# Multidimensional analysis of lignins, humins and derivatives by Size Exclusion Chromatography x Pyrolysis-GC-MS

Alan García[1], Mario Schilder[1], Sandra Constant[2], Henrik Cornelisson[2] and Hans-Gerd Janssen[1,3]

[1]Analytical Chemistry, University of Amsterdam, The Netherlands

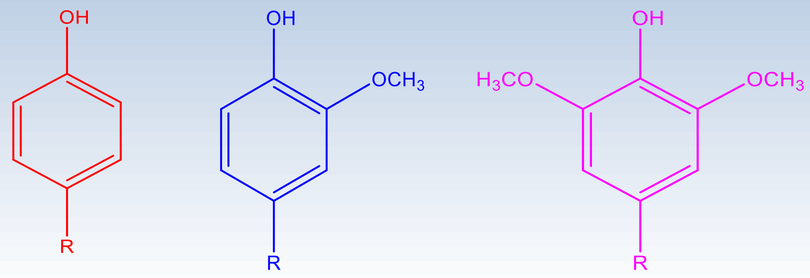
[2]Avantium Holding B.V., The Netherlands

[3]Unilever Research and Development, The Netherlands

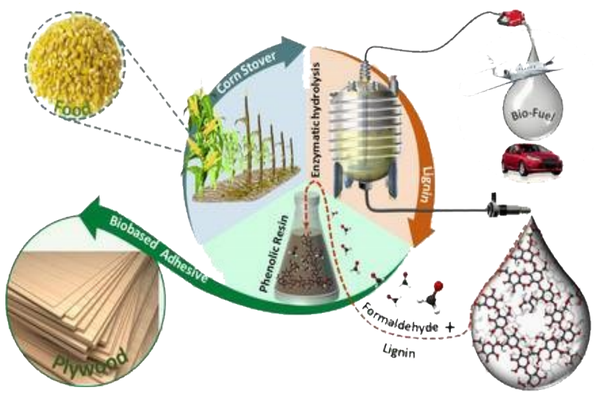
E-mail: a.r.garciacicourel@uva.nl

## Introduction

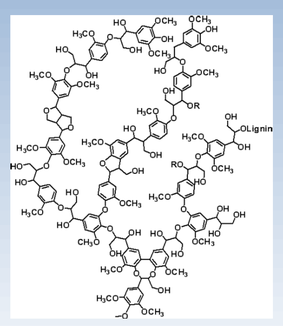
Lignin is a complex polymer with a highly branched aromatic structure consisting of three propanephenyl molecules: p-coumaril, p-coniferyl and p-sinapyl alcohol connected by ether and C=C bonds forming hydroxyphenols (H), guaiacols (G) and siringols (S), respectively.



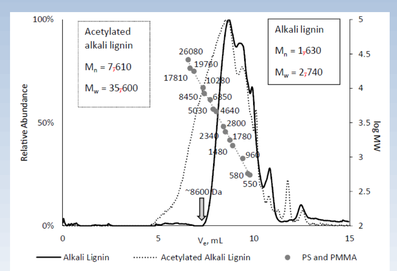

It is mostly used as a low grade fuel after its extration from celluose in the paper industry. However, with an increasing focus on bio-renewable products, lignin could prove to be a valuable feedstock: it can be turned into bio-oil using fast pyrolysis, it can be used as an adheasive in asphalts, it can act as an anti-oxidizing agent, and finally, smaller aromatic compounds could be obtained if controlled decomposition is achieved. The potential usefullness of lignin samples is determined by its structure, which differs between softwoods (gymnosperms), hardwoods (angiosperms) and grasses (herbaceous cops) as well as by the method of pretreatment. The purity and structure of the aquired lignin is dependent on the method of pretreatment and extraction and understanding these differences is critical for further valorization of the lignin biopolymers. Numerous analytial methods exist to characterize lignins. Chemical degradation methods are commonly used to analyze monomeric content, where techniques such as FTIR and NMR are used to determine functional groups, lignin components and structual information .




## Analytical methods



Size Exclusion Chromatography

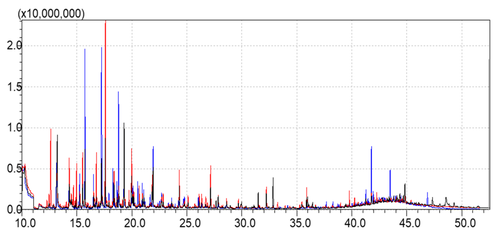



Pyrolysis

Or

PTV Optic 3 (600 °C)

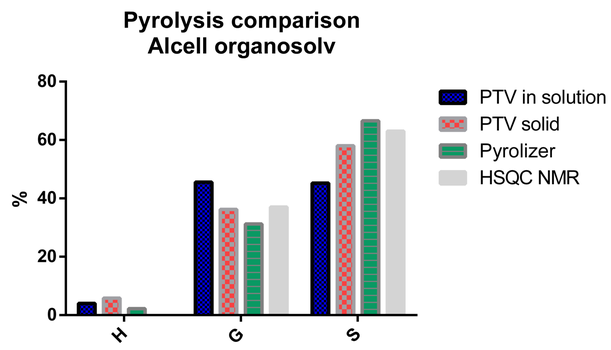
Pyroprobe 5000 (600 and 750 °C)

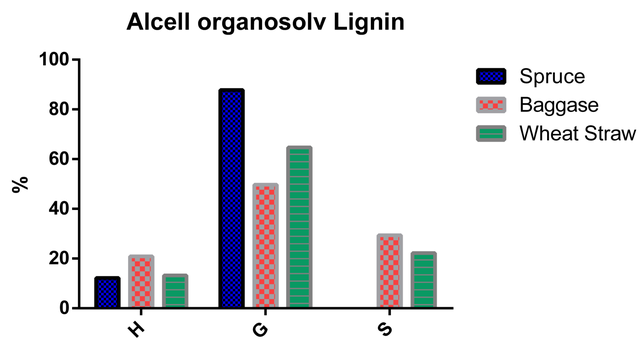


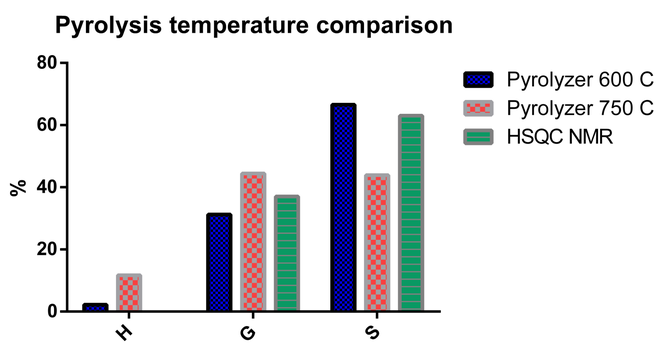
GC-MS

## Results

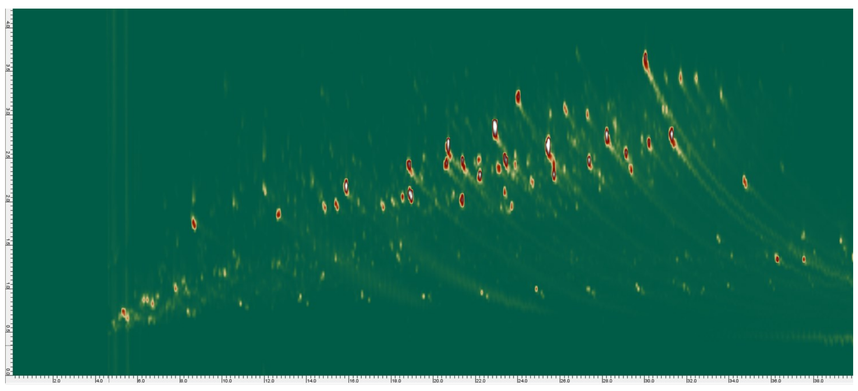
### Pyrolysis-GC-MS

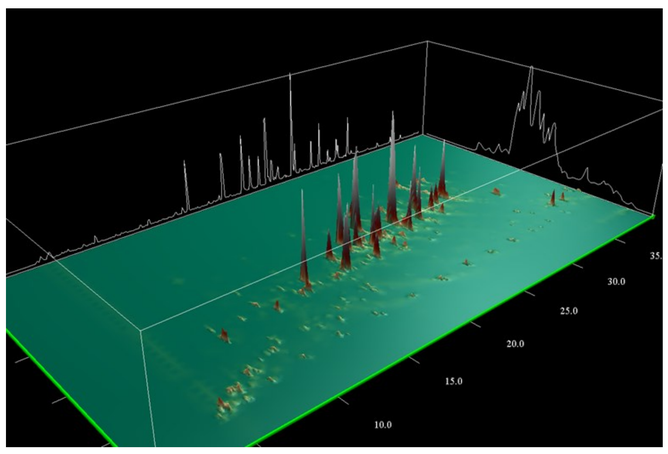



### Pyrolysis-GCxGC-MS





## Conclusions

- Pyrolysis-GC-MS is a good alternative for lignin characterization.
- Lignin composition results for both pyrolyzers (PTV and Pyroporobe) were comparable to other methods like HSQC NMR.
- Pyrolysis at 750 C increased the amount of secondary reaction products (H). Ratios of H, G and S obtained at 600 °C are in line with ratios established with HSQC NMR.
- Pyrolysis of lignin in solution (THF or water) was possible by prior solvent evaporation in the PTV.
- Differences of lignin samples from different feedstock but same isolation process were corroborated using the proposed methods.
- Pyrolysis-GCxGC-MS is a potential tool for a better lignin characterization

## Further work

- Development and optimization of the SEC method for lignin analysis
- Interface the SEC to the pyrolysis-GC-MS for an online characterization of lignin samples
- Optimization of the pyrolysis-GCxGC-MS method
- Application of the method to different lignin and humin samples

## References

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