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Extracting high β-O-4 content lignin and by-producing substrate susceptible to enzymatic hydrolysis by a green flow through process

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ABSTRACT

Maleic acid (MA), a solid dicarboxylic acid can be obtained from renewable lignocellulose, was used to extract lignin through flow through (FT) process for the first time. Due to the high boiling point and flash point of MA, the FT process was carried out at atmospheric pressure without VOCs release and explosion risk. 50 wt% MA aqueous solution could extract 60 % lignin from birch wood, and the dilution factor for precipitating lignin was only 3. MA-extracted lignin preserved more than 80 % of β—O—4 bonds and a monophenol yield (> 30 %) comparable to that of milled wood lignin was obtained by catalytic hydrogenolysis. The recyclability of MA was demonstrated through three rounds of lignin extraction by recovered MA. And the cellulose-rich residue could be efficiently converted into glucose (glucose yield > 90 %) at a low cellulase loading of 10 FPU/g glucan due to the rich carboxyl groups of lignin. In addition, the low corrosiveness of MA and the mild operating conditions make the process have strong industrial application prospects.

1. Introduction

Lignin accounts for 15–40 % of the content of lignocellulosic biomass and is the most abundant natural aromatic compound [1]. The special three-dimensional network structure and abundant groups of lignin make it widely used in various fields, such as materials, construction, cosmetics, agriculture, energy and so on [2–6]. Because lignin and carbohydrates are tightly intertwined, extraction of lignin usually requires relatively severe conditions, such as high temperature and high pressure [7]. The severe extraction conditions result in an altered chemical structure of the extracted lignin, such as C—O bond cleavage and C—C bond formation, as well as the generation of chromophores [8]. As a result, the extracted lignin is usually in dark brown color, to limit its subsequent application in high-end materials and preparation chemicals [9–11].

Extracting lignin by flow through (FT) process, in which the extraction solution flows through a reactor containing lignocellulose to extract lignin, currently receiving extensive attention [12,13]. Due to the short residence time of the dissolved lignin in the reactor during FL process, lignin is not easily reacted to cause structural changes [14]. Wang et al. [14,15] used formic acid to extract lignin through FT process, 76 % of lignin in wheat straw could be extracted at 130 °C and a liquid–solid ratio of 26, and the extracted lignin preserved more than 75 % of the total β—O—4 bonds. David et al. [16] used methanol as solvent to extract lignin close to native lignin by FT process at 225 °C, proving that simultaneous catalytic degradation of lignin to obtain monophenolic compounds is not necessary in the FT process. Douwe et al. [17] extracted 57 % of lignin in walnut shells by FT process at 120 °C with acidic *n*-propanol/water (80:20, v/v) system, the resulting lignin contains 66 β—O—4 bonds per 100 aromatic rings. However, the solvents used to extract lignin typically have low boiling points (Table S1), resulting in high pressures in the reactor during extraction, requiring pressure-resistant reactors. At the same time, the open system of FT process is prone to volatile organic compounds (VOCs) and explosion risks. And the utilization of cellulose-rich residue, the main part of feedstocks, is often neglected, resulting in potential waste of resources.

Recently, some organic solid acids have been successively used to fractionate lignocellulosic feedstocks at normal pressure and low temperature, among which aromatic sulfonic acids are the most widely studied [18–21]. Zhu et al. [22] pioneered the application of *p*-toluenesulfonic acid (*p*-TsOH) to treat poplar wood, and found that more than 90 % delignification and more than 85 % xylan dissolution were achieved at 80 wt% *p*-TsOH concentration and a temperature of 80 °C. Next, *p*-TsOH was used to extract pinkish lignin from poplar by FT process

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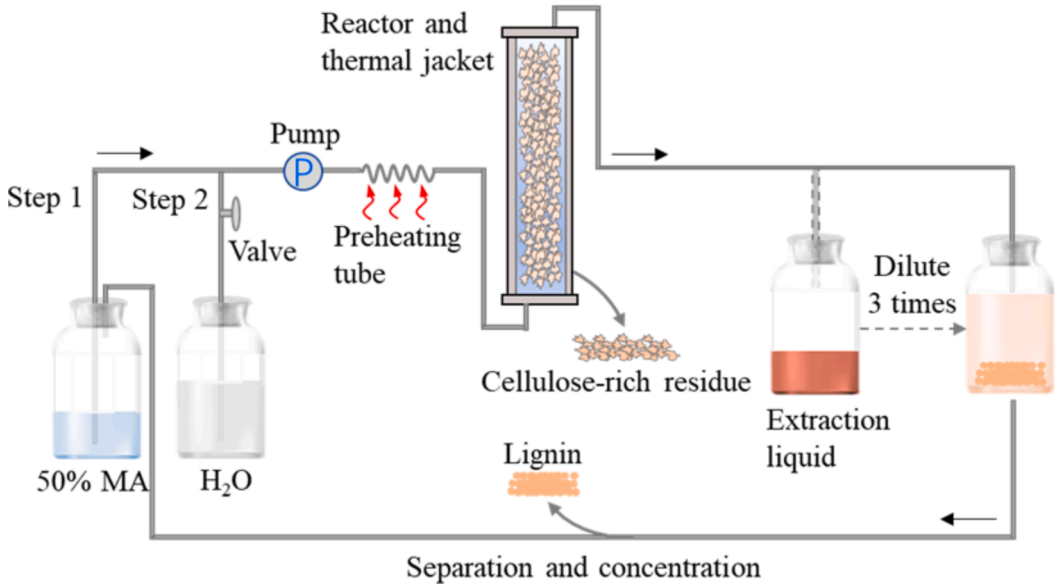

Scheme 1. Schematic diagram of MA extraction of lignin by FT process. Step 1: injected 50 wt% MA solution; step 2: injected DI water twice the mass of MA solution.

$$Yield_{monophenol}(\%) = M_{monophenol}/(20\ mg \times Purity) \times 100\% \quad (3)$$

where $M_{monophenol}$ and Purity were the mass of the monophenols after hydrogenolysis and the purity of the corresponding lignin, respectively.

2.6. Enzymatic hydrolysis

Cellulose-rich residue was hydrolyzed by cellulase CTec2 as before [30], with a solid content of 10 % and an enzyme loading of 10 FPU/g glucan. The initial pH of buffer was set to different values, from 4.0 to 7.0. Dilute acid (DA)-treated birch was used as a reference, the pre-treatment conditions referred to previous work [31]. Composition analysis of the two substrates was shown in Table S2.

3. Results and discussion

3.1. Lignin extraction by FT process

Due to the acidity of MA, part of lignin and carbohydrates (mainly hemicellulose) were degraded, and they were also esterified to introduce free carboxyl groups as shown in Fig. 1 [26]. Extracting lignin from birch wood under different temperature, acid flow rate and liquid–solid ratio was investigated.

When the acid flow rate was 8 mL min^{-1} at liquid–solid ratio of 15:1, increasing the extraction temperature from 110 °C to 120 °C could effectively increase the yield of lignin from 34.4 % to 60.6 %, and the purity of lignin also increased from 88.4 % to 91.5 % (Table 1). When the extraction temperature was further increased to 130 °C, the yield and purity of lignin were slightly improved. Under extraction temperature 120 °C with liquid–solid ratio of 15:1, increasing the flow rate of MA solution from 5 to 8 mL min^{-1}, the yield and purity of lignin decreased slightly because the reaction time was significantly shortened.

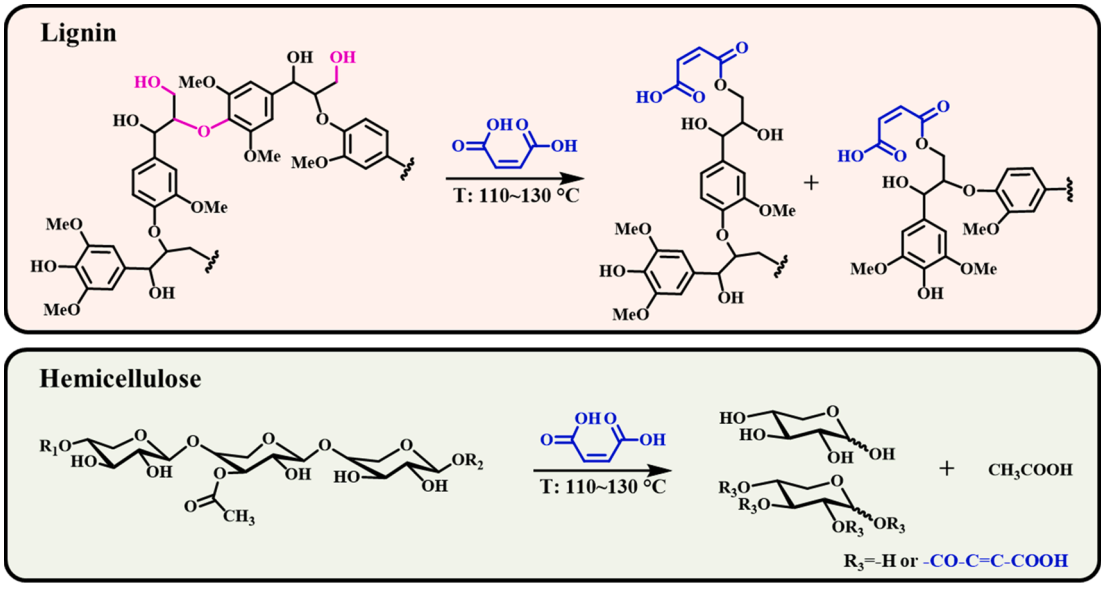

Fig. 1. Chemical reactions of lignin and hemicellulose with MA during FT process.

Table 1
Yield and purity of extracted lignin under different conditions.

No.	Temperature (°C)	Flow rate (mL/min)	Liquid solid mass ratio	Lignin yield (%)	Purity (%)
1	110	8	15:1	34.0.4	88.4
2	120	8	15:1	60.6	91.5
3	130	8	15:1	63.5	92.3
4	120	5	15:1	62.3	92.1
5	120	10	15:1	52.2	89.4
6	120	8	10:1	48.6	88.6
7	120	8	20:1	63.1	92.1

When the acid flow rate was further increased to 10 mL min^{-1}, the lignin yield decreased from 60.6 % to 52.2 %. At 120 °C and the acid flow rate 8 mL min^{-1}, increasing the liquid–solid ratio from 10:1 to 15:1, the yield of lignin was increased from 48.6 % to 60.6 %. Further increasing the liquid–solid ratio to 20:1, the yield of lignin slightly increased to 63.1 %, suggesting lignin yield was not significantly improved at the late stage of extraction. After comprehensive consideration, the extraction temperature of 120 °C, the flow rate of 8 mL min^{-1} and the liquid–solid ratio of 15:1 were selected as the subsequent lignin extraction conditions.

3.2. Physical and chemical properties of extracted lignin

3.2.1. Component and molecular weight analysis

MA-extracted lignin was divided into DL1 and DL2 (precipitated from extraction liquid before and after 15 min) to study the structure variation of lignin fraction at different extraction stages, and compare them with MWL.

Yield and component analysis of different kinds of lignin were shown in Table 2. Since MWL has been repeatedly purified by various organic reagents, its purity was the highest at 93.8 %, but its yield was only 8.6 %. Compared with DL 2, DL 1 had a lower purity of 89.3 %, and the content of carbohydrates was higher. Which was due to the shorter contact time between lignin in DL 1 and acid solution, resulting in less chemical bond breakage between lignin and carbohydrates. The yield of DL 1 was significantly higher than that of DL 2, which shown that the extraction efficiency in the early stage of the FL process was higher than that in the later stage. Although the purity of lignin extracted by MA was slightly lower than that of MWL, its yield was 7 times higher than the yield of MWL, which was beneficial to reflect the overall properties of lignin in the raw materials and the large-scale application of lignin.

As shown in Fig. 2, both MWL and DL1 were creamy color, and the color of DL1 was slightly darker. While the color of DL2 was slightly pinkish creamy, and the color of the whole extracted lignin (abbreviated as Whole) was between DL1 and DL2. The color is an indicative of the formation of chromophores through the FT process, and more chromophores in DL2 than in DL1, due to longer exposure time in the MA solution before dissolution. Overall, the extracted lignin was very light in color compared to commercial technical lignin.

Since the extraction of MWL only used non-polar solvents, the chemical bonds in lignin molecules were less broken, so the molecular weight of MWL was relatively large, with a number average molecular weight (Mn) of 3443 Da and a weight average molecular weight (Mw) of 14142 Da (Table S2). Compared with MWL, the molecular weight of the whole lignin extracted by MA was lower, with a Mn of 1318 Da and a Mw of 4185 Da. Because the ether bonds and ester bonds of lignin were easier to break under acidic conditions. Compared with DL1, the distribution of DL2 is broader. DL2 contains very low MW lignin due to more extensive depolymerization by MA, and high MW lignin due to lignin repolymerization as reflected from the second peak shown in Fig. 2, as a result DL2 has a greater polydispersity index than DL1 (Table S3).

Table 2
Yield and component analysis of lignin.

Sample	Yield (wt%)	Purity (%)	Glucose (%)	Xylose (%)	Others (%)
MWL	8.6	93.8	2.4	1.3	4.5
DL1	38.4	89.3	3.6	2.1	5.0
DL2	22.2	92.4	2.1	1.2	4.3
Whole	60.6	91.5	2.6	1.4	4.5

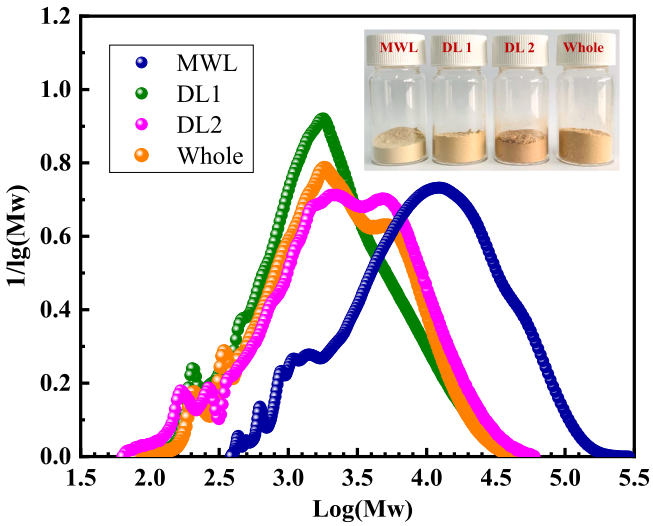

Fig. 2. Molecular weight distribution of different kinds of lignin.

3.2.2. 2D ^{1}H–^{13}C NMR analysis

The structural information of aromatic rings and side chains in lignin molecules can be detected by 2D ^{1}H–^{13}C NMR. Compared with MWL, the overall signal of MA-extracted lignin in the aromatic region and side chain region did not change significantly, which indicated that the MA-extracted lignin was structurally similar to MWL (Fig. 3). MA-extracted lignin showed a condensed $S_{2/6}$ signal response, indicating that condensation occurred in lignin. MA-extracted lignin contained 53.2 β—O—4 bonds per 100 aromatic rings, which was 83.4 % of the amount in MWL (Table 3). Compared with MWL, the relative content of β—β bond in MA-extracted lignin was slightly increased, indicating slightly more C—C condensation. The relative content of β—O—4 bond in DL2 was decreased and the relative content of β—β bond increased compared with their corresponding value in DL1 due to the longer lignin exposure time to acid, as a result, S/G ratio in DL2 was increased compared with that in DL1.

The whole lignin was also compared with lignin extracted by batch reaction (L-Batch, with a condition of 60 wt% MA and 120 °C for 30 mins), both had a yield around 60 % [29]. It could be seen that the signal of condensed $S_{2/6}$ in L-Batch was stronger, and the ratio of S/G was larger. The relative content of β—O—4 bonds in L-Batch was only 50 % of the whole lignin extracted by FT process, which shown that the FT process could effectively prevent the condensation of lignin and retain more β—O—4 bonds.

3.2.3. ^{31}P NMR and FTIR spectra analysis

Hydroxyl group is an important active functional group in lignin, which not only increases the hydrophilicity of lignin, but also facilitates various chemical reactions of lignin. The content of different types of hydroxyl groups was calculated via ^{31}P NMR results (Fig. 4A). The content of alcoholic hydroxyl groups in both MWL and MA-extracted lignin was the highest, above 3.0 mmol/g, but the alcoholic hydroxyl group in MA-extracted lignin was slightly less than that in MWL. Compared with MWL, the contents of 5-substitued OH and Guaiacyl OH were increased in MA-extracted lignin, because more phenolic hydroxyl groups were generated by the cleavage of phenolic ether bonds under acidic conditions. However, comparing DL2 with DL1, Guaiacyl OH was

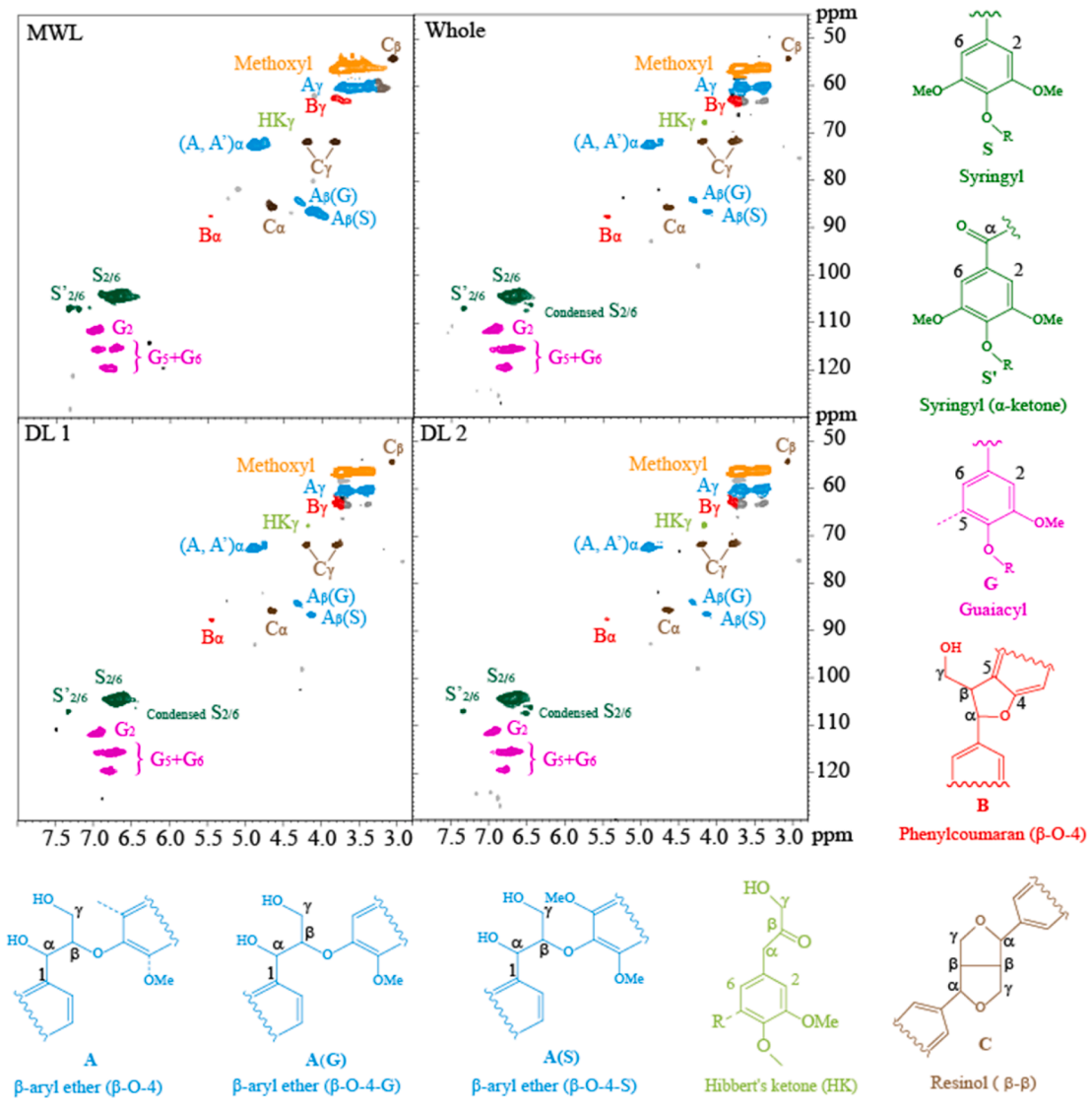

Fig. 3. 2D ^{1}H–^{13}C NMR spectrum of MWL and MA-extracted lignin.

Table 3
Structural characteristics (interunit linkages, aromatic units, and S/G ratio) of lignin from integrating ^{1}H–^{13}C correlation peaks in the HSQC spectra (the condensed $S_{2/6}$ is abbreviated as S_{Cond}).

Sample	$S_{2/6}$	$S'_{2/6}$	S_{Cond}	S	G	S/G	β–O–4 (%)	β–5 (%)	β–β (%)
MWL	76.7	4.1	–	80.8	19.2	4.2	64.0	1.1	11.8
DL 1	79.0	3.3	1.8	84.1	15.9	5.3	57.2	1.0	12.5
DL 2	74.9	3.2	12.4	90.5	9.5	9.5	45.6	0.5	14.5
Whole	73.7	3.3	9.5	86.5	13.5	6.4	53.2	0.8	13.6
L-Batch	62.9	3.2	25.4	91.5	8.5	10.7	26.7	0.1	8.9

decreased, perhaps partly due to the low content of G units in DL2 (Table 4). The content of carboxyl groups in MA-extracted lignin was obviously increased due to esterification reaction of MA with lignin alcohol hydroxyl groups to introduce a free carboxyl group [26]. which could also explain the decrease in the alcoholic hydroxyl groups in lignin. Furthermore, DL2 from longer exposure time with acid (or a greater reaction severity) has a lower amount of alcoholic OH but a substantially greater amount of carboxy groups than DL1 does.

The FTIR spectra of MWL and MA-extracted lignin were shown in Fig. 4B. It could be seen that the FTIR spectra of MWL and MA-extracted lignin samples were very similar, and there were no obvious differences between the FTIR spectra of DL1 and DL2. Their FTIR spectra all have clear characteristic absorption peaks of benzene ring (835, 1595, 1505, 1464 cm^{-1}), methoxy group (1423 cm^{-1}), methyl group (2935, 2845 cm^{-1}), carboxyl group (1730 cm^{-1}) and hydroxyl group (3420 cm^{-1}) [32]. An obvious difference was that the absorption peak at 1730 cm^{-1} in DL2 was the strongest among them four lignin samples, as a result of the greatest lignin carboxylation (Table 4).

3.3. Catalytic hydrogenolysis

Hydrogenolysis of lignin to prepare aromatic compounds can be an important pathway to achieve high-value lignin utilization [33]. The yield of monophenols is an indicative measurer of the potential for

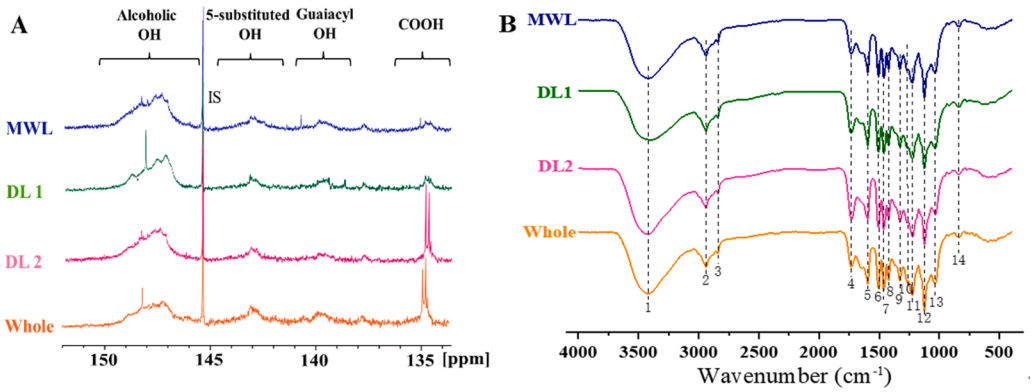

Fig. 4. (**A**) ^{31}P NMR spectrum of MWL and MA-extracted lignin. (**B**) FTIR spectra of MWL and MA-extracted lignin.

Table 4
Content of different types of hydroxyl groups calculated according to ^{31}P NMR.

Sample	Aliphatic OH (mmol/g)	5-substituted OH (mmol/g)	Guaiacyl OH (mmol/g)	COOH (mmol/g)
MWL	3.69	0.40	0.31	0.20
DL 1	3.54	0.61	0.45	0.39
DL 2	3.14	0.68	0.35	0.81
Whole	3.32	0.66	0.40	0.67

producing aromatic compounds from lignin. As shown in Fig. 5. The main catalytic hydrogenolysis products from all four lignin samples were dihydroeugenol, 4-propyl syringol, dihydroconiferyl alcohol, and dihydrosinapyl alcohol. Among them, the yields of dihydroeugenol and dihydroconiferyl alcohol were higher than 4-propyl syringol and dihydrosinapyl alcohol because there were more S units than G units in birch MWL and MA-extracted birch lignin. The monophenol yield from DL1 after catalytic hydrogenolysis was 34.2 %, almost identical to 34.4 % from MWL. This indicate that the content of β—O—4 linkages is not the only factor affecting the yield of monophenols. The smaller molecular weight of DL1 may be beneficial to increase molecular contact with catalyst to improve the efficiency of hydrogenation reaction. The monophenol yield of DL2 was 25.2 %, lower than that from DL1, perhaps due to the lower β—O—4 content and partially condensed structure. The monophenol yield of the whole lignin extracted by MA was 30.3 %, which was quite good, and the product distribution is relatively uniform, conducive to subsequent high-value conversions.

Compared with the monophenol yield of L-Batch (which was 20.2 %) [29], the monophenol yield of the whole lignin extracted by FT process was increased by 50 %. Although the conditions of catalytic hydrogenolysis in the two systems were different, taking MWL as a reference, the monophenol yield of the whole lignin obtained by FT process (87.9 % of MWL's) was significantly higher than that obtained by batch reaction (56.3 % of MWL's).

3.4. Recycling of MA

To verify the recyclability of MA, the diluted extraction liquid (120 °C; flow rate: 8 mL/min; liquor to solid: 15:1) after separating lignin was concentrated to 50 wt% MA and reused to extracting lignin. As shown in Fig. 6A, with the increase of the recovery times of MA, the extraction yield of lignin decreased slightly, and 54.3 % of lignin in birch powder could still be extracted by MA after three rounds of recovery. And the purity of extracted lignin by recovered MA did not decrease, it was all about 92 %. The 2D ^{1}H–^{13}C NMR spectra of the extracted lignin by recovered MA (mixed three rounds of lignin together) was shown in Fig. 6B. It could be seen that the NMR signal of the extracted lignin by recovered MA had no obvious change compared with that by fresh MA. The relative contents of β—O—4, β—β and β—5 were 52.1 %, 0.9 % and 14.1 %, respectively (Table S4). This indicated that the recycling of MA did not significantly affect the quality of the extracted lignin.

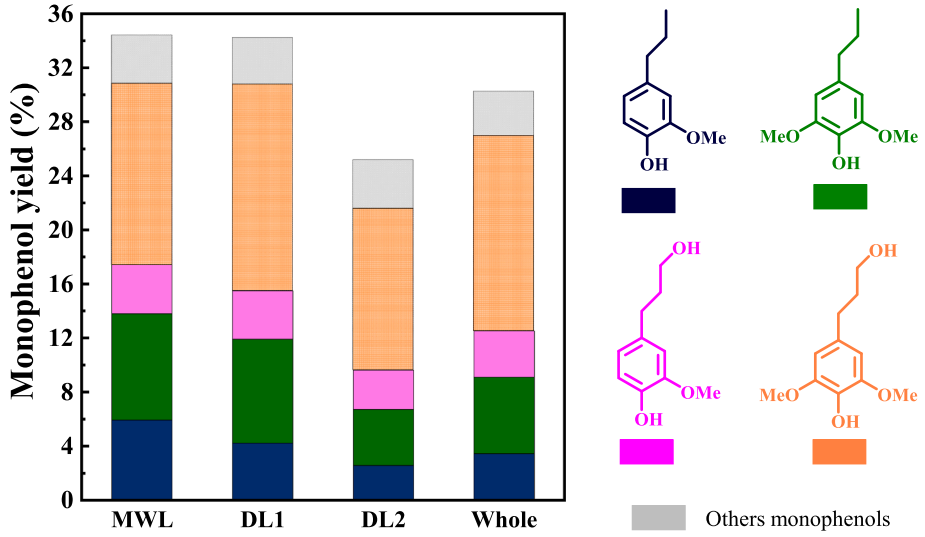

Fig. 5. The monophenol yields of MWL and MA-extracted lignin after catalytic hydrogenolysis by Ru/C catalyst (reaction temperature: 200 ℃, catalyst loading: 20 wt% based on lignin, hydrogen pressure: 2 MPa, reaction time: 12 h).

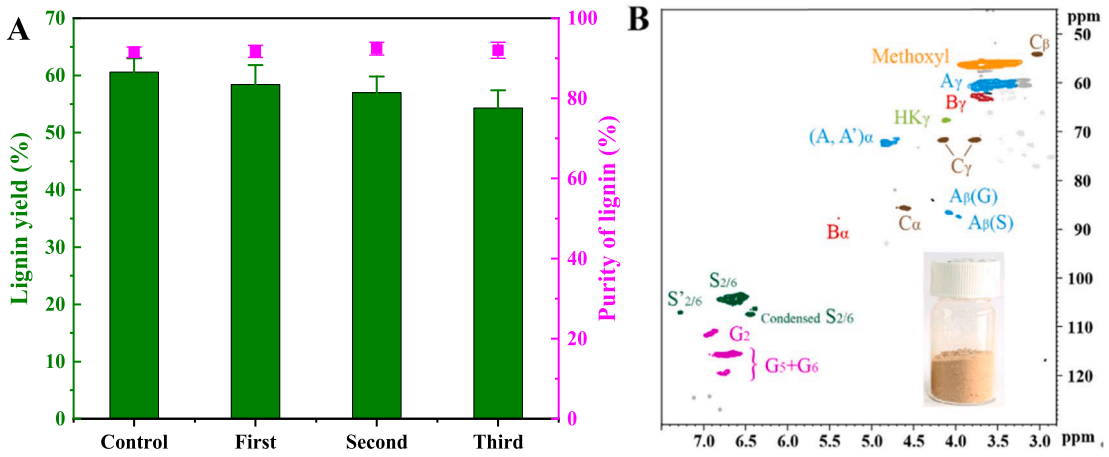

Fig. 6. **(A)** Yields and purities of lignin samples from different round of extraction by recovered MA; **(B)** 2D ^{1}H–^{13}C NMR spectra of extracted lignin (mixed different round of lignin together) by recovered MA.

After repeated use of MA solution, monosaccharides, degraded by hemicellulose and cellulose, accumulated in the solution, and their massive accumulation would affect the extraction of lignin. However, our previous work has proved that high purity of MA can be recovered from MA aqueous solution by cooling and crystallization [29,34], and the degraded monosaccharides can also be obtained after purification.

3.5. Enzymatic hydrolysis of cellulose-rich residue

To realize the comprehensive utilization of all components, high-value utilization of cellulose-rich residues is also required. Enzymatic hydrolysis of cellulose to glucose, and further biological and chemical conversion into different chemicals and materials is an important part of biorefinery.

Here, the experiments compared the differences of enzymatic hydrolysis between DA-treated and MA-treated Birch. As shown in Fig. 7A, with the increase of the pH, the enzymatic hydrolysis yields of the two substrates increased first and then decreased. Typically, the enzymatic activity of cellulase CTec2 was highest at around pH 5.0, but the hydrolysis yield of substrates treated by DA and MA reached the highest at pH 5.5 and pH 6.5, respectively, which were 48.4 % and 91.3 %. Because the negative charge of cellulase (with an isoelectric point of about 3.6) and lignin in the substrate increased at higher pH, the electrostatic repulsion between them increased, so the non-productive adsorption of the cellulase on lignin reduced, resulting in an improved substrate hydrolysis yield [35,36].

However, compared with DA-treated substrate, the hydrolysis yield of the MA-treated substrate was increased more significantly with the increase of pH. When the pH was increased from 4.8 to 6.0, the enzymatic hydrolysis yield of the MA-treated substrate increased from 42.5 % to 83.4 %, and the DA-treated substrate increased from 33.6 % to 47.0 %. It is speculated that the reason was that the content of carboxyl groups in the MA-treated substrate was higher. At higher pH, these carboxyl groups carried obvious negative charges after ionization, which effectively reduced the hydrophobic interaction between cellulase and lignin, and increased the electrostatic repulsion between them. Therefore, the non-productive adsorption of cellulase was reduced, and the enzymatic hydrolysis yield of the substrate was improved (Fig. 7B).

4. Conclusions

Extracting lignin with MA aqueous solution by FT process was carried out at atmospheric pressure without VOCs release and explosion risk. MA-extracted lignin preserved more than 80 % of β—O—4 bonds which was twice that of L-Batch. And it can be effectively hydrogenolyzed into four monophenols by Ru/C catalyst (monophenol yield exceeded 30 %). During the FT process, MA solution could be recycled after simple concentration, and the quality of the extracted lignin by recovered MA was not obviously affected. The cellulose-rich residue was easily hydrolyzed to glucose by cellulases at relative high pH due to its

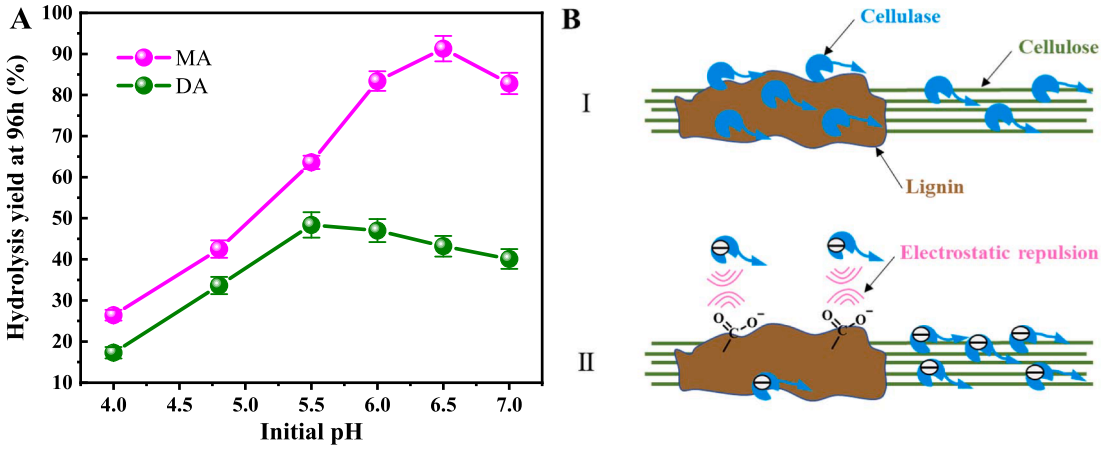

Fig. 7. **(A)** Enzymatic hydrolysis yields of DA-treated and MA-treated substrates at different initial pH; **(B)** Schematic diagram of the adsorption of cellulase on different substrates, I: DA-treated substrate, II: MA-treated substrate.

rich carboxyl groups. In a word, the renewable extraction reagent, the mild operating conditions, and the high-value utilization of all components make the extraction process green and sustainable.

CRediT authorship contribution statement

Cheng Cai: Conceptualization, Data curation, Funding acquisition, Writing – original draft. **Ning Li:** Funding acquisition, Software, Validation. **Huifang Liu:** Formal analysis, Visualization. **Jian Zhang:** Methodology, Resources. **J.Y. Zhu:** Investigation, Supervision, Writing – review & editing. **Feng Wang:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2022.139730.

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