Lignocellulose Biorefinery:

Monitoring the Conversion of Wood into Platform Chemicals after Organosolv- and Steaming-Pretreatment

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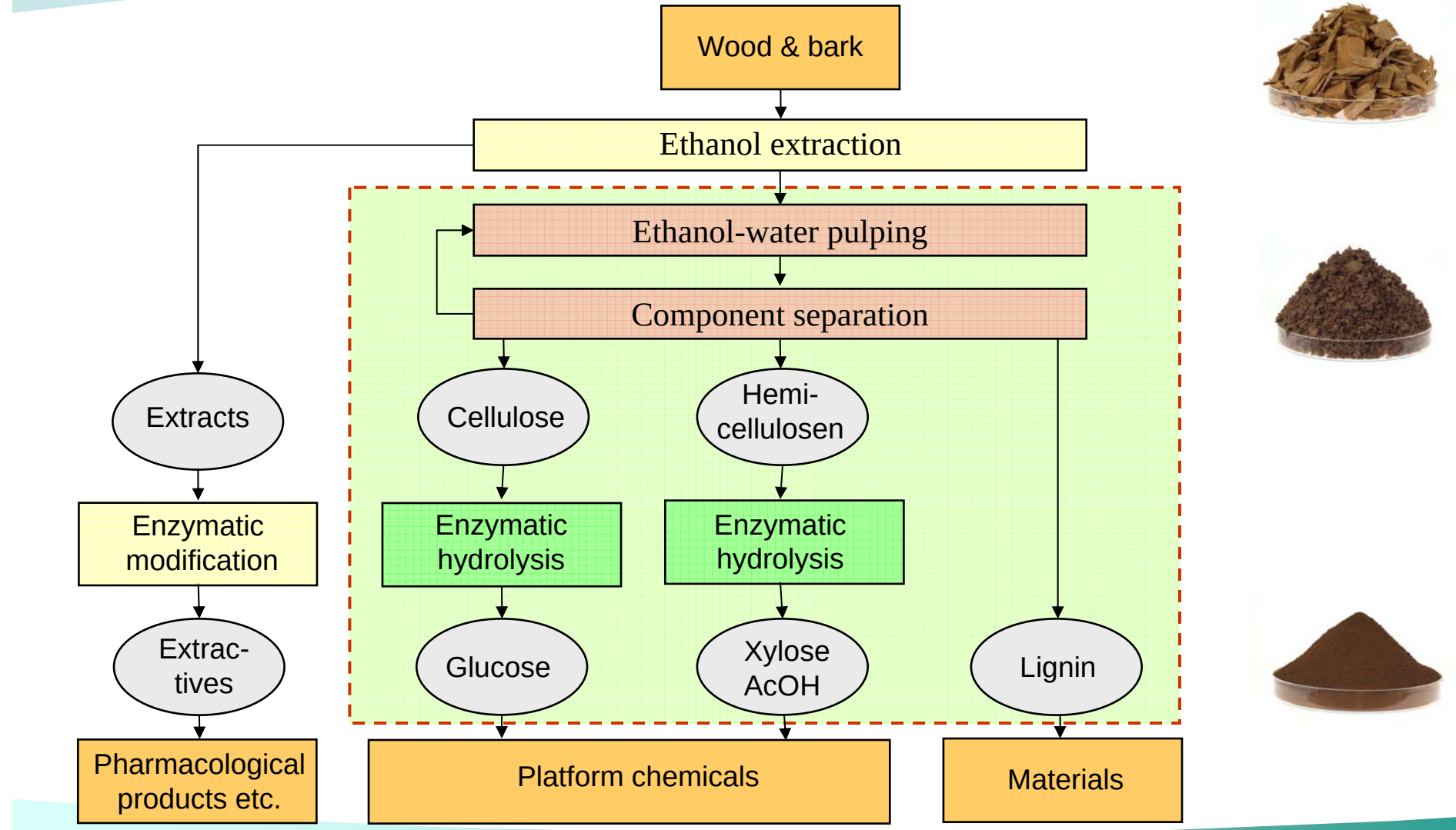
Monitoring the Conversion of Wood into Platform Chemicals after Organosolv- and Steaming-Pretreatment

Outline

- Processes under consideration: Ethanol:water pulping, steaming pretreatment
- Process variables
- Test values for process evaluation
- Applied methods for carbohydrate, lignin, extraction, and transformed products evaluation
- Conclusion

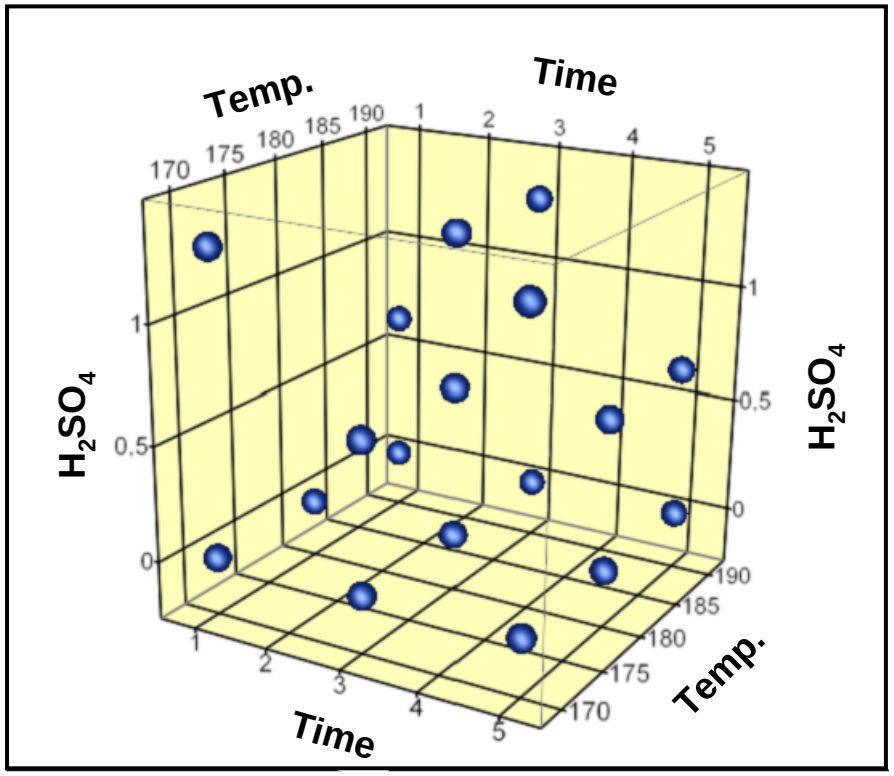
Hardwood biorefinery based on alcohol:water pulping process

Process steps and products



Ethanol:Water-Pulping

Statistical design



100 g scale

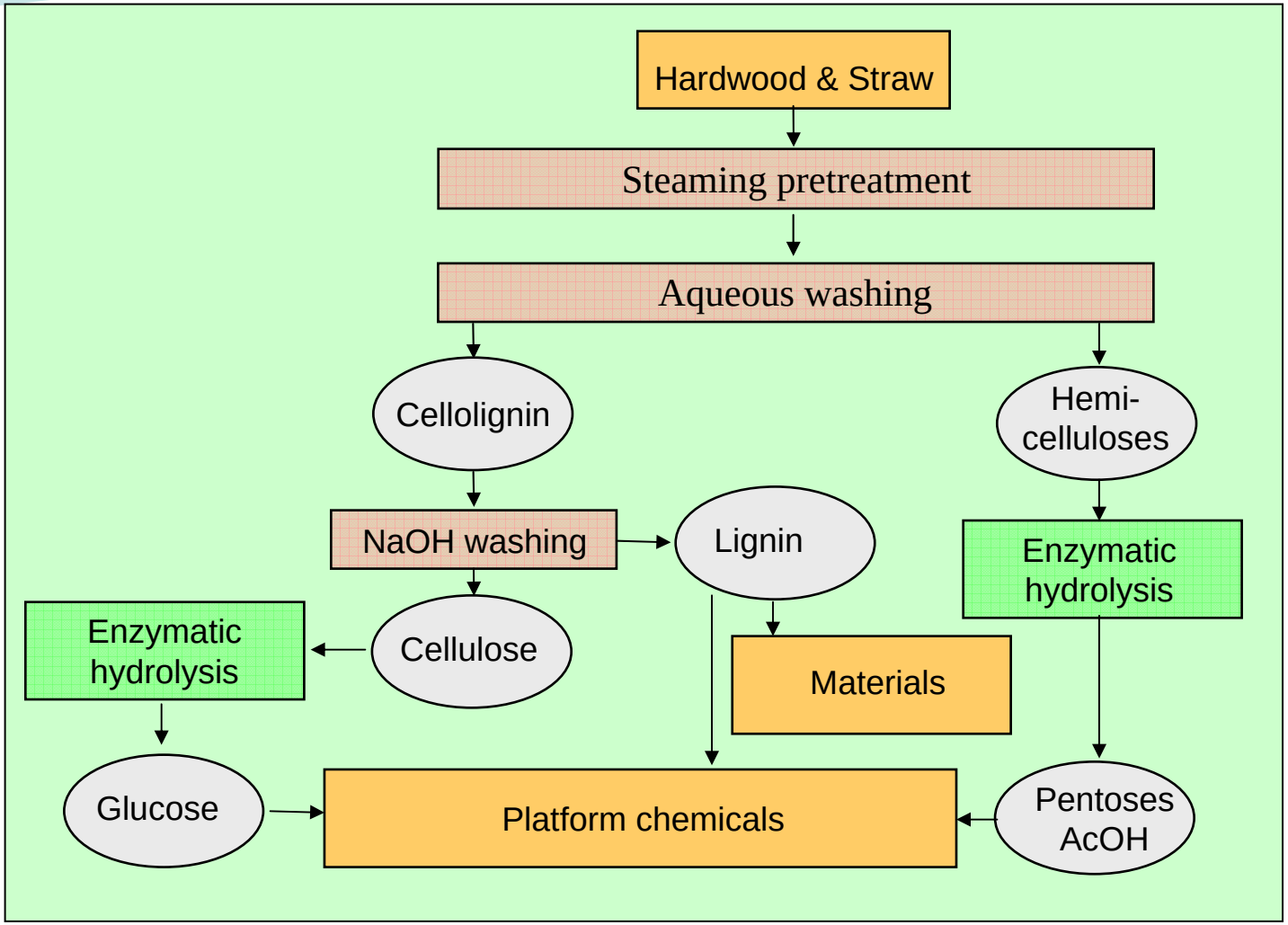
10 kg scale

1 kg scale

1 l digesters; liquor:wood = 6:1; ethanol : water 1:1 (w/w)

Hardwood & straw biorefinery based on steaming pretreatment

Process steps and products



Optimization of steaming conditions

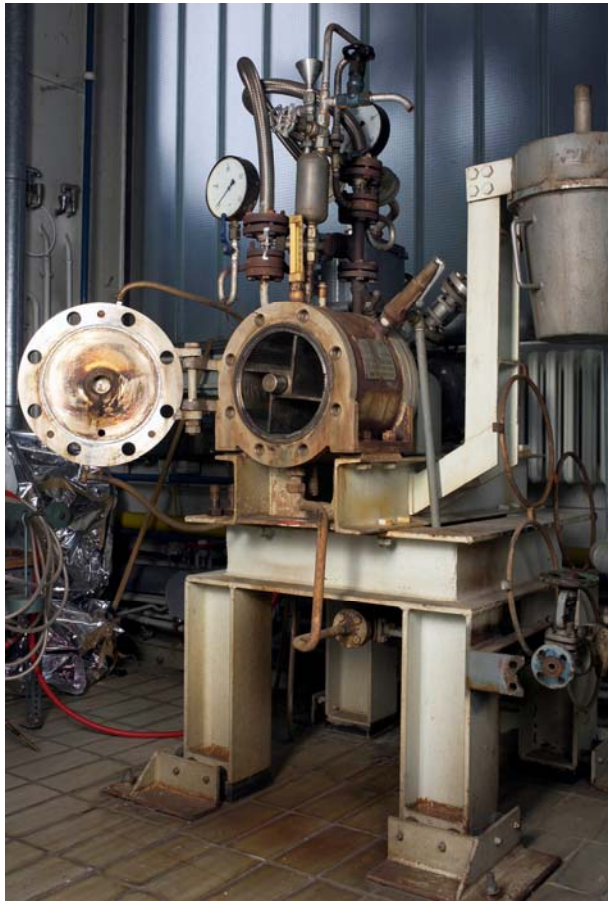
Statistical design:

Temp.: 170, 182.5, 195, 207.5, 220°C	Time: 3, 9.75, 16.5, 23.25, 30 min.

17 experiments
13 levels
4 levels as double-tests

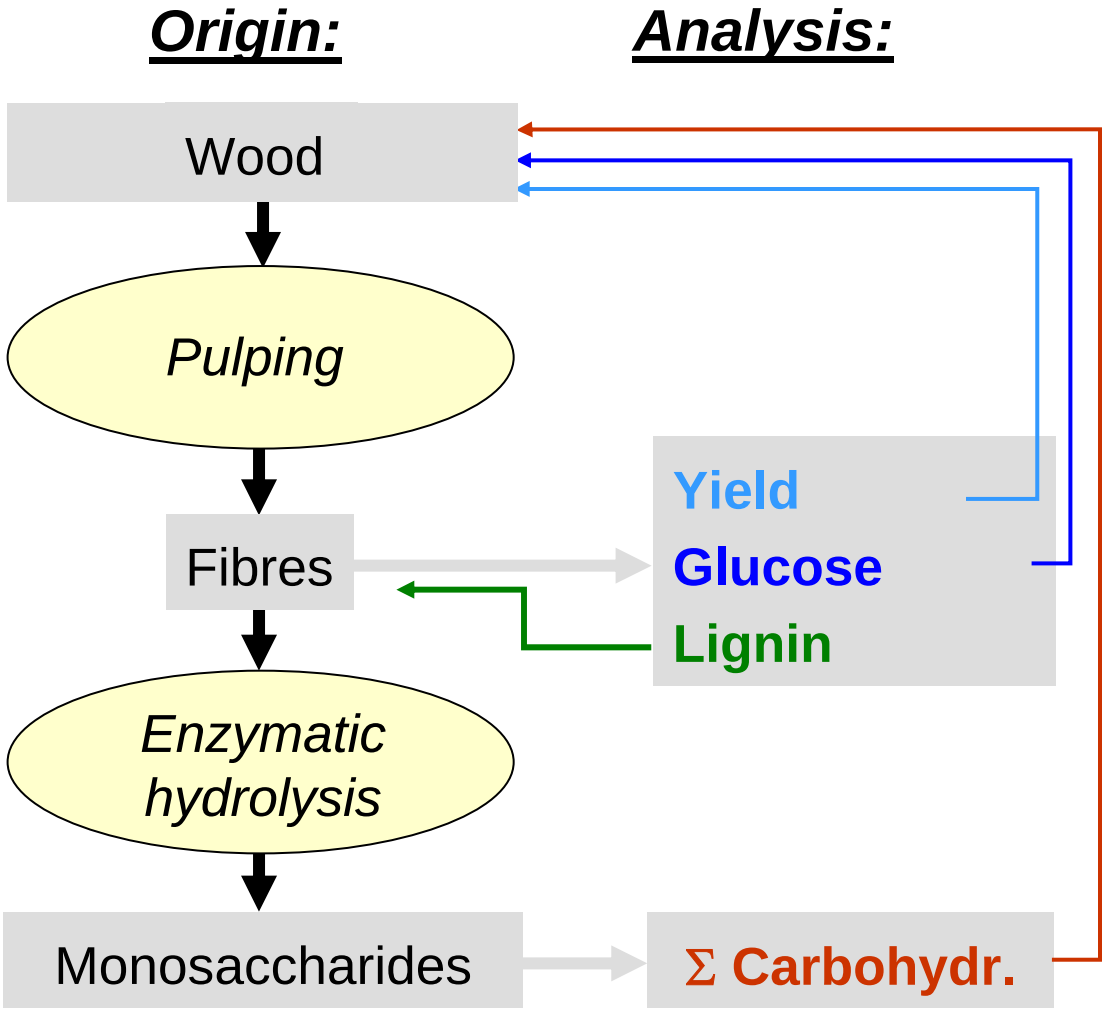
R0 = t exp [T-100/14.5]

➔ Severity factor (Overend and Chornet 1987)



Pulping & enzymatic hydrolysis

Test values for process evaluation



Denotation of test value:

Fibre yield (% wood)

Cellulose (% wood)

Lignin (% fibre)

Yield (% wood)
after enzymatic hydrolysis (EH)

Process Analytics: Arsenal of Applied Methods /1

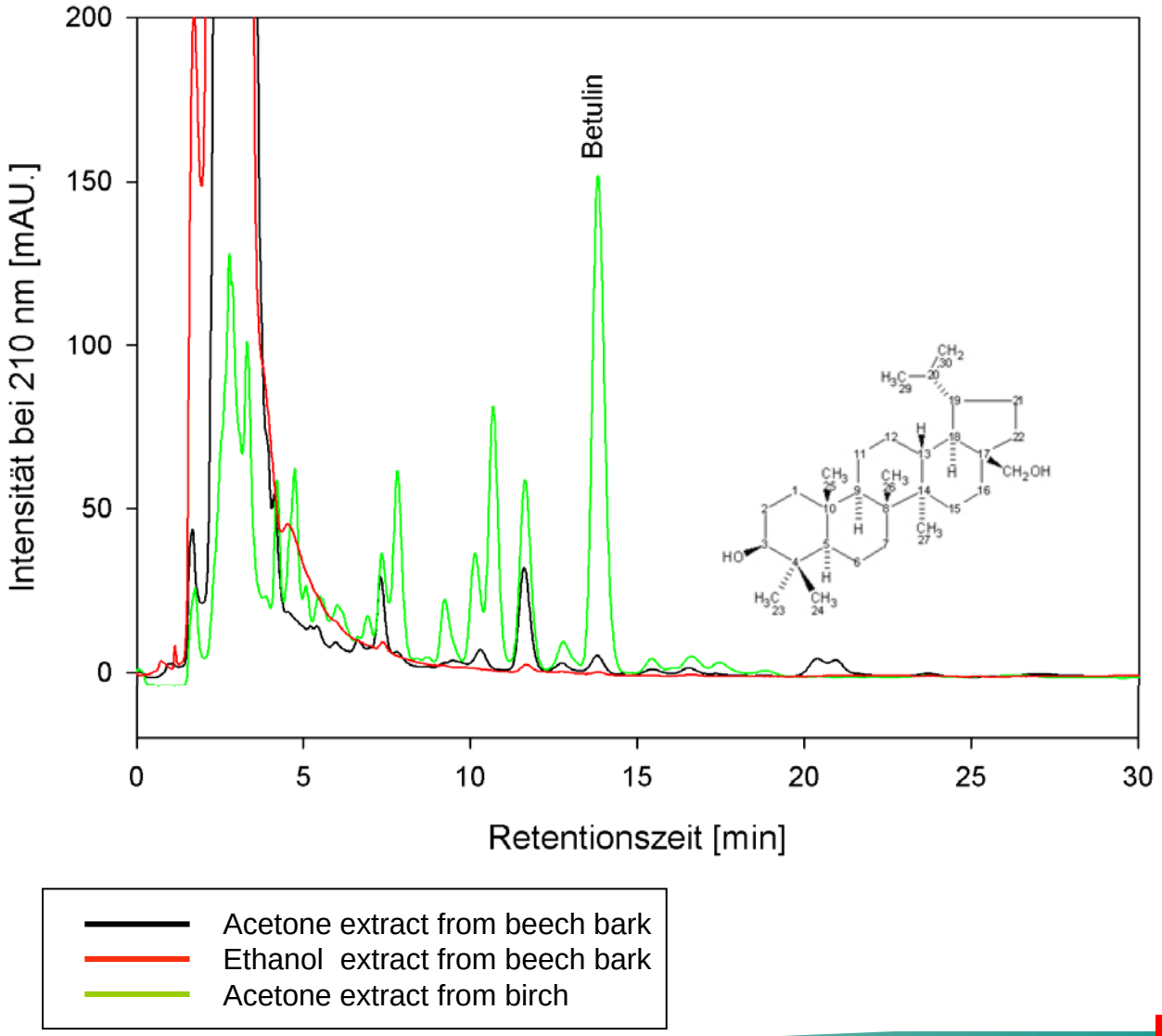
- Accelerated solvent extraction (ASE) and reversed phase HPLC for wood extractives
- Different acid hydrolysis methods
- Borate complex ion exchange chromatography for acid hydrolysates
- Anion exchange chromatography for neutral wood sugars and oligosaccharides
- Enzymatic test combination for acetic acid determination
- HPLC for furfural and 5-HMF determination

Process Analytics: Arsenal of Applied Methods /2

- Quantitative lignin determination: as residue after sulphuric acid treatment (Klason-lignin, acid-soluble lignin) or after K-permanganate oxidation (Kappa-No)
- Qualitative lignin characterization: ^{1}H-NMR after acetylation for methoxyl- and proton determination, ^{31}P-NMR for aliphatic and aromatic OH-group determination
- Size exclusion chromatography for molar mass determination of cellulose, hemicelluloses and lignin
- Elemental analysis: Carbon-, hydrogen-, oxygen-, nitrogen content determination
- Relative comparison of accessibility of fibres for cellulolytic enzymes under standardized conditions

Wood extractives: Removal from woody tissue by accelerated solvent extraction (ASE) and analysis by HPLC

Is **beech** bark a proper source for ***Betulin*** similar to **birch** bark?

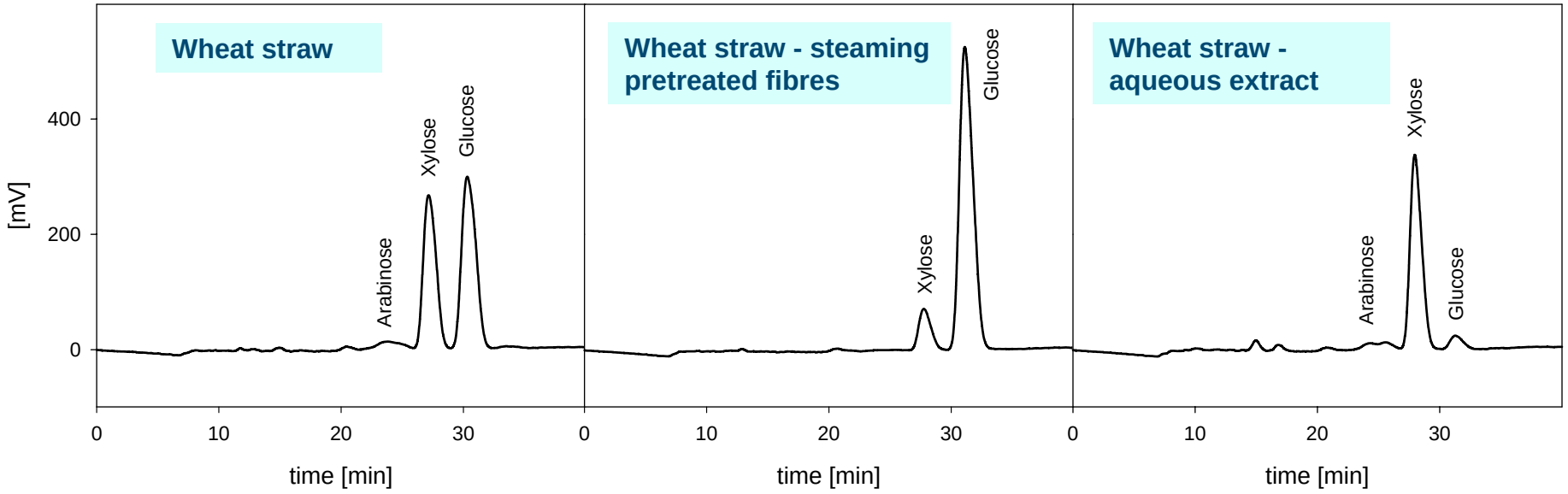


Borate complex anion exchange chromatography

Quantification of xylan extraction by steaming pretreatment of wheat straw

Stationary phase:
MCI Gel CA08F (Mitsubishi)
115 x 6.6mm, 60°C

Mobile phase:
Linear gradient of 0.3 to 0.9 M K-borate buffer pH 9.2 within 35 min. 0.7 ml/min. Cu-bicinchonate detection

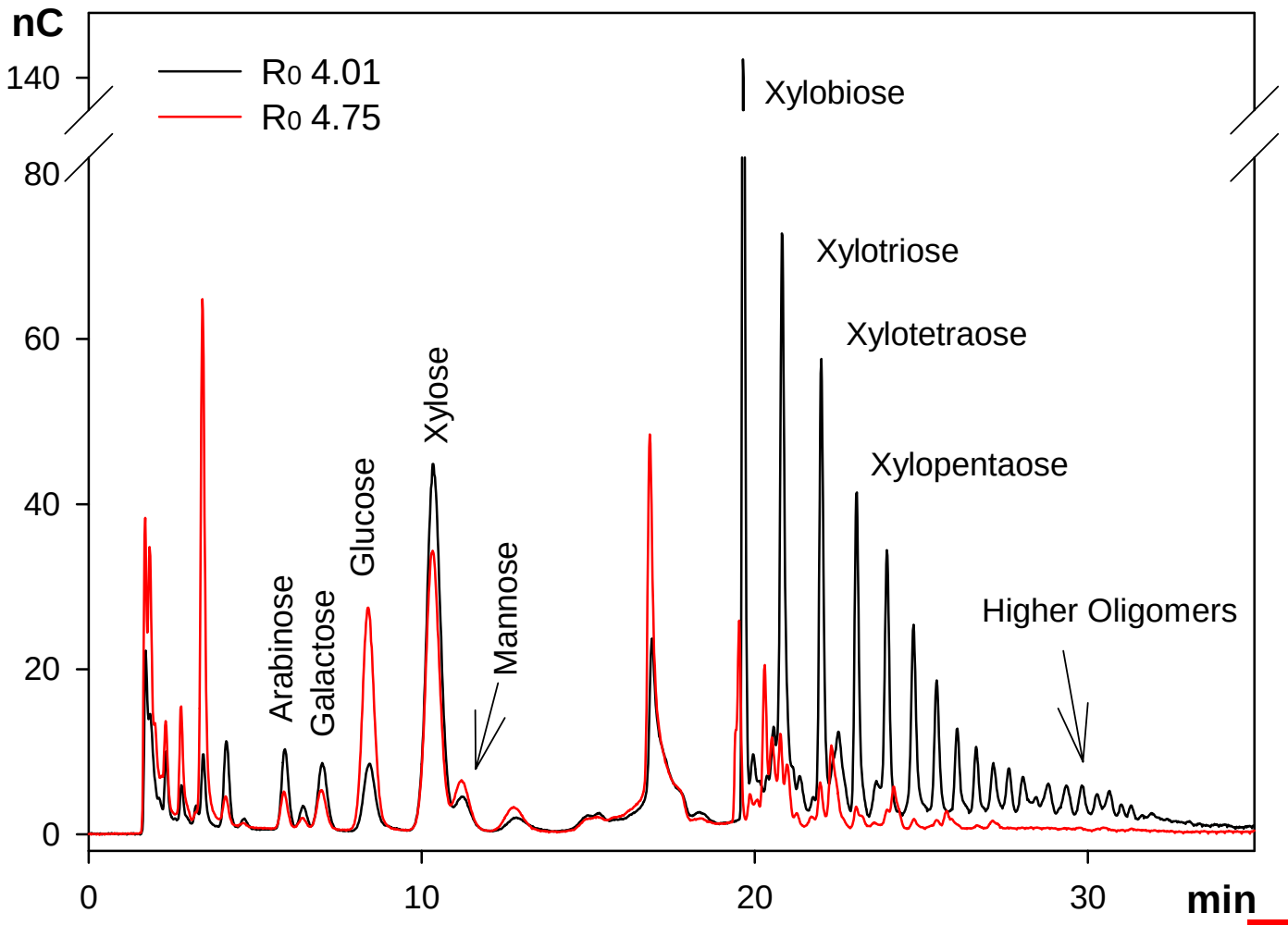


Anion exchange chromatography in NaOH-Medium

Aquous extracts from steaming pretreatment

195°C; 16.5 min
=> R0 = 4.01

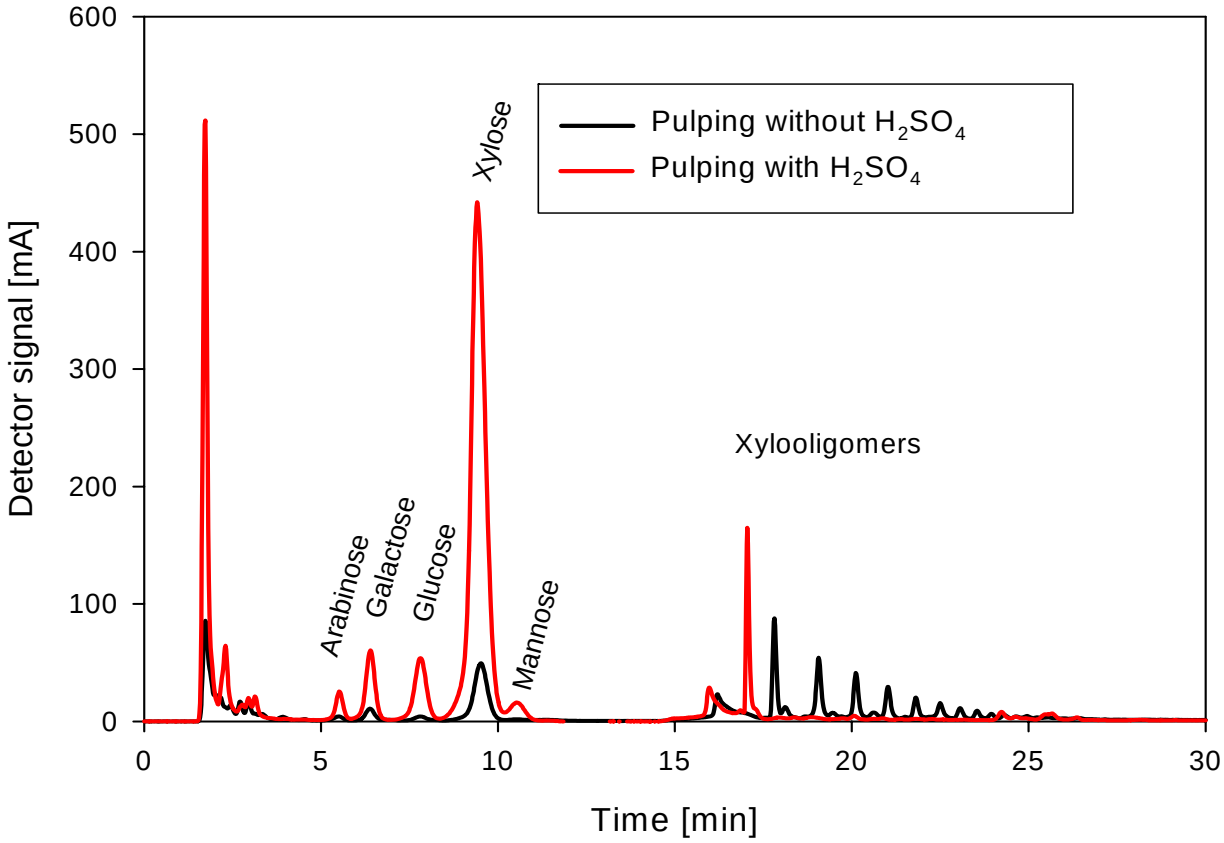
220°C; 16.5 min
=> R0 = 4.75



Recovered organosolv hemicellulose fractions

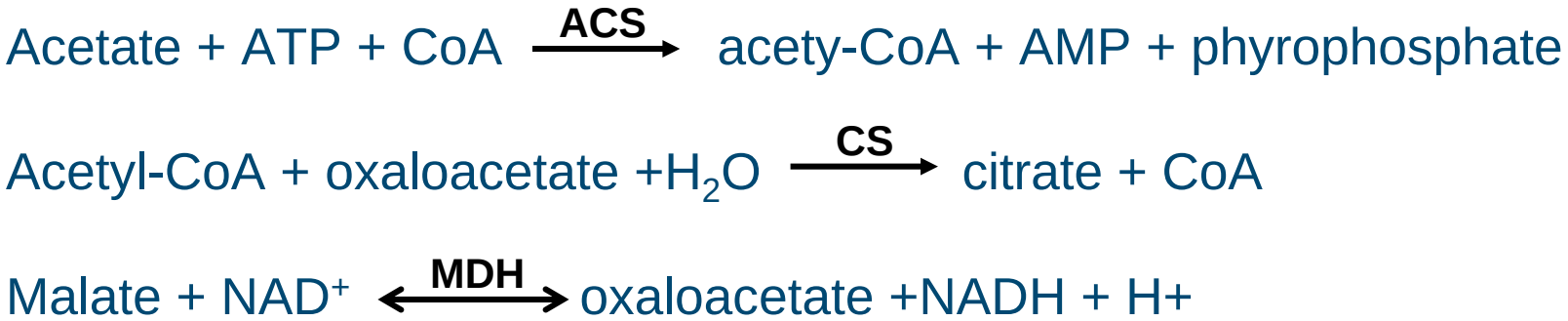
HPAEC-chromatographic analysis

- Acetyl groups are completely cleaved off in the organosolv pulping process
- Xylan main chain is fragmented into oligo-saccharides in the absence of catalyst
- Sulphuric acid addition converts xylan into xylose and traces of xylobiose



Liberated acetic acid

By UV enzymatic test combination



ACS = Acetyl-COA-Synthetase
MDH = Malate Dehydrogenase

The method is specific for acetic acid
Detection limit is 0.15 mg/l
Linearity exists from 0.15 mg acetic acid/l to 0.3g acetic acid/l

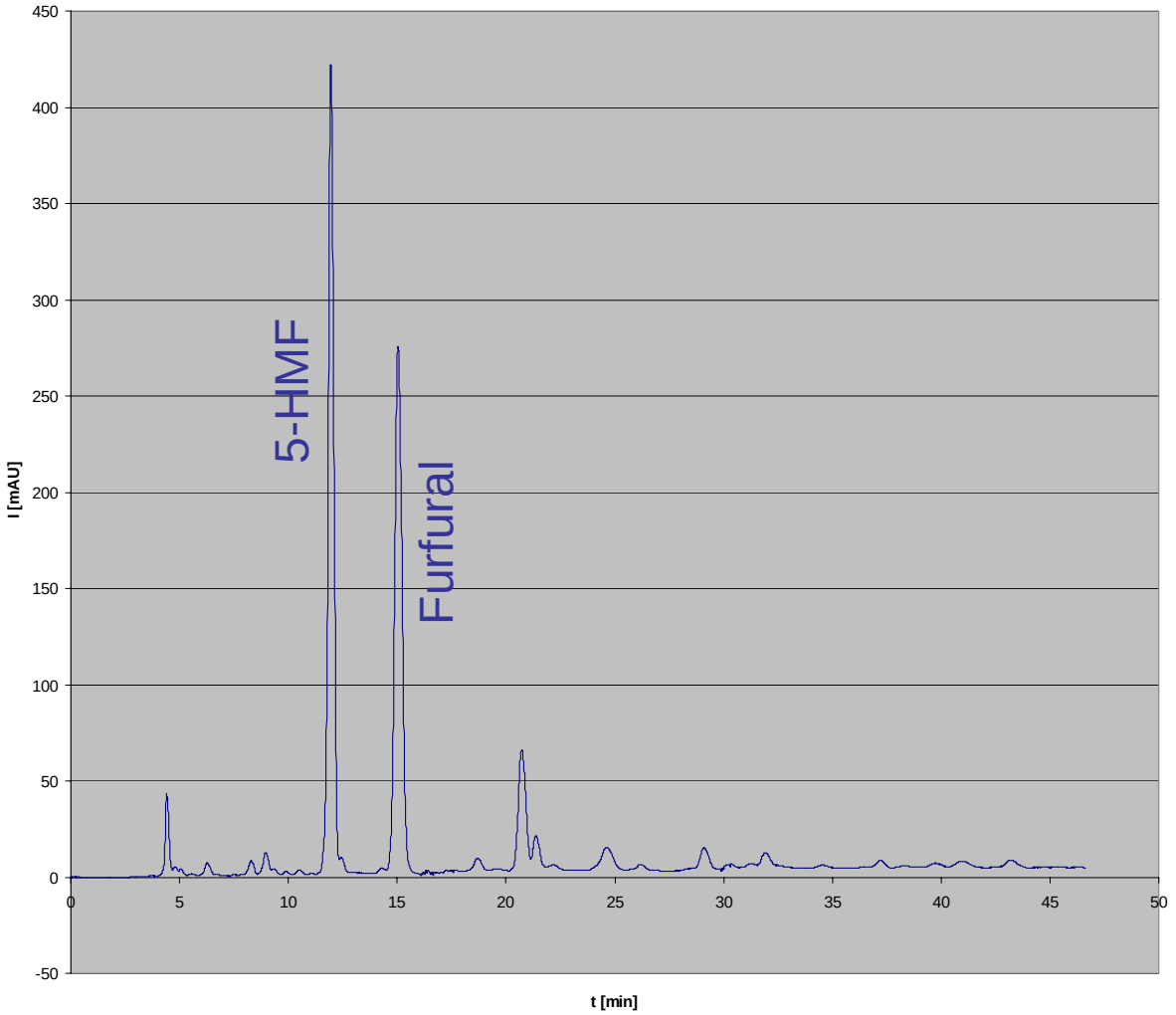
UV enzymatic test combinations are also available for:

- Formic acid
- 5-HMF
- Glucose
- Ethanol

Reversed phase HPLC for Furfural and 5-HMF determination

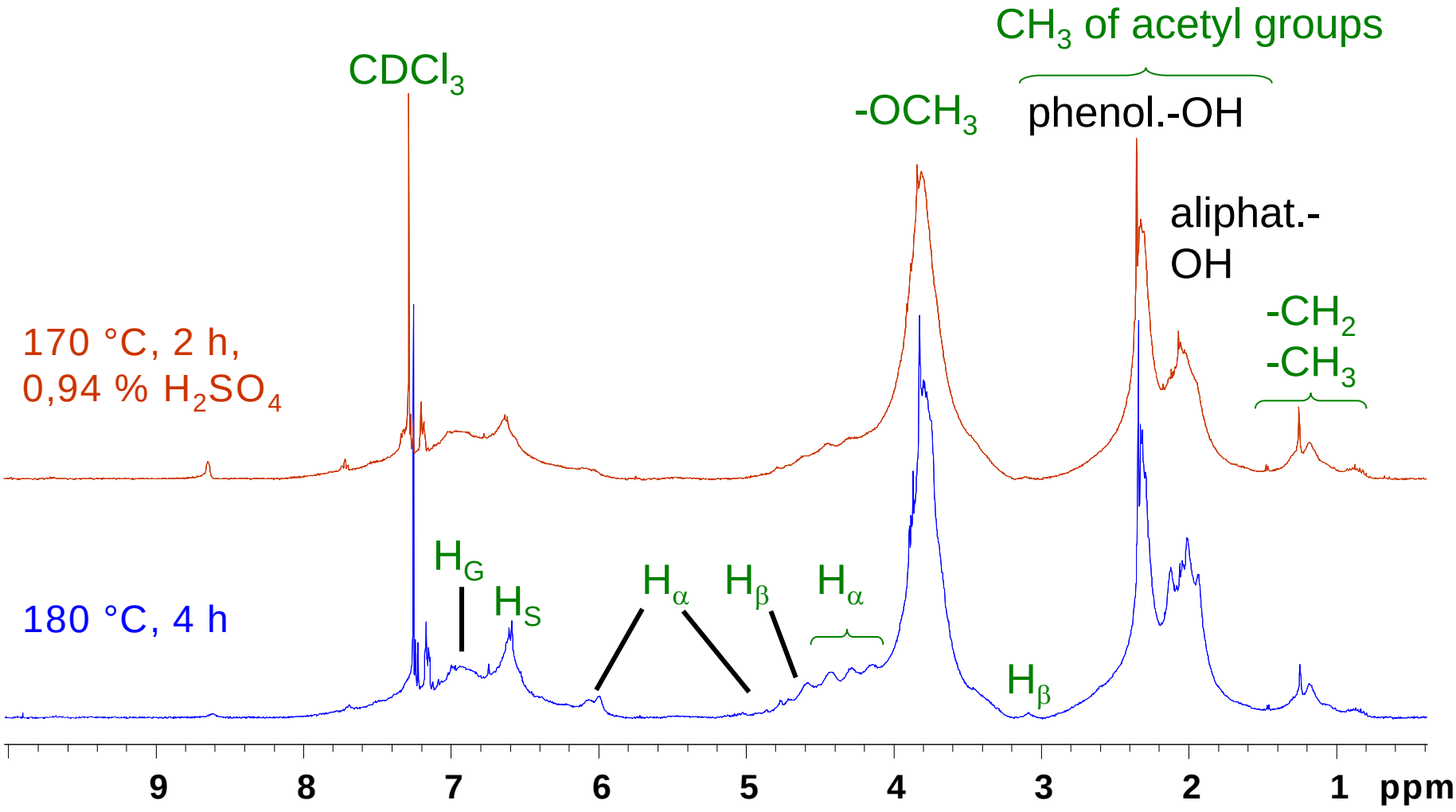
Stationary phase:
AQUASIL C18 5µ
250 x 4.6mm

Mobile phase:
1mM phosphoric acid in acetonitrile
1ml/min



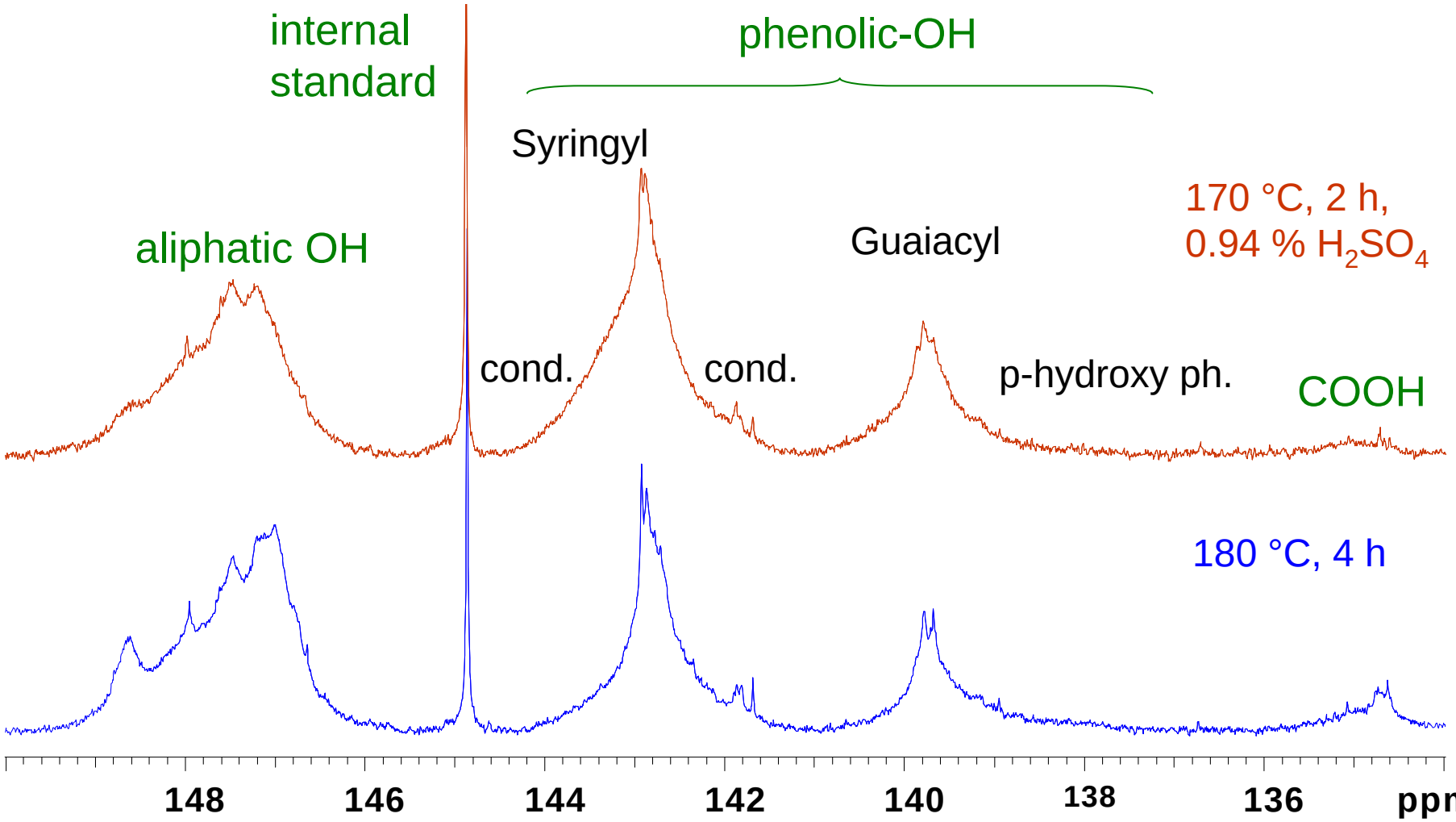
Characterisisation of Organosolv lignins (L:W 6:1)

^{1}H-NMR after acetylation:



Characterisation of Organosolv lignins (L:W 6:1)

^{31}P-NMR for OH-group determination*):



*) Phosphitylation reagent: 2-Chloro-4,4,5,5,-tetramethyl-1,3,2-dioxaphospholane

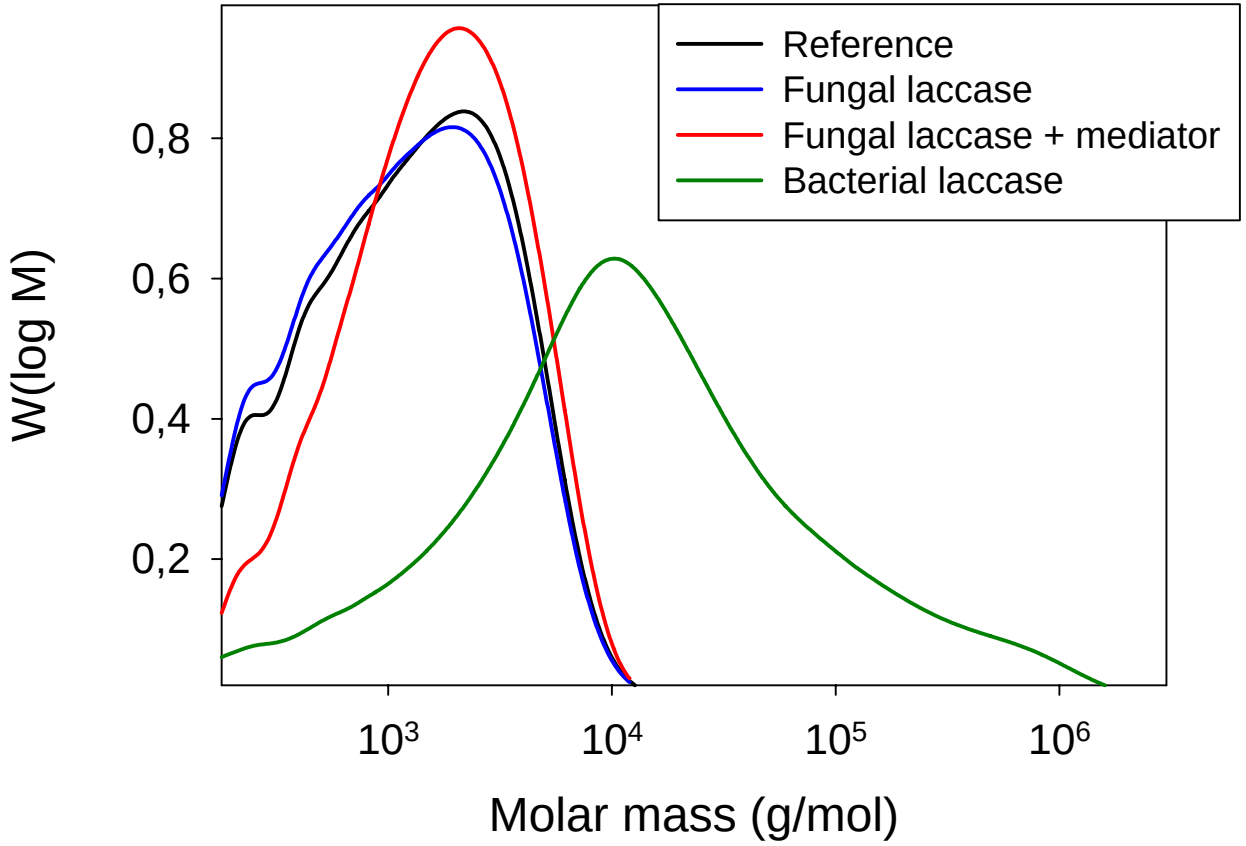
Size exclusion chromatography of lignin

Organosolv lignin from beech after different laccase treatments

Stationary phase:
2x PolarGel M
300 x 7.5mm
60°C

Mobile phase:
0.1% LiBr in DMSO
0.6 ml/min

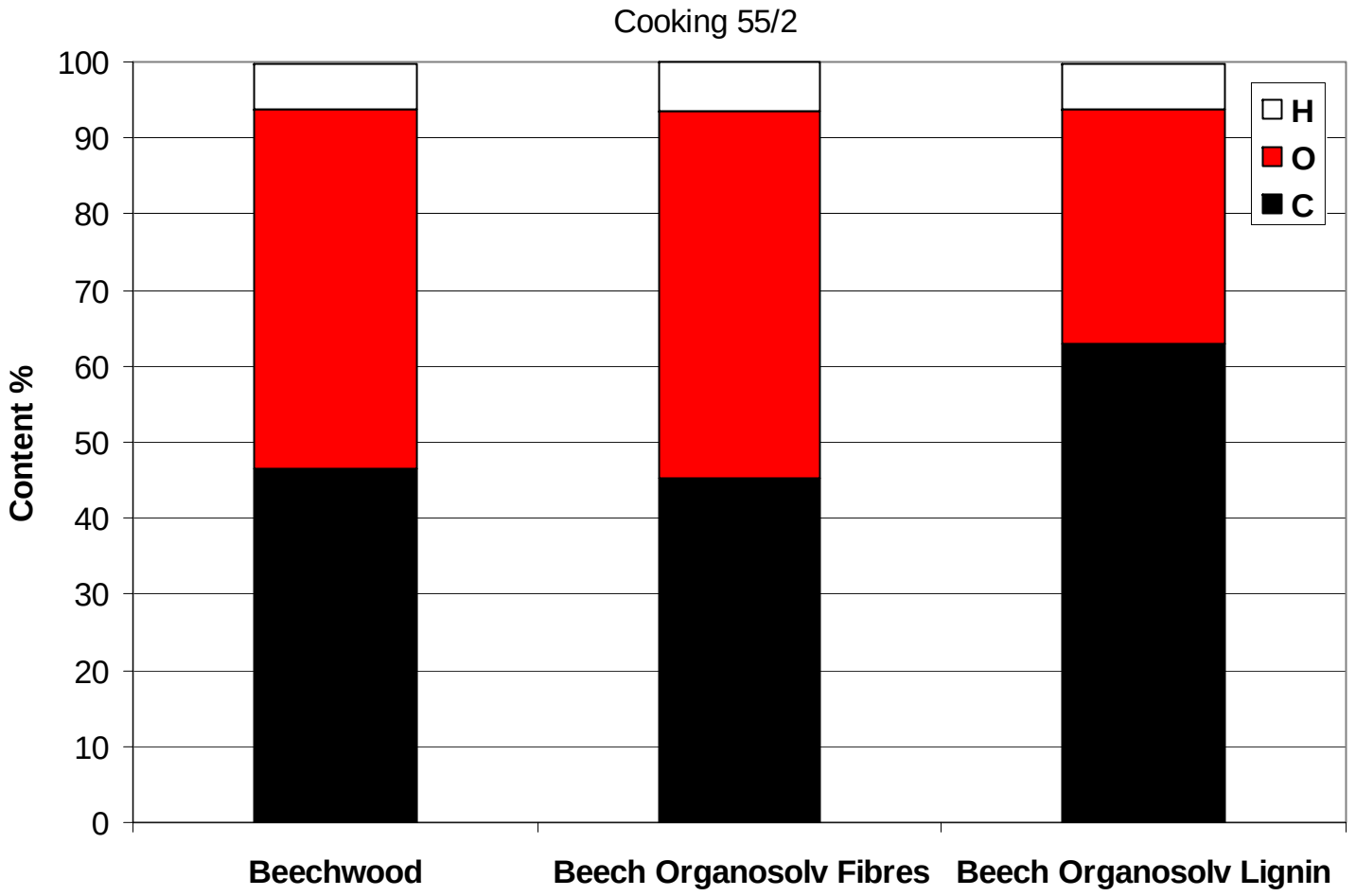
Calibration with polyethylenglycol standards



Elemental analysis:

Carbon, oxygen, hydrogen balance of ethanol-water pulping

Relative shift of carbon content into the lignin fraction



Organosolv lignins from beechwood biorefinery

C_{900} formular

Methoxyl- & OH-groups, protons on aromatic ring & side chains; molar masses

	OCH_3	Σ OH	$H_{Syringyl}$	$H_{Gyacacyl}$	$H_{\alpha\beta\gamma}$	$-CH_2$ $-CH_3$	M_W (g/mol)
Variants with H_2SO_4							
L:W 6:1	149	132	70	60	82	50	5700
L:W 3:1	156	149	80	68	122	34	5200
Variants without H_2SO_4							
L:W 6:1	135	148	91	69	138	41	6100
L:W 3:1	127	139	86	68	117	34	5300

B. Saake, J. Puls 2009

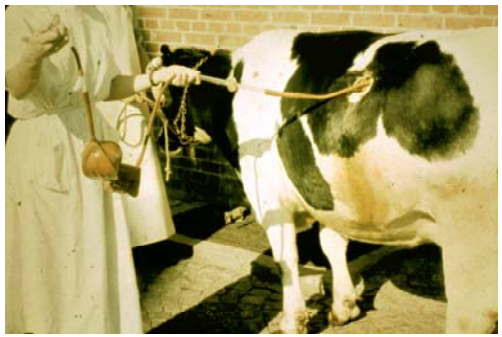
Enzymatic degradability of wood fibres after treatment

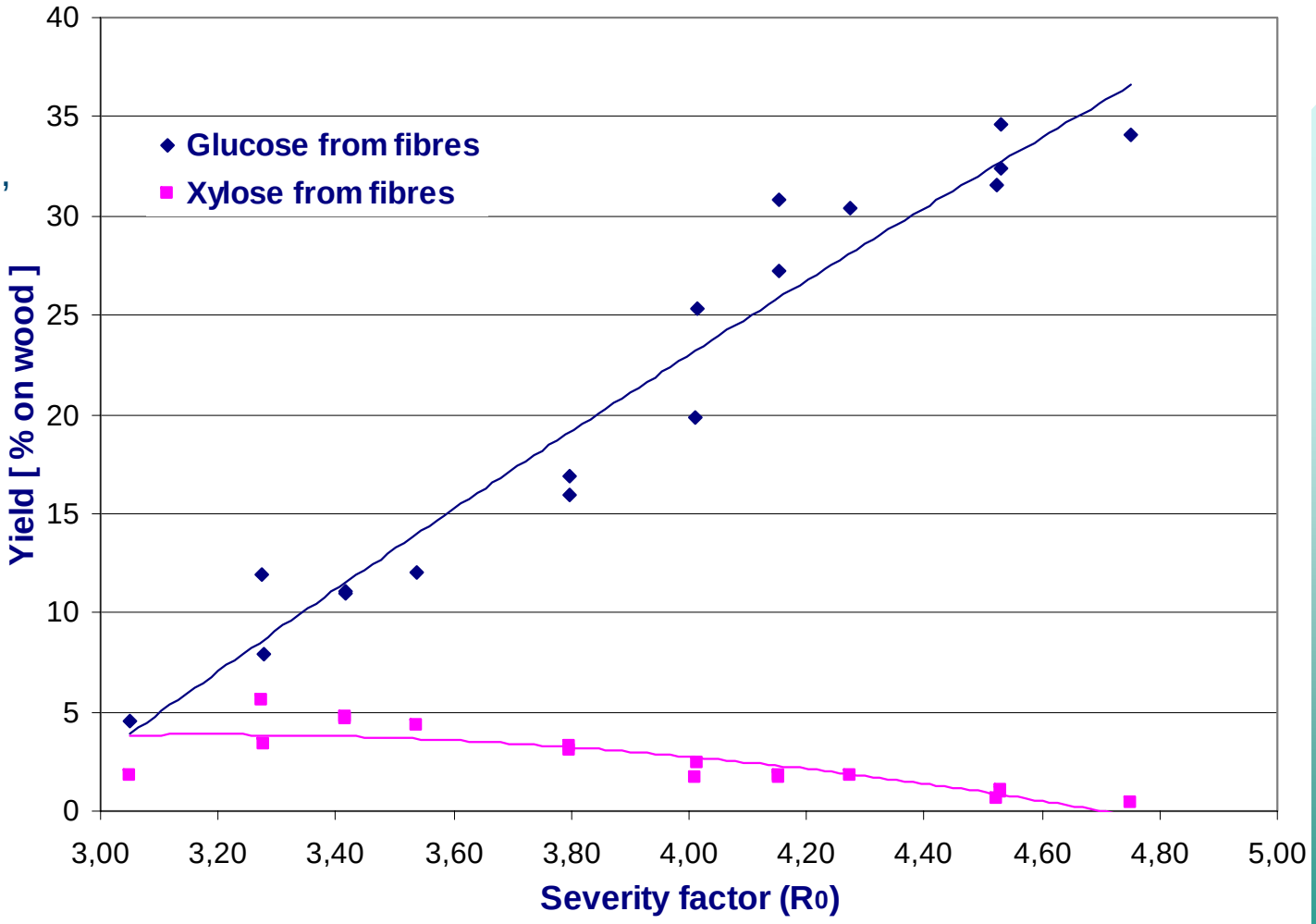
In *vitro* test using standard extracellular enzyme mixture:

- 2% fibre density, 72h, 45°C, pH 5
- 75 FPU/g DM (Celluclast + Novozym 188)

In *vivo* test using fistulated cow:

- 20g fibres in nylon bag
- 72 h rumen incubation





Conclusion

- In spite of our severe efforts yields from individual fractions do not end up in 100% total yield
- This is partly due to hydrolysis losses in analytical hydrolysis (e.g. uronic acids are more or less completely destructed)
- Although a large variety of methods is being applied, not all of the transformed products after organosolv- and thermal treatment are included into the material balance. This is specially true for volatile compounds
- There is also a loss of non-precipitated lignin products

EWLP 2010

16th - 19th August 2010 in Hamburg, Germany

EWLP 2010 - 11th European Workshop on Lignocellulosics and Pulp - Hamburg Germany

The meeting will specifically address "Biorefinery and lignin chemistry".

The following topics will be covered:
Lignocellulose based biorefineries – New products and uses of lignin
Advances in pulping and bleaching – New analytical methods
Advances in lignocellulose chemistry – Biotechnology in lignocellulose utilisation

http://www.ewlp-2010.org

2nd circular is available at the information desk !

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EWLP-workshop dinner will be organized on Wednesday August 18th 2010 on board the bark *Rickmer Rickmers* at the Hamburg harbour front

MC-meeting of COST Action FP0901 is planned for the afternoon of Thursday August 19th followed by a workshop on Friday/Saturday August 20th/21st