Mechanistic insight in the selective delignification of wheat straw by three white-rot fungal species through quantitative 13C-IS py-GC–MS and whole cell wall HSQC NMR

ABSTRCT

Background The white-rot fungi Ceriporiopsis subvermispora (Cs), Pleurotus eryngii (Pe), and Lentinula edodes (Le) have been shown to be high-potential species for selective delignification of plant biomass. This delignification improves polysaccharide degradability, which currently limits the efficient lignocellulose conversion into biochemicals, biofuels, and animal feed. Since selectivity and time efficiency of fungal delignification still need optimization, detailed understanding of the underlying mechanisms at molecular level is required. The recently developed methodologies for lignin quantification and characterization now allow for the in-depth mapping of fungal modification and degradation of lignin and, thereby, enable resolving underlying mechanisms. Results Wheat straw treated by two strains of Cs (Cs1 and Cs12), Pe (Pe3 and Pe6) and Le (Le8 and Le10) was characterized using semi-quantitative py-GC–MS during fungal growth (1, 3, and 7 weeks). The remaining lignin after 7 weeks was quantified and characterized using ^{13}C lignin internal standard based py-GC–MS and whole cell wall HSQC NMR. Strains of the same species showed similar patterns of lignin removal and degradation. Cs and Le outperformed Pe in terms of extent and selectivity of delignification (Cs ≥ Le >> Pe). The highest lignin removal [66% (w/w); Cs1] was obtained after 7 weeks, without extensive carbohydrate degradation (factor 3 increased carbohydrate-to-lignin ratio). Furthermore, though after treatment with Cs and Le comparable amounts of lignin remained, the structure of the residual lignin vastly differed. For example, Cα-oxidized substructures accumulated in Cs treated lignin up to 24% of the total aromatic lignin, a factor two higher than in Le-treated lignin. Contrarily, ferulic acid substructures were preferentially targeted by Le (and Pe). Interestingly, Pe-spent lignin was specifically depleted of tricin (40% reduction). The overall subunit composition (H:G:S) was not affected by fungal treatment. Conclusions Cs and Le are both able to effectively and selectively delignify wheat straw, though the underlying mechanisms are fundamentally different. We are the first to identify that Cs degrades the major β-O-4 ether linkage in grass lignin mainly via Cβ–O–aryl cleavage, while Cα–Cβ cleavage of inter-unit linkages predominated for Le. Our research provides a new insight on how fungi degrade lignin, which contributes to further optimizing the biological upgrading of lignocellulose. Electronic supplementary material The online version of this article (10.1186/s13068-018-1259-9) contains supplementary material, which is available to authorized users.

Keyword: Ceriporiopsis subvermispora; Lentinula edodes; Pleurotus eryngii; Selectivity; Lignin degradation; Lignin quantification; Cα-oxidation; Ligninolytic enzymes.