XXVIII Congress of the Analytical Chemistry Division
Bari 22 – 26 September 2019

O3 SS4

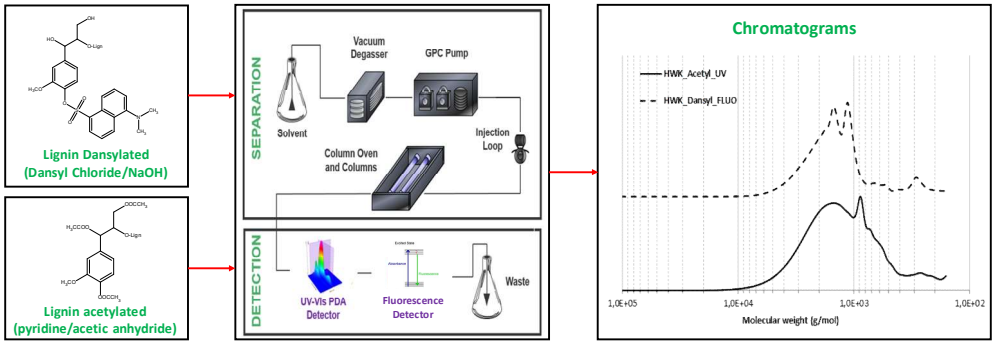
FLUORESCENCE LABELLING FOR THE STUDY OF PHENOLIC GROUPS DISTRIBUTION IN TECHNICAL LIGNIN AS A FUNCTION OF THE MOLECULAR WEIGHT

A. Salanti, L. Zoia, M. Orlandi

Department of Earth and Environmental Sciences, University of Milano-Bicocca, Milano, Italy

Lignin is a three-dimensional polymer and the second most abundant natural polymer after cellulose. With hemicelluloses, those two biopolymer constitute the so-called lignocellulosic materials. The lignin structure consists of three phenolic monomer, p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) which are linked through ether and carbon-carbon bonds resulting in heterogenic and irregular macromolecules [1]. Moreover, to separate lignin from the lignocellulose compound, intermolecular linkages are broken and modified during the pulp and paper and/or biorefinery processes. Molecular weight as well as the functional group (hydroxy, methoxy, carboxyl) are highly affected by the separation process [2]. The resulting technical lignins are indeed complex, irregular, polyphenolic compounds: this heterogeneity is the main drawback for a reliable lignin valorisation, one of the most important point in the field of biorefinery [3]. This is the reason why recently many papers were focused on lignin fractionation [4, 5]. In general, from an analytical point of view, the understanding of technical lignins is set back by the common analysis approach putting together fragments with known structural features and perhaps some newly identified motifs, and complementing this by analysing many functional groups. As reported by Potthast and co-worker, however, we have not yet arrived at a stage where we can state that we comprehend the whole picture of this fascinating molecule [6]. In order to overcome this problem and to increase our understanding of the structure of technical lignins, an alternative analytical approach have been set up. In particular, the approach in based on the fluorescence labelling of lignin with dansyl chloride, selectively and quantitatively on phenolic groups. Phenolic groups have been selected because: i) they are the main functional groups on lignin; ii) they are ease to modify; iii) in term of valorisation they are the more valuable chemical group: they have antioxidant properties and they can be converted in other reactive functionalities. The selectivity and the yield of the labelling reaction was checked by ^{31}P-NMR. Then the fluorescence labelled lignin was submitted to Gel Permeation Chromatography (GPC) coupled with a fluorescence spectrometer. The comparison of the GPC profile of a simply acetylated lignin sample (detect by UV, bearing the information related to the biopolymer molecular weight distribution) with the GPC profile of the same lignin sample, but dansyl labelled on phenolic groups, give us the opportunity to obtain information about the distribution of this important functionality as a function of the molecular weights. After data elaboration (from GPC comparison) and total phenol content measurement (by ^{31}P-NMR) it is possible to defined the phenol concentration at different molecular weight ranges. In Table 1 are reported the phenol

contents of different technical lignins at different molecular weight ranges. This information is extremely valuable for many reasons: i) it is possible to understand how the extractive process affect the lignin structure; ii) it is possible to evaluate which fraction of lignin is more suitable for one specific application. In future perspectives, this approach could be apply to other chemical group such as alcohols and carboxylic acid. In this view, we can obtain interrelations between functional groups and the molecular weight ranges, for different lignin sources. This could help to establish for technical lignins structure-property-application relationships (SPARs) that are required for any future large-scale application.



MW range (g/mol)	SWK (mmol/g)	HWK (mmol/g)	SG (mmol/g)	WS_{SE} (mmol/g)	MS_{Acid} (mmol/g)
20000-10000	0.00	0.07	0.00	0.00	0.04
10000-5000	0.99	1.41	0.14	0.36	0.29
5000-3000	2.67	2.39	1.03	1.02	0.76
3000-2000	4.07	2.77	2.14	1.65	1.37
2000-1000	6.35	3.63	4.78	2.57	1.44
1000-500	3.70	1.14	4.60	2.28	1.17
500-160	4.76	2.24	3.30	1.82	0.52

References

[1] Gellerstedt, G., Henriksson, G. (2008). Lignins: major structure, properties and applications, 1st edn. In M. lgacem & A. Gandini (Eds.), Monomers, Polymers and Composites from Renewable Resources (pp. 201-224). Amsterdam: Elsevier Science.

[2] del Rio, J. C., Rencoret, J., Prinsen, P., Martinez, A. T., Ralph, J., Gutierrez, A. (2012). Journal of Agricultural and Food Chemistry, 60(23), 5922-5935.

[3] Claudia Crestini, Heiko Lange, Marco Sette, Dimitris S. Argyropoulos. Green Chem., 2017, 19, 4104.

[4] Viktoria Rohde, Sarah Böringer, Beatrice Tübke, Christian Adam, Nicolaus Dahmen, Detlef Schmiedl. GCB Bioenergy. 2019;11:206-217.

[5] Carina A. Esteves Costa, Paula C. Rodrigues Pinto, Alírio E. Rodrigues. Separation and Purification Technology 192 (2018) 140-151.

[6] Grigory Zinovyev, Ivan Sumerskii, Philipp Korntner, Irina Sulaeva, Thomas Rosenau & Antje Potthast. Journal of Wood Chemistry and Technology, 0:1-13, 2016.