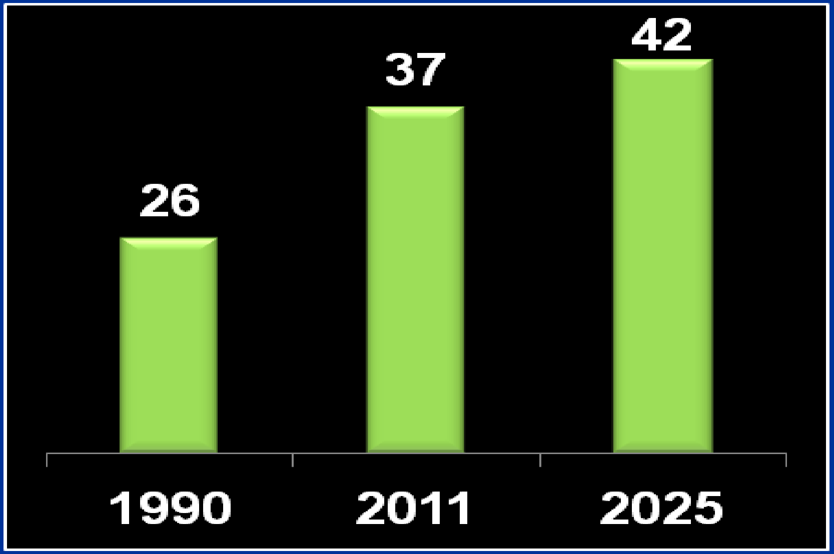
PRODUCTIVITY (AAI), m³/ha/year

Eucalyptus spp.



7 year rotation

Pinus spp.



12 year rotation

Productivities up to 100 m³/ha/year have been reported for *E. grandis X E. urophylla* hybrids in certain sites in the state of Bahia (*Fernandes et al., 2011*)

Source: ABRAF, STPC, 2012.

Outline:

- –Wood quality
- –Cooking
- –Bleaching
- –Brightness stability

Important Definitions

- AAI = annual average increment (m^3/ha/yr)
- Yield = gravimetric yield (t pulp/t wood)
- Density = t wood/ m^3 wood
- SWC = specific wood consumption (m^3 wood/ t pulp)
  - SWC = 1.00 ton pulp/ (yield * density)
- AAICell = AAI / SWC (t pulp/ha/yr)

Wood Quality Traits

↗Wood Density

SWC

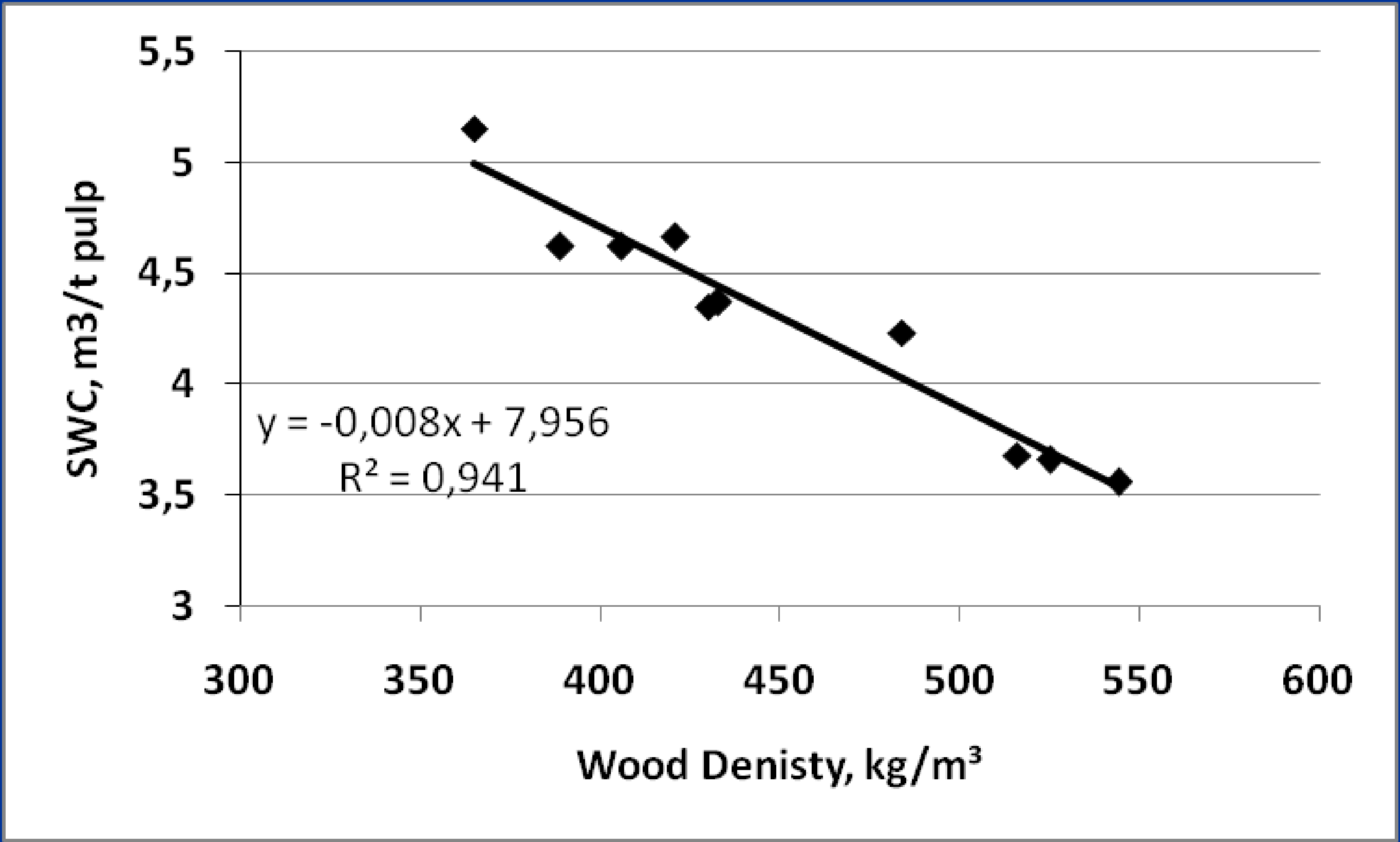
↗Wood Chemistry:

- Cellulose
- Extractives
- Lignin
  - Lignin S/G
- Hemicelluloses
- Uronic Acids

YIELD

SWC = Specific Wood Consumption (m^3 wood/ ton of pulp)

7-8 yr old eucalyptus samples cooked to kappa 17-18



Source: Colodette et al. (7)

Effect of wood density and pulping yield on SWC for *Eucalyptus grandis* and *Eucalyptus urophylla* cooked to kappa 17-18

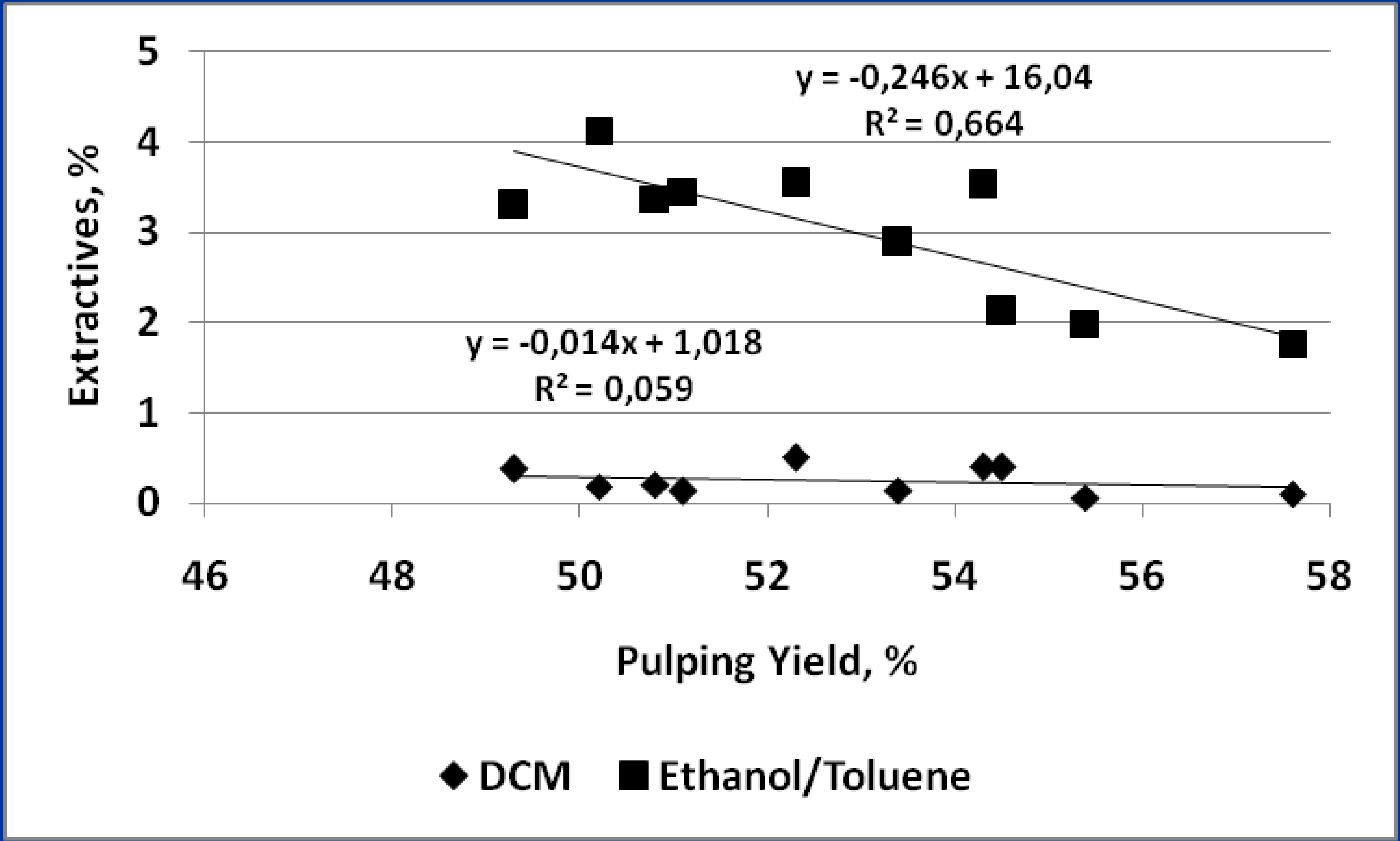
Trait	*Eucalyptus grandis*	*Eucalyptus urophylla*
Wood density, t/m^3	389	544
Pulping yield, %	55.9	51.7
SWC, m^3/odt pulp	4.60	3.56

Source: Colodette et al. [7]

Wood Density

- Overall, one should strive for high wood densities and pulping yields
- However, there are more opportunities to change wood density (350-600 kg/m^3) than pulping yield potential (50-55%), through tree improvement programs

Effect of wood ethanol/toluene and DCM extractive contents on pulping yield at kappa 18±0.5 for ten seven-year old *Eucalyptus*

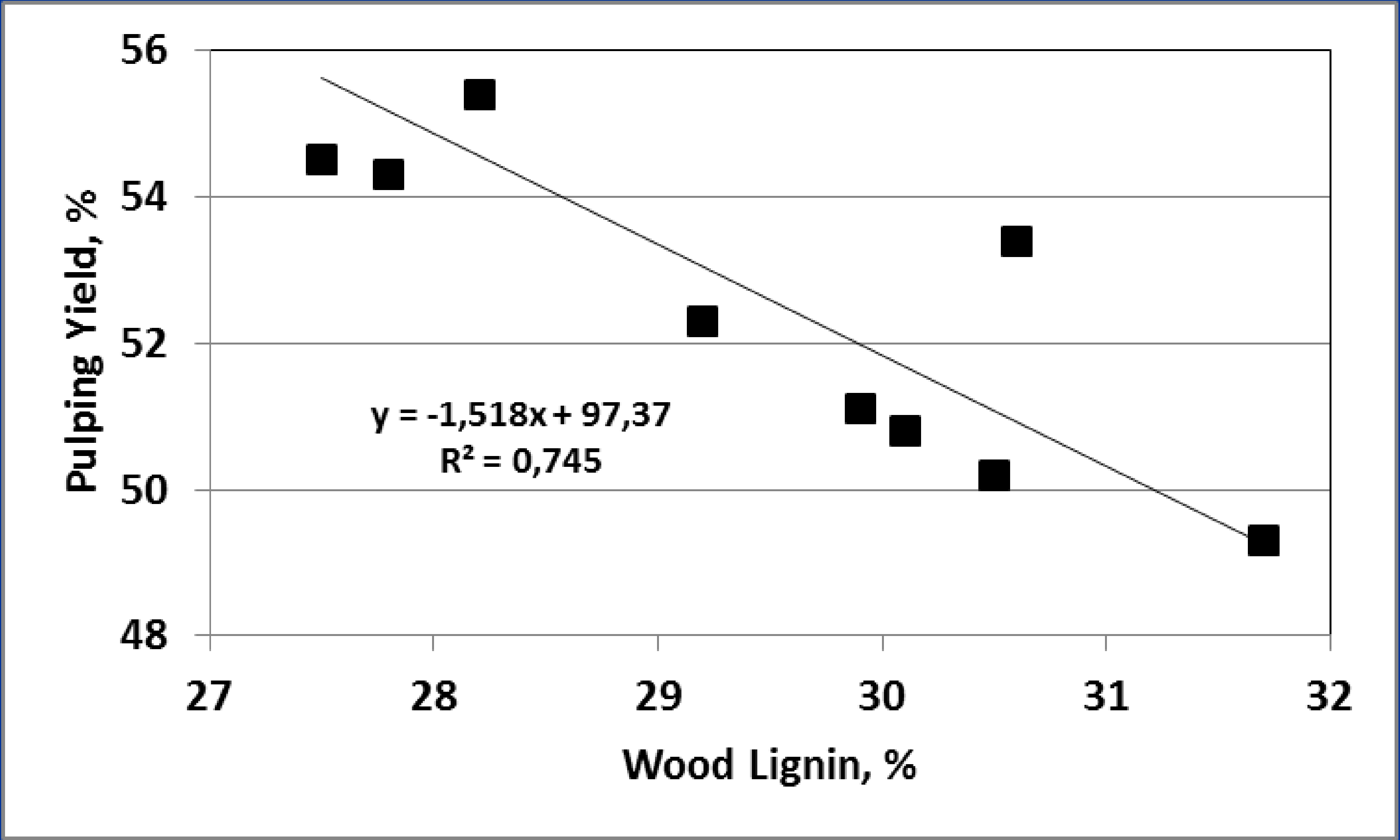


Source: Gomide & Colodette (9)

Extractives

- Extractives negatively affect pulping yield;
- Brazilian grown eucalyptus contains low extractives because of young harvesting age, but content increases fast with aging (premature formation of heartwood)
- Eucalyptus lipophyllic extractive fraction causes severe pitch problems (steryl esters)

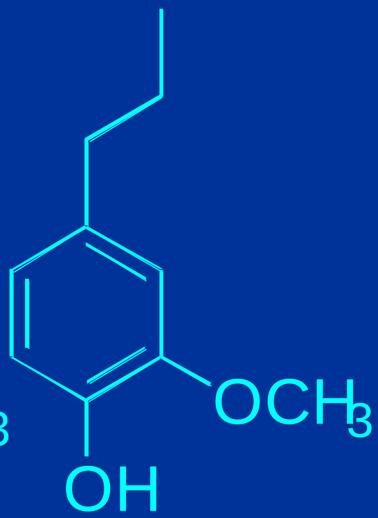
Effect of lignin content on pulping yield to kappa 18±0.5 for ten seven-year old samples



Source: Gomide & Colodette (8)

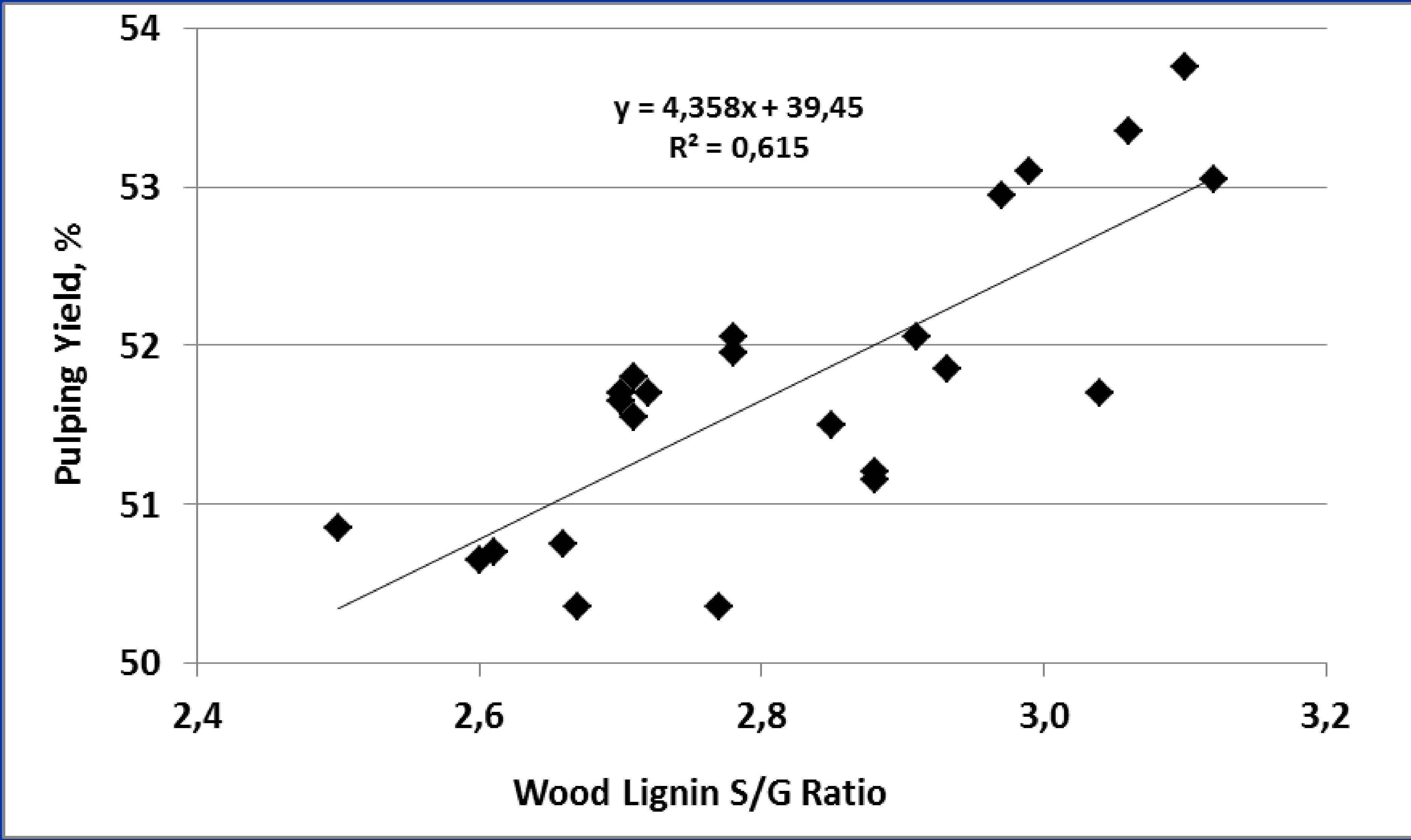
Wood Lignin Syringyl (S)/ Guaiacyl (G)

S



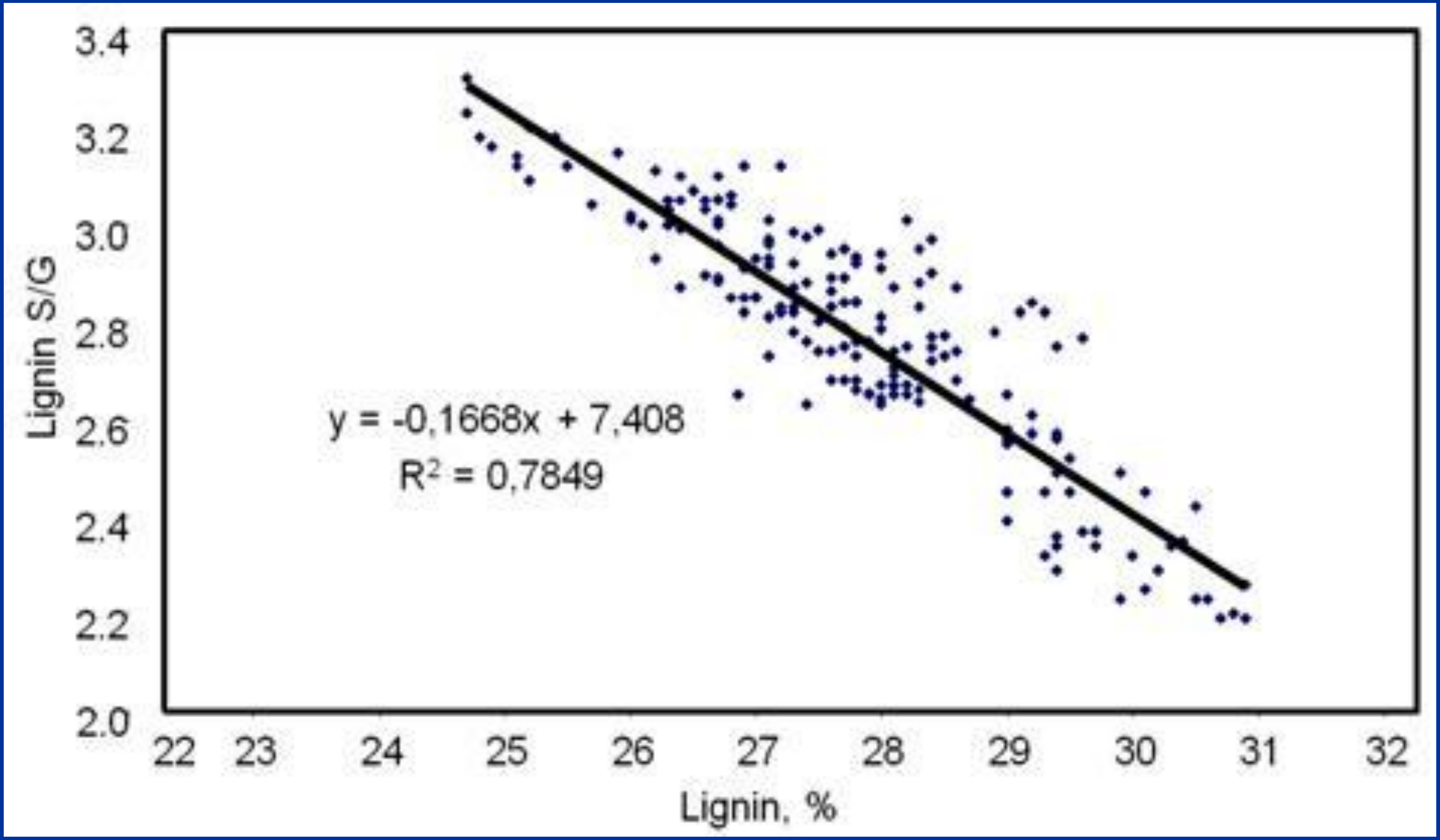
G

Effect of lignin S/G ratio on pulping yield at kappa 17 for twenty four three-year old *E. urograndis* wood samples.



Source: Gomes & Colodette (10).

Relationship between wood lignin content and syringyl/guaiacyl ratio for 100 samples of three-year old *Eucalyptus urograndis*



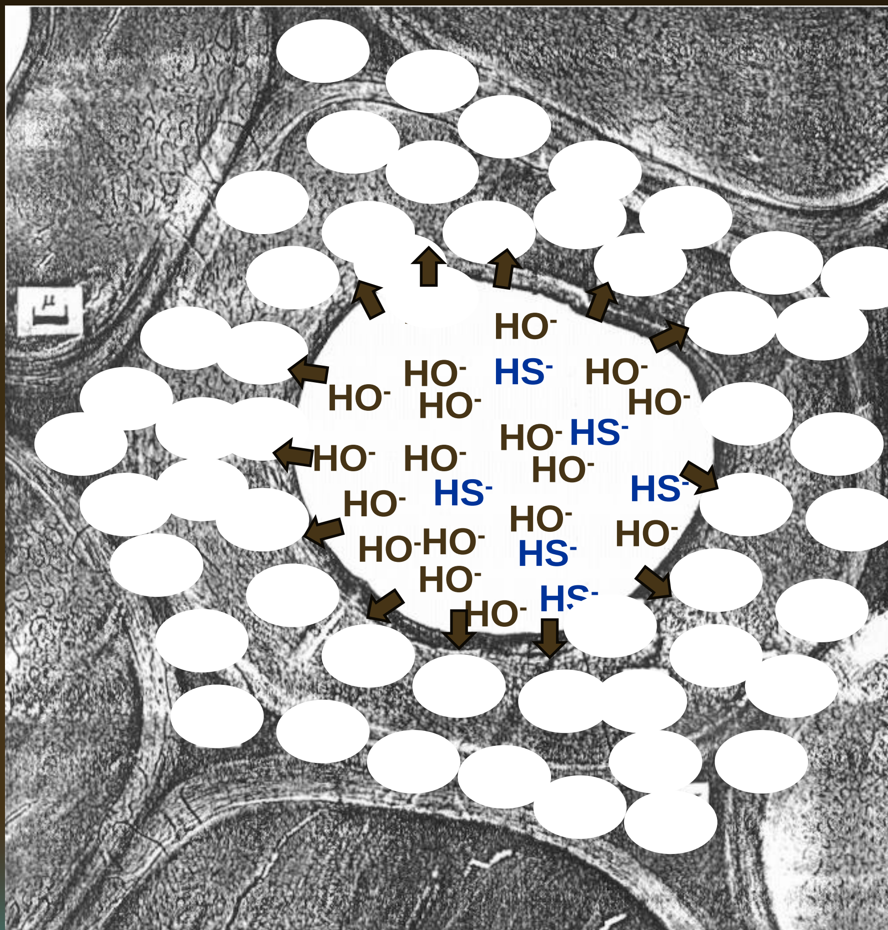
Source: Colodette et al. (20).

Relevance of the Lignin S/G Ratio

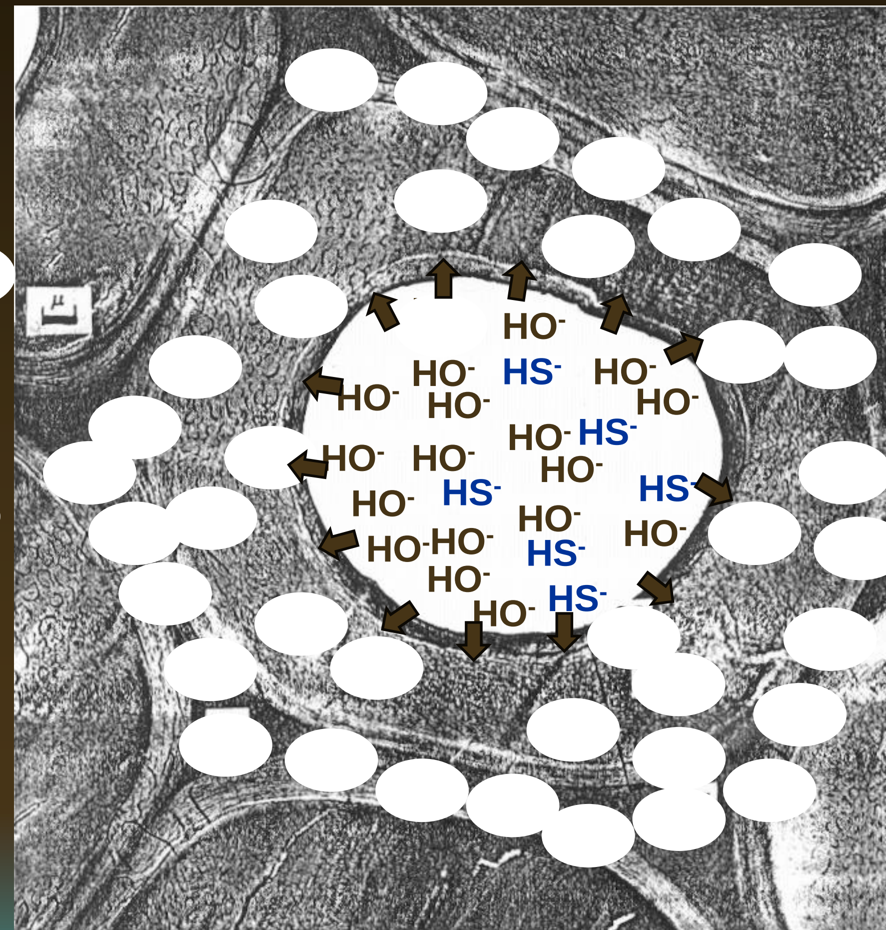
Wood containing lignin of high S/G ratio will defiberize at lower kappa numbers during cooking, without excessive alkali charges and yield penalties

In other words, there will be a lower lignin content in the high S/G derived pulp before the fibers are chemically separable; thus decreasing bleaching costs.

High S/G Lignin (defiberization at low kappa)



Low S/G Lignin (defiberization at high kappa)

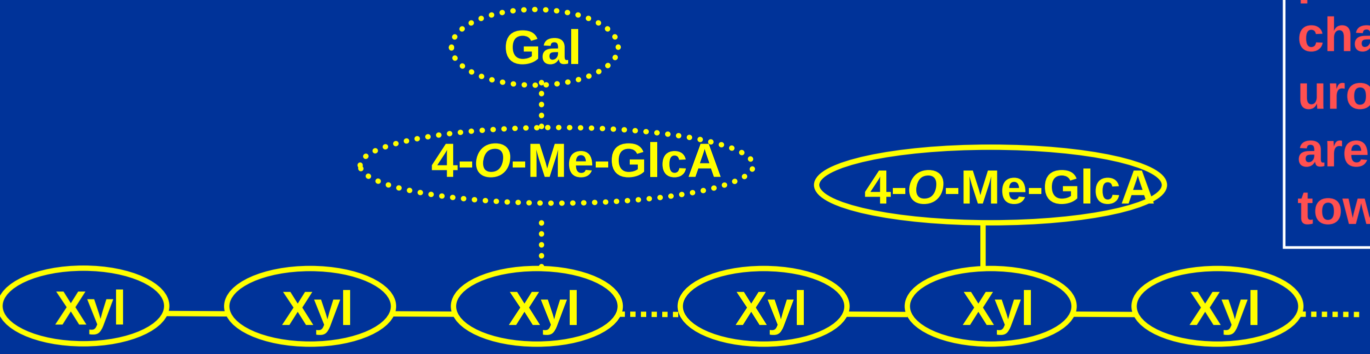


Lignin Content and Nature (S/G)

- Overall, one should strive for low lignin content and high S/G ratios, if fiber line yield is main priority

Eucalyptus Special Xylan

Eucalyptus xylans possess galactose side chains, unusually high uronic acid contents, and are reasonably stable towards kraft pulping



- [β-D-Xyl*p*]-(1→4)-[β-D-Xyl*p*]$_7$-(1→4)-[β-D-Xyl*p*]$_{79}$-(1→4)-[β-D-Xyl*p*]$_3$-(1→4)-[β-D-Xyl*p*] -

2 ↑ 1 4-*O*-Me-α-D-Glc*p*A

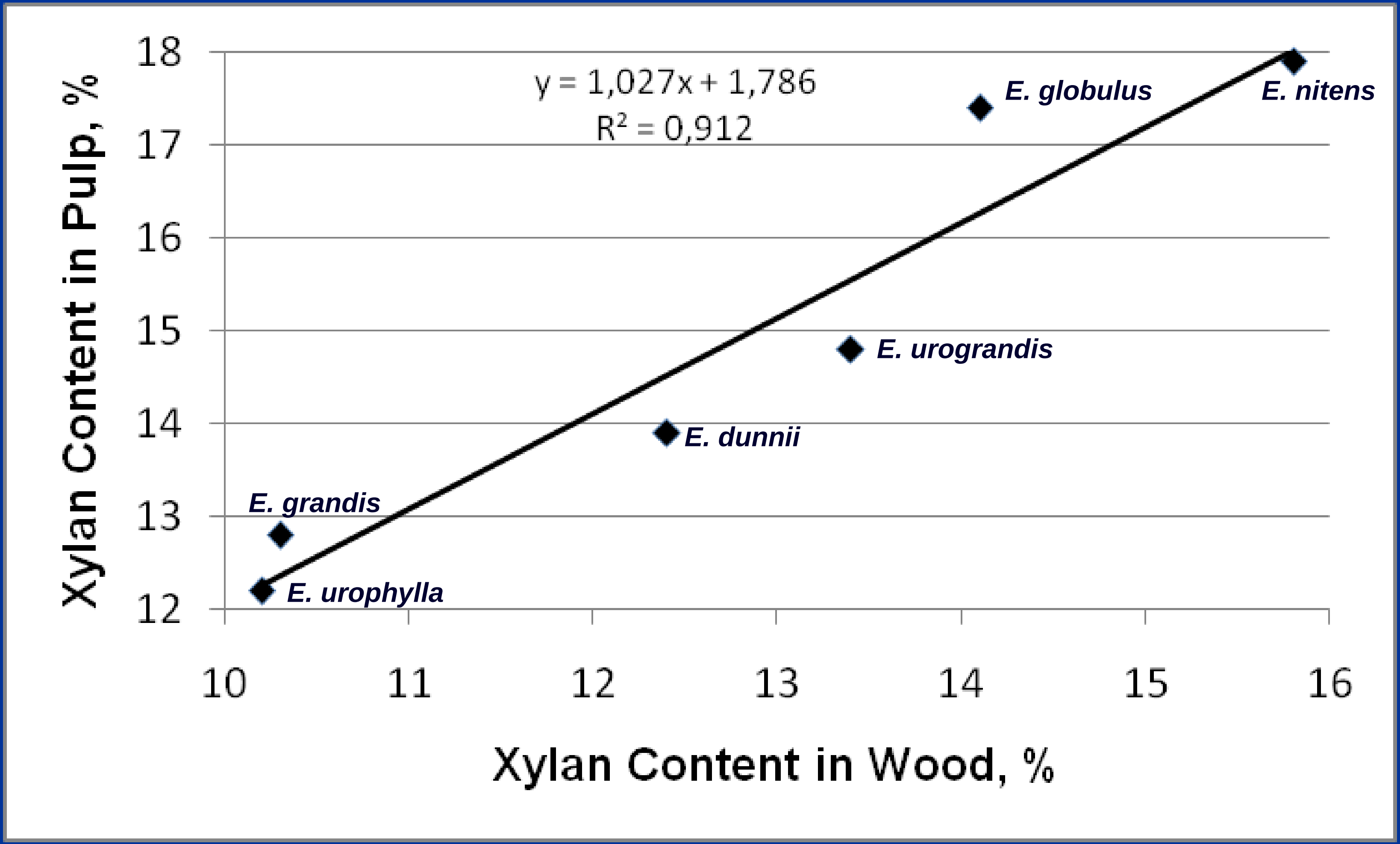
2 ↑ 1 4-*O*-Me-α-D-Glc*p*A 2 ↑ 1 α-D-Gal*p*

O_2 Substituted 4-O-MeGUA

2-*O*-α-D-galactopiranosyl-4-*O*-methyl-α-D-glucurono-D-xilan

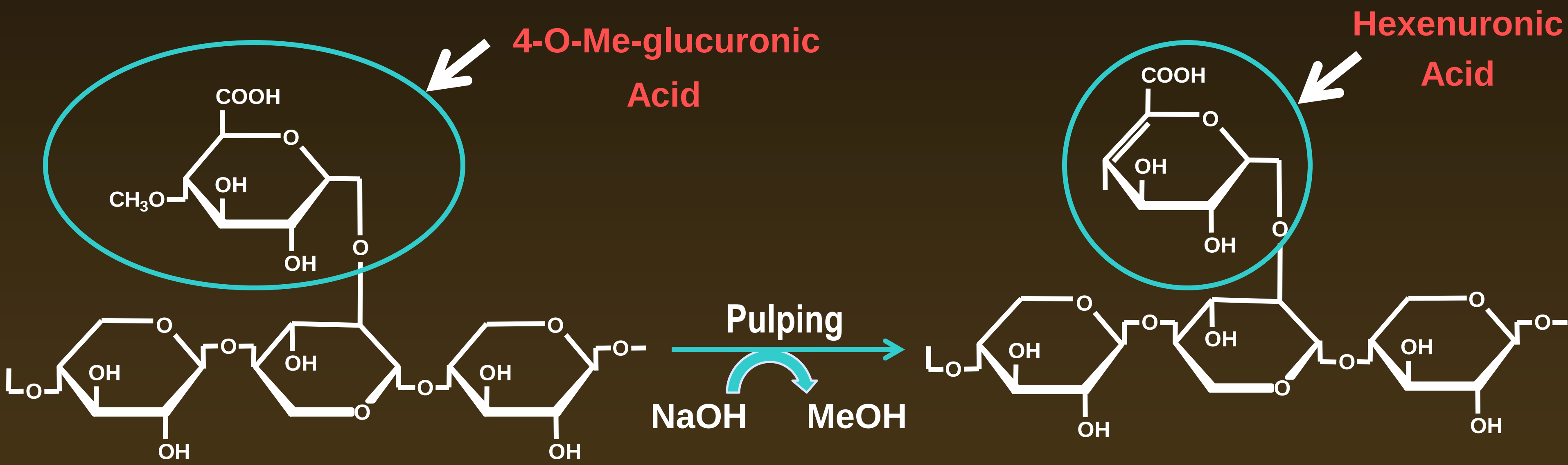
Shatalov, A. A. et al. Carbohydrate Research, 320, 93-99, 1999.

Effect of wood xylan content on kraft pulp xylan content for various eucalyptus species at kappa 17



Source: Magaton & Colodette (5).

Eucalyptus has twice as much uronic acids compared to northern HWD



4-O-Me-glucuronic Acid
|
—Xil— Xil—Xil—

Hexenuronic Acid
|
—Xil— Xil—Xil—

Distribution of eucalyptus wood xylans after kraft pulping to kappa 17, expressed in % of wood original value

Wood Species	Xylans, % of original wood		
	Pulp	Black Liquor	Degraded
E. dunni	51.3 **(2.1)***	7.3	41.4
E. globulus	54.1 **(2.6)**	7.7	38.2
E. grandis	57.3 **(2.8)**	6.9	35.8
E. nitens	52.6 **(2.1)**	4.0	43.4
E urograndis	49.7 **(1.9)**	6.4	44.1
E. urophylla	58.7 **(2.6)**	7.5	33.8

***Values in brackets indicate MeGlA/ 10 xylose molar ratio measured by ^{1}H NMR.**

Source: Magaton & Colodette (5).

Molecular weight (kDa) of xylans in the wood and in the corresponding kraft pulp: harvesting age eucalyptus clones of various origins cooked to kappa number 17

Species	Wood	Kraft Pulp	Black Liquor
E. dunni	36.7 (2.1)*	19.4	13.4
E. globulus	33.0 (2.6)	19.6	14.3
E. grandis	37.9 (2.8)	20.9	14.7
E. nitens	33.2 (2.1)	19.8	13.8
E. urograndis	34.9 (1.9)	19.9	14.3
E. urophylla	39.4 (2.6)	21.1	18.1

*values in brackets indicate MeGlA/ 10 xylose molar ratio measured by ^{1}H NMR.

Xylans/ Uronic Acids

- **High xylans in the wood means high xylans in the pulp, but xylans are very sensitive to EA dosed during pulping (needs gentle cooking)**

Final Remarks: Wood Quality

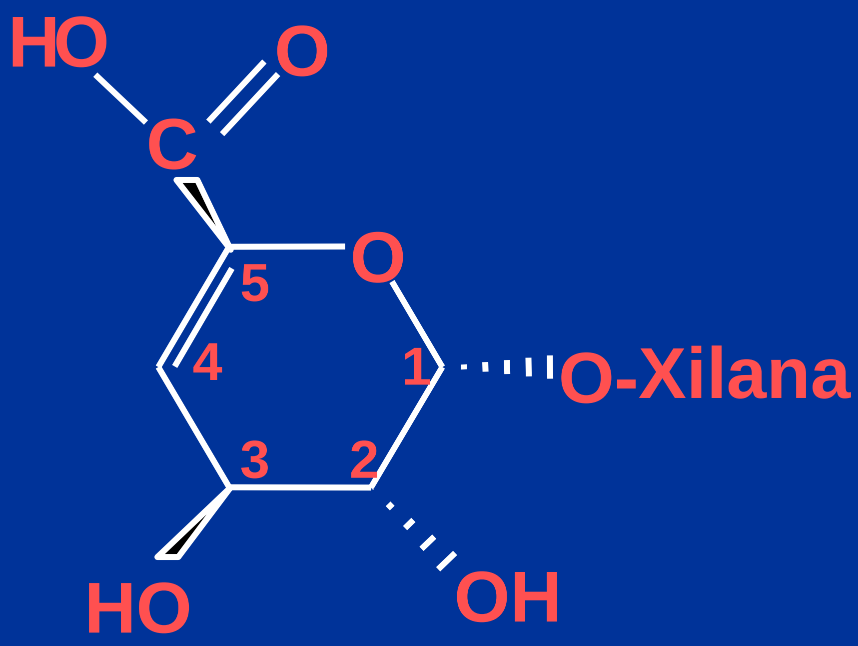
- Efficient production of kraft pulp is achieved with eucalyptus wood having reasonably high density, low extractives and lignin quantities and high lignin S/G ratio
- Xylans highly substituted with uronic acids are desirable as well (pulp quality)

Cooking

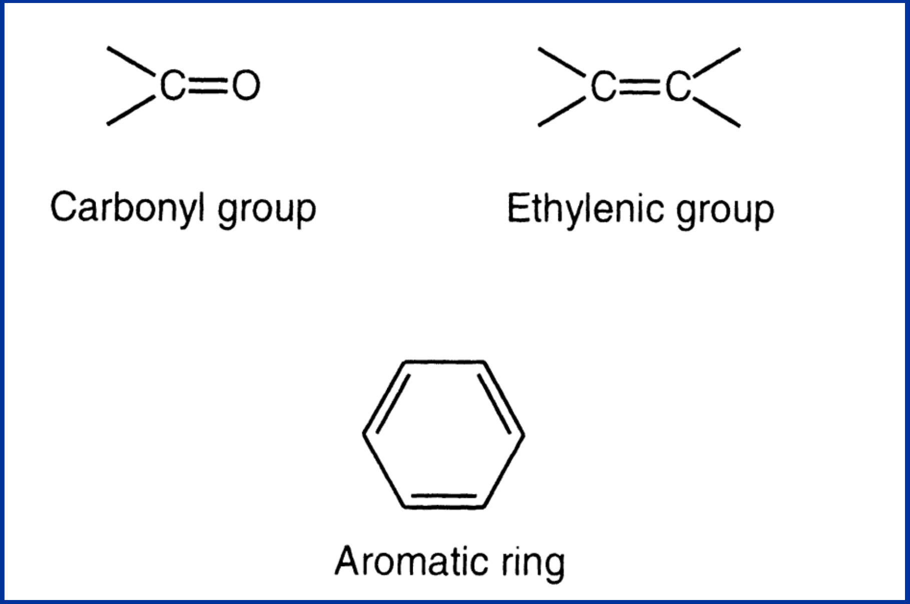
- Mostly continuous
  - Few conventional Kraft
  - Mostly modified Kraft (gentle cooking)
    - Compact
    - Lo-solids
    - Few other modified (EMCC, MCC, ITC, KM)
  - No modified batch
- Cooking Aids
  - Anthraquinone frequently used
  - Other additives (surfactants, PS)

The ratio HexA/lignin is the main factor determining yield and bleachability

HexA is the main source of leuco-chromophores



Lignin is the main source of chromophores



Cooking Eucalyptus to High Yield and Bleachability

- ✓Highest HexA/Lignin ratio ⇒ highest yield and bleachability*
- ✓But, how to attain the highest HexA/Lignin ratio in kraft pulps?

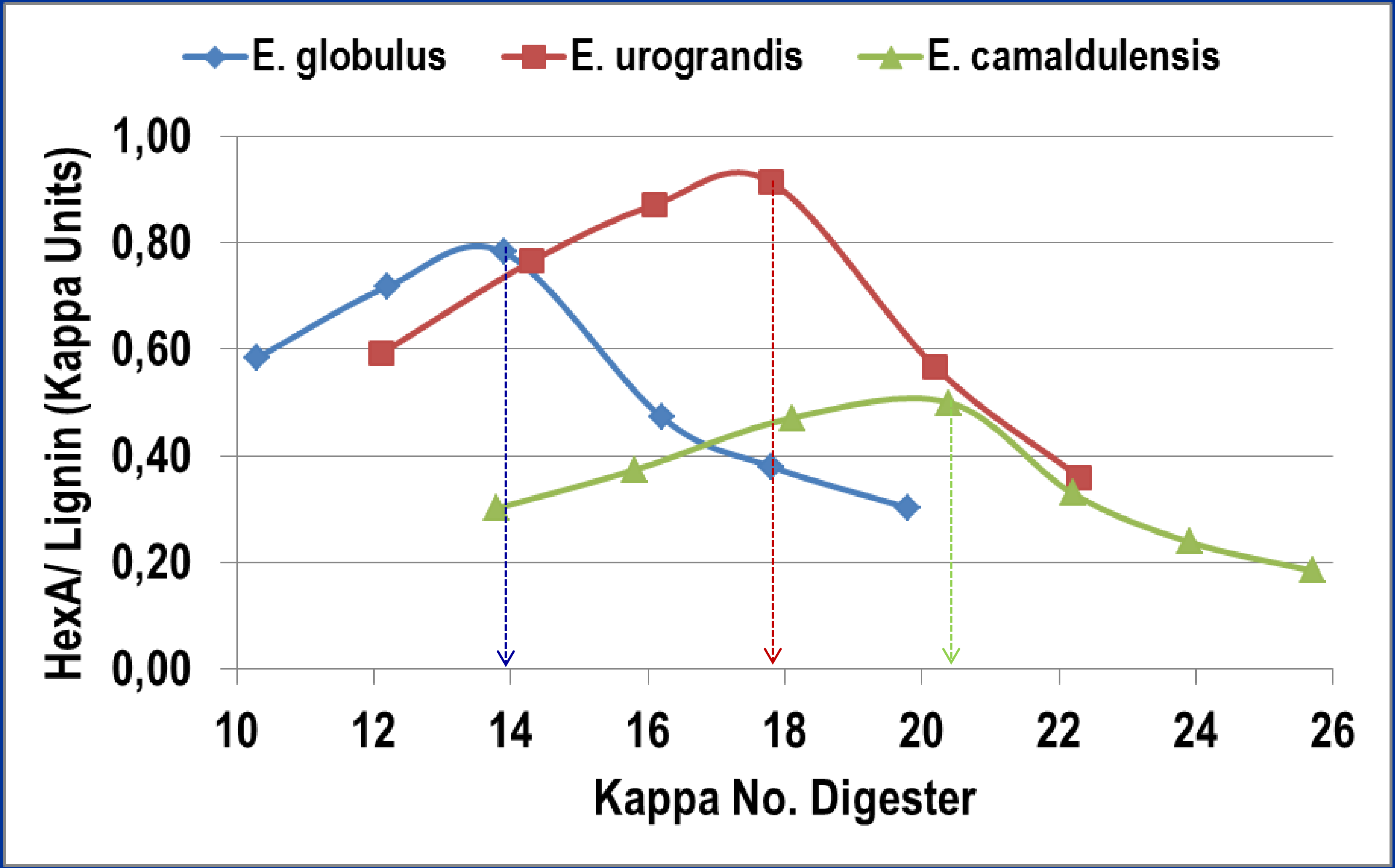
* Bleachability = Δ Kappa/ TAC across bleaching

TAC = Total Active Chlorine

Attaining a high HexA/Lignin ratio

- Selecting wood of high 4-O-MeGluA content (difficult task)
- Gentle cooking
- **Terminating cooking at the proper kappa number for the wood supply available**

Kappa # that maximizes HexA/Lignin depends on wood

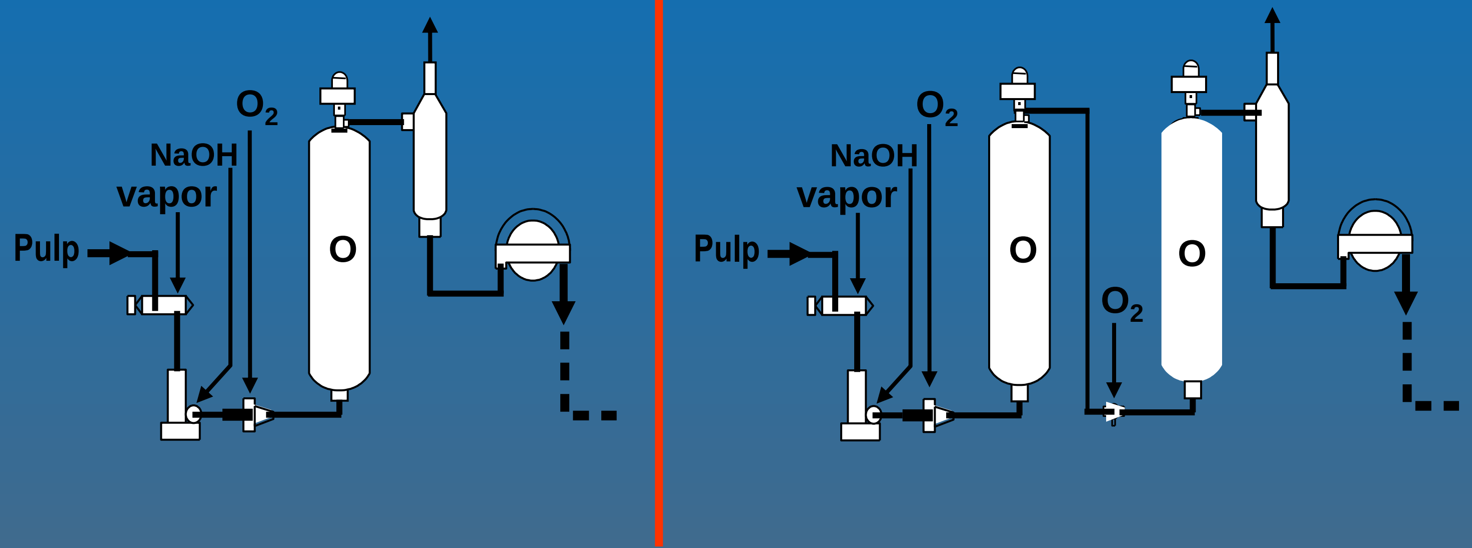


E. globulus* with low lignin content and high lignin S/G ratio maximized HexA at low kappa, with the opposite occurring for *E. camaldulensis

Oxygen Delignification

Oxygen Delignification

Single *vs* Double Stage



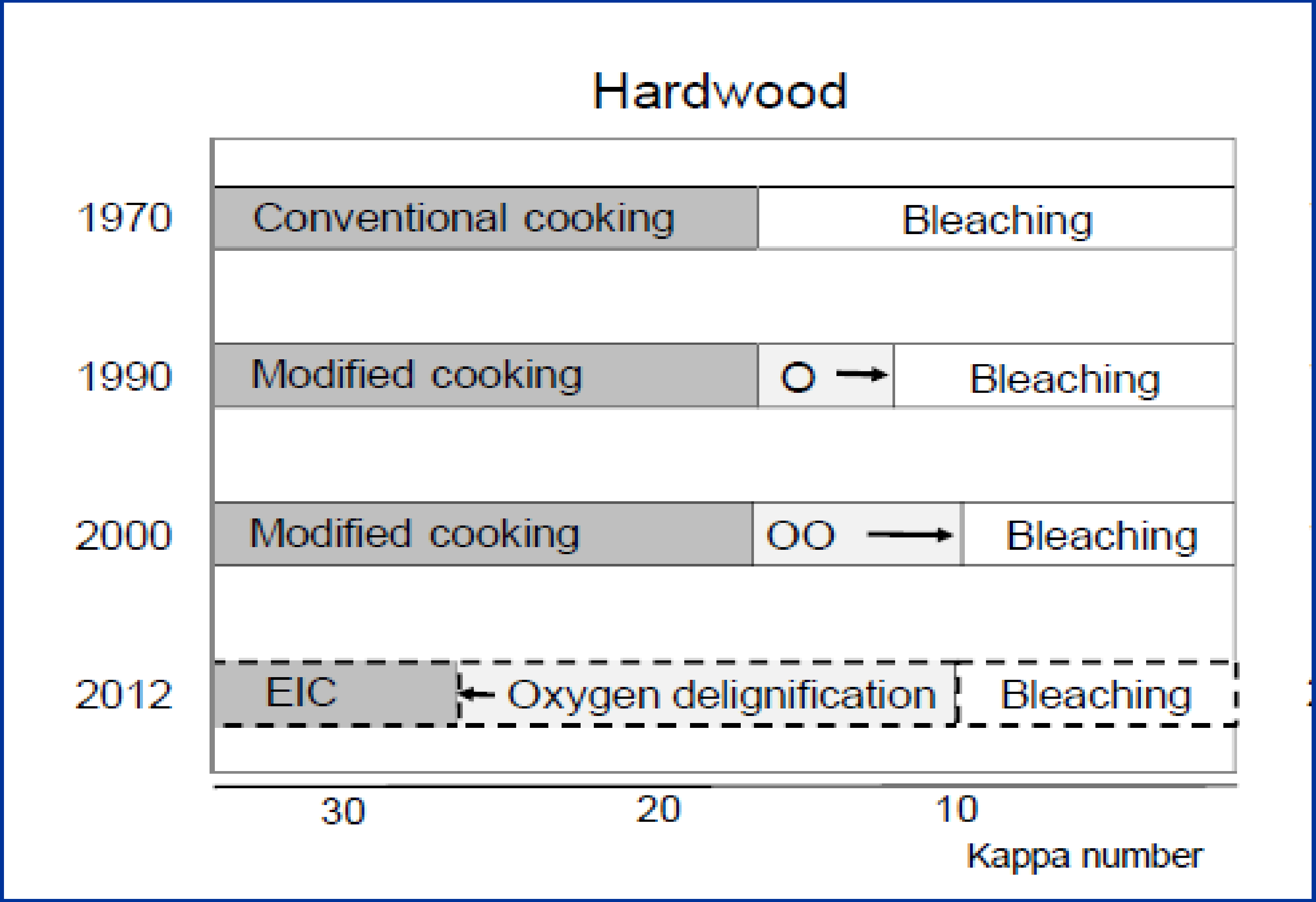
✓ **For Softwoods: two stages is standard technology**

- **Higher delignification and brightening efficiency**
- **Higher selectivity**
- **Easier operation (less channeling, better mass transfer)**
- **First stage at lower time-temperature and higher pressure-alkalinity than the second**

Oxygen Delignification

- ✓ For hardwoods, choice between single and double stage determined by pulp "true" lignin content
  - second stage of little significance for pulps of high HexA content and cooked to low Kappa No.
  - second stage attractive when pulping is terminated at high kappa (25-30) – more "true" lignin and yield gains
- ✓ New installations tend to install double-stage systems

Terminating cook at high kappa makes O_2 delig more attractive for HWD kraft pulps



Wedin and Lindström, 2012

ECF BLEACHING

Bleaching Drivers

- – Capital, steam/energy (back to 3-stage?)
- – bleaching chemical consumption
- – brightness and brightness stability
  - ➢ 90^+ % ISO
  - ➢ 2% ISO reversion (Tappi UM 200)
- – pulp strength
- – pulp OX (only special markets)
- – bleaching yield
- – water consumption
- – effluent load & treatability

ECF Bleaching

First bleaching Stage

First Bleaching Stage – Kraft Pulp

- **Z/D, Z/E and AZ**
  - Z/D-(EPO)-D
  - Z/E-D-P
  - A-Z-D-P

Very interesting approaches for improved brightness stability and water reuse

- **D, D/A and A/D**
  - **D-(EP)-D**
  - **D/A-(EP)-D**
  - **A/D-(EP)-D-P**

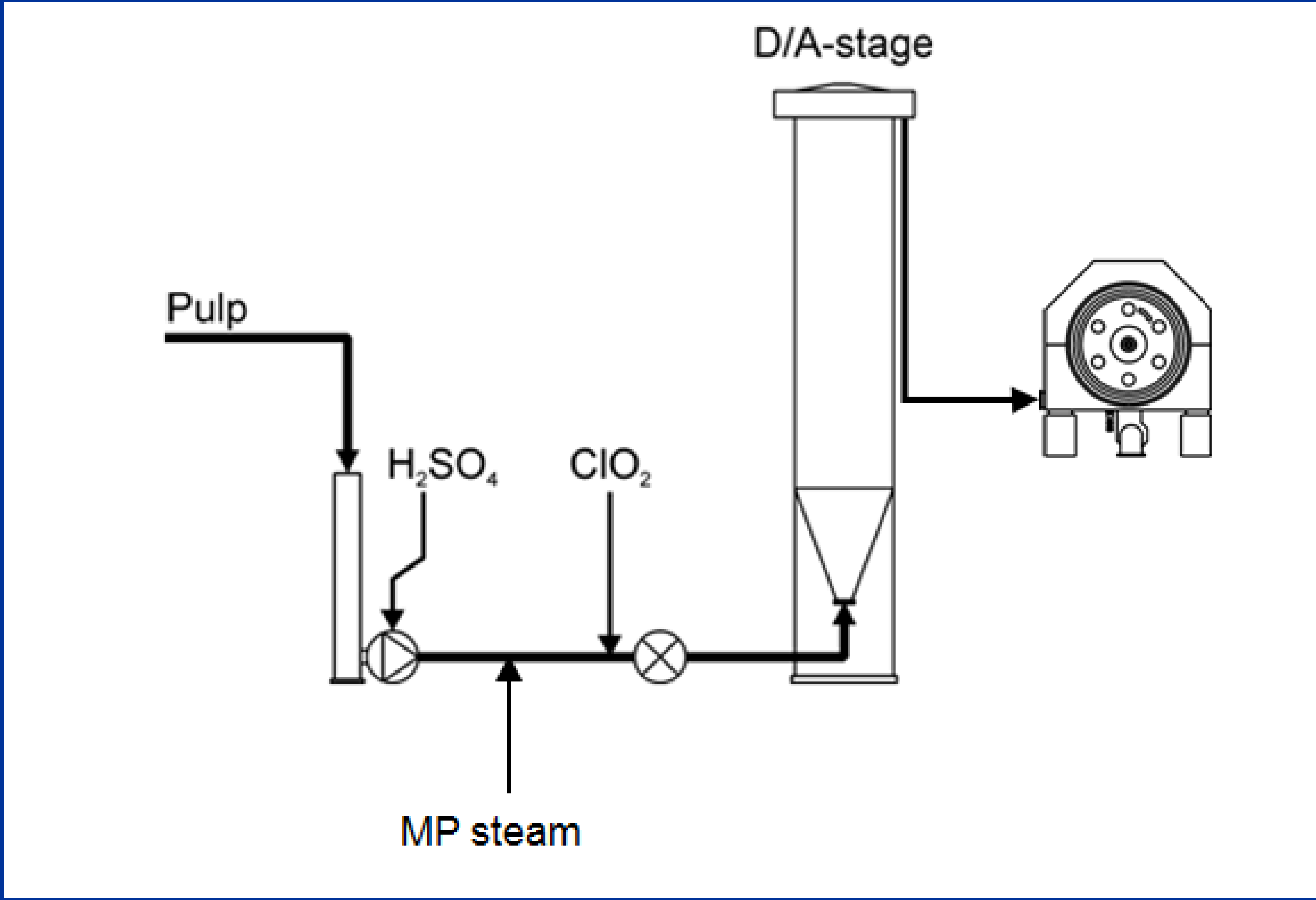
Lower active chlorine demands:more cost effective

Sequences and Chemical Consumptions – O_2 delignified pulps

Sequence	Total Active Chlorine, kg/adt	
	Paper Pulp	Dissolving Pulp
D*-(EPO)-D	45-50	-
D*-(EPO)-D-P	35-40	20-30
Z/D-(EPO)-D	35-40	-
Z/E-D-P	55-65	-
A-Z-P	-	30-40

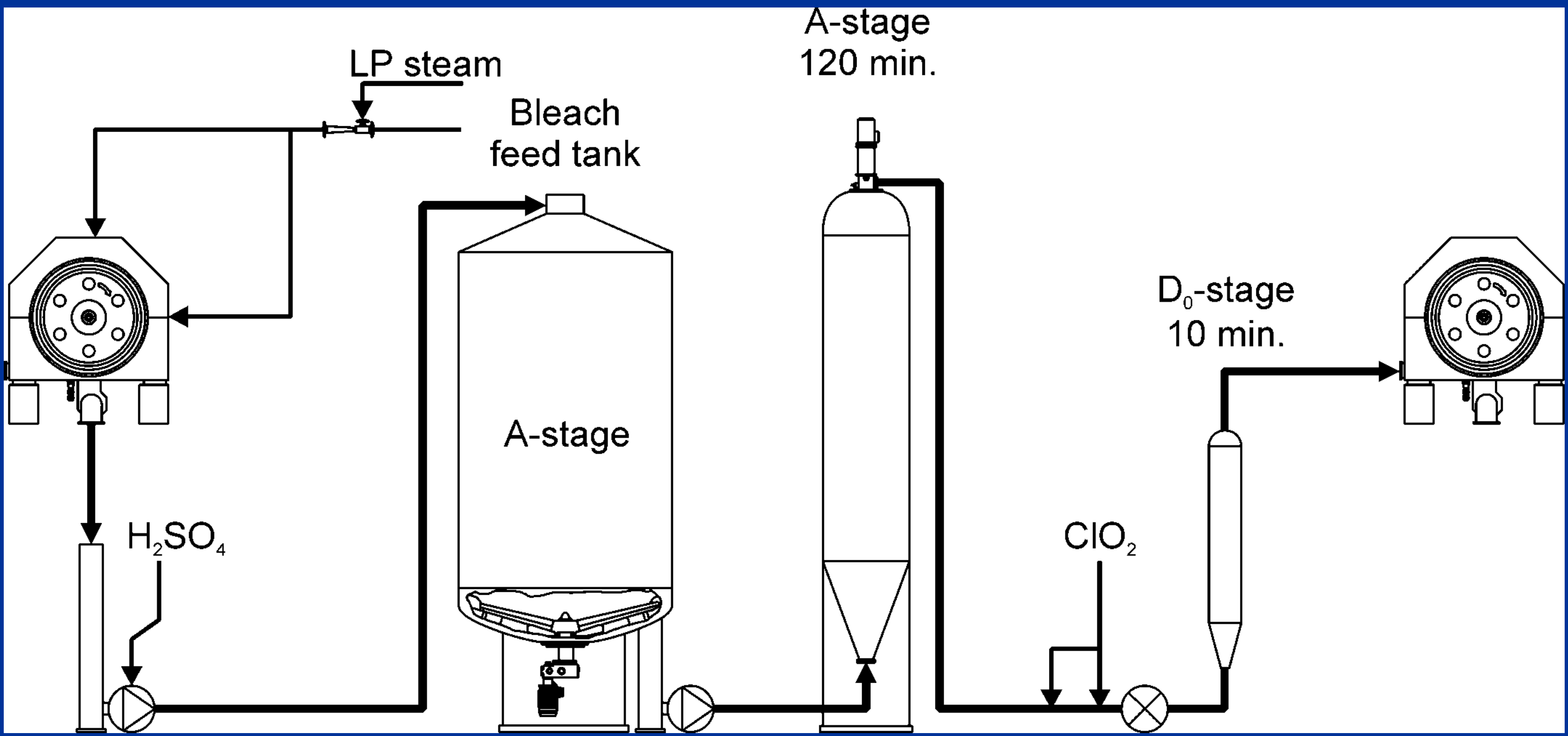
***D/A or A/D technology**

The D/A Technology



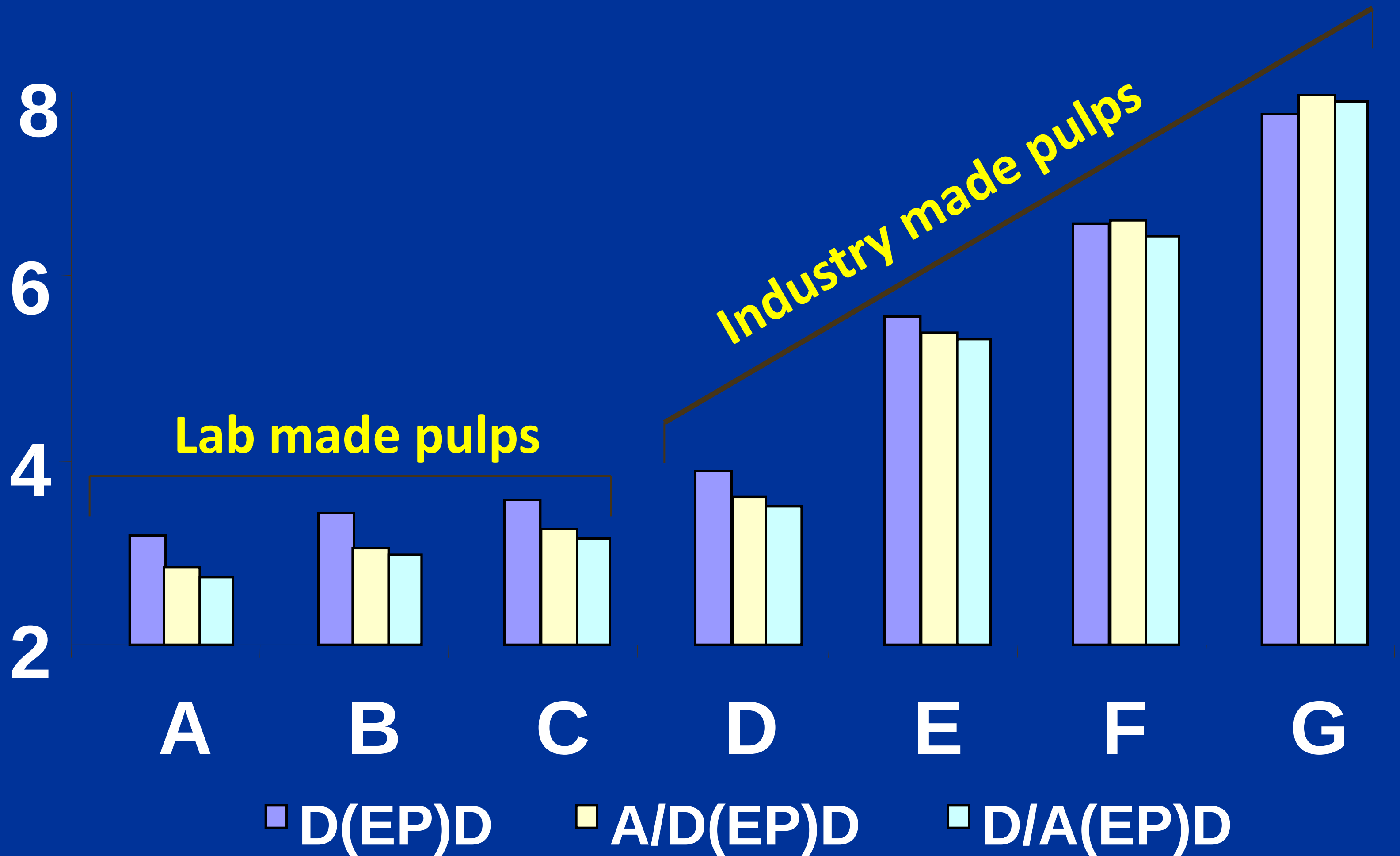
- Very successful if low kappa factors are used
- 9 installations in South America

The Advanced A/D Technology



- A-stage **done in combined down-flow and up-flow towers**
- **6 installations in South America**

Active Cl Consumption (%) for 90.0% ISO brightness



- **Hot acid/ hot chlorine dioxide bleaching is effective for high bleachability pulps but ineffective for low bleachability ones, particularly those with high carryover**

ECF Bleaching

Second Bleaching Stage

Second Bleaching Stage

- Oxidative extraction using lowest possible alkali dose (end pH 10 -10.5)
  - (EP)
  - (EPO)
  - (PO) – New Installations
- Approach slightly different when using hot acid/ hot chlorine dioxide bleaching in first stage
  - Higher temperatures
  - Need for oxygen ?

ECF Bleaching

Final Bleaching Stage

Final Bleaching

- ✓ Single Stage
  - D
  - D_N/D
- ✓ Double Stage
  - DD
  - DP

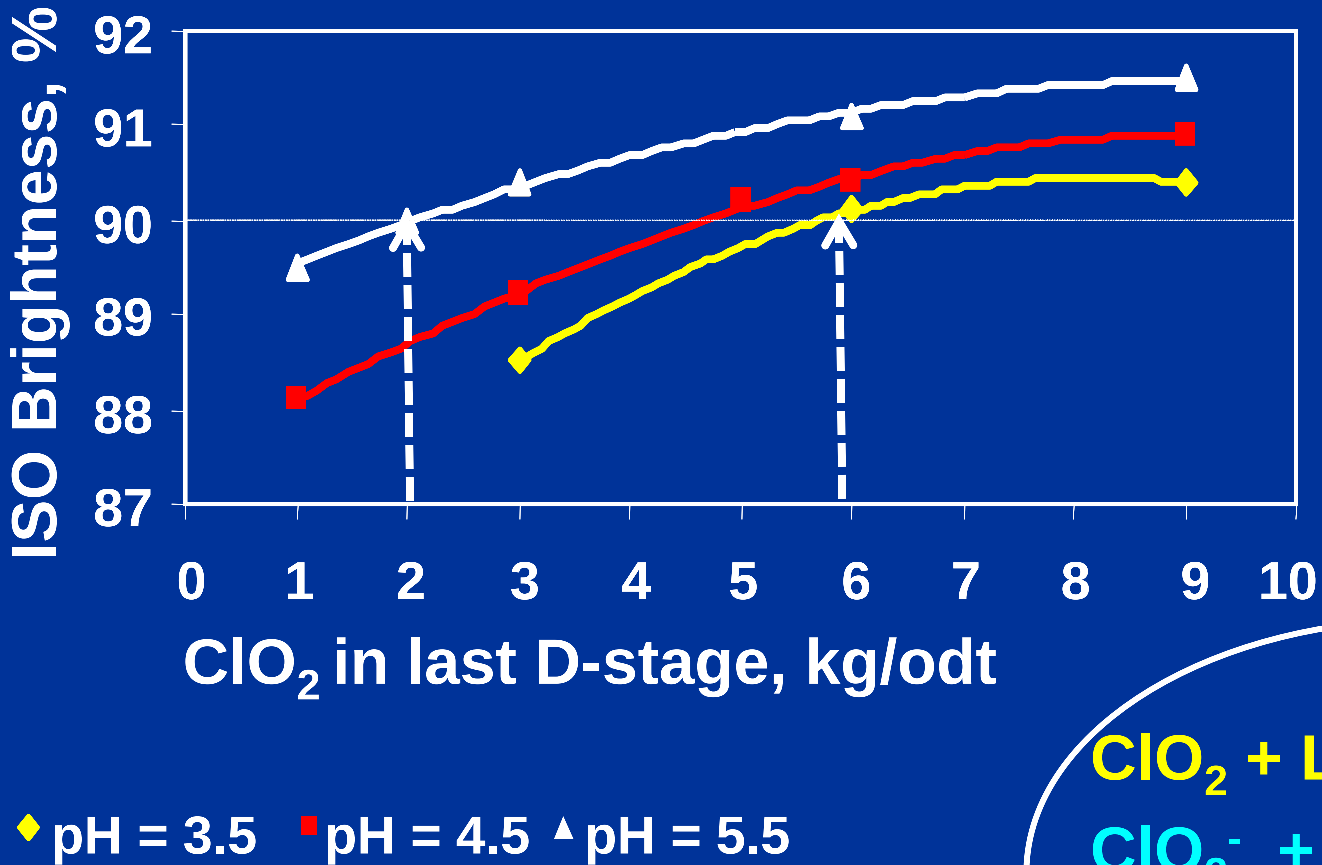
Bleaching O_2 delignified pulp* to 90.0% ISO

Bleaching Results	D/A(EP)D	D/A(EPO)D_N/D	D/A(EP)DD	D/A(EP)DP
Total Act. Cl, % **	**3.51**	**3.30**	**3.10**	**3.32**
Relative Cost, %	**100**	**102.5**	**103**	**103.8**
Viscosity, mPa.s	14.8	15.6	16.0	14.5
Reversion, % ISO	2.0	2.0	1.7	1.4
Yield Loss, %	**2.2**	**2.1**	**2.2**	**2.5**

***Kappa 10.5, HexA´s 67.2 mmol/kg, brightness 53.5% ISO and viscosity 36.8 mPa.s.**

****Total active Cl = ClO_2*2.63 + H_2O_2*2.09**

Last D-stage end pH *vs* Brightness : D/A-(PO)-D



Last D-stage ClO_2 bleaching is more effective at pH 5.5. $HClO_2$ is slowly regenerated as needed from chlorite.

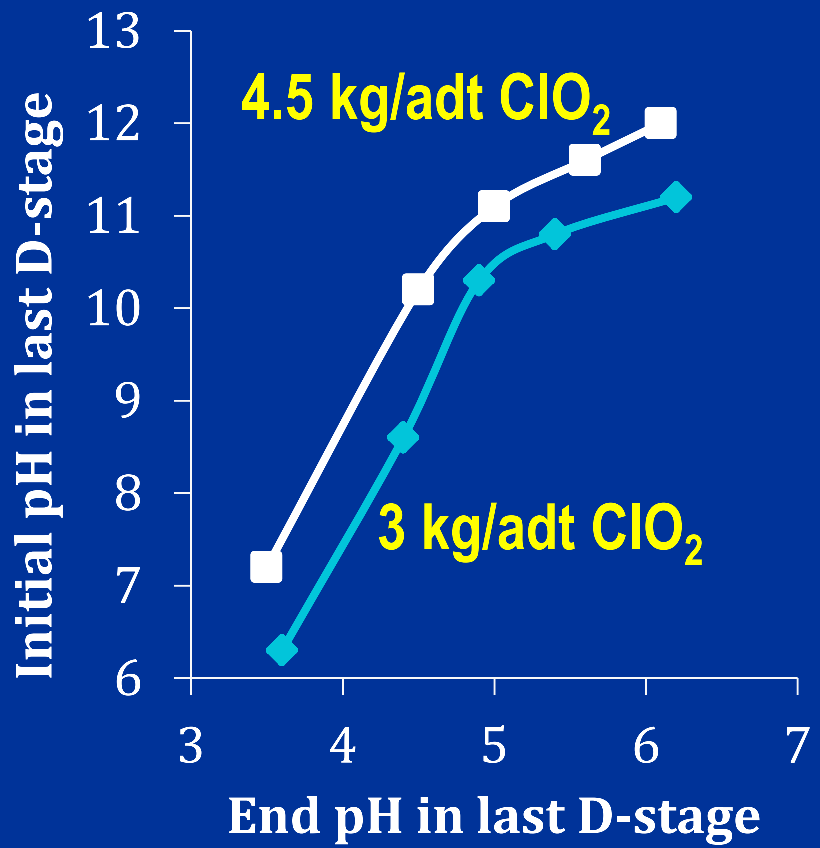
ClO_2 + Lignin → ClO_2^-

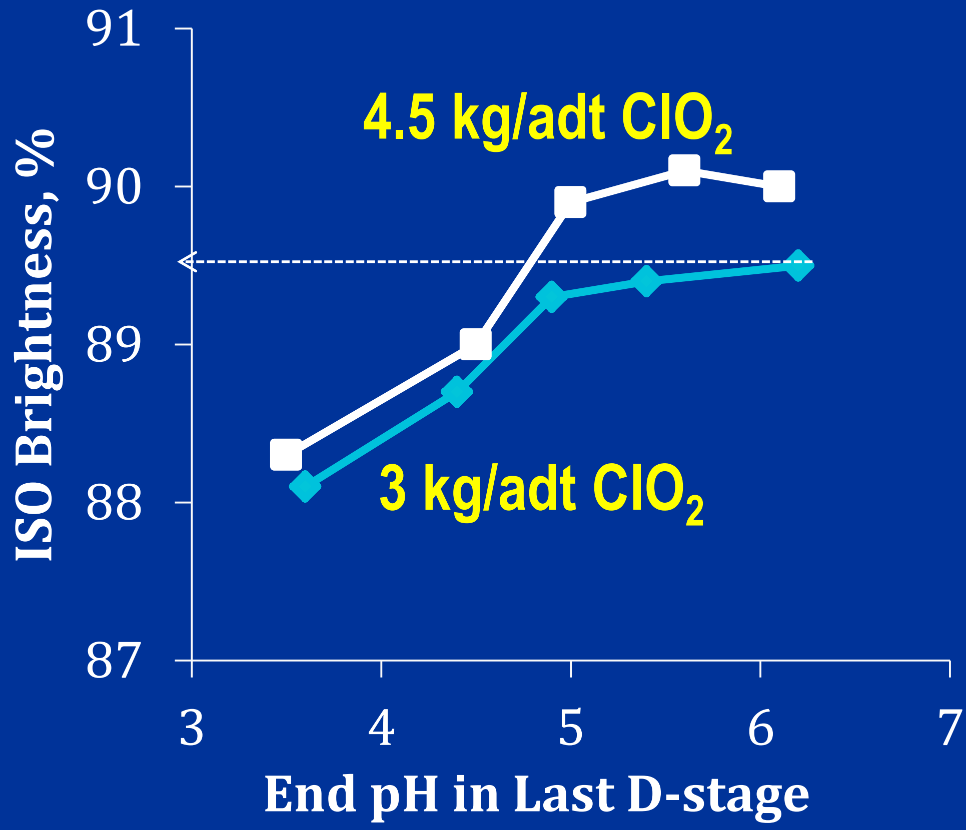
ClO_2^- + H^+ ↔ $HClO_2$

$HClO_2$ + lignin → HClO + oxidized lignin

Robles, Colodette and Milanez, IPBC 2005

Unbuffered Near Neutral ClO_2 Bleaching





"process works better on high HexA pulps and requires significant time/temperature"

The Near Neutral ClO_2 bleaching

- **Unbuffered:** End pH of 5-6.5 difficult to attain at high ClO_2 dose (initial pH of 11.5-12.0 required)

  $$2ClO_2 + 2OH^- \rightarrow H_2O + ClO_2^- + ClO_3^-$$

- **Buffered:** The use of a bicarbonate buffering system has been proposed (Jiang, Z-H & Berry, R., 2011 IPBC, Portland, USA)
  - Carryover + $CO_2 \Rightarrow NaHCO_3$
  - $NaOH + CO_2 \Rightarrow NaHCO_3$
  - $Na_2CO_3 + CO_2 \Rightarrow NaHCO_3$

Xylanase Bleaching

- ✓ Potentially very interesting for eucalypt pulp bleaching since the large majority of the residual lignin is linked to xylans
- ✓ Currently, there are powerful xylanases in the market (4 kappa units decrease for 100 g/adt xylanase application
- ✓ ClO_2 savings in the order 4 kg/adt has been achieved in long term mill trials with 40 g/adt enzyme application
- ✓ There are issues:
  - ✓ Effluent COD in open loops
  - ✓ Loss of O-stage efficiency in close loops
  - ✓ Some xylans losses (yield?)

Brightness Stability

Brightness Reversion

Color Reversion

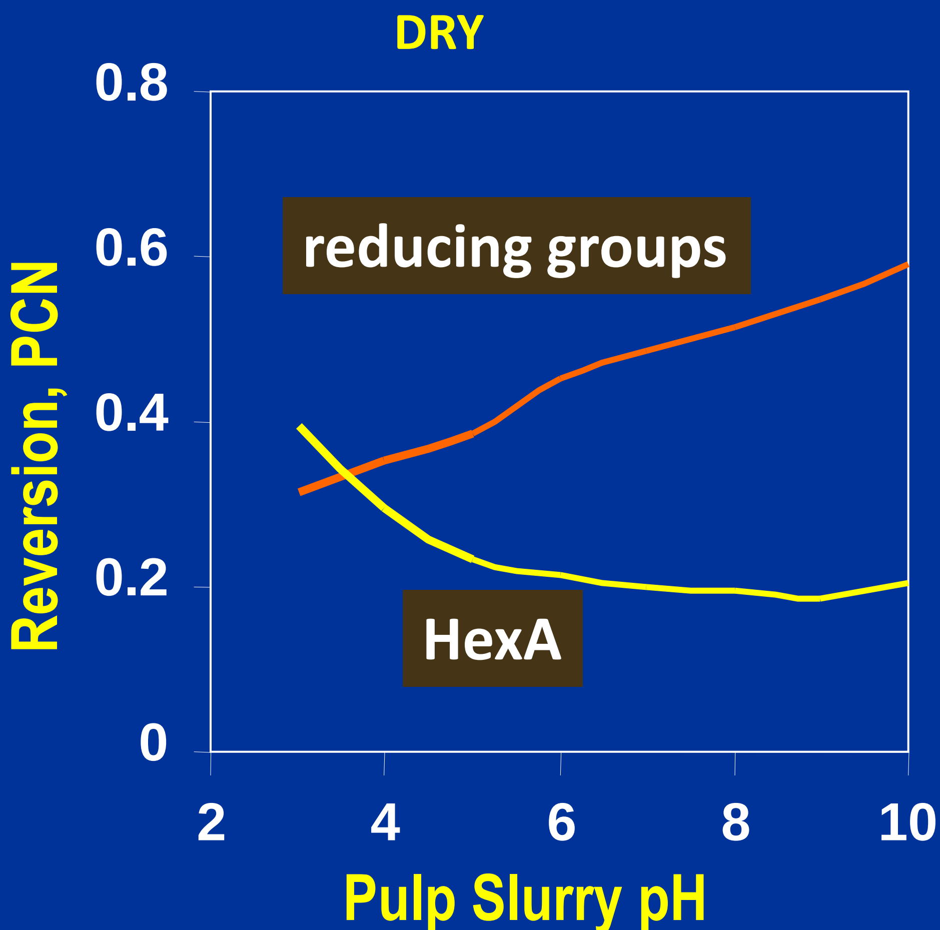
Yellowing, etc

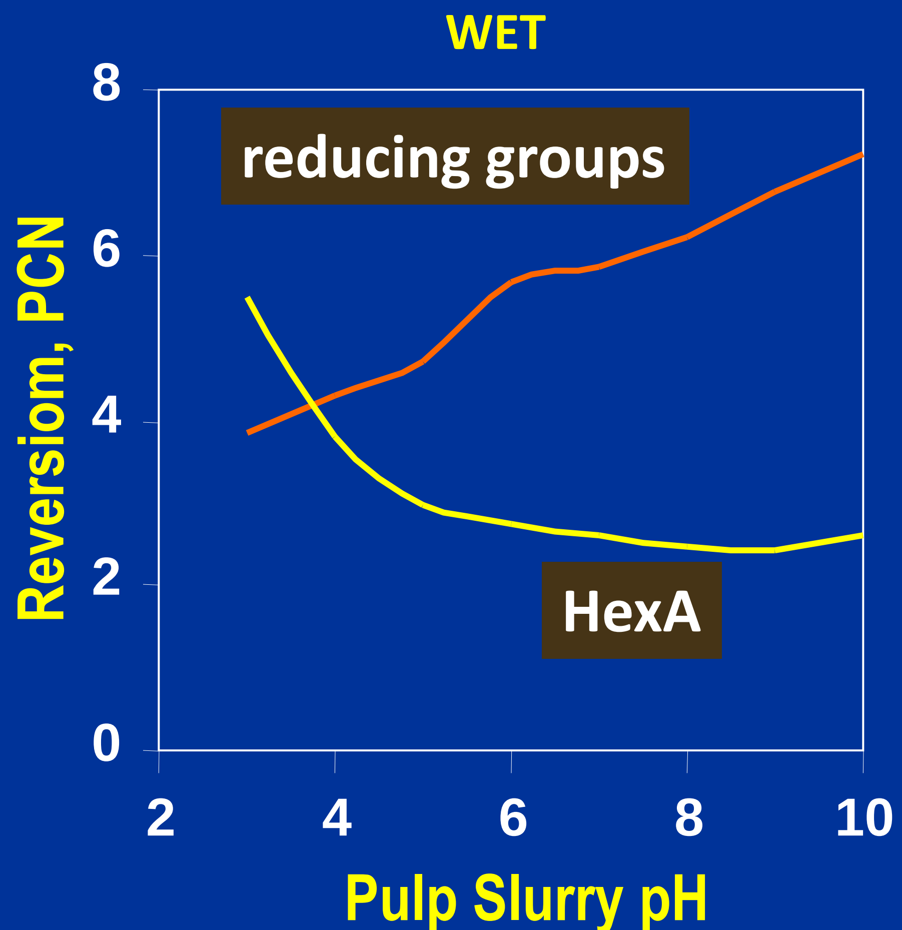
Causes of Reversion – Bleaching Related

- Residual lignin (quinones)
- Residual HexA
- Reducing groups
- Organically bound chlorine (pulp OX)

"Brightness reversion is strongly influenced by pulp slurry pH, before drying"

Effect of pulp pH on Reversion





(DC)(EPO)DD (0.2 mmol/kg HexA, 0.32 meqCu_2O/100g)

D (EPO)DP (11.2 mmol/kg HexA, 0.06 meq Cu_2O/100g

Brightness Reversion

- The reversion caused by HexA is more severe when pulp is dried under acidic conditions
- The reversion caused by reducing groups is more severe when pulp is dried under alkaline conditions
- ECF bleached pulps contain only trace amounts of reducing groups but may contain significant amounts of HexA
- Pulp drying at pH around 7 (suspension) would solve reversion problems for eucalyptus pulps, but machine drainability issues prevent this practice

Final Remarks – Cooking & Bleaching

- ✓ Cook to high HexA/Lignin ratios at a given kappa for given wood
- ✓ Double O-stage recommended, particularly for low bleachability pulps (low HexA)
- ✓ D*-(EP)-D type sequence suffice for ECF bleaching of eucalypt pulps
- ✓ Hot acid/hot chlorine dioxide technologies are effective, especially for high bleachability pulps
- ✓ Chemical consumption strongly influenced by pulp origin (high HexA ⇨ high bleachability)
- ✓ Final chlorine dioxide stage more efficient at pH 5-5.5
- ✓ Xylanase bleaching has potential but need further work
- ✓ A certain amount of HexA is tolerable in bleached pulp, if slurry is adjusted to pH neutrality before drying