Electronic Supplementary Information

Effects of hydrothermal pretreatment on the structural characteristics of organosolv lignin from Triarrhena lutariioriparia

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The acetylation of lignin

50 mg of lignin sample was dissolved in a 3 mL solution of DMSO: N-Methylimidazole (2: 1, v/v). The dissolution was performed on a shaker at room temperature for 24 h in the dark. After that, 1 mL of acetic anhydride was added into the solution for an additional 1.5 h. At the end of the designated time, the solution was dropped slowly into 300 mL of acid water (pH = 2.0) adjusted by HCl to induce precipitation, and the precipitate was washed thoroughly with acid water (pH = 2.0) until significant reducing of pungent odor, and then freeze-dried to obtain the acetylated lignin. Extracted lignin samples were synchronous acetylated, which can be well compared with acetylated DELs.

The calculation of severity log $R_0$

In this section, the severity of hydrothermal treatment was mentioned in terms of the severity log $R_0$, which quoted the results of Wang 2016 to demonstrate that the oligosaccharides were mainly released among the hydrothermal conditions in this study.

Wang et al reported that the severity log $R_0$ was calculated by the following formula according to previous paper [1],

$$\log R_0 = \log \left[ R_{\text{HEATING}} + R_{\text{ISOTHERMAL}} + R_{\text{COOLING}} \right]$$

$$= \left[ \log \int_{t_H}^{t_C} \exp \left( \frac{T(t) - T_{\text{REF}}}{\omega} \right) \cdot dt \right] + t_C \cdot \exp \left( \frac{T(t) - T_{\text{REF}}}{\omega} \right) \cdot \omega$$

where $t_H$ (min) is the time needed to achieve the target temperature, $t_C$ (min) is the time needed for the whole heating–cooling period, $t$ (min) is the retention time, and $T(t)$ represents the treatment temperature (°C). Calculations were made based on the values reported in the literature ($\omega$ and $T_{\text{REF}}$ are 14.75 and 100 °C, respectively) [1, 2].

References

[1] Overend, R.P.; Chornet, E.; Gascoigne, J.A. Fractionation of Lignocellulosics by Steam-Aqueous
Pretreatments [and Discussion]. *Philos Trans R Soc Lon A Math Phys Eng Sci*. **1987**, *321*, 523-36; DOI: 10.1098/rsta.1987.0029.

[2] Kim, Y.M.; Kreke, T.; Mosier, N.S.; Ladisch, M.R. Severity factor coefficients for subcritical liquid hot water pretreatment of hardwood chips. Biotechnol Bioeng. **2013**, *111*, 254-63; DOI: 10.1002/bit.25009.

**Table S1.** The abbreviations and elaboration of product obtained from hydrothermal and organic acid treatment

| Name       | Add hydrothermal process | Reaction temperature (°C) | Reaction time (min) | Description                                                                 |
|------------|--------------------------|---------------------------|---------------------|-----------------------------------------------------------------------------|
| H170-30    | Yes                      | 170                       | 30                  | The liquid product obtained from hydrothermal process                       |
| H170-60    | Yes                      | 170                       | 60                  | The liquid product obtained from hydrothermal process                       |
| H180-30    | Yes                      | 180                       | 30                  | The liquid product obtained from hydrothermal process                       |
| P170-30    | Yes                      | 170                       | 30                  | The residue obtained from hydrothermal pretreatment                         |
| P170-60    | Yes                      | 170                       | 60                  | The residue obtained from hydrothermal pretreatment                         |
| P180-30    | Yes                      | 180                       | 30                  | The residue obtained from hydrothermal pretreatment                         |
| Ocontrol   | No                       | -                         | -                   | The residue obtained from direct organic acid treatment of TL                |
| OP170-30   | Yes                      | 107                       | 180                 | The residue obtained from organic acid treatment of P170-30                 |
| OP170-60   | Yes                      | 107                       | 180                 | The residue obtained from organic acid treatment of P170-60                 |
| OP180-30   | Yes                      | 107                       | 180                 | The residue obtained from organic acid treatment of P180-30                 |
| Lcontrol   | No                       | 107                       | 180                 | The lignin obtained from organic acid treatment of TL                        |
| L170-30    | Yes                      | 107                       | 180                 | The lignin obtained from organic acid treatment of P170-30                  |
| L170-60    | Yes                      | 107                       | 180                 | The lignin obtained from organic acid treatment of P170-60                  |
| L180-30    | Yes                      | 107                       | 180                 | The lignin obtained from organic acid treatment of P180-30                  |

All the samples were soaked in organic acid (formic acid/ acetic acid/water, 3/5/2, v/v/v)
at 60 °C for 1 h before treated with organic acid.

**Table S2.** Assignments of $^{13}$C-$^1$H correlated signals in the HSQC spectra of the lignin

| Labels | $\delta_c/\delta_H$ (ppm) | Assignment |
|--------|--------------------------|-------------|
| $C_\beta$ | 52.9/3.47 | $C_\beta$-$H_\beta$ in phenylcomaran structures(C) |
| $B_\beta$ | 53.5/3.07 | $C_\beta$-$H_\beta$ in resinol substructures(B) |
| -OCH$_3$ | 55.4/3.71 | C-H in methoxyls |
| $A_\gamma$ | 59.8/3.59 | $C_\gamma$-$H_\gamma$ in $\beta$-O-4 substructures(A) |
| $I_\gamma$ | 61.3/4.08 | $C_\gamma$-$H_\gamma$ in cinnamyl(sinapyl/coniferyl) alcohol end groups(I) |
| X$_5$ | 62.8/3.12 | $C_5$-$H_5$ $\beta$-D-xylopyranoside substructures(X) |
| $A'_\gamma$ | 62.9/4.27 | $C_\gamma$-$H_\gamma$ in $\gamma$-acylated $\beta$-O-4 substructures(A') |
| $B_\gamma$ | 70.8/3.76 and 4.18 | $C_\gamma$-$H_\gamma$ in resinol substructures(B) |
| $A_a$ | 71.8/4.85 | $C_a$-$H_a$ in $\beta$-O-4 substructures(A) |
| $A'_a$ | 74.2/5.95 | $C_a$-$H_a$ in $\alpha$-acylated $\beta$-O-4 substructures(A') |
| $A'_\beta$(G/H) | 80.5/4.56 | $C_\beta$-$H_\beta$ in $\beta$-O-4 linked to a G/H unit(A) |
| $A_\beta$(G/H) | 83.3/4.35 | $C_\beta$-$H_\beta$ in $\beta$-O-4 linked to a G/H unit(A) |
| $B_a$ | 84.7/4.62 | $C_a$-$H_a$ in resinol substructures(B) |
| $A_\beta$(S) | 85.9/4.11 | $C_\beta$-$H_\beta$ in $\beta$-O-4 linked to a S unit(A) |
| $C_a$ | 86.9/5.47 | $C_a$-$H_a$ in phenylcomaran structures(C) |
| $S_2,6$ | 106.2/7.34 | $C_2,6$-$H_2,6$ in syringyl units(S) |
| $S'_2,6$ | 106.2/7.34 | $C_2,6$-$H_2,6$ in oxidized(C=O) phenolic syringyl units(S') |
| $G_2$ | 110.8/6.96 | $C_2$-$H_2$ in guaiacyl units(G) |
| $F_{A_2}$ | 110.9/7.26 | $C_2$-$H_2$ in ferulate (FA) |
| $pCE_8$ | 113.5/6.25 | $C_8$-$H_8$ in $p$-coumarate ($p$CE) |
| $G_5$ | 115.5/6.76 | $C_5$-$H_5$ in guaiacyl units(G) |
| $G_6$ | 118.8/6.78 | $C_6$-$H_6$ in guaiacyl units(G) |
| $H_{2,6}$ | 127.7/7.18 | $C_2,6$-$H_2,6$ in $p$-hydroxyphenyl units(H) |
| $pCE_{2,6}/pCA_{2,6}$ | 129.9/7.45 | $C_2,6$-$H_2,6$ in $p$-coumarate ($p$CE) |
| $pCE_{7}/pCA_{7}$ | 144.4/7.39 | $C_7$-$H_7$ in $p$-coumarate ($p$CE) |
**Fig. S1.** Mass balance of the hydrothermal and organic acid delignification process

All data are calculated based on the dry weight of 73.