

# Intensive Interaction Region during Co-pyrolysis of Lignin and Cellulose: Experimental Observation and Kinetic Assessment

Shiliang Wu, Dekui Shen, Jun Hu, Huiyan Zhang, and Rui Xiao\*

Interactions between biomass constituents (cellulose, hemicelluloses, and lignin) under pyrolytic conditions have received more and more attention in recent years. A synthesized sample was prepared through mixing of cellulose and lignin with a mass:mass ratio of 1:1. The cellulose-lignin mixture (C-L-M) was heated from 20 to 800 °C using a thermogravimetric analyzer coupled with a Fourier transform infrared spectrometer (TG-FTIR). The presence of the cellulose-lignin complex was theoretically confirmed by the suggestion of a hydrogen bond network between cellulose- and lignin-related oligomers through the density functional theory (DFT) method. To estimate the strength of the interaction between cellulose and lignin in different regions, correlation coefficients  $r$  were employed to nominate three regions: region I (20 to 305 °C), in which lignin and cellulose were pyrolyzed into oligomers without interacting with one another; region II (305 to 432 °C), which was deemed the intensive interaction region, with an  $r$  value of about 0.2; and region III (432 to 800 °C), in which the pyrolysis of cellulose ceased and only lignin was further degraded. A kinetic scheme was also proposed to model the co-pyrolysis of cellulose and lignin.

*Keywords: Cellulose; Lignin; Co-pyrolysis; Interaction; Kinetic scheme*

*Contact information: Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University, Nanjing 210096, PR China; \*Corresponding author: ruixiao@seu.edu.cn*

## INTRODUCTION

Pyrolysis is a promising technology for converting biomass into liquid fuel and chemicals (Bridgwater 2012; Ma *et al.* 2012). Biomass is mainly composed of cellulose, hemicellulose, and lignin, with contents of about 40 to 60%, 20 to 40%, and 10 to 25% on a dry basis, respectively (McKendry 2002). To understand the pyrolysis characteristics of biomass and establish kinetic models for the design of biomass pyrolysis reactors, a number of studies on the pyrolysis of individual biomass components (cellulose (Jacques 2011; Patwardhan *et al.* 2011c; Shen and Gu 2009; Shen *et al.* 2011; Wang *et al.* 2011a; Wu *et al.* 2013; Yang *et al.* 2007), hemicellulose (Lv *et al.* 2010; Patwardhan *et al.* 2011a; Shen *et al.* 2010a; Wang *et al.* 2013; Yang *et al.* 2007), and lignin (Chu *et al.* 2013; Ferdous *et al.* 2002; Hu *et al.* 2012; Jiang *et al.* 2010; Patwardhan *et al.* 2011b; Shen *et al.* 2010b)) have been done. These studies have consolidated the understanding of the component's individual pyrolytic behaviors and have helped to understand the pyrolytic mechanism of whole biomass systems. Because of differences in chemical structures, the three components of biomass have different pyrolysis characteristics. Cellulose is a linear polymer of glucopyranose linked by  $\beta$ -1,4-glycosidic bonds. The decomposition of cellulose occurs mostly within a small temperature interval, around 312 to 404 °C, at a 20

°C/min heating rate; when the decomposition of cellulose is finished, 8.23% char residue is found (Shen and Gu 2009). Hemicellulose is a polymer that is composed of hexoses (*e.g.*, mannose, glucose, and galactose) and pentoses (*e.g.*, xylose and arabinose). The decomposition temperature range of hemicellulose is about 192 to 366 °C. The decomposition of hemicellulose is generally considered easier than that of cellulose (Shen *et al.* 2010a). The structure of lignin is very complex, but generally, it is described as an irregular polymer of various phenolic-C3 alkyl side chain monomeric (C9) units. Lignin exhibits continuous weight loss throughout the entire pyrolysis process at a 20 °C/min heating rate. The final residue is about 40%, which is higher than that of cellulose or hemicellulose (Shen *et al.* 2010b). Compared to the numerous studies on biomass and its three components, the study on the interactions between the three components is relatively small. An overlap of the main decomposition temperature ranges has been observed between the three components, so their interactions may play an important role in the biomass pyrolysis process.

Thermogravimetric characteristics are important for biomass kinetic analysis. Normally, to validate the rationality of a proposed kinetic model, the predicted thermogravimetric characteristics are compared with experimental results. To discuss the interaction between biomass components, thermogravimetric characteristics are checked. Usually, these three components are thought to pyrolyze separately with no interaction. Raveendran *et al.* (1996) conducted biomass components and synthetic biomass analyses using a thermogravimetric analyzer, showing that interactions between the components are not as important as the composition of biomass (Raveendran *et al.* 1996). Direct summative correlations based on biomass component pyrolysis adequately explained both the pyrolysis characteristics and product distribution of biomass. Biagini *et al.* (2006) used thermogravimetric (TG) analysis coupled with infrared spectroscopy to study the devolatilization of biomass fuels and their three components. They found that the summative law is suitable for both thermogravimetric curves and the extended Fourier transform infrared spectrometer (FTIR) profiles and that the calculated values obtained using this summative law are in agreement with experiment results, suggesting that there were no interactions. Yang *et al.* (2006) examined synthesized samples containing two or three of the biomass components with a thermogravimetric analyzer. Their results indicated that interaction between the three components is negligible.

Recently, several researchers found evidence of interactions between the components under pyrolytic conditions. Hosoya *et al.* (2007) discovered significant interactions between cellulose and lignin at 800 °C, stating that lignin inhibited the thermal polymerization of levoglucosan formed from cellulose and enhanced the formation of the low molecular weight products, while cellulose reduced the secondary char formation from lignin. Comparatively weak interactions were also observed in cellulose-hemicellulose co-gasification. Worasuwannarak *et al.* (2007) investigated pyrolysis behaviors of rice straw, rice husk, and corncob using the thermogravimetric analyzer coupled with mass spectrometry (TG-MS) technique, indicating that there were interactions between cellulose and lignin during pyrolysis. The interactions lead to a decrease in tar yields but an increase in char yields. Couhert *et al.* (2009a,b) doubted whether the additivity law suitably predicts gas yields of biomass after rapid pyrolysis at high temperatures, so they carried out an experiment in an entrained flow reactor (EFR), showing that interactions occurred both outside (*i.e.*, in the gas phase) and inside the mixed samples. Wang *et al.* (2011) tested the pyrolysis characteristics of biomass using a thermogravimetric analyzer coupled with a Fourier-transform infrared spectrometer (TG-

FTIR) and an experimental pyrolyzer. By analyzing the main products with gas chromatography-mass spectrometry (GC-MS), they concluded that the pyrolysis characteristics of biomass cannot be predicted *via* the behaviors of its three components. Studies regarding a possible interaction mechanism between the three components under pyrolysis conditions have great potential to improve the current understanding of the whole biomass pyrolysis systems.

In this work, a thermogravimetric analyzer coupled with a Fourier-transform infrared spectrophotometer (TG-FTIR) was employed to explore the interactive behavior between cellulose and lignin under pyrolysis conditions. From the kinetic point of view, the isoconversional method was used to determine the intensive interaction region between cellulose and lignin. Chemical information regarding the possible interaction mechanism was proposed and confirmed using density functional theory (DFT). A comprehensive kinetic scheme for the co-pyrolysis of cellulose and lignin in TG was proposed according to the interaction region.

## EXPERIMENTAL

### Materials

Cellulose tested in the experiment is a commercial product (Sigma Chemical Co., USA) and was used without further processing. Lignin was precipitated from black liquor, following a previously introduced method (Hu *et al.* 2012, 2013).

To make the cellulose-lignin mixture, cellulose and lignin were mixed with a mass:mass ratio of 1:1 and ground to form small particles (around 40  $\mu\text{m}$ ). The mixture was then manually pressed and agglomerated using a hydraulic press machine under 20 MPa. Finally, the pressed and agglomerated mixture was milled to fit through a 100-mesh screen (particle size is smaller than 149  $\mu\text{m}$ ) (Couhert *et al.* 2009a,b).

### TG-FTIR

A thermogravimetric analyzer (STA 409 PC, NETESCH, Germany) coupled with an FTIR spectrophotometer (Nicolet iN10, OMNIC, USA) was used to investigate the thermogravimetric characteristics of samples and the gaseous product evolution from cellulose, lignin, and the cellulose-lignin mixture. The samples were heated from 20 to 800  $^{\circ}\text{C}$  at the heating rates of 10, 20, and 30  $^{\circ}\text{C}/\text{min}$  in an open  $\text{Al}_2\text{O}_3$  crucible under nitrogen gas flow. The flow rate of nitrogen was held at 60 mL/min to maintain an inert atmosphere for the decomposition process. The masses of the samples were less than 5 mg to avoid a possible temperature gradient and to ensure kinetic control of the process. The FTIR spectrophotometer was connected to the thermogravimetric analyzer by a flow cell, which was heated to 180  $^{\circ}\text{C}$  to avoid condensation of gases onto the cell wall. The scanning range was set to 4000 to 800  $\text{cm}^{-1}$ , and the resolution factor was selected to be 1  $\text{cm}^{-1}$ . The start time difference between the FTIR spectrophotometer and the thermogravimetric analyzer was about 4 min due to the time required for nitrogen to fill the cell volume of the spectrometer.

### DFT

Density functional theory (DFT) was used to simulate the possible linkages in cellulose-related and lignin-related complexes. Zhang *et al.* (2011) investigated connections between cellulose and hemicellulose and hemicellulose and lignin using

different kinds of quantum calculation methods including the semi-empirical Austin method 1 (AM1), Hartree-Fock (HF), and density functional theory (DFT). It has been reported that B3LYP/6-31G is a reasonably accurate method to calculate the hydrogen bond network in woody biomass. B3LYP/6-31G was employed to estimate the possible molecular structure of and linkages within cellulose-lignin complexes. The calculations were carried out for the ground state. The stabilities of the optimized structures were certified by frequency analysis. All calculations were performed using the Gaussian 03 package (Frisch 2004).

### Isoconversional Method

According to the ICTAC kinetics committee recommendations (Vyazovkin *et al.* 2011), the isoconversional method has the advantage of giving an unambiguous (independent of  $f(\alpha)$  model) value of the activation energy related to a given conversion. Typically, kinetic models used in the area of thermal analysis consider the rate to be a function of only two variables,  $T$  and  $\alpha$ ,

$$\frac{d\alpha}{dT} = k(T)f(\alpha) \quad (1)$$

where  $f(\alpha)$  is the reaction model that shows the dependence of the process rate on the extent of conversion, and the dependence of the process rate on temperature is represented by the rate constant  $k(T)$ .

The degree of conversion is calculated as follows,

$$\alpha = \frac{m - m_{20}}{m_{800} - m_{20}} \quad (2)$$

where  $m$  is the mass of the sample during the heating process, and  $m_{20}$  and  $m_{800}$  are the sample masses at 20 and 800 °C, respectively,

$k(T)$  is parameterized through the Arrhenius equation,

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where  $A$  and  $E$  are represent the pre-exponential factor and the activation energy, respectively, and  $R$  is the universal gas constant.

When taking the logarithmic derivative of the reaction rate (Eq. 1) at constant  $\alpha$ ,

$$\left[\frac{d \ln(d\alpha / dt)}{dT^{-1}}\right]_{\alpha} = \left[\frac{d \ln k(T)}{dT^{-1}}\right]_{\alpha} + \left[\frac{d \ln f(\alpha)}{dT^{-1}}\right]_{\alpha} \quad (4)$$

where the subscript  $\alpha$  indicates the value at a given extent of conversion. When  $\alpha$  is constant,  $f(\alpha)$  is also constant. Therefore, the second term in the right hand side of Eq. (4) is zero. Combining Eq. (3) yields:

$$\left[ \frac{d \ln(d\alpha / dt)}{dT^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (5)$$

The activation energy at a given degree of conversion  $\alpha$  can be calculated using Eq. 5. A significant variation of  $E_{\alpha}$  with  $\alpha$  indicates that a process is kinetically complex.  $E_{\alpha}$  vs.  $T_{\alpha}$  dependency derived from the  $E_{\alpha}$  vs.  $\alpha$  dependency is also useful for kinetic analysis (Vyazovkin *et al.* 2011). Tihay *et al.* (2011) and Friedman (1964) have successfully used this method to evaluate the effect of oxygen concentration on cellulose wadding and plastic. So here the isoconversional method was used to evaluate the interaction between cellulose and lignin.

### Statistical Method

There are few objective methods to evaluate the strength of the interaction, making an unambiguous conclusion as to whether there are interactions between the three components. In this work, statistical methods were used to evaluate the interaction between cellulose and lignin. For random variables  $X$  and  $Y$ , their expected values are  $E(X)$  and  $E(Y)$ , respectively. The covariance of  $X$  and  $Y$  can be presented as follows,

$$Cov(X, Y) = E[(X - E(X))(Y - E(Y))] \quad (6)$$

where  $Cov(X, Y)$  is the covariance of  $X$  and  $Y$ . If  $Cov(X, Y) = 0$ , it means that variables  $X$  and  $Y$  are mutually independent.

The variances of  $X$  and  $Y$  are denoted as  $D(X)$  and  $D(Y)$ . The correlation coefficient  $r$  is defined based on variances and covariances:

$$r = Cov(X, Y) / \sqrt{D(X)D(Y)} \quad (7)$$

The value of  $r$  is between -1 and 1. If  $X$  and  $Y$  have a positive correlation, the value for  $r$  is 1. The bigger the absolute value of  $r$  is, the stronger the correlation between  $X$  and  $Y$ . In this article, the predicted and experimental TG and DTG data were the variables  $X$  and  $Y$ . If there is no interaction between cellulose and lignin, the correlation coefficient  $r$  is 1; if there is interaction between cellulose and lignin, the smaller the value of the correlation coefficient is, the stronger the interaction is.

## RESULTS AND DISCUSSION

### TG-FTIR Analysis

Results from the three heating rates (10, 20, 30 °C/min) showed the same trend. TG and DTG curves for a 20 °C/min heating rate for cellulose, lignin, and the cellulose-lignin mixture are shown in Fig. 1, while the curves for 10 and 30 °C/min heating rates are shown in the appendix (Supplementary Material) in Figs. S1 and S2, respectively. The characteristic points of the TG and DTG curves are listed in Table 1. No significant differences were found for samples pyrolyzed under different heating rates. The predicted cellulose-lignin mixture weight loss calculated by the direct summative law (based on mass ratio) is also presented in Fig. 1 and Table 1. The pyrolysis of cellulose begins at

313 °C, from which point it lost mass sharply with increasing temperature and reached its maximum mass loss rate at 351 °C. When the temperature was over 438 °C, the decomposition of cellulose has nearly been completed, obtaining a solid residue of 10.24%. The decomposition temperature range for lignin stretched from 194 to 631 °C. The maximum mass loss rate of 0.45 %/°C for lignin pyrolysis (at 390 °C) was much smaller than that of cellulose (2.24 %/°C at 351 °C). The solid residue from lignin pyrolysis was 34.19%, which is consistent with reports in other literature (Yang *et al.* 2006).

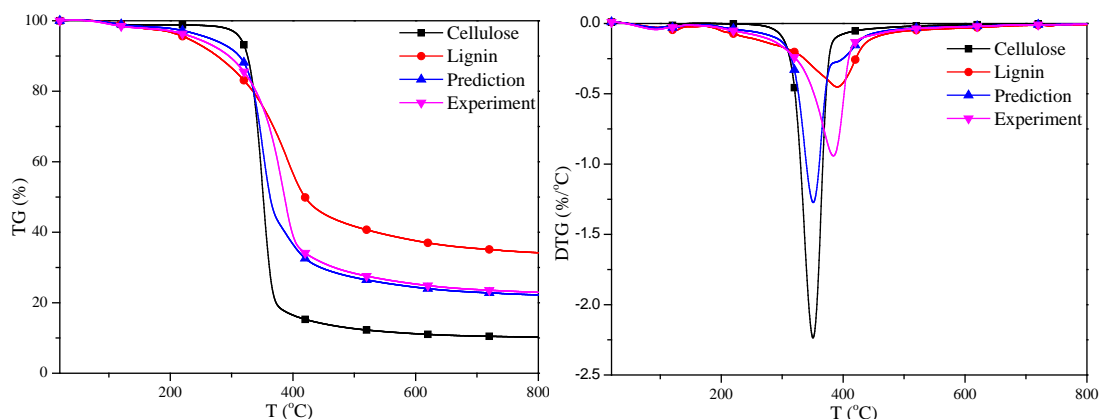


Fig. 1. TG and DTG curves of the sample at 20 °C /min

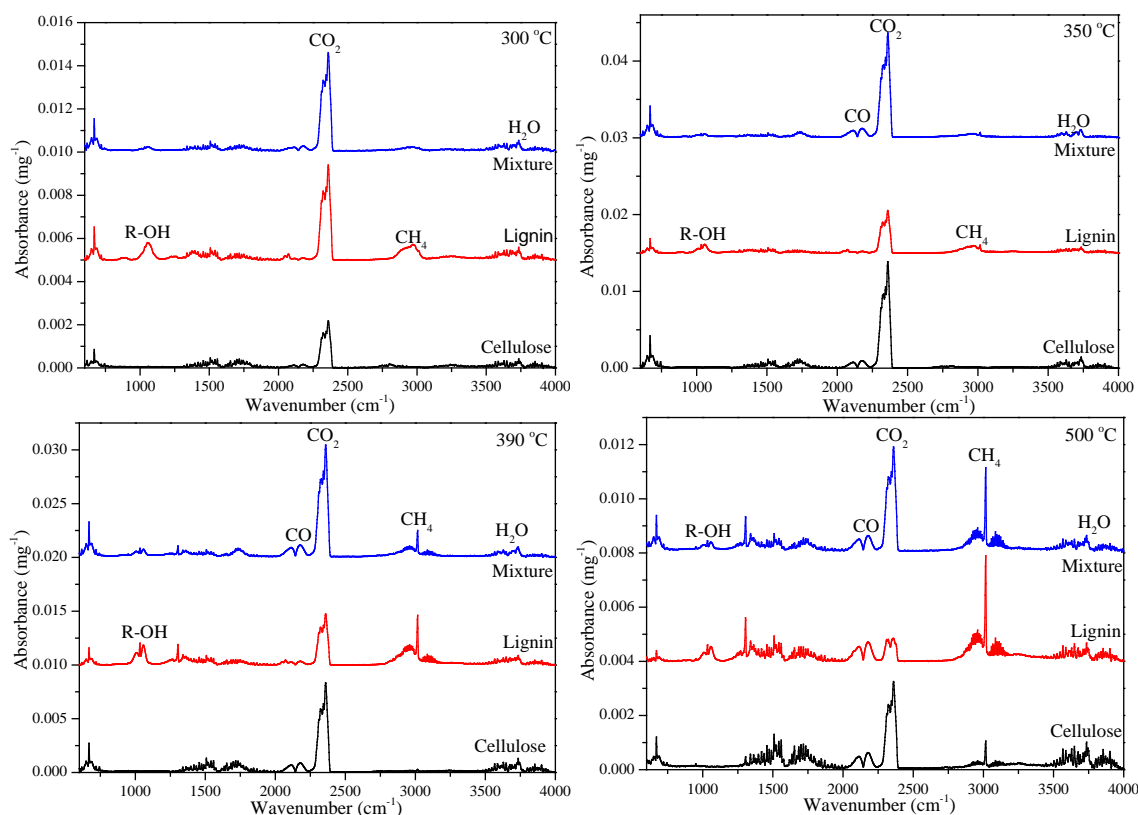
Table 1. Characteristic Points of TG and DTG Curves for the Samples (20 °C/min)

Sample	$T_{in}^a$ (°C)	$T_{end}^b$ (°C)	$T_{max}^c$ (°C)	DTG <sub>max</sub> (%/°C)	Residue <sup>d</sup> (%)
Cellulose	313	438	351	-2.24	10.24
Lignin	194	631	390	-0.45	34.19
Prediction	245	532	351	-1.27	22.21
Experimental	195	567	377	-0.89	22.95

<sup>a</sup> Decomposition initiation temperature, where 5% mass loss of the total mass loss is reached  
<sup>b</sup> Decomposition end temperature, where 95% mass loss of the total mass loss is reached  
<sup>c</sup> Where the absolute value of DTG reaches its maximum  
<sup>d</sup> The mass (%) at 800 °C/min

When cellulose and lignin were co-pyrolyzed, the experimental results were different from the predictions. The experimental decomposition temperature range (195 to 567 °C) was larger than predicted (245 to 532 °C), but there was no significant difference for the char residue (22.21% predicted versus an experimental result of 22.95%). The predicted maximum mass loss rate (1.27%/°C) was larger than the experimental result (0.89%/°C). The corresponding predicted temperature of the maximum mass loss (351 °C) was lower than the experimental result (377 °C). This is consistent with other reported results (Wang *et al.* 2008, 2011b). Wang *et al.* (2008) compared the calculated results and experimental results of cellulose-lignin mixtures, finding that the calculated maximum mass loss rate was about 0.5 %/°C larger than the experimental, and that the calculated temperature corresponding to the maximum mass loss rate was about 30 °C lower than the experimental result. All of these phenomena suggest that the interaction between cellulose and lignin cannot be ignored under co-pyrolysis conditions. The cellulose-lignin interaction inhibits the decomposition of

cellulose, since the mass loss rate peak of the cellulose-lignin mixture shifts from that of cellulose (351 °C) towards that of lignin (377 °C). Further, its value was lower than the predicted value.



**Fig. 2.** FTIR spectra of evolved gases at different temperatures

The FTIR spectra of evolved gases from cellulose, lignin, and the cellulose-lignin mixture pyrolyzed at different temperatures (300, 350, 390, and 500 °C) were analyzed in order to explore the cellulose-lignin interaction (Fig. 2). At 300 °C, the decomposition of cellulose (313 to 438 °C) had not happened, so only a small amount of CO<sub>2</sub> from cellulose had evolved (Li *et al.* 2001). Though characteristic peaks for R-OH and CH<sub>4</sub> appeared on FTIR spectra for lignin, there were no signs of them in the cellulose-lignin mixture's spectra.

At 350 °C, where  $T_{max}$  for cellulose (351 °C) was reached, CO appeared for both cellulose and the mixture. However, there was no peak for R-OH or CH<sub>4</sub> for the mixture. Typically, R-OH and CH<sub>4</sub> are formed from the breakage of side chains of lignin and its oligomers. The interaction between cellulose and lignin may inhibit the decomposition of lignin into R-OH and CH<sub>4</sub>.

When the temperature increased to  $T_{max}$  for lignin (390 °C), a peak indicating the presence of CH<sub>4</sub> appeared for the mixture, but the peak for R-OH was still absent. This confirms that cellulose-lignin interaction inhibits the decomposition of lignin. At 500 °C, the evolution of gas products are much smaller than those at 350 °C and 390 °C. The FTIR spectra of the cellulose-lignin mixture are similar to those of lignin. It could be concluded that cellulose-lignin interaction not only inhibits the decomposition of cellulose, but also prevents the decomposition of lignin.

### Isoconversional Method

From the analysis of the TG-FTIR experiment, the effect of cellulose-lignin interaction on the thermogravimetric characteristics is shown. To modify the kinetic model of cellulose-lignin co-pyrolysis and shed light on the biomass pyrolysis kinetic model based on the individual components' models, the kinetic scheme of cellulose, lignin, and their co-pyrolysis was identified by the isoconversional method.

A series of data from different heating rates (10, 20, and 30 °C/min) were used to calculate the dependencies of  $E_\alpha$  on  $\alpha$  and of  $E_\alpha$  on  $T_\alpha$ . The results are shown in Fig. 3. Attributed to the influence of external conditions (such as the heating process), the linearly dependent coefficient for  $E_\alpha$  vs.  $\alpha$  is under 0.95 when  $\alpha > 0.8$ , so only  $0.05 < \alpha < 0.8$  is shown in Fig. 3.

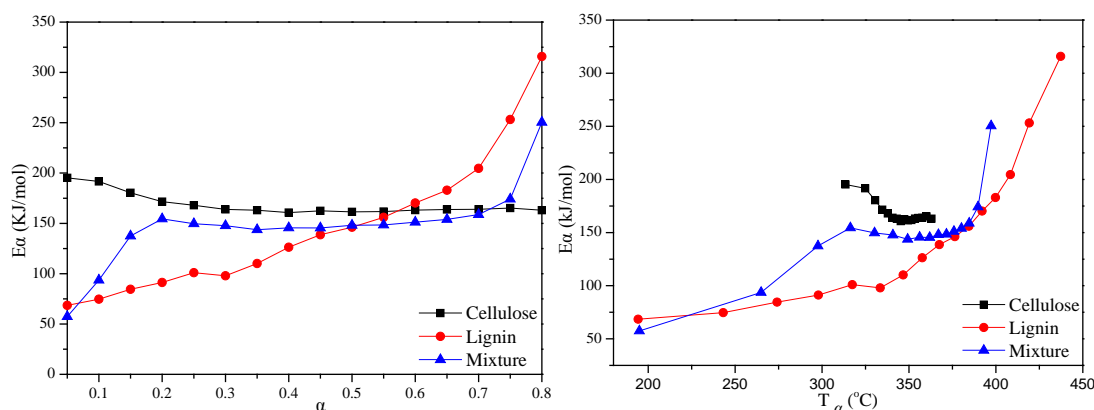


Fig. 3. Dependency of  $E_\alpha$  on  $\alpha$  and  $T_\alpha$

The decomposition of cellulose can be divided into two distinct stages: the first stage is for  $0.05 < \alpha < 0.1$ , in which the activation energy  $E_\alpha$  is around 195 kJ/mol; the second stage is for  $\alpha > 0.2$ , in which the activation energy  $E_\alpha$  is about 163 kJ/mol; the region  $0.1 < \alpha < 0.2$  is the transitional region. The most frequently used kinetic model for cellulose is the Broido-Shafizadeh model (Bradbury *et al.* 1979). The model suggests that cellulose transforms into active-cellulose first (the activation energy  $E_\alpha$  is around 270 kJ/mol) and then that active-cellulose decomposes into volatiles and char (the activation energies  $E_\alpha$  for char and volatiles are all around 200 kJ/mol) (Conesa *et al.* 1995). The results from the isoconversional method are consistent with the Broido-Shafizadeh model for a smaller activation energy model. The different value of activation energy may be caused by using a different calculation method, temperature range, or experimental data processing method. For lignin, the activation energy increased from 68 to 315 kJ/mol with increasing  $\alpha$  and the corresponding  $T_\alpha$ . This is consistent with the work of Ferdous *et al.* (2002). They created the distributed activation energy model (DAEM) for kraft lignin, finding that the activation energy increased from 129 to 361 kJ/mol when the temperature increased from 545 to 805 K (272 to 532 °C). This suggests that the decomposition of lignin involves numerous reactions with different activation energies. For the cellulose-lignin mixture, it is obvious that there are three different stages. The first stage is before  $\alpha = 0.2$ , where the activation energy increases from 57 to 154 kJ/mol; in the second stage ( $0.2 < \alpha < 0.7$ ), the activation energy remains constant at around 145 kJ/mol with only small fluctuations; and in the third stage the activation energy increased



to 250 kJ/mol. Noticing the dependency of  $E_{\alpha}$  vs.  $T_{\alpha}$ , the variation of activation energy for cellulose-lignin mixture follows the trend for lignin, but when the decomposition of the mixture was located within the cellulose decomposition temperature range (313 to 438 °C), the activation energy for the mixture was significantly influenced by cellulose. The decomposition of the cellulose-lignin mixture can be divided into three regions from the isoconversional method of analysis. Regions I and III are before and after the cellulose decomposition range, respectively. These two regions are dominated by the decomposition of lignin, while the second region (Region II) is dominated by cellulose decomposition.

### Intensive Interaction Region

The calculated correlation coefficients  $r$  between predicted and experimental results gathered across the temperature range 20 to 800 °C, at different heating rates, are shown in Table 2. The correlation coefficient  $r$  for TG was near 1 for all heating rates. For DTG, the  $r$  value was between 0.65 to 0.75, indicating that interaction had indeed happened between cellulose and lignin. The strength of the interaction was influenced by the heating rates, with the strongest interaction observed at the 20 °C/min heating rate.

The correlation coefficients  $r$  for these three regions were also calculated and are presented in Table 2 to validate the three regions for cellulose-lignin co-pyrolysis found in section “Isoconversional Method”. The  $r$  values of TG and DTG for Regions I and III are all near 1, suggesting that there is no significant interaction in these regions. However, for Region II, the  $r$  values for DTG are all smaller than 0.4 (especially for a heating rate of 20 °C/min, in which the  $r$  value was only about 0.1818). It can be concluded that Region II is the intensive interaction region.

**Table 2.** Correlation Coefficient  $r$  for Different Regions

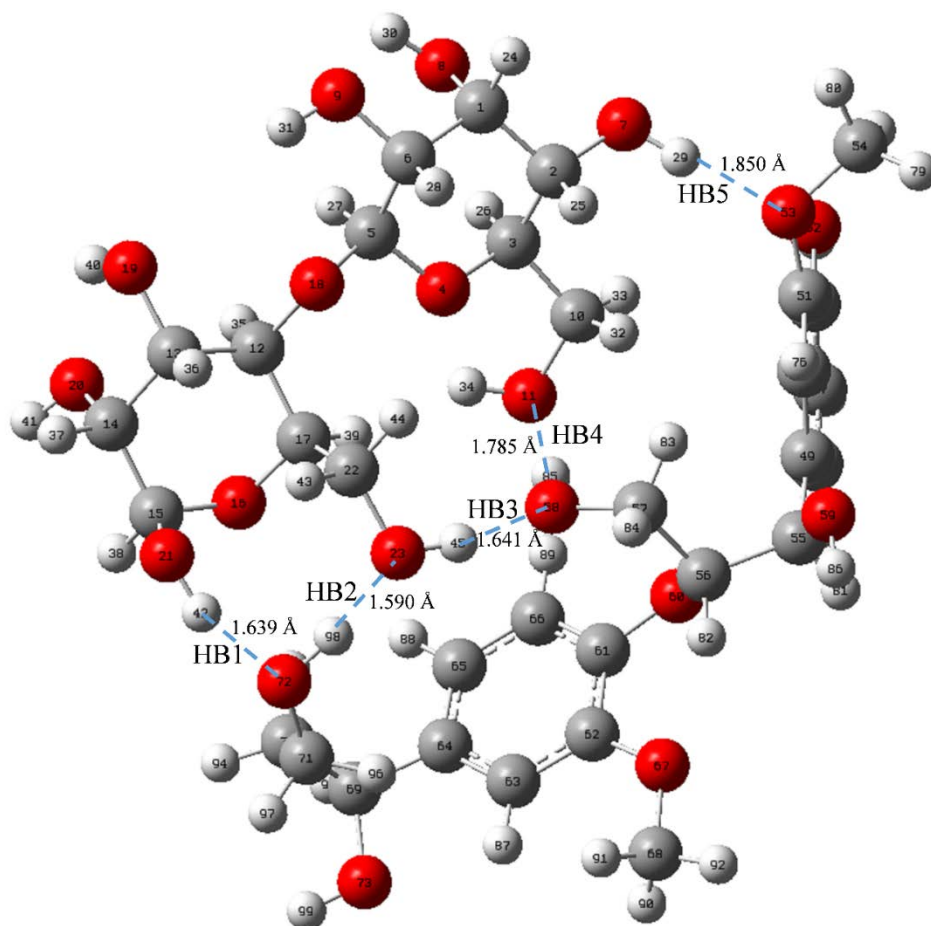
	Correlation Coefficient					
	TG			DTG		
	10	20	30	10	20	30
Total	0.9965	0.9943	0.9957	0.7276	0.6812	0.7540
Region I	0.9982	0.9997	0.9979	0.9902	0.9884	0.9960
Region II	0.9601	0.9385	0.9526	0.3916	0.1818	0.2488
Region III	1.000	0.9999	0.9999	0.9981	0.9988	0.9861

### Cellulose-Lignin Co-Pyrolysis Kinetic Scheme

Though the intensive reaction region has been confirmed, the detailed cellulose-lignin interaction mechanism is still in question.

According to the above discussion (both experimental and theoretical), a “cellulose-lignin complex” interaction mechanism for the co-pyrolysis of cellulose and lignin was proposed to take place during the intensive reaction region. The oligomers and intermediates from cellulose and lignin formed cellulose-lignin complexes *via* hydrogen bonds. In the intensive reaction region, there are many primary products from cellulose and lignin formed by the breakage of weak bonds, most of which are in the liquid phase. Both cellulose and lignin have numbers of -OH groups, so the formation of cellulose-lignin complexes is possible. The chemical structure of a possible cellulose-lignin complex was calculated by density functional theory (DFT) to confirm the proposed mechanism. The cellulose-lignin complex was composed of cellobiose and lignin-derived dimers with  $\beta$ -O-4 linkages (Fig. 4). There are five hydrogen bonds forming the network

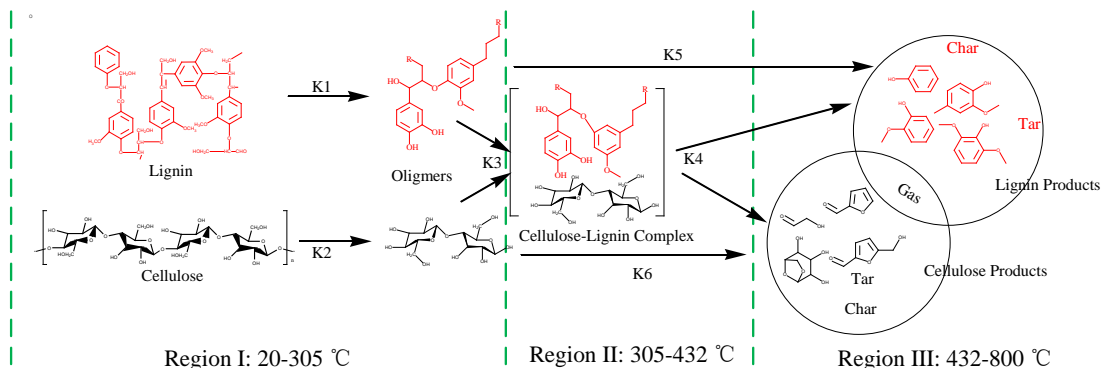
that connects the cellulose-derived and lignin-derived oligomers together. The bond length of the hydrogen bonds was between 1.590 and 1.850 Å. They are shorter than the hydrogen bonds between cellulose and hemicellulose, which are typically around 2 Å (Zhang *et al.* 2011). This could be attributed to CH- $\pi$  interaction between the C-H (cellulose) and  $\pi$  electron system (lignin), which helps to stabilize the cellulose-lignin complex (Hosoya *et al.* 2006). As the cellulose-lignin complex is stabilized by the hydrogen bond network and CH- $\pi$  interaction, the mass loss rate peak shifts to higher temperatures and the maximum value decreases. However, the hydrogen bond network and CH- $\pi$  interactions are both weak. When temperature is increased, these weak connections are broken up, resulting in no significant difference between the predicted and experimental char residue values.



**Fig. 4.** Hydrogen bond network between oligomers (intermediates) from cellulose and lignin pyrolysis

A kinetic scheme for cellulose and lignin is proposed in Fig. 5. In Region I (before cellulose decomposition range, 20 to 305 °C), cellulose and lignin pyrolyzed into oligomers without interaction. When the temperature was increased into the cellulose decomposition temperature range (Region II, 305 to 432 °C), the cellulose-derived and lignin-derived oligomers could go through secondary reactions separately into volatiles and char. The cellulose-lignin complex was also formed and decomposed through the reaction pathway differently from the secondary reactions of oligomers. In Region III,

cellulose completes its decomposition reaction, while lignin decomposition continues. No obvious interaction within this region was observed.



**Fig. 5.** Kinetic scheme for co-pyrolysis of cellulose and lignin

## CONCLUSIONS

1. The interaction between cellulose and lignin was tested and verified by TG-FTIR. The predicted maximum mass loss rate (1.27%/°C) was larger than the experimental result (0.89%/°C), and the corresponding temperature of the maximum mass loss (351 °C) was lower than the experiment (377 °C), confirming that the interaction between cellulose and lignin cannot be neglected.
2. The isoconversional method suggested that the process of cellulose-lignin mixture pyrolysis can be divided into three regions: Region I and Region III are before and after cellulose decomposition range, whereas Region II is the cellulose decomposition range. Evaluated by statistical method, there are no significant interactions in Region I and III, while Region II is the intensive interaction region.
3. “Cellulose-lignin complexes” is proposed by as the interaction mechanism, and this was confirmed by DFT calculation. “Cellulose-lignin complexes” interaction mechanism could explain the results from TG-FTIR well.
4. A kinetic scheme of the interaction mechanism was proposed involving cellulose-lignin complexes produced in the intensive reaction region. This scheme allowed for the modification of the kinetic model for biomass pyrolysis.

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## REFERENCES CITED

- Bradbury, A. G. W., Sakai, Y., and Shafizadeh, F. (1979). "A kinetic model for pyrolysis of cellulose," *Journal of Applied Polymer Science* 23(11), 3271-3280.
- Bridgwater, A. V. (2012). "Review of fast pyrolysis of biomass and product upgrading". *Biomass and Bioenergy* 38(0), 68-94.
- Chu, S., Subrahmanyam, A.V., and Huber, G.W. (2013). "The pyrolysis chemistry of a  $\beta$ -O-4 type oligomeric lignin model compound," *Green Chemistry* 15(1), 125-136.
- Conesa, J. A., Caballero, J. È. A., Marcilla, A., and Font, R. (1995). "Analysis of different kinetic models in the dynamic pyrolysis of cellulose," *Thermochimica Acta* 254, 175-192.
- Couhert, C., Commandré, J. M., and Salvador, S. (2009a). "Failure of the component additivity rule to predict gas yields of biomass in flash pyrolysis at 950° C," *Biomass and Bioenergy* 33(2), 316-326.
- Couhert, C., Commandre, J. M., and Salvador, S. (2009b). "Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin?" *Fuel* 88(3), 408-417.
- Ferdous, D., Dalai, A., Bej, S., and Thring, R. (2002). "Pyrolysis of lignins: Experimental and kinetics studies," *Energy & Fuels* 16(6), 1405-1412.
- Friedman, H. L. (1964). "Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic," *Journal of Polymer Science Part C: Polymer Symposia*, Wiley Online Library, pp. 183-195.
- Frisch, M. J., Trucks, G.W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. M., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Peterson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda R., Hasegawa, J., Ishida, M., Nakajima T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P.Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., AlLaham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., and Pople, J. A. (2004). "Gaussian 03," Gaussian, Inc., Pittsburgh, PA, 2003.
- Hosoya, T., Kawamoto, H., and Saka, S. (2006). "Thermal stabilization of levoglucosan in aromatic substances," *Carbohydrate Research* 341(13), 2293-2297.
- Hu, J., Shen, D., Xiao, R., Wu, S., and Zhang, H. (2012). "Free-radical analysis on thermochemical transformation of lignin to phenolic compounds," *Energy & Fuels* 27(1), 285-293.
- Hu, J., Xiao, R., Shen, D., and Zhang, H. (2013). "Structural analysis of lignin residue from black liquor and its thermal performance in thermogravimetric-Fourier transform infrared spectroscopy," *Bioresource Technology* 128, 633-639.
- Jacques, L. (2011). "Cellulose pyrolysis kinetics: an historical review on the existence and role of intermediate active cellulose," *Journal of Analytical and Applied Pyrolysis* 94, 17-32.

- Jiang, G., Nowakowski, D. J., and Bridgwater, A.V. (2010). "Effect of the temperature on the composition of lignin pyrolysis products," *Energy & Fuels* 24(8), 4470-4475.
- Li, S., Lyons-Hart, J., Banyasz, J., and Shafer, K. (2001). "Real-time evolved gas analysis by FTIR method: An experimental study of cellulose pyrolysis," *Fuel* 80(12), 1809-1817.
- Lv, G.-J., Wu, S.-B., Lou, R. (2010). "Characteristics of corn stalk hemicellulose pyrolysis in a tubular reactor," *BioResources* 5(4), 2051-2062.
- Ma, L., Wang, T., Liu, Q., Zhang, X., Ma, W., and Zhang, Q. (2012). "A review of thermal-chemical conversion of lignocellulosic biomass in China," *Biotechnology Advances* 30(4), 859-873.
- McKendry, P. (2002). "Energy production from biomass (part 1): Overview of biomass". *Bioresource Technology* 83(1), 37-46.
- Patwardhan, P. R., Brown, R. C., and Shanks, B. H. (2011a). "Product distribution from the fast pyrolysis of hemicellulose," *ChemSusChem* 4(5), 636-643.
- Patwardhan, P. R., Brown, R. C., and Shanks, B. H. (2011b). "Understanding the fast pyrolysis of lignin," *ChemSusChem* 4(11), 1629-1636.
- Patwardhan, P. R., Dalluge, D. L., Shanks, B. H., and Brown, R. C. (2011c). "Distinguishing primary and secondary reactions of cellulose pyrolysis," *Bioresource Technology* 102(8), 5265-5269.
- Raveendran, K., Ganesh, A., and Khilar, K. C. (1996). "Pyrolysis characteristics of biomass and biomass components," *Fuel* 75(8), 987-998.
- Shen, D., and Gu, S. (2009). "The mechanism for thermal decomposition of cellulose and its main products," *Bioresource Technology* 100(24), 6496-6504.
- Shen, D., Gu, S., and Bridgwater, A. V. (2010a). "Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR," *Journal of Analytical and Applied Pyrolysis* 87(2), 199-206.
- Shen, D., Gu, S., Luo, K., Wang, S., and Fang, M. (2010b). "The pyrolytic degradation of wood-derived lignin from pulping process," *Bioresource Technology* 101(15), 6136-6146.
- Shen, D., Xiao, R., Gu, S., and Luo, K. (2011). "The pyrolytic behavior of cellulose in lignocellulosic biomass: A review," *RSC Adv.* 1(9), 1641-1660.
- Tihay, V., Boulnois, C., and Gillard, P. (2011). "Influence of oxygen concentration on the kinetics of cellulose wadding degradation," *Thermochimica Acta* 525(1-2), 16-24.
- Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C., and Sbirrazzuoli, N. (2011). "ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data," *Thermochimica Acta* 520(1-2), 1-19.
- Wang, G., Li, W., Li, B., and Chen, H. (2008). "TG study on pyrolysis of biomass and its three components under syngas," *Fuel*, 87(4-5), 552-558.
- Wang, S., Guo, X., Liang, T., Zhou, Y., and Luo, Z. (2011a). "Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies," *Bioresource Technology* 104, 722-728.
- Wang, S., Guo, X., Wang, K., and Luo, Z. (2011b). "Influence of the interaction of components on the pyrolysis behavior of biomass," *Journal of Analytical and Applied Pyrolysis* 91(1), 183-189.
- Wang, S., Ru, B., Lin, H., Luo, Z. (2013). "Degradation mechanism of monosaccharides and xylan under pyrolytic conditions with theoretic modeling on the energy profiles". *Bioresource Technology*, 143, 378-383.

- Worasuwannarak, N., Sonobe, T., and Tanthapanichakoon, W. (2007). "Pyrolysis behaviors of rice straw, rice husk, and corncob by TG-MS technique." *Journal of Analytical and Applied Pyrolysis*, 78(2), 265-271.
- Wu, S., Shen, D., Hu, J., Xiao, R., and Zhang, H. (2013). "TG-FTIR and Py-GC-MS analysis of a model compound of cellulose – glyceraldehyde," *Journal of Analytical and Applied Pyrolysis* 101, 79-85.
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12-13), 1781-1788.
- Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D. H., and Liang, D. T. (2006). "In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin," *Energy & Fuels* 20(1), 388-393.
- Zhang, X., Yang, W., and Blasiak, W. (2011). "Modeling study of woody biomass: interactions of cellulose, hemicellulose, and lignin," *Energy & Fuels* 25(10), 4786-4795.

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## APPENDIX

## Supplementary Material

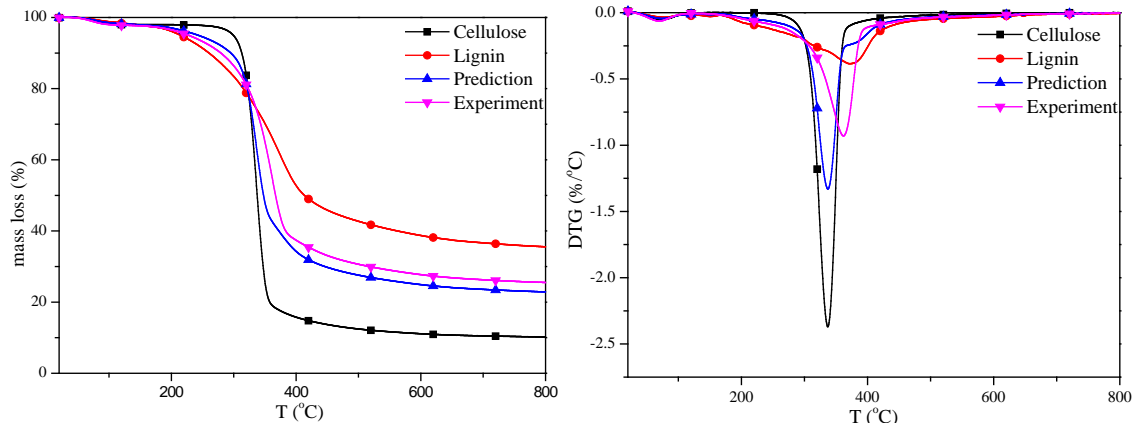


Fig. S1. TG and DTG curves of the sample pyrolysis at 10 °C /min

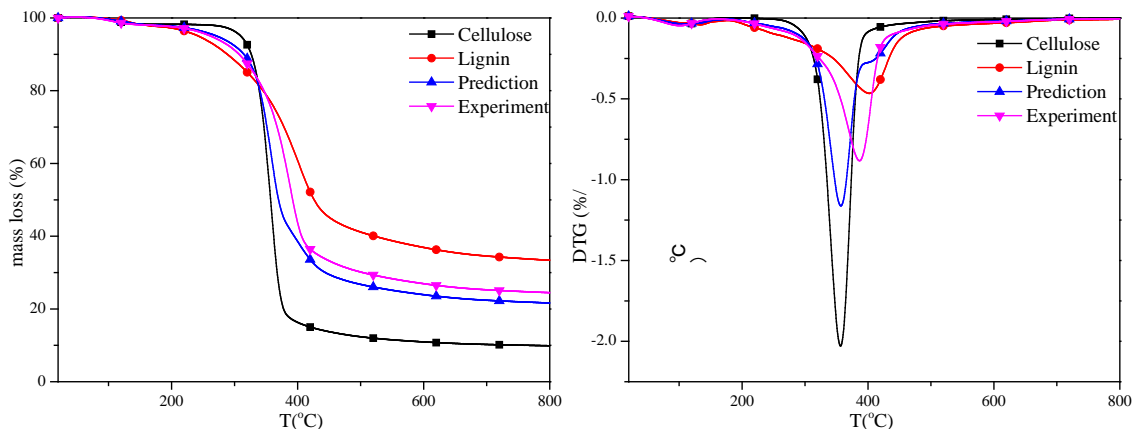


Fig. S2. TG and DTG curves of the sample pyrolysis at 30 °C /min