Validation and optimization of analytical methods for samples from the wood-based biorefinery

Anna Jacobs & Fredrik Aldaeus

INNVENTIA

Outline

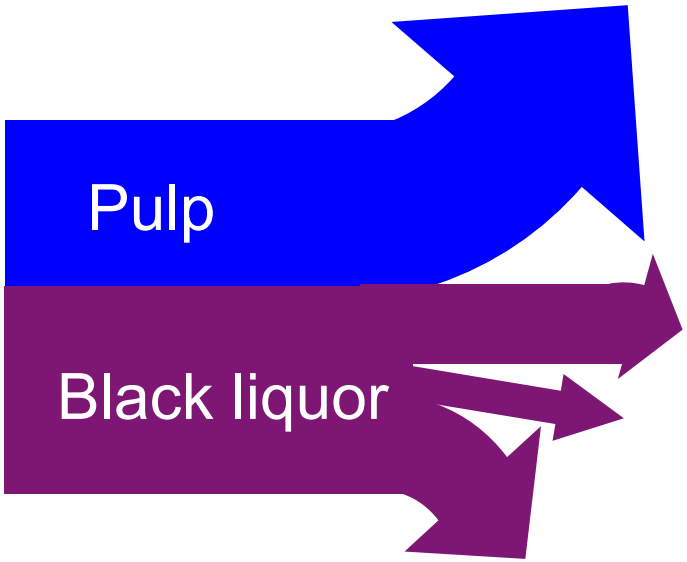
- Biorefinery activities at INNVENTIA
- Lignin characterisation methods
- Lignin analysis development and validation
    - Klason and acid-soluble lignin
    - Carbohydrate content
    - Determination of lignin content by UV spectroscopy
    - Determination of malodorous components by head-space GC/MS
    - Extractives content
    - Moisture content

Biorefinery activities at Innventia

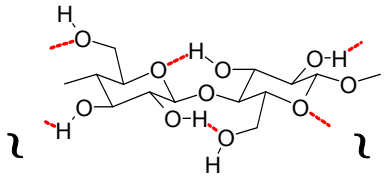
- Cluster Biorefinery II, 2009-2011
- Separation processes
- Biorefinery products
  - *Lignin*: Carbon fibres, adsorbents, surfactants
  - *Hemicellulose*: Fibre activating agents (improve paper chemical performance); polymers for biobased composite materials

Large amounts of organic by-products from chemical pulping − Today used as internal fuel

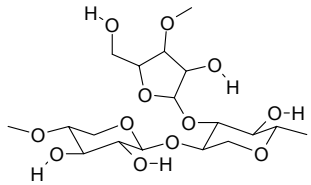
Wood to kraft pulp mill



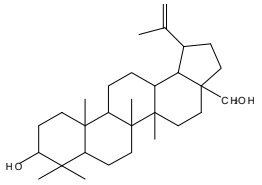
Cellulose



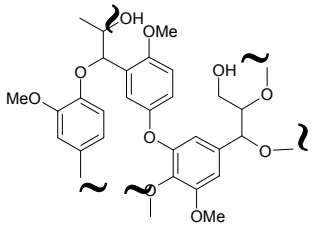
Carbo-hydrates



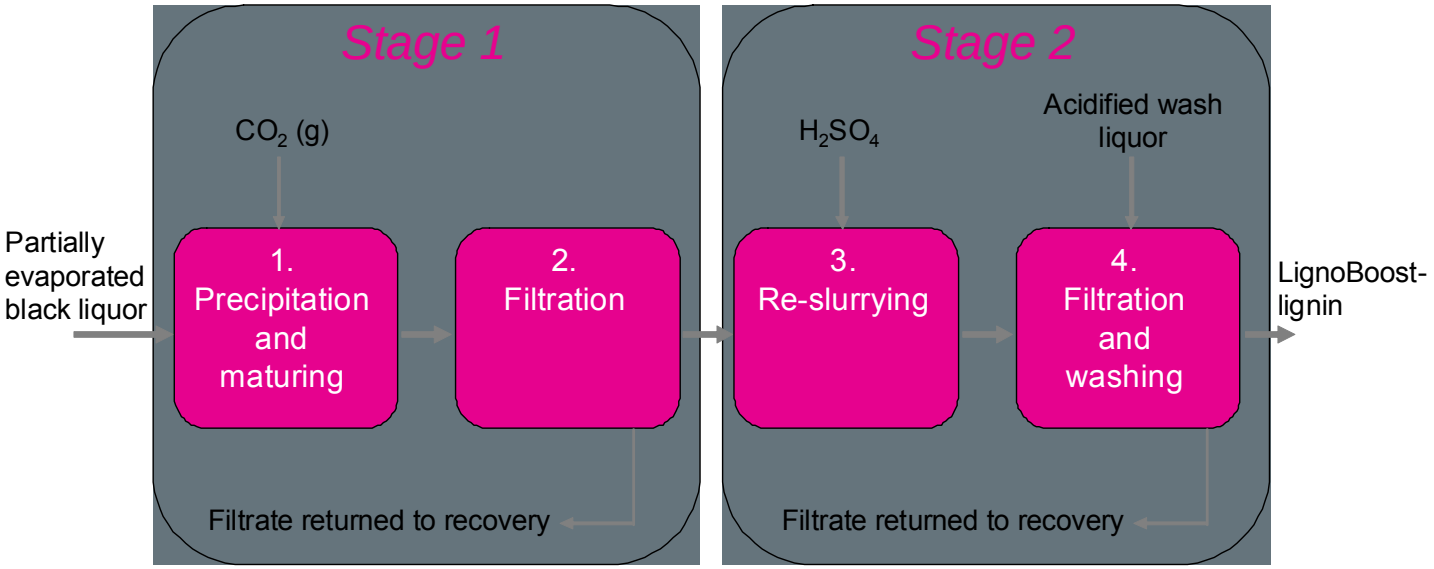
Extractives



Lignin



The LignoBoost process



Need for chemical analysis:

- Amount and purity of LignoBoost lignin
- Lignin properties

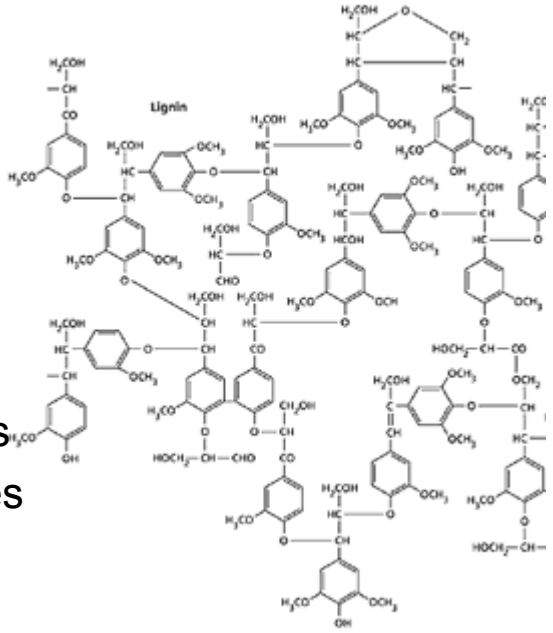
Lignin characterisation methods at INNVENTIA
Examples

- Composition
  - Acid-insoluble lignin
  - Acid-soluble lignin
  - ”UV lignin”
  - Volatile components
  - (Extractives)
  - (Carbohydrates)
  - (Ash + metals)
  - (Anionic ions)
  - (Sulphur)
  - (Moisture)

- Thermal characterisation
  - *-T_s, T_d, etc*

- Physical characterisation
  - Molecular mass distribution (MMD)
  - Diffusion coefficent
  - Conformation in solution

- Structural elucidation
  - Phenol groups
  - Carboxyl groups
  - Carbonyl groups
  - Syringyl & guaiacyl groups
  - Amount of β-O-4 structures
  - etc…



Acid hydrolysis of black liquor and lignin samples

TAPPI-methods

TAPPI METODEN

CAUTION

This method may require the use of some chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used are potentially hazardous and, if so, should follow strictly the procedures specified by both the manufacturer, as well as state and federal authorities, for safe use of these chemicals.

T 222 om-83

TENTATIVE STANDARD—1943
OFFICIAL STANDARD—1954
REVISED—1974
OFFICIAL TEST METHOD—1983
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Acid-insoluble lignin in wood and pulp

1. Scope

1.1 This method describes a procedure which can be applied to the determination of acid-insoluble lignin in wood and in all grades of unbleached pulps. In semi-bleached pulp the lignin content should not be less than about 1% to provide a sufficient amount of lignin, about 20 mg, for an accurate weighing. The method is not applicable to bleached pulps containing only small amounts of lignin.

1.2 Some of the lignin dissolves in acid solution during the test and is not included in the test result. In softwoods (coniferous woods) and in sulfate pulps, the amount of soluble lignin is small, about 0.2 to 0.5%. In hardwoods (deciduous woods), non-wood fibers, and in sulfite pulps, the content of soluble lignin is about 3 to 5%. In semi-bleached pulps, soluble lignin could amount to about one-half or more of the total lignin content.

NOTE 1: The acid-soluble lignin can be determined in a solution, after filtering off the insoluble lignin, by a spectrophotometric method based on absorption of ultraviolet radiation. The most often used wavelength is 205 nm (*1*).

1.3 The total lignin content in pulps can be estimated fairly closely by rapid, indirect methods based on chlorination of the lignin (TAPPI T 253 "Hypo Number of Pulp") or oxidation of the lignin (TAPPI T 236 "Kappa Number of Pulp").

2. Summary of method

The carbohydrates in wood and pulp are hydrolyzed and solubilized by sulfuric acid; the acid-insoluble lignin is filtered off, dried, and weighed.

3. Significance

Wood contains from about 20 to 30% lignin, removal of which is a main objective of pulping and bleaching processes. Determination of lignin content in wood and pulps provides information for evaluation and application of the processes. Hardness, bleachability, and other pulp properties, such as color, are also associated with the ligni

4. Definiti

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5.1 *Filtra*
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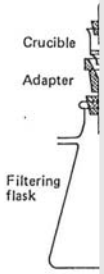

Fig. 1 Lignin filtra

T 249 cm-00

PROVISIONAL METHOD – 1975
CLASSICAL METHOD – 1985
REAFFIRMED – 2000
©2000 TAPPI

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Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography

1. Scope

carbohydrate composition
lucan, mannan, arabinan,
ermined. The method is

olyzate is neutralized, and
tic anhydride and sulfuric
for injection into the gas

to processing conditions
in wood have different
s of the monosaccharide
absolute values for paper

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counted for by subjecting
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can be chromatographed
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rmally at 190°C with an
be used with a flow rate

d Product Quality Division
TAPPI

CAUTION

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UM 250

Acid-soluble lignin in wood and pulp

Scope

This method describes a procedure which can be applied to the determination of acid-soluble lignin in wood and pulp, supplementing the determination of acid-insoluble ligin described in TAPPI T 222 "Acid-Insoluble Lignin in Wood and Pulp."

The sum of the acid-soluble lignin in per cent, as determined by this method, and of the acid-insoluble lignin according to T 222, should represent the total lignin content in a wood or pulp sample.

Summary

Absorbence of ultraviolet radiation at a wavelength of 205 nm is measured on a filtrate obtained after isolation of the acid-insoluble lignin according to T 222. The absorbence is related to the dissolved lignin content in the filtrate.

Apparatus

1. *Spectrophotometer,* suitable for measuring absorbence at the UV range of radiation.
2. *Absorption cells* (cuvettes), fused silica, with 10-mm light path.

Lignin characterisation methods at INNVENTIA
Examples

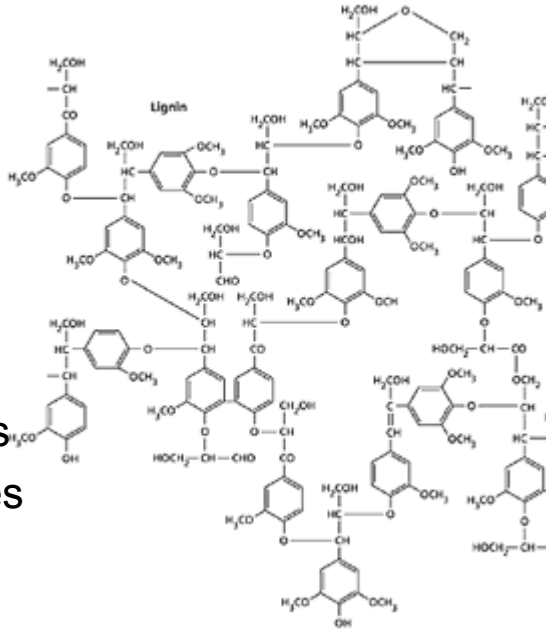
- Composition
  - **Acid-insoluble lignin**
  - **Acid-soluble lignin**
  - **”UV lignin”**
  - Volatile components
  - **(Extractives)**
  - **(**Carbohydrates**)**
  - **(Ash + metals)**
  - **(Anionic ions)**
  - **(Sulphur)**
  - **(**Moisture**)**

- Thermal characterisation
  - *-T_s, T_d, etc*

- Physical characterisation
  - Molecular mass distribution (MMD)
  - Diffusion coefficent
  - Conformation in solution

- Structural elucidation
  - Phenol groups
  - Carboxyl groups
  - Carbonyl groups
  - Syringyl & guaiacyl groups
  - Amount of β-O-4 structures

  - etc…



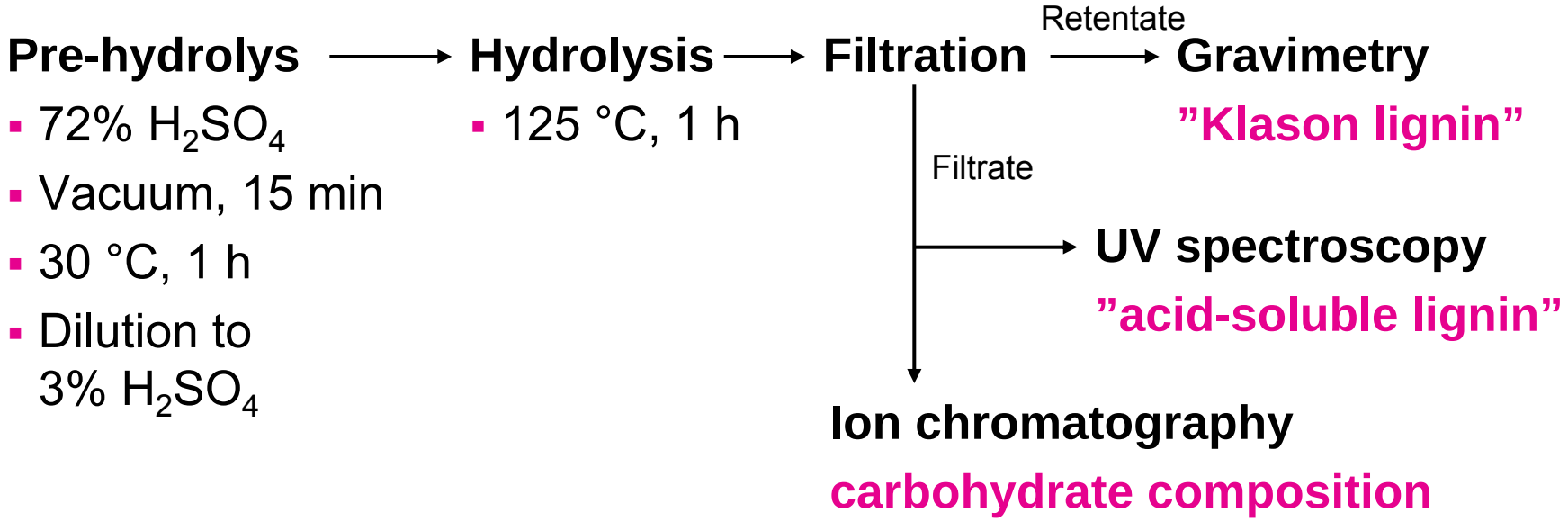
Acid hydrolysis of black liquor and lignin samples
Experimental

- Four samples:
  - Black liquor
    - HW, SW

  - LignoBoost lignin
    - HW, SW

Acid hydrolysis of black liquor and lignin samples

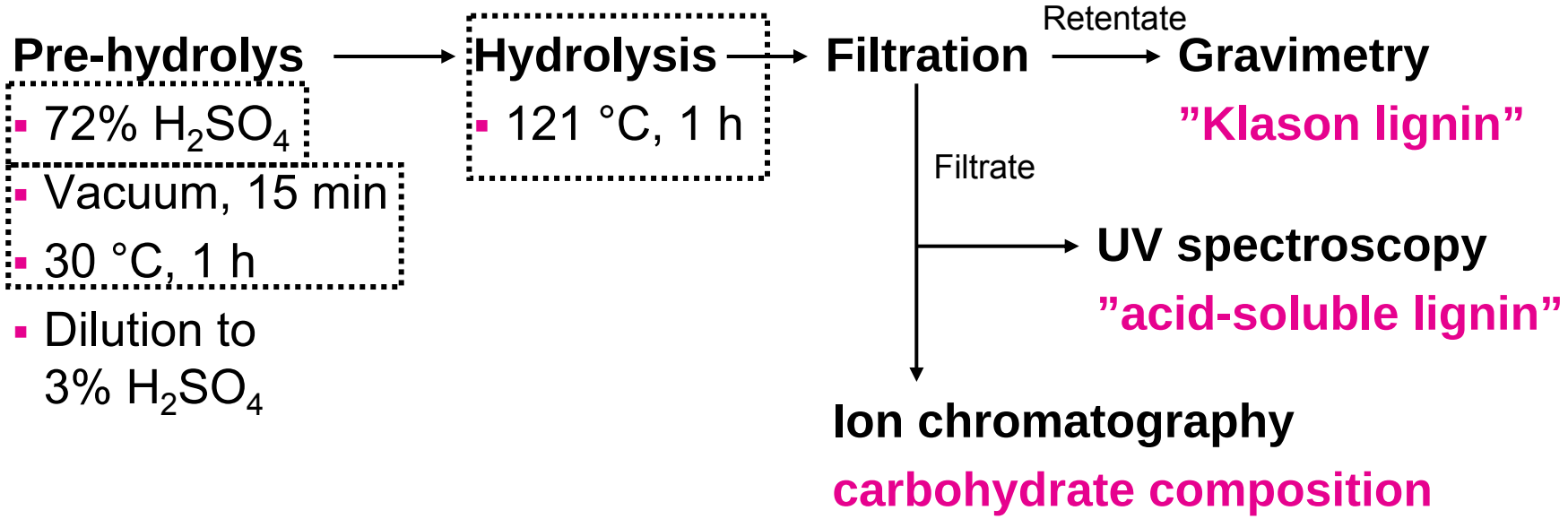
Experimental protocol



Is the method applicable for lignin and BL samples?
Are all steps necessary?

Acid hydrolysis of black liquor and lignin samples

Experimental protocol



Part 1 (Hydrolysis):

Alt. 1 = All moments (standard method)

Alt. 2 = No vacuum/pre-heating

Alt. 3 = No strong acid

Alt. 4 = No hydrolysis

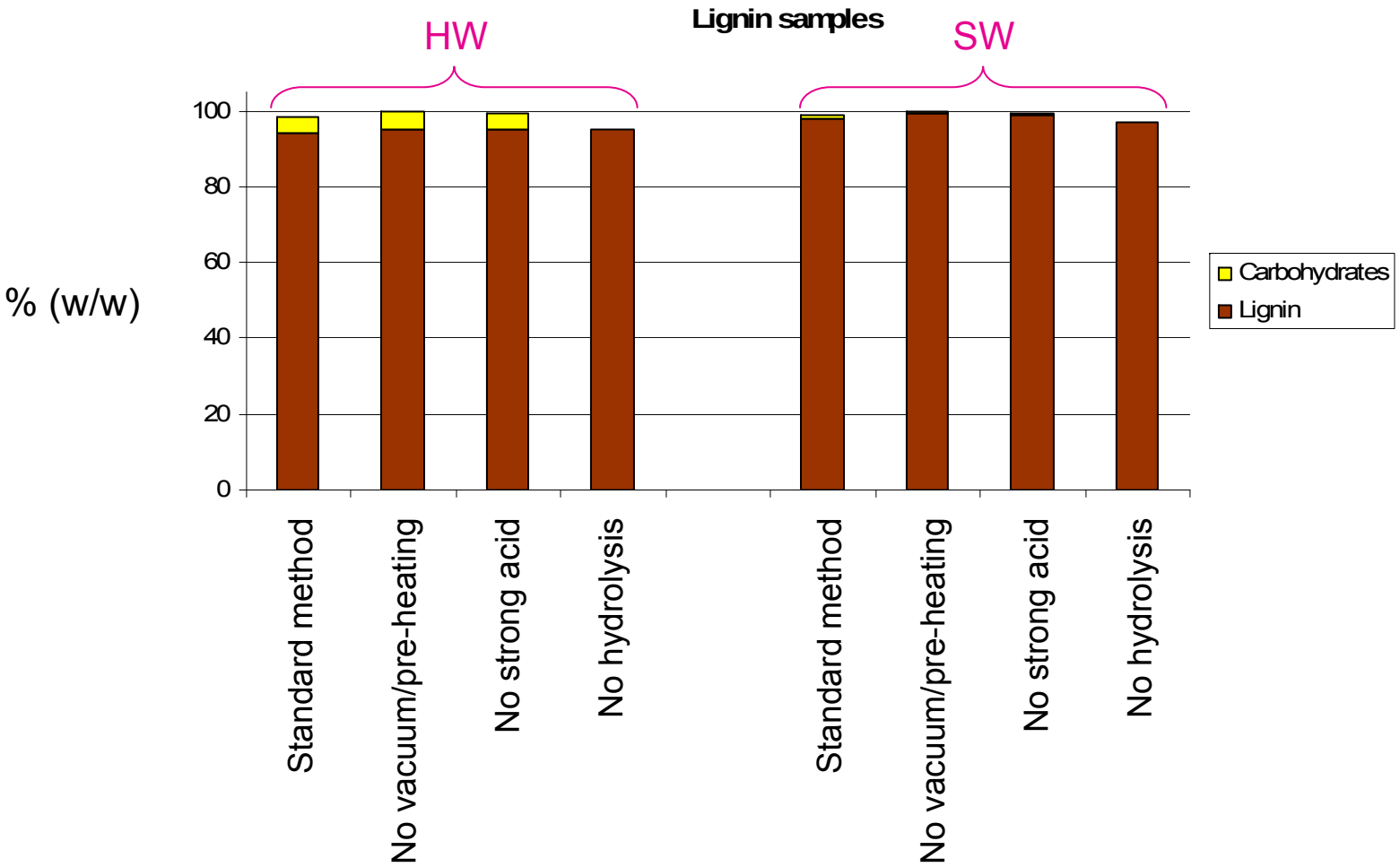
Part 2 (Determination):

Structures in "Klason lignin"

UV absorptivities

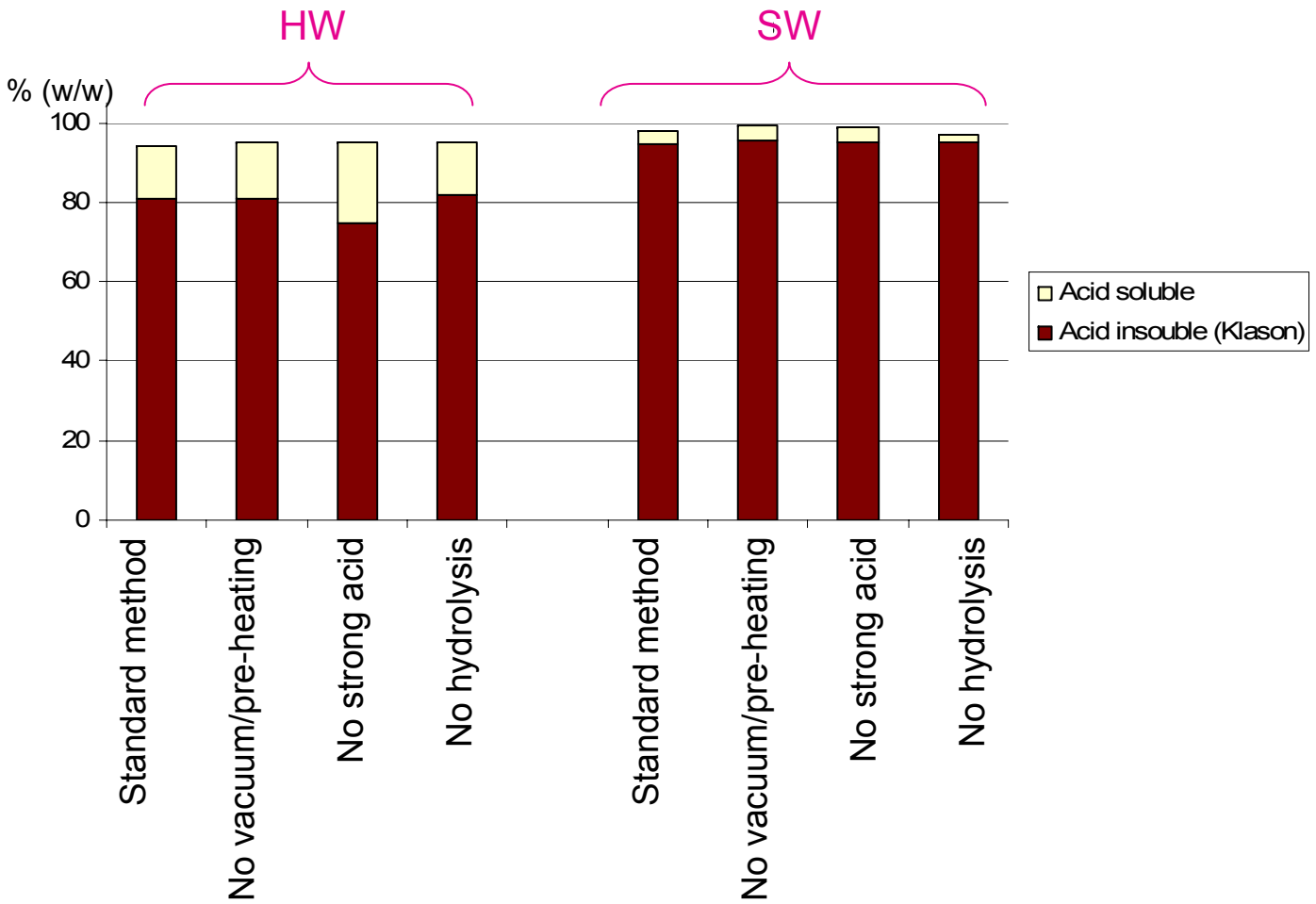
Acid hydrolysis of black liquor and lignin samples

Lignin samples after different pre-hydrolyses



Acid hydrolysis of black liquor and lignin samples

Lignin composition after different pre-hydrolyses

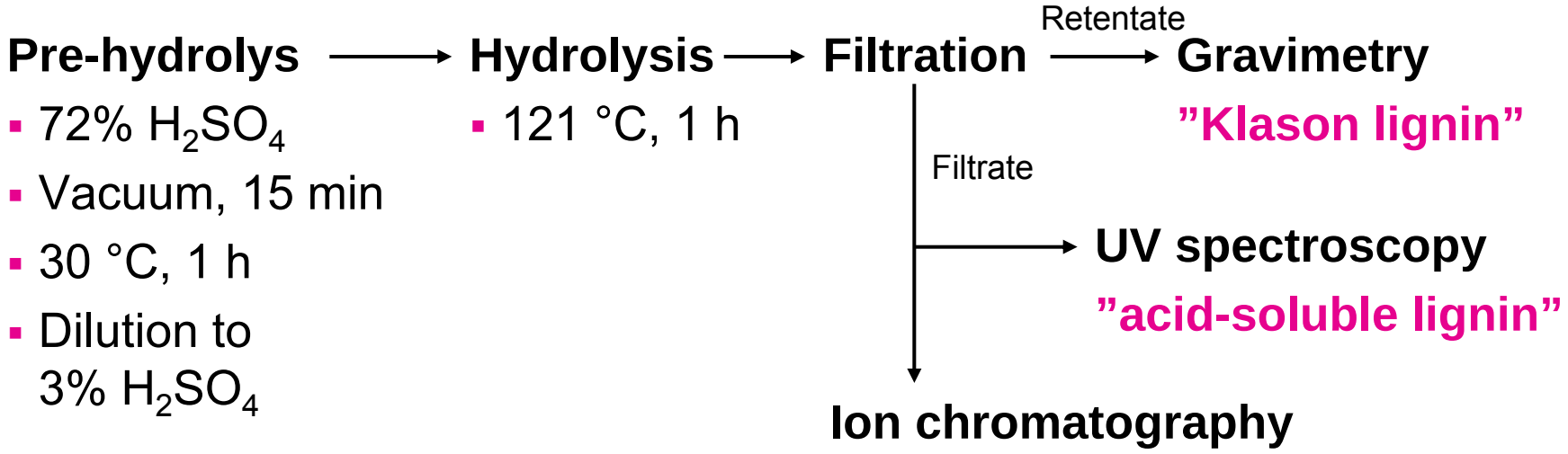


Acid hydrolysis of black liquor and lignin samples
Conclusions from Part 1 (hydrolysis).

- No major differences between different hydrolysis parameters
- No indication of sample degradation
- The procedure may be simplified

Acid hydrolysis of black liquor and lignin samples

Experimental protocol



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Alt. 3 = No strong acid

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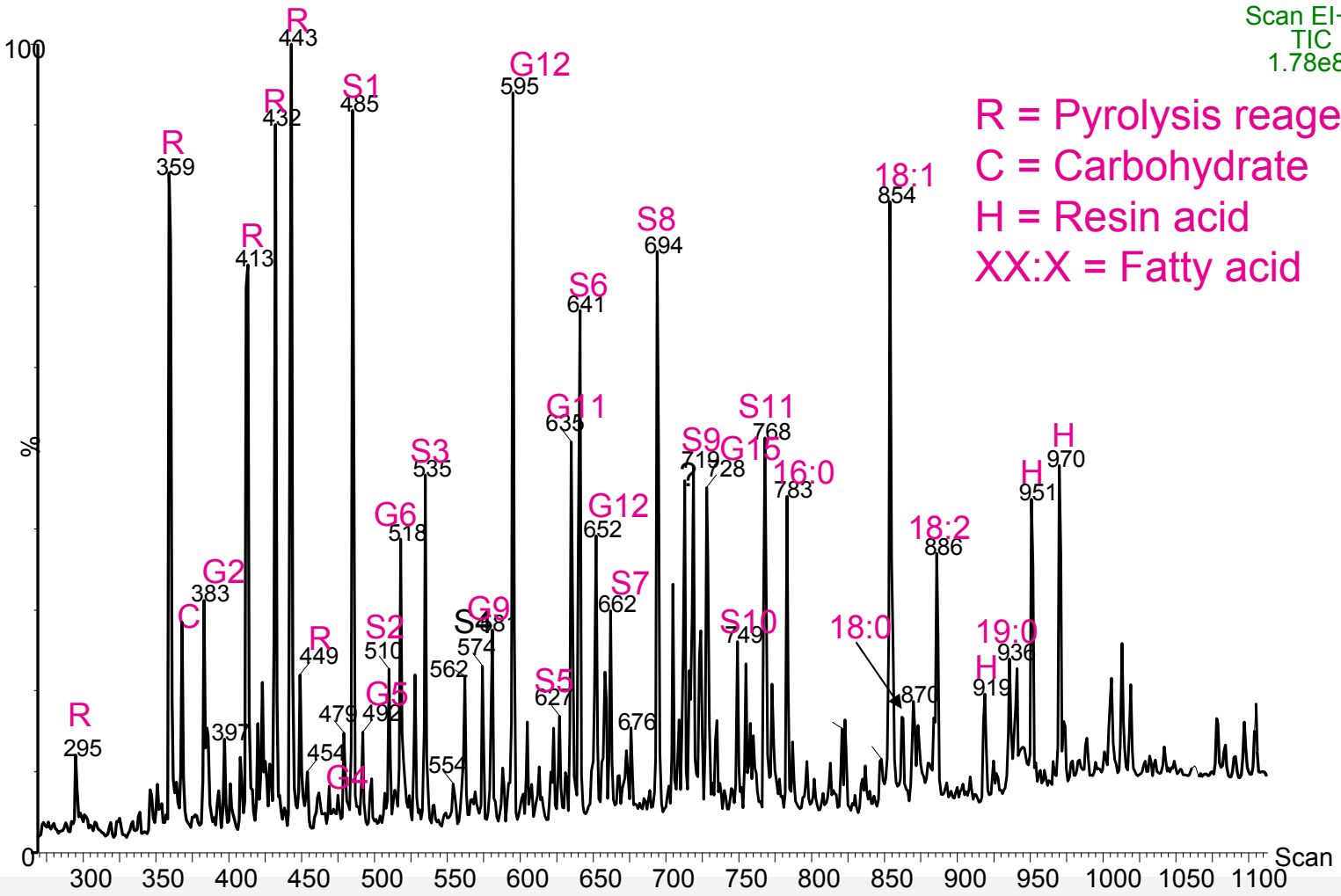
Part 2 (Determination):

Structures in ”Klason lignin”

UV absorptivities

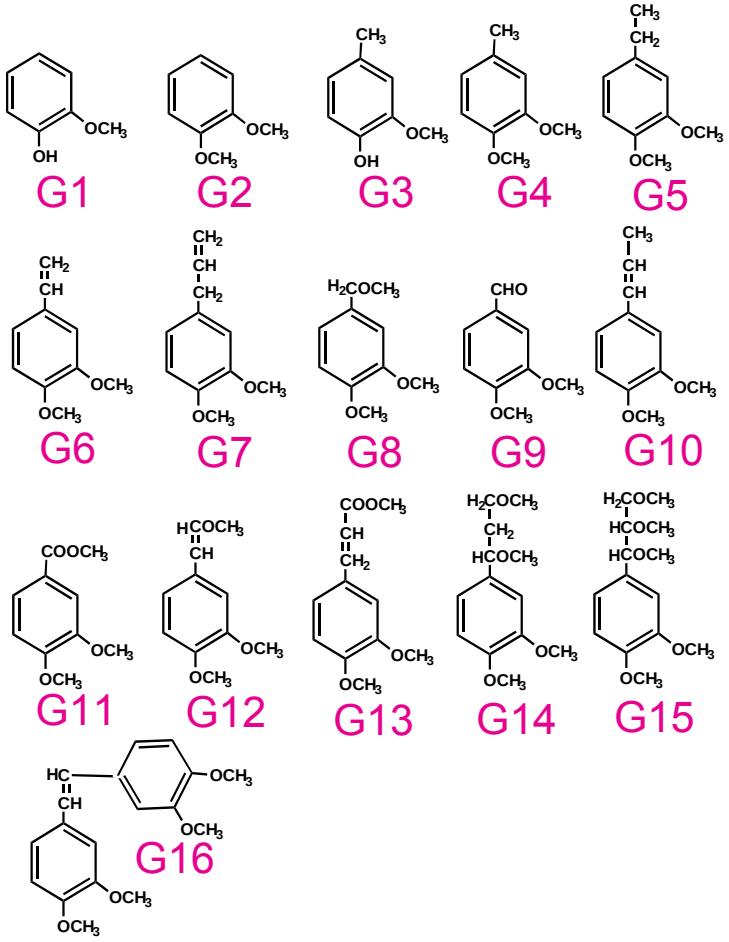
Lignin structures in “Klason” lignin

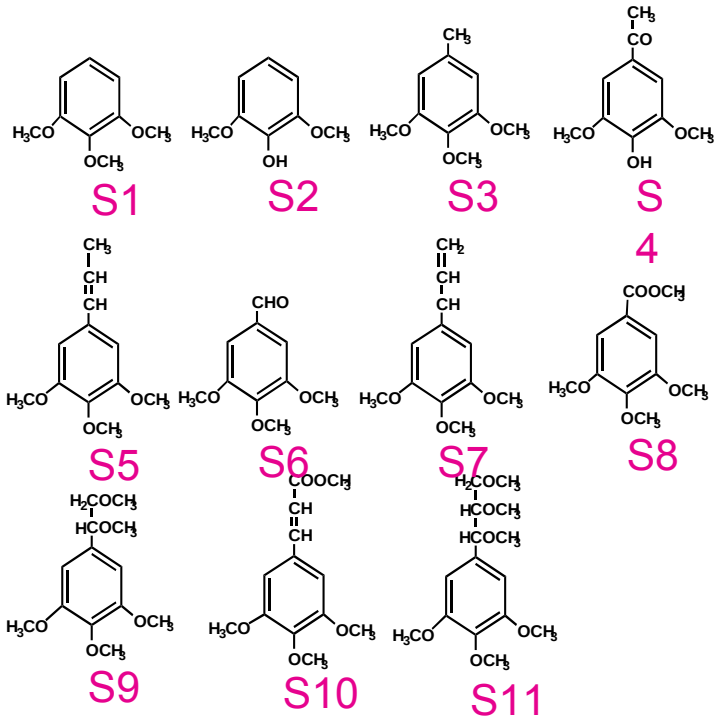
Pyrogram of HW lignin sample



Acid hydrolysis of black liquor and lignin samples

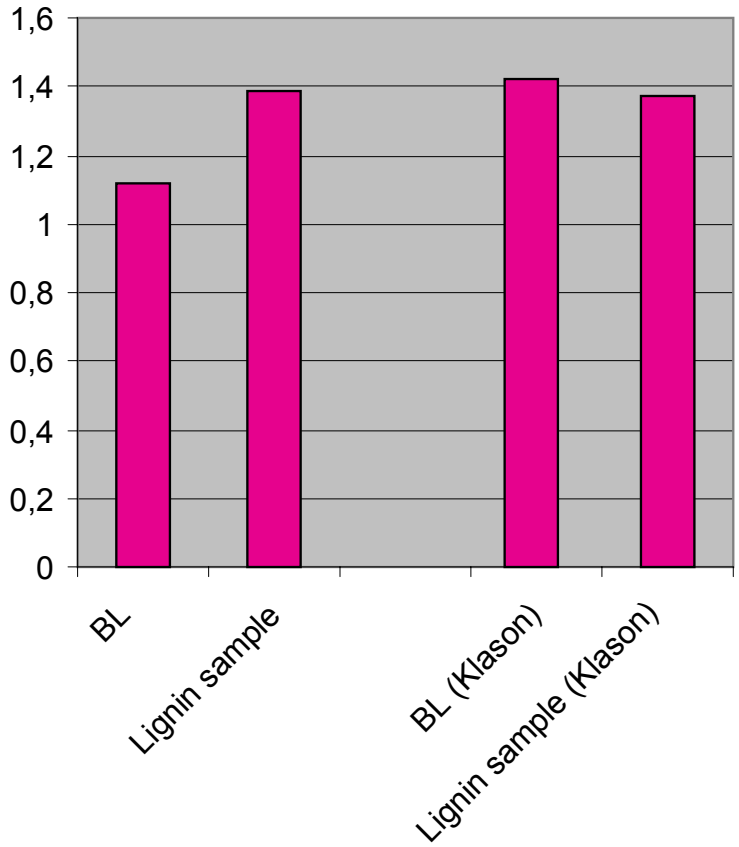
Identified guaiacyl & syringyl fragments





Acid hydrolysis of black liquor and lignin samples

Syringyl/Guaiacyl ratio (S/G) in HW samples



UV absorptivity after acid hydrolysis

Beers law: c = A/(a*b) *where:* *c = sample conc.*
A = UV absorbance
a = UV absorptivity
b = cuvette length

UV absorptivities at 205 nm.

Sample	**a (L/g*cm)**	**Reference**
All samples	110	TAPPI T222 om-00
Hardwood and HW pulp	113	Swan, 1956, Sv. Papperstidn. 68, 791
Softwood and SW pulp	128	Krogerus,1974, KCL Report 1196
Semi bleached pulp	80	Krogerus,1974, KCL Report 1196

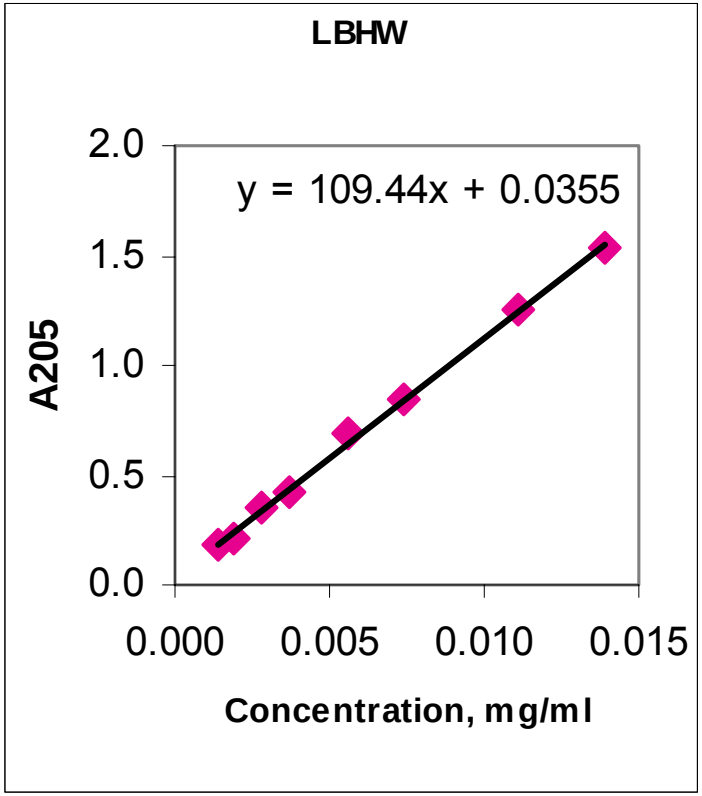
UV absorptivity at 205 nm
Experimental

- Acid hydrolysis
  TAPPI T222 om-00
- Filtration + gravimetric determination (Klason)
- Calculation of lignin concentration in filtrate (i.e. correction for hemi, ash & Klason lignin)
- Dilution
- UV absorption measurement at 205 nm

Sample	Origin
LignoBoost SW 1	Pilot scale
LignoBoost SW 2	Lab./ pH 9.5
LignoBoost SW 3	Lab./ pH 11.5
LignoBoost HW 1	Lab./ pH 9.5
LignoBoost HW 2	Lab./ pH 10.5 Ultrafiltrated
LignoBoost HW 3	Lab./ pH 10.5 Heat treated

UV absorptivity at 205 nm
Results

UV absorptivities at 205 nm.	
Sample	**a (L/g*cm)**
LignoBoost SW 1	86
LignoBoost SW 2	94
LignoBoost SW 3	103
LignoBoost HW 1	109
LignoBoost HW 2	123
LignoBoost HW 3	110



Acid hydrolysis of black liquor and lignin samples
Conclusions from Part 2 (determination)

- The lignin composition (i.e. guaiacyl/syringyl ratio) is changed during the LignoBoost process.
- The G/S ratio in the Klason lignin is similar to that in the LignoBoost lignin

- The UV aborptivites after acid hydrolysis may differ from those used in the standard methods
- The difference is more pronounced for softwood lignins (up to 35%)

UV absorptivity at 280 nm
Experimental

- Dissolution in 0.1 M NaOH
- Dilution
- UV absorption measurement at 280 nm

Sample	Origin
LignoBoost SW 1	Pilot scale
LignoBoost SW 2	Lab./ pH 9.5
LignoBoost SW 3	Lab./ pH 11.5
LignoBoost HW 1	Lab./ pH 9.5
LignoBoost HW 2	Lab./ pH 10.5 Ultrafiltrated
LignoBoost HW 3	Lab./ pH 10.5 Heat treated

UV absorptivity at 280 nm
Results

UV absorptivities at 280 nm.			
	a (L/g*cm)	**Ref. value**	**Δ (%)**
Indulin AT	21.3	21.6[1]	1.4
LB SW 1	23.4	24.5[2]	4.5
LB SW 2	26.8		-9.4
LB SW 3	26.6		-8.6
LB HW 1	24.3	21.7[3]	-12.0
LB HW 2	27.8		-28.1
LB HW 3	25.3		-16.6

1) Douek & Allen
Pulp Paper Canada 81:11(1980)

2) Norrström
Sv. Papperstidn. 73:19 (1970)

3) Marton
Tappi 50:7 (1967)

Overall conclusions
Summary

- The traditional methods developed for wood and pulp samples may not be suitable for analysis of black liquor and lignin samples.
- The procedure for acid hydrolysis could be simplified
- The methods using UV absorptivities may be used for estimation of lignin content, but not for exact measures
- Further investigation is in progress!

Malodorous compounds in lignin samples
Experimental

- Four samples:
  - Eucalyptus LignoBoost lignin, unwashed (Stage 1 only), sealed
  - Eucalyptus LignoBoost lignin, sealed
  - Eucalyptus LignoBoost lignin, air dried 5 months
  - SW LignoBoost lignin (Bäckhammar), air dried 12 months

- Samples suspended in 6 mL NaCl-saturated water

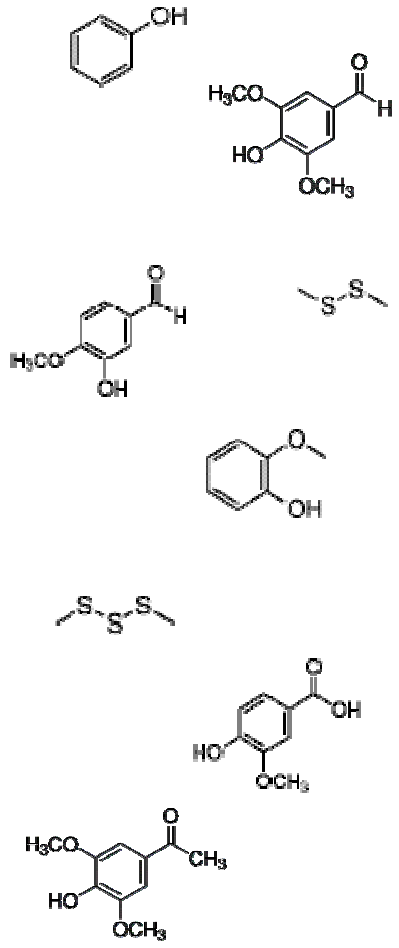
- Analysis of headspace with SPME-GC-MS

- Sampling at 80 °C during 30 min

Malodorous compounds in lignin samples

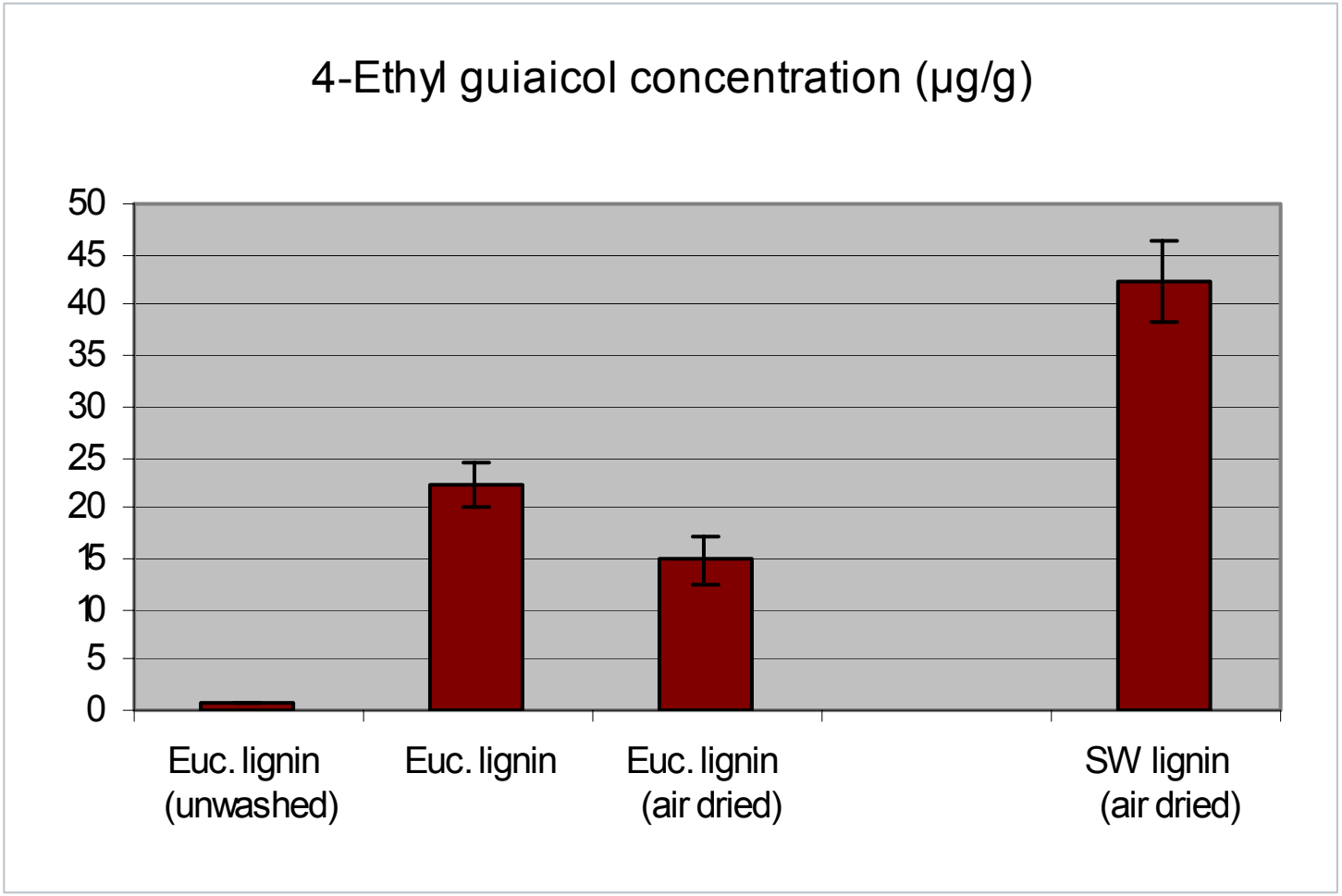
Identified volatile organic compounds (VOCs)

- Eucalyptus lignin, unwashed
  - 38 VOCs (more sulfides and phenols)
- Eucalyptus lignin
  - 28 VOCs
- Eucalyptus lignin, air dried
  - 26 VOCs
- SW lignin, air dried
  - 26 VOCs



Malodorous compounds in lignin samples

Quantification of 4-ethyl guaiacol



Malodorous compounds in lignin samples
Summary

- Headspace-SPME-GC-MS may be used to quantify malodorous compounds in lignin samples.
- Less good method for sulfides.
- The headspace content of guaiacol vary drastically during the LignoBoost process and during sample storage.

Moisture/dry content

Is the dry content value affected by drying temperature?
Does the drying affect the lignin?

- Air drying (25°C) – drying at 40/150°C – reconditioning (25°C)

- Four LignoBoost samples:
  - SW
  - HW
  - HW (high sulphur content)
  - Eucalyptus

Moisture/dry content - results

Dry content (weight difference after reconditioning)		
	40°C	**105°C**
LignoBoost SW	97% (-0,1%)	95% (-2,2%)
LignoBoost HW	96% (-0,6%)	95% (-3,0%)
LignoBoost eucalyptus	92% (1,2%)	89% (-1,2%)
LignoBoost HW (high sulphur content)	99% (<0,1%)	98% (-0,3%)

Conclusion: Drying should be performed at 40°C

Extractives content

Different solvents are suggested for removal of extractives. Which is the most suitable?

- Petroleum ether, bp 40-60°C
- Petroleum ether, bp 60-80°C
- Hexane

- Three LignoBoost samples:
  - SW
  - HW
  - Eucalyptus

Extractives content - results

Extractives content (% of dry sample)			
	p-ether bp 40-60°C	**p-ether bp 60-80°C**	**Hexane**
LignoBoost SW	0.70	0.73	0.58
LignoBoost HW	0.34	0.37	0.37
LignoBoost eucalyptus	0.12*	0.18*	0.18*

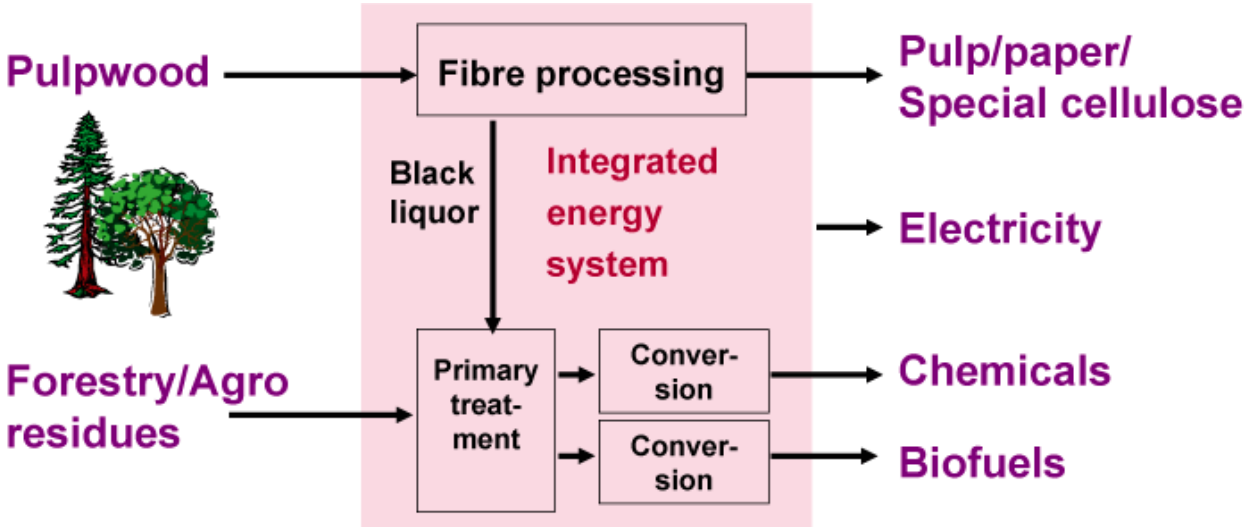
*) Value below the limit for correct weighing

Conclusion: No solvent can be pointed out as better

Chemical Analysis group at INNVENTIA

Thank you for listening!

Cluster Biorefinery II, 2009-2011



Goals

Value-added chemical products and materials from wood-derived components in process liquors and forestry residues.

System solutions for integration of the new technologies with the pulp mill

Contact: Birgit Backlund
birgit.backlund@innventia.com

Separation processes

Ultrafiltration is one of the methods used in the separation systems

Methods are developed for separation and upgrading of lignin and hemi-cellulose (xylan) from process liquors.

Among the tools are e.g. ultrafiltration and the LignoBoost process, developed by Innventia, for separation of lignin.

System studies and techno-economical evaluation of new processes are made.

Biorefinery products

New chemicals and materials are developed from wood-derived lignin and hemicellulose. Examples:

- *Lignin*: Carbon fibres, adsorbents, surfactants
- *Hemicellulose*: Fibre activating agents (improve paper chemical performance); polymers for biobased composite materials

Market aspects are evaluated for potential products