Round Robin on lignins
plus discussion about the Py-GC/MS technique

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INNVENTIA

Objective

- Settle common methods of isolated lignin samples to determine
  - the thermal characteristics esp. Tg as determined with DSC
  - the lignin content

Why?

- Isolated lignins are a potential value-added product for the industry
- Different methods and evaluation procedures are applied
- Thermal properties is of increasing importance
- Standard method for quantification is developed for wood/pulp etc
- All structural analysis is related to dry content of lignin

... it's tricky to compare lignin properties and follow mass balances

How to reach the objective

- Evaluate proposed methods using a RR procedure and compare with in-house methods in use today at respective laboratory
  - Participants: 9 for T_g and T_d and 15 for quantification
  - Common samples
  - Initial analysis following the same protocol and
  - In-house analysis
  - Discussions at meetings, and whatever we find suitable...
  - Interactive procedure

Active participation is important!

Samples

- Selected samples representing lignins
  - of different origin and processing
  - of interest in today's research & development

- Hardwood (birch/aspen) Kraft lignin – KLHM
- Softwood (pine/spruce) Kraft lignin – KLSM
  - Innventia
- Spruce Organosolv lignin – Org.solv
  - VTT/Tamminen
- Soda (wheat straw) lignin – Soda
  - WUR/Gosselink
- Enzymatic treated Steam Explosion lignin (poplar) – ESEL
  - vTi /Bodo & Fokko Schutt

Fundamental characteristics

Hardwood and Softwood Kraft lignins

isolated according to the LignoBoost procedure

	KLHM lignin		KLSM lignin	
Ash, %-w	0.7		1.0	
Acid insoluble lignin, %-w	88.1		93.0	
Acid soluble lignin, %-w	10.1		5.6	
Carbohydrates total, %-w	1.7		1.4	
Extractives, %-w	n.d.		0.23	
	Carbohydrate composition			
	rel %	**%-w**	**rel %**	**%-w**
Arabinose	16.3	0.3	16.1	0.2
Galactose	16.9	0.3	48.6	0.7
Glucose	25.0	0.4	13.0	0.2
Xylose	41.7	0.7	21.0	0.3
Mannose	0	0	1.3	0

Used methods
for characterisation of kraft lignins

- Ash: ignition at 525 °C, ISO 1762:2001
- Hydrolysis with sulphuric acid, Tappi T249-cm 00
- Acid insolubles (”Klason”)
- ASL: UV 205nm; coeff. 128 l/g (SWKL), 113 l/g (HWKL), Tappi T222-om 00
- Carbohydrates: HPAEC-PAD
- Extractives: p-ether solubles, Soxtec,
  - conditions according to SCAN-CM 49:03

Fundamental characteristics
Spruce Organosolv lignin

- ash content: 6.9 %
- extractives content: 3 % ether-soluble
- carbohydrate content & composition: 1.2%
  - Rha~Ara~Fructose<0.1%
  - Xyl 0.03%
  - Gal 0.1%
  - Glc 0.4%
  - Man 0.46%

Used methods

for characterisation of Spruce Organosolv lignin

- Ash : at 780 ºC (heating up to 1000ºC)
- Extractives: 2h extraction at RT, filtration, evaporation-vacuum drying
- Carbohydrates: H_2SO_4 hydrolysis - HPAEC/PAD

- Details in Willför et al. 2009

Fundamental characteristics

Soda (wheat straw) lignin

- characterized without removal of extractives
- ash content: 9.7%
- Klason lignin, ash-free: 63.51%; ASL: 1.45%
- carbohydrate content & composition: 13%
  - Arabinan 1.87%
  - Xylan 8.52%
  - Galactan 0.43%
  - Glucan 0.97%
- Other: tot. uronic acid total 1.38%, protein 7.2% (N=1.2%)

Used methods
for characterisation of Soda (wheat straw) lignin

- Ash: 800 ºC for 4-8 hours (ILI protocol)
- Lignin and carbohydrate content after 2-step sulfuric acid hydrolysis and gravimetric and HPAEC
- Details in Gosselink et al. Holzforschung, 64, 2010

About the thermal analysis
Tg determination

The methods to be used should be

1. with DSC, as described below (“Innventia”)
2. your in-house DSC method and/or
3. your in-house DTA method

- The results from 2 and 3 should be reported along with a description of your method

Results so far, thermal RR

- To few reported results at date
- New request will be sent to WG1 and WG2 leaders for further distrib.,
  – Samples will be provided if possible (limited amount left)
- **New dead-line: May 15**
- **General comment**
- Please note that both analysis (Tg and TD determination) should be performed in inert atmosphere, e.g. under nitrogen
- **Please report the av. and SD for n=5** for each sample and analysis