PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

DETERMINATION OF LIGNIN CONTENT FOR EXTRACTS OBTAINED BY PRESSURISED HOT WATER

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Acknowledgements

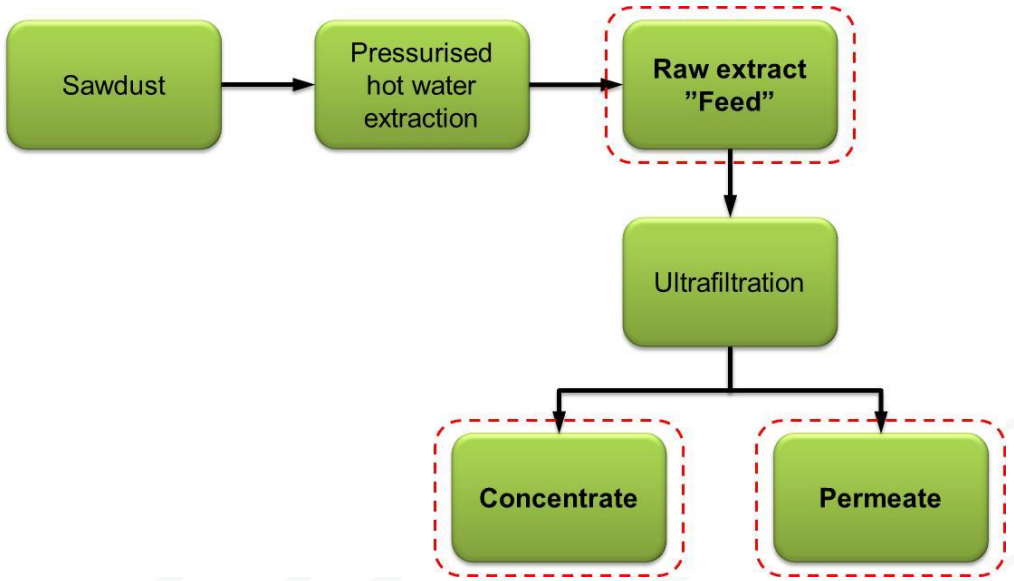
Open your mind. LUT.
Lappeenranta University of Technology

Background

- Purity of hemicellulose-rich extracts is important for their further usage
- The major impurity in GGM/xylan is usually **lignin**
  - Can be reactive when extracts are produced into new products
  - Gives undesired colour and lignin-derived products may emit odour
- The accurate lignin content of the extracts must be known

Raw materials

- Industrial spruce and birch sawdusts
- PHW extracted at Metla
  - Flow-through technique
- Ultrafiltered at LUT
  - Regenerated cellulose membrane
  - 10 kDa cut-off



Mass balance on the ultrafiltration

	Amount extract, kg	Dry solids content, %	Amount dry solids, kg
Spruce feed	1570	1.02	16.01
Spruce concentrate	30	19.16	5.75
Spruce permeate	1540	0.69	10.63
Difference			-0.36
Birch feed	1570	1.57	24.65
Birch concentrate	30	25.00	7.50
Birch permeate	1540	1.05	16.17
Difference			0.98

Lignin determination methods

- Determination of chlorine consumption, “Chlorine number“
  - ISO 3260 or SCAN-C 29
- Acetyl bromide
  - Yokoyama, T; Kadla, J.F; Chang, H-M. J. Agric. Food. Chem. 2002, 50, 1040
- Acid-insoluble & acid-soluble lignin
  - KCL N:o 115b:82
  - TAPPI Test Method T 222 and TAPPI Useful Methods UM 250
  - National Renewable Energy Laboratory, Laboratory Analytical Procedure (LAP)
  - TAPPI and Goldschmid UV lignin

Chlorine number

- Acidification of sample by 4 M HCl
- NaClO addition ➔ formation of Cl_2-gas
- Reaction 15 min at 25 °C
- Addition of 1 M KI
- Titration with 0.2 M $Na_2S_2O_3$ starch as indicator
- Result g Cl_2/100 g sample
- Lignin content, % = 0.9 * Chlorine number
  - Kyrklund, B. and Strandell, G. (1969) Pap. Puu 51(4a):299–305

Acetyl bromide

- Sample treatment with 25% w/w AcBr in glacial acetic acid + $HClO_4$ (catalyst)
- Heating at 70 °C during 30 min
- Reaction mixture poured into flask containing NaAc-buffer
- Volume adjusted with AcOH to 50 ml
- UV at 280 nm
- Calibration curve done with softwood and hardwood milled wood lignin

KCL N:o 115b:82

- Sample treatment with 72% H_2SO_4 for 2 hours
- Addition of water and wait for 4 hours
- Addition of water and wait overnight
- Refluxing for 4 hours
- Filtering, washing and drying the solid lignin
- Acid-soluble lignin by UV

TAPPI T 222 and UM 250 (and Goldschmid)

- Sample treatment with 72% H_2SO_4 for 2 hours
- Addition of water and boiling in open flask for 4 hours
- Filtering, washing and drying of solid lignin
- Acid-soluble lignin by UV

Laboratory analytical procedure (LAP)

- Sample treatment with 72% H_2SO_4 for 1 hour
- Addition of water and autoclavation at 121 °C for 1 hour
- Filtering, washing and drying of solid lignin
- Acid-soluble lignin by UV

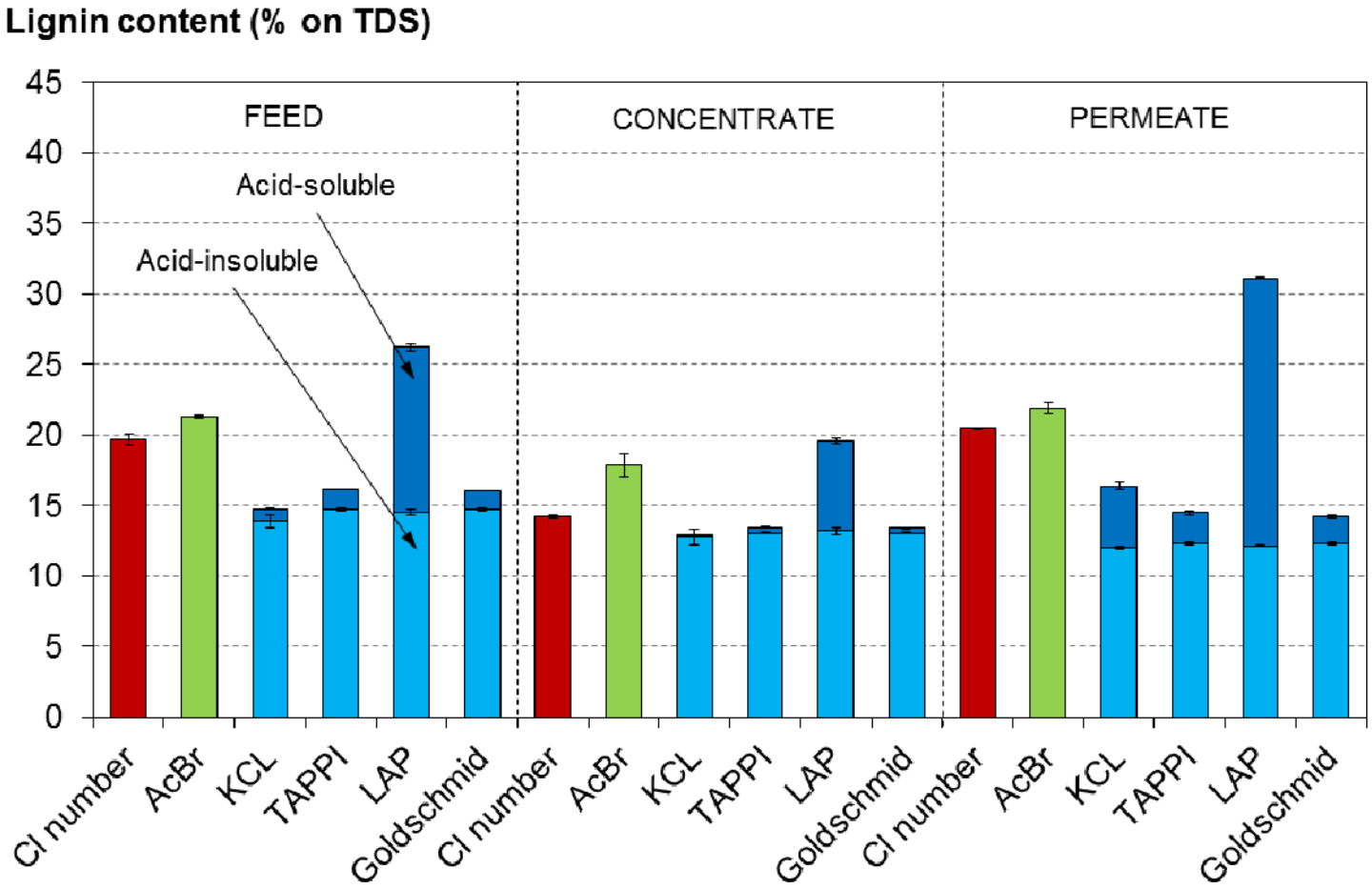
Wavelengths and extinction coefficients for Klason lignin

Method	Wavelength	Absorbance	Extinction coefficient
KCL	203 nm	0.2–0.7	128 L/gcm for SW 110 L/gcm for HW
LAP	240 nm	0.7–1.0	12 L/gcm for SW 25 L/gcm for HW
Tappi	205 nm	0.2–0.7	110 L/gcm for SW and HW
Golschmid*	215 and 280 nm		

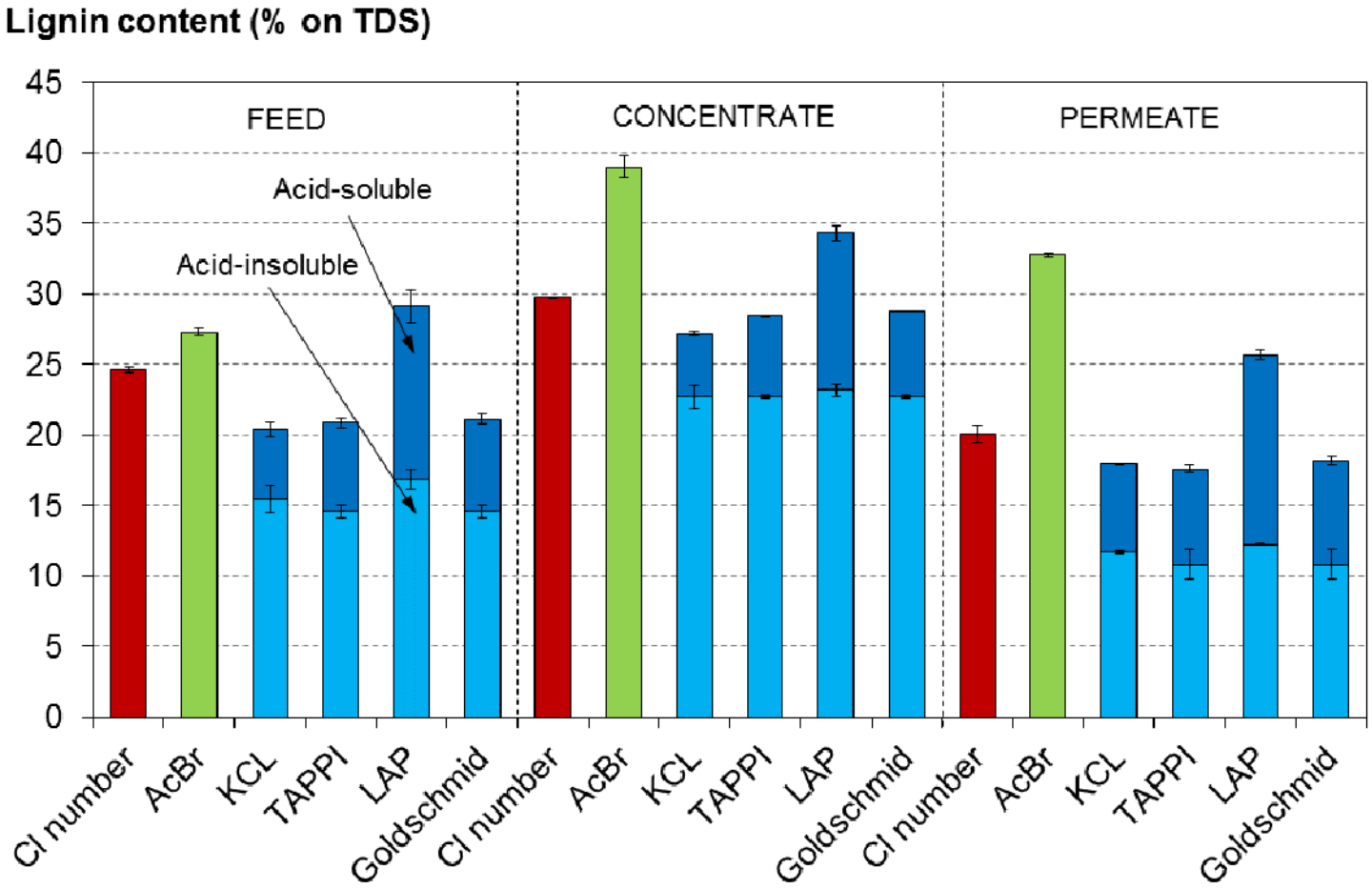
*)

$$C_L = \frac{4.53 \cdot A_{215\,nm} - A_{280\,nm}}{300}$$

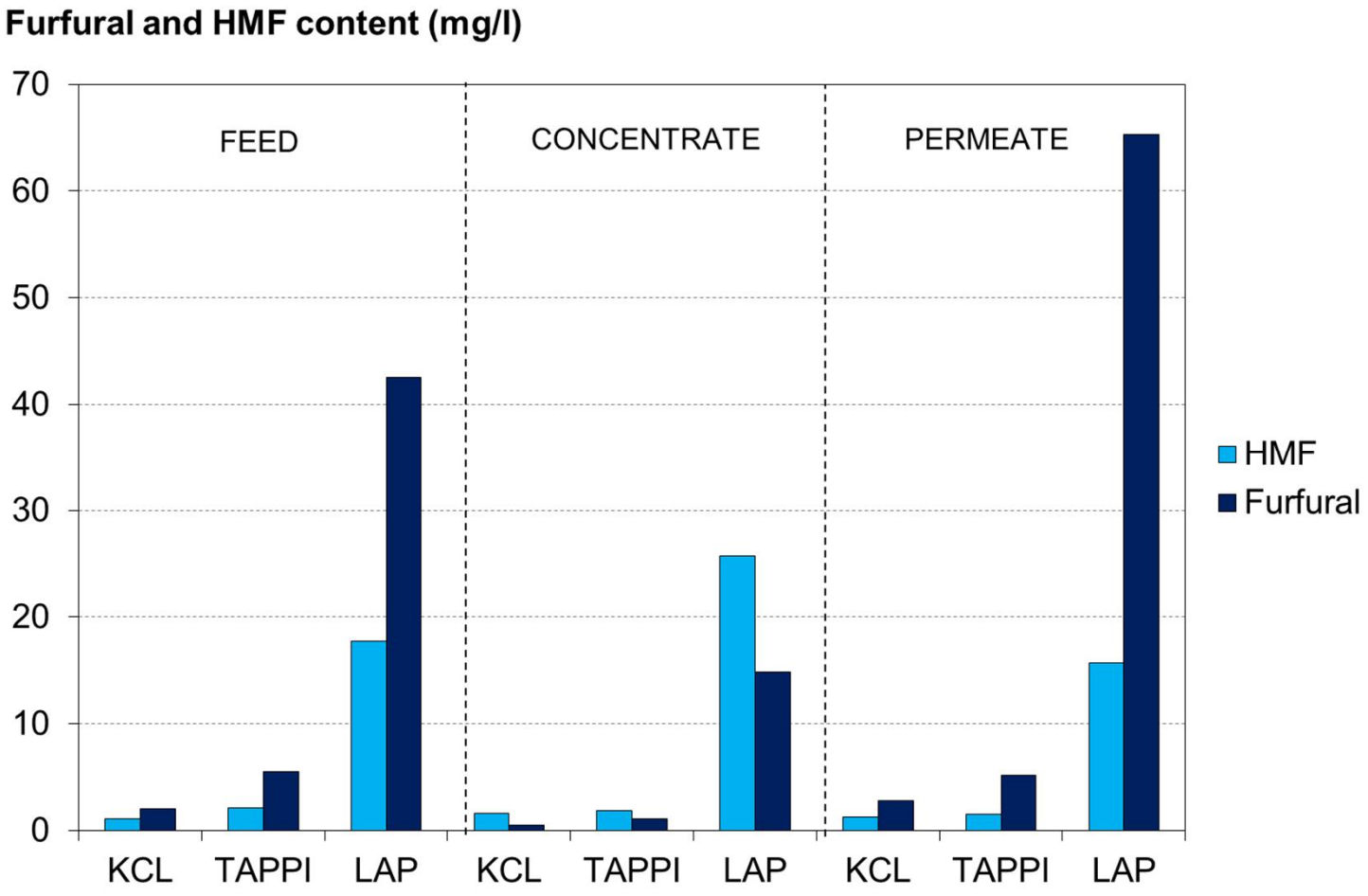
Lignin content in **spruce** raw extract and filtrates



Lignin content in **birch** raw extract and filtrates



Furfural and HMF content in Klason lignin hydrolysates (spruce)



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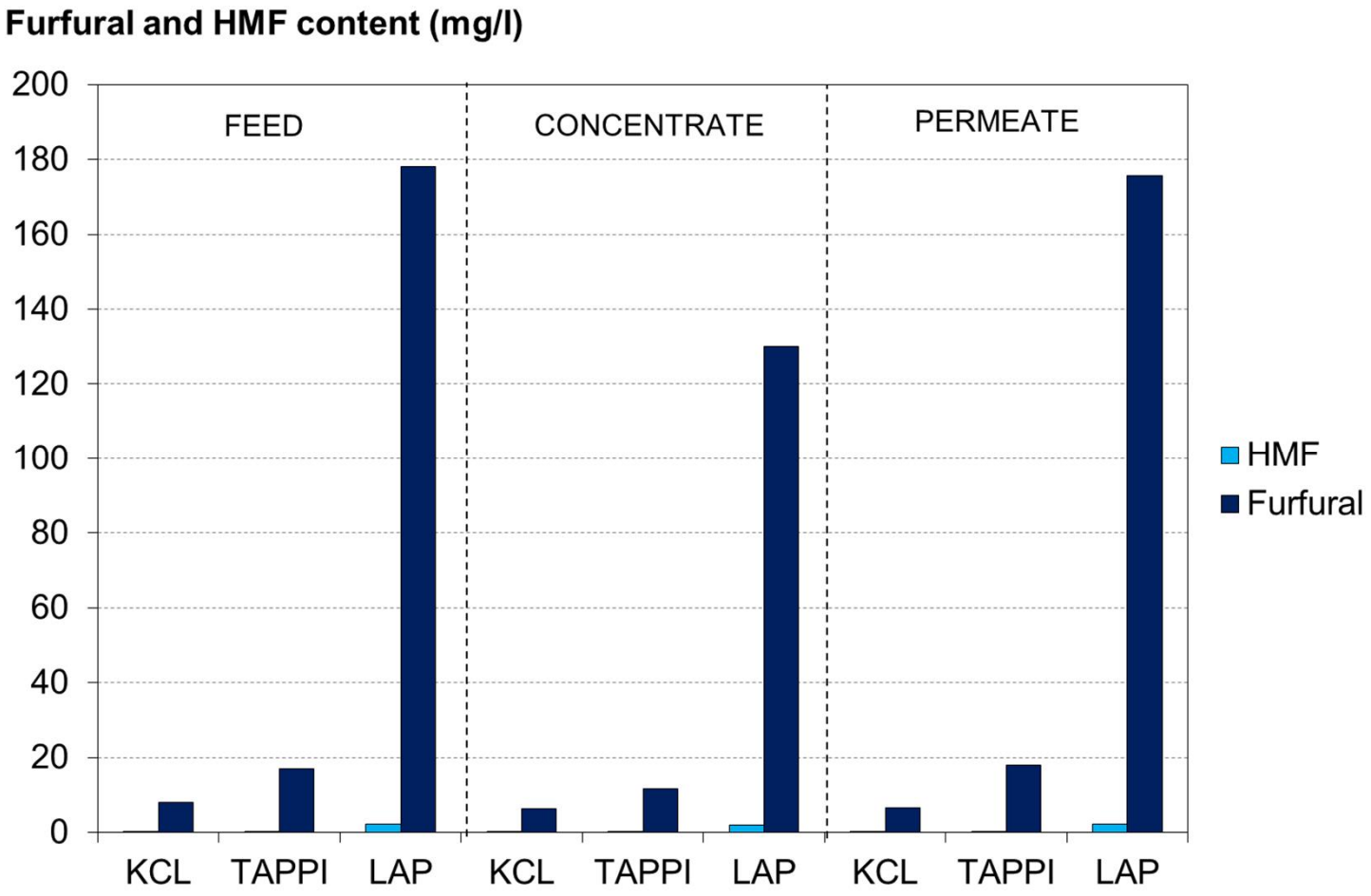
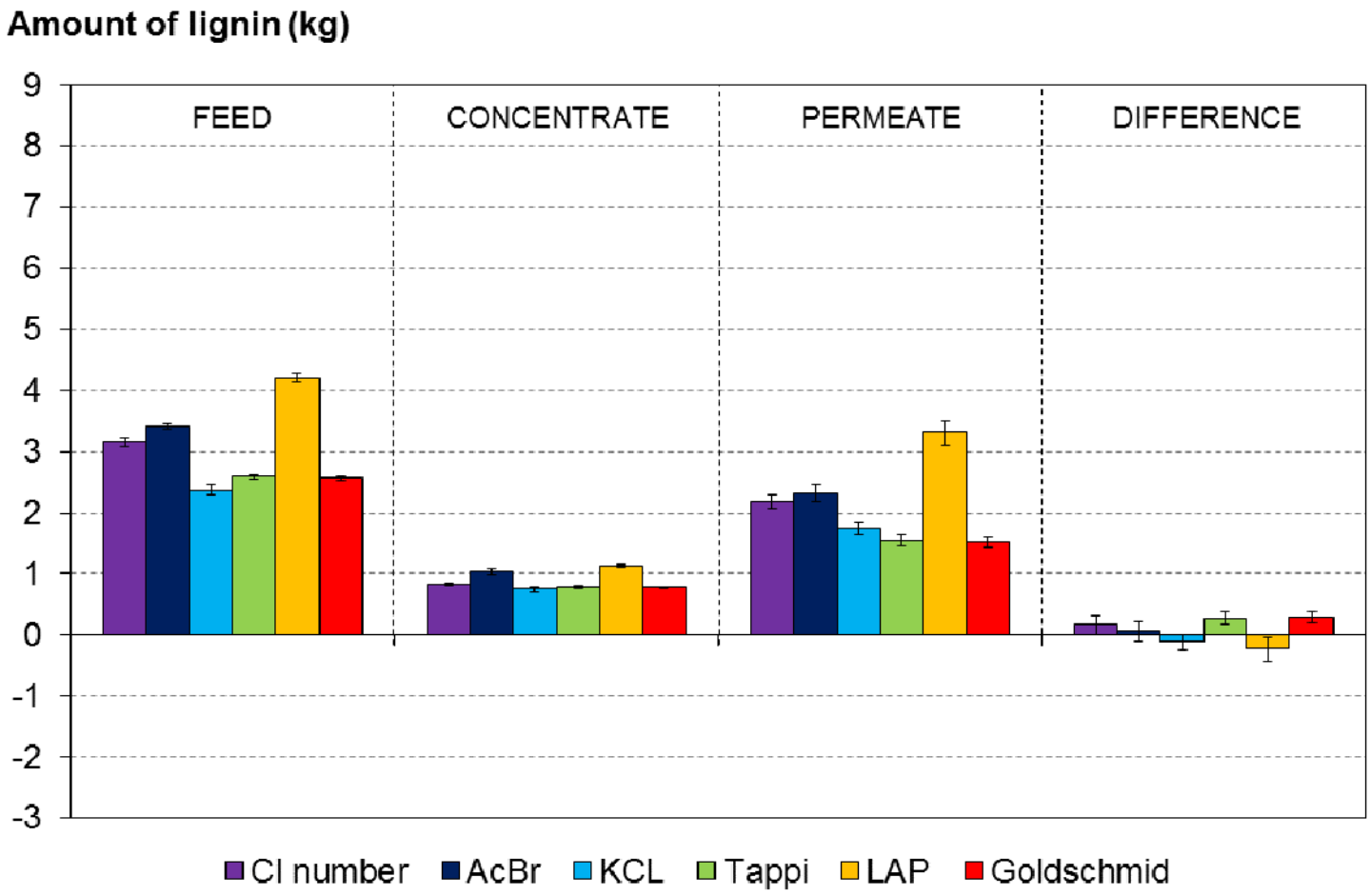


Chlorine number and AcBr

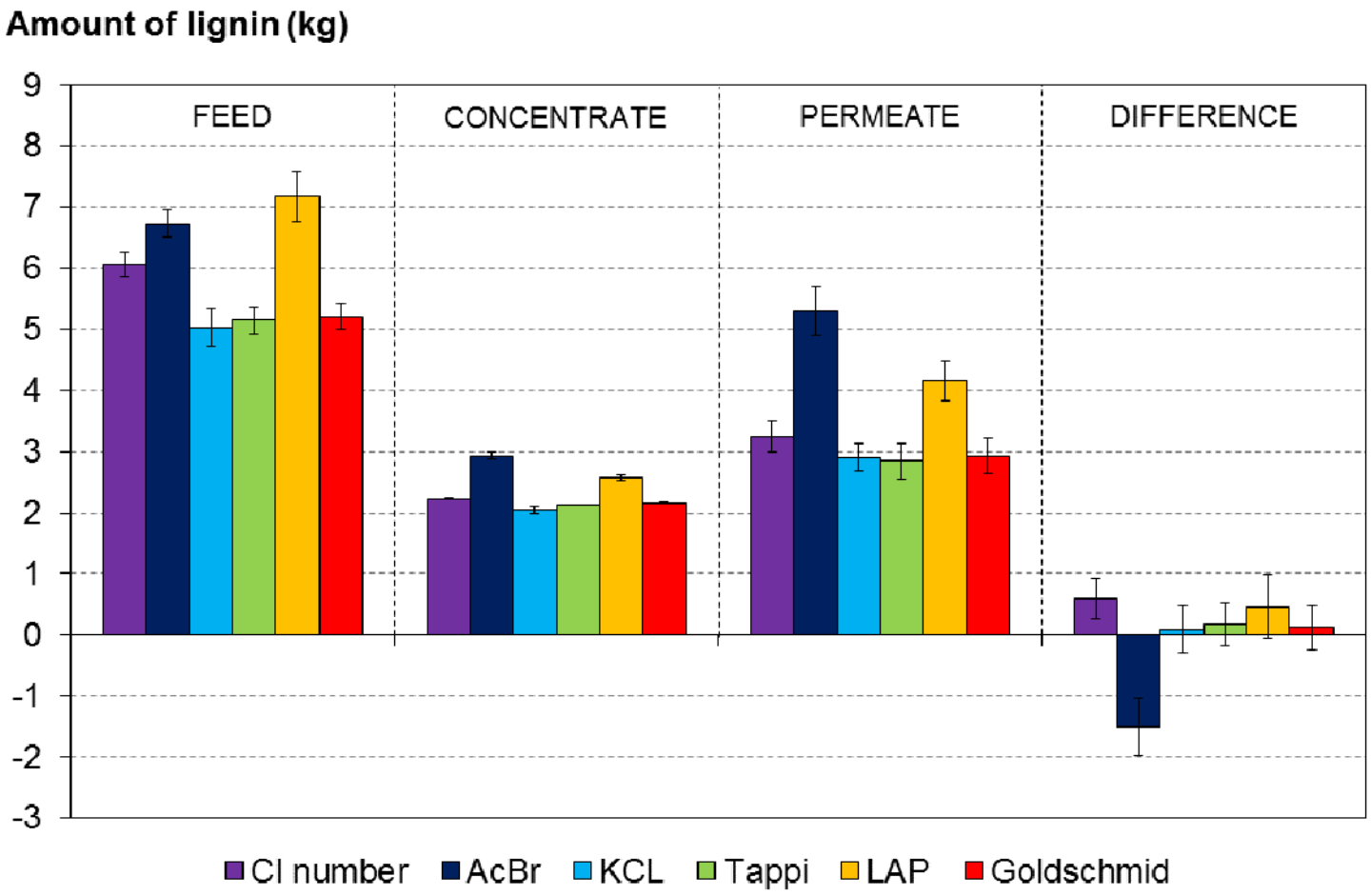
- Cl number
  - Chlorine gas can react with altered carbohydrates, lipophilic extractives and low molar mass phenolics
- AcBr
  - Isolated MWL used for calibration
    - Less oxidised and degraded compared to lignin release from wood at high temperature
  - Pentose degradation products formed during the analysis

Lignin mass balance of **spruce** extract filtration



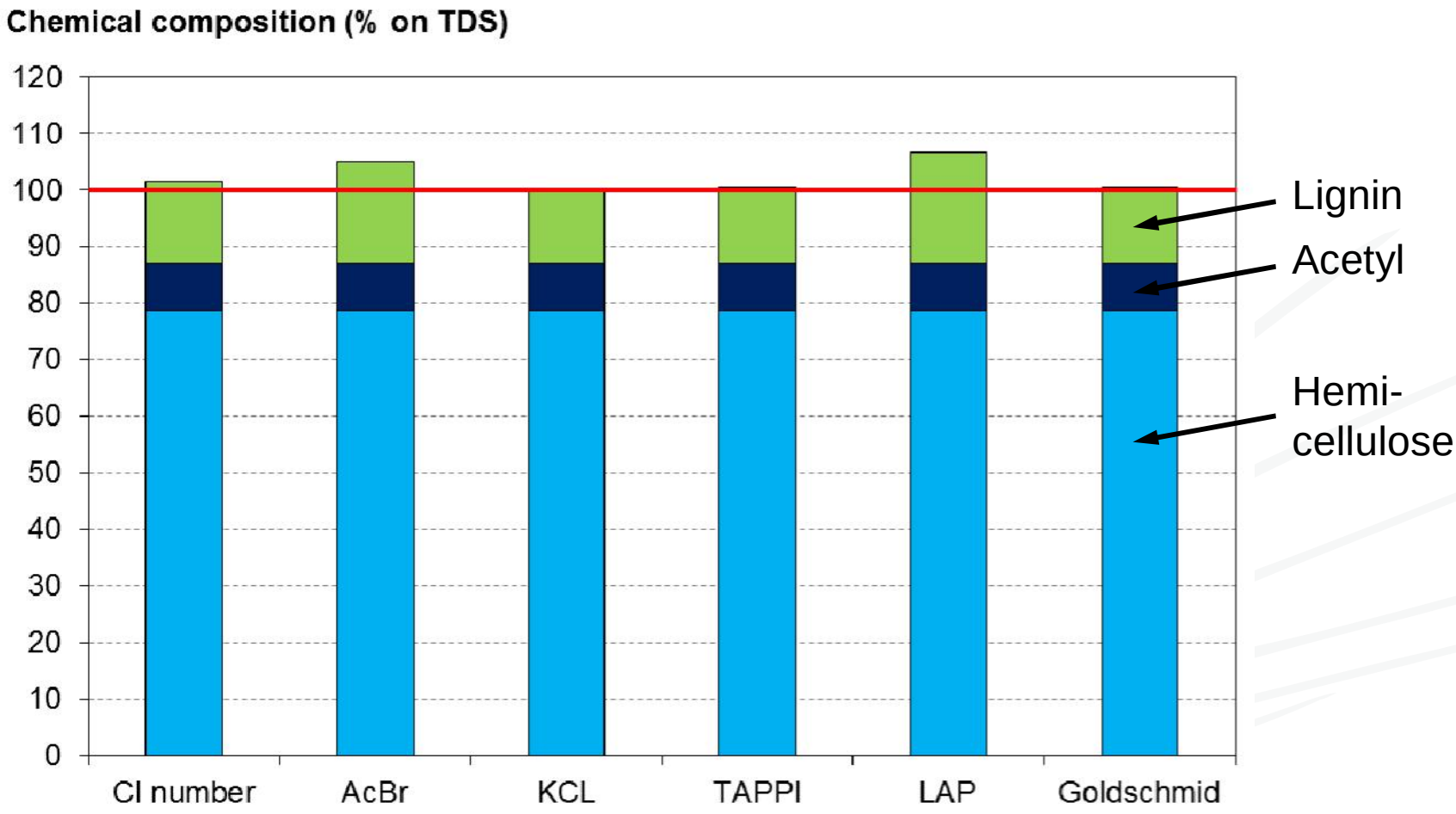
Difference = Feed - (Concentrate + Permeate)

Lignin mass balance of **birch** extract filtration

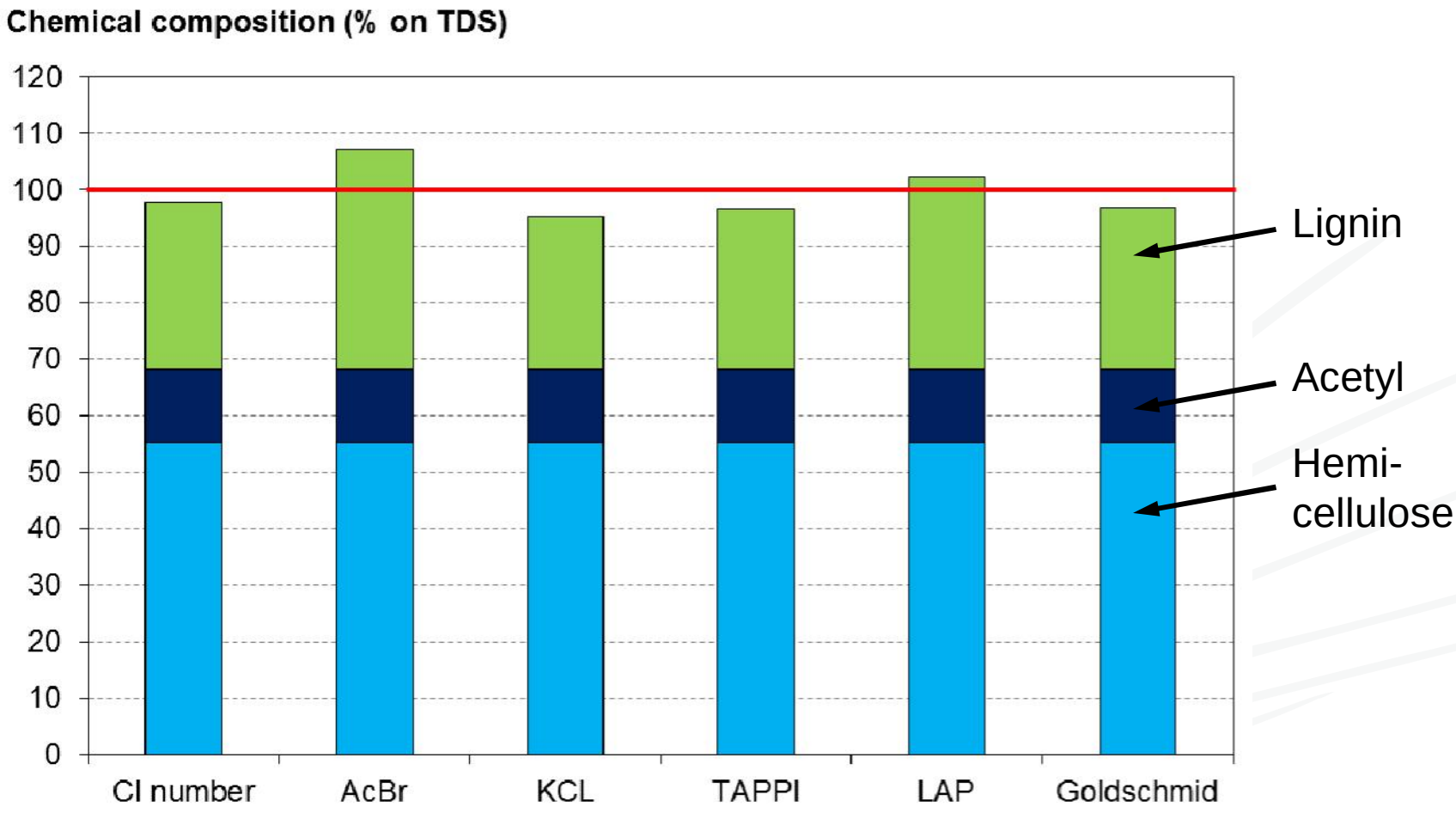


Difference = Feed - (Concentrate + Permeate)

Spruce concentrate



Birch concentrate



Summary

- Klason lignin (solid) for extracts obtained at relatively mild conditions up to 170 °C was the most accurate and repeatable
  - Most of variation due to acid-soluble lignin
- In case of spruce extracts all methods tested can be used for monitoring lignin balance during ultrafiltration

THANK YOU!