Supporting Information

Selective Modification of Aliphatic Hydroxy Groups in Lignin Using Ionic Liquid

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Table of Contents

The file includes: Experimental and Characterization sections including Figure S1−S7 and Table S1

Comparison of acyl donor activities of PhOAc and IPAc

To verify the activity of PhOAc as an acyl donor for acetylation of Ph-EtOH under the EmimOAc catalyst, a model transesterification of Ph-EtOH with an equimolar amount of PhOAc was performed at 80 ºC and analyzed by in situ ^{1}H NMR. As shown in Figure S1, acetyl (Ac) conversion of Ph-EtOH with PhOAc rapidly reached to 90% for only 3 h, whereas that with IPAc remained less than 70% until 12 h. This result demonstrated that the PhOAc works as an acyl donor with higher activity than that of IPAc.

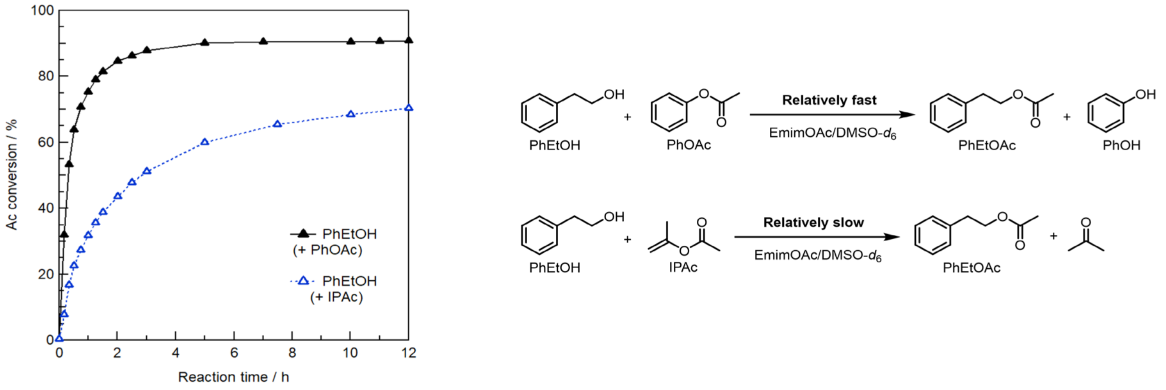

Figure S1. Conversions of Ph-EtOH (0.38 mol L^{-1}) in transesterification reaction with different acyl donors of PhOAc or IPAc (each 0.38 mol L^{-1}) for 12 h at 80 ºC catalyzed by EmimOAc (0.38 mol L^{-1}), as determined by in situ ^{1}H NMR in DMSO-d_6.

Transesterification of a mixture of Ph-EtOH and PhOH using excess IPAc and a catalytic amount of EmimOAc

To investigate an effect of the excess use of IPAc (3 eq./[R-OH]) in transesterification of a mixture of PhOH and Ph-EtOH under a catalytic amount of EmimOAc (1 eq./[R-OH]). Figure S2 shows the difficulty in complete deacetylation of the generated PhOAc until 10 h because PhOH was continuously acetylated by the excess IPAc. In addition, the rack of required proton donor such as Ph-EtOH could prevent the effective deacetylation of PhOAc.

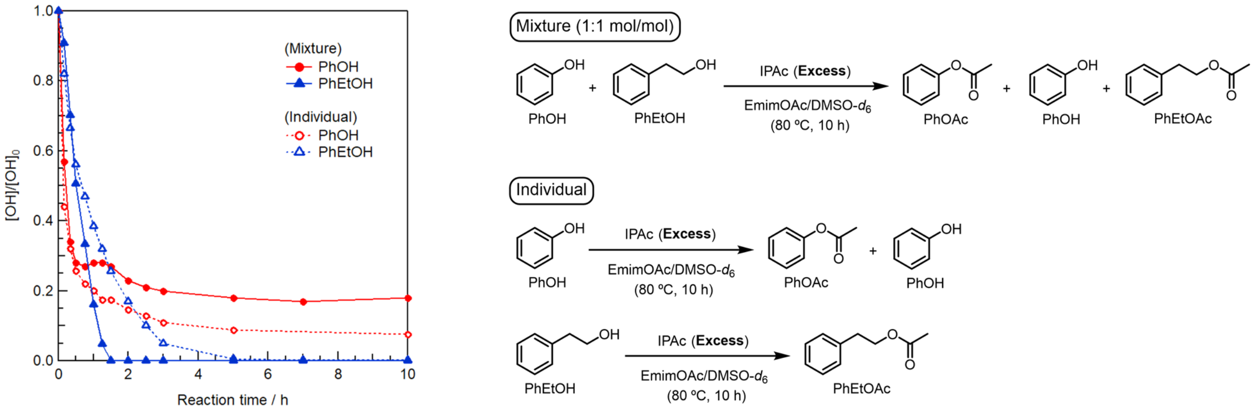

Figure S2. Changes in the relative contents of PhOH and Ph-EtOH (each 0.38 mol L^{-1}) in transesterification of the mixture with excess IPAc (1.14 mol L^{-1}) for 10 h at 80 ºC catalyzed by EmimOAc (0.38 mol L^{-1}), compared with those in transesterification of individual PhOH or Ph-EtOH under the same condition, as determined by in situ ^{1}H NMR in DMSO-d_6.

Effect of reaction time on selective modification of R-OH group within Kraft lignin

In order to investigate an effect of reaction time in the step (ii) on the deacetylation of Ar-OAc groups, the one-pot two-steps reaction using an excess IPAc (12 eq./[R-OH]) was preliminary performed with changing the time from 0 to 24 h. As shown in Figure S3, the generated Ar-OAc groups in the step (i) was gradually deacetylated, demonstrating that a resultant selective modification of R-OH groups in Kraft lignin with Ac group was realized by the prolongation of deacetylation time in the step (ii), even when the excess IPAc was applied.

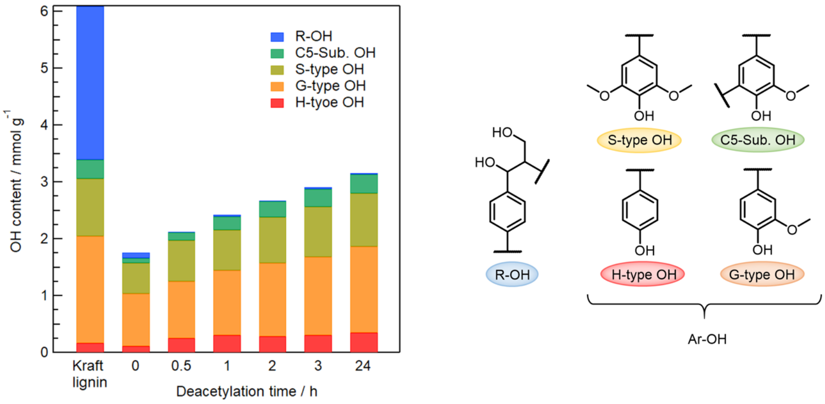

Figure S3. OH contents of R-OH and Ar-OH (H/G/S-types and C5-Sub. OH) groups in Kraft lignin before and after acetylation using IPAc (12 Equation/[R-OH]) at 80 ºC for 1 h and subsequent selective deacetylation with added water (2 Equation/[Ar-OH]) at 80 ºC for 0–24 h in an EmimOAc/DMSO mixed system.

Quantitative ^{31}P NMR measurements after phosphitylation

The determined OH content of the Kraft lignin used in this study and detail assignments of each kind of OH group were summarized in Table S1. Figure S4 shows the observed quantitative ^{31}P NMR spectra of the phosphitylated original Kraft lignin and the acetyl derivatives, Lig-Ac (Selective) and Lig-Ac (Full).

Table S1 OH contents of the used Kraft lignin and the assignments in quantitative ^{31}P NMR

OH group		Assignment / ppm	OH content / mmol g^{-1}
Aromatic OH		137.1–144.0	3.69
	C5-substituted	140.0–144.5	1.07
	Syringyl	141.9–143.0	0.24
	Guaiacyl	138.7–140.2	2.06
	p-Hydroxyphenyl	137.4–137.8	0.21
Aliphatic OH		145.4–150.0	2.46
Carboxylic OH		133.6–136.0	0.46
Total			6.61

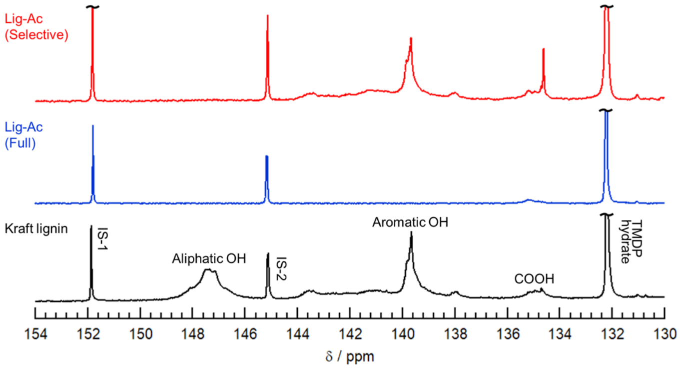

Figure S4. Quantitative ^{31}P NMR spectra of the phosphitylated Lig-Ac (Selective), Lig-Ac (Full), and Kraft lignin measured in $CDCl_3$/pyridine mixed solvent using two kinds of ISs and a relaxation reagent.

Size Exclusion Chromatography (SEC)

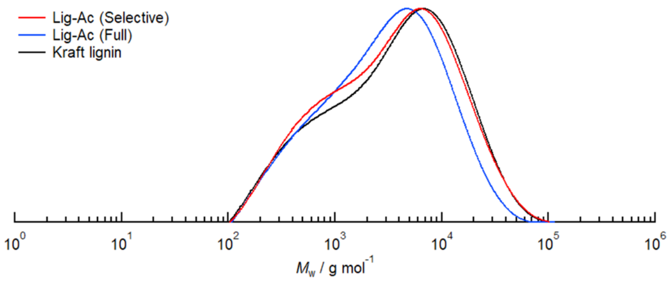

Figure S5. Molecular weight distributions of Lig-Ac (Selective), Lig-Ac (Full), and Kraft lignin measured by SEC in 0.01 mol L^{-1} LiBr/DMF solution.

Solubility test

Figure S6 shows the representative pictures of Lig-Ac (Selective), Lig-Ac (Full), and Kraft lignin in chloroform/methanol mixed solvent (8:2, v/v). The original Kraft lignin hardly dissolved, but both the acetyl derivatives sufficiently dissolved in it, indicating that the selective acetylation of R-OH groups in Kraft lignin sufficiently contributed to improve the solubility of Lig-Ac (Selective), despite of the low substitution degree compared with that of Lig-Ac (Full).

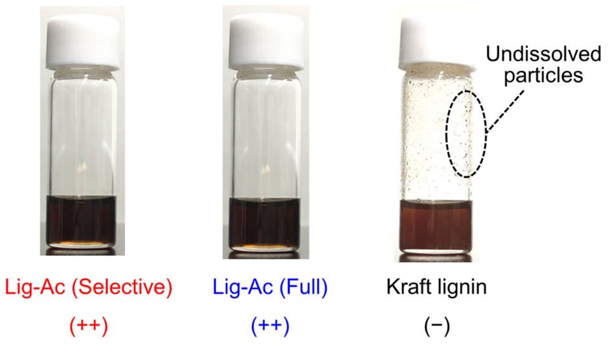

Figure S6. Pictures of solutions of Lig-Ac (Selective), Lig-Ac (Full), and Kraft lignin in chloroform/methanol (8:2, v/v) solution.

Heat-flow tester

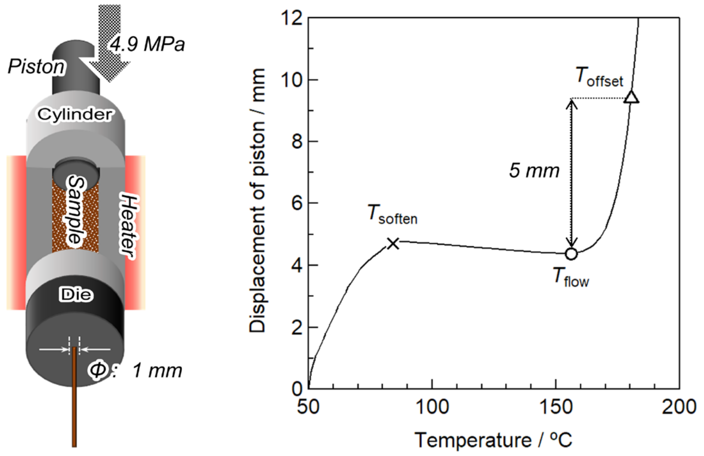

Figure S7. Heat-flow tester diagrams.