Supplementary information

Towards an environmentally and economically sustainable biorefinery: heavy metal contaminated waste wood as a low-cost feedstock in a low-cost ionic liquid process

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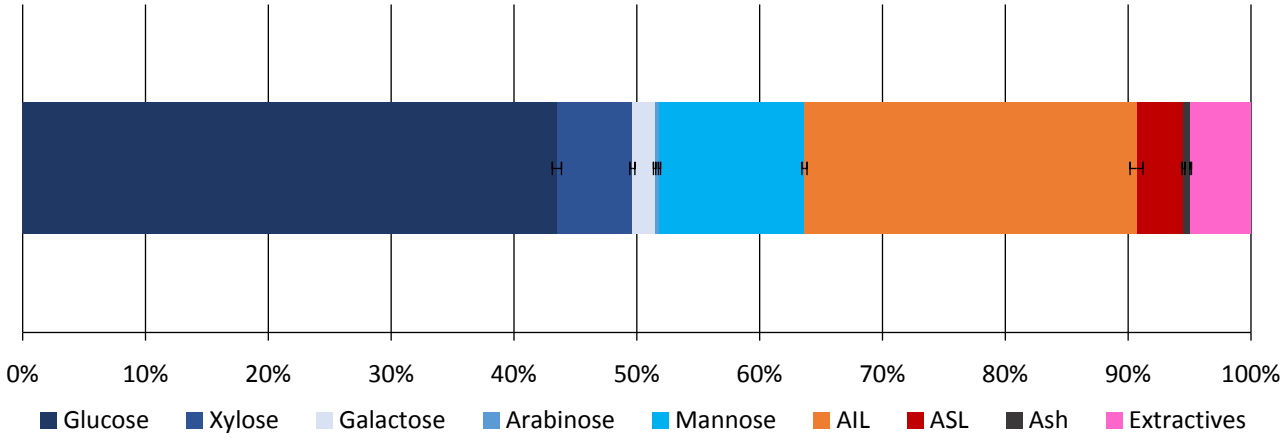

Figure S1 Compositional analysis of CCA treated wood used in the experiments. AIL: Acid insoluble lignin. ASL: Acid soluble lignin.

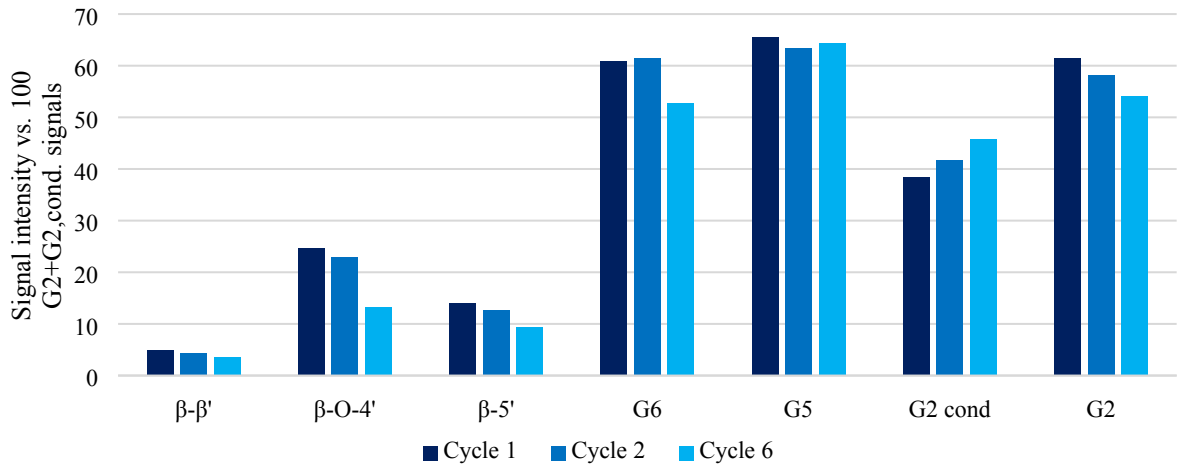

Figure S2 HSQC NMR results of lignin recovered after pretreatment of CCA treated softwood at 170°C for 30 min with fresh, recycled and 5 times recycled [HC_1im]Cl with a biomass to solvent ratio of 1:5 g/g and a final water content of 20wt%.

Metal mass balance

Using the metal content of the lignin (from ICP), the metals' mass closures were calculated (Table 1 in SI). For As and Cu the mass closures were in the vicinity of 100% for the various cycles. In the case of Cu, numbers fluctuated around 100% while they were consistently below 100% for As. Volatilisation of As compounds is a possible explanation for this observation, however it is unclear whether this would have happened during one of the biomass processing steps or during the sample preparation for ICP analysis. Also, it should be noted that the errors associated with the various measurements result in a relatively large overall error. In the case of Cr often more than 100% of the theoretical maximum was found and large variations were observed across the triplicate experiments. While all numbers are corrected for a blank IL which went through the same process steps of ethanol and water addition and evaporation, it cannot be excluded that minor Cr contamination was introduced to one or more of the samples, e.g. from the use of stainless steel spatulas.

Despite the deviation within the triplicate experiments being fairly small, a spike is observed at cycle 4 where 102% of Cu appeared to have been found in the IL liquor while also the As percentage in the liquor showed an increase. Inhomogeneity in the sample or external contamination were considered unlikely, owing to the narrow range within the triplicate repeats and the lack of external As sources in the laboratory. It is therefore considered most likely to be a minor error in the ICP analysis. An apparently higher concentration of As and Cu in one cycle would then reflect negatively on the next cycle, where the concentration of the IL in the earlier cycle is the baseline for the consecutive cycle. Cr appeared to be unaffected by this outlier, quite possibly due to the system having reached a saturation limit (1100-1200 ppm) as we saw in Figure 2 (b) where Cr concentration in the IL stagnated after cycle 4.

Table S1 Mass closures from ICP-OES analysis of pulp, lignin and brown liquor isolated after each cycle of pretreatment of CCA treated timber. CCA treated wood was pretreated with [HC_1im]Cl for 30 min at 170°C at a biomass to solvent ratio of 1:5 g/g and a final water content of 20wt%. Standard errors were calculated for triplicate measurements.

	Cu	**Cr**	**As**
Cycle 1	94.7±4.3%	95.1±4.3%	92.3±3.0%
Cycle 2	93.8±0.7%	111.4±2.9%	98.1±0.8%
Cycle 3	99.0±2.4%	125.9±0.2%	97.6±1.8%

Cycle 4	105.4±2.9%	133.1±26.4%	99.6±6.7%
Cycle 5	98.9±7.2%	109.7±19.6%	92.9±6.3%
Cycle 6	105.4±2.3%	128.9±4.2%	97.8±0.9%

Table S2 Metal contents relative to the initial metal content found in the brown liquor after applying a potential of -0.7 V on a screen-printed electrode. Recycled [HC_1im]Cl was obtained from 6 cycles of pretreatment of CCA treated timber for 30 min at 170°C at a biomass to solvent ratio of 1:5 g/g and a final water content of 20wt%. Standard errors were calculated for triplicate measurements.

	after 2 min	after 5 min	after 10 min
Cu	93.8±4.8%	93.6±0.7%	91.6±3.6%
Cr	89.0±4.6%	89.0±0.9%	88.9±2.9%
As	84.6±5.2%	86.4±1.7%	85.3±2.5%