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Identification and quantification of lignin monomers and oligomers using GC × GC - FID/MS from reductive catalytic fractionation of pine wood

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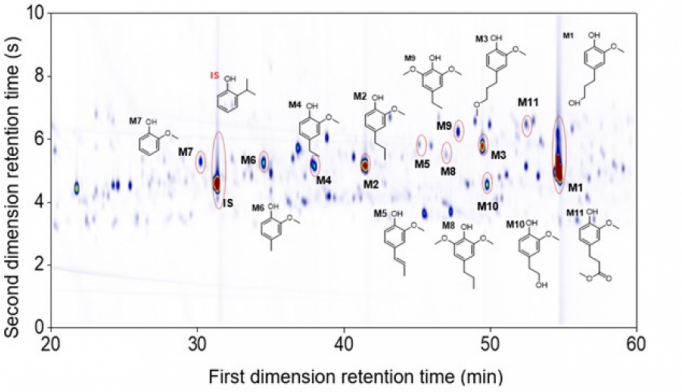
PURPOSE OF THE ABSTRACT

Thorough lignin characterization is vital to reveal and appreciate the physicochemical properties of lignin and to evaluate lignocellulose biorefinery processes. Comprehensive two-dimensional GC × GC is a powerful analytical technique widely applied for complex mixtures due to its effective separations, large peak capacity, and high sensitivity. In this study, an in-depth characterization of lignin oil, obtained from Reductive Catalytic Fractionation (RCF) of pine wood, was performed with quantitative GC × GC - FID analysis and qualitative GC × GC - MS. By utilizing high-temperature resistant column sets in the GC × GC system and by applying a derivatization step, unambiguous detection of lignin monomers, dimers, and trimers is enabled. In addition to confirming the identity of eleven monomers, corresponding to 34 wt% of the RCF lignin oil, thirty-six dimers (16 wt%) and twenty-one trimers (7 wt%) were comprehensively identified and quantified, molecularly describing an additional 23 wt% of the RCF lignin oil. The proposed structures reveal structural details of the interlinkages present in the dimeric and trimeric oligomers, containing ?-5, ?-1, ?-?, 5-5, and a minor number of ?-O-4 and 4-O-5 bonds. Furthermore, aliphatic end-units in the dimeric and trimeric molecules were identified, consisting of multiple 4-position substituents that have been previously observed in RCF-derived lignin monomers. The identified structures of individual dimer and trimer molecules by GC × GC align with and further complement the recent findings from 1H-13C HSQC NMR spectroscopy, demonstrating meaningful complementarity between both 2D techniques to obtain a holistic view on both the molecular structures and the distribution of bonds and end-units in RCF oil. Furthermore, the RCF oil was separated into six fractions and analyzed. The structural motifs (inter-unit linkages and end-units) found in the fractions vary significantly, such that lignin fractions extracted in more polar solvents contained higher molecular weight fragments and more hydroxyl containing structural motifs.

FIGURES



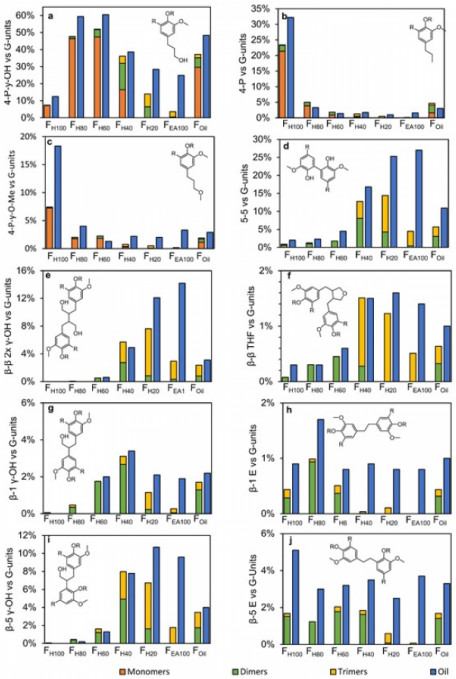


FIGURE 1

GC ? GC chromatogram of bio-oil monomeric region in the Foil sample.

FIGURE 2

Distribution of the end-units and inter-unit linkages

Distribution of the end-units and inter-unit linkages found in the monomers, dimers and trimers in the different fractions and compared to their amounts found in the entire sample.

KEYWORDS

Monophenols | Reductive Catalytic Fractionation | Biorefinery | Lignin structure

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