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Figure S1: Solubility of 65%, 75%, 85% and 95% EOL (4 h reflux) in THF (50 mg/mL).



Figure S2: Partial short range ¹³C-¹H (HSQC) correlation spectra (aromatic region only) of organosolv lignins **a** 95% EOL-4 h, **b** 95% AOL-4 h, **c** 95% DOL-4 h isolated from *Miscanthus giganteus*.



Figure S3: Partial **a** HSQC and **b** HMBC spectra of 95% EOL-4 h, establishing the long range correlations between signals 5 in Ara*f* and alpha and beta positions in *p*CA/FA to the carbonyl in the ester linkage.



Figure S4: Partial (oxygenated aliphatic region) **a** HSQC and **b** HSQC-TOCSY spectra of 95% AOL-4 h showing *p*-coumaric acid is linked to C5 of arabinofuranose.



Fig. S5: Partial **a** HSQC (aliphatic region) and **b** HMBC (oxygenated aliphatic region) and **c** HMBC (oxygenated aliphatic region) spectra of 95% AOL-4 h showing modification of hydroxyl groups at C1 and C2 of arabinofuranose by acetone.



Figure S7: FTIR spectra of 95% EOL with 2, 4 and 8 h reflux time.

Labels	δ_C/δ_H (ppm)	Assignment
S _{2,6}	103.6/6.62	C _{2,6} -H _{2,6} in etherified syringyl units (S)
G_2	110.8/6.92	C ₂ -H ₂ in guaiacyl units (G)
FA ₂	110.9/7.32	C ₂ -H ₂ in ferulate units (FA)
FA_{β}	113.7/6.30	C_{β} -H _{β} in ferulate units (FA)
pCA_{β}	114.4/6.47	C_{β} -H _{β} in <i>p</i> -coumarates units (<i>p</i> CA)
G_{5}/G_{6}	114.8/6.94 and 119.8/6.76	C_5 - H_5 and C_6 - H_6 in guaiacyl units (G)
<i>p</i> CA _{3,5}	115.1/6.75	$C_{3,5}$ -H _{3,5} in <i>p</i> -coumarates units (<i>p</i> CA)
FA ₆	122.9/7.14	C ₆ -H ₆ in ferulate units (FA)
<i>p</i> CA _{2,6}	130.0/7.55	$C_{2,6}$ -H _{2,6} in <i>p</i> -coumarates units (<i>p</i> CA)
pCA_{α}	144.4/7.55	C_{α} -H _{α} in <i>p</i> -coumarates units (<i>p</i> CA)
FA _α	144.6/7.46	C_{α} -H _{α} in ferulate units (FA)

Table S1: Assignments of the main ${}^{13}C{}^{-1}H$ correlation signals in the HSQC spectra of organosolv lignins from *Miscanthus giganteus* (aromatic area).