Supplementary information

Understanding the in-situ state of lignocellulosic biomass during ionic liquids-based engineering of renewable materials and chemicals

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Table S1 NMR chemical shift assignments for lignocellulose-derived structures

Component origin	Specific functional group	Chemical shift (ppm)
	^{13}C NMR*	
Lignin	Aldehyde/ketone (C═O)	220−187
	−COO/CH_3COO	173
	Aromatic C—O ($G_{3(e)}$ and $G_{3(ne)}$)	153−147
	Aromatic C—O ($G_{4(e)}$ and $G_{4(ne)}$)	147−143
	Aromatic C—C ($G_{1(e)}$)	137−134
	Aromatic C—C ($G_{1(ne)}$)	131
	Aromatic C—H (G_6)	120
	Aromatic CH (G_5)	115
	Aromatic CH (G_2)	112
Hemicellulose	OCHO of (C_1)	109−97
Cellulose	OCHO of (C_1)	105
	CHOH of (C_4)	89
	CHOH of (amorphous C_4)	84
Lignin	C_β-OR	86−82
Hemicellulose	Arabinan CHOH of (C_2, C_3, C_4)	86−80
	Xylan CHOH of (C_2, C_3, C_4)	80−73
Cellulose	CHOH of (C_2, C_3, C_5)	75
Lignin	C_α-OR of lignin	76−72
Cellulose	CHOH of (C_2, C_3, C_5)	72
	CH_2OH of (crystalline C_6)	66
	CH_2OH of (amorphous C_6)	63
Hemicellulose	CH_2OH of (amorphous C_5)	63-61
Lignin	C_γ—OR	64−60
	OCH_3	56
	α, β methylene groups	29−31
Hemicellulose	CH_3	21.6
Lignin	γ methyl in *n*-propyl side chain	15.5

	^{1}H NMR*	
Hemicellulose	OCH_3	2.2–3.2
	CH_2OH of (amorphous C_5)	3.2−3.9
	Xylan CHOH of (C_1, C_2, C_3, C_4)	3.2−4.3
	Arabinan CHOH of (C_1, C_2, C_3, C_4)	3.6−5.2
Lignin	H_β in β–β structure	3.2–3.4
	Methoxyl proton	3.4–4
	Hγ in β-*O*-4 aryl ether	4.1–4.6
	H_β in β-*O*-4 aryl ether	4.8
	H_β in benzyl aryl ether	5.3–5.8
	Aromatic H in syringyl unit	6.6
	Aromatic H in guaiacyl unit	6.7–6.9
	Ethylenic and aromatic protons in *p*-coumaric and ferulic acids	7.3–7.6
	^{31}P NMR#	
Lignin/ Cellulose	Aliphatic OH	150.0-145.0
Lignin	5-Substituted OH	145.0–141.0
	Guaiacyl OH	141.0–138.5
	p-Hydroxyphenyl OH	138.5–136.5
	COOH	136.0–133.5

Sources: *Holtman et al., 2010. DOI: 10.1021/jf101258x; Wen et al., 2010. DOI: 10.1021/jf1032153; #Pu et al., 2011. DOI: 10.1039/C1EE01201K; Balakshin & Capanema, 2015. DOI: 10.1080/02773813.2014.928328; Ben et al., 2018. DOI: 10.3389/fenrg.2018.00013

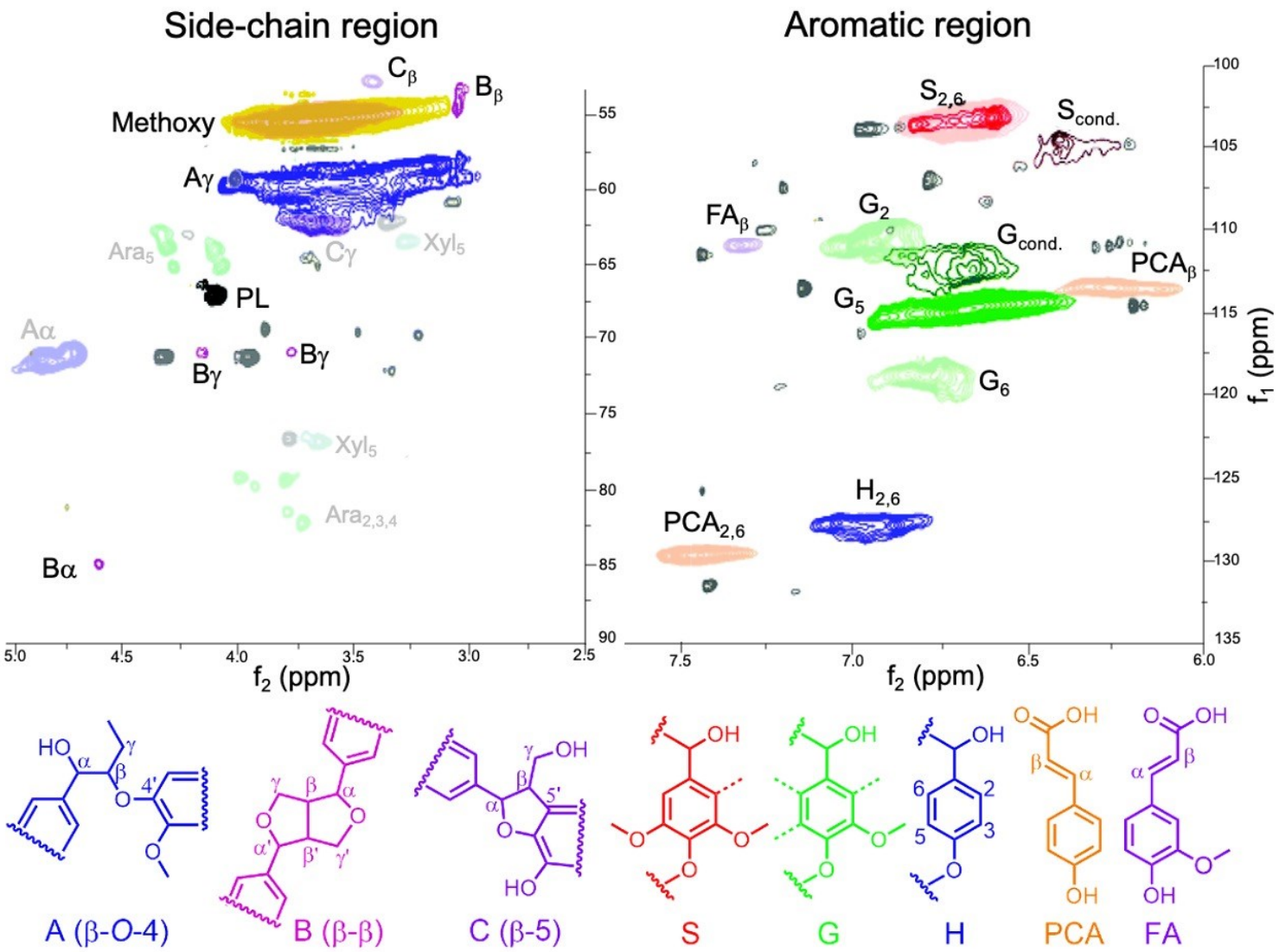
Side-chain region
Aromatic region
Cβ
Bβ
Methoxy
Aγ
Ara5
Cγ
Xyl5
PL
Aα
Bγ
Bγ
Xyl5
Ara2,3,4
Bα
f2 (ppm)
S2,6
Scond.
FAβ
G2
Gcond.
PCAβ
G5
G6
H2,6
PCA2,6
f2 (ppm)
f1 (ppm)
A (β-O-4)
B (β-β)
C (β-5)
S
G
H
PCA
FA

Fig. S1 2D-HSQC (heteronuclear single quantum coherence) NMR spectra of *Miscanthus* lignin extracted using 4:1 triethylammonium hydrogen sulfate and water (v/v) at 120 °C for 3 days. Differences between the faded spectra, which was recorded after 1 h, and the darkened spectra, which was recorded after 3 days, elucidate the disappearance of carbohydrate moieties, aryl ether, phenylcoumaran and lignin-carbohydrate sub-unit linkages (PCA, FA), as well as conversion of phenolic sub-units into condensed and demethoxylated (H-lignin) forms (adapted from Brandt-Talbot et al., 2017, DOI: 10.1039/C7GC00705A).