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Structural characterization of lignocellulosic-based pyrolysis oil by two-dimensional mass spectrometry

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Pyrolysis oils produced during biofuel manufacturing from lignocellulosic biomass, are complex organic mixtures with unpredictable compositions. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables high-confidence assignments of elemental compositions, but cannot differentiate between isomers without fragmentation [1]. Ion isolation before fragmentation is not practical for complex mixtures. Here, we use two-dimensional mass spectrometry (2D MS), in which precursor and fragment ions are correlated without isolation, for the structural characterization of pyrolysis oil.

2D mass spectra were recorded on an FT-ICR MS coupled with gated trapped ion mobility spectrometry (gTIMS) [2,3] and electron induced dissociation. For data processing, visualization, and analysis, the SPIKE and PyC2MC open-source softwares were used [4,5].

2D mass spectra enable visual identification of compounds with structural similarities from their fragmentation patterns. Resolving powers of 120,000 at *m/z* 400 were obtained for fragment ion peaks, and of 2000 at *m/z* 400 for precursor ion peaks. The autocorrelation line was extracted for elemental composition assignments, which were compared to those obtained from one-dimensional mass spectra. The correlation between precursor and fragment ion peaks was obtained for differences of the order of 10 mDa (e.g. CH_4 vs. O). Neutral loss lines were extracted and the elemental composition of the neutrals could be assigned with high confidence. Some of them corresponded to well-known compounds in pyrolysis oils (e.g. levoglucosan at $C_6H_{10}O_5$) and others were more unexpected [6]. Here, we show the performance of 2D MS of pyrolysis oil, the workflow that was established in SPIKE and PyC2MC, and we discuss the structural information that was gained for lignocellulosic-based biomass pyrolysis oil.

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