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

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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_1 and L_2) were investigated by the NMR spectra that were obtained on a Bruker AVIII 400 MHz spectrometer (Germany). The ^{13}C NMR and the ^{31}P NMR analyses of the lignin samples were performed according to the method given in a previous article.[1]

The molecular structural features of the two isolated lignins were investigated via the ^{13}C NMR technique and the spectra of L_1 and L_2 are shown in Fig. S1. The assignments of these lignin signals were achieved by the reported literature.[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.[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 ^{31}P NMR technique is an effective method to quantify various hydroxyl groups in lignin.[4] The Fig. S2 displays the ^{31}P NMR spectra of L_1 and L_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.[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 ^{31}P NMR to obtain a good performance and low formaldehyde emission.[3, 6] There were slightly more non-condensed G-type phenolic hydroxyl groups in L_2 (0.53 mmol g^{-1}) than in L_1 (0.41 mmol g^{-1}). The content of non-condensed H-type phenolic hydroxyl groups were the same. Therefore, L_2 was more reactive in the synthesis of lignin-based phenolic resin than L_1. The aliphatic-OH

content of L_2 (1.70 mmol g^{-1}) was greater than that of L_1 (0.81 mmol g^{-1}), and the -COOH content of L_1 (0.63 mmol g^{-1}) was slightly less than that of L_2 (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 (LR_3 and LR_4) 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 LR_3 and LR_4 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 LR_3 and LR_4 was obviously lower than FRs owing to the absence of carbohydrate and protein. The bonding strength of LR_3 and LR_4 was nearly the same. Although L_2 was more active than L_1 as shown in Table S1, L_2 had much more hydrophilic groups, which could have a negative effect on bonding strength. It was noteworthy that the bonding strength of LR_3 and LR_4 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 LR_3 and LR_4 was extremely higher than FRs and even E_0 grade.

The chemical structures of LR_3 and LR_4 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 LRs. The spectra of LR_3 and LR_4 have some obvious distinctions compared with LR_1 and LR_2. The substituted urea was mainly disubstituted (161.0 ppm) in LR_3 and LR_4. Most importantly, the signals of methylene ether linkages of LR_3 and LR_4 (72.3 ppm) were distinctly higher than those of LR_1 and LR_2. The methylene ether bonds in the resins were found to be mainly associated with the urea units.[7] The only condensation of urea under alkaline conditions is to form methylene ether bridges between methylol urea groups.[8] However, these methylene ether linkages in resins would decompose to form methylene bridges and eliminate formaldehyde at high temperature during the curing process.[9-11] Therefore, the high formaldehyde emission of LR_3 and LR_4 could be brought about by the methylene bridges.

3. References

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Tables and figures

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

Sample	-OH (mmol g^{-1})						
	Total aliphatic	Total S	Substituted G	Non-condensed phenolic		-COOH	Active site
				G	H		
L_1	0.81	0.38	0.14	0.41	0.21	0.63	0.83
L_2	1.70	0.47	0.19	0.53	0.21	0.83	0.95

Table S2 Adhesive properties and plywood performances of the LR_3 and LR_4

Adhesive	Adhesive properties			Plywood performances	
	Solid content (%)	pH (25 °C)	Viscosity (22 °C, mPa·s)	Bonding strength (MPa)	Formaldehyde emission (mg L^{-1})
LR_3	51.2	12.1	1545.0	0.72	0.69
LR_4	50.8	12.7	1029.0	0.73	0.92
GB/T 14074-2017	≥35.0	≥7.0	≥60.0	≥0.70[a]	≤0.50

[a] The plywood performances were tested according to the Chinese National Standard GB/T 17657-1999.

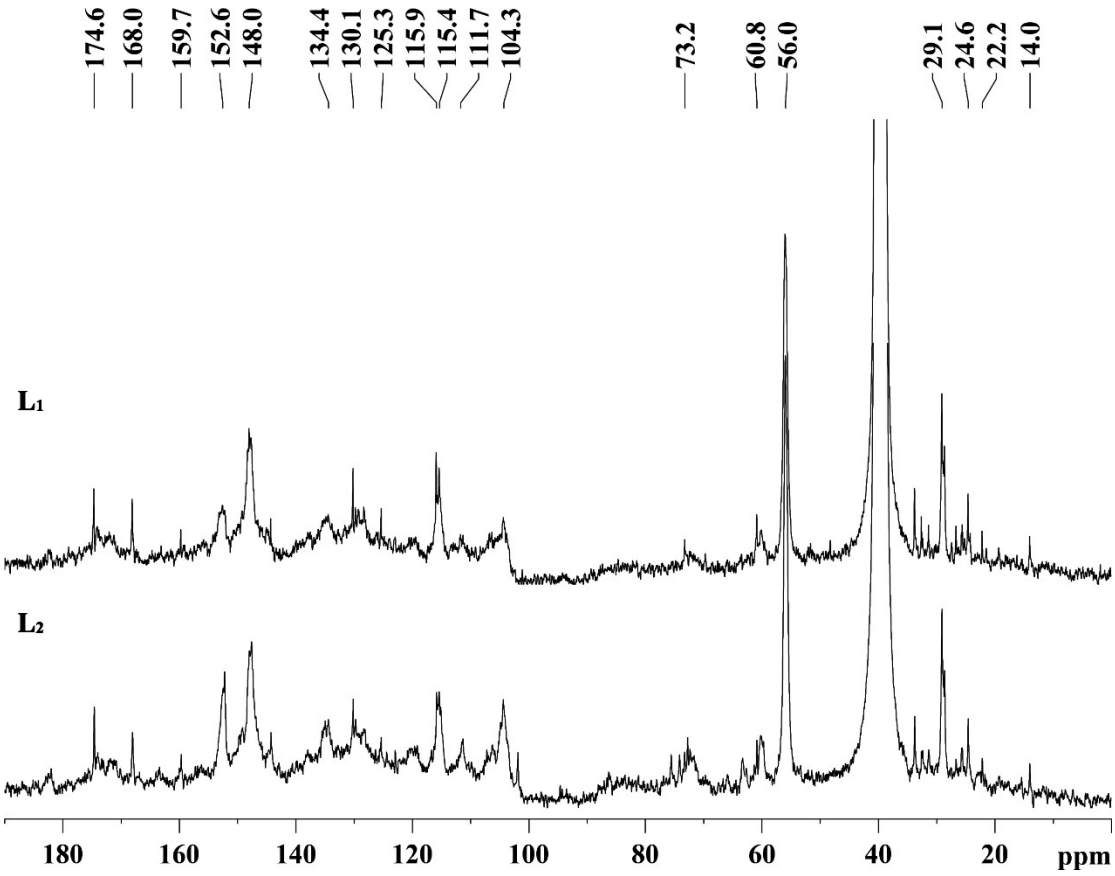

Fig. S1. ^{13}C NMR spectra of the lignin samples

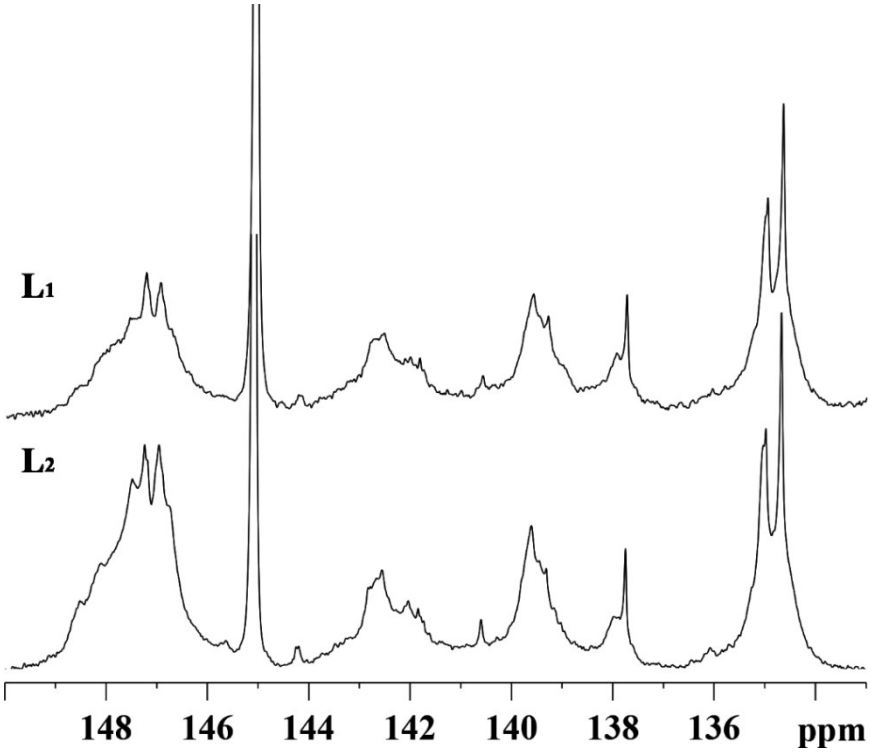

Fig. S2. ^{31}P NMR spectra of the lignin samples

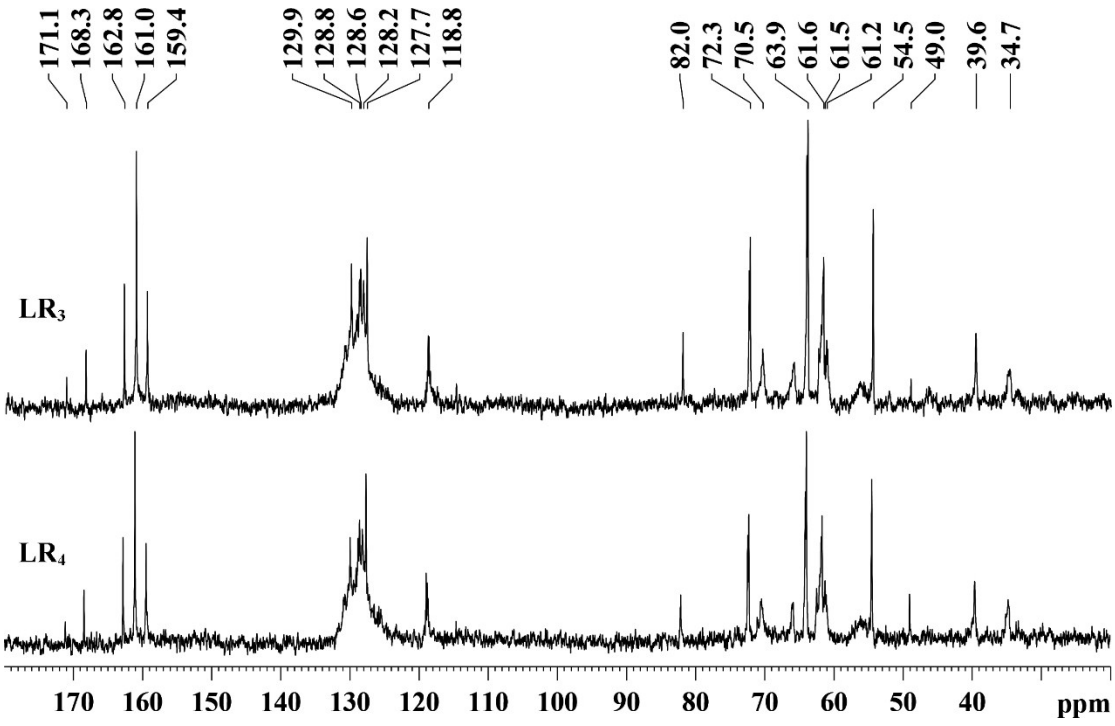

Fig. S3 Solution-state ^{13}C NMR spectra of LR_3 and LR_4

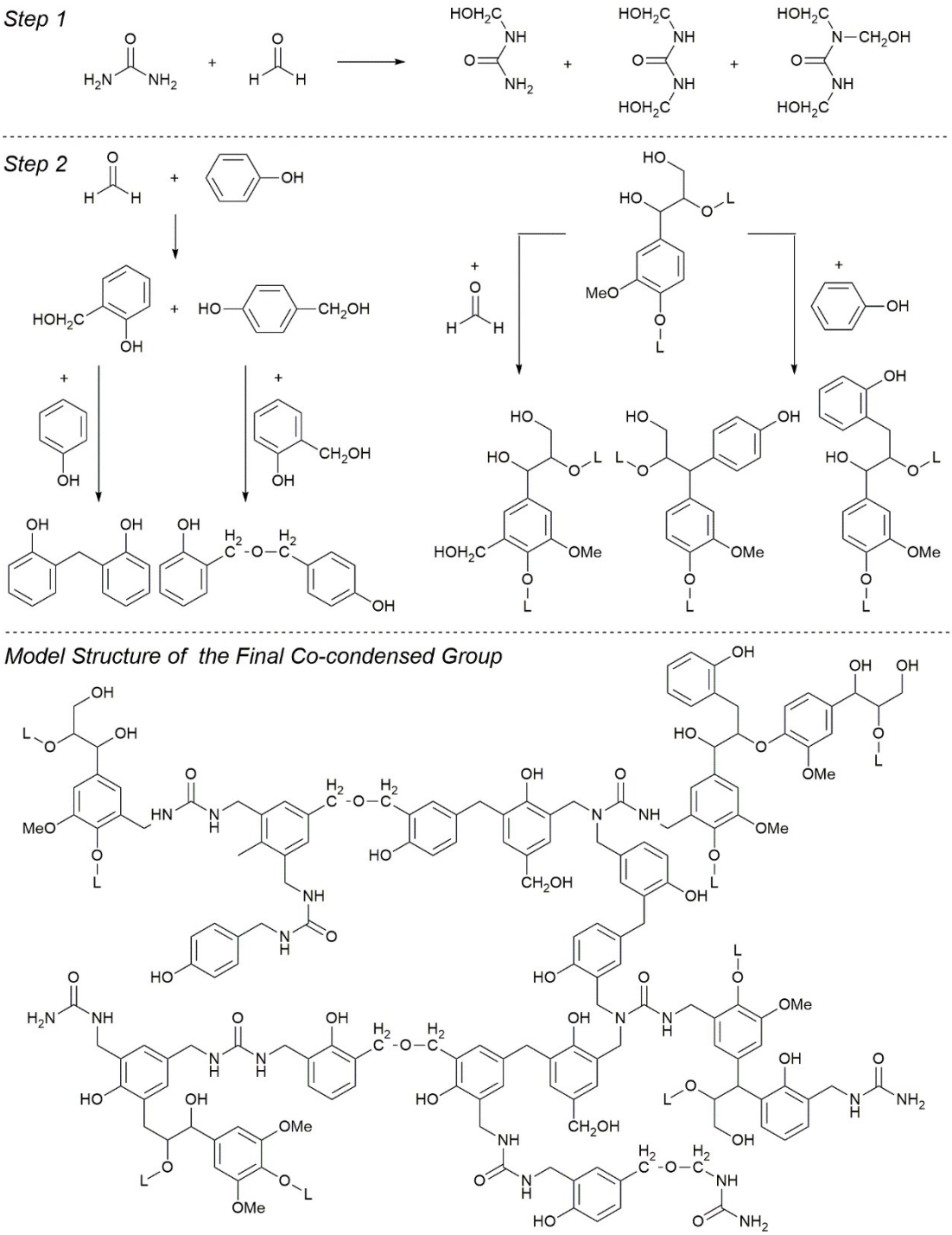

Fig. S4 Schematic of the main synthetic route of FRs