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Composition Analysis of Organosolv Lignin and Its Catalytic Solvolysis in Supercritical Alcohol

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S Supporting Information

ABSTRACT: The structural analysis and catalytic solvolysis performance of organosolv lignins from Chinese fir (softwood) and maple (hardwood) were investigated. Fourier transformation infrared spectroscopy (FTIR) analysis revealed that both Chinese fir lignin and maple lignin exhibited a guaiacyl–syringyl structure. Chinese fir lignin consisted of guaiacyl units principally, while maple lignin consisted of syringyl units mainly. The ratios of guaiacol-/syringol-type products obtained by pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) were 2.53 for Chinese fir lignin and 0.29 for maple lignin, respectively. The catalytic solvolysis degradation was studied in supercritical ethanol/1-butanol at 300 °C with Ru/C to produce phenolic compounds. The degradation products of Chinese fir lignin were mainly guaiacol-type products, while the products of maple lignin consisted of both guaiacol- and syringol-type compounds. The yields of most products of maple lignin were much higher than those of Chinese fir lignin. The results show that the organosolv maple lignin is a potential feedstock for producing phenolic products through the solvolytic method.

1. INTRODUCTION

Lignin, one of the main components of biomass, has been widely studied as a potential sustainable feedstock for production of energy, fuels, and chemicals through different kinds of thermochemical transformation methods.^{1,2} Lignin is a three-dimensional amorphous polymer consisting of a methoxylated phenylpropane structure, which is greatly dependent upon the biomass species and isolation methods.^{3–5}

Lignin from softwood (gymnosperms) and hardwood (angiosperms) species exhibits different relative abundance of the *p*-coumaryl, coniferyl, and sinapyl alcohols.⁶ The structure of softwood lignin is derived principally from coniferyl alcohol (more than 95%), together with *p*-coumaryl-alcohol-type units and a trace amount of sinapyl-alcohol-type units, while roughly equal proportions of coniferyl-alcohol-type units and sinapyl-alcohol-type units could be found in hardwood lignin.^{2,7}

Lignin liquefaction is estimated as a promising technique to convert lignin to valuable chemicals, especially phenolic compounds.^{8–11} Wahyudiono et al. investigated the decomposition of alkali lignin in near and supercritical water, reporting monomeric compounds as the primary liquid product.¹² Ye et al. degraded organosolv lignin from corn stalk in ethanol/water at 260 °C with the Ru/C catalyst, and 4-ethylphenol and 4-ethylguaiacol were identified as the main products.^{13,14} Wang et al. studied the hydrogenolysis of organosolv lignin from poplar (hardwood) with Raney Ni in methylcyclohexane and 2-propanol at 300 °C, finding that the solvent played a key role in directing the selectivity.¹⁵ Tang et al. investigated the catalytic hydrocracking of pyrolytic lignin of rice husk to liquid fuels in supercritical ethanol, reporting phenolic compounds as the dominant products.¹⁶

Thermochemical transformation behavior of lignin is tightly related to its chemical structure.^{3,17} The structural difference between softwood lignin and hardwood lignin would result in a

different distribution of degradation products and yields. Therefore, it is important to study the structural characteristics of softwood lignin and hardwood lignin to understand the degradation performance better and give guidance on how to improve the yields of desired products.

The target of this work is to understand the difference of composition and solvolysis performance between organosolv lignins isolated from Chinese fir (*Cunninghamia*, softwood) and maple (hardwood). The structural characterization of the two lignins was carried out with Fourier transformation infrared spectroscopy (FTIR) and pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) to study the functionality groups and distribution of three units (syringyl/guaiacyl/*p*-coumaryl). The solvolysis degradation performance was investigated in supercritical ethanol/1-butanol to produce high-value phenolic products with the Ru/C catalyst, which was reported as an active catalyst in both C–C and C–O bond cleavage reactions for lignin degradation.^{16,18,19}

2. MATERIALS AND METHODS

2.1. Materials. The solvents used in the study were purchased from Nanjing Reagent Co. and used as received. A 5% Ru/C catalyst was purchased from Aladdin. Chinese fir and maple were obtained from a manufacturer in southern Anhui Province, China.

Lignin was prepared from the woods according to the method described in published work.¹⁵ In brief, 20 g of wood pellets and 120 mL of ethanol/water (1:1, v/v) were loaded into a 200 mL autoclave. Then, the reactor was heated by electricity to 180 °C and kept for 2 h with a stirring speed of 200 rpm. After the reactor was cooled to room

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temperature, the mixture products were filtrated to obtain a brownish solution. This solution was heated at 65 °C under 0.4 MPa to remove the solvent. The remaining solid lignin was dried at 80 °C for 12 h and stored in a dry atmosphere for the following solvolysis. Proximate analyses of Chinese fir lignin and maple lignin are given in Table 1.

Table 1. Proximate Analyses of Chinese Fir Lignin and Maple Lignin^a

lignin	volatile matter (wt %)	fixed carbon (wt %)	ash (wt %)
Chinese fir lignin	71.83	25.98	2.19
maple lignin	72.78	26.78	0.94

^aDry basis.

2.2. Solvolysis of Lignin. The solvolysis of lignins was conducted in a high-pressure autoclave (AC 150, ESTANIT). The 150 mL autoclave was made of 316 TI, with a maximum working pressure of 40 MPa at 600 °C. The lignin sample (2 g) and Ru/C catalyst (0.2 g) were loaded into the reactor with 15 mL of ethanol and 65 mL of 1-butanol solvent. The air in the reactor was driven out by purging and evacuating hydrogen 3 times. Then, the reactor was injected with hydrogen to 3 MPa and electrically heated to 300 °C. This heating process took about 40 min. After the reactor was kept at 300 °C for 2 h at a stirring speed of 400 rpm, it was cooled to room temperature by a water coil. Each reaction condition was repeated 2–3 times. After the pressure was released, the reactor was opened and all liquid and solid products were collected. The reactor was rinsed with ethanol. Solid product that adhered to the wall was removed with a metal spatula. The liquid product was isolated by filtration under vacuum. The total solid char were dried at 85 °C overnight and weighed.

The liquid products were calibrated to 200 mL by adding ethanol. Then, the ethanol and 1-butanol solvent was removed from 10 mL of liquid product in rotary at 80 °C under 0.1 MPa. The remaining oil products were weighed and dissolved in 10 mL of ethanol for GC/MS analysis.

2.3. Characterization of the Products. The FTIR of the two lignins and their chars were recorded on a FTIR spectrophotometer (Bruker Vector 22) using a KBr disc containing 1% samples. A total of 16 scans were conducted for each sample in the range from 4000 to 400 cm⁻¹, with a resolution of 4 cm⁻¹. The precision was no more than 0.01 cm⁻¹.

Py-GC/MS has been used to investigate the structural characterization of lignin in terms of the syringyl/guaiacyl/*p*-coumaryl unit ratio and lignin content in biomass.^{20–22} A fast pyrolysis analyzer (CDS5250) was coupled with GC/MS (Agilent 5975C) to identify

the volatile products. A total of 1 mg of lignin sample was loaded in the pyrolysis tube, and the pyrolysis temperature was set to be 500 °C, with the flash heating rate of 20 000 °C/s. The residence time for the sample was 20 s. The evolved volatiles were identified by GC/MS, the conditions of which were set to be as follows: the injector temperature was kept at 300 °C; the chromatographic separation was performed with a HP-5MS capillary column; the oven temperature was programmed from 50 °C (2 min) to 290 °C (1 min) with a 8 °C/min heating rate; and the mass spectra were operated in electron impact (EI) mode at 70 eV. The mass spectra were obtained from *m/z* 50 to 650. The chromatographic peaks were identified according to the National Institute of Standards and Technology (NIST) MS library and previously published work.^{17,21,23}

GC/MS analysis for the liquid products was carried out on GC/MS (Agilent 5975C). The oven temperature was programmed from 40 °C (3 min) to 180 °C (2 min) with a 5 °C/min heating rate and then to 280 °C (2 min) with a 10 °C/min heating rate.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis of Lignin. The FTIR spectra of the two lignins are shown in Figure 1, and the notable peak assignments are listed in Table 2.^{6,7} Both Chinese fir lignin and maple lignin

Table 2. Bands Assignments for FTIR Spectra of Lignin

number	wavenumbers (cm ⁻¹)	band origin
1	3425	O–H stretch in hydroxyl groups
2	2920	C–H stretch in methyl and methylene groups
3	1715–1705	C=O stretch in conjugated carbonyls
4	1605–1595	aromatic skeletal vibrations
5	1510–1505	aromatic skeletal vibrations
6	1457	C–H deformations in methyl and methylene groups
7	1430–1425	aromatic skeletal vibrations
8	1370–1365	aliphatic C–H stretch in CH ₃
9	1326–1325	C–O stretch in syringyl rings
10	1270	C–O stretch in guaiacyl rings
11	1215	C–O stretch in guaiacyl rings
12	1120	aromatic C–H in-plane deformation of the syringyl rings
13	1030	aromatic deformation in-plane and C–O deformation in primary alcohols

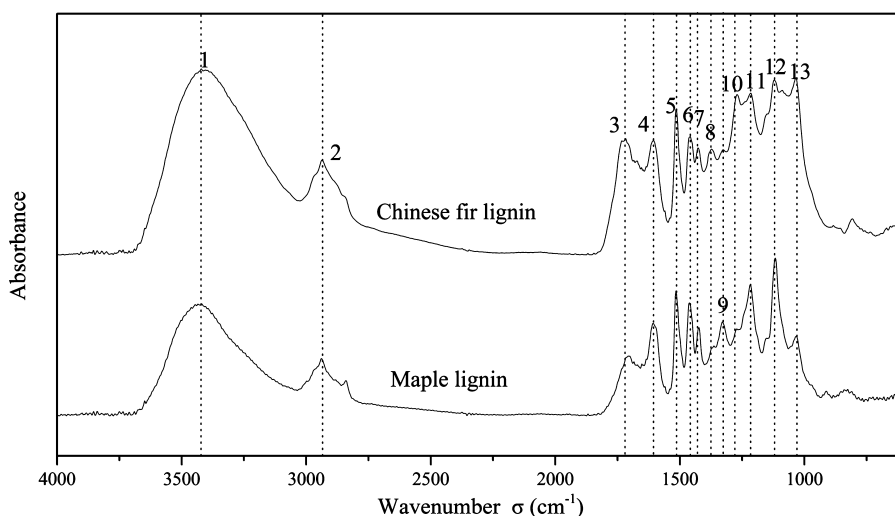


Figure 1. FTIR spectra of Chinese fir lignin and maple lignin.

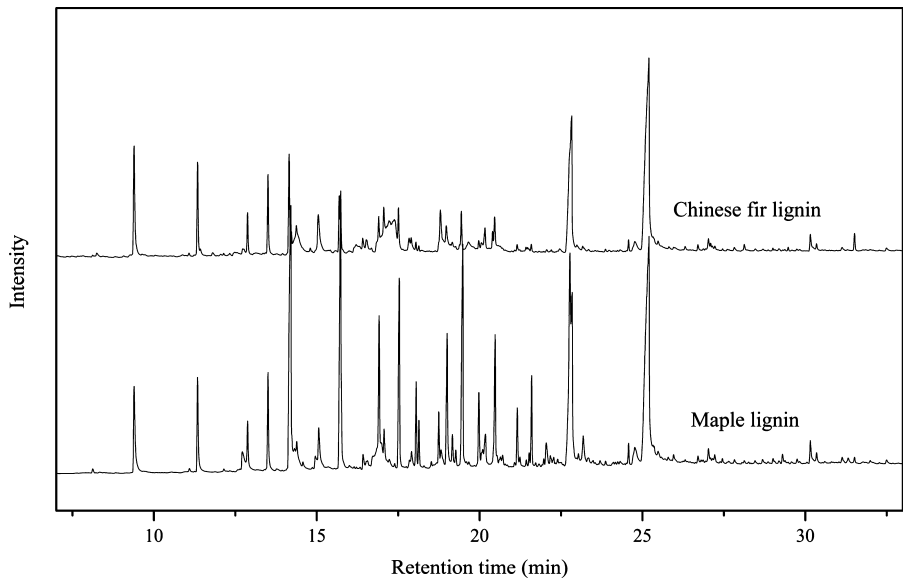


Figure 2. Py–GC/MS spectra of Chinese fir lignin and maple lignin at 500 °C.

Table 3. Peak Areas and Peak Area Ratios of Products of Chinese Fir Lignin and Maple Lignin in Py–GC/MS

type	retention time (min)	compounds	Chinese fir lignin		maple lignin	
			peak area	peak area ratio	peak area	peak area ratio
G	9.39	guaiacol	5.57×10^8	3.11	4.63×10^8	1.85
G	11.09	4-methylguaiacol	3.45×10^8	1.92	4.03×10^8	1.62
CA	12.72	1,2-benzenediol, 3-methoxy-			1.72×10^8	0.69
G	12.88	4-ethylguaiacol	1.71×10^8	0.95	2.56×10^8	1.03
G	13.5	4-ethenylguaiacol	3.18×10^8	1.77	3.80×10^8	1.52
S	14.2	syringol	3.77×10^8	2.1	1.64×10^9	6.54
G	14.22	phenol, 2-methoxy-4-(1-propenyl)-, (E)-	9.35×10^7	0.52		
G	14.39	4-propylguaiacol	5.33×10^8	2.97	2.40×10^8	0.96
S	14.58	phenol, 4-methoxy-3-(methoxymethyl)-			8.97×10^7	0.36
G	15.06	vanillin	4.12×10^8	2.3	3.05×10^8	1.22
S	15.69	1,2,4-trimethoxybenzene	1.90×10^8	1.06	1.34×10^9	5.37
G	15.73	phenol, 2-methoxy-4-(1-propenyl)-	2.52×10^8	1.41		
G	16.42	ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.06×10^8	0.59	7.79×10^7	0.31
S	16.92	benzene, 1,2,3-trimethoxy-5-methyl-			7.77×10^8	3.11
G	17.07	2-propanone, 1-(4-hydroxy-3-methoxyphenyl)-	3.97×10^8	2.21	2.46×10^8	0.98
S	17.54	ethanone, 1-(3,5-dimethoxyphenyl)-			7.75×10^8	3.1
S	18.05	phenol, 2,6-dimethoxy-4-(2-propenyl)-			2.78×10^8	1.11
S	18.14	benzene, 1-ethyl-3-(phenylmethyl)-			1.80×10^8	0.72
S	18.75	phenol, 2,6-dimethoxy-4-(2-propenyl)-	5.90×10^7	0.33	1.98×10^8	0.79
G	18.82	benzeneacetic acid, 4-hydroxy-3-methoxy-	3.84×10^8	2.14	1.57×10^8	0.63
S	19.01	benzaldehyde, 4-hydroxy-3,5-dimethoxy-	2.25×10^8	1.26	6.17×10^8	2.47
S	19.17	2-allyl-1,4-dimethoxy-3-methyl-benzene		0	1.60×10^8	0.64
S	19.49	phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.71×10^8	0.95	1.08×10^9	4.31
S	19.98	ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	7.11×10^7	0.4	3.08×10^8	1.23
S	20.4	benzenebutyric acid, 2,3-dimethoxy-	1.06×10^8	0.59		
S	20.48	desaspidinol	2.08×10^8	1.16	5.77×10^8	2.31
S	21.16	ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-			2.19×10^8	0.87
S	22.05	3,5-dimethoxy-4-hydroxyphenylacetic acid			1.61×10^8	0.65
S	23.18	3,5-dimethoxy-4-hydroxycinnamaldehyde			2.59×10^8	1.04

showed the peaks of hydroxy groups (O–H stretching at 3425 cm^{-1} ; 1 in Figure 1), methy groups (C–H stretching at 2920 cm^{-1} ; 2 in Figure 1), and aromatic rings (aromatic skeletal vibrations at 1600 , 1510 , and 1430 cm^{-1} ; 4, 5, and 7 in Figure 1).

Fingerprint regions between 1800 and 900 cm^{-1} of the two lignins exhibited an obvious difference. Chinese fir lignin

showed a higher peak of conjugated carbonyl groups (C=O stretching between 1715 and 1705 cm^{-1} ; 3 in Figure 1) than maple lignin. C–O stretching vibrations at 1268 cm^{-1} (10 in Figure 1) of Chinese fir lignin showed the abundant existence of guaiacyl rings. Chinese fir lignin showed a stronger peak at 1268 cm^{-1} (10 in Figure 1) than the peak at 1215 cm^{-1} (11 in Figure 1). However, in maple lignin, the peak at 1268 cm^{-1} was

weaker than the peak at 1215 cm^{-1} . This opposite distribution was also observed between *Acacia auruculaeformis* lignin (hardwood lignin) and *Pinus roxburghii* lignin (softwood lignin).⁶ Maple lignin exhibited obvious peaks at 1328 cm^{-1} (9 in Figure 1) and 1120 cm^{-1} (12 in Figure 1), which corresponded to C–O stretching vibrations and aromatic C–H in-plane deformation of the syringyl rings, respectively, indicating a typical characterization of hardwood lignin. The peak at 1030 cm^{-1} (13 in Figure 1) corresponding to C–O deformation in primary alcohols or ethers was weaker in maple lignin than in Chinese fir lignin. This indicated a better removal of polysaccharides for Chinese fir lignin, which might be attributed to the different lignin–carbohydrate complex structure.⁴

Softwood lignin, such as lignin from pine and spruce, mainly consists of guaiacyl units (more than 95%), together with *p*-coumaryl units and a trace amount of syringyl units. While hardwood lignin, such as poplar and birch, consists of both guaiacyl and syringyl units in a great amount with varying proportions.^{6,7} It is interesting that a certain intensity of peak at 1120 cm^{-1} could be identified in Chinese fir (softwood) lignin, showing the considerable existence of the syringyl unit, and this existence could be further confirmed in the following Py–GC/MS analysis.

3.2. Py–GC/MS Analysis of Lignin. The GC spectra of fast pyrolysis products at $500\text{ }^{\circ}\text{C}$ of Chinese fir lignin and maple lignin are presented in Figure 2. The peak areas and peak area ratios of main products are given in Table 3. Peaks were identified by the NIST library and previous studies.^{21,23} Because the chromatographic peak area of one compound is considered to be linear with its quantity and the peak area ratio is linear with its concentration, the absolute peak areas and peak area ratios of the products of different lignins can reflect their yields and relative content qualitatively.²⁴

Guaiacol-type compounds were the main products of Chinese fir lignin, accounting for 19.89% of the total peak area. Guaiacol, 4-methylguaiacol, 4-ethenylguaiacol, 4-propylguaiacol, and vanillin were the main identified guaiacol-type products. The absence of phenol-type products implied that the pyrolysis of lignin under $500\text{ }^{\circ}\text{C}$ was mainly comprised of the cleavage of interunit linkages and cracking of side chains, while the methoxy groups and phenolic hydroxyl groups were rarely fragmented.¹⁷ Consistent with the FTIR analysis, which revealed the existence of syringyl units, we found syringol-type compounds from the pyrolysis products of Chinese fir lignin, which accounted for 7.85% of the total peak area. The peak area ratio of guaiacol-/syringol-type compounds was 2.53. Cresol- and catechol-type products appeared in a slight amount at this temperature. Besides, levoglucosan, which is a typical pyrolysis product of cellulose and hemicellulose, can be identified at the retention time of 17.37 min in the products of Chinese fir lignin.²⁵ The identification of levoglucosan indicated the existence of the remaining polysaccharides in Chinese fir lignin.

For maple lignin, the syringol-type compounds were the main products, amounting to 34.62%. Guaiacol-type products were also identified in a great amount of 10.12%. The peak area ratio of guaiacol-/syringol-type compounds of maple lignin was 0.29, and the methoxyl content per phenylpropanoid unit was about 1.77. Levoglucosan, which was identified in the products of Chinese fir lignin, was not found in those of maple lignin, indicating a good removal of polysaccharides.

Pyrolysis products of lignin usually consisted of permanent gases, volatile compounds, and non-volatile oligomers, and only the volatile compounds can be identified by GC/MS.²⁴ According to the proximate analyses given in Table 1, the volatile of Chinese fir lignin (71.83%) was only slightly lower than that of maple lignin (72.78%). However, the absolute peak areas of GC/MS showed that the yields of most pyrolysis products of maple lignin were much higher than that of Chinese fir lignin, including both guaiacol- and syringol-type products. The lower yields of phenolic compounds of Chinese fir lignin might be the result of its higher remaining polysaccharides, which has also been revealed by the FTIR analysis.

3.3. FTIR Analysis of Char. Figure 3 shows the FTIR spectrum of the Ru/C catalyst. Figure 4 shows the FTIR

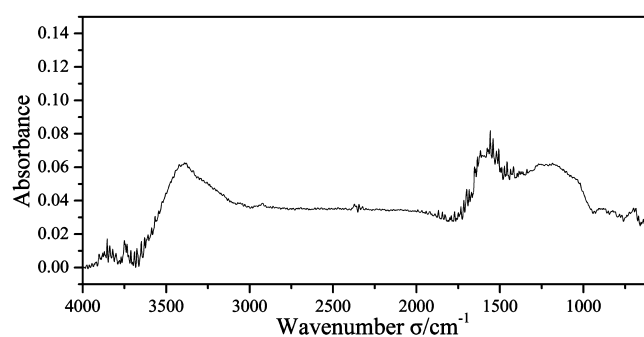


Figure 3. FTIR spectrum of the Ru/C catalyst.

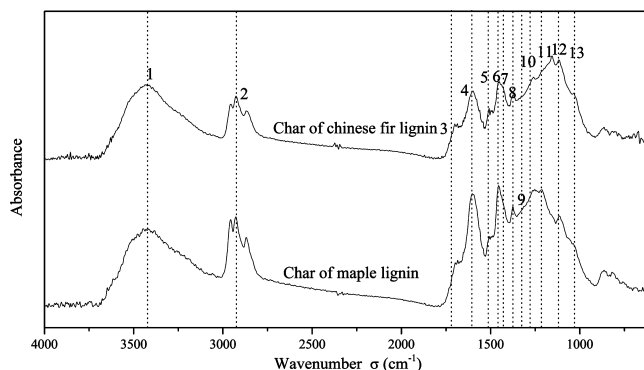


Figure 4. FTIR spectra of chars of Chinese fir lignin and maple lignin.

spectra of the char residue of Chinese fir lignin and maple lignin. The Ru/C catalyst was difficult to be isolated from the solid char. As a result, the FTIR of char given in Figure 4 was the spectrum of Ru/C plus that of the produced char. Nevertheless, the spectra of Ru/C observed in Figure 3 only exhibited bands of hydroxy groups and aromatic rings, which had little impact on our qualitative analysis of the produced char.

Chars of Chinese fir lignin and maple lignin both showed a lower intensity of the conjugated carbonyl group compared to that of the lignins. Our previous work on solvolysis of alkali lignin in subcritical water showed that the hydroxy groups in that char were much more than the hydroxy groups in alkali lignin, because of the cleavage of the $\text{ArCO}-\text{CH}_3$ bond.²⁶ In the present work, however, the peak intensity of hydroxy groups in char was weaker than that in lignins. This indicated that the hydroxy groups might have reacted with the alcohol

solvent during the solvolysis. This reaction also caused the higher intensity of the methy group and a new appeared peak around 2956 cm^{-1} in the chars.

Fingerprint regions of the chars also showed great differences from that of the lignins. Bands of 1600 and 1424 cm^{-1} of aromatic skeleton vibrations remained in the chars. However, the peak of 1515 cm^{-1} disappeared after the solvolysis. C–O stretching vibrations at 1270 and 1215 cm^{-1} of guaiacyl rings in char of Chinese fir lignin became weaker. Peaks observed at 1328 and 1120 cm^{-1} of the syringyl rings in maple lignin also became weaker after the degradation. The weakening of these peaks indicated partial removal of methoxyl groups.

Differences can also be identified between the spectra of chars of Chinese fir lignin and maple lignin. Taking the band at 1601 cm^{-1} corresponding to the aromatic rings as the reference, the intensity of specific groups based on one aromatic ring can be studied qualitatively.²⁷ The intensity of the band corresponding to hydroxy groups in char of Chinese fir lignin was higher than that in char of maple lignin. Besides, after the solvolysis, the char of Chinese fir lignin exhibited an obvious peak at 1156 cm^{-1} corresponding to C–O in alcohol or ether groups.

3.4. Characterization of Liquid Products. The products of lignin depolymerization were comprised of liquid product, gaseous product, and solid char. In this work, the liquid product was focused and gaseous product was not collected. The selectivity of the detected products (S_i) was defined as²⁸

$$S_i (\%) = \frac{A_i}{A_{\text{total detected}}} \times 100 \quad (1)$$

The total detected peak area was obtained on the basis of the area intergration of 40 major peaks of GC/MS spectra.

The yields of solid product of Chinese fir lignin and maple lignin were 26.22 and 27.82%, respectively, which were much higher than that of the degradation of pyrolytic lignin (0.3–5.12%) in supercritical ethanol,¹⁶ while the oil yield in the present work was slightly lower (32.12% for Chinese fir lignin and 41.11% for maple lignin). The difference may be the result of different lignin origins and different degradation conditions.

Figure 5 displays the peak area of main liquid products of Chinese fir lignin and maple lignin. The products of Chinese fir lignin were mainly guaiacol-type compounds, while the products of maple lignin consisted of both great amounts of guaiacol- and syringol-type compounds. Besides, some long-chain alkyl products were identified for Chinese fir lignin, which, however, were not found for maple lignin (see Table S1 of the Supporting Information). The difference of lignin origin can lead to different distributions of products. The degradation products of corn stock lignin consisted of mainly 4-ethyl phenol and guaiacol.¹⁸ The hydrocracking of pyrolytic lignin of rice husk in supercritical ethanol produced mainly phenolic compounds of phenol and guaiacol-type compounds, while syringol-type products were not found, which was attributed to the occurrence of demethoxylation reactions during the degradation.¹⁶

There were four main guaiacol-type products formed from Chinese fir lignin, i.e., guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol. According to the peak areas in Figure 5, 4-propylguaiacol was the most abundant guaiacol-type product. Wahyudiono et al. and Yong et al. reported that products in subcritical water were mainly comprised of guaiacols with little side chains.^{12,29} The significant amount of

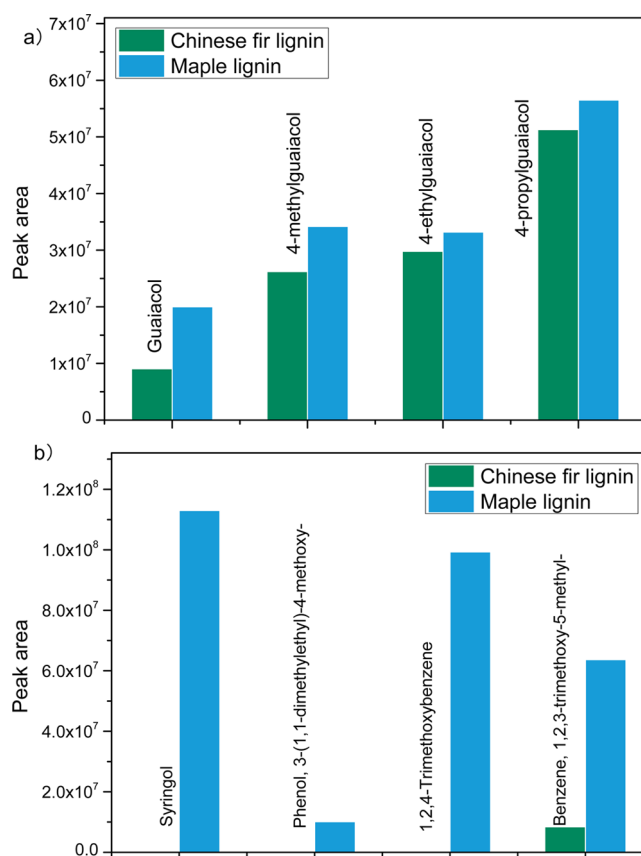


Figure 5. Peak areas of main liquid products of Chinese fir lignin and maple lignin.

4-propylguaiacol in the present work indicated a good perseverance of the side chain, which should be attributed to the alcohol condition used. The existence of side chains was also observed in the degradation products of lignin in ethanol/water.¹⁸

For maple lignin, syringol-type products were the main products and syringol was the most abundant product. Besides, the yields of guaiacol-type products of maple lignin were also high. According to the peak areas, the yields of guaiacol-type products of maple lignin were even higher than those of Chinese fir lignin, consistent with the results of Py–GC/MS. No vanillin or other oxidized products were identified because of the alcohol solvent used and hydrogen injected, which served as the hydrogen source.

Figure 6 shows the peak area ratios of main liquid products of Chinese fir lignin and maple lignin, corresponding to the selectivities of the products. 4-Propylguaiacol possessed the highest selectivity of 14.29% for Chinese fir lignin. For maple lignin, syringol showed the highest selectivity of 14.32%. Table 4 shows the peak areas of guaiacol- and syringol-type products of pyrolysis and solvolysis of Chinese fir lignin and maple lignin. The relative content of guaiacol-type compounds of Chinese fir lignin was summarized to a total value of 32.41%, and the value of maple lignin was much lower, at 18.31%. The selectivity of syringol-type products of maple lignin was as high as 36.36%. The ratio of guaiacol-/syringol-type products were 13.85 for Chinese fir lignin and 0.50 for maple lignin. These values were much higher than the guaiacol-/syringol-type product ratios identified by Py–GC/MS (2.53 for Chinese fir lignin and 0.29 for maple lignin), indicating that methoxy

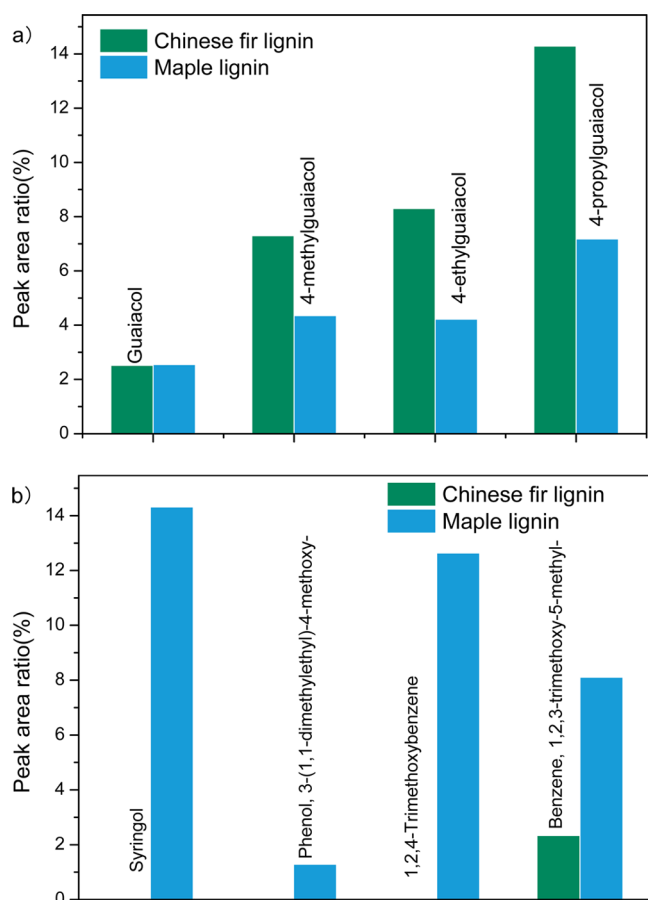


Figure 6. Peak area ratios of main liquid products of Chinese fir lignin and maple lignin.

Table 4. Peak Areas of Guaiacol- and Syringol-Type Products of Pyrolysis and Solvolysis of Chinese Fir Lignin and Maple Lignin

product compounds	Chinese fir lignin		maple lignin	
	pyrolysis (%)	solvolysis (%)	pyrolysis (%)	solvolysis (%)
guaiacol-type (sum)	19.89	32.41	10.12	18.30
syringol-type (sum)	7.82	2.34	34.62	36.36
guaiacol-/syringol-type	2.53	13.85	0.29	0.50

groups were partly removed in the solvent–lignin system, which might be enhanced by the addition of the Ru/C catalyst.

4. CONCLUSION

Both lignins from Chinese fir (softwood) and maple (hardwood) exhibited a guaiacyl–syringyl structure. The ratios of guaiacyl/syringyl units identified by Py–GC/MS were 2.53 for Chinese fir lignin and 0.29 for maple lignin. The phenolic products of solvolysis were mainly guaiacol-type monomers for Chinese fir lignin, while both considerable amounts of guaiacol- and syringol-type compounds were formed for maple lignin. Alcohol solvents can inhibit the repolymerization reaction and help to preserve the side chain. The yields of most solvolysis products of maple lignin were much higher than those of Chinese fir lignin. The results show that the organosolv maple lignin is a potential kind of feedstock for solvolysis to produce phenolic products.

■ ASSOCIATED CONTENT

● Supporting Information

Peak area and peak area ratio of products for Chinese fir lignin and maple lignin in Py–GC/MS (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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