

# Advanced methods to interpret lignin $^{31}\text{P}$ NMR spectra

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## INTRODUCTION

**Different types of hydroxyl groups are the key functional groups in respect to lignin reactivity. Derivatization followed by  $^{31}\text{P}$  NMR has established its positions as a powerful analysis method in lignin chemistry in this particular area.**

Two ideas were tested in the present study, aiming at further improving the method.

- Syringyl type phenolic structures cannot be separated from the condensed G type lignin structures bearing a similar aromatic ring substitution pattern. Peak deconvolution was applied as a potential means to quantify the condensed G type phenolic structures and S type phenolic structures separately.
- The content of carboxylic acids (COOH) has in some cases been surprisingly high. Lignins were now redissolved in water and small molecular acidic degradation products were quantified by capillary electrophoresis (CE). The content of COOH bound to the polymeric lignin was then corrected accordingly.

## EXPERIMENTAL

### Lignins

- Softwood (SW) and hardwood (HW) kraft lignins were oxidized in alkali under oxygen delignification conditions: 0,6 MPa, 90°C. A series of samples were taken at 5, 10, 20, 30, 60, 120, 180 and 240 minutes. The samples were acidified to pH 2.5 and freeze-dried. By this means, all non-volatile lignin-originating reaction products were recovered.

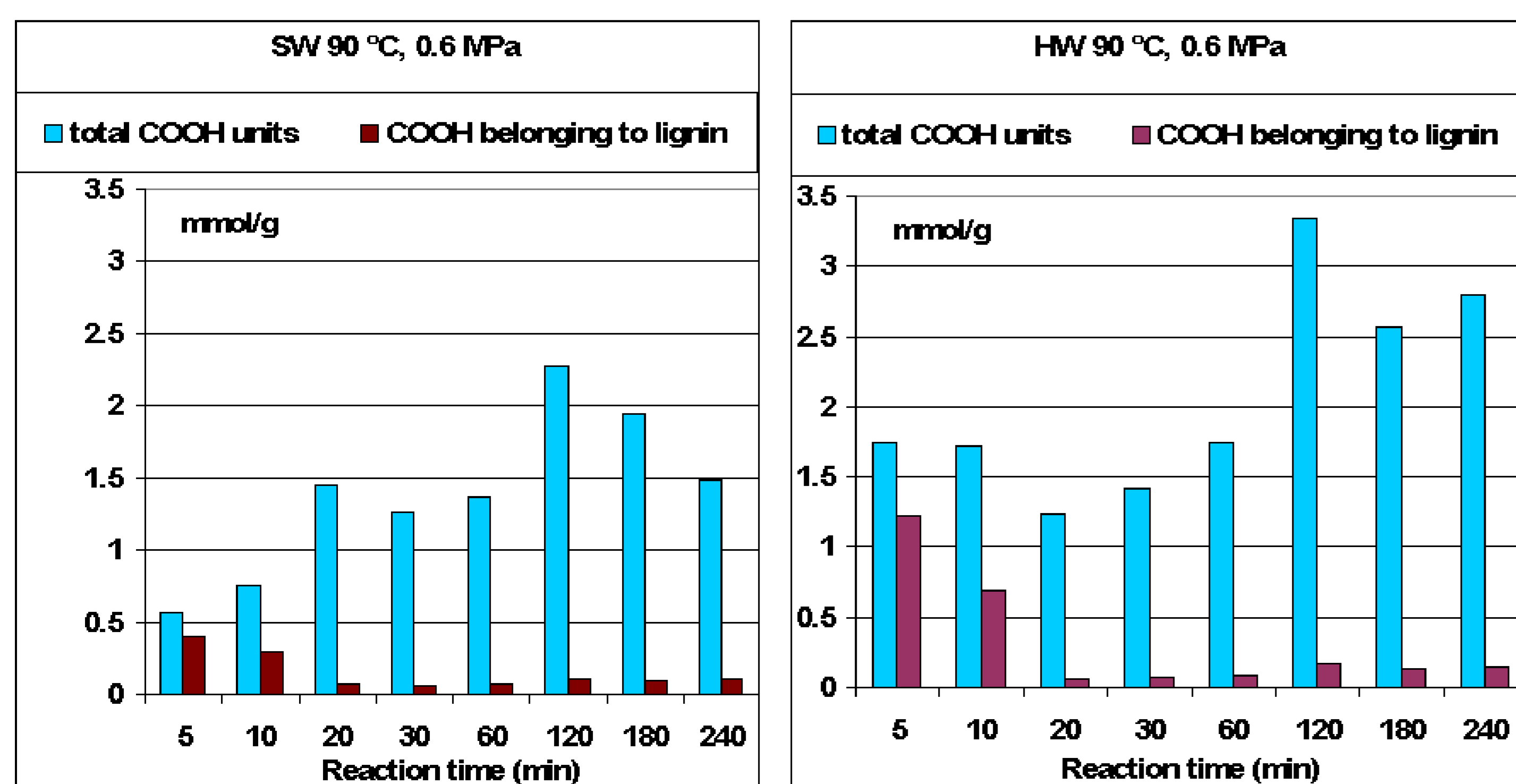
### Analyses

- $^{31}\text{P}$  NMR method was applied according to literature [1].
- Deconvolution was applied to the range of 137 - 144 ppm using GSim software and Origin program. The aim was to get detailed information about the overlapping signals of the condensed structures to be later applied for the separation of S type units from the condensed G units.
- Quantification of the small molecular carboxylic acids the re-dissolved lignin were carried out using capillary electrophoresis [2].

## RESULTS

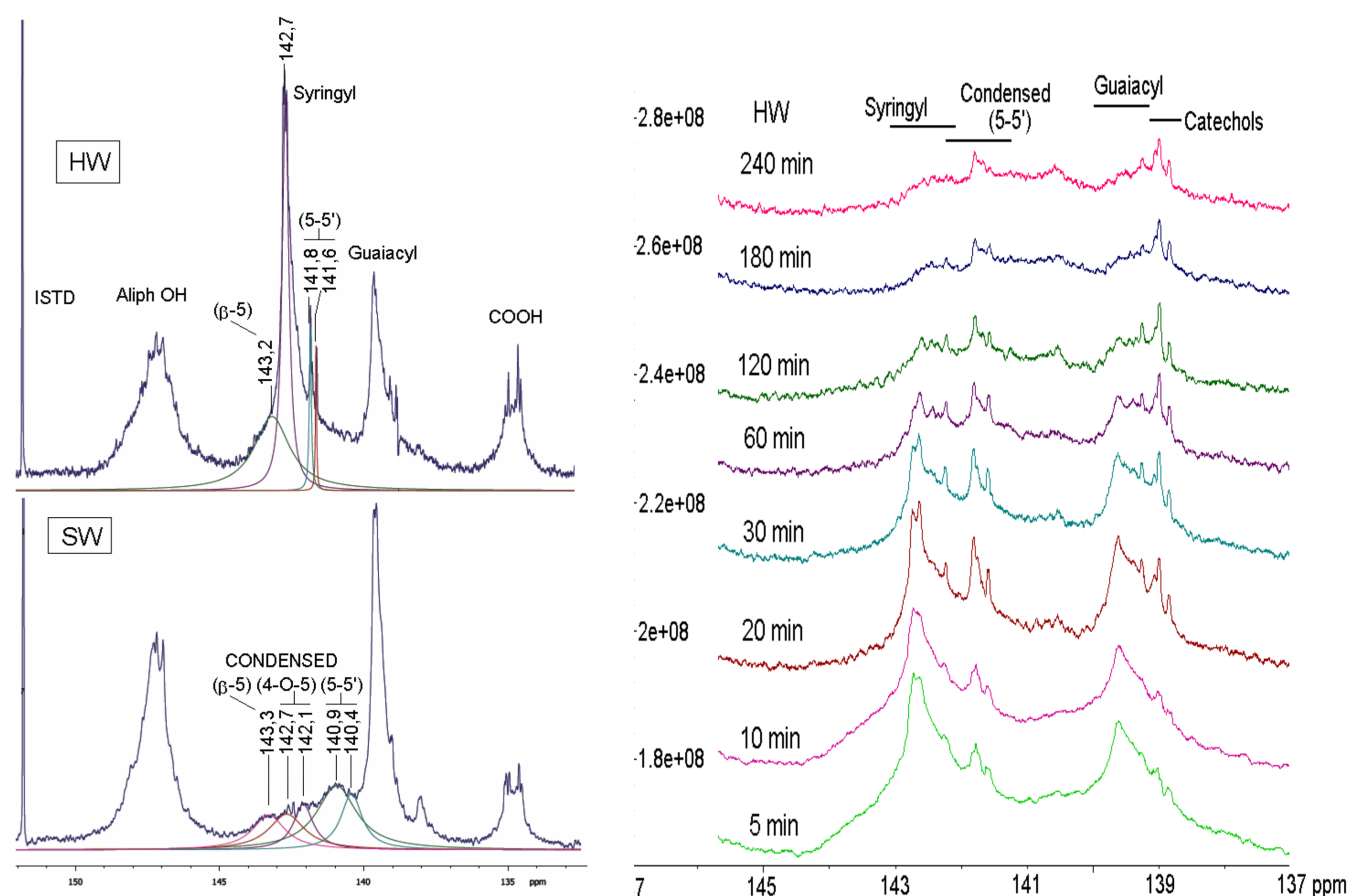
As seen in Figure 1, the total amount of non-volatile carboxylic acids formed per one gram of starting lignin increased until about 120 min oxidation in both SW and HW series, reaching values 2.3 - 3.4 mmol/g, respectively.

Analysis of the small molecular acids formed as lignin degradation products from the re-dissolved samples revealed that in fact they explain 30% - 95% of the total COOH units. Oxalic acid was the dominating acid detected. Only minor portion, i.e. 0.06 - 1.2 mmol/g of the COOH units were bound to the polymeric lignin. In this study, freeze-drying of the whole reaction solution after pH adjustment was applied as the method for sample recovery, which increased the contribution from small molecular acids. However, some acid co-precipitation is expected to take place even when lignin is recovered by acidification. Thus, the CE analysis combined with  $^{31}\text{P}$  NMR is widely applicable for lignin analyses.



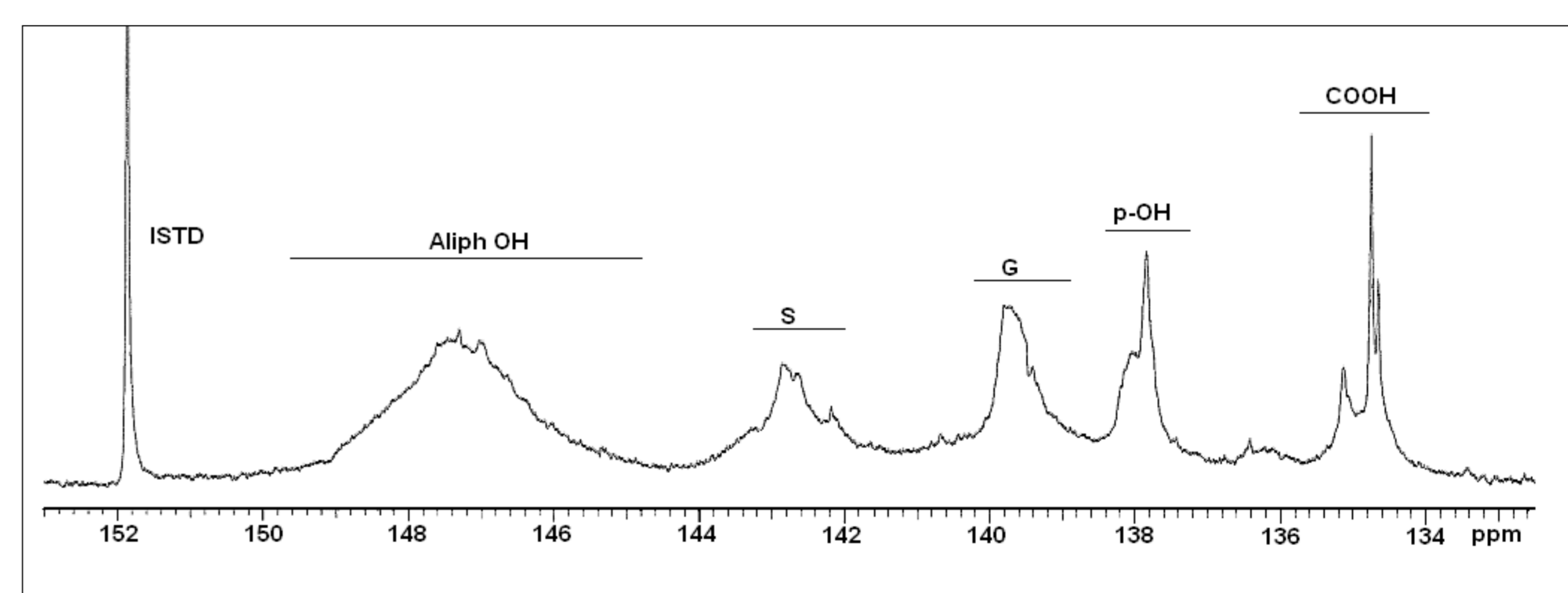
**Figure 1.** Distribution of the total COOH units vs. COOH units bound to the polymeric lignin as a function of oxidation time of SW and HW lignin and comparison to the total acid concentration found in reaction solution, relative to the amount of starting lignin.

The total amount of phenolic S type lignin and condensed G type lignin in the SW and HW samples was around 0.9 - 1.2 mmol/g and 0.3 - 0.6 mmol/g, respectively. Deconvolution of both the HW and SW samples revealed that the non-resolved signals belong mainly to 5-5' biphenylic structures and to a lesser extent to 4-O-5' structures (Figure 2, left). In HW samples the ratio of signals of S and condensed structures decreases as a function of time roughly from 1:1 to less than 0.3:1 (Figure 2, right).



**Figure 2.**  $^{31}\text{P}$  NMR spectra with deconvoluted signals of the SW and HW samples (Left).

Even if the methods were developed using wood lignins, they are applicable to a wide range of raw materials, as exemplified by the  $^{31}\text{P}$  NMR spectrum of reed canary grass lignin in Figure 3.



**Figure 3.**  $^{31}\text{P}$  NMR spectra of a reed canary grass lignin from VTT organosolv cooking (courtesy of Hannu Mikkonen and Sami Alakurtti, VTT)

## CONCLUSIONS

- The formation of carboxylic acids can be followed by  $^{31}\text{P}$  NMR. In addition, the formation of small molecular acidic degradation products can be determined using CE. This way, it is possible to distinguish the carboxylic acids bound to the lignin macromolecule from the cleaved reaction products.
- Deconvolution of the  $^{31}\text{P}$  NMR spectra is a promising means to get more detailed information of the various types of substituted phenolic structures.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] Granata, A., Argyropoulos, D.S. *J. Agric. Food Chem.* 43 (1995)1538 - 544.
- [2] S. Rovio, A. Kalliola, H. Sirén, T. Tamminen, Determination of the carboxylic acids in acidic and basic process samples by capillary zone electrophoresis. *J. Chromatogr. A* 2010, 1217, 1407 - 1413.