The direct transformation of bioethanol fermentation residues for production of high-quality resins

Bo Pang\textsuperscript{a,b}, Xue-Fei Cao\textsuperscript{b}, Shao-Ni Sun\textsuperscript{b}, Xi-Luan Wang\textsuperscript{b}, Jia-Long Wen\textsuperscript{a}, Su Shiung Lam\textsuperscript{c}, Tong-Qi Yuan\textsuperscript{*,a,b}, Run-Cang Sun\textsuperscript{d}

\textsuperscript{a}Beijing Advanced Innovation Center for Tree Breeding by Molecular Design, Beijing Forestry University, No. 35 Tsinghua East Road Haidian District, Beijing, 100083, P. R. China.

\textsuperscript{b}Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, No. 35 Tsinghua East Road Haidian District, Beijing, 100083, P. R. China.

\textsuperscript{c}Pyrolysis Technology Research Group, Institute of Tropical Aquaculture and Fisheries Research (Akuatrop) & Institute of Tropical Biodiversity and Sustainable Development (Bio-D Tropika), Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

\textsuperscript{d}Center for Lignocellulose Science and Engineering, Dalian Polytechnic University, No. 1 Qing Gongyuan Gan Jingzi District, Dalian, 116034, P. R. China.

\* Corresponding author: Beijing Advanced Innovation Center for Tree Breeding by Molecular Design, Beijing Forestry University, No.35 Tsinghua East Road Haidian District, Beijing, 100083, P. R. China. Tel./fax: +86-010-6233-6903; E-mail address: ytq581234@bjfu.edu.cn (T. Q. Yuan).
1. Characterization of the lignins separated from fermentation residues

The fermentation residues were firstly dissolved into 5% sodium hydroxide solution for 1 hour under stirring at room temperature. After the preswollen process, the temperature rose to 90 °C and maintained 2 hours. The resulted mixtures were centrifuged, and the solution was directly adjusted to pH=2.0 with hydrochloric acid. The residual lignins were separated via centrifuging and then air-dried. The chemical structure of isolated lignins (L\textsubscript{1} and L\textsubscript{2}) were investigated by the NMR spectra that were obtained on a Bruker AVIII 400 MHz spectrometer (Germany). The \textsuperscript{13}C NMR and the \textsuperscript{31}P NMR analyses of the lignin samples were performed according to the method given in a previous article.\textsuperscript{1}

The molecular structural features of the two isolated lignins were investigated via the \textsuperscript{13}C NMR technique and the spectra of L\textsubscript{1} and L\textsubscript{2} are shown in Fig. S1. The assignments of these lignin signals were achieved by the reported literature.\textsuperscript{2} The signals at 124-140ppm were the aromatic signals. The G-type and H-type lignin units would lead to the formation of the stable C-C linkages that had relatively high bond energy.\textsuperscript{3} As shown in Fig. S1, there was scarce signals of carbohydrate at 102-90 ppm, which indicated that there was little residual carbohydrate in the lignins. As compared with Fig. 2, most of lignin signals were not obviously observed in the spectra of LRs. This deduced that the lignins in residues had sufficiently co-condensed with urea, formaldehyde, and phenol.

The \textsuperscript{31}P NMR technique is an effective method to quantify various hydroxyl groups in lignin.\textsuperscript{4} The Fig. S2 displays the \textsuperscript{31}P NMR spectra of L\textsubscript{1} and L\textsubscript{2} and the values of the various -OH groups in the lignin samples are listed in Table S1. The assignments and quantitative calculation methods were conducted according to previous literature.\textsuperscript{5} Generally, the non-condensed G-type and H-type phenolic hydroxyl groups are considered to be the active sites in the synthesis of lignin-based resins. Accurate and effective formulations for lignin-based resin can be designed based on the active site measurements obtained via \textsuperscript{31}P NMR to obtain a good performance and low formaldehyde emission.\textsuperscript{3, 6} There were slightly more non-condensed G-type phenolic hydroxyl groups in L\textsubscript{2} (0.53 mmol g\textsuperscript{-1}) than in L\textsubscript{1} (0.41 mmol g\textsuperscript{-1}). The content of non-condensed H-type phenolic hydroxyl groups were the same. Therefore, L\textsubscript{2} was more reactive in the synthesis of lignin-based phenolic resin than L\textsubscript{1}. The aliphatic-OH
content of L₂ (1.70 mmol g⁻¹) was greater than that of L₁ (0.81 mmol g⁻¹), and the -COOH content of L₁ (0.63 mmol g⁻¹) was slightly less than that of L₂ (0.83 mmol g⁻¹). Low content of these hydrophilic groups could favor the water resistance of resins.

2. Synthesis and characterize of LR resins

The lignins isolated from fermentation residues were used to prepare urea-formaldehyde-phenol-lignin resins (LR₃ and LR₄) with the same methods of FRs. The properties of LRs were also tested. Before preparing plywood, the solid content of LRs was firstly adjusted to the same with FRs. The LR₃ and LR₄ then mixed with 30% (w/w, based on resin) wheat flour as filler.

The adhesive properties and plywood performances of LR are listed in Table S2. The viscosity of LR₃ and LR₄ was obviously lower than FRs owing to the absence of carbohydrate and protein. The bonding strength of LR₃ and LR₄ was nearly the same. Although L₂ was more active than L₁ as shown in Table S1, L₂ had much more hydrophilic groups, which could have a negative effect on bonding strength. It was noteworthy that the bonding strength of LR₃ and LR₄ was both lower than FRs. This confirmed further that the carbohydrates existing in FRs were conducive for improving bonding strength. Furthermore, the formaldehyde emission of LR₃ and LR₄ was extremely higher than FRs and even E₀ grade.

The chemical structures of LR₃ and LR₄ were also investigated by employing a solution-state $^{13}$C NMR spectra. Fig. S3 shows the $^{13}$C NMR spectra of the freeze-dried uncured LR s. The spectra of LR₃ and LR₄ have some obvious distinctions compared with LR₁ and LR₂. The substituted urea was mainly disubstituted (161.0 ppm) in LR₃ and LR₄. Most importantly, the signals of methylene ether linkages of LR₃ and LR₄ (72.3 ppm) were distinctly higher than those of LR₁ and LR₂. The methylene ether bonds in the resins were found to be mainly associated with the urea units. The only condensation of urea under alkaline conditions is to form methylene ether bridges between methylol urea groups. However, these methylene ether linkages in resins would decompose to form methylene bridges and eliminate formaldehyde at high temperature during the curing process. Therefore, the high formaldehyde emission of LR₃ and LR₄ could be brought about by the methylene bridges.
3. References

Tables and figures

Table S1 Different hydroxyl group contents and active sites in the lignin samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total aliphatic</th>
<th>Total S</th>
<th>Substituted</th>
<th>Non-condensed phenolic</th>
<th>-COOH</th>
<th>Active site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₁</td>
<td>0.81</td>
<td>0.38</td>
<td>0.14</td>
<td>0.41</td>
<td>0.63</td>
<td>0.83</td>
</tr>
<tr>
<td>L₂</td>
<td>1.70</td>
<td>0.47</td>
<td>0.19</td>
<td>0.53</td>
<td>0.83</td>
<td>0.95</td>
</tr>
<tr>
<td>Adhesive</td>
<td>Adhesive properties</td>
<td>Plywood performances</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>---------------------</td>
<td>----------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solid content (%)</td>
<td>pH (25 °C)</td>
<td>Viscosity (22 °C, mPa·s)</td>
<td>Bonding strength (MPa)</td>
<td>Formaldehyde emission (mg L⁻¹)</td>
<td></td>
</tr>
<tr>
<td>LR₃</td>
<td>51.2</td>
<td>12.1</td>
<td>1545.0</td>
<td>0.72</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>LR₄</td>
<td>50.8</td>
<td>12.7</td>
<td>1029.0</td>
<td>0.73</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>GB/T 14074-2017</td>
<td>≥35.0</td>
<td>≥7.0</td>
<td>≥60.0</td>
<td>≥0.70ᵃ</td>
<td>≤0.50</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ The plywood performances were tested according to the Chinese National Standard GB/T 17657-1999.
Fig. S1. $^{13}$C NMR spectra of the lignin samples
Fig. S2. $^{31}$P NMR spectra of the lignin samples
Fig. S3 Solution-state $^{13}$C NMR spectra of LR$_3$ and LR$_4$
Fig. S4 Schematic of the main synthetic route of FRs