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Effect of cellulose-lignin interactions on char structural changes during fast pyrolysis at 100 – 350 °C

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Colloquium 8: SOLID FUEL COMBUSTION

Estimation of length using the provided method

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Abstract

This study investigates the cellulose-lignin interactions during fast pyrolysis at 100–350 °C for better understanding fundamental pyrolysis mechanism of lignocellulosic biomass. The results show that co-pyrolysis of cellulose and lignin (with a mass ratio of 1:1) at temperatures < 300 °C leads to a char yield lower than the calculated char yield based on the addition of individual cellulose and lignin pyrolysis. The difference between the experimental and calculated char yields increases with temperature, from ~2% at 150 °C to ~6% at 250 °C. Such differences in char yields provide direct evidences on the existence of cellulose-lignin interactions during co-pyrolysis of cellulose and lignin. At temperatures below 300 °C, the reductions in both lignin functional groups and sugar structures within the char indicate that co-pyrolysis of cellulose and lignin enhances the release of volatiles from both cellulose and lignin. Such an observation could be attributed to two possible reasons: (1) the stabilization of lignin-derived reactive species by cellulose-derived reaction intermediates as hydrogen donors, and (2) the thermal ejection of cellulose-derived species due to micro-explosion of liquid intermediates from lignin. In contrast, at temperatures ≥ 300 °C, co-pyrolysis of cellulose and lignin increases char yields, i.e., with the difference between the experimental and calculated char yields increasing from ~1% at 300 °C to ~8% at 350 °C. The results indicate that the cellulose-derived volatiles are difficult to diffuse through the lignin-derived liquid intermediates into the vapour phase, leading to increased char formation from co-pyrolysis of cellulose and lignin as temperature increases. Such an observation is further supported by the increased retention of cellulose functional groups in the char from co-pyrolysis of cellulose and lignin.

Keywords: Cellulose; Lignin; Co-pyrolysis; Char Structure; Cellulose-Lignin Interactions

1. Introduction

Lignocellulosic biomass is a renewable feedstock widely utilized in thermochemical processes such as pyrolysis [1] and comprises of three major components (cellulose, hemicellulose and lignin) [2, 3]. Each component exhibits different pyrolysis behaviour upon heating. Under non-catalytic conditions, hemicellulose decomposes rapidly at ~220 °C, followed by cellulose decomposition at ~300 °C, while lignin decomposes over a wide range of temperatures from 160 to 900 °C [3, 4]. The differences in properties and compositions of these biomass components strongly affect both pyrolysis mechanisms and product distributions [5, 6].

During lignocellulosic biomass pyrolysis, different biomass components may interact with each other. Hosoya et al. [6] observed significant interactions between cellulose and lignin at 800 °C, while interactions between cellulose and hemicellulose are weak. On one hand, the presence of cellulose inhibits the polymerization of lignin-derived species and enhances the formation of light compounds (such as guaiacol) from lignin. On the other hand, the presence of lignin also influences cellulose pyrolysis. It is known that cellulose pyrolysis mainly produces anhydro-sugars (i.e., levoglucosan) as primary products [7], which tend to polymerize into char within the liquid intermediate phase, or evaporate into volatiles [8]. The presence of lignin not only suppresses the polymerization of levoglucosan into char, but also promotes the formation of some light compounds such as furfural, 5-HMF and acetic acid [8, 9].

However, previous studies on the interactions of cellulose and lignin mainly focused on the product yields [6, 10-13], the kinetic modelling [10, 14], and the characteristics of the volatiles [6, 9, 15, 16] from co-pyrolysis of cellulose and lignin. The knowledge on the characteristics and properties of chars produced from co-pyrolysis of lignin and cellulose is limited, while such knowledge is essential to understanding the pyrolysis mechanism of lignocellulosic biomass for various thermochemical applications especially for bio-oil/biochar production. Therefore, the main objective of this study is to understand the effect of cellulose-lignin interactions on char structure changes during co-pyrolysis of cellulose and lignin at 100–350 °C.

2. Experimental

2.1. Sample preparation

The lignin (kraft, alkali) and cellulose (Avicel PH-101) samples were purchased from Sigma-Aldrich. All samples were first sieved to a size fraction of 75–106 μm . Prior to the preparation of cellulose-lignin mixture, both cellulose and lignin samples were leached in ultrapure water under agitation to remove the water-soluble compounds and the inorganic species. The leaching of both samples was repeated for several times until no further water-soluble compounds or inorganic species could be detected in the washing solution. The cellulose-lignin mixture sample (with a mass ratio of 1:1 to represent the ratio of cellulose-to-lignin in lignocellulosic biomass) was then prepared by wet mixing method to obtain a more homogeneous mixture compared to dry mixing. Table 1 lists the properties of the cellulose, lignin and cellulose-lignin mixture samples used in this study. All samples were dried a 40 °C in oven to remove excessive moisture for experiment use.

2.2. Fast pyrolysis experiments

A series of fast pyrolysis experiments were carried out using a drop-tube/fixed-bed quartz reactor with pulsed-feeding (detailed description given elsewhere [17]) at 100–350 °C. It should be noted that temperatures higher than 350 °C were not considered due to the difficulties in collecting sufficient char samples for detailed characterization. Briefly, the reactor was preheated to the desired pyrolysis temperature in a furnace with a stream of ultra-high-purity argon (flowrate: 1.1 L/min) as carrier gas. Approximately 0.4 g of each sample was fed into the reactor in a single shot, followed by holding the reactor at the pyrolysis temperature for a further 15 min. Upon completion of the pyrolysis, the reactor was immediately removed from the furnace, and cooled to room temperature with argon continuously flowing through the reactor. The char yield (on a dry basis) was calculated by the weight difference of the reactor before and after the experiment. The char product was collected for further structural characterization.

2.3. Sample characterization

The raw samples (i.e., cellulose, lignin and cellulose-lignin mixture) and char products were characterised via a series of techniques. The ultimate analyses were performed using an elemental analyser (Perkin-Elmer 2400 Series II), whereas the proximate analyses were conducted using a thermogravimetric analyser (TGA Mettler) according to ASTM E870-92. The ultimate and proximate analyses results of the raw samples are presented in Table 1. Post hydrolysis experiments were also carried out to analyse the sugar contents of the solid samples, according to the NREL method [18].

Table 1. Properties of the cellulose, lignin and cellulose-lignin mixture samples used in this study.

Sample	Moisture (wt%, ar ^a)	Proximate (wt%, db ^b)			Ultimate (wt%, daf ^c)			
		Ash	VM ^c	FC ^d	C	H	N	O ^f
Lignin	3.0	0.8	56.3	42.9	63.3	6.1	0.37	30.2
Cellulose	2.4	0.1	91.5	8.4	42.6	6.2	-	51.1
Cellulose-lignin	2.3	0.3	71.9	27.8	52.8	6.1	0.14	40.9

^aar = air-dried (as received). ^bdb = dry basis. ^cVM = volatile matter. ^dFC = fixed carbon. ^edaf = dry ash free. ^fby difference.

The chemical functional groups of the solid samples were characterized by a Fourier transform infrared (FT-IR) spectrometer (Bruker IFS 66) using a KBr pellet method detailed elsewhere [19]. According to our previous method [19], the intensities of FT-IR spectra linearly change with char concentration in the KBr pellet. Thus, all spectra were corrected for background and then normalized to the unit mass (per mg on a dry basis) of the sample fed into the reactor for direct comparisons. The UV fluorescence spectra of the THF-soluble portions of the solid samples were also obtained using an UV fluorescence spectrometer (Perkin-Elmer LS 55) to understand the change of aromatic ring structures, as detailed elsewhere [20]. Our previous study [19] has also shown that the intensities of UV fluorescence linearly change with the sample concentration in the THF solvent. Thus, the UV fluorescence spectra were also normalized to the unit mass (per mg on a dry basis) of the sample fed into the reactor for direct comparisons. The solid state ¹³C CP/MAS NMR spectra of the solid samples were acquired to study the changes of carbon structures via a Varian 400 MHz NMR spectrometer equipped with a 4 mm CP/MAS probe, following a method detailed elsewhere [19].

3. Results and Discussion

3.1. Yields and properties of the chars produced from the fast pyrolysis of cellulose, lignin and cellulose-lignin mixture

Fig. 1 presents the char yields of the fast pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C. Cellulose decomposition is slow at temperatures < 250 °C, with char yields reducing from ~99% at 100 °C to ~96% at 250 °C, but becomes substantial at temperatures > 250 °C with a char yield of only ~6% at 350 °C. Compared to cellulose, lignin decomposes gradually as temperature increases, with char yields reducing from ~96% at 100 °C to ~46% at 350 °C. For cellulose-lignin mixture, the char yield decreases gradually from ~98% at 100 °C to ~64% at 300 °C, but decreases rapidly to ~34% at 350 °C. The char yields were also calculated based on the mass ratio (1:1) of cellulose and lignin in the mixture and the individual char yields at various temperatures, assuming the pyrolysis of cellulose and lignin takes place independently. The experimental and calculated char yields are also compared in Fig. 1. It can be clearly seen that the calculated char yields are higher than the experimental results at below 300 °C, with the difference increasing from ~2% at 150 °C to ~6% at 250 °C. There is almost no difference between the char yields from experiment and calculation at 300 °C, but such a difference increases to ~8% at 350 °C. These results clearly demonstrate the existence of cellulose-lignin interactions during co-pyrolysis of cellulose and lignin.

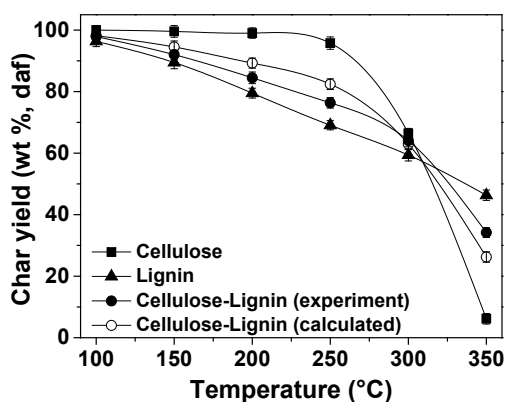


Fig. 1. Char yields from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C.

The sugar contents (i.e., glucose) of char samples from the fast pyrolysis of cellulose, lignin and cellulose-lignin at 100–350 °C were determined via acid hydrolysis, with the results presented in Fig. 2. After post hydrolysis, all sugar structures in the char samples are converted into glucose. Very little amount of glucose (i.e., ~0.1%) could be detected from lignin post hydrolysis. The glucose yield of the char from cellulose decreases progressively with temperature, from ~98% at 100 °C to ~58% at 300 °C, then to zero at 350 °C, indicating the complete destruction of sugar structures at 350 °C. For the cellulose-lignin mixture, the glucose yield of the char reduces from ~49% at 100 °C to ~22% at 300 °C, then to zero at 350 °C. To study the effect of cellulose-lignin interactions on the sugar structures, the sugar yields of the chars were also calculated based on the mass ratio (1:1) of cellulose and lignin in the mixture and their corresponding glucose yields at various temperatures, and the experimental and calculated results are also presented in Fig. 2. It can be seen that there are no obvious differences between the experimental and calculated sugar yields at 150 °C or below. However, the glucose yields from experiments are slightly lower than the calculated results at temperatures > 150°C, demonstrating that the presence of lignin indeed affects the decomposition of sugar structures during cellulose pyrolysis. The difference between the experimental and calculated sugar yields increases slightly from ~5% at 200 °C and ~7% at 300 °C. At 350°C, since all sugar structures are decomposed, there are no differences between the experimental and calculated results. Clearly, these results demonstrate that the presence of lignin enhances the decomposition of sugar structures during cellulose pyrolysis, leading to reduced sugar yields in the char.

The elemental compositions of all raw samples and chars are listed in Table S1 of the Supplemental Material. The carbon content of cellulose char only increases slightly from ~42.7% at 100 °C to ~47.5% at 350 °C, accompanied by the decreasing hydrogen and oxygen contents from ~6.1 to ~5.5 and ~46.9% at 100 °C to ~5.5 and ~46.9% at 350 °C, respectively. This leads to reductions in the atomic H/C and O/C ratios from 1.72 and 0.90 at 100 °C to 1.39 and 0.74 at 350 °C, respectively. In comparison, the carbon content of lignin char increases from ~64.6 to ~71.4% with increasing temperature from 100 to 350 °C, accompanied by the decreasing hydrogen and oxygen contents from

~5.8 and ~23.9% at 100 °C to ~5.0 to ~23.4% at 350 °C, respectively. This leads to a reduction in the H/C atomic ratio from 1.08 at 100 °C to 0.84 at 350 °C, as expected because lignin char becomes more condensed as temperature increases. As for the chars from the cellulose-lignin mixture, the carbon content also increases from ~52.8% at 100 °C to ~58.8% at 350 °C, with the hydrogen and oxygen contents reducing from ~6.0 to ~40.2% at 100 °C and ~5.4 to ~35.7% at 350 °C. The atomic H/C and O/C ratios also decrease from 1.33 and 0.56 at 100 °C to 1.10 and 0.46 at 350 °C, respectively. To further investigate the effect of cellulose-lignin interactions on elemental composition of char during co-pyrolysis, the calculated atomic ratios of H/C and O/C based on the mass ratio (1:1) of cellulose and lignin in the mixture and their corresponding elemental compositions at various temperatures are also presented in Table S1 for comparisons. The experimental H/C ratio is slightly lower than the calculated H/C ratio at 250 °C or below, but higher at temperatures > 250 °C. Similar trends can be observed for the O/C ratio. The results further demonstrate that the cellulose-lignin interactions enhance cellulose decomposition at temperatures \leq 250 °C but suppress the condensation reactions at temperatures > 250 °C.

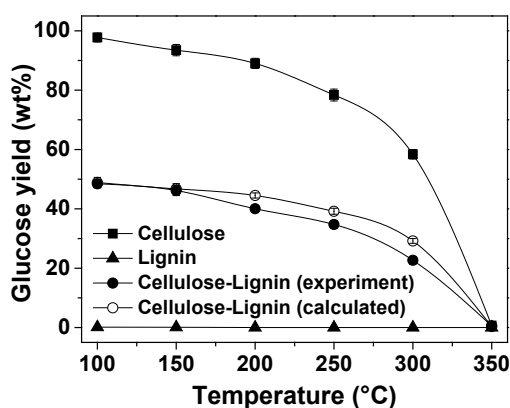


Fig. 2. Glucose yields from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C.

3.2. Structural changes of the chars produced from the fast pyrolysis of cellulose, lignin and cellulose-lignin mixture

The structures of chars from cellulose, lignin and cellulose-lignin mixture were further characterised by a series of analytic instruments including FT-IR, UV fluorescence and NMR. The FT-IR spectra of the raw samples and their chars produced from pyrolysis at 100–350 °C are shown in Fig. 3. The presented spectra of the char samples were all normalized to the unit mass (per mg on a dry basis) of the raw sample for direct comparisons. The peak assignments of various functional groups are summarized in Table S2 of the Supplemental Material. For the cellulose chars, the main peaks identified are –OH stretches (3352 cm^{-1}), C–H bonds (2900 cm^{-1}), C=O bonds (1730 cm^{-1}), OH of methyl or absorbed H₂O (1638 cm^{-1}) and C–O–C vibrations (1050 cm^{-1}). According to the spectra shown in Fig. 3, the absorbance intensities of the chars show slight decreases at low temperatures ($\leq 250\text{ °C}$), and significant changes are only observed when the temperature increases to 300 °C. The slow decrease of –OH stretching at 3352 cm^{-1} can be attributed to dehydration reactions of hydroxyl groups [21, 22]. The band associated to C–H at 2900 cm^{-1} shows the rupture of aliphatic groups of alkyl compounds in cellulose char. It is important to point out that the peak at 1730 cm^{-1} begins to form at $\geq 300\text{ °C}$, indicating the formation of new C=O functional groups (via mechanisms such as dehydration, ring opening and polymerization reactions [23]). The band observed at 1638 cm^{-1} is reported as the –OH bending (due to the absorption of water [22]), known to be produced from dehydration reactions of polysaccharides to form anhydro-sugars [23]. The peak at 1050 cm^{-1} is the C–O–C bridge stretching of pyranose saccharide rings, and its intensity decreases with temperature.

As for the lignin chars, the main functional groups also reduce as temperature increases, including –OH stretches (3419 cm^{-1}), aliphatic C–H (2938 cm^{-1}), –CH₃ stretches (2844 cm^{-1}), C=O bonds (1704 cm^{-1}), aromatic ring vibrations (1513 cm^{-1}) and C–O bonds (1033 cm^{-1}). However, the absorbance intensities of the lignin chars show obvious reductions even at 150 °C, which is expected since lignin decomposition starts at a lower temperature (i.e., $\sim 100\text{ °C}$) than that ($\sim 200\text{ °C}$) for cellulose [20]. It is noted that the intensities at 350 °C are very weak. This can be attributed to the transformation of these functional groups into highly aromatic structures (invisible to FT-IR) via various reactions (e.g.

fragmentation, demethylation and decarbonylation [24]), eliminating aliphatic and phenolic components [25].

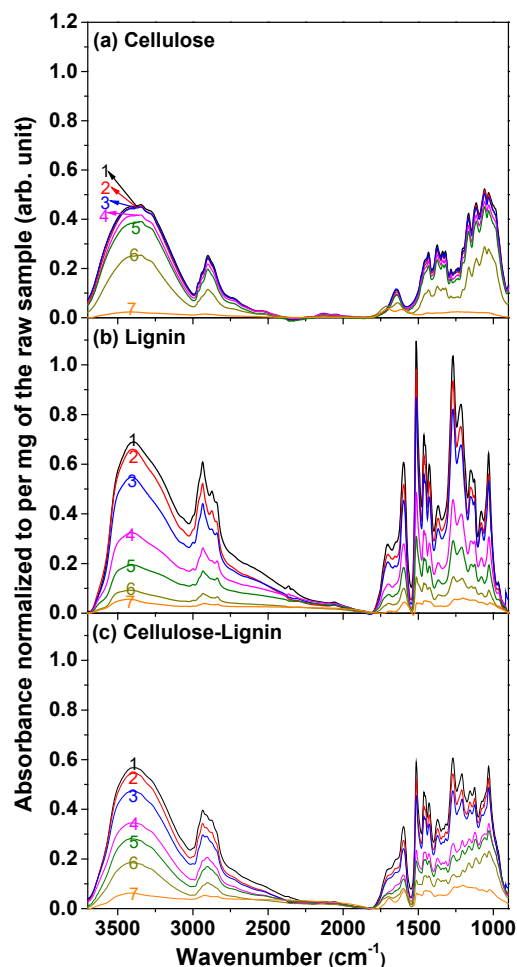


Fig. 3. FT-IR spectra of the chars from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C. Panel (a) cellulose and its chars: (1) cellulose; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C; (7) 350 °C. Panel (b) lignin and its chars: (1) raw lignin; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C; (7) 350 °C. Panel (c) cellulose-lignin mixture and its chars: (1) cellulose-lignin mixture; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C; (7) 350 °C.

For the chars from cellulose-lignin mixture, all the absorption bands decrease with increasing temperature. The major difference lies in the wavenumber of 1000 – 1700 cm^{-1} . The intensities of various functional groups gradually decrease as temperature increases. However, the spectra of the chars at 1000 – 1700 cm^{-1} appear to decrease greatly at 200 °C, mainly due to lignin pyrolysis. The –

OH stretching and aliphatic groups C–H decrease with increasing temperature, showing the release of alkyl chains substituent and phenolic compounds (monomers or oligomers). The aromatic bands mostly between 1513 and 1125 cm^{-1} also decrease with increasing temperature. Major reductions in functional groups take place at 300 $^{\circ}\text{C}$, mainly due to cellulose pyrolysis. The C–O–C bonds derived from saccharides decrease rapidly and majority of them diminish at 350 $^{\circ}\text{C}$.

The FT-IR spectra of the chars from experiments were compared with the calculated spectra based on the mass ratio (1:1) of cellulose and lignin in the mixture and the corresponding FT-IR spectra of chars produced from pyrolysis individually. The differences between the experimental and calculated intensities of the spectra (i.e., subtracting the calculated spectra from the experimental spectra) are presented in Fig. 4. At temperatures < 250 $^{\circ}\text{C}$, negative intensities between the experimental and calculated FT-IR spectra can be seen, i.e., the experimental results are lower than the calculated results. It seems that the release of the lignin-derived volatiles can be enhanced during co-pyrolysis of cellulose and lignin. When the pyrolysis temperature increases to > 250 $^{\circ}\text{C}$, positive intensities between the experimental and calculated FT-IR spectra can be found, indicating that more chemical functional groups from cellulose are retained in the chars at above 250 $^{\circ}\text{C}$.

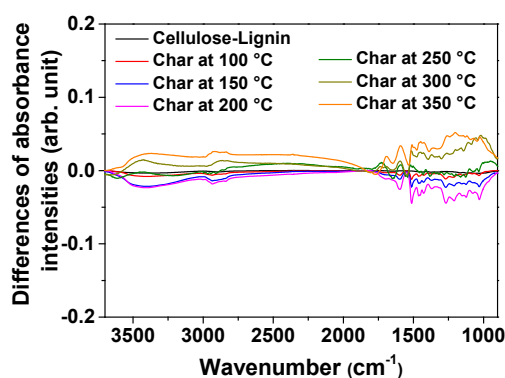


Fig. 4. Differences between the experimental and calculated FT-IR absorbance intensities of chars for the pyrolysis of cellulose-lignin mixture at 100–350 $^{\circ}\text{C}$.

The lignin, cellulose-lignin mixture and respective char samples were dissolved in THF, and the dissolved samples were analysed by UV fluorescence spectrometer to investigate the changes of the

aromatic fused ring structures during pyrolysis. Fig. 5 shows the UV fluorescence spectra of the chars produced from the pyrolysis of lignin and cellulose-lignin mixture at 100–300 °C. It should be noted that there are no UV fluorescence intensities from the cellulose chars. For the chars from lignin and cellulose-lignin mixture, a broad peak can be seen from the spectra in the wavelength range of 250–400 nm, with mono ring at < 290 nm, 2–3 fused rings at 290–340 nm, 3–5 fused rings at 340–390 nm [19]. To enable direct comparisons, all the UV fluorescence spectra were normalized to the unit mass (per mg on a dry basis) of the raw sample, and the results are shown in Fig. 5. For lignin pyrolysis, the UV fluorescence intensities decrease slowly as temperature increases to 150 °C, indicating the slow release of light lignin compounds (i.e., the so-called low-molecular-weight portion of lignin [26]). However, significant reductions in the UV fluorescence intensities can be found at 200 °C, and almost no signals can be detected at 250 °C. This can be attributed to the softening and melting of lignin at ~140 °C, generating a liquid intermediate phase that suppresses the release of volatile compounds from lignin hence forming a char with more aromatic characteristics. The UV fluorescence intensities of the chars from the pyrolysis of cellulose-lignin mixture follow a similar trend, but the reductions in aromatic fused ring structures are much slower at 200 °C, indicating polymerization of lignin-derived aromatic structures being suppressed during co-pyrolysis.

The UV fluorescence intensities of the chars from experiments were also compared with the calculated spectra based on the mass ratio (1:1) of cellulose and lignin in the mixture and their corresponding UV fluorescence intensities of chars produced at various temperatures. The differences between the experimental and calculated UV fluorescence intensities (i.e., subtracting the calculated intensities from the experimental intensities) are plotted in Fig. 6. The experimental results are higher than the calculated results, due to the positive UV fluorescence intensities between the experimental and calculated results. As the temperature increases, the differences of UV fluorescence intensities increase slowly and reach maximum at 200 °C, followed by decreases as temperature further increases. More aromatic structures of 2–5 fused rings are retained in the char during co-pyrolysis of

lignin and cellulose, especially at 200 °C, demonstrating that the presence of cellulose suppresses the polymerization of aromatic structures in lignin during co-pyrolysis of cellulose and lignin.

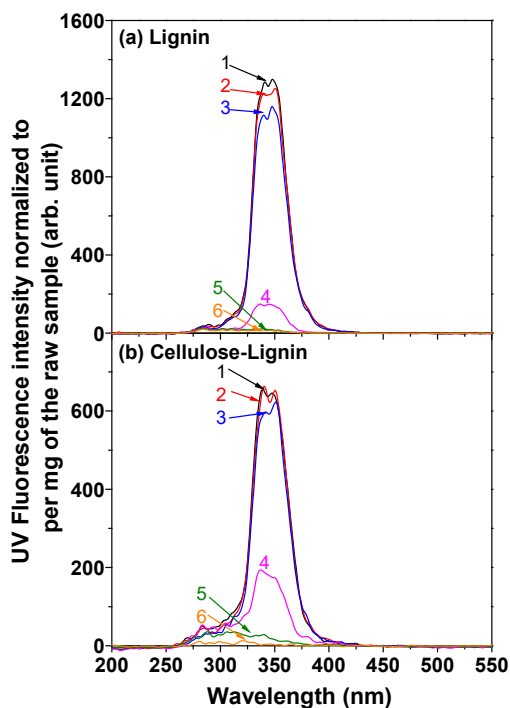


Fig. 5. UV fluorescence spectra of the chars from the pyrolysis of lignin and cellulose-lignin mixture at 100–300 °C. Panel (a) lignin and its chars: (1) lignin; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C. Panel (b) cellulose-lignin mixture and its chars: (1) cellulose-lignin mixture; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C.

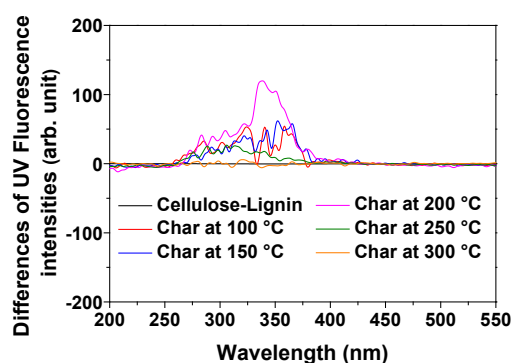


Fig. 6. Differences between the experimental and calculated UV fluorescence intensity of the chars for the pyrolysis of cellulose-lignin mixture at 100–300 °C.

The solid state ^{13}C CP/MAS NMR analysis was also used to study the changes of carbon structure in the chars from the pyrolysis of cellulose, lignin and cellulose-lignin mixture, and the results are

presented in Fig. S1 of the Supplemental material. The assignment of carbons in cellulose are listed as: C1 at 100–108 ppm, combination of C2/C3/C5 at 70–78 ppm, C4 at 81–91 ppm and C6 at 60–66 ppm [27]. For cellulose pyrolysis, there are negligible changes in the spectra of chars at temperatures ≤ 200 °C, as expected. At 300 °C, the spectrum shows the decomposition of sugar structures, since cellulose decomposition starts at 250 °C. The sharp resonance peaks of the NMR spectra of cellulose char also disappear at 300 °C. For lignin pyrolysis, the carbon groups are assigned as follows: aliphatic C at 10–50 ppm, methoxyl C at 50–90 ppm, aromatic C at 102–155 ppm and carbonyl C at 160–220 ppm [28]. The spectra of lignin chars show decreasing peaks of aliphatic and methoxyl carbons but increasing peaks of aromatic carbons as temperature increases from 100 to 300 °C. The NMR spectra indicate that the aliphatic and methoxyl carbon structures are gradually transformed into more condensed aromatic structures as temperature increases during lignin pyrolysis.

The spectra of chars from the pyrolysis of cellulose-lignin mixture show overlapping characters from both lignin and cellulose structures. As the temperature increases from 100 to 300 °C, the NMR spectra show decreasing aliphatic and methoxyl carbon structures from lignin, while the sugar structures from cellulose only experience slight reductions at 300 °C. It is interesting to see that the sugar structures are still present in the char from cellulose-lignin co-pyrolysis even at 300 °C, in contrast to the significant destruction of sugar structures during cellulose pyrolysis alone. The results demonstrate that part of sugar structures are preserved during co-pyrolysis of cellulose and lignin.

3.3. Discussion on the cellulose-lignin interactions during co-pyrolysis of cellulose and lignin

The experimental results presented in this study clearly demonstrate the existence of interactions between cellulose and lignin during co-pyrolysis. The cellulose-lignin interactions affect both char yields and char structures during co-pyrolysis. At temperatures < 300 °C, pyrolysis of cellulose-lignin mixture leads lower char yields than the theoretically-calculated values (assuming no synergies), with the differences between the experimental and calculated char yields increasing from $\sim 2\%$ at 150 °C to a maximal value of $\sim 6\%$ at 250 °C. This demonstrates co-pyrolysis of cellulose and lignin enhances

the release of volatiles at low temperatures. The reduced char yield during co-pyrolysis of cellulose and lignin at low temperatures can be due to two possible reasons, according to results in this study and relevant literature.

First, the presence of cellulose enhances the release of lignin-derived light compounds due to the hydrogen donation from the cellulose-derived compounds to stabilize the reactive species from lignin pyrolysis. It is known that liquid intermediates (mainly sugar and anhydro-sugar oligomers) can be produced from cellulose pyrolysis even at 150 °C [29]. Those intermediates can easily participate in lignin pyrolysis reactions as hydrogen donors. Eventually, this leads to suppressed polymerization of lignin-derived species and increased release of light compounds from lignin pyrolysis, resulting in reduced char yields. The UV fluorescence spectra in Fig. 6 clearly demonstrate that more aromatic structures with 2-5 fused rings are retained in char during co-pyrolysis of cellulose and lignin. This indicates that the polymerization of lignin-derived species is suppressed at temperatures < 250 °C, due to the positive UV fluorescence intensities between the experimental and calculated results. The results are consistent with a recent study [16], which has reported that the lignin-derived compounds (i.e., phenolics) are enhanced during co-pyrolysis of cellulose and lignin.

Second, the presence of lignin also enhances the thermal ejection of cellulose-derived liquid intermediates at low temperatures. It is reported that liquid intermediates can be produced from lignin pyrolysis even at ~150 °C [30], leading to increased micro-explosion during lignin pyrolysis [31]. Since cellulose is also partially melted at such low temperatures [29], the thermal ejection of the cellulose-derived liquid intermediates can be enhanced during co-pyrolysis with lignin. The glucose yield data in Fig. 2 demonstrates that the loss of sugar structures is enhanced even at 200 °C, indicating that the release of cellulose-derived liquid intermediates may be enhanced. This is supported by a recent study [16], which has reported that the cellulose-derived compounds (i.e., anhydrosugars such as levoglucosan) are enhanced during co-pyrolysis of cellulose and lignin.

At higher temperatures (i.e., > 250 °C), cellulose pyrolysis becomes dominant during co-pyrolysis of cellulose and lignin. The FT-IR and NMR results (see Fig. 4 and Fig. S1) in this study show

increased retention of cellulose-derived structures at temperatures $> 250\text{ }^{\circ}\text{C}$, indicating that cellulose decomposition is suppressed at increased temperatures. This could be at least due to two reasons. First, once the cellulose-derived volatiles (i.e., anhydrosugars) are formed, it is more difficult to diffuse through the liquid intermediate phase from both cellulose and lignin, leading to enhanced decomposition in the liquid intermediate phase. Second, the stabilization of the reactive species from lignin pyrolysis may lead to the partial destruction of sugar structures at low temperatures, thus reducing the formation of volatiles at increased temperatures. As a result, pyrolysis of cellulose-lignin mixture leads higher char yields than the theoretically-calculated values at increased temperatures, with the difference between the experimental and calculated char yields increasing from $\sim 1\%$ at $300\text{ }^{\circ}\text{C}$ to $\sim 8\%$ at $350\text{ }^{\circ}\text{C}$.

4. Conclusions

This study reports the effect of cellulose-lignin interactions on the structural changes of chars during fast pyrolysis at $100\text{--}350\text{ }^{\circ}\text{C}$. Co-pyrolysis of cellulose and lignin leads to a reduced char yield at low temperatures ($< 300\text{ }^{\circ}\text{C}$) but an increased char yield at high temperatures ($\geq 300\text{ }^{\circ}\text{C}$), compared to the calculated char yield from the pyrolysis of cellulose and lignin individually. At below $250\text{ }^{\circ}\text{C}$, both lignin functional groups and sugar structures are found to reduce in the char from co-pyrolysis of cellulose and lignin, indicating enhanced release of volatiles from both cellulose and lignin. Lignin pyrolysis is enhanced likely due to the stabilization of lignin-derived reactive species by cellulose-derived reaction intermediates (i.e., anhydro-sugars) as hydrogen donors, while cellulose pyrolysis is promoted possibly by increased thermal ejection of cellulose-derived liquid intermediates due to micro-explosion of liquid intermediates from lignin. The differences between the experimental and calculated char yields increase with temperature, from $\sim 2\%$ at $150\text{ }^{\circ}\text{C}$ to $\sim 6\%$ at $250\text{ }^{\circ}\text{C}$. At $300\text{ }^{\circ}\text{C}$ or above, cellulose decomposition is suppressed mainly because the cellulose-derived volatiles are difficult to diffuse through the lignin-derived liquid intermediates into the vapour phase, as evidenced by increased retention of cellulose functional groups in the char from co-pyrolysis of cellulose and

lignin. This leads to increased char formation during co-pyrolysis of cellulose and lignin at increased temperatures, with the difference between the experimental and calculated char yields increasing from ~1% at 300 °C to ~8% at 350 °C.

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List of Figure Captions

Fig. 1. Char yields from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C.

Fig. 2. Glucose yields from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C.

Fig. 3. FT-IR spectra of the chars from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C. Panel (a) cellulose and its chars: (1) cellulose; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C; (7) 350 °C. Panel (b) lignin and its chars: (1) raw lignin; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C; (7) 350 °C. Panel (c) cellulose-lignin mixture and its chars: (1) cellulose-lignin mixture; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C; (7) 350 °C.

Fig. 4. Differences between the experimental and calculated FT-IR absorbance intensities of chars for the pyrolysis of cellulose-lignin mixture at 100–350 °C.

Fig. 5. UV fluorescence spectra of the chars from the pyrolysis of lignin and cellulose-lignin mixture at 100–300 °C. Panel (a) lignin and its chars: (1) lignin; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C. Panel (b) cellulose-lignin mixture and its chars: (1) cellulose-lignin mixture; (2) 100 °C; (3) 150 °C; (4) 200 °C; (5) 250 °C; (6) 300 °C.

Fig. 6. Differences between the experimental and calculated UV fluorescence intensity of the chars for the pyrolysis of cellulose-lignin mixture at 100–300 °C.

List of Supplemental Material

A Word File (named as Supplemental Material) including the following contents:

Table S1. Elemental compositions of the chars from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–350 °C.

Table S2. Peak assignments for FT-IR spectra of lignin and cellulose samples [1,2].

Fig. S1. ^{13}C CP/MAS NMR spectra of the chars from the pyrolysis of cellulose, lignin and cellulose-lignin mixture at 100–300 °C. (a) Cellulose and its chars; (b) lignin and its chars; (c) cellulose-lignin mixture and its chars.