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New insights into the molecular structure of kraft lignins and an IR-based method for rapid lignin structure characterization

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PURPOSE OF THE ABSTRACT

Biorefinery operations preferably need to find ways to utilize lignin as a source for value-added production of renewable chemicals and materials. However, its highly complex and variable chemical structure not only hampers its utilization, but also requires an extensive suite of analytical instruments to characterize. Lignin valorization, and indeed biorefinery operations in general, would therefore benefit from more detailed insight into the structure of lignin, as well as from more rapids methods to obtain this information.

Here, we report that straightforward Attenuated Total Reflection-FTIR analysis combined with Principle Component Analysis (PCA) and Partial Least Squares (PLS) modelling can provide remarkable insight into the structure of technical lignins, giving quantitative results that are comparable to standard GPC and 2D HSQC NMR methods. A large calibration set of different technical (fractionated) lignin samples, covering kraft, soda and organosolv processes, were prepared and analyzed using traditional GPC and NMR methods, as well as by readily accessible ATR-FTIR spectroscopy. PLS models correlating the ATR-FTIR spectra of the broad set of lignins with GPC and NMR measurements were found to predict the molecular weight (Mn, Mw) and inter-unit abundances (?-O-4, ?-5 and ?-?) very well, with low relative errors as estimated from cross-validation results. The resulting model could thus accurately predict the structural characteristics of an independent validation set of lignins with good accuracy. The results demonstrate that simple lignin ATR-FTIR analysis, combined with multivariate analysis techniques such as PCA and PLS modelling, can provide a wealth of structural information, at the same time improving the reproducibility of routine lignin characterisation measurements and reducing time, cost and equipment requirements [1].

Furthermore, we report the most detailed description of the kraft lignin structure to date, based on NMR analyses of the prototypical kraft lignin Indulin AT and de novo synthetic kraft lignins obtained from (13C-labeled) dimeric and polymeric lignin models.[2] Analysis of the 2D HSQC spectra of Indulin AT and a set of polarity-separated fractions allowed for approximately 40-50% of the aromatic groups to be quantified, as part of native or kraft-generated linkages. Interestingly, linkage abundance varied greatly as function of Mw, providing better understanding of the chemistry that occurs during kraft pulping and offering opportunities for Mw-specific valorization processes. The synthetic kraft materials allowed a new, minor component to be isolated, which proved highly diagnostic and led to the discovery of a new condensation pathway involving homovanillin as key intermediate. Notably, this new linkage could be identified in a range of different kraft lignins, suggesting that the newly discovered pathway is involved in most, if not all, kraft lignins.

FIGURES

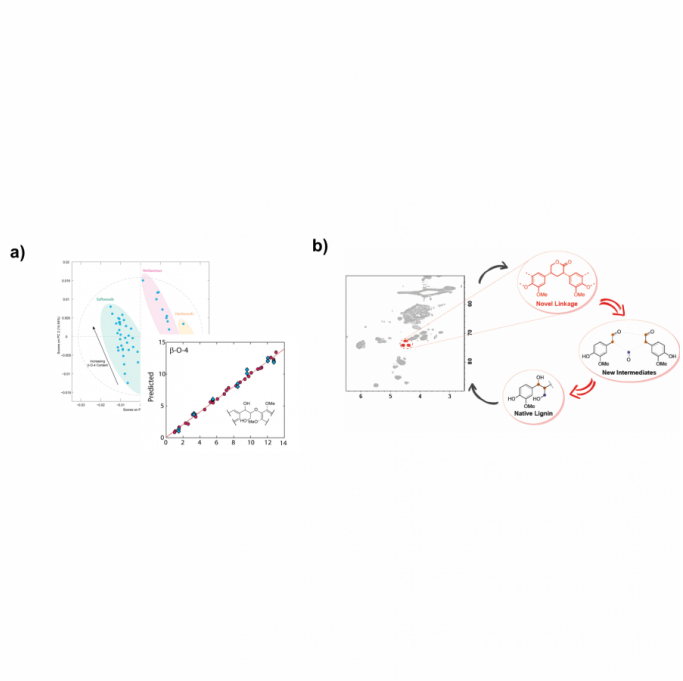

FIGURE 1

Figure 1

a) Chemometrics analysis of simple ATR-IR spectra of technical lignins provides a wealth of structural data; b) Detailed NMR analysis of kraft lignins revealed a new diagnostic structural motif.

FIGURE 2

KEYWORDS

lignin | biorefinery | analytics | chemometrics

BIBLIOGRAPHY

[1] C. S. Lancefield, S. Constant, P. de Peinder, P. C. A. Bruijnincx, submitted for publication.

[2] C. S. Lancefield, H. L. J. Wienk, R. Boelens, B. M. Weckhuysen, P. C. A. Bruijnincx, Chem. Sci. 2018, 9, 6348-6360