Business from technology

Analytical pyrolysis as tool in biorefinery-related research

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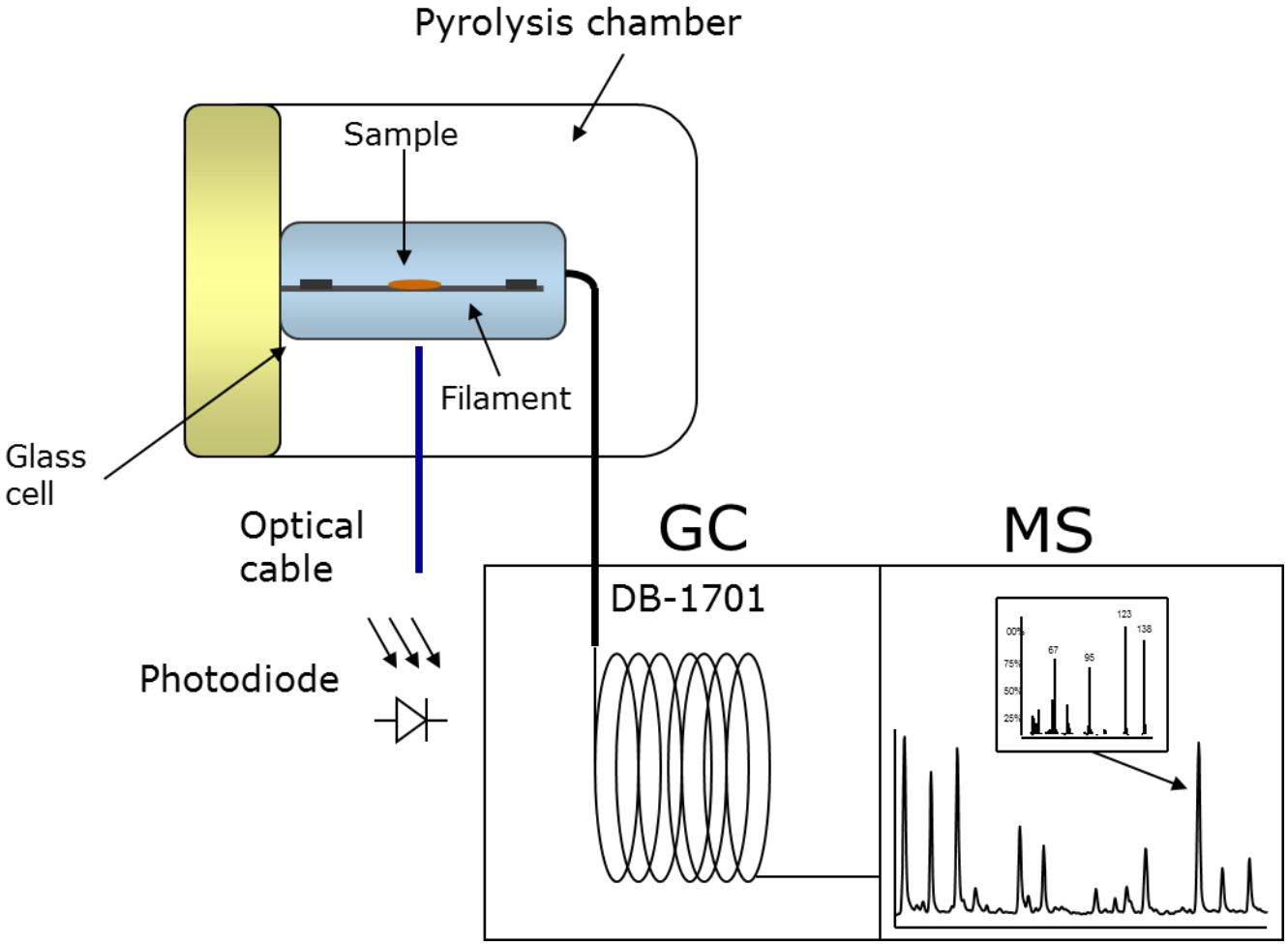
Aim of the study

- Biomass and its components are typically complex mixtures of biopolymers with random structures. Therefore, also the structural changes induced by chemical or enzymatic conversions are difficult to follow by analytical techniques.
- Poor solubility limits the choice of possible analysis techniques.
- The aim of the presentation is to demonstrate the potential of pyrolysis combined with GC/MS detection (Py-GC/MS) for the characterisation of various lignocellulosic biomass raw materials and biomaterials.

Pyrolysis-GC/MS method

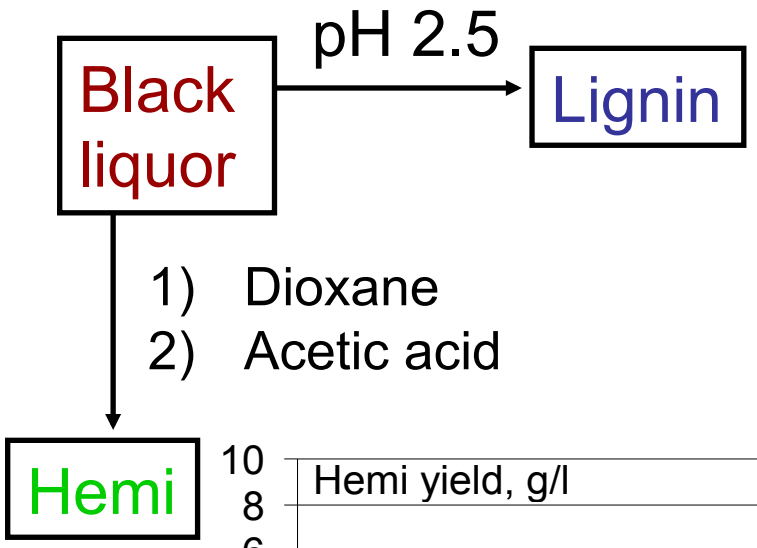


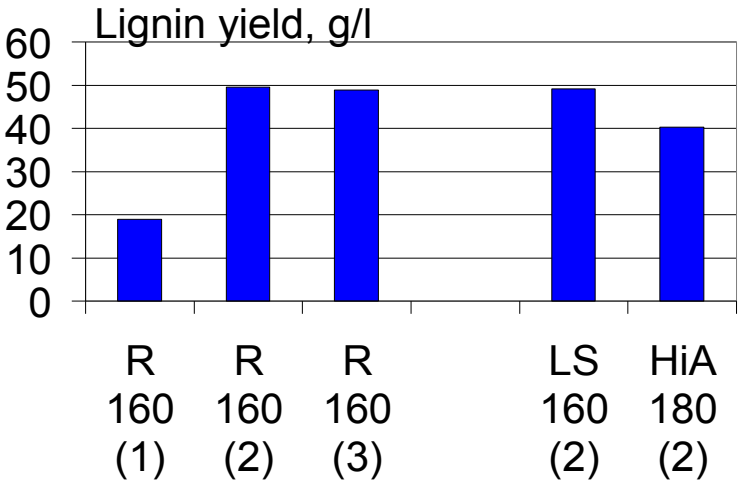
- Peak integration can be done using pre-selected ions or as TIC.
- Integrated peak areas are normalized to 100% for qualitative analysis
- The sum of lignin derived products is calculated and normalized to sample weight (*ca* 100 µg) for semiquantitative analysis

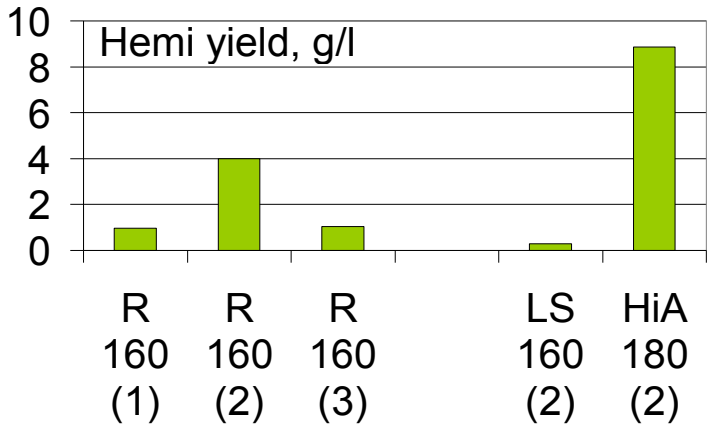
Application cases related to biorefinery research

- Biomasses and their fractions
  - Dissolved lignin and hemicelluloses in SW kraft pulping
  - Chemistry of organosolv cooking: analysis of wood, pulp and isolated lignin
  - Lignin structure and S/G ratio in Brazilian Eucalyptus hybrids
  - Analysis of the composition of fractions obtained by mechanical and enzymatic treatments from brewer's spent grain (BSG)
- Modified biomass fractions for material applications
  - *In-situ* methylation combined with Py-GC/MS for the detection of the degree of esterification
  - Thermal desorption-GC/MS as a tool to simulate the formation of volatile organic compounds (VOCs) during thermal processing of lignin

Application of Py-GC/MS to study the hemicellulose and lignin fractions from kraft cooking black liquor





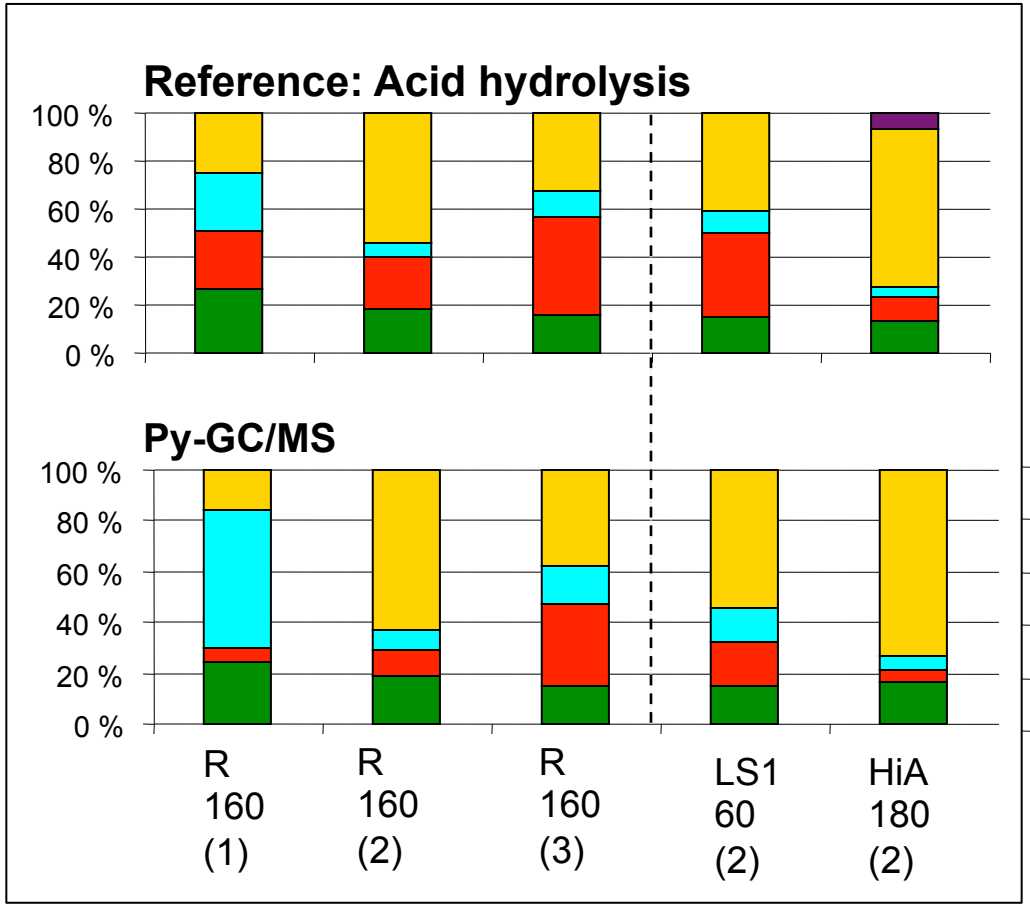


Samples from SW kraft cooking: differences in cooking parameters and phase

R160 (1)	**R**eference160ºC, impregnation
R160 (2)	**R**eference160ºC, bulk phase
R160 (3)	**R**eference160ºC, residual phase
LS160 (2)	**L**ow **S**ulphidity 160ºC, bulk phase
HiA180 (2)	**Hi**gh **A**lkalinity 180ºC, bulk phase

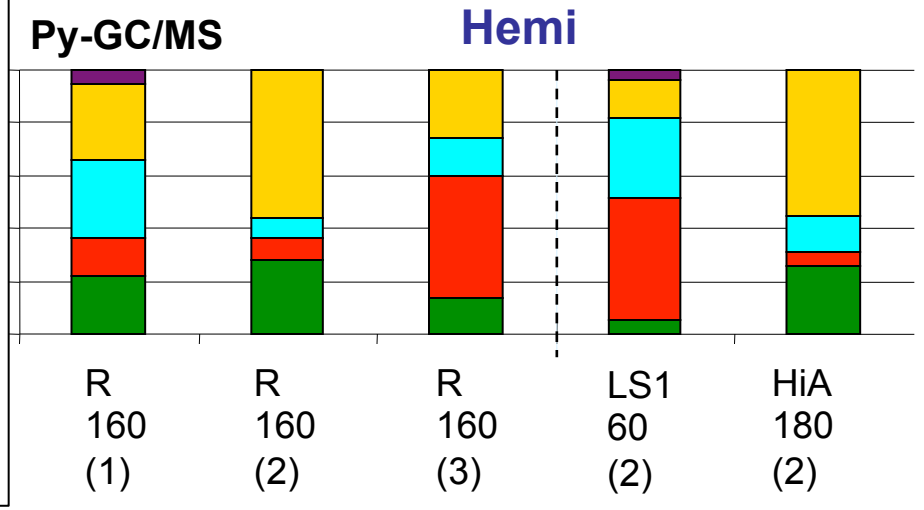
Carbohydrate composition in the lignin and hemi fractions

Lignin

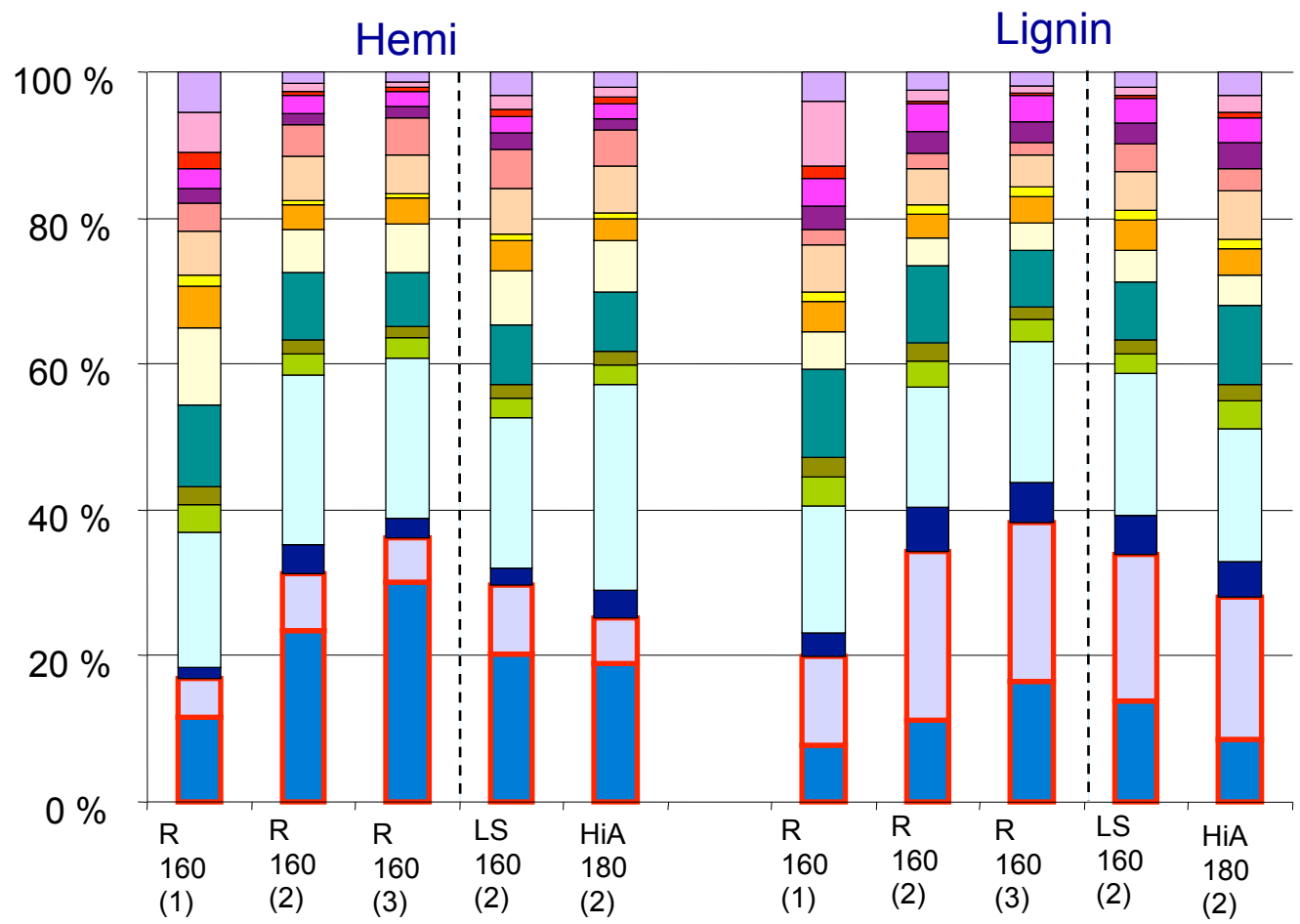


- Similar trends by both methods, but differences in the response between individual components.
- Similar composition (not content) in the lignin and hemi fractions

Hemi



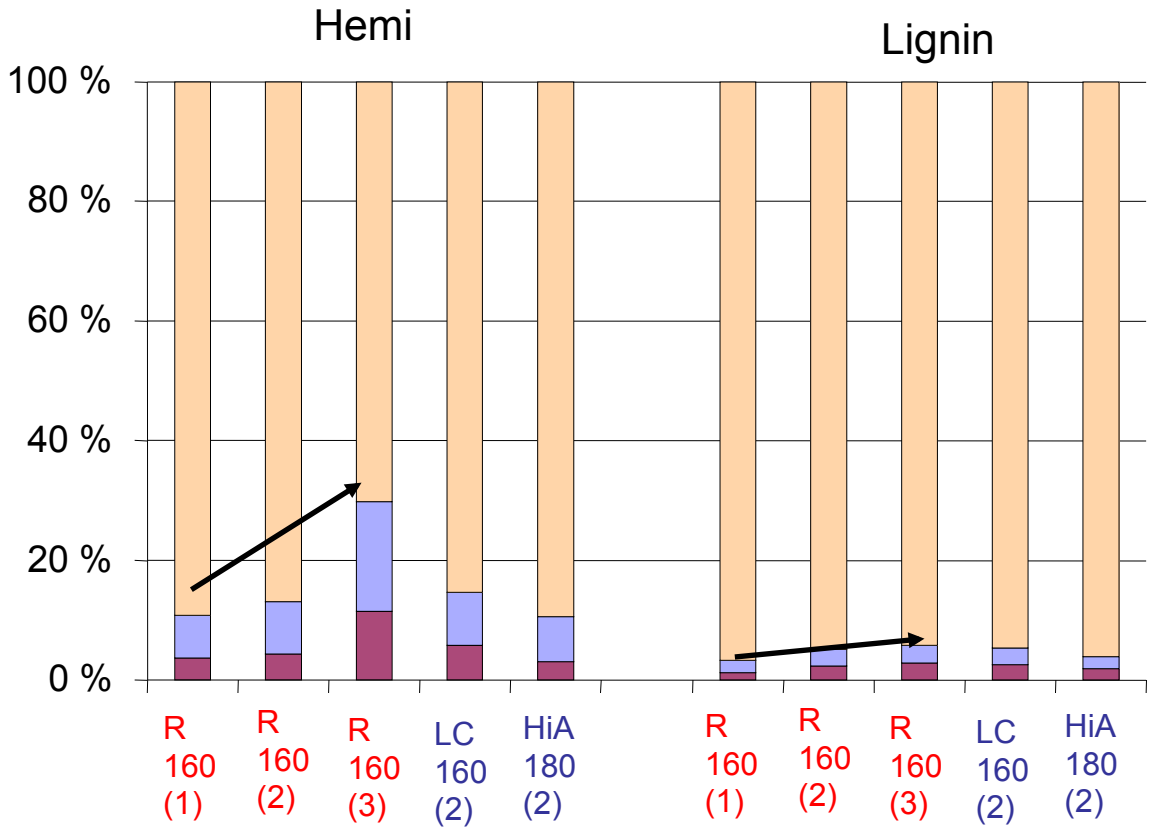
Lignin structure (G) by pyrolysis



- Coniferaldehyde
- trans-Coniferyl alcohol
- cis-Coniferyl alcohol
- Dihydroconiferyl alcohol
- 4-(1-hydroxy-prop-2-enyl)guaiacol
- Guaiacylacetone
- Homovanillin
- 4-(oxy-allyl)guaiacol
- Acetoguaiacone
- Vanillin
- trans-Isoeugenol
- cis-Isoeugenol
- Eugenol
- 4-Vinylguaiacol
- 4-Ethylguaiacol
- 4-Methylguaiacol
- Guaiacol

- Same products distribution in hemi and lignin fractions except for the ratio between guaiacol and 4-Me/ Guaiacol, due to
  - Differences in lignin structure
  - matrix effects
  - LCC

Trace components: markers for modified structures



Guaiacyl lignin (G)

Phenol

Hydroquinone

- Trace aromatics more abundant in hemi compared to lignin
- Increase during cooking
  - Polysaccharide-derived compounds

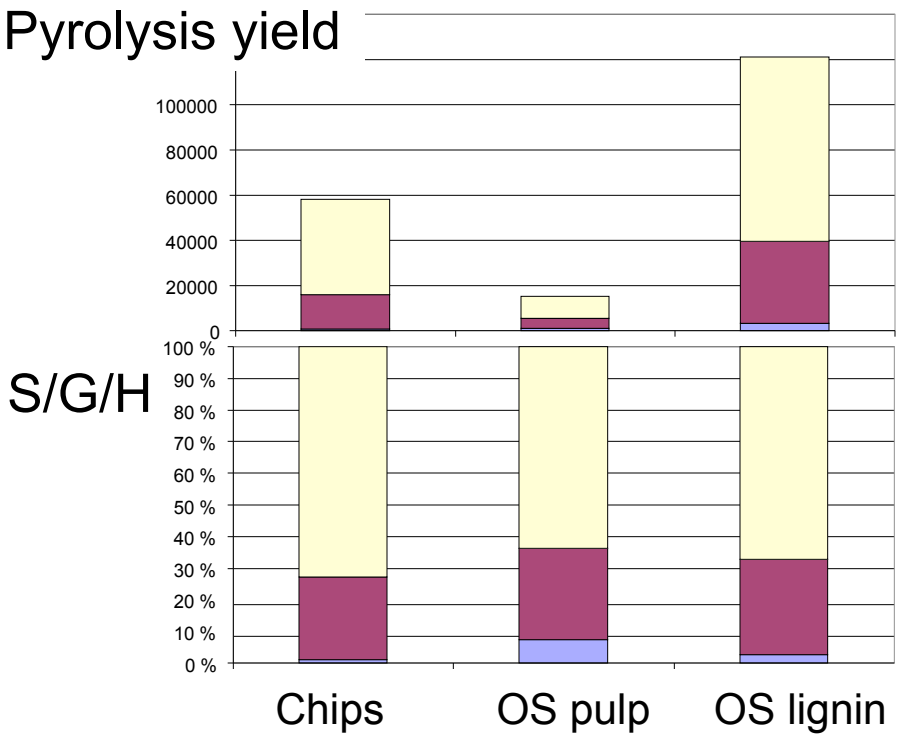
Conclusions related to the chemistry of kraft cooking followed by Py-GC/MS

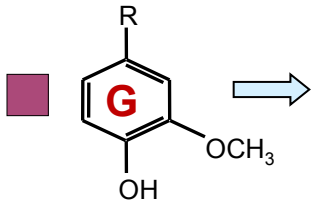
- For both the hemicellulose and lignin fractions, Py-GC/MS gives information about
  - Carbohydrate composition
  - Structural differences in lignin
  - Indication of the presence of modified structures formed in lignin and hemicelluloses during cooking
- Matrix effects may distort direct comparison between sample types (hemi *vs* lignin).

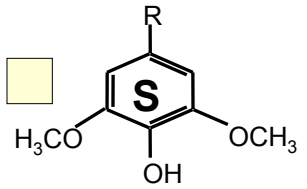
KCL re-inventing paper

Niemelä, K., Tamminen, T., Ohra-aho, T. Black liquor components as potential raw materials, 14th ISWFPC, Durban, South Africa, June 25th-28th, 2007

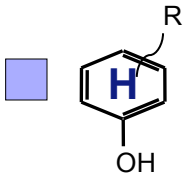
Organosolv (OS) pulping of Birch by acetic acid / phosphinic acid







Corresponding structures in the S series

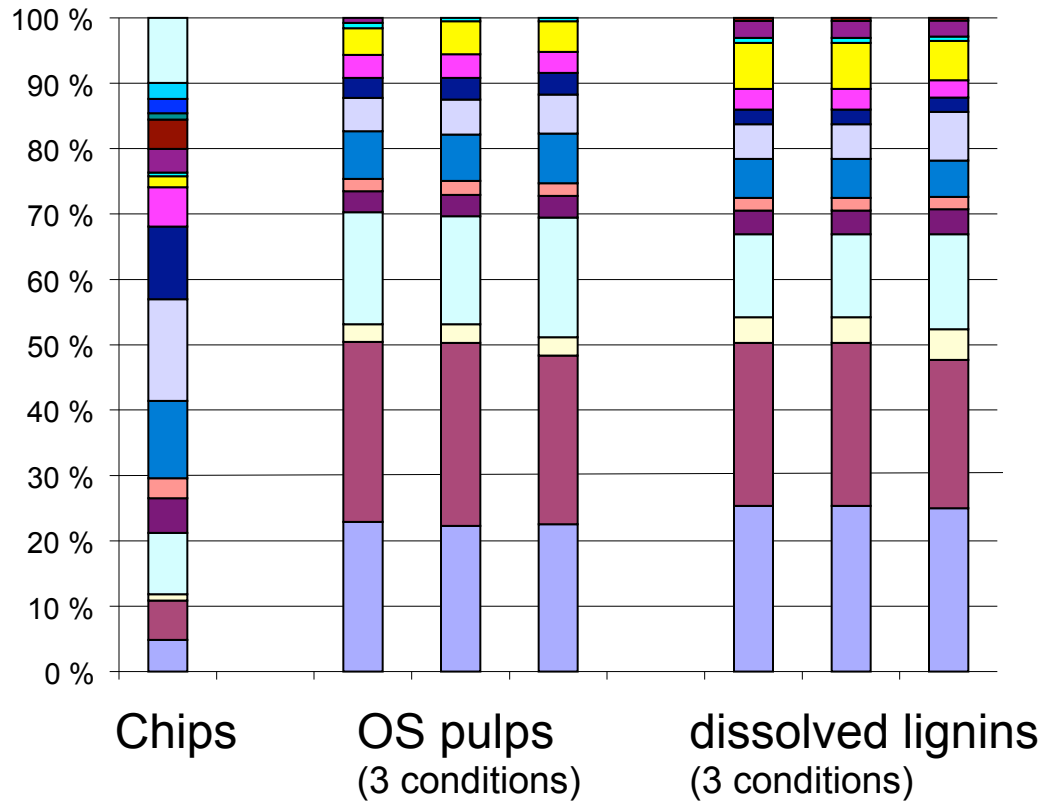


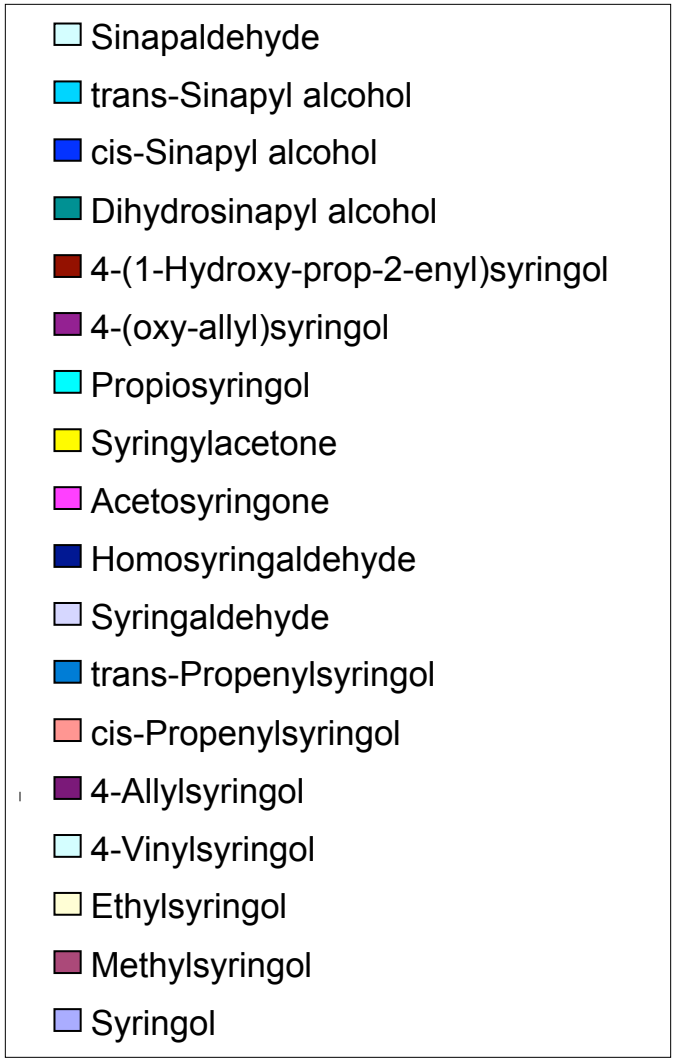
R = H or CH_3

- Coniferaldehyde
- trans-Coniferyl alacohol
- cis-Coniferyl alcohol
- Dihydroconiferyl alcohol
- 4-(1-Hydroxyprop-2-enyl)guaiacol
- 4-(oxy-allyl)guaiacol
- Guaiacylacetone
- Acetoguaiacone
- Homovanillin
- Vanillin
- trans-Isoeugenol
- cis-Isoeugenol
- Eugenol
- Vinylguaiacol
- 4-Ethylguaiacol
- 4-Methylguaiacol
- Guaiacol

- Pyrolysis yield (total content of degradation products normalised to sample amount) reflects lignin content
- G/S ratio constant, H enriched in pulp

Lignin structure in *E. globulus* after OS cooking (only S series shown)





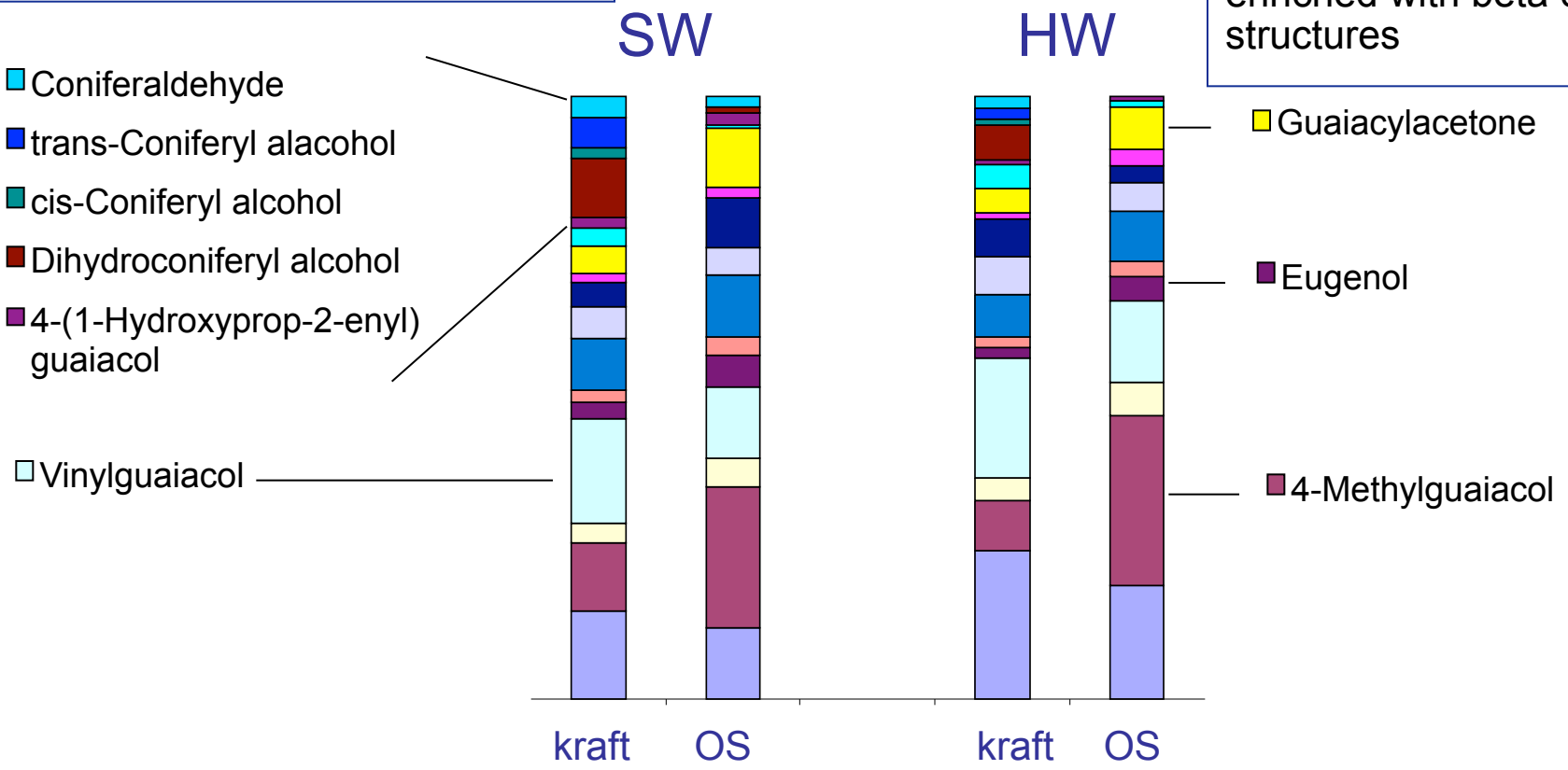
- Residual pulp lignin and the dissolved lignin are similar to each other, but differ from the chip lignin

⇒ cooking changes lignin structure, but no lignin structural type is dissolved preferentially

Comparison between kraft and OS lignins (only G series presented for HW samples)

Kraft lignins: increased proportion of degradation products containing 3-carbon side chain

Organosolv lignins: increased proportion of degradation products containing short side chain, enriched with beta carbonyl structures



Conclusions related to the application of Py-GC/MS to study organosolv pulping

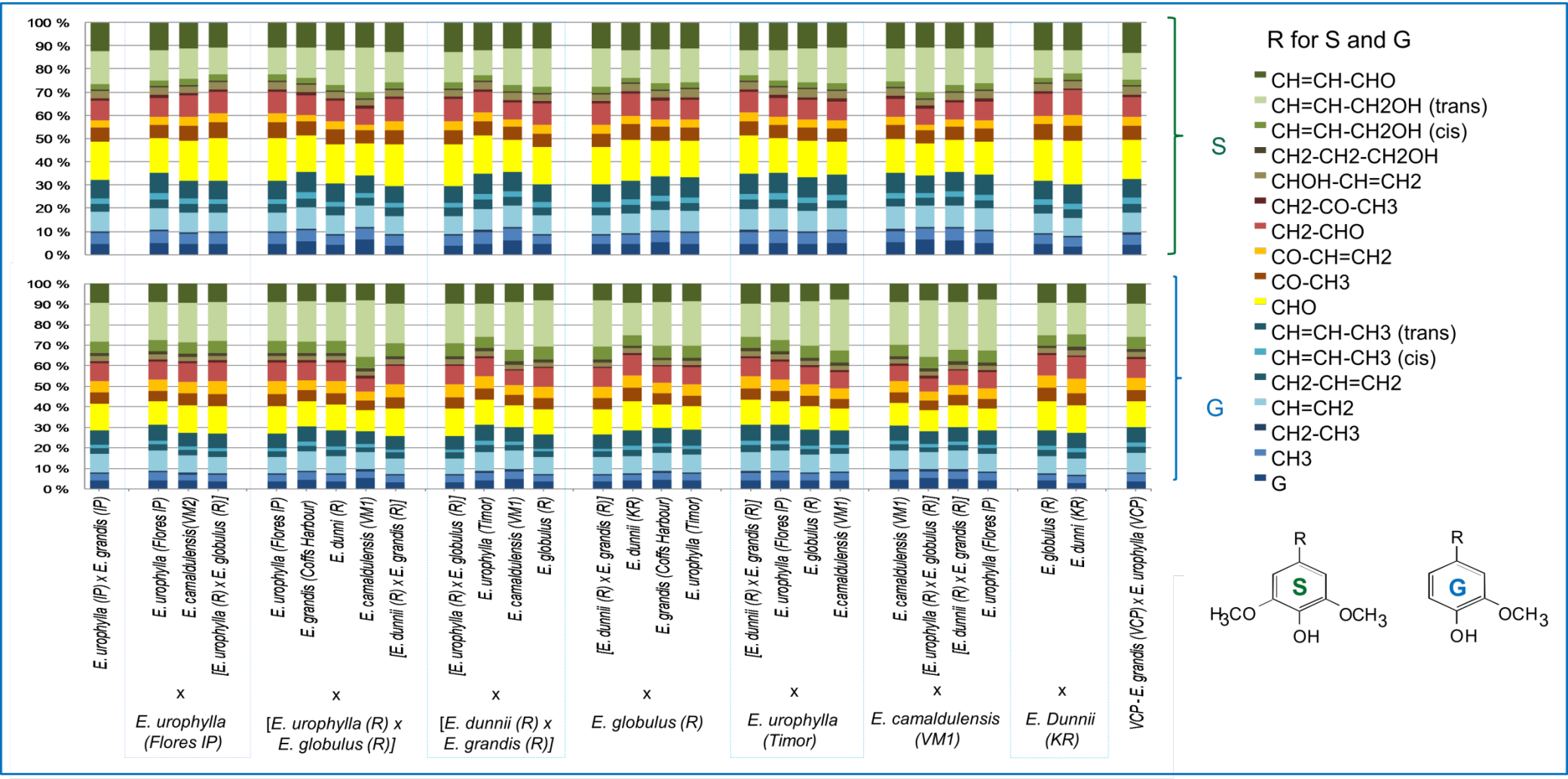
- Generally, the same distribution of lignin degradation products was detected
  - from pulp and isolated dissolved lignin
  - in the guaiacyl and syringyl series
- Cooking changes lignin structure, but no lignin structural type is dissolved preferentially

afore

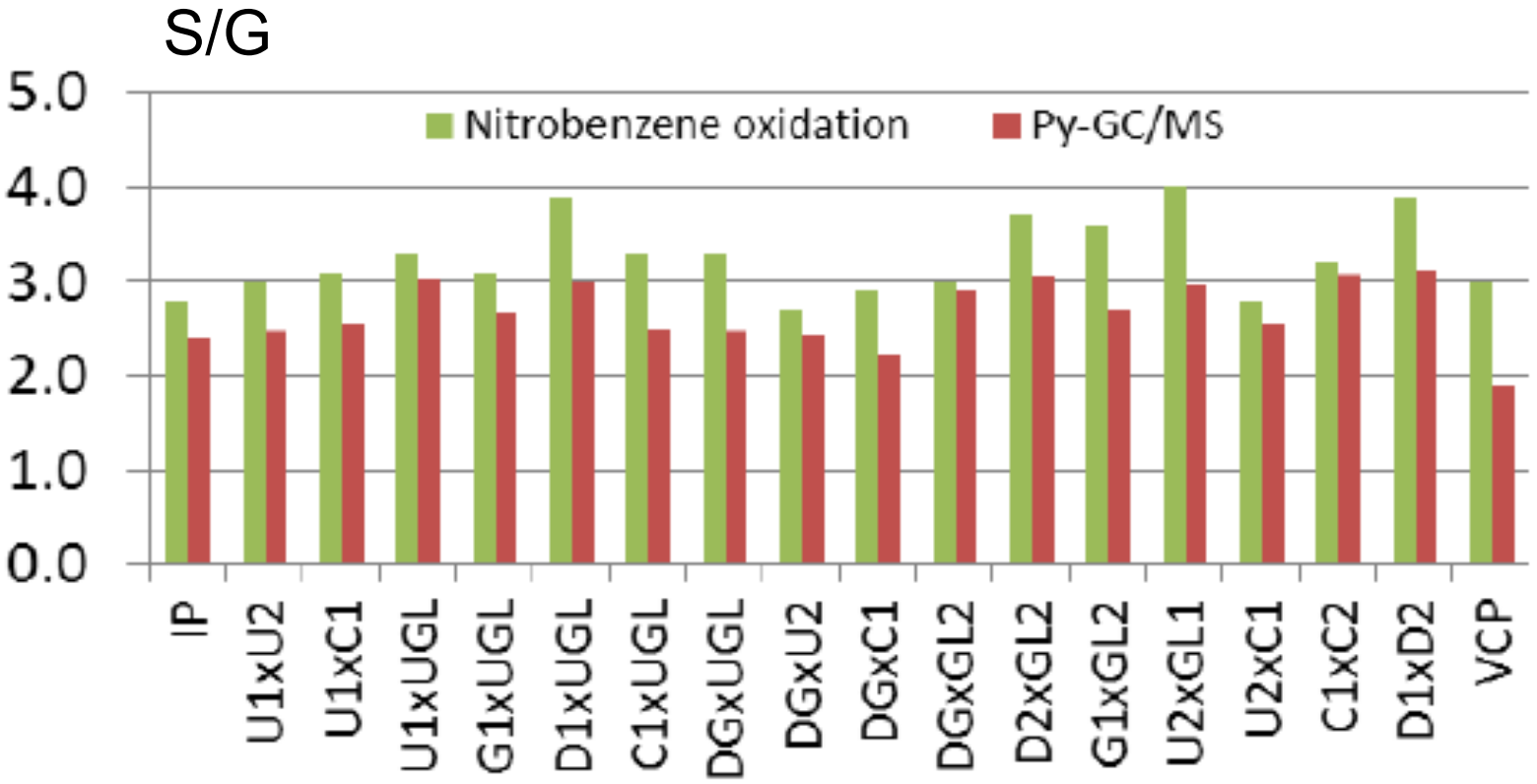
SEVENTH FRAMEWORK PROGRAMME

Tamminen, T., Mikkonen, H., Hyvärinen, S., Hakala, T., Liitiä, T., Ohra-aho, T., Alakurtti, S., Rovio, S., Lappas, A., Suurnäkki, A. Novel type of technical lignins by organosolv cooking with phosphinic acid in various solvents, ACS 2011, March 27-31, 2011, Anaheim, USA

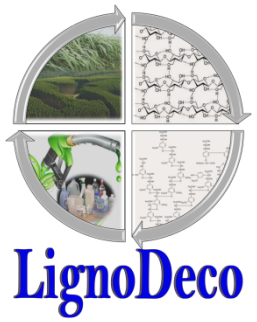
Differences in lignin structure between Brazilian Eucalyptus hybrids



Determination of S/G ratio in the Eucalyptus hybrids – comparison with nitrobenzene oxidation



Conclusions related to the Eucalyptus hybrid comparison by Py-GC/MS

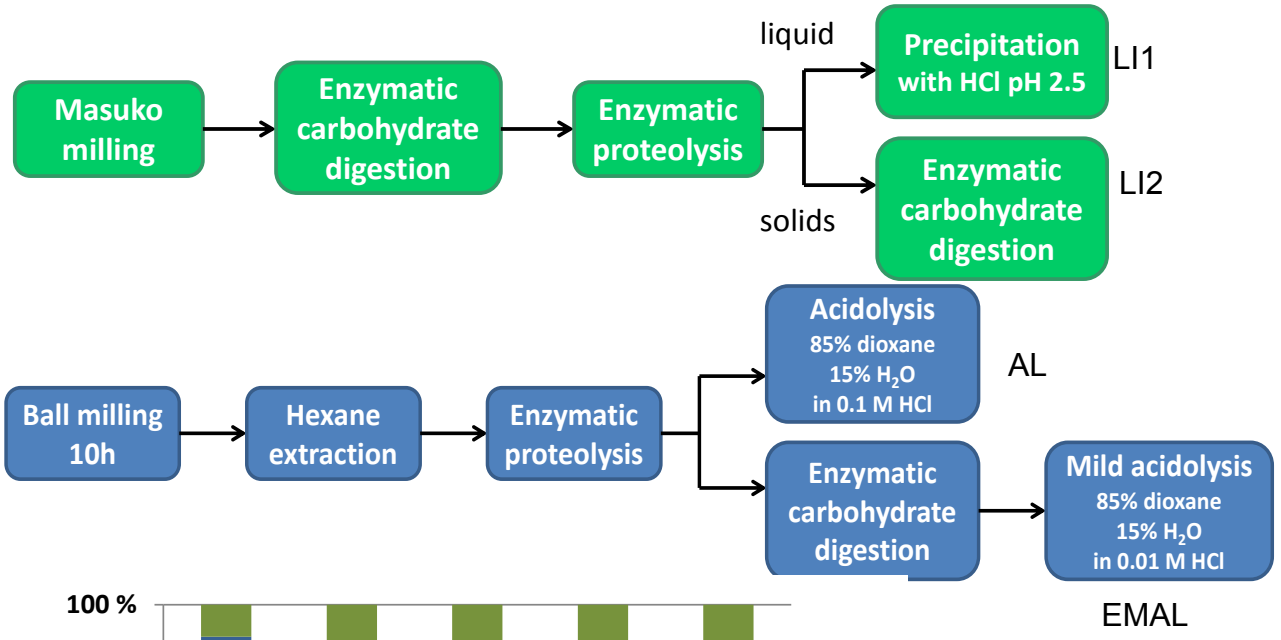


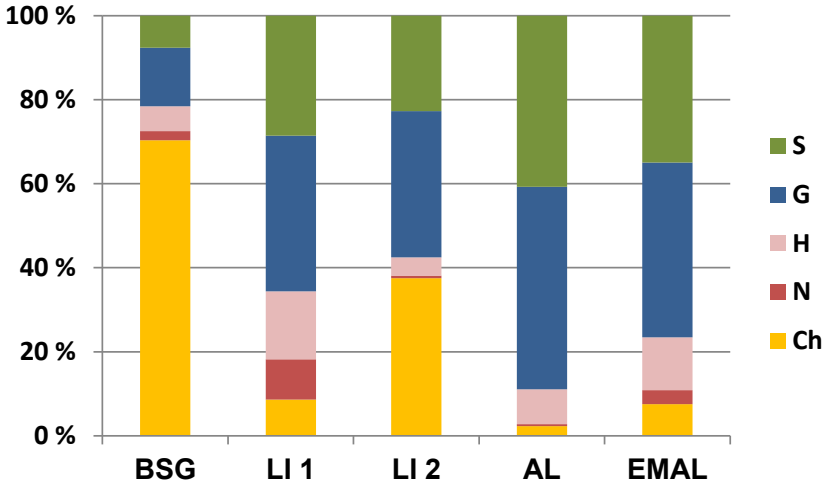
- Pyrolysis-GC/MS detects differences in lignin structure between Eucalyptus hybrids.
- Same trends are seen in the G and S series.
- The S/G ratios determined with pyrolysis-GC/MS and nitrobenzene oxidation were close to each other. However, there was no linear correlation between the methods

Ohra-aho, T., Tamminen, T., Gomes, F.J.B., Colodette, J. Structural differences in lignin between Eucalyptus clones determined by analytical pyrolysis-gas chromatography/mass spectrometry, 5th Brazilian Colloquium on Eucalyptus Pulp, May 2011

Ohra-aho, T., Gomes, F.J.B, Colodette, J., Tamminen, T., S/G ratio and lignin structure among Eucalyptus hybrids determined by Py-GC/MS and nitrobenzene oxidation, JAAP, accepted

Analysis of Brewer's spent grain (BSG), a potential biorefinery feedstock



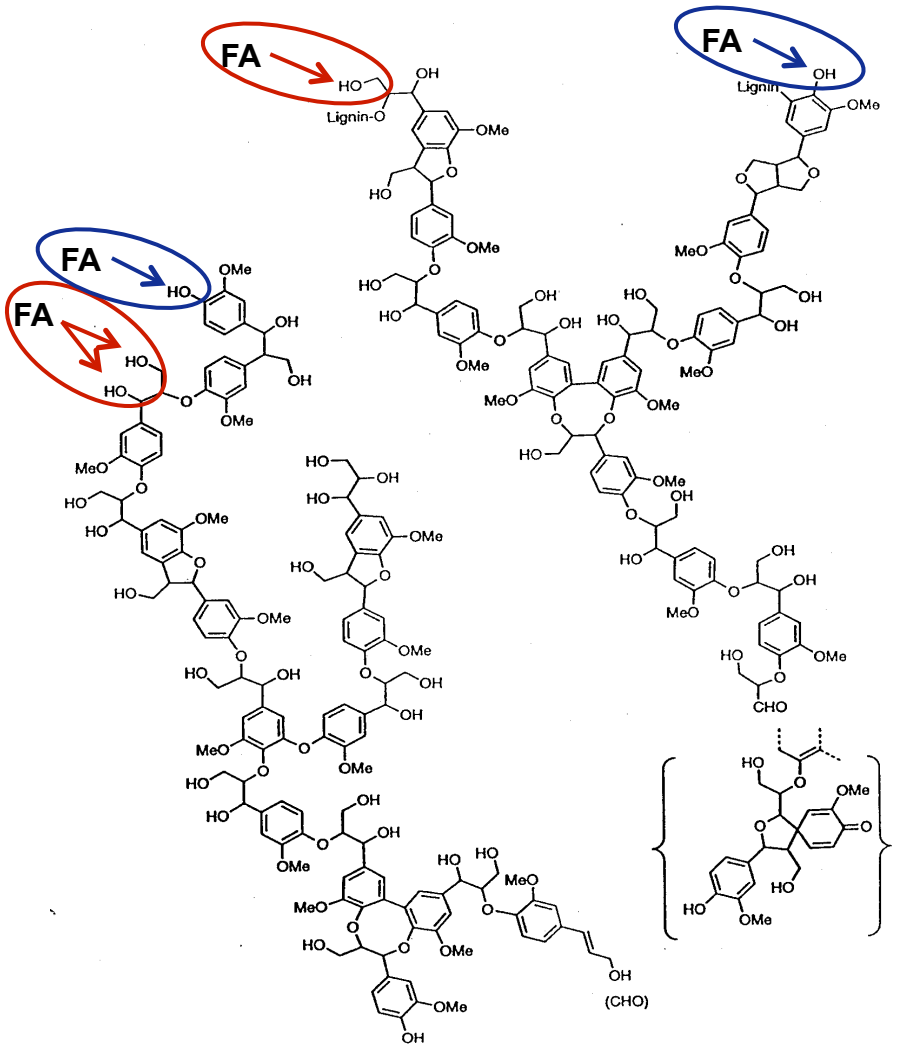


- BSG fractionated both chemically and enzymatically, yielding samples enriched with
  - Lignin with protein contamination (LI1)
  - Carbohydrates resistant to enzymatic hydrolysis (LI2)
  - Lignin (AL, EMAL)
- Phenolic acids and protein complicate lignin analysis in non-wood samples. Origin of H structures is not clear.

Niemi, P., Tamminen, T., Ohra-aho, T., Rovio, S., Faulds, C., Orlandi, M., Poutanen, K., Buchert, J. Fractionation of brewer's spent grain and characterization of the obtained lignin-rich fractions, COST FP 0901 Workshop, Espoo, Finland, Aug 2012

The Academy of Finland, BIOREGS and COST FP0901 are gratefully acknowledged for financial support.

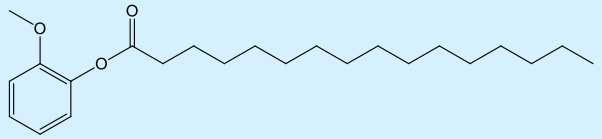
Thermochemolysis (*in-situ* derivatisation py-GC/MS) to study the degree of esterification in modified biomaterials



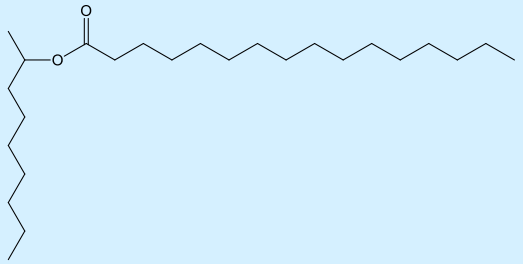
Source: Syrjänen and Brunow , J Chem Soc Perkin Trans, (1998)

- Fatty acids (FA) react with free
  - → Aliphatic OH-groups
  - → Aromatic OH-groups

Model compounds were synthetised representing aromatic and aliphatic ester bonds between FA and lignin



Guaiacyl palmitate

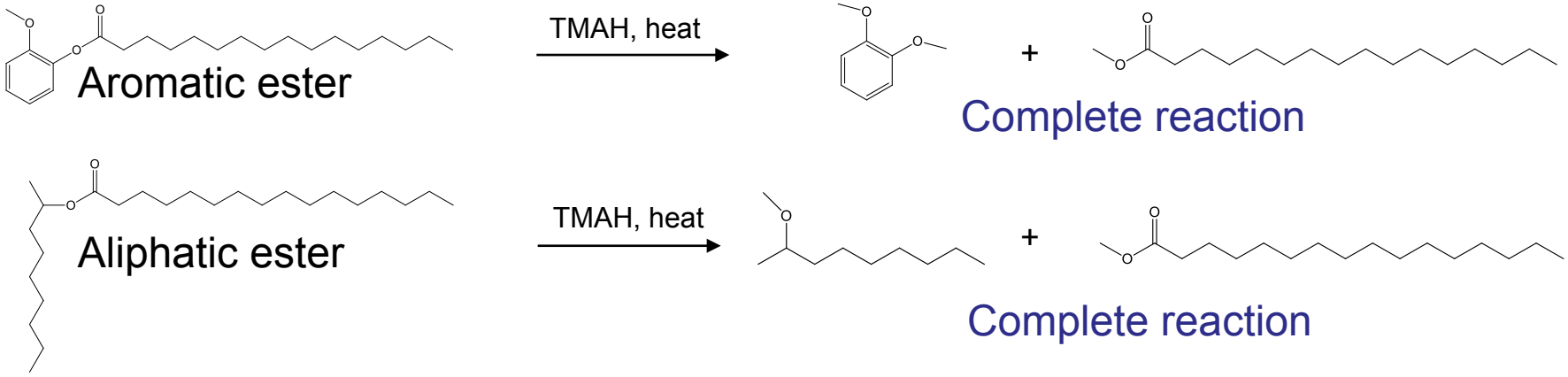


2-Nonanyl palmitate

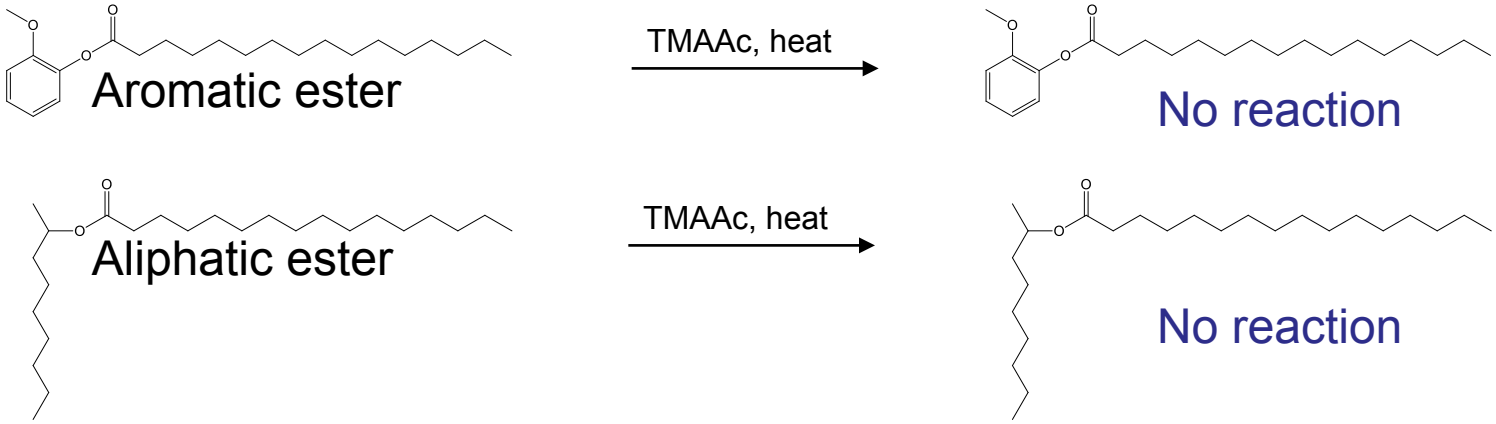
Thermochemolysis using on-line derivatisation by two reagents:

Expected selectivity based on wood extractive analysis

TMAH



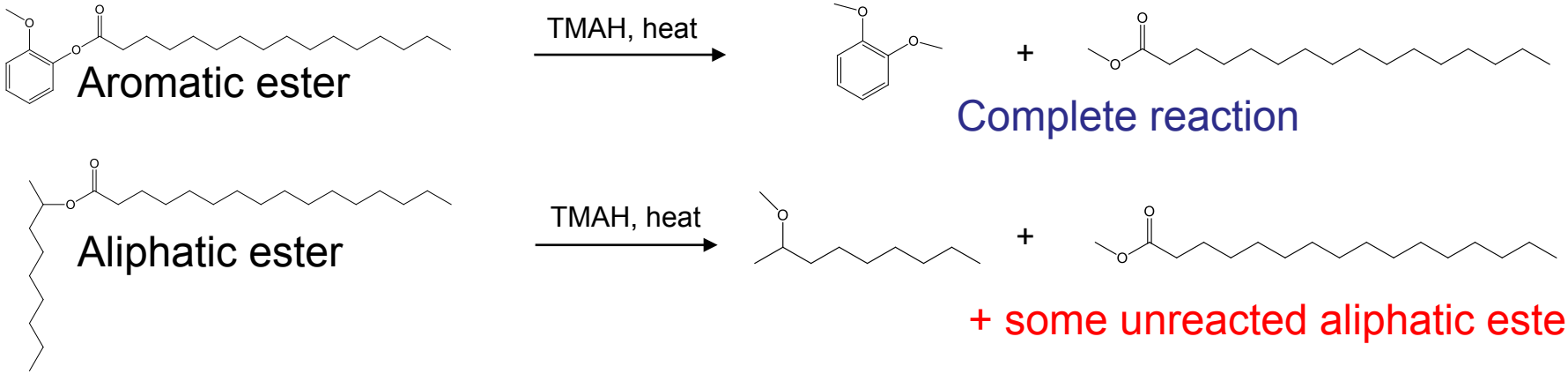
TMAAc



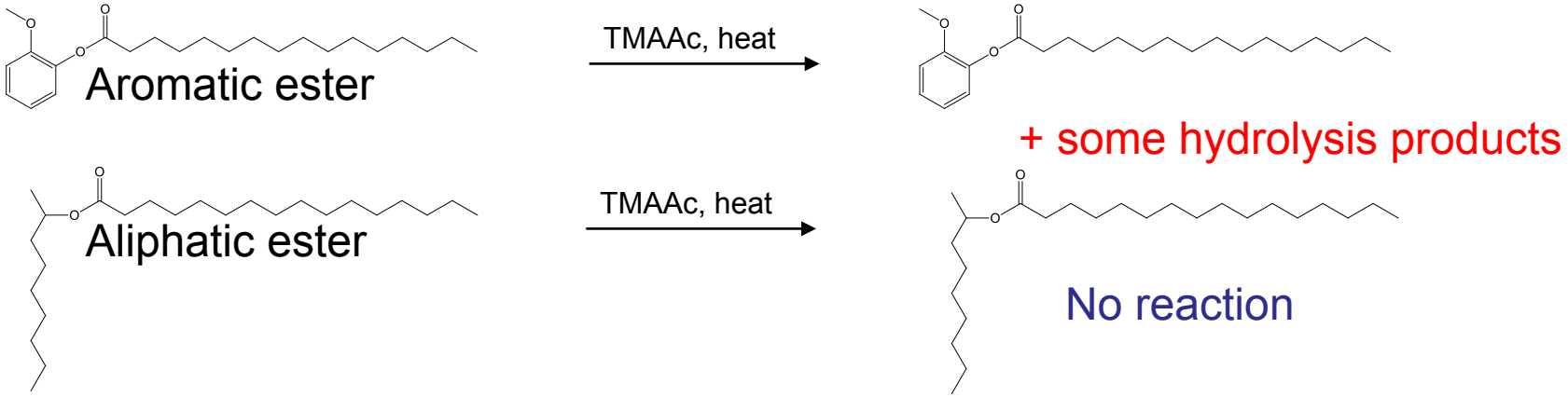
Thermochemolysis using on-line derivatisation by two reagents:

Model compound results: incomplete selectivity for aromatic esters

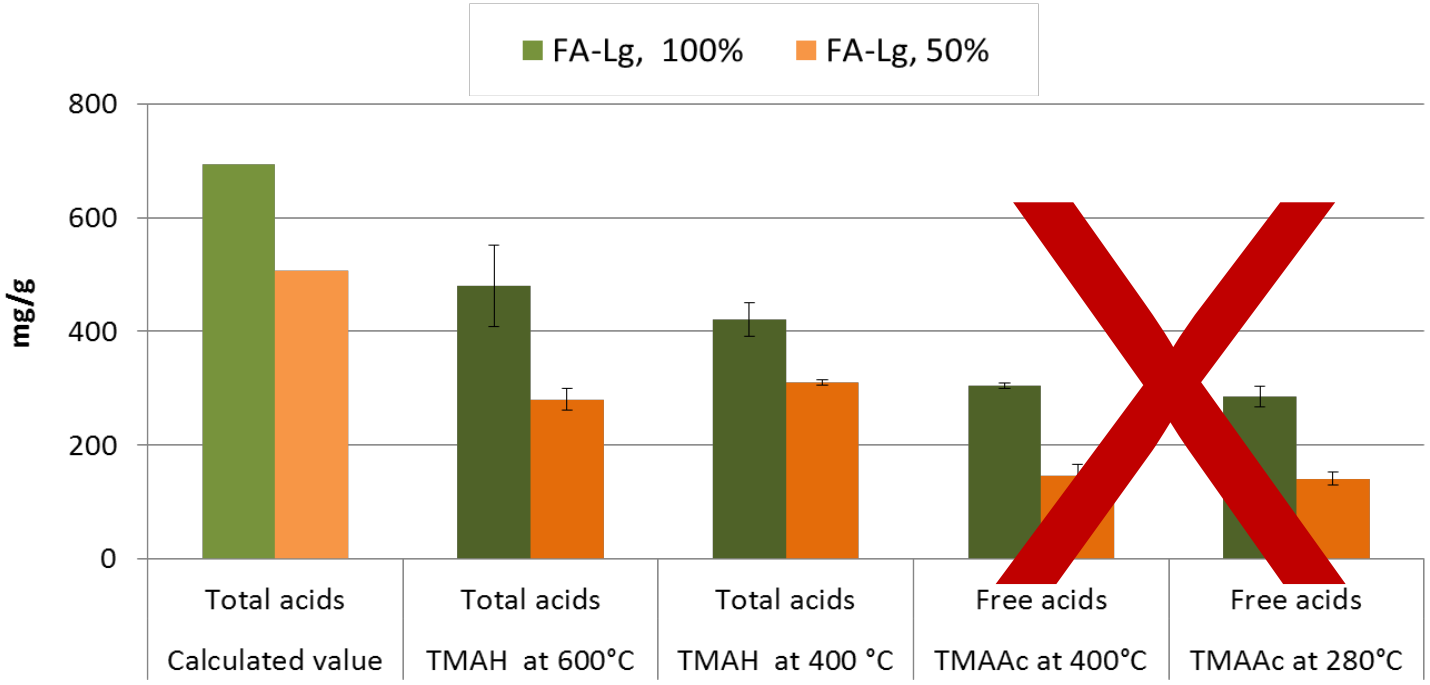
TMAH



TMAAc



Application of thermochemolysis to the real case: Quantitation of total acids in lignin esters



BioRefine

Tekes

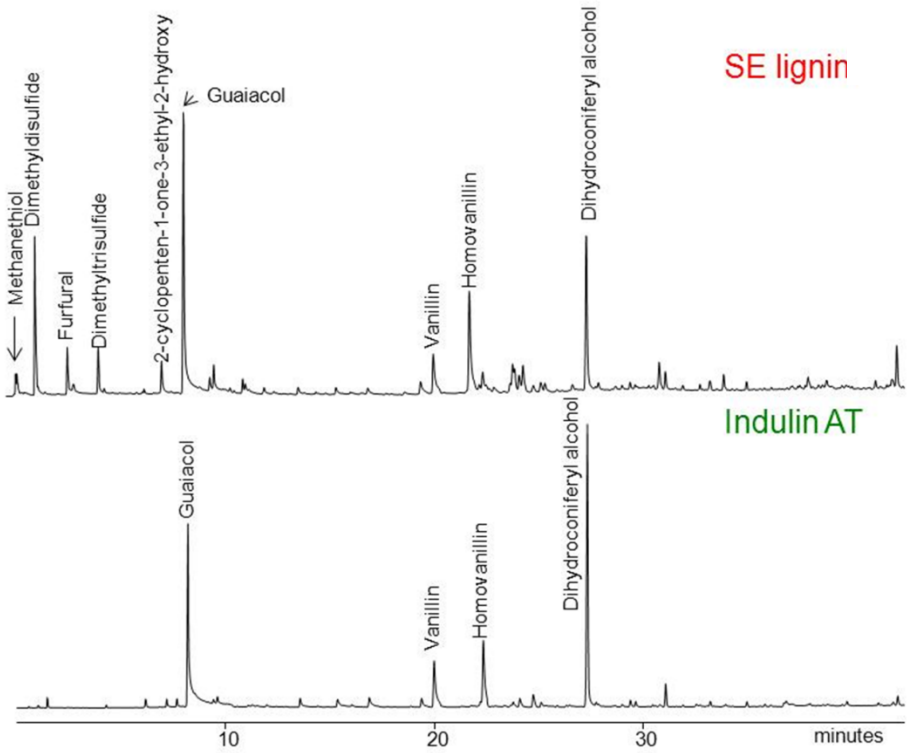
- Total fatty acids can be determined by TMAH
- Free acid content unreliable due to the partial hydrolysis of aromatic ester bond by TMAAc

Suomen Akatemia
Tieteen rahoittaja ja asiantuntija

Ohra-aho, T., Ropponen, J., Tamminen, T. Thermochemolysis using TMAAc and TMAH reagents as means to differentiate between free acids and esters, Journal of Analytical and Applied Pyrolysis, in press

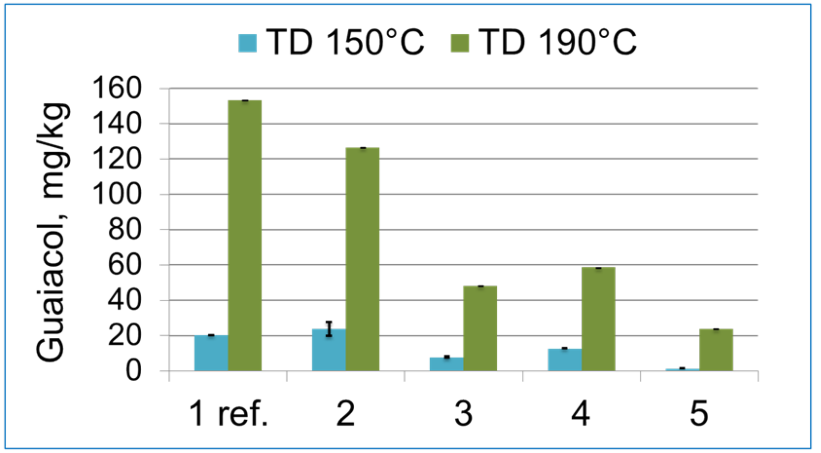
Thermal desorption (TD-GC/MS) as means to analyse VOC from lignin

Qualitative



Quantitative

- Amount of sample 2.5 mg
- TD at 150°C and 190°C for 5 min
- GC/MS identification
- Quantification of guaiacol using external standard calibration.



- Enzymatic and chemical treatments (2-5) reduce the release of the VOC component guaicol

ERA IB
Tekes

Ohra-aho, T., Kalliola, A., Tamminen, T. Novel TD-GC/MS method to simulate the VOC formation in the temperature range of thermoplastic processing, COST FP 0901 Workshop, Espoo, Finland, Aug 2012

Conclusions

- Pyrolysis combined with GC/MS detection (Py-GC/MS) has wide potential for the characterisation of various types of biomass as such or after fractionation or chemical modification.
- Structural information is obtained for lignin, *e.g.* the syringyl / guaiacyl ratio.
- Thermal desorption-GC/MS, has been developed as a tool to simulate the formation of VOCs during thermal processing of lignin.

Acknowledgements

- The research examples presented come from projects funded by
  - Tekes via the ERA IB and Biorefine programs
  - EU FP7 projects LignoDeco and Afore
  - Academy of Finland projects Defibre (AKA/CNPq in the SusEn program), Lignin Fibre and Bioregs

VTT creates business from technology