FT-IR CHARACTERISATION OF LIGNINS WITH HELP OF PCA

Cost E41 Spectrometric techniques used for the analysis
of Carbohydrates, Lignin and Extractives

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Aim of the research

- Characterize lignin samples from different sources with a fast analytical technique as FT-IR

- Evaluate the applicability of IR for characterization of lignins (quality control)

- Build predictive IR-models for characterisation of lignin samples

Samples

- Over 30 different lignins used for predicting IR-models

- Kraft, lignosulphonate, soda, steam explosion lignins

- Resources: ao. soft wood, hard wood, annual plants

FT-IR protocol

- Diffuse Reflectance Infrared Fourier Transform method (DRIFT)

- Mixture of 5% w/w lignin in KBr

- Spectra recorded between 700 - 4000 cm^{-1}

- 64 scans

Chemical analysis by standard protocols

- **Lignin** content after 2-step sulphuric acid hydrolysis (AIL+ASL)
- **Sugar residues** quantified by HPAEC-PAD
- **Uronic acids** after colouring with m-hydroxydiphenyl
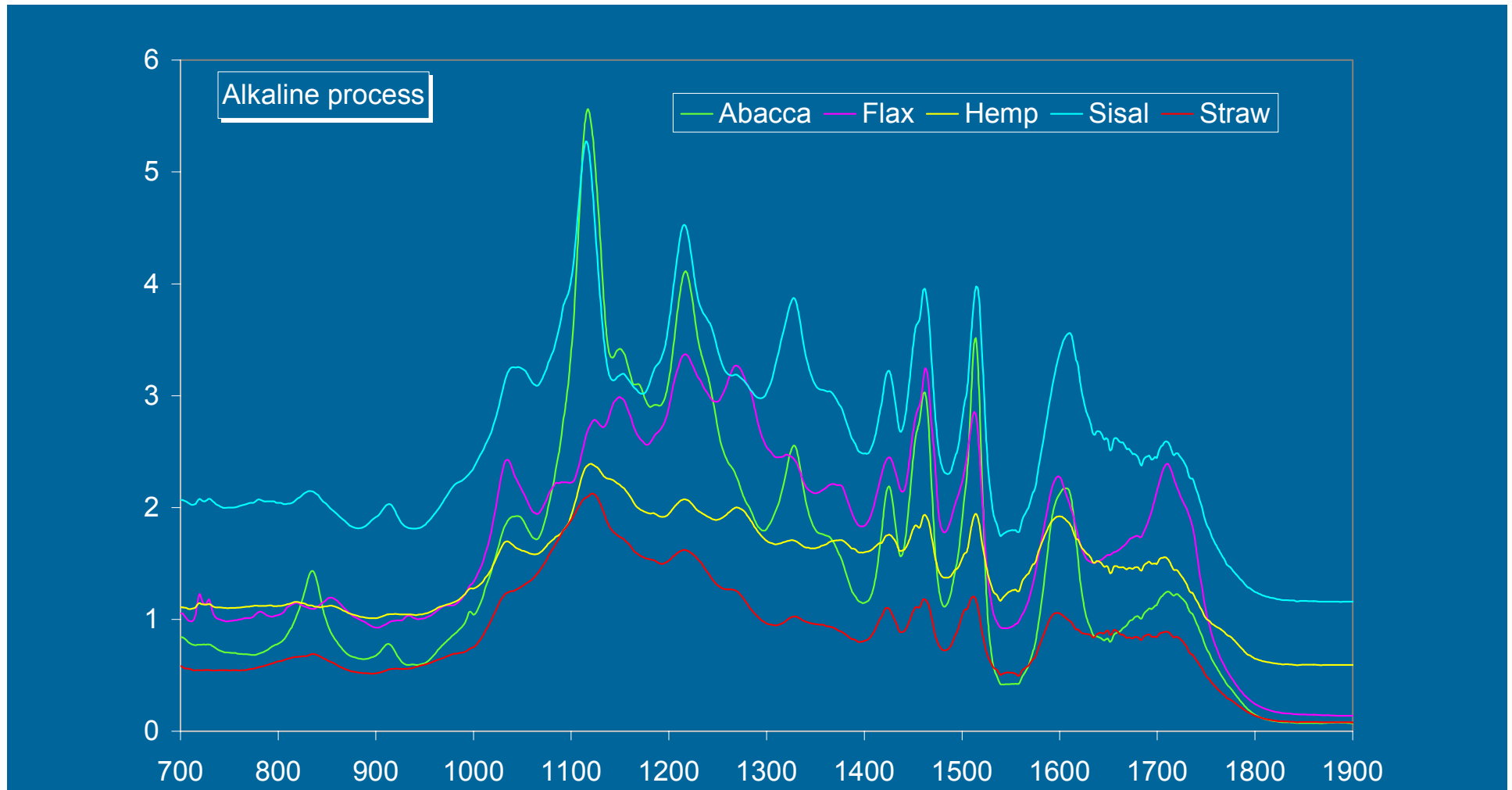- **Phenolic hydroxyl** and **carboxylic groups** by non-aqueous titration with TnBAH
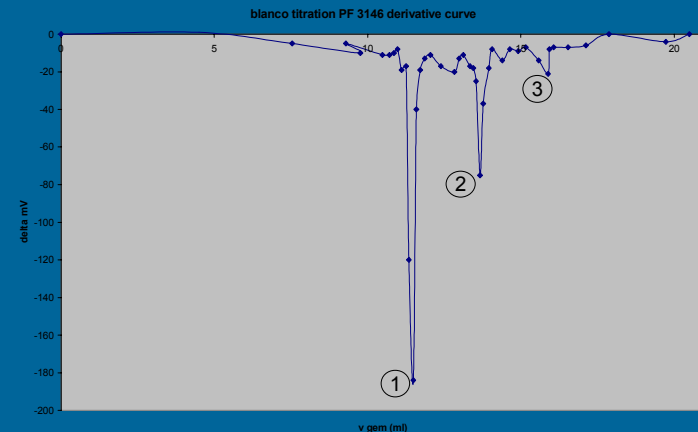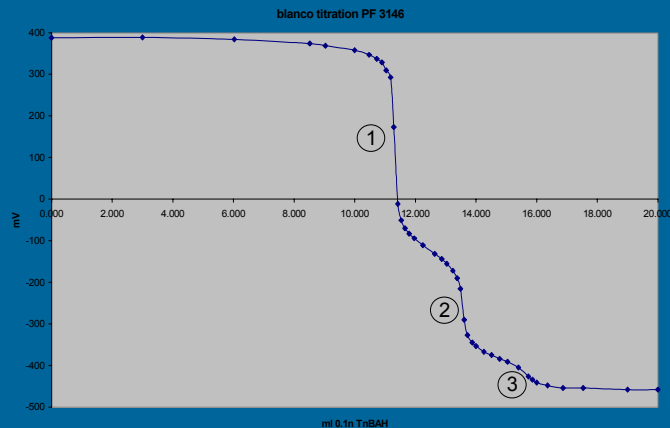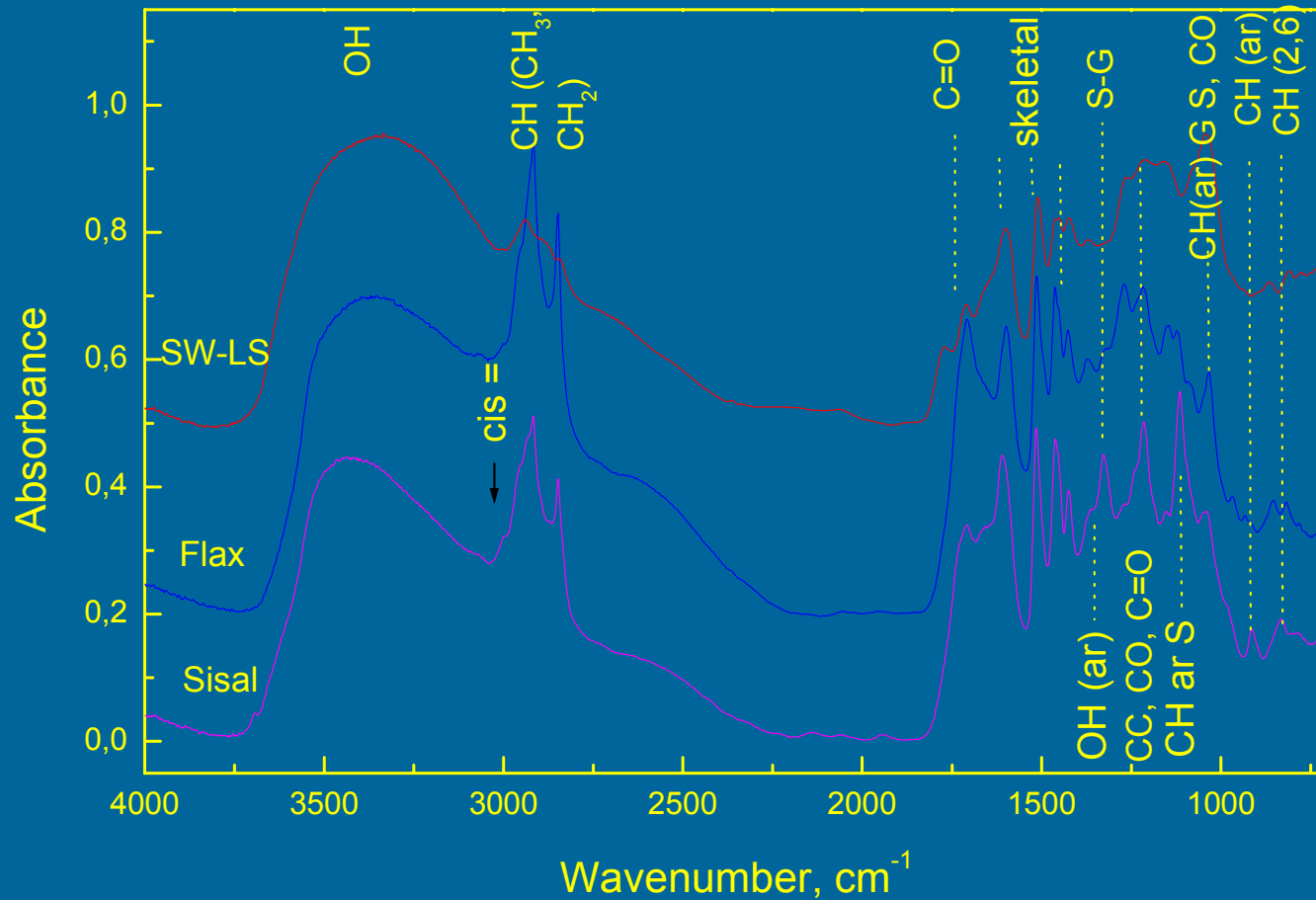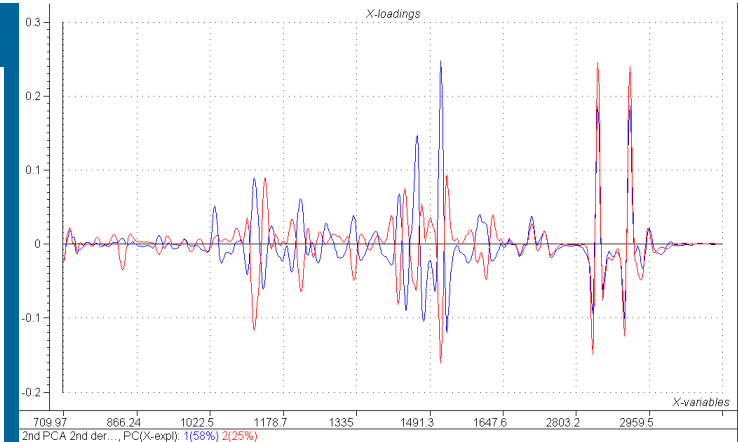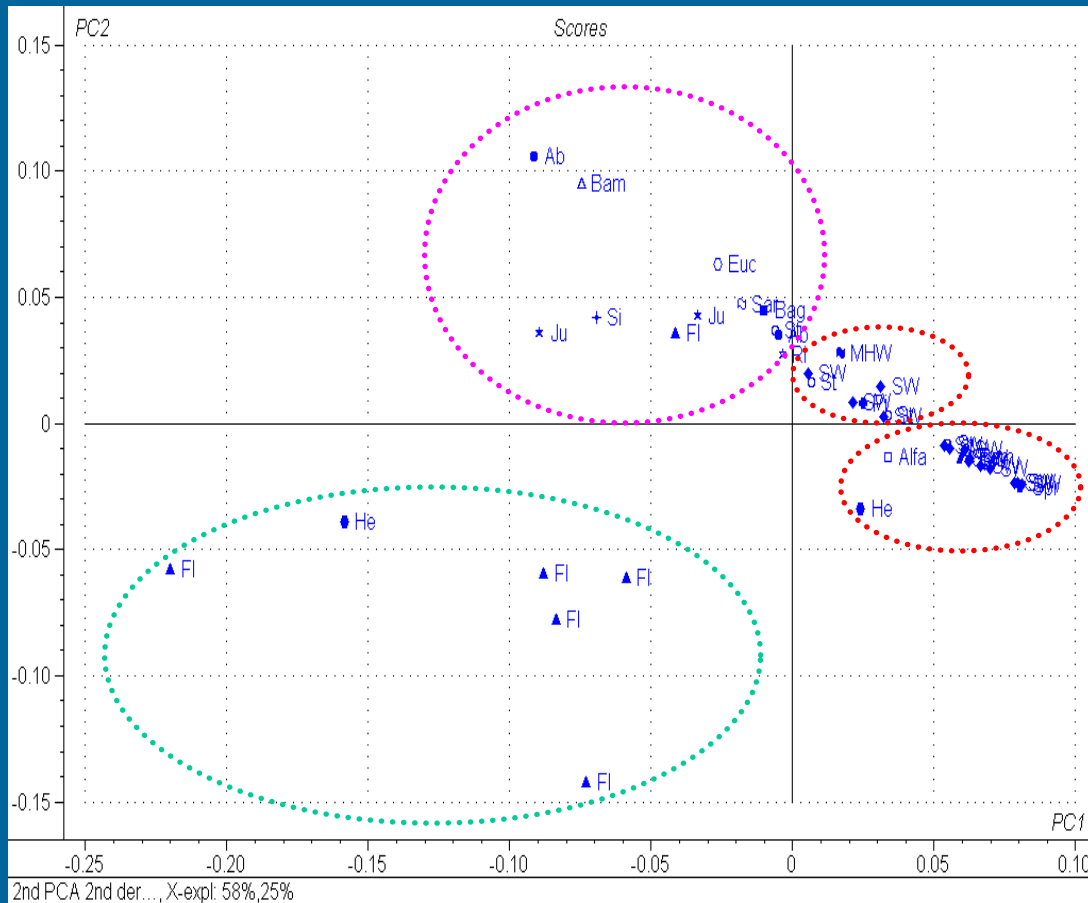
FT-IR spectra of lignins

FT-IR spectra of lignins

Bamboo & Wheat Straw lignin IR spectra : 700-1800cm-1
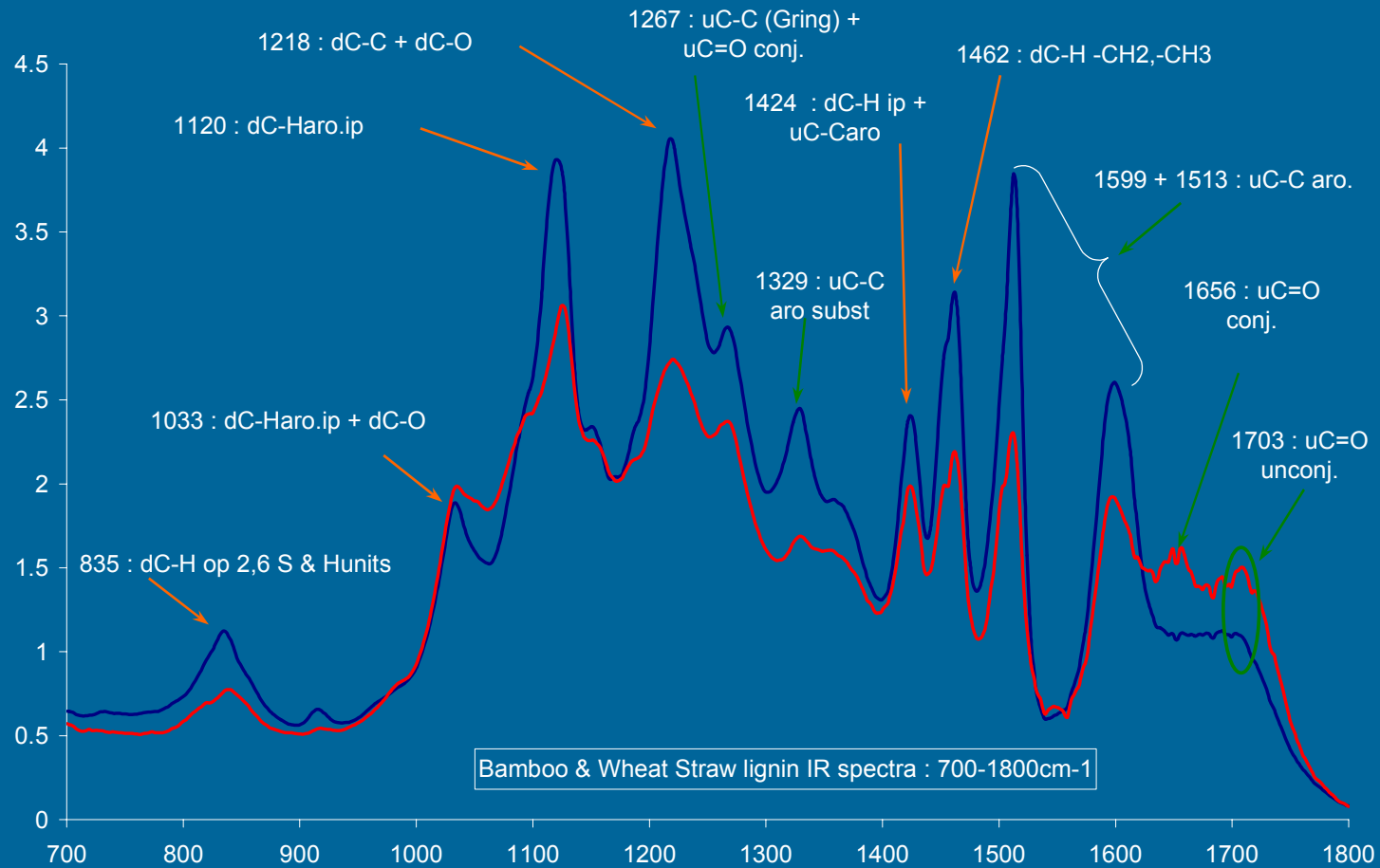
FT-IR spectra of soda lignins from different plants

FT-IR: Classification of lignins

PC 1

(+) 2915, 2851, 1709, 1614, 1516, 1466, 1221, 1120, 1032 cm⁻¹

(-) 2905, 2837, 1527, 1479, 1441, 1136 cm⁻¹

PC 2

(+) 2917, 2851, 1630, 1529, 1435, 1142, 870, 789 cm⁻¹

(-) 2947, 2907, 2837, 1593, 1516, 1464, 1427, 1331, 1219, 1118, 837 cm⁻¹

IR-based calibration models

- To develop quantitative models for the characterisation of lignin-containing materials, multivariate analysis has been used

- PLS-1 models were developed:
    - X matrix: spectral region 700-1800 cm^{-1}, 2800-3800 cm^{-1}
    - Y matrix: chemical parameters

- Calibration models were validated with:
    - statistical cross-validation
    - prediction set of samples

IR calibration & prediction: Lignin content

Calibration model:

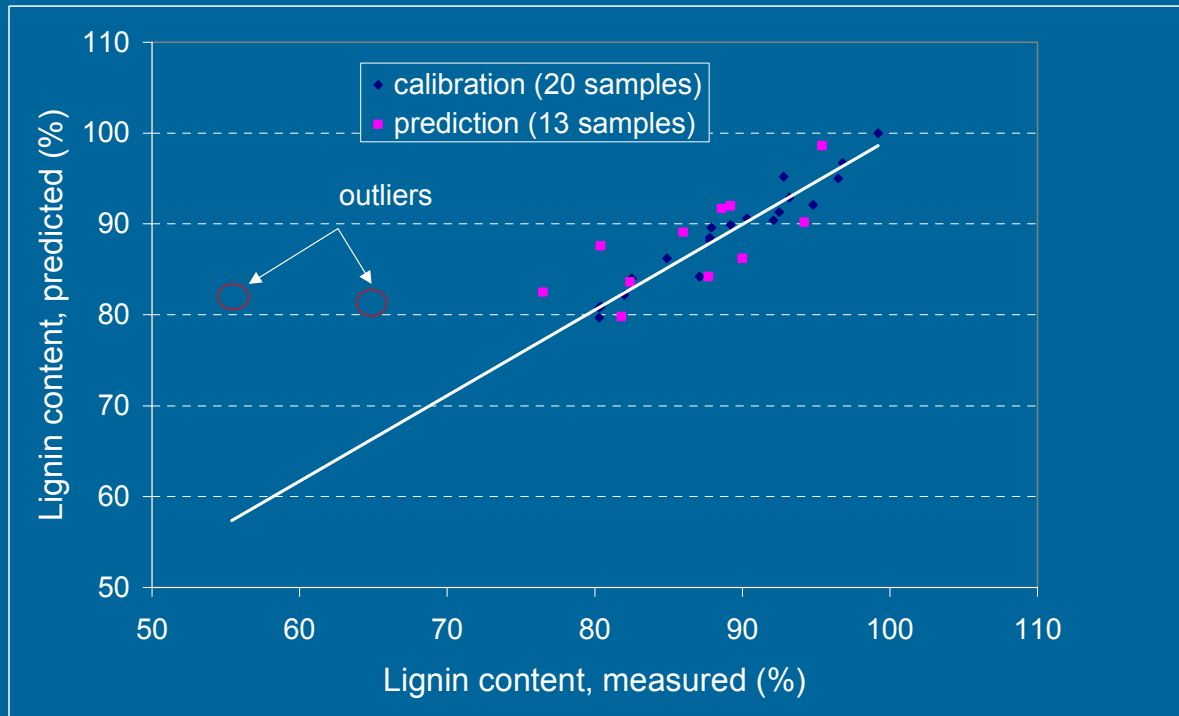|	
set:	20 samples
PC:	5
R^2c:	0.97
RMSEC:	1.39

Validation:

set:	13 samples
R^2v:	0.88
RMSEP:	2.78

IR calibration & prediction: -COOH content

Calibration model:

set: 18 samples
PC: 5
R^2c: 0.92
RMSEC: 0.25

Validation:

set: 11 samples
R^2v: 0.73
RMSEP: 0.46

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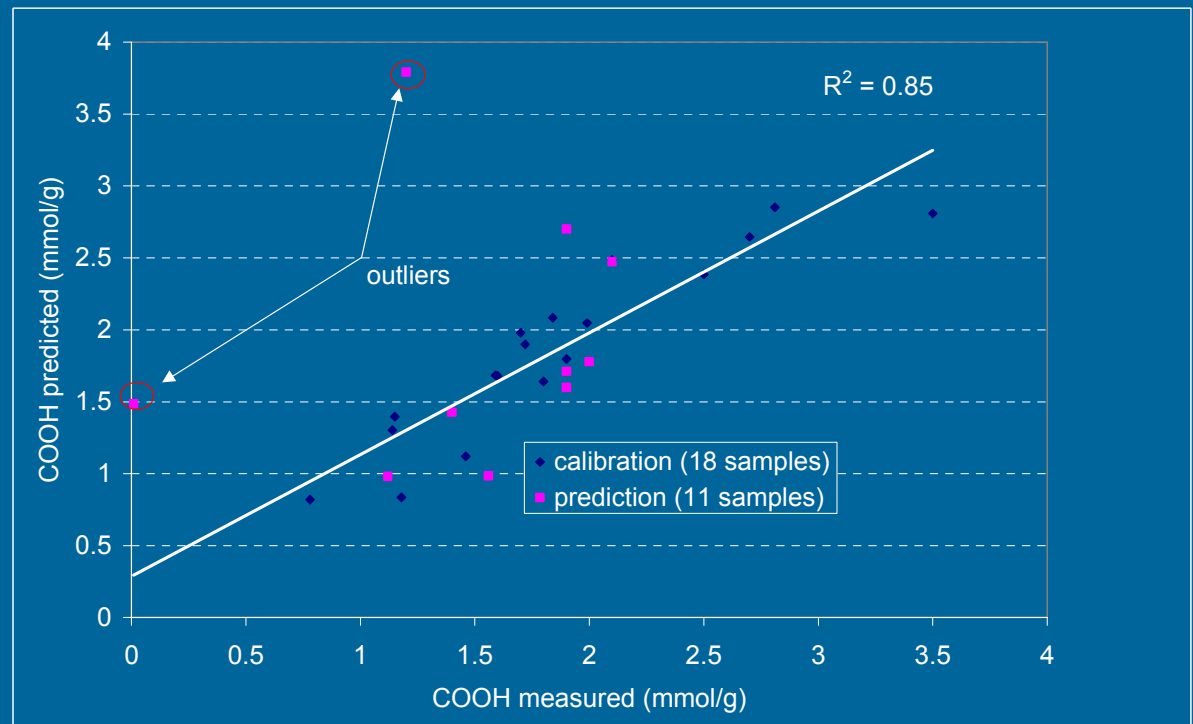
IR calibration & prediction: Phenolic OH

Calibration model:
set: 18 samples
PC: 6
R^2c: 0.98
RMSEC: 0.087

Validation:
set: 13 samples
R^2v: 0.90
RMSEP: 0.24

Scatter plot — X-axis: Phenolic OH, measured (mmol/g); Y-axis: Phenolic OH, predicted (mmol/g). Legend: calibration (18 samples); prediction (13 samples).

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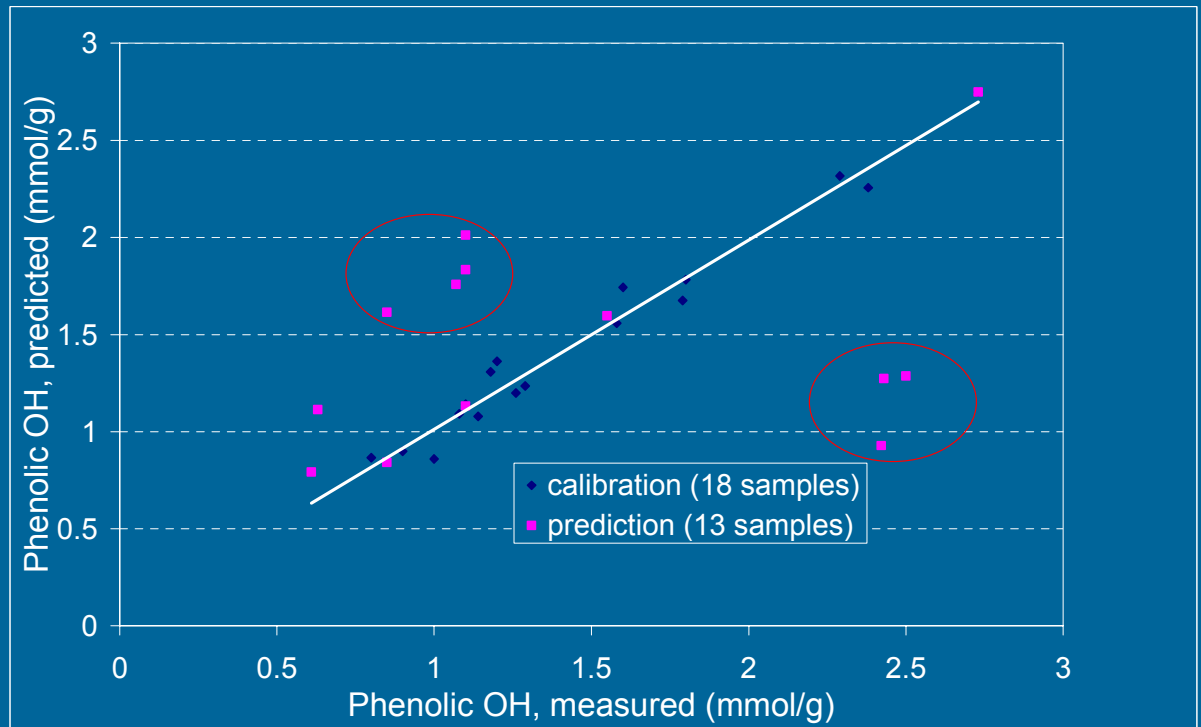
IR calibration & prediction: Sugar content

Calibration model:

set: 25 samples

PC: 6

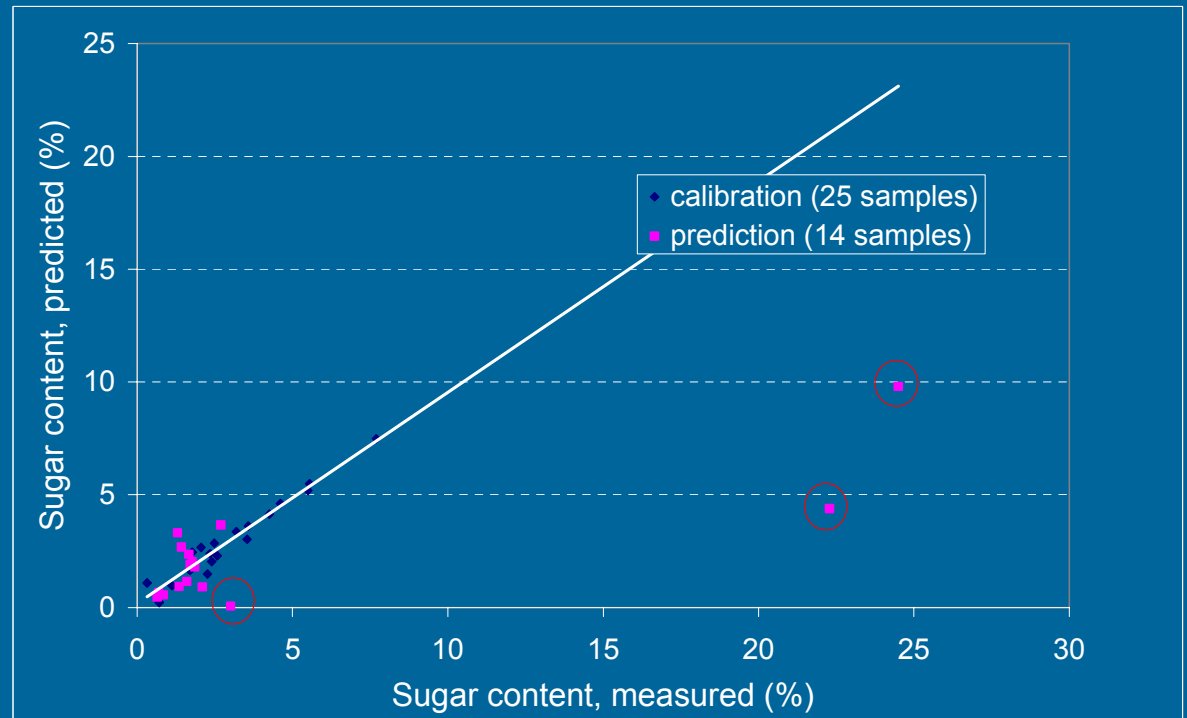R^2c: 0.96

RMSEC: 0.38

Validation:

set: 14

R^2v: 0.81

RMSEP: 0.82

Conclusions

- IR spectroscopy can be used as a fast, non-destructive tool for the characterisation of lignins and for quality control

- Prediction value increases with lignin purity

- Based on IR, lignin samples can be classified according to source and processing