Structural Changes of Wheat Straw Lignin during Formic Acid Treatment

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Abstract: The aromatic nature of lignin makes it a potential renewable source of chemicals and other valuable products. Isolation of lignin from lignocellulosic biomass using organic solvents enables the production of high-purity lignin. The use of formic acid in the organosolv pulping and fractionation process has been widely studied. Characterization of lignin is necessary to achieve value-added applications of lignin. To simplify the isolation of formic acid-treated lignin, herein, milled wheat straw lignin (MWSL) was employed as an archetype for characterization of the structural changes of lignin during formic acid treatment. The results showed that the MWSL was GSH-type (comprising *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) monolignols) and underwent structural changes during formic acid treatment. Lignin was esterified during the formic acid treatment. The content of alkyl hydroxyl groups in lignin decreased upon formic acid treatment, corresponding to an increase of the number of double bond equivalents (DBE). Lignin units with active reaction sites were liable to slight condensation, which resulted in a moderate increase of the molecular weight. The molecular weight distribution of formic acid-treated MWSL (FMWSL) was wider than that of the MWSL, although the molecular weight of both species did not differ significantly. The β-*O*-4 linkage in lignin was partially cleaved during formic acid treatment, resulting in the production of new phenolic structures. This improved the solubility of lignin in the cooking liquor and its reactivity for downstream applications.

Keywords: formic acid; wheat straw lignin; structural characterization

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1 Introduction

Wheat straw, as an agricultural residue from the production of cereals, is an attractive and low-cost lignocellulosic resource for bio-based chemicals and material industries because of its annual renewability and abundance[1-2]. In China, wheat straw is still extensively used as a raw material in the pulp and paper industry. Formic acid is recognized as a promising agent for organosolv pulping and fractionation. Formic acid can effectively delignify many woody and non-woody materials, such as beech[3], *Eucalyptus globulus*[4], wheat straw[5], *Miscanthus*[6-7], etc, and can efficiently promote fractionation of lignocellulosic materials into their constituents, for example, cellulose, hemicellulose, and lignin[5]. This process can be performed under atmospheric pressure and low temperature conditions. Further, formic acid is inexpensive and can be recovered simply by evaporation and distillation. Lignin originates from three aromatic alcohol precursors. These cross-linked monolignol substructures are defined as *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)[8]. Cereal straw lignin is a GSH-type lignin containing all three monolignols[9]. The major inter-unit linkages within lignin are ether types with about 50% β-*O*-4 linkages[8]. The monolignols form a complex network closely associated with hemicellulose during the biological lignification process. These structures are termed lignin-carbohydrate complexes (LCC).

The aromatic nature of lignin makes it a potential renewable source of chemicals and other valuable products[10-14]. The potential applications of lignin include the production of chemicals such as phenols[15-17] and BTX (benzene, toluene, and xylene)[18]. The use of lignin in various material applications, such as phenolic resins[19], polyurethanes[13,20-21], epoxy resins[22-24], and carbon fibers[25-26], has been studied. In spite of the various potential applications, industrial use of lignin currently remains difficult due to the limited industrial supply and the challenges associated with the properties of lignin, such as its complex and non-uniform chemical structure[27].

High-purity lignin (low in ash and residual carbohydrates, etc) is preferred for many applications. Isolation of lignin from lignocellulosic biomass by using organic solvents (organosolv) enables the production of high-purity lignin. Pilot-scale organosolv processes such as ethanol-based processes[28] and acetic and formic acid-based processes[29-30] are reported to have great potential for integration of pulping and biorefinery.

Characterization of organosolv lignin is a prerequisite for the development of high value-added applications. To date, the lignin extracted by ball milling process is considered as the best archetype of natural lignin for study of the structural changes and the underlying mechanisms. In this study, milled wheat straw lignin (MWSL) is employed to simplify the isolation of formic acid-treated lignin for characterization of the effects of formic acid treatment on the structure and molar mass distribution of treated lignin. The investigation aims to provide valuable information for the valorization of formic acid lignin.

2 Experimental

2.1 Preparation of MWSL

MWSL was prepared according to the method reported by Björkman[31]. An ultrasonic device was employed during dioxane extraction to improve the yield.

2.2 Formic acid treatment

A total of 200 mg (dry weight) of MWSL was charged into a glass reactor and 85% formic acid aqueous solution was added at a liquid-to-solid ratio of 20∶1 to dissolve the lignin. The reactor was kept at 95℃ on a water bath for 60 min. After a specified reaction time, the reaction was immediately quenched by immersion of the reactor in a cold water bath. The lignin was then precipitated by adding distilled water with 1% HCl to the lignin solution and the suspension was centrifuged. The isolated lignin was purified according to the method reported by Björkman[31]. The formic acid-treated MWSL (FMWSL) was obtained after vacuum freeze-drying.

2.3 FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectra of the lignin

samples were obtained using a BRUKER Tensor 27 FT-IR spectrometer. Each spectrum comprised an average of 32 scans, recorded with OPUS software in the wavenumber range of 400 ~ 4000 cm^{-1} with a resolution of 2 cm^{-1} using a potassium bromide (KBr) disc. The KBr was pre-dried in the laboratory oven to reduce interference from water.

2.4 Acetylation of lignin

For gel permeation chromatography (GPC) and ^1H NMR analyses, the lignin samples were subjected to acetylation to enhance the solubility in organic solvents. Lignin (20 wt%) was placed in an acetyl anhydride/acetyl acid mixture (1∶1 by weight) containing sodium acetate as a catalyst (0.5 mole per mole of acetyl anhydride)[32]. The reactions were carried out at room temperature (25℃) for 48 h and the solution was subsequently refluxed for 1 h. The products obtained by precipitation in ice-cold water with 1% HCl were filtered, washed with distilled water, and freeze-dried.

2.5 GPC analysis

The molecular weight distribution of lignin was determined by GPC using a Perkin-Elmer instrument equipped with three Water Stryragel columns (HR 1, HR 2, and HR 3) and a Refractive Index detector (Series 200). Tetrahydrofuran (HPLC grade) was used as the mobile phase at a flow rate of 1.0 mL/min. The columns were calibrated using narrow molecular weight monodisperse polystyrene standards at concentrations ranging from 350 g/mol to 2 300 000 g/mol. Lignin samples were dissolved in the eluent at a concentration of 1 mg/mL. The solution was filtered using a 0.45 μm filter and 20 μL of the filtered solution was then injected into the HPLC system.

2.6 NMR spectroscopy

^1H NMR spectra of acetylated lignin were recorded in $CDCl_3$ solution on a Japan Electronic AL300 superconducting Fourier transform NMR spectrometer. The spectra were collected in the δ range of 0 ~ 15 ppm with 128 scans using a pulse angle of 60° and a pulse delay of 1.551 s. ^{13}C NMR spectra were recorded on a Bruker-Spectrospin 400 UltraShield™ spectrometer using DMSO-d_6 solution with 20 000 scans. Tetramethylsilane (TMS) was used as an internal reference.

2.7 Elemental analysis

In preparing the samples for elemental analysis, the lignin powder was dried at 105℃ in a vacuum oven until constant weight was achieved. The content of carbon, hydrogen, nitrogen, and sulfur in the sample was analyzed using a Thermo Flash2000 analyzer. The percentage of oxygen was calculated by subtracting the C, H, N, and S contents from 100%. Based on the elemental composition and the methoxy groups in the lignin samples (from ^1H NMR), the empirical C_9 units of lignin were calculated and the average double bond equivalents (DBE) was calculated according to Eq. (1), as presented in the literature[33].

$$DBE = \frac{(2a+2)-b}{2} \quad (1)$$

Here, a is the number of carbon atoms and b is the number of hydrogen atoms in the empirical formula.

3 Results and discussion

3.1 FT-IR analysis

The FT-IR spectra of MWSL and FMWSL were displayed in Fig. 1. The wide and strong absorption bands at 3200 ~ 3433 cm^{-1} indicated the presence of hydroxyl groups in MWSL as well as FMWSL. The intensified peaks at 2940, 2843, 1462, and 1359 cm^{-1} in the profile of FMWSL indicated an increase in the number of methyl and methylene groups. This was attributed to

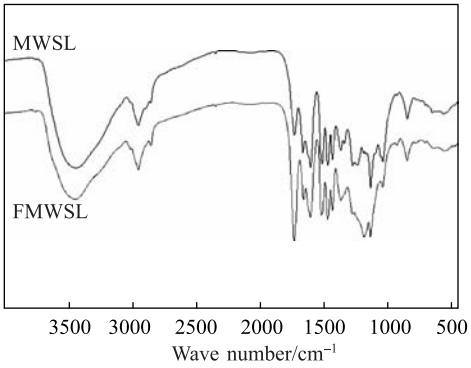


Fig. 1 FT-IR spectra of MWSL and FMWSL

dehydration and condensation reactions during formic acid treatment.

More esterified structures were present in FMWSL (based on the peaks at 1722 and 1178 cm^{-1}), indicating esterification of the hydroxyl groups in lignin. Both MWSL and FMWSL contained aromatic ketones (1651 cm^{-1}). The intensity of the peaks corresponding to the C_3, C_5 substituted structure (841 cm^{-1} and 919 cm^{-1}) in the phenyl ring increased after formic acid treatment, suggesting that condensation reactions occurred at the C_5 position of the G unit or the C_3, C_5 positions of the H unit.

3.2 NMR analysis

The ^1H NMR spectra of MWSL and FMWSL were presented in Fig. 2 and the corresponding peak assignments and peak areas were presented in Table 1. The signals of the three basic monomers, i. e., the G (6.7 ~ 7.2 ppm), S (6.25 ~ 6.70 ppm), and H (7.35 ~ 7.65 ppm) units, were clearly observed, which confirmed the presence of GSH-type lignin in the wheat straw. The intensified signals at 7.70 ~ 8.40 ppm in the spectral profile of FMWSL suggested the esterification of lignin after formic acid treatment, which agreed well with the FT-IR analysis. After formic acid treatment, the intensity of the signals corresponding to the protons on the aromatic rings decreased. For example, the signal of the H unit (7.35 ~ 7.65 ppm) of FMWSL vanished, whereas that of the G unit (6.7 ~ 7.2 ppm) was attenuated. These changes implied that the H and G units were liable to attack at the C_3 and C_5 position. The obviously attenuated signal of H_α (5.70 ~ 6.25 ppm) and H_β (4.05 ~ 5.20 ppm) implied partial decomposition of the β-*O*-4 linkage in lignin. The intensity of the proton signals of the aromatic hydroxyl groups (2.15 ~ 2.70 ppm, acetylated) of FMWSL increased compared with that of MWSL, which was consistent with cleavage of the β-*O*-4 linkages. Decomposition of the β-*O*-4 linkages resulted in the production of new phenolic structures, improving the solubility of lignin in the cooking liquor and its reactivity for downstream application.

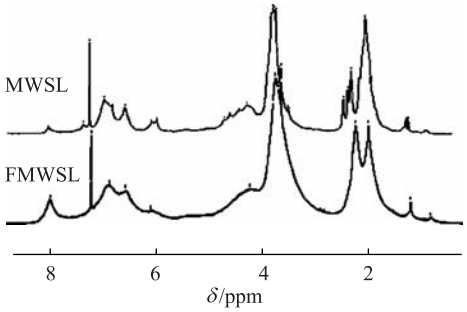


Fig. 2 ^1H NMR spectra of MWSL and FMWSL

Table 1 Peak assignments of ^1H NMR spectra of MWSL and FMWSL

δ/ppm	Relative peak area/%		Assignment
	MWSL	FMWSL	
7.70 ~ 8.40	0.85	3.26	Protons in carboxyl and aldehyde groups
7.35 ~ 7.65	1.22	—	Protons in the aromatic *p*-hydroxyphenyl ring
7.25			$CDCl_3$
6.70 ~ 7.20	8.54	7.31	Protons in the aromatic guiacyl ring
6.25 ~ 6.70	4.21	5.38	Protons in the aromatic syringyl ring
5.70 ~ 6.25	2.93	2.66	H_α in β-*O*-4 and β-1 structure
			H_β in β-*O*-4 structure
4.05 ~ 5.20	14.51	11.30	H_α, H_γ in β-β structure
			H_γ in β-1 and β-5 structure
3.10 ~ 4.05	30.79	34.42	Protons in methoxyl groups
2.15 ~ 2.70	8.23	11.23	Protons in acetylated phenolic groups
1.45 ~ 2.15	22.56	12.62	Protons in acetylated alkyl hydroxyl groups

The ^{13}C NMR spectra of MWSL and FMWSL were presented in Fig. 3, and the corresponding peak assignments were displayed in Table 2. The strong signals of acetyl carbons at 168.9 ~ 170.4 ppm and 20.6 ppm signified the presence of hydroxyl groups in MWSL. In the case of FMWSL, the intensity of these signals was obviously reduced. Signals of the alkyl hydroxyl groups and the phenolic hydroxyl groups were evident at 170.4 ppm and 169.8 ~ 168.9 ppm, respectively. The concentration of alkyl hydroxyl groups declined considerably (based on the peak at 170.4 ppm) after formic acid treatment, while the number of phenolic hydroxyl groups increased (based on the signals at 169.8 ~ 168.9 ppm and 20.6 ppm). The increase in the intensity of the peaks corresponding to the formyl groups (162.0 ppm) in FMWSL indicated esterification of the hydroxyl groups during formic acid treatment. The decrease in the num-

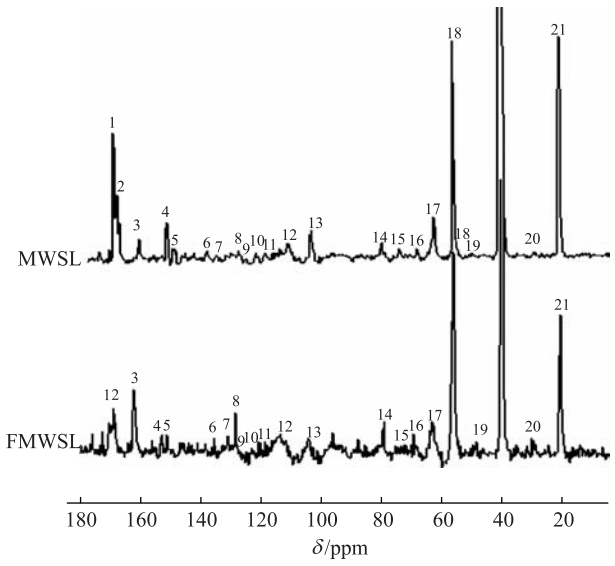


Fig. 3 ^{13}C NMR spectra of MWSL and FMWSL

Table 2 Peak assignments of the ^{13}C NMR spectra of MWSL and FMWSL

Number	δ/ppm	Assignment
1	172.5,170.4	C═O in acetylated alkylhydroxyl groups
2	169.8 ~ 168.9	C═O in acetylated phenolic hydroxyl groups
3	162.0	Carbon in formyl groups
4	153.4	C_5/C_3 in etherified syringyl ring
5	151.3	C_3 in acetylated guiacyl groups and C_4 in etherified guiacyl groups
6	139.4	C_1/C_4 in etherified syringyl groups
7	135.5	C_4 of syringyl and C_1 in guiacyl groups with *β-O*-4 structure
8	129.6	C_α/C_β in unsaturated side chains
9	128.7	C_1 in *p*-hydroxyphenyl groups
10	124.0	C_5 in acetylated guiacyl groups and C_β in cinnamyl alcohol
11	119.9	C_6 in etherified guiacyl groups
12	112.5	C_2 in guiacyl groups
13	105.1	C_2, C_6 in acetylated syringyl groups
14	80.4	C_β in *β-O*-4 structure
15	74.6	C_α in *β-O*-4 structure
16	69.4	Acetylated side chains (—CH(OAc)—)
17	63.2	C_γ in *β-O*-4 structure
18	56.3	Methoxyl groups
19	51.3	C_β in *β-β* and *β*-5 structure
20	29.6	Diphenyl methane
21	20.6	CH_3— in acetyl groups

ber of phenolic ether components (based on the peaks at 153.4 ppm and 139.4 ppm) and the increase in the intensity of the signal corresponding to free phenolic hydroxyl groups (acetylated) suggested cleavage of the aryl ether bond and release of the phenolic hydroxyl groups. The increased intensity of the signal of diphenyl methane suggested condensation of the lignin units during formic acid treatment.

3.3 Elemental and GPC analyses

The results of elemental analysis were listed in Table 3. After the treatment of MWSL with formic acid, the hydrogen and oxygen content decreased, accompanied by an increase in the number of double bond equivalents (DBE). These observations suggested dehydration and *β*-elimination in the side chains and condensation of lignin during the treatment.

Table 3 Results of elemental analysis, the empirical C_9 formula, and DBE of MWSL and FMWSL

Samples	Element content/%			Empirical formula of lignin (C_9)	DBE
	C	H	O		
MWSL	57.51	5.74	36.75	$C_9H_{8.35}O_{3.61}(OCH_3)_{1.342}$	5.15
FMWSL	59.81	5.35	34.84	$C_9H_{6.72}O_{3.07}(OCH_3)_{1.52}$	5.88

Fig. 4 and Table 4 summarized the results of GPC analysis. The molecular weight of FMWSL increased from 6627 to 8933. The FMWSL sample had a slightly wider molecular weight distribution and slightly higher polydispersity than MWSL. However, the dispersity was still low. The GPC signal of FMWSL was detected 1 ~ 2 min earlier than that of MWSL, which suggested the production of larger molecules via condensation reactions

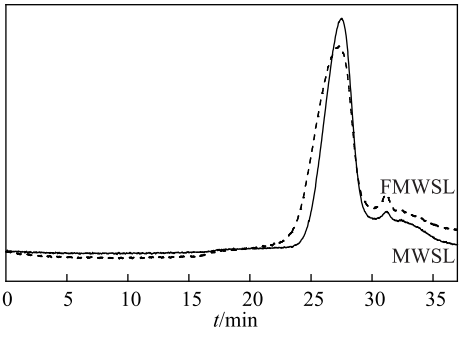


Fig. 4 GPC spectra of MWSL and FMWSL

Table 4 Molecular weight of MWSL and FMWSL

Samples	*M*n	*M*w	Dispersity
MWSL	4611	6627	1.437
FMWSL	5340	8933	1.673

between lignin molecules in the former case. However, the molecular weight of FMWSL was not significantly different from that of MWSL.

4 Conclusions

The aromatic nature of lignin makes it a potential renewable source of chemicals and other valuable products. Isolation of lignin from lignocellulosic biomass using organic solvents enables the production of high-purity lignin. The use of formic acid in the organosolv pulping and fractionation process has been widely studied. Characterization of lignin is necessary to achieve high value-added applications of lignin. To simplify the isolation of formic acid-treated lignin, herein, milled wheat straw lignin (MWSL) was employed as an archetype for characterization of the structural changes of lignin during formic acid treatment. The results showed that the MWSL was GSH-type (comprising *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) monolignols) and underwent structural changes during formic acid treatment. Lignin was evidently esterified during the formic acid treatment. The decrease in the content of alkyl hydroxyl groups in lignin corresponded to an increase of the number of double bond equivalents (DBE). Lignin units with active reaction sites at the C_3 or C_5 position were liable to condensation. However, condensation between lignin units occurred to a limited extent, resulting in a moderate increase of the molecular weight of lignin. The molecular weight of formic acid-treated MWSL had a slightly wider distribution, but didn't differ significantly from that of the parent lignin. The β-*O*-4 linkage in lignin underwent cleavage during formic acid treatment. Structural decomposition of lignin resulted in the production of new phenolic structures, which should improve the solubility of lignin in the cooking liquor and enhance the reactivity of lignin for downstream application.

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