Cellulose-lignin and Xylan-lignin Interactions on the Formation of Lignin-derived Phenols in Pyrolysis Oil

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To gain a better understanding of the effect of the interactions between two biomass components (cellulose-lignin and xylan-lignin) on lignin-derived phenolic products, two analysis methods are introduced. With 3:1, 2:1, and 1:1 ratios of cellulose and lignin, and xylan and lignin, the mixtures were subjected to fast pyrolysis, which was carried out in a fixed-bed tubular furnace at 450 to 600 °C. The phenolic content in the bio-oils was analyzed by gas chromatography-mass spectrometry. The product distributions showed that cellulose, xylan, and lignin were the main contributors to the mass of biomass bio-oil, gas, and char, respectively. The char yields decreased and the bio-oil and gas yields increased in the presences of cellulose and xylan. Comparative analyses of both the phenol content and peak area of the two methods suggest that in the case of cellulose and lignin co-pyrolysis, the formation of three kinds of phenolic products is promoted. The strength of this positive effect increased with increasing lignin content. However, the production of hydroxyphenols is promoted, while the productions of guaiacols and syringols are inhibited by the effect of xylan, which creates a different interaction between xylan and lignin.

INTRODUCTION

Excessive use of traditional fossil energy has caused serious damage to ecological and social environments. There is a pressing need to study and develop clean and renewable energy. Biomass is recognized as the third largest primary energy resource in the world (Huber *et al*. 2006), and it has been widely used to produce valuable fuels and chemicals by pyrolysis technology (Czernik and Bridgwater 2004; Mohan *et al*. 2006). Bio-oil produced by biomass pyrolysis is a promising second-generation renewable energy carrier that can be utilized for bio-fuels and biochemicals. Bio-oil contains sugars, phenols, furfural, and other chemical substances. Phenolic compounds, which can be obtained from bio-oil, have great potential in perfumes, phenolic resin adhesives, dyes, photostabilizers, and medical disinfection (Saiz-Jimenez and Leeuw 1986; Simoneit *et al.* 1993; Kim *et al.* 2010).

The practical and industrial value of bio-oil can be increased by upgrading chemical substances within it (Yang *et al.* 2014). However, because of the complexity of the biomass structure, there are still many difficulties with the formation mechanism of these chemical products. It is known that the main constituents of biomass are cellulose, xylan, and lignin. In general, polysaccharides and lignin account for 90 wt%. Among

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these constituents, cellulose, xylan, and lignin account for 25 to 50 wt%, 20 to 40 wt%, and 5 to 30 wt% of the dry weight of lignocellulose, respectively (Ragauskas *et al.* 2006; Wang *et al.* 2011). The lignin component has a unique chemical structure formed by p-coumaryl-, coniferyl-, and sinapyl alcohols (C9 unit) connected by ether bonds and C=C bonds (Qu *et al.* 2011; Lv *et al.* 2013; Shen *et al.* 2015a). Therefore, it is generally believed that lignin is the principal source of phenols (Qu *et al*. 2011; Xin *et al*. 2013). A number of studies have proposed that there is no obvious interaction when the three components undergo co-pyrolysis (Alén *et al.* 1996; Kjeldsen *et al.* 1996; Biagini *et al.* 2006; Qu *et al.* 2011). Alén *et al.* (1996) investigated the thermochemical behavior of pine wood and its main structural constituents (cellulose, hemicelluloses, and lignin) using py-GC/MS and indicated that the composition of the volatile phase from wood pyrolysis behaved as the sum of its constituents in the temperature range of 400 to 1000 °C. A similar conclusion was drawn by Biagini *et al.* (2006), in that the calculated sums are in good agreement with the experimental results under the study of TG-FTIR (a thermogravimetric analyzer coupled with Fourier transform infrared analysis). Using thermogravimetric analysis (TGA) technology, Kjeldsen *et al.* (1996) established that there is no interaction between the components by comparing the thermal weight loss characteristics of 14 kinds of biomass samples and 7 components (Whatman cellulose, cellulose in wood, alkali lignin, acid lignin, hemicellulose, xylan, and extracts).

The interactions that exist between two components cannot be neglected (cellulose-lignin, xylan-lignin, and cellulose-xylan) during the pyrolysis process according to previous studies. Some reports focus on the interactions between cellulose and lignin (Gani and Naruse 2007; Hosoya *et al.* 2007; Wang *et al.* 2011; Dorez *et al.* 2014; Jing *et al.* 2015). Cellulose and lignin interactions during pyrolysis at 800 °C were investigated by Hosoya *et al.* (2007). They found that lignin inhibited the thermal polymerization of levoglucosan formed from cellulose and enhanced the formation of low-molecular weight products, while cellulose reduced the secondary char formation from lignin and enhanced the formation of products including guaiacol, 4-methyl-guaiacol, and 4-vinyl-guaiacol from lignin pyrolysis. By means of TG analysis of the pyrolysis of seven biomasses with different contents of the three components, the presence of a low content of lignin was found to impede the cellulose degradation pathway, leading to the promotion of a higher than expected char yield (Dorez *et al.* 2014).

There are also a few studies that proposed some interactions that existed under hemicellulose and lignin co-pyrolysis conditions. Wang *et al.* (2011) analyzed the pyrolysis products by GC-MS and GC and found that the amount of the lignin-derived phenol, 2,6-dimethoxy phenol, is enhanced by the integrated influence of hemicellulose. A similar conclusion has been reported by Kawamoto *et al.* (2015), in which xylan activated the formation of both phenolic and nonphenolic dimers.

Cellulose and hemicellulose do not act independently during pyrolysis, according to previous studies. Wang *et al.* (2011) also have shown that the interaction of cellulose and hemicellulose strongly promotes the formation of 2,5-diethoxytetrahydrofuran and inhibits the formation of altrose and levoglucosan, while cellulose enhances the formation of hemicellulose-derived acetic acid and 2-furfural. For a native cellulose-hemicellulose mixture, no significant interaction was identified by Jing *et al.* (2015).

The phenolic compounds in the bio-oil obtained from fast pyrolysis of biomass are high value-added chemical products. Due to the complexity of the secondary cell wall structure of biomass, the formation process of phenolic compounds is affected by many

factors, among which the interaction of components are particularly significant. Therefore, in the study, the target product was the phenolic compounds, and the research objective was the lignin-producing phenolic compounds. Cellulose, hemicellulose, and lignin were used as the experiment materials. One-component and two-component mixtures (cellulose-lignin and hemicellulose-lignin were mixed with mass ratios of 3:1, 2:1, 1:1) were subjected to pyrolysis in a tubular furnace at different temperatures (450 to 600 °C). The influence of cellulose and hemicellulose on the phenolic products distribution of lignin was studied by means of the calculation method based on weights, the peak area ratio method, and a statistical method for evaluation. The study of these effects of biomass components on the phenolic production can provide basic data for the production of high value-added products for the directional transformation of biomass.

EXPERIMENTAL

Materials

The cellulose sample used in the study was in powder fibrous form and was purchased from Aladdin Industrial Corporation (CN). Xylan, which was obtained from beechwood, was used as a representative for hemicellulose. The alkali lignin sample was in the form of a brown powder. Xylan and lignin samples were purchased from Sigma-Aldrich Corporation (USA).

The volatiles, fixed carbon, and ash content of samples were analyzed according to Chinese National Standards (GB/T 28731), and elemental analysis of samples was determined using a EURO EA3000 Analyzer (LEEMAN LABS INC., Hudson, USA). The proximate and ultimate analysis results are summarized in Table 1.

To study the interaction of cellulose and lignin, and xylan and lignin, different ratios of mixing were conducted before two-component fast pyrolysis: the mass ratios of cellulose and lignin of 3:1, 2:1, 1:1, the mass ratios of xylan and lignin of 3:1, 2:1, 1:1.

Table 1. Proximate and Ultimate Analyses of the Three Components

Materials	Elemental Analysis (wt %)					Proximate Analysis (wt %)		
	C	H	O	N	S	Volatiles	Fixed carbon	Ash
Cellulose	39.95	6.20	52.77	0.00	1.08	94.35	5.65	0.00
Xylan	41.40	5.92	52.64	0.01	0.03	76.28	21.82	1.90
Lignin	48.53	4.49	43.86	0.10	3.02	8.19	37.69	4.12

Pyrolysis Experiments

The fast pyrolysis experiments were conducted with a fixed bed tubular furnace, as shown in Fig. 1. The pyrolysis system includes an electrical heater, tubular reactor (with an inner diameter of 55 mm and length of 680 mm), and two cooling and collecting bottles. Nitrogen with a purity of 99.99% was used as a carrier gas. Pure component and two-component mixture (cellulose-lignin and xylan-lignin) were used to be experiment materials that were placed into porcelain boats (with sizes of 50 mm $\times$ 20 mm $\times$ 10 mm). Experimental procedures are summarized as follows: prior to experiments, the pyrolysis temperature was set to 450, 500, 550, and 600 °C by the electrical controller and the reaction tube was purged with nitrogen (with a flow rate of 300 mL/min). When the temperature reached the set temperature, the porcelain boats filled half way were pushed rapidly into the heating area one after another. The heating rate of materials was

approximately 1000 °C/s. The pyrolysis time for each porcelain boat was approximately five minutes. The pyrolysis volatile gases accompanied by nitrogen flowed into the cooling system. The condensable volatile gases were condensed into bio-oil and mainly collected in collection bottles, and the non-condensable volatile gases were collected in gas collector bag. The waste collecting bottles that filled with ethanol water used to remove particles from the gas.
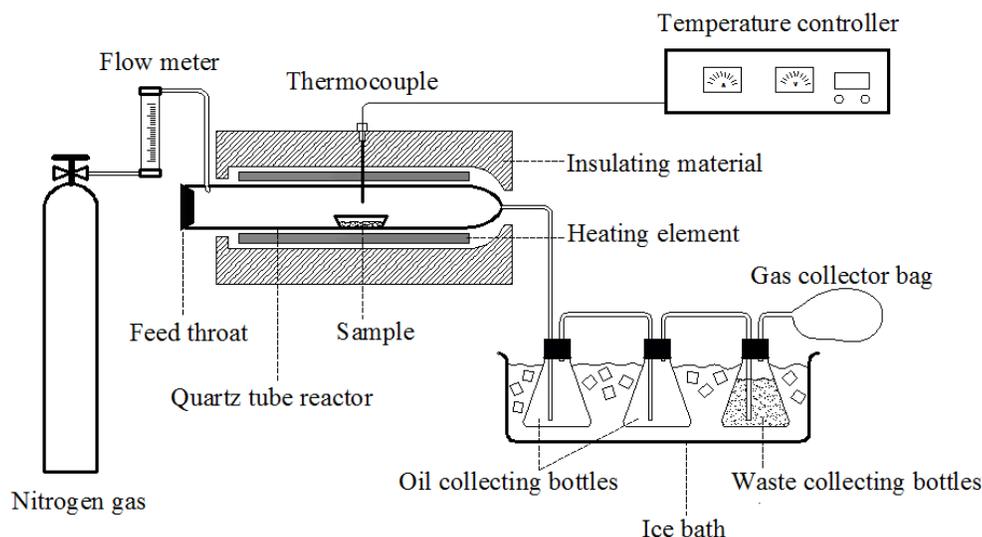
Fig. 1. Fixed bed tubular furnace

GC-MS Analysis

Gas chromatography-mass spectrometry (GC-MS), which is a popular chemical analytical instrument, was used to analyze the chemical composition of bio-oil in this study (Kloos *et al.* 2014; Wang *et al.* 2011). The GC-MS analysis was carried out using a 6890 gas chromatograph (Agilent, USA) and 5973N mass spectrometer (Agilent, USA). The chromatographic column used in the study was a DB-1701 GC capillary column (with a length of 60 m, inside diameter of 0.25 mm, and film thickness of 0.25 mm). Split injection mode was used with a ratio of 60:1 at 290 °C. Helium (99.999% high purity) was used as the carrier gas with a flow rate of 1 mL/min. The temperature program was as follows: the GC oven temperature was programmed from 40 to 240 °C at a rate of 5 °C/min and then held at 240 °C for 5 min. The inlet temperature was maintained at 250 °C. The temperature of the transfer line between GC and MS was set at 280 °C, and the ion source temperature was set at 250 °C for MS. The composition of bio-oil was obtained from the final ion chromatogram. The analytical run time was 45 min in total.

RESULTS AND DISCUSSION
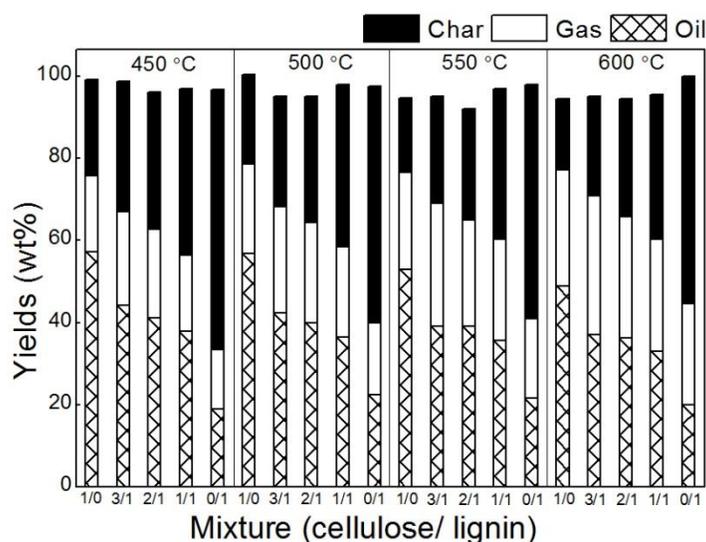
Product Distribution

To investigate the influence of the interactions between two components (cellulose-lignin and xylan-lignin) on the pyrolysis product distribution, cellulose-lignin and xylan-lignin were pre-mixed with weight ratios of 3:1, 2:1, and 1:1. The distribution of gas, bio-oil, and char obtained from fast pyrolysis of the three components is shown in

Fig. 2. The calculation methods for product yield have been reported in previous studies (Lv *et al*. 2013).

As can be seen from Fig. 2, the gas yield increased while the char yield decreased with increasing temperature during pyrolysis. Moreover, the yield of bio-oil first increased and then decreased as the temperature increased from 450 to 600 °C. These results are consistent with the pyrolysis products obtained from native biomass (Lv *et al*. 2013). The maximum yields of bio-oil and gas were obtained from cellulose and xylan, respectively (Ayhan and Gönenç 2002; Qu *et al.* 2011; Giudicianni *et al.* 2014; Shen *et al*. 2015). This may be because lignin acted as a promoter for primary cracking of cellulose-produced volatiles (Giudicianni *et al.* 2014). The maximum yield of char was obtained from lignin pyrolysis, which may because lignin contains the highest fixed carbon content and is also the most thermally resistant among the three components (Ayhan and Gönenç 2002; Qu *et al*. 2011; Xin *et al*. 2013; Shen *et al*. 2015).

It also can be seen in Fig. 2 that the char yield decreased and the bio-oil and gas yields increased with increasing cellulose content. Particularly, the gas yield from co-pyrolysis of cellulose and lignin was remarkably higher than that from their separate pyrolysis. This phenomenon shows that the presence of cellulose promotes the formation of gas product. Gas products from biomass fast pyrolysis were mainly primary non-liquefied vapors, and there was some light oxide generated by secondary cracking of liquefied vapors, although the residence time of vapors in the oven was less than 2 s. The increases in bio-oil yields with increases in cellulose content were not obvious, which indicated that lignin inhibited the pyrolysis of cellulose to produce bio-oil and probably promoted the decomposition of primary volatiles for cellulose. These results are in agreement with previous studies (Wang *et al*. 2011).

As shown in Fig. 2, the change trends with respect to bio-oil and char in the co-pyrolysis of xylan and lignin were similar to that of cellulose and lignin. It can be seen that the co-pyrolysis of cellulose and lignin was similar to that of xylan and lignin. In addition, the effect of the interaction between xylan and lignin on the gas products was somewhat weaker than that of cellulose and lignin. This may be due to the fact that xylan has many side chains that are susceptible to heat cracking at low temperatures, generating small molecules of gas (Xin *et al*. 2013). Therefore, in the temperature range of 450 to 600 °C, the effect of xylan and lignin co-pyrolysis on gaseous products was not as obvious as that of cellulose and lignin.

a. Distribution of products obtained from cellulose and lignin co-pyrolysis
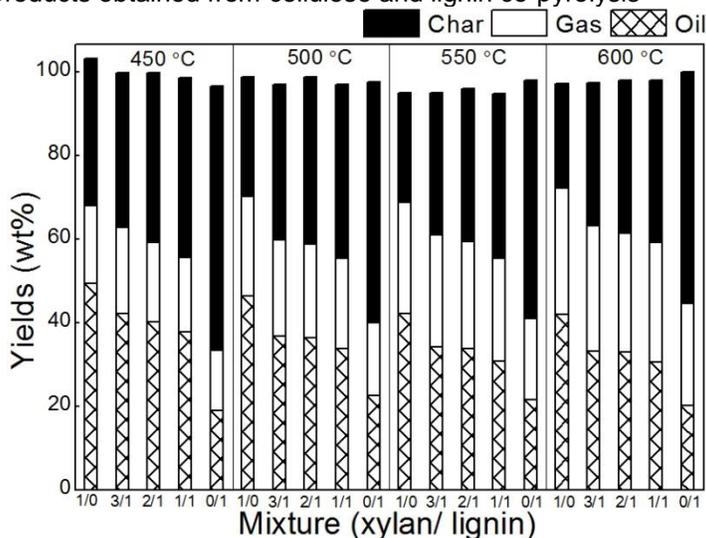
b. Distribution of products obtained from xylan and lignin co-pyrolysis

Fig. 2. Distribution of products obtained from co-pyrolysis of two components

Influence of the Interactions on Phenolic Products

Bio-oil rich in phenol can be used for preparation of high-value-added chemical products. The phenolic products in bio-oil are primarily produced by lignin pyrolysis, which occurs because of the unique structure of lignin; this structure is primarily composed of three phenylpropane (Shen *et al*. 2015a) units connected by ether bonds (*e.g.*, β-β, 5-5) and C=C bonds (Mansouri and Salvadó 2006). Therefore, the phenolic compounds from lignin pyrolysis can be categorized into several groups according to the number of –OCH$_3$ groups on the benzyl ring (Shen *et al*. 2015b): hydroxyphenols (namely phenol and alkylphenol, *e.g.*, phenol, 4-methyl phenol, and 3,4-dimethyl phenol), guaiacols (*e.g.*, 2-methoxyl phenol), and syringols (*e.g.*, 2,6-dimethoxyl phenol).

The difference between one-component pyrolysis and two-component co-pyrolysis can be used to study the effects of components on the phenolic production (Qu *et al*. 2011). When two components are subjected to co-pyrolysis, the resulting phenolic

content can be calculated by multiplying the bio-oil yield and the phenolic content of the bio-oil. Lignin in the two-component mixture is the main source of phenolic compounds; therefore, based on an assumption that there is no interaction between the components having an effect on the phenolic products, the calculated results of the phenolic content of lignin pyrolysis can be calculated by multiplying the weight of lignin in the mixture, bio-oil yield from lignin pyrolysis and phenolic content in the bio-oil.

The differences between the calculated and experimental GC-MS relative peak areas (content %) of the phenolic products from the two-component pyrolysis are shown in Fig. 3. When comparing the experimental and calculated results, it is clear that the chemical interactions occurred when cellulose and lignin, and xylan and lignin, were pyrolyzed simultaneously. Furthermore, the content of hydroxyphenols increased, but that of guaiacols and syringols decreased, with increasing temperature. Studies have shown that phenol and alkylphenols are mostly generated from the secondary cleavage reaction of guaiacols and syringols (Shen *et al*. 2010; Bai *et al*. 2014; Hu *et al*. 2012). In addition to temperature, the interactions during two-component co-pyrolysis also influenced the formation of phenolic products. It is known that cellulose, xylan, and lignin have different heat capacities (Hatakeyama *et al*. 1982). Therefore, different mass ratios resulted in different heat capacities, which might be one reason for the influence of two-component co-pyrolysis on the characteristics and distribution of products (Wu *et al*. 2016).

As shown in Fig.3, there was an upward trend in the difference between experimental and calculated results with increasing temperature during co-pyrolysis of cellulose and lignin, suggesting that the yield of lignin-derived phenolic products was promoted by the positive effect of cellulose. This could be due to the stabilization effect of the CH-π interaction between laevoglucose from cellulose pyrolysis and π-electrons in the benzene ring from lignin pyrolysis, which would facilitate the decomposition reaction of lignin and inhibit the secondary decomposition of the product in phenolic form (Hosoya *et al*. 2006). With increasing lignin content, the promotion of phenolic product content was enhanced. Moreover, as the temperature increased, there was an increase in the difference between experimental and calculated results. This further confirms that temperature and cellulose both have notable influences on the production of phenolic compounds from lignin pyrolysis. The same conclusions have been reached in previous studies (Hosoya *et al*. 2007; Kawamoto *et al*. 2015; Jing *et al*. 2015). The effects of the interaction of cellulose and lignin on the phenolic products have been investigated at temperatures ranging from 150 to 800 °C. When the pyrolysis temperature is below 300 °C, cellulose exerts a passive influence on the formation of lignin-derived products (Kawamoto *et al*. 2015), while with increasing temperature, the lignin-derived product content increases under the promotion of cellulose (Hosoya *et al*. 2007; Jing *et al*. 2015).

The interactions between xylan and lignin also play important roles in the formation of phenolic products. It can be seen from Fig. 3 that there were differences between experimental and calculated results under co-pyrolysis of xylan and lignin, suggesting that the reaction pathways of xylan and lignin are different from those of cellulose and lignin. In the presence of xylan, the formation of guaiacols and syringols was remarkably inhibited, and that of hydroxyphenols was promoted. The effects of xylan on the formation of phenolic products became stronger with increasing content of lignin. Moreover, an increase in temperature enhanced these effects. The above results indicate that the interactions of xylan and lignin accelerated the decomposition process of lignin and the secondary cracking of lignin primary phenolic products to generate many

light oxygen compounds. These results are similar to those of Kawamoto *et al*. (2015) and Wang *et al*. (2011), in which xylan activated both phenolic and non-phenolic dimers from lignin pyrolysis. The ratios of experimental and calculated peak areas of typical phenolic products obtained from lignin and two-component pyrolysis at 550 °C are listed in Table 2. The calculated and experiment peak areas are calculated based on the bio-oil yield and phenolic peak area in the bio-oil as the above mentioned. If the ratio is 1, that would suggest that there is no interaction between two components. However, when the ratio is greater than 1 or less than 1, there is promotion (>1) or suppression (<1) of phenolic production. It can be seen from Table 2, for the co-pyrolysis of cellulose and lignin at 550 °C, that when the mass ratio of cellulose and lignin was 1:1, the ratio of experiment and calculated peak area of phenol, 2-methylphenol, 2,4-dimethylphenol, and 4-methoxy-3-methylphenol was 2.81, 3.10, 2.76, and 0.66, respectively. These findings indicated that the presence of cellulose enhanced most phenolic compound production from lignin pyrolysis, especially phenol and alkyl phenol, except 4-methoxy-3-methylphenol. Table 2 also shows the effects of xylan-lignin interactions on phenolic compounds. Most hydroxyphenols were promoted and most guaiacols were inhibited by the presence of xylan. Taking the mass ratio of xylan and lignin of 1:1 as example, the ratio of experimental and calculated peak area of phenol, 2-methylphenol, 2,4-dimethylphenol, 2-methoxyphenol, 2-methoxy-4-methylphenol, and 4-ethyl-2-methoxyphenol was 2.73, 2.80, 1.86, 0.27, and 0.61, respectively. Also, these effects are both enhanced with increasing content of cellulose and xylan. The conclusions are similar to the analysis of the phenolic relative content.
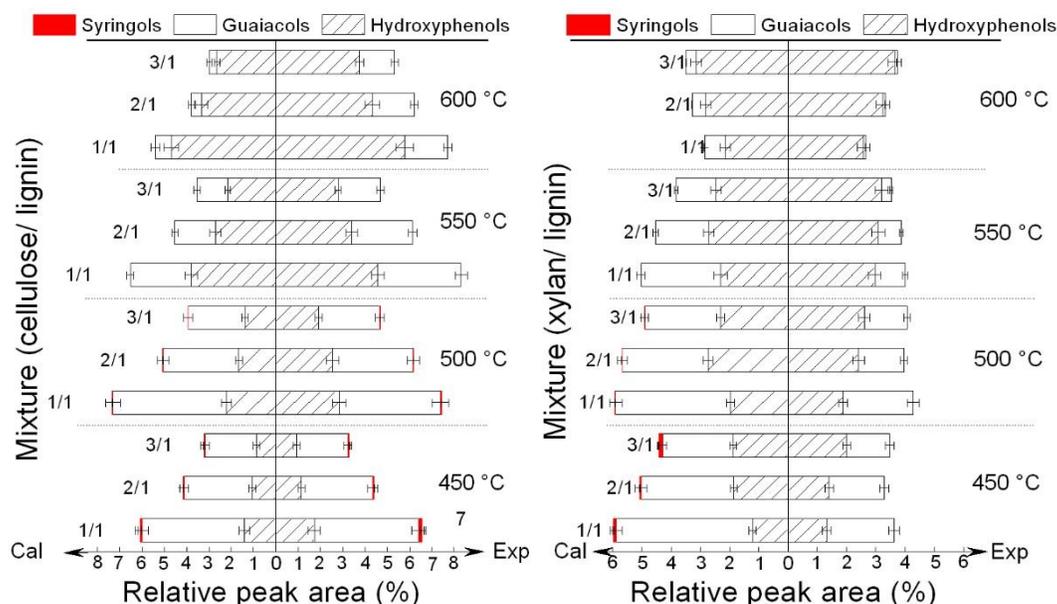

Fig. 3. Distribution of phenolic products obtained from two-component co-pyrolysis

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Table 2. Ratio of Experimental and Calculated Results Obtained from Lignin and Two-Component Pyrolysis at 550 °C

Phenolic compounds	Experimental [a]/calculated [b] peak area ratio					
	C:L-1:1	C:L-2:1	C:L-3:1	X:L-1:1	X:L-2:1	X:L-2:1
Phenol	2.81	2.05	1.98	2.73	2.18	1.61
Phenol, 2-methoxy-	1.31	1.27	1.23	0.27	0.88	0.91
Phenol, 2-methyl-	3.10	2.50	2.41	2.80	0.77	1.03
Benzene, 1,2-dimethoxy-	1.59	1.51	1.21	0.51	0.66	0.83
Phenol, 3-methyl-	2.75	1.91	1.65	1.84	1.92	1.11
Phenol, 4-methyl-	3.41	2.88	2.64	1.70	1.08	1.18
Phenol, 4-methoxy-3-methyl-	2.63	1.12	0.90	0.52	0.76	0.86
Phenol, 4-methoxy-3-methyl-	0.66	0.45	0.31	0.40	0.55	0.60
Phenol, 2-methoxy-4-methyl-	1.67	1.16	0.32	0.80	0.87	0.94
Phenol, 2,4-dimethyl-	2.76	2.69	2.20	1.86	1.68	1.48
Phenol, 3,5-dimethyl-	2.78	2.73	2.07	0.47	0.44	0.44
Phenol, 4-ethyl-	1.48	1.58	1.32	1.58	1.04	0.96
Phenol, 3,4-dimethyl-	1.53	1.41	1.25	1.89	1.78	1.04
Phenol, 4-ethyl-2-methoxy-	1.57	0.88	0.86	0.61	0.84	0.92
2-Methoxy-4-vinylphenol	1.25	1.15	1.21	0.46	0.71	0.92
Benzaldehyde, 3-hydroxy-4-methoxy-	1.75	0.76	0.73	0.51	0.66	0.62
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.38	1.25	1.09	2.54	1.98	1.56

a. The peak areas obtained from the co-pyrolysis of cellulose-lignin and xylan-lignin
b. The calculated peak areas are based on the weight of lignin in the mixture.

Statistical Method for Evaluation of Cellulose-Lignin and Xylan-Lignin Interaction

The strength of cellulose-lignin and xylan-lignin interactions can be evaluated using a statistical method that has been reported in previous studies (Wu *et al*. 2016). The correlation coefficient, R, has been introduced as an index for interaction strength. The correlation coefficient ranged from 0 to 1. When the correlation coefficient is 0, there is no interaction between the two components for phenolic production, but there is the strongest interaction when it is 1. This method can be used to evaluate the overall interactions between cellulose and lignin as well as xylan and lignin with 1:1, 2:1, and 3:1 ratios during pyrolysis. The phenolic product distribution and correlation coefficient of co-pyrolysis of cellulose-lignin and xylan-lignin are illustrated in Fig. 4.
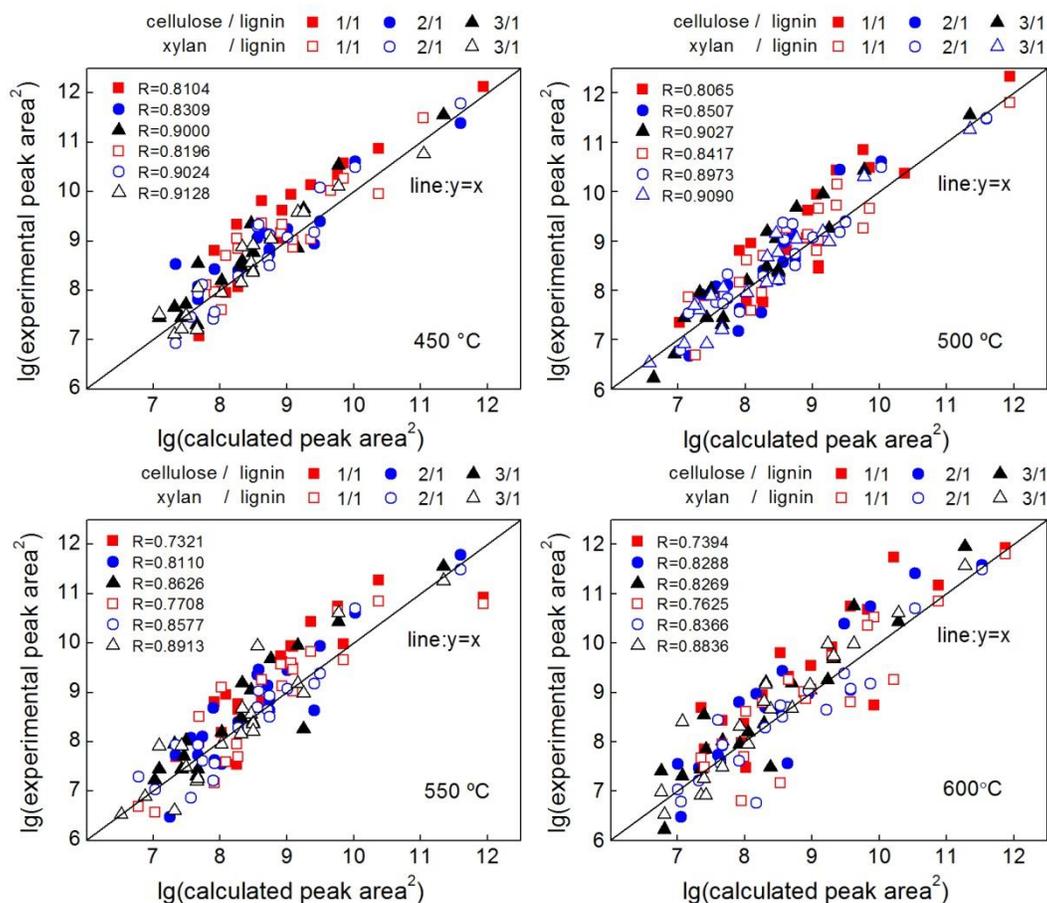
Fig. 4. Phenolic product distribution and correlation coefficient of co-pyrolysis of cellulose-lignin and xylan-lignin mixtures

It can be seen from Fig. 4 that the R-value was 0.7321 when the mass ratio of cellulose and lignin was 1:1; the R-value was 0.8110 when the mass ratio was 2:1; and the R-value was 0.8626 when the mass ratio was 3: 1, in the case of pyrolysis temperature of 550 °C. For the co-pyrolysis of xylan and lignin, at 550°C, the R-value was 0.7708 when the mass ratio of xylan and lignin was 1:1, the R-value was 0.8577 when the mass ratio was 2:1, and the R-value was 0.8913 when the mass ratio was 3:1. Under the other pyrolysis temperature conditions, with the change of mass ratio of two components mixture (cellulose-lignin and xylan-lignin), the change of R-value was similar to that of 550 °C. These indicated that with the decrease in cellulose or xylan content in mixture, The correlation coefficient R was always lower than 1 and had a downward trend. Therefore, the promotion of cellulose and xylan on phenolic formation from lignin pyrolysis were weakened with the decrease of cellulose and xylan content. The difference of the correlation coefficient R-value between cellulose-lignin and xylan-lignin may due to the different heat capacities of the mixtures. Based on the above analyses, cellulose and xylan can promote the demethoxylation reaction of lignin. However, the presence of cellulose promotes the secondary cracking of the primary phenolic products of lignin, which may be due to the fact that some of the products formed in the low-temperature region provide sufficient side-chain initiation groups for the subsequent thermal cracking of lignin, thereby inhibiting the fused cyclization of lignin and other side effects.

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For the effect of temperature on the influence strength, the R-values were decreased with the temperature increasing from 450 °C to 600 °C. There was a clear trend of enhanced effects with increasing temperature. Taking the mass ratio of the mixture as 1:1 as an example, when the mass ratio of cellulose to lignin was 1:1, the R-values were decreased from 0.8104 to 0.7394; and when the mass ratio of xylan to lignin was 1: 1, the R-values were decreased from 0.8196 to 0.7625. The strength of the cellulose-lignin and xylan-lignin interactions increased dramatically with co-pyrolysis at 600 °C. The effect of temperature on cellulose-lignin interactions is a comprehensive result of H-transfer mechanism, cellulose-lignin complex mechanism, covalent bonds, and morphology (Wu *et al*. 2016). The low thermal stability of guaiacols and syringols may be the reason why the xylan-lignin interactions were enhanced with increasing temperature.

CONCLUSIONS

1. In this study, the effects of two parameters (mixture ratio and temperature) on cellulose-lignin and xylan-lignin interactions were investigated. The product distribution and the phenolic product content during two-component pyrolysis were used to characterize the interaction between components with mixture ratios of 3:1, 2:1, and 1:1.

2. For the distribution of pyrolysis products, cellulose, xylan, and lignin were the main contributors to the mass of biomass bio-oil, gas, and char, respectively. The char yields decreased and bio-oil and gas yields increased in the presence of cellulose and xylan. The xylan-lignin interactions are also somewhat weaker than those of cellulose-lignin.

3. During two-component co-pyrolysis, cellulose promotes an increase in lignin-derived phenolic products, including hydroxyphenols, guaiacols, and syringols. There is a different phenomenon for xylan-lignin interactions. The formations of guaiacols and syringols are inhibited, while the formation of hydroxyphenols is enhanced in the presence of xylan. The relative content and peak area can both be used to support this conclusion.

4. The presences of a lower content of cellulose and a higher content of xylan in biomass can promote the production of lignin-derived hydroxyphenols. However, when the cellulose content is higher and the xylan content is lower in biomass, the production of guaiacols and syringols will be enhanced, especially 2-methoxyphenol and 1,2-dimethoxybenzene. This study of the interaction between cellulose and lignin, as well as xylan and lignin, provides the basic theoretical data needed to characterize the selectivity of biomass feedstocks and the directional transformation of pyrolysis products.

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