

# **Key-note presentation**

## **“The future pine and eucalyptus pulp mill multi-product biorefinery”**

**By Peter Axegård, INNVENTIA AB (STFI-Packforsk)  
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# **STFI-Packforsk AB is now INNVENTIA AB**

**INNVENTIA AB**

Visit: Drottning Kristinas väg 61

Mail: Box 5604, SE-114 86 Stockholm, Sweden

[peter.axegard@innventia.com](mailto:peter.axegard@innventia.com)

[www.innventia.com](http://www.innventia.com)

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# **Presentation will cover**

**Energy export from kraft pulp mills**  
**Lignin - removal and utilization**  
**Hemicellulose - removal and utilization**  
**ClO<sub>2</sub>-bleaching and TCDD/F**  
**Water closure**  
**2nd generation ethanol**

# Drivers for pulp mill biorefining

- Competition for biomass from the energy sector
- Processing of large volumes of biomass
- New efficient separation processes available
- Attractive to add “side” processes for low value biomass
- Opportunities for new pulp mill products



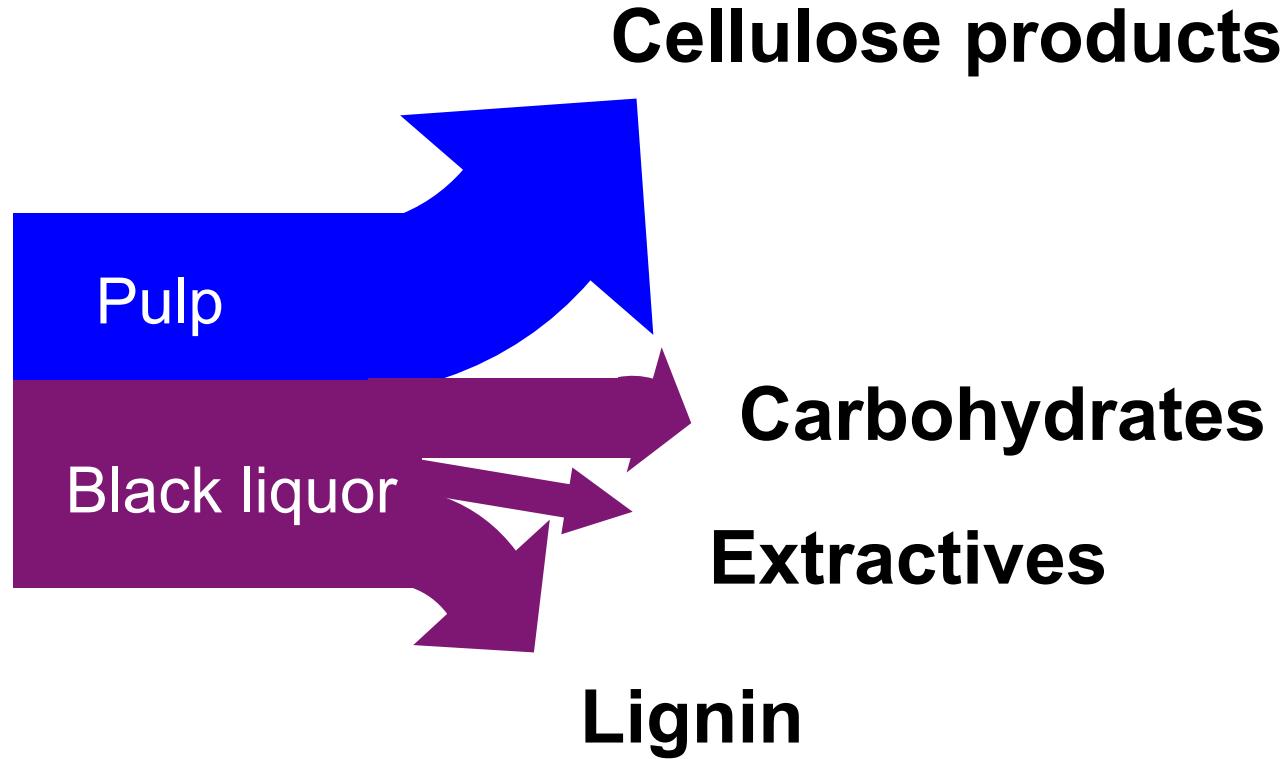
# **Modern bleached kraft pulp mills**

## **- highly energy efficient**

<b>Model Mill Case</b>	<b>Sold Fuel</b>	<b>Produced Power</b>	<b>Sold power</b>	<b>Fossil CO<sub>2</sub></b>
	<b>GJ/ADt</b>	<b>kWh/ADt</b>	<b>kWh/ADt</b>	<b>kg/ADt</b>
<b>Modern mill – bark boiler</b>	<b>0,6</b>	<b>1520</b>	<b>730</b>	<b>-260</b>
<b>Modern Mill – no bark boiler</b>	<b>3.1</b>	<b>1255</b>	<b>545</b>	<b>-260</b>
<b>Typical mill</b>	<b>-0.6</b>	<b>645</b>	<b>-140</b>	<b>+320</b>

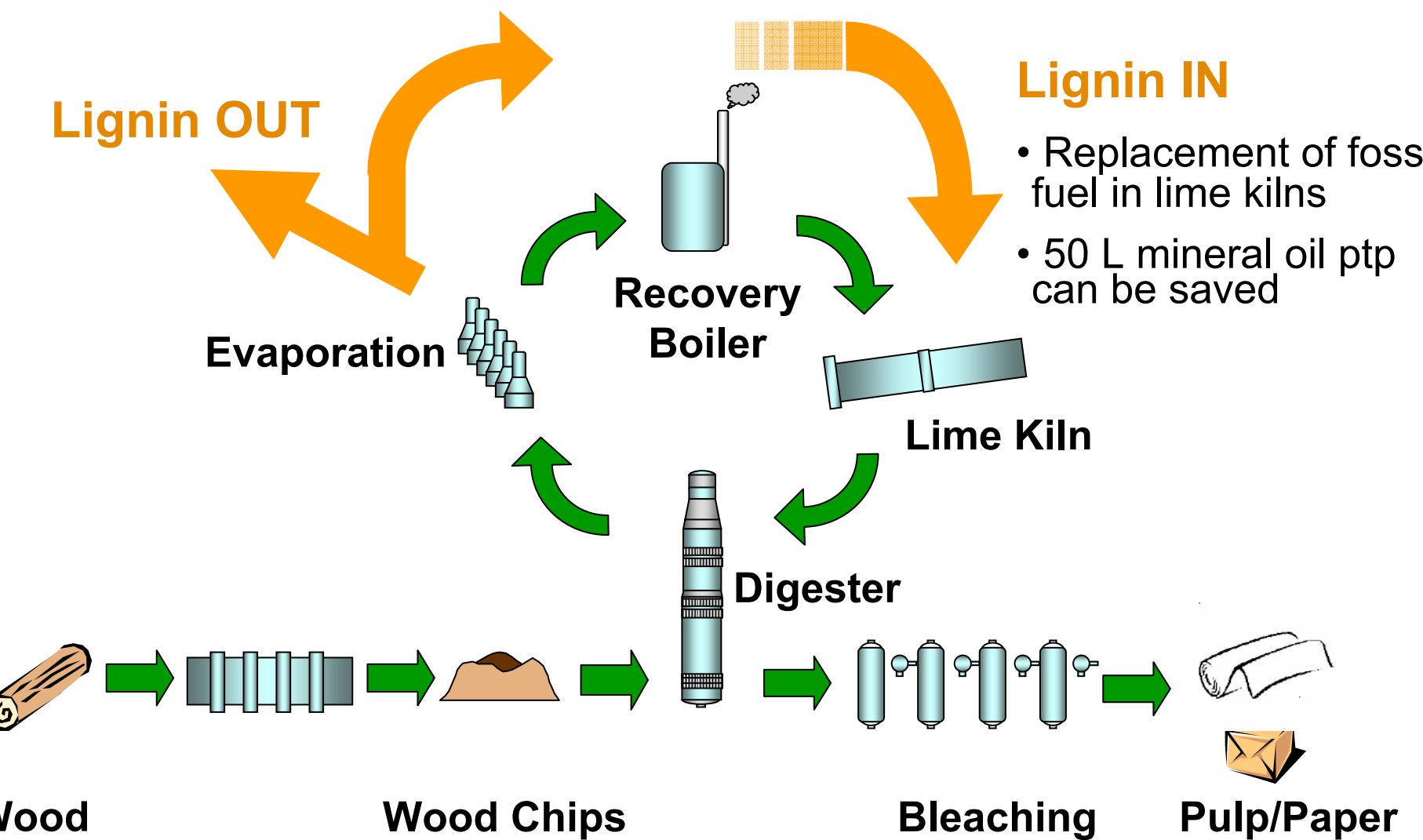
# About 50% of the wood ends up in cooking liquor and is used as fuel

Wood to kraft  
pulp mill

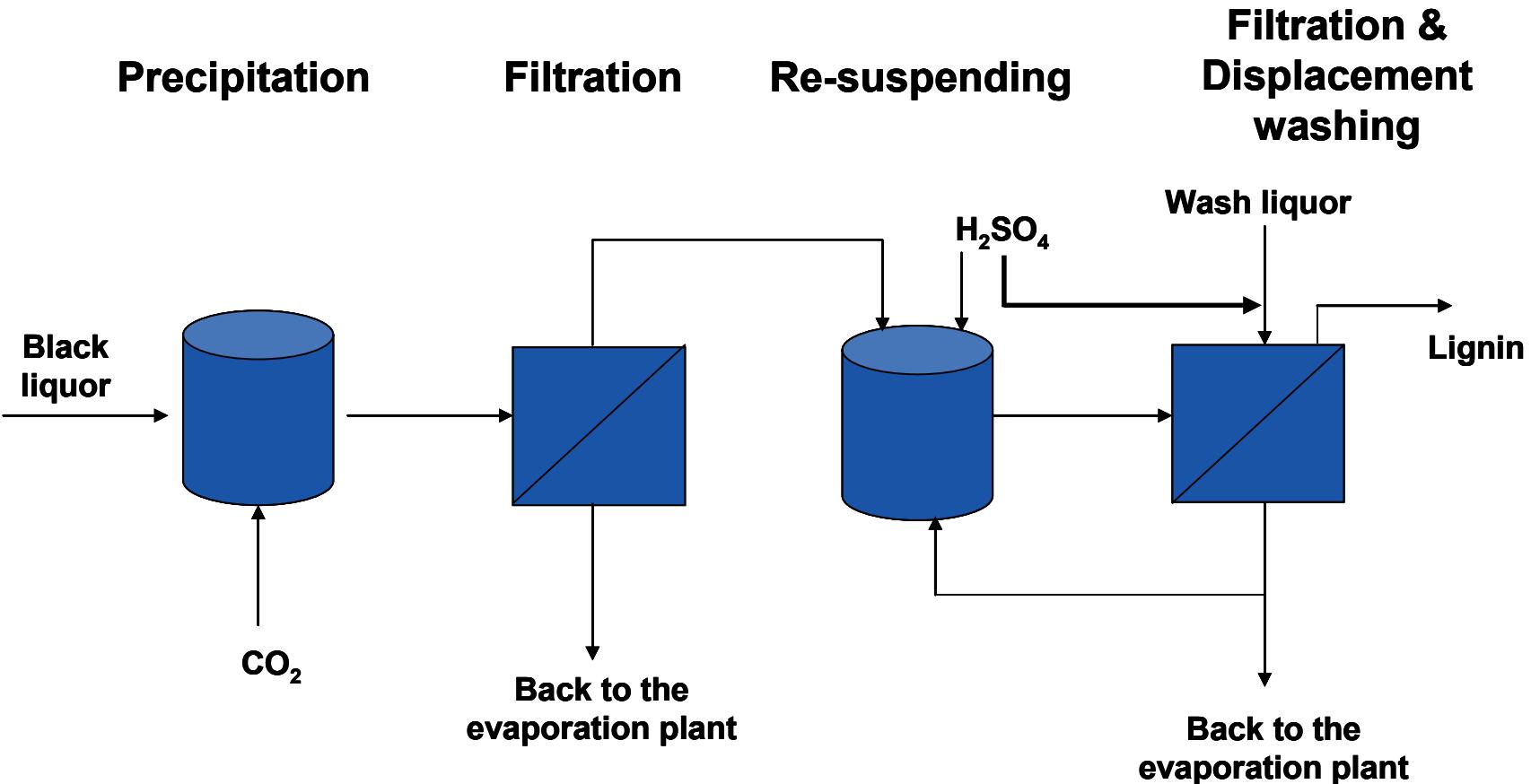


55-60 % of energy ends up in the black liquor

# The LignoBoost process



# The LignoBoost process



# Metso filter in lignin demo plant

VPA 1040  
24 chambers  
1-1.2 t lignin/h



# Dried LignoBoost lignin



# Lignin from LignoBoost

## Lignin in fuel oil



## Typical composition

C	64 – 66 %
O	26 – 27.5 %
H	5.7 – 5.8 %
N	0.1 %
S	1 – 3 %

HHV: 25-26.5 GJ/t

## Biofuel in lime kilns



## Pellets



## Carbon fibres



Mill trial with 100 % lignin 2008

Pelletizing trials 2006

Own development & co-op

# Wood/plants – a mine for valuable polymers

## -Hemicellulose

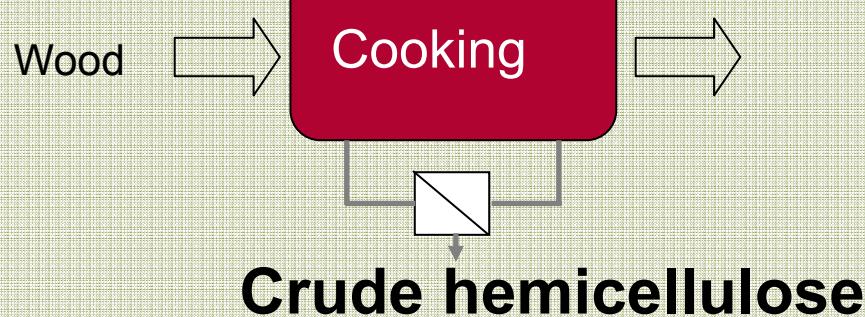
	Softwoods		Hardwoods			Agro/annual	
	Spruce	Pine	Birch	Euca. glob.	Euca. urogr.	Hemp	Bagasse
Xylan, %	9	8	26	21	16	29	28
Glucomannan, %	19	18	3	4	3	2	2

- Glukomannan degrades in alkali
- Xylan is relatively stable in alkali

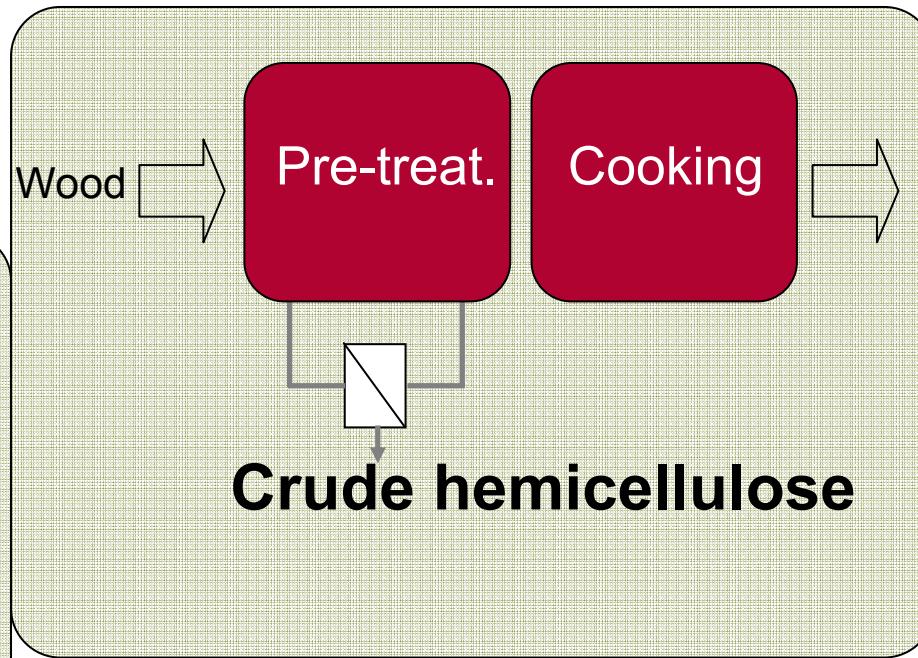


# Hemicellulose from wood and black liquor

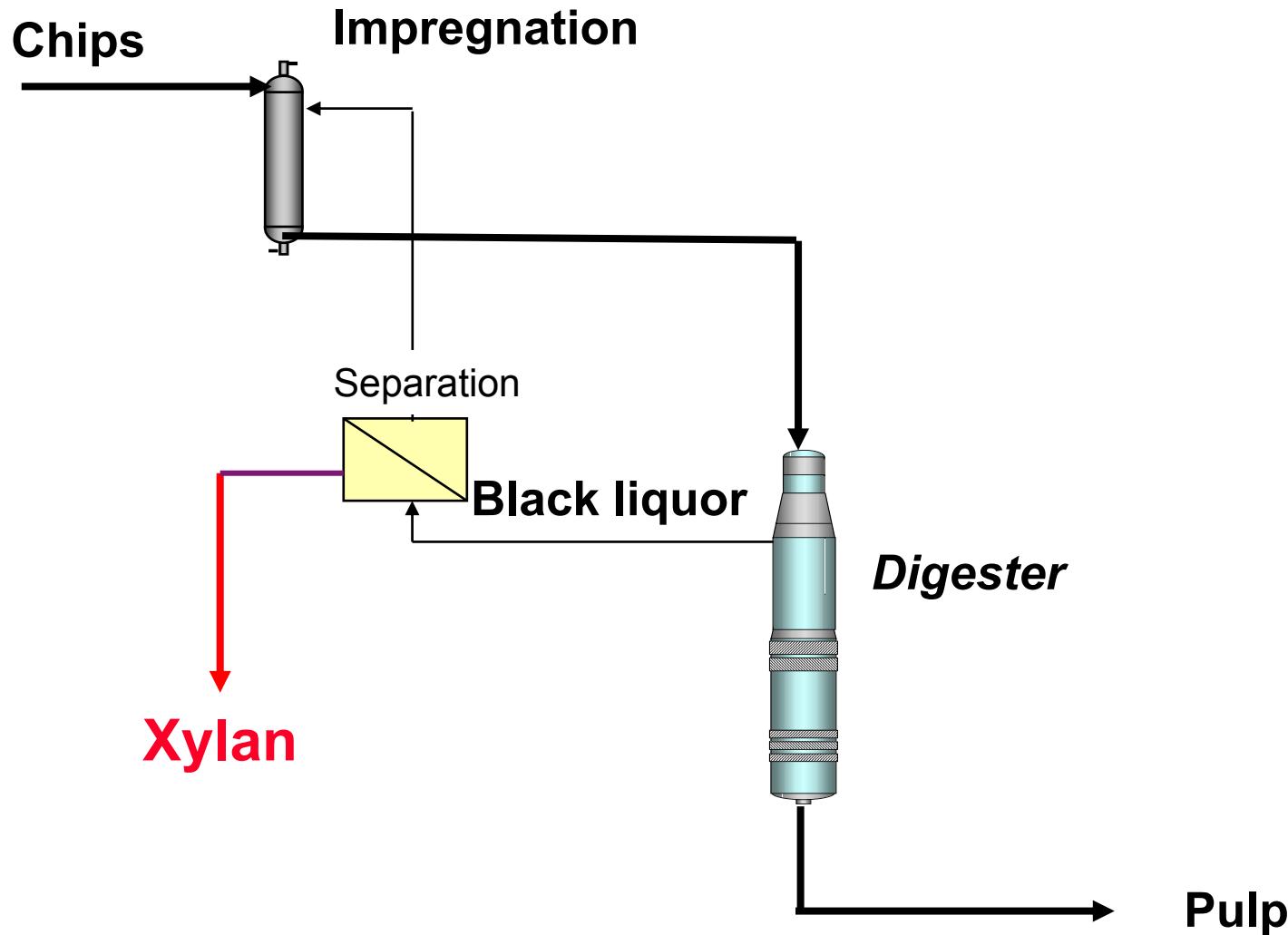
## *Hemi-separation from BL*



## *Hemi-separation prior cooking*



# Mill trial with xylan removal



# Hemicellulose - Nano-fibril cellulose composite films



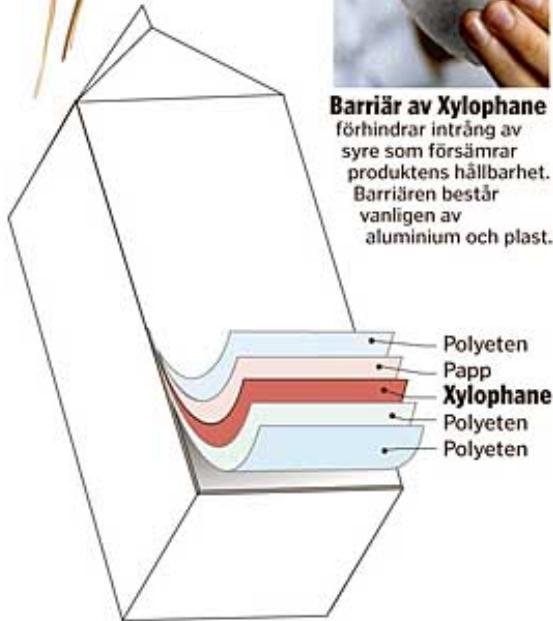
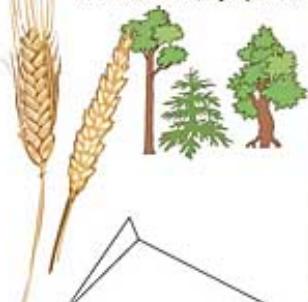
**Glucomannan based film**



**Xylan based film**

# Hemicellulose barriers almost commercial

**Restprodukter** från jordbruk eller skog används för att producera råvaran xylan. Xylanet blandas med tillsatser och levereras i pulverform till förpackningstillverkaren, som gör en beläggning av materialet, Xylophane.

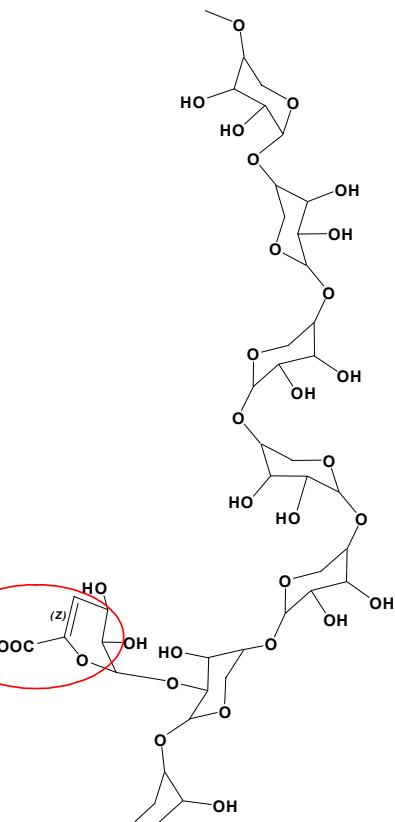


**Barriär av Xylophane**  
förhinderar inträng av  
syre som försämrar  
produktens hållbarhet.  
Barriären består  
vanligen av  
aluminium och plast.



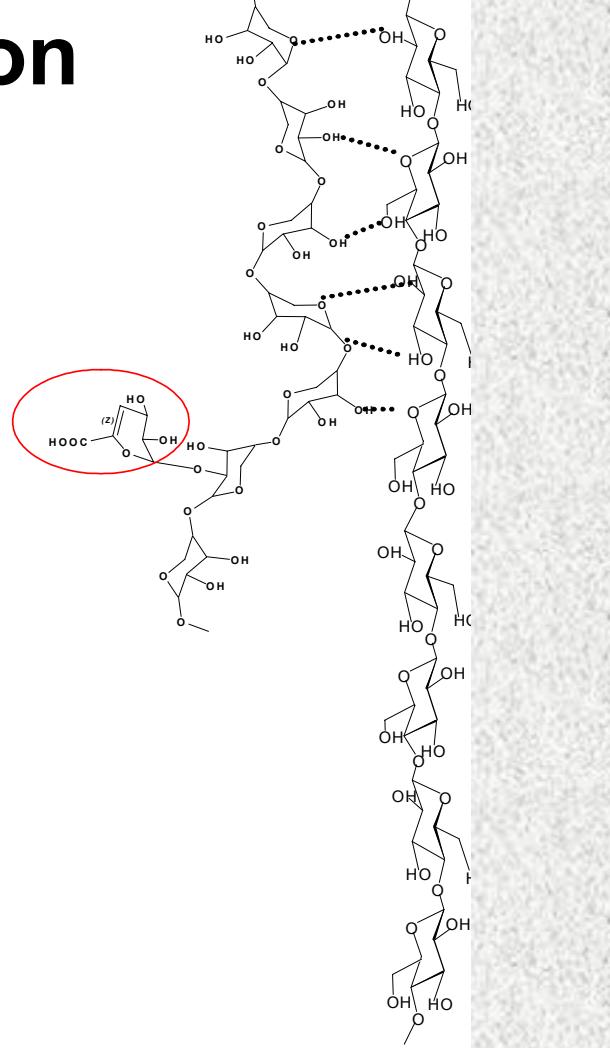
**Source: Xylophane**

# Sorption of HW xylan on SW fibres



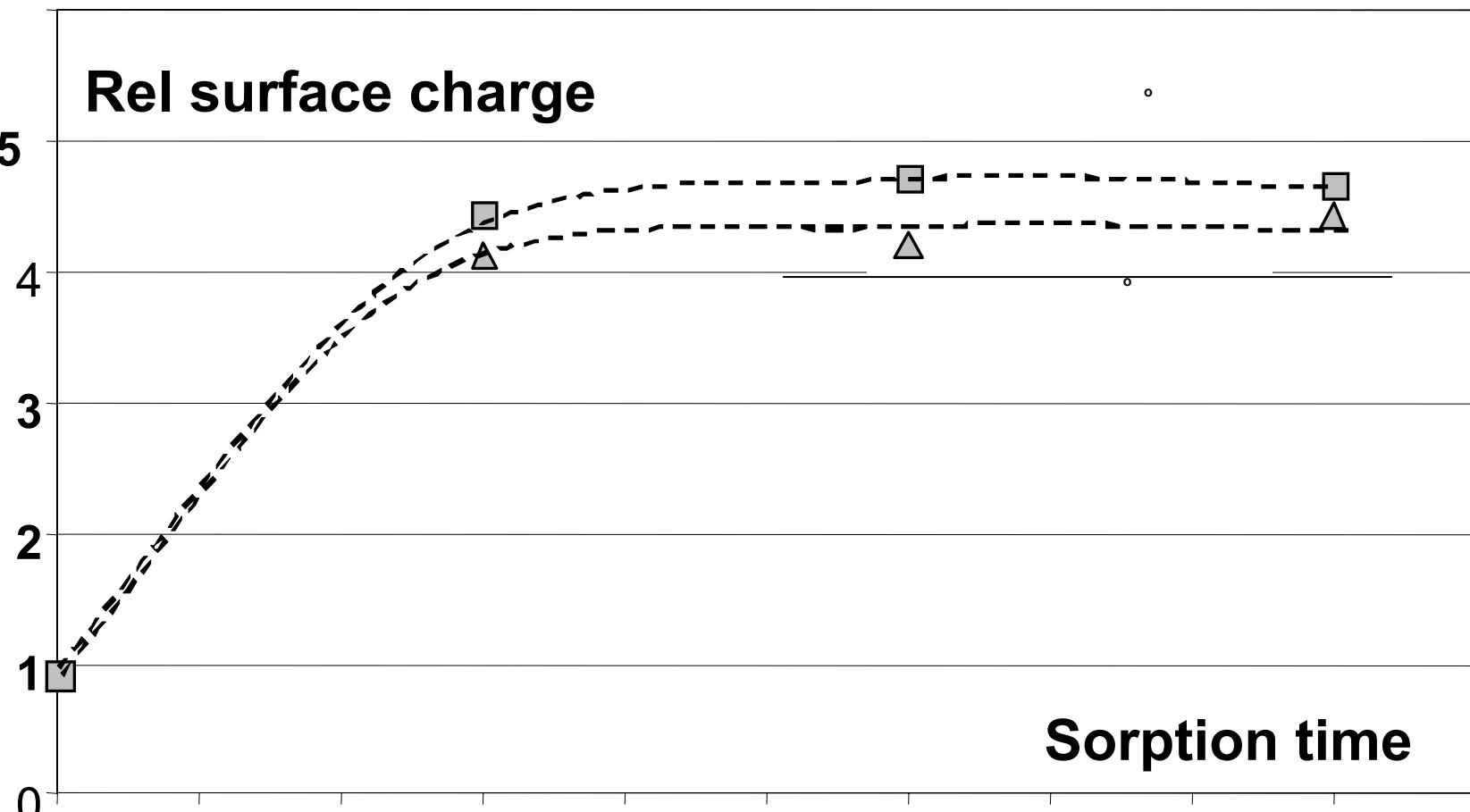
Charged HW xylan

Sorption



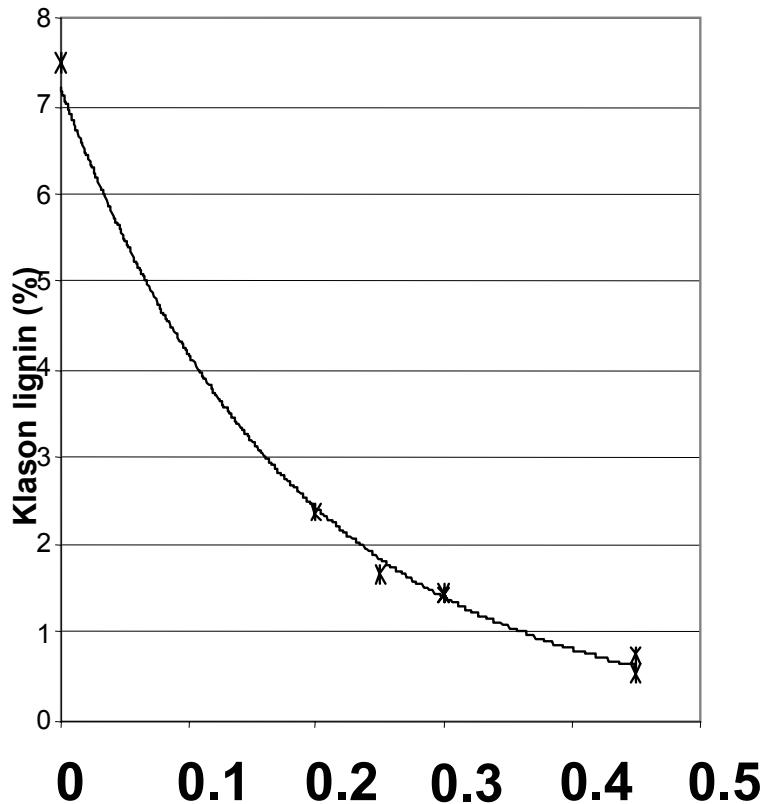
HW xylan on SW  
fibre surface

# High SW fibre surface charge with euca xylan

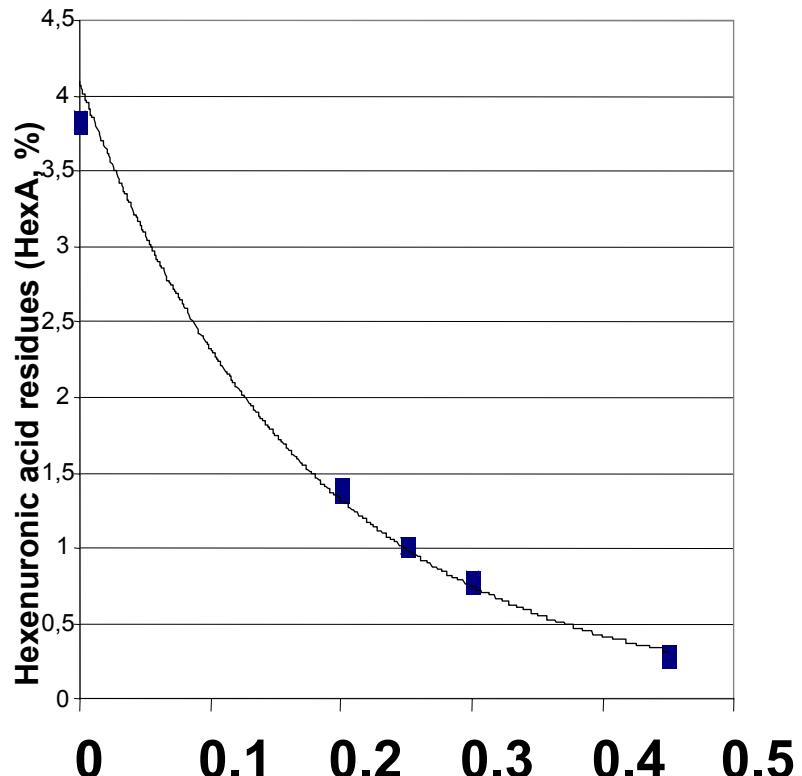


# $\text{ClO}_2$ bleaching of xylan from black liquor

Lignin



HexA



$\text{ClO}_2$  charge, act Cl x Kappa No

# PCDD/F in the Baltic Sea

- Concerns regarding ECF bleaching raised 2005 (Olsson)



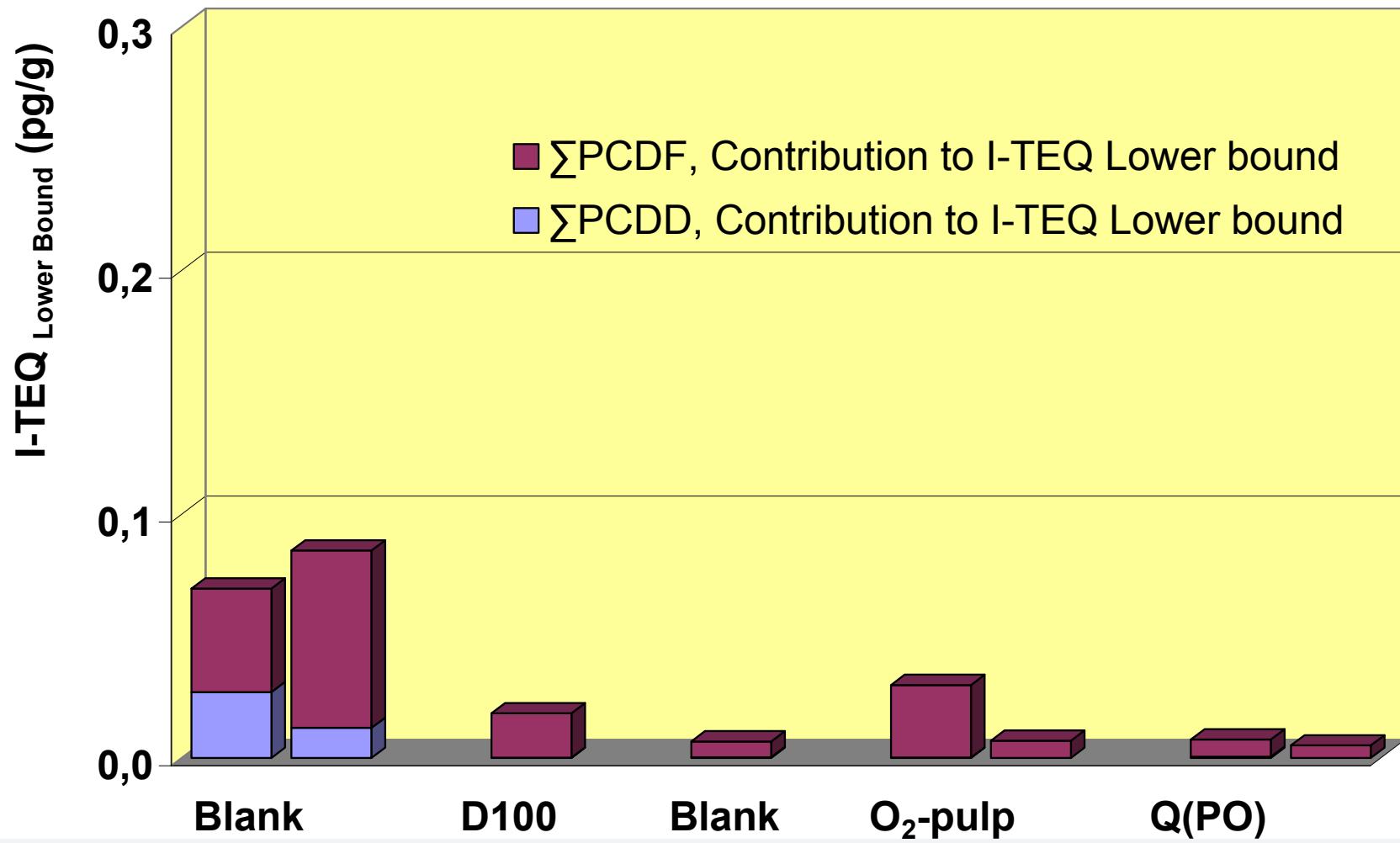
# STFI-Packforsk study on PCDD/F 2007/08

- Studied bleaching parameters
  - Addition of DBF (0-100 ng/g) before D100-stage
  - Final pH in D100-stage
  - Comparison of lab vs. industrial ClO<sub>2</sub> solutions
  - Carry over of oxygen stage filtrate to D100-stage
  - Unbleached, TCF- and ECF- bleached pulps studied
  - Cl<sub>2</sub> - content in ClO<sub>2</sub> solution
- TCDD/F analyses at Umeå University, Sweden
  - 17 congener analysis

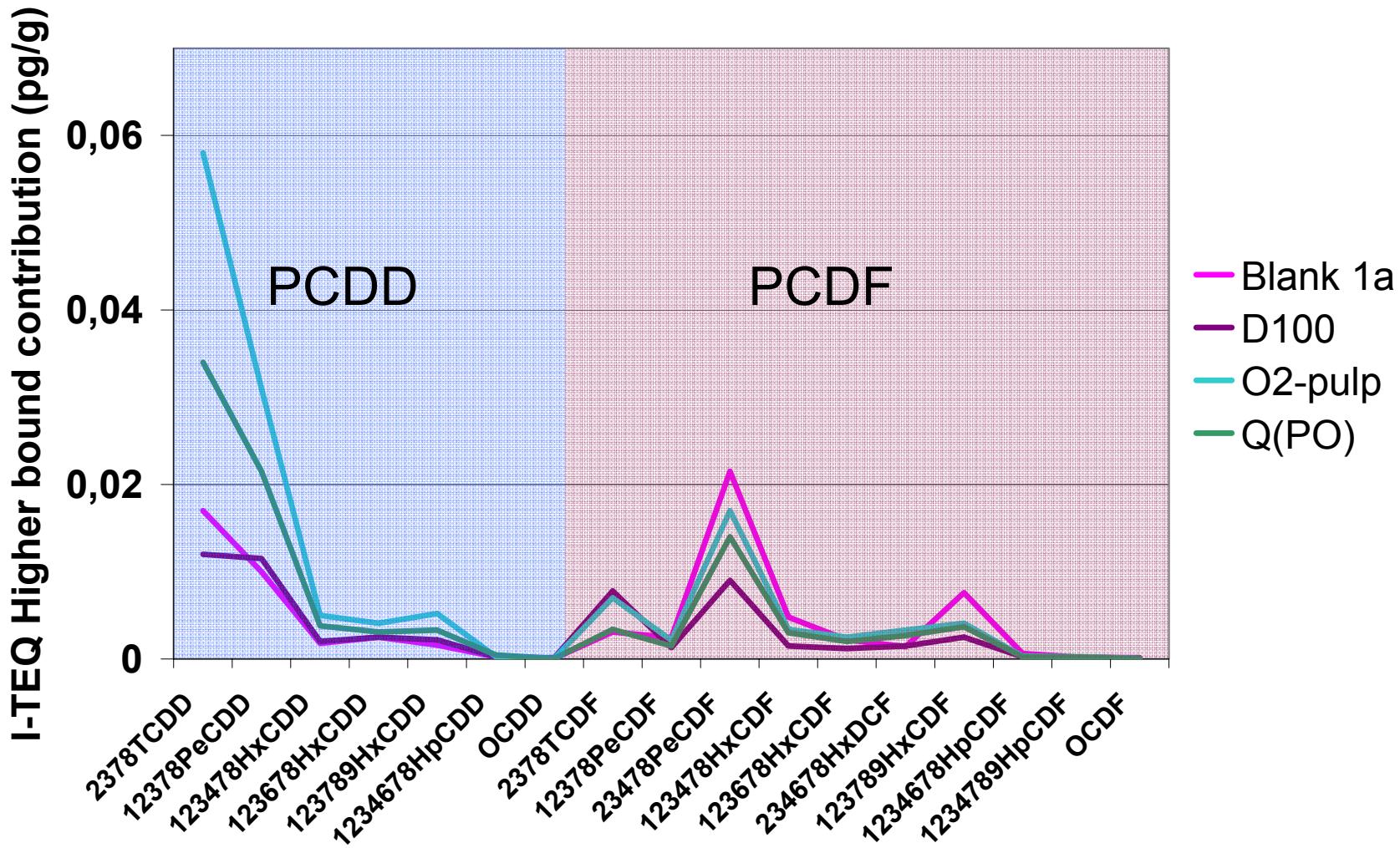


# PCDD/F in UKP-ECF-TCF-blank

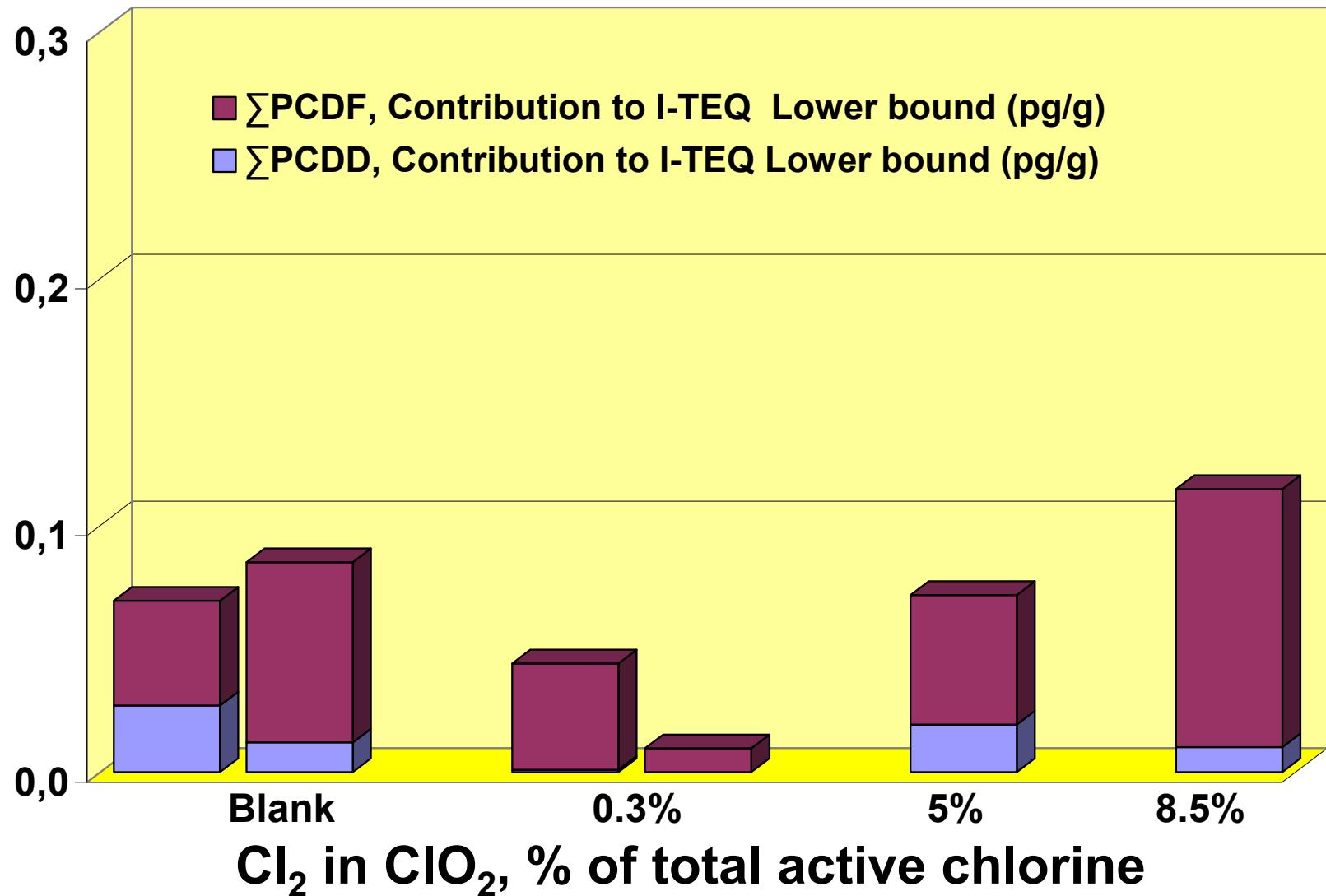
## I-TEQ Lower Bound (ND=0)



# PCDD/F congeners in UKP-ECF-TCF-blank



# PCDD/Fs formation vs. Cl<sub>2</sub> in ClO<sub>2</sub>



**By Eka Chemicals recommended processes for manufacturing of chlorine dioxide:**

- SVP-SCW
- SVP-LITE
- HP-A
- SVP-HP
- SVP-Pure

**The guarantee level on elemental chlorine in these processes are <0.2 g Cl<sub>2</sub>/dm<sup>3</sup> chlorine dioxide solution.**

- This amount equals <0.8-0.9% of the active chlorine being elemental chlorine, the remainder being chlorine dioxide.

**Other ClO<sub>2</sub> processes must be evaluated on a case by case basis.**



# Conclusions STFI-Packforsk PCDD/F study

- **Earlier findings and conclusions on PCDD/F confirmed**
  - Alliance for Environmental Technology (1996)
  - IPPC Reference Document on Pulp and Paper Industry BAT (European Commission, 2001)
  - United Nations Environment Programme (UNEP, 2003)
  - Hartsfield Consultants, report for IFS world bank (2006)
  - Dioxin formation in Pulp and Paper Mills of India (Thacker et al, 2007)
- **Swedish EPA Report, January 2009:**
  - The Pulp and paper industry is not a significant source of PCDD/F to the Baltic sea
  - Main source airborne precipitation from combustion



# Conclusions STFI-Packforsk PCDD/F study

- **Cl<sub>2</sub>-free ClO<sub>2</sub> (less than 2% of active chlorine Cl<sub>2</sub>) does not contribute to the formation of PCDD/Fs**
- **ClO<sub>2</sub> products from modern ClO<sub>2</sub>-generators are essentially free from elemental chlorine**
- **Modern ClO<sub>2</sub> bleaching (ECF) is not likely to cause any formation of PCDD/Fs**
- **ClO<sub>2</sub>-bleaching should be used in future biorefineries**

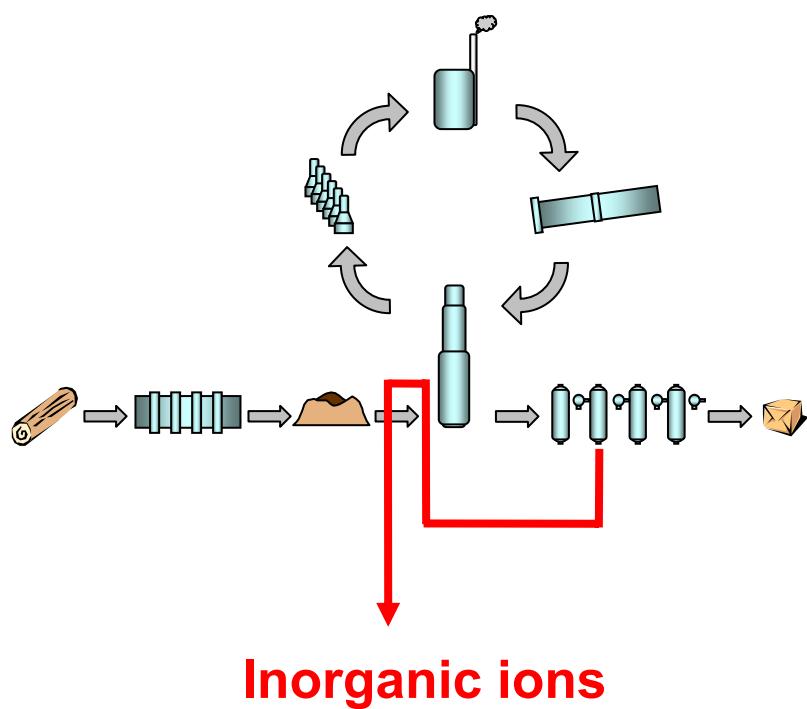


# **Reduced fresh water use in bleaching**

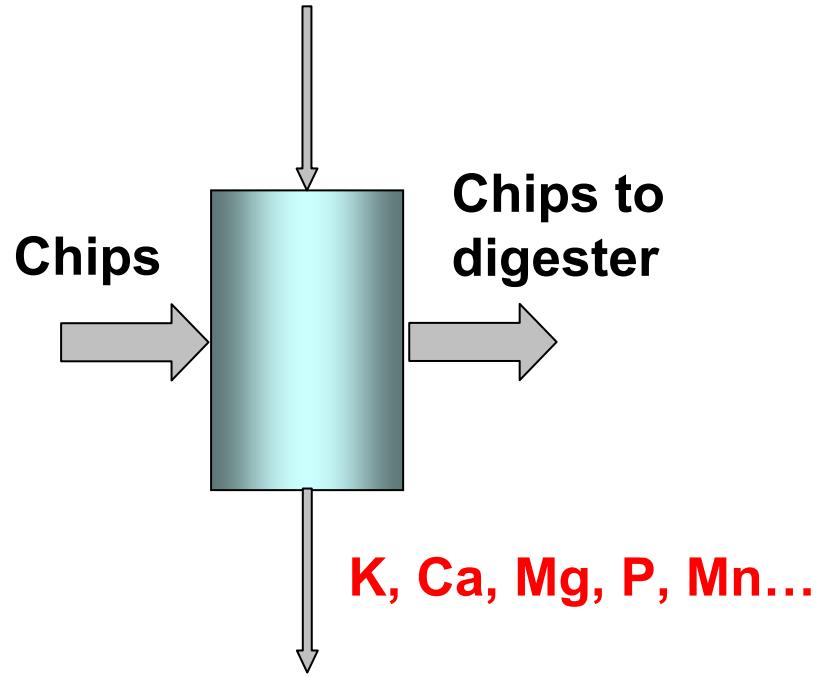
- **Effluent volume ~ 10 m<sup>3</sup> ptp achieved in some mills**
- **Futher water closure is limited by**
  - accumulation of K/Cl in recovery system
  - scaling of Ca- and Ba-salts
  - organic substances in finished pulp



# Chip leaching for water closure



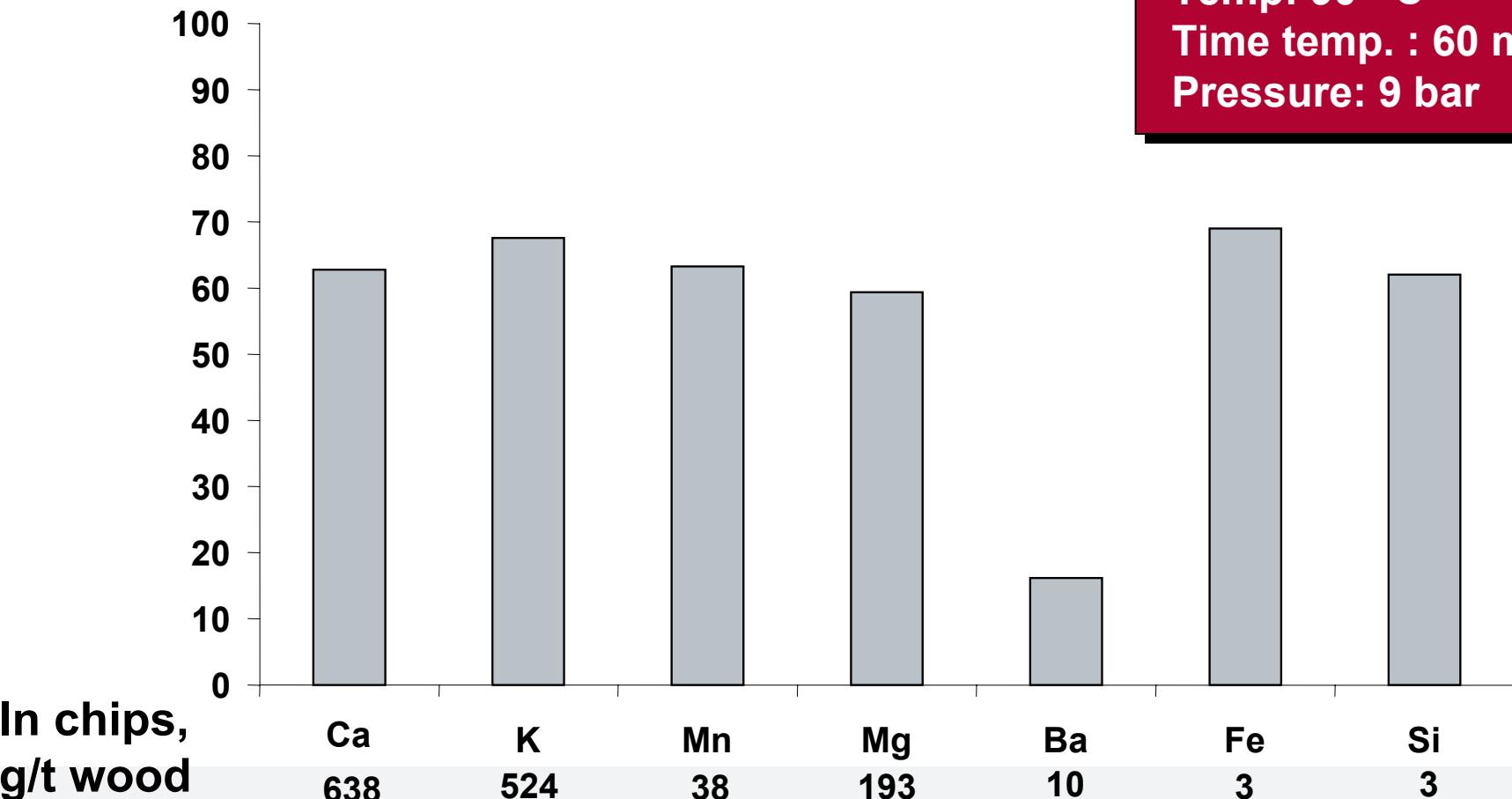
Bleach plant filtrate



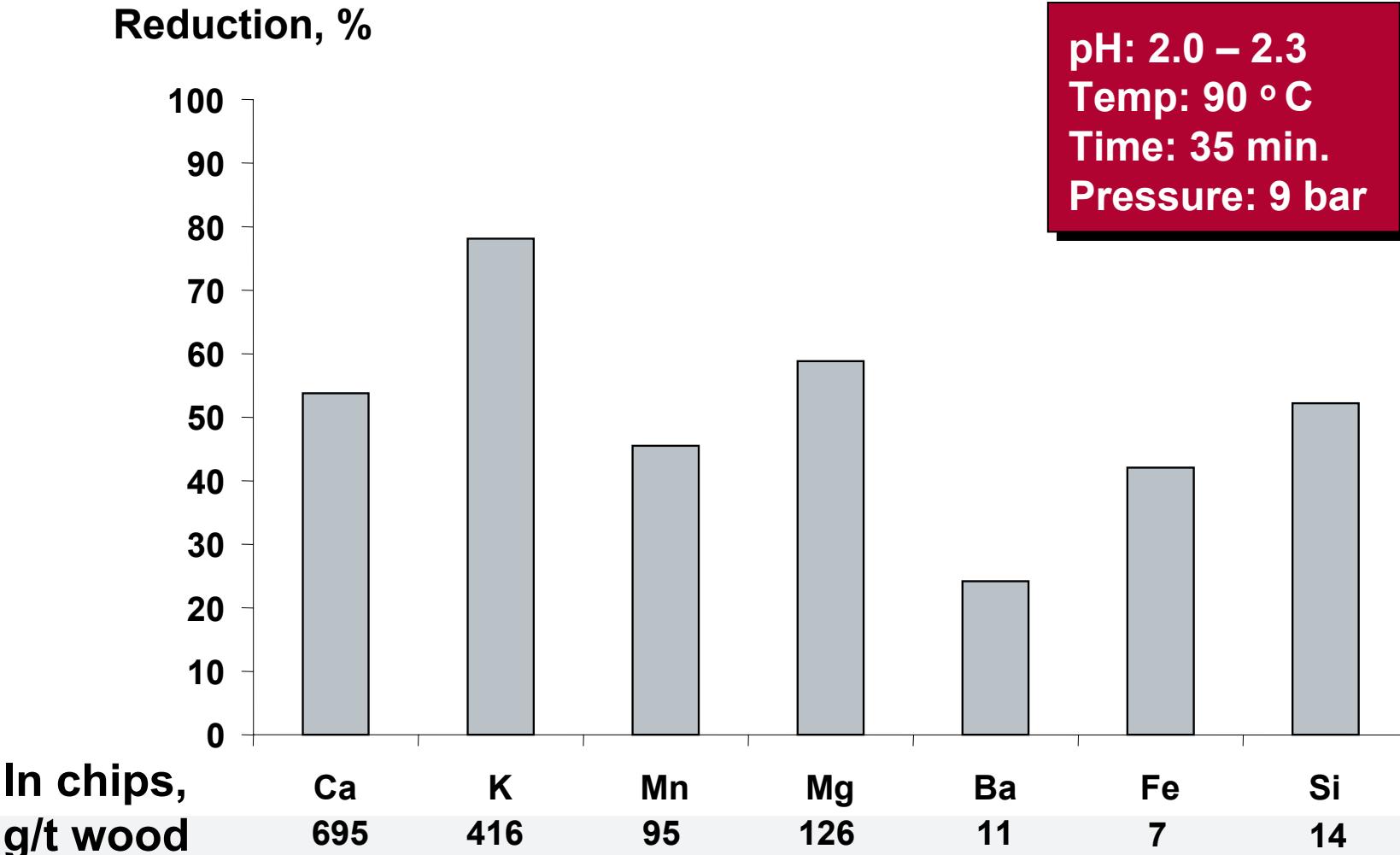
# HW mill trials- Reduced intake of NPEs

Reduction, %

pH: 2.0 – 2.3  
Temp: 90 °C  
Time temp. : 60 min  
Pressure: 9 bar



# SW mill trials - Reduced intake of NPEs



# **Effluent “free” BKP with chip leaching**

- **COD below 1 kg ptp**
- **Mill effluent 6 - 7 m<sup>3</sup> ptp**
- **Minimal external treatment**
- **Efficient spill liquor handling system needed**
- **Extra evaporation needed using low grade steam**



# Mill effluent from a BKP mill with tertiary treatment



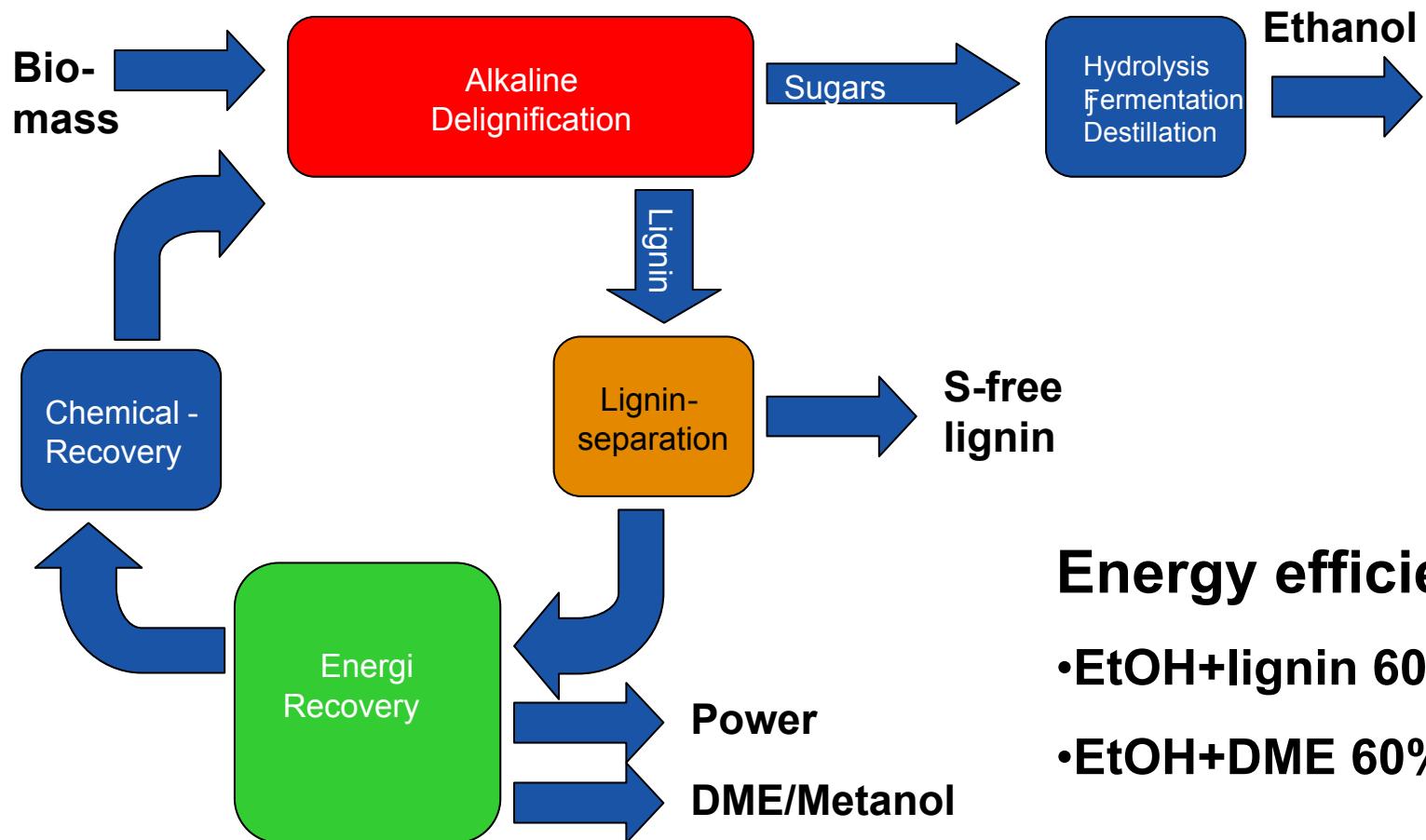
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# **Second generation EtOH from wood**

- **Acid/enzymatic hydrolysis and fermentation**
- **Alkaline delignification, hydrolysis and fermentation**
  - can handle all wood/forestry residues/annual plants
  - good separation of cellulose and lignin
  - established technology



# Ethanol- Alkaline Process



**Energy efficiency**

- EtOH+lignin 60%
- EtOH+DME 60%

# Ethanol- Alkaline Process

Concept has just been demonstrated

- S-free chemical pulp and black liquor
- S-free lignin from LignoBoost demo plant
- Hydrolysis and fermentation of pulp in pilot scale



# Biorefining - Full utilization of wood

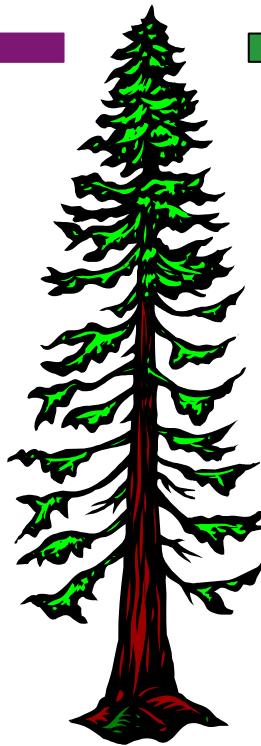
Energy



Chemicals/Materials

*DME*  
*Ethanol*  
*FT-diesel*  
*Biooil*  
*Heat*  
*Electricity*  
*Solid fuel*

Lignin  
Cellulose  
Bark  
Forestry residues



Lignin

Hemi-cellulose  
Cellulose

Extractives

- *Functional polymers*
- *Bioactive compounds*

- *Phenols*
- *Carbon fiber*
- *Binders*
- *Dispersants*
- *Activated carbon*
- *Fiber additives*
- *Barriers*
- *Hydrogels*
- *Fibers*
- *Derivatives*
- *Nanocellulose*

# Implementation in kraft pulp mills 1-5 years

**Reference**      Existing kraft pulp mill = platform

**Step 1**

**1-5 years**

- Pulp and some special cellulose
- Reduced water use
- ECF-bleaching without Cl<sub>2</sub>
- LignoBoost lignin
- Hemicelluloses from black liquor and wood
- Ethanol and lignin from low value biomass



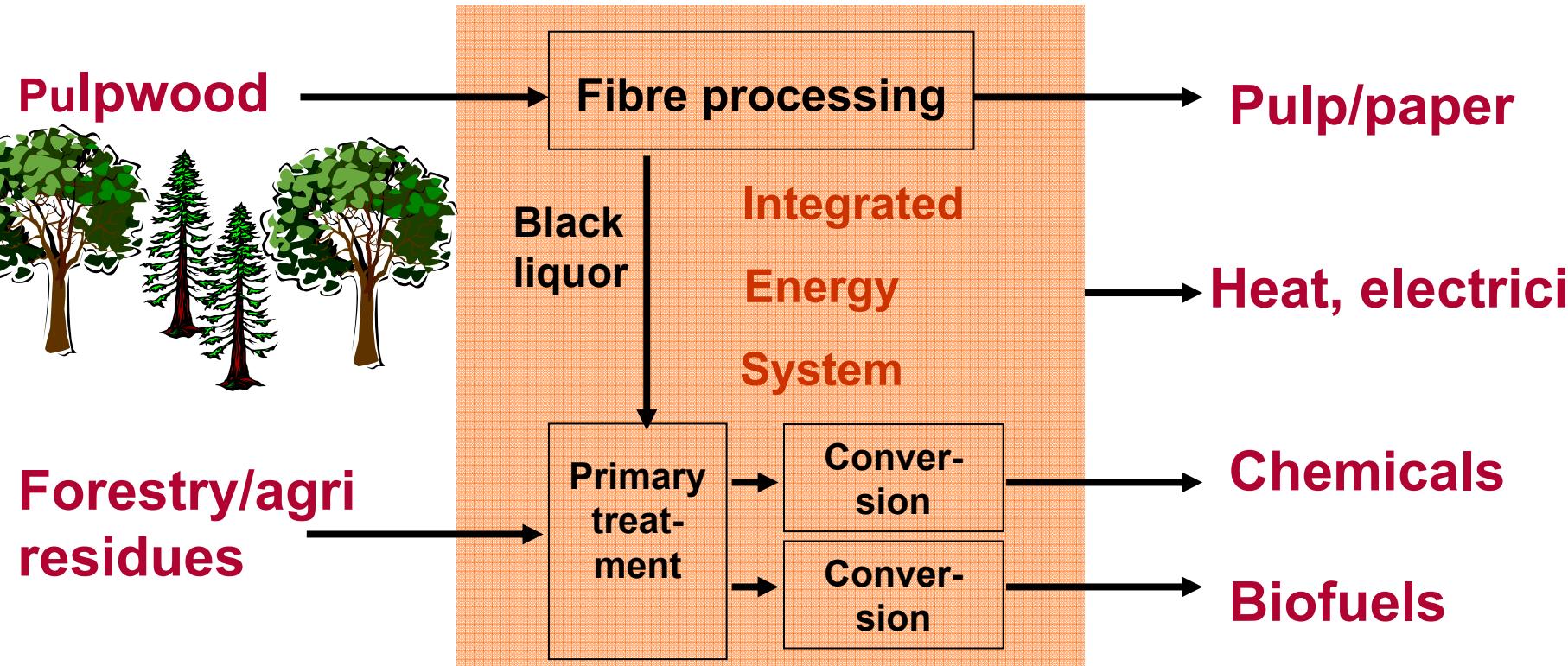
# Implementation in kraft pulp mills 1-5 years

**Reference**      **Existing kraft pulp mill = platform**

<b>Step 1</b> <b>1-5 years</b>	- Pulp and some special cellulose - Reduced water use - ECF-bleaching without Cl2 - LignoBoost lignin - Hemicelluloses from black liquor and wood - Ethanol and lignin from low value biomass
<b>Step 2</b> <b>5-10 years</b>	- <b>Torrefaction</b> - <b>Pyrolysis</b> - <b>Black liquor gasification</b> - <b>Biomass gasification</b>



# The Future Pulp Mill Biorefinery

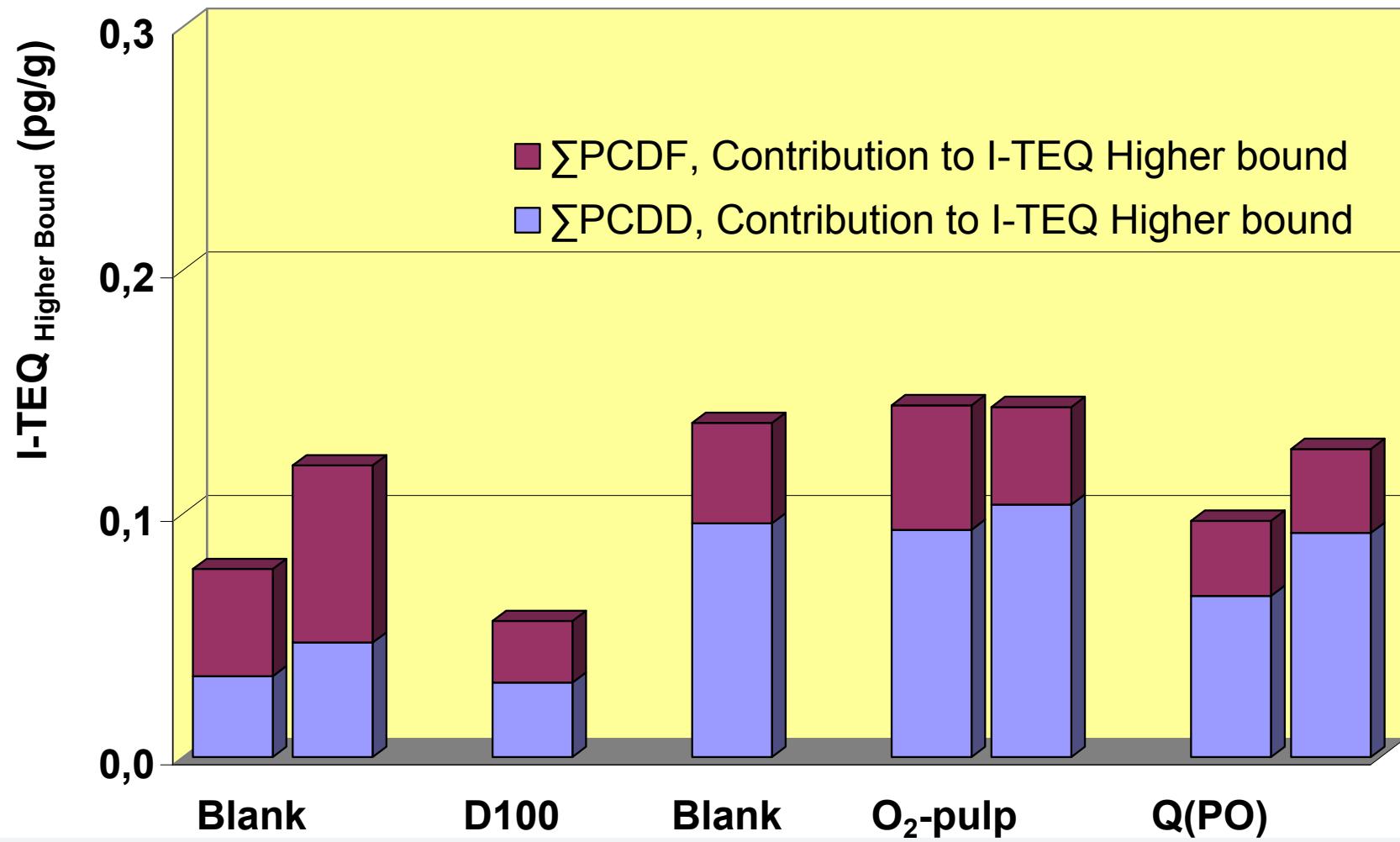


# EXTRA SLIDES

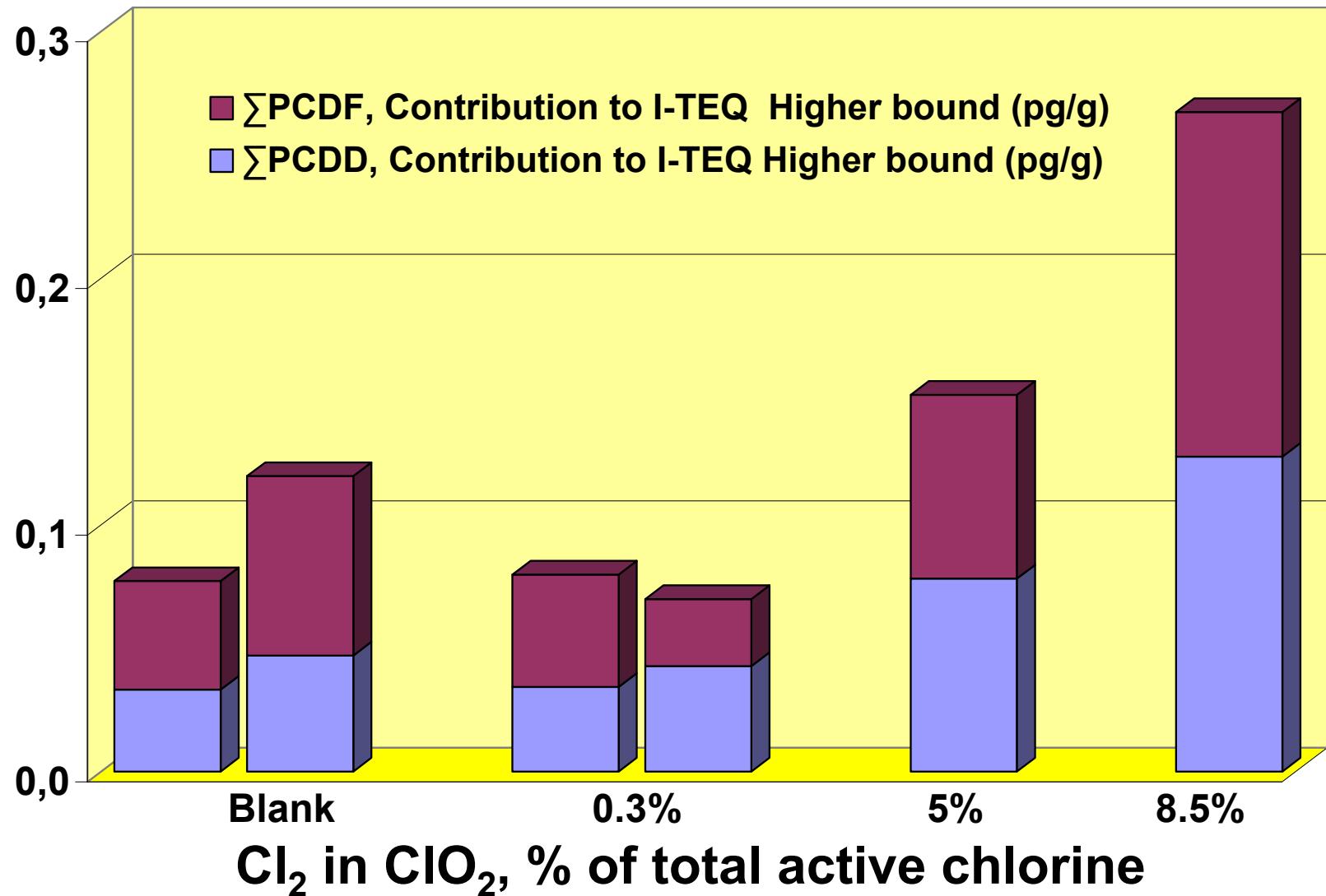


# PCDD/F in UKP-ECF-TCF-blank

## I-TEQ Higher Bound (ND=LOD)



# PCDD/Fs formation vs. Cl<sub>2</sub> in ClO<sub>2</sub>



# By-products from a kraft pulp mill, kg ptp

	Softwood	Birch	Eucalypt
<b>Xylan</b> - black liquor - wood chips	30 15 - 150	100	40

