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Interactions among biomass components during co-pyrolysis in (macro)thermogravimetric analyzers

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Abstract−The interactions of biomass components (hemicellulose, cellulose, and lignin) during co-pyrolysis were investigated in a thermogravimetric analyzer (TGA) as well as a self-designed Macro-TGA with higher heating rate and larger amount of sample. The overlap ratio (OR) was used to evaluate the interaction of biomass components quantitatively. In TGA, the pyrolysis of xylan was not significantly affected by cellulose, whereas the pyrolysis of cellulose was markedly influenced by xylan. The interactions between xylan and lignin were weak with an overlap ratio of 0.9869, whereas co-pyrolysis of cellulose and lignin was strongly inhibited by interactions with the overlap ratio of 0.9737. In Macro-TGA, interactions between components were stronger than that in TGA due to more considerable heat and mass transfer effect.

Keywords: Biomass, Interaction, Pyrolysis, TGA, Cellulose, Lignin

INTRODUCTION

As is well known, fossil fuels, including coal, petroleum and natural gas will be exhausted in the future. Meanwhile, the 2015 United Nations Climate Change Conference (COP21) emphasizes the crisis of global warming once again. Bioenergy is a significant sustainable and renewable energy which may ease these two issues [1]. Pyrolysis can produce versatile bio-char, bio-oil, and syngas that can be further used as chemical materials and transportation fuels, which is therefore regarded as a promising technology [2,3]. Meanwhile, pyrolysis is the fundamental process of other thermochemical processes, such as combustion and gasification [4,5].

Biomass is mainly composed of hemicellulose, cellulose, and lignin [6,7]. Hemicellulose is a group of pentose, including xylan, xyloglucan, glucuronoxylan, and so on [8], which is considered helpful to cross-link cellulose, lignin or pectin, supporting the secondary cell wall of the plant [9]. Cellulose owns the largest proportion in biomass, making it the most important component. The cell wall of plants is mainly supported by cellulose [10]. Lignin is a complicated aromatic polymer, with three main monomers synapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol [11-13]. Since biomass samples vary from place to place, research focusing on hemicellulose, cellulose, and lignin can provide more mechanisms and universal information of biomass pyrolysis.

Hemicellulose, cellulose, and lignin are usually present in biomass together, and research has shown that the interactions between these three components during pyrolysis should not be neglected [14]. Therefore, it is necessary to study their interactions during co-pyrolysis [15,16]. Giudicianni et al. reported that interactions between biomass components are non-ignorable from the experimental results that syngas heating value is lower for xylan\lignin mixture and surface area of char is decreased for all kinds of mixtures [3]. The pyrolysis of hemicellulose, cellulose, and lignin was investigated by Wang et al. in TGA under syngas and hydrogen. The results showed that lignin and hemicellulose could affect the pyrolysis of cellulose, while they did not interact with each other during the pyrolysis process [17]. Worasuwannarak et al. also reported that significant interactions could be observed for the co-pyrolysis of cellulose and lignin. The interactions decreased the tar yields and increased the char yields [18].

Basic kinetic characteristics are useful to predict thermal behavior during the co-pyrolysis process and for the design of more suitable reactors [19-22]. TGA is the most commonly used apparatus to study the pyrolysis rate and mass loss kinetics of interactions of biomass components [23]. Nevertheless, the temperature of TGA is usually elevated after the sample is placed in the furnace, which limits the heating rate of TGA to tens of degree per minute [24]. However, heating rate is considered to have a critical influence on biomass thermal behavior [25]. At slow heating rate, different components decompose at different temperature range. When one component begins to decompose, the decomposition of the other may be finished; thus the interaction between these two components may be very limited [26]. Meanwhile, the sample mass in TGA is approximately 5-20 mg, and the heat and mass transfer during the pyrolysis process can be neglected, which is quite different from industrial reactors [27]. In other words, the interactions of components in TGA may be weakened due to the limited heat and mass transfer process. Therefore, the interactions in a macro-reactor which can simulate the real industrial reactor are expected. There are some fixed bed reactors used to investigate the interaction of

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Table 1. Proximate and ultimate analyses of xylan, cellulose, and lignin

Samples	Proximate analysis[d] (%)			Ultimate analysis[daf] (%)				
	A	V	FC	C	H	N	O	S
Xylan	2.11	78.57	19.33	39.18	6.32	0.00	54.50	0.01
Cellulose	0.00	95.21	4.79	44.51	6.25	1.29	47.93	0.01
Lignin	16.15	54.61	29.25	63.86	4.45	0.18	25.83	5.67

A: ash; V: volatile; FC: fixed carbon; [d]: dry basis; [daf]: dry ash free basis

biomass components during co-pyrolysis. However, only the product characteristics could be obtained from these reactors. There is no such a reactor that can show the kinetics of interactions during co-pyrolysis of biomass components.

In this paper, the interactions of hemicellulose, cellulose, and lignin are studied in a TGA as well as a self-designed Macro-TGA under inert atmosphere. The higher heating rate and larger amount of sample in Macro-TGA may provide different results compared to TGA. The TG curve overlap ratio (OR) is proposed to evaluate the interactions between components quantitatively.

MATERIALS AND METHODS

1. Materials

Hemicellulose (represented by xylan) and microcrystalline cellulose were both provided by Sigma-Aldrich. Dealkaline lignin was purchased from Tokyo Chemical Industry. First, all the samples were dried at 105 °C to remove the influence of water. Table 1 shows the proximate and ultimate analyses of the samples, which has also been reported in our previous research [27]. As shown in Table 1, cellulose has the highest amount of volatile fraction, with no ash left. Lignin has the highest amount of fixed carbon and ash content [27].

2. Thermogravimetric Analysis

The TGA experiments were operated in a NETZSCH STA 449F with a N_2 flow rate of 100 ml min^{-1}. Temperature was elevated from 50 to 1,000 °C at a heating rate of 10 °C min^{-1}. Repeated experiments substantiated the good reproducibility of TG curves.

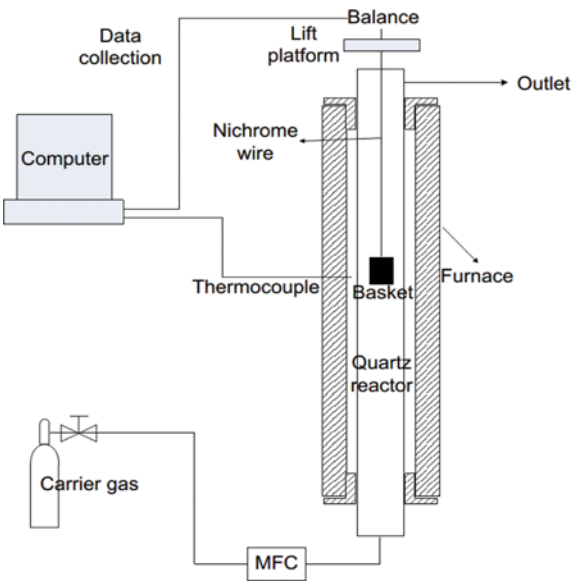

Fig. 1. Schematic diagram of Macro-TGA system.

3. Macro-TGA Experiments

As is displayed in Fig. 1 [27], the samples examined in TGA were also tested in Macro-TGA. The reaction system consisted of a reactor and a mass monitoring system. A three-section furnace, a quartz reactor and a basket formed the pyrolysis reactor. Approximately 1.5 g of the sample was placed in the basket in the experiment. Through a nichrome wire, the mass of the basket was monitored by a balance. The online data acquisition unit collected the balance data and the sample temperature. The carrier gas in this experiment was N_2 with the flow rate of 1 L min^{-1}.

In the experiments of fast pyrolysis, the reactor was initially heated to 800 °C. When the temperature stabilized, the sample was placed in the hot zone of the reactor and pyrolysis happened quickly. The temperature of the reactor was maintained at 800 °C till the reaction finished.

To obtain the background of the signal, blank test was administered before. For each experiment, the background data was subtracted to get the real results. Repeated experiments demonstrated the good reproducibility of Macro-TGA.

Compared to regular TGA, the advantage of Macro-TGA was that it was actually a fixed bed reactor, which is more similar to industrial reactors. With several grams of sample that could be pyrolyzed, the heat transfer and mass transfer in Macro-TGA was more significant than that in regular TGA, which made it suitable to investigate interactions. In addition, the heating rate of Macro-TGA could be as fast as hundreds of degrees per minute, which was much larger than that of regular TGA. The drawback of Macro-TGA is that samples experienced more complex processes in Macro-TGA, which made it difficult to study the chemistry.

RESULTS AND DISCUSSIONS

1. Pyrolysis of Single Biomass Components

1-1. Pyrolysis of Single Biomass Components in TGA

The TG and derivative thermogravimetric (DTG) curves of pyrolysis of xylan, cellulose, and lignin in TGA are shown in Fig. 2. The pyrolysis of xylan and lignin starts very early (~200 °C). Yang et al. showed that the pyrolysis of xylan starts from approximately 220 °C [28], and Shen et al. also showed that the pyrolysis of xylan in TGA happens in a very narrow range of temperature (200-350 °C) [29]. As shown in Fig. 2(a), cellulose pyrolysis starts from a higher temperature (approximately 300 °C). The residue mass of lignin at 1,000 °C is the highest (~46.2%), followed by xylan (~27.3%). Two

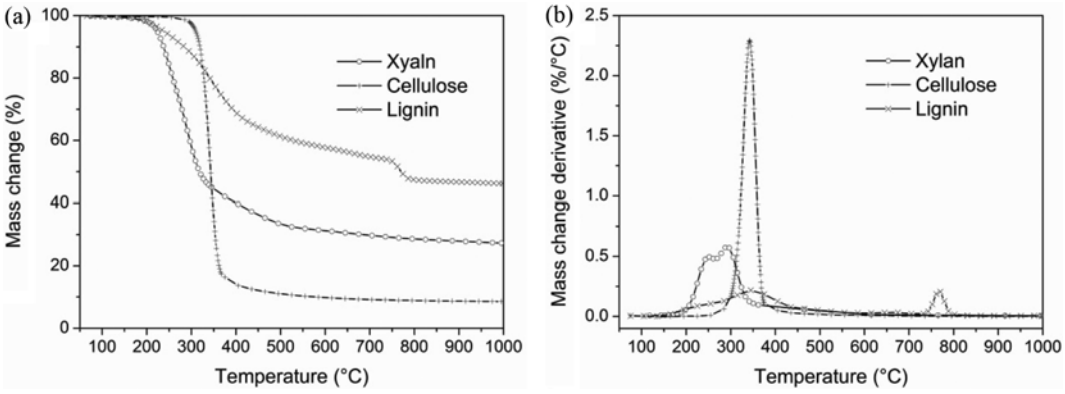

Fig. 2. TG and DTG curves of pyrolysis of xylan, cellulose, and lignin in TGA.

main peaks are present at the pyrolysis of xylan, at 245 and 296 °C, as shown in Fig. 2(b). The first peak can be ascribed to the cleavage of the glycosidic bonds between xylan units and the decomposition of the side chain structure, while the second peak is considered to be derived from the opening of xylan unit at higher temperature [3]. The pyrolysis of cellulose presents only one peak at 344 °C. According to the report of Zhang et al., cellulose decomposes from 287 to 387 °C [20]. The pyrolysis of lignin is complicated, with two main peaks at 338 and 768 °C. Yang et al. reported that lignin decomposition happened in a wide range of temperature from 100 to 900 °C, which is consistent with the results in this paper [28].

1-2. Pyrolysis of Single Biomass Components in Macro-TGA

The pyrolysis of three biomass components in Macro-TGA is shown in Fig. 3. Xylan pyrolysis ends quite early (approximately 50 s); cellulose pyrolysis lasts longer time (~75 s); while lignin pyrolysis presents a slower process, which lasts more than 300 s. As shown in Fig. 3(b), the DTG peak of xylan and cellulose is high. Peaks present in TGA are usually merged in Macro-TGA due to higher heating rate. As reported by Shen et al., because the decomposition of xylan units are enhanced, the two peaks from pyrolysis of xylan will overlap [29]. As shown in Fig. 2(a) and Fig. 3(a), pyrolysis in Macro-TGA produces less residue content than that in TGA. The reason may be that during the fast pyrolysis in Macro-TGA, a large amount of soot may be generated due to the high heating rate and violent perturbation of the sample, which reduces the final residue content of pyrolysis.

2. Interactions of Biomass Components During Co-pyrolysis

Binary mixture experiments (1 : 1) were performed to compare with the linear superposition results of single components (Eq. (1)).

$$X_{cal}=(X_1+X_2)/2 \quad (1)$$

where X_{cal} denotes calculated results from the linear superposition of single components; X_1 and X_2 denotes the experimental results from pyrolysis of xylan, cellulose, or lignin.

There are two TG curves from the experimental results and calculated results. Therefore, an overlap ratio (OR) of TG curves was proposed to quantitatively evaluate the interactions between components [30], which was defined as Eq. (2). From the geometrical perspective, OR is the area sandwiched by two curves divided by the total area; from the algebraic perspective, OR is the absolute-value norm of the difference of two sets of data.

$$OR=1-\frac{\text{The area sandwiched by two curves}}{\text{The total area}}=1-\frac{\int_{t_s}^{t_e}|\Delta m(t)|dt}{(t_e-t_s)(m_s-m_e)} \quad (2)$$

In Eq. (2), represents the absolute value of mass difference of two TG curves at the same temperature; t_s and t_e represent start temperature and end temperature, respectively; m_s and m_e represent start mass (100%) and residue mass, respectively. Further explanation of OR can be found in Supplementary Material.

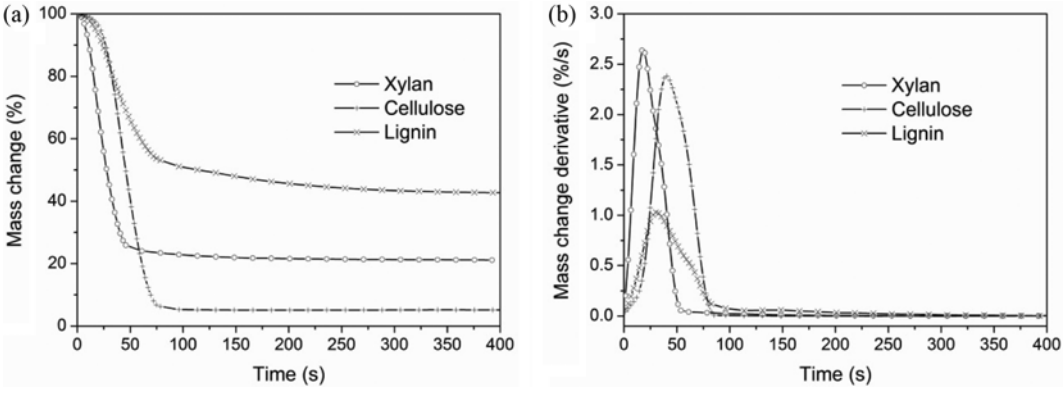

Fig. 3. TG and DTG curves of pyrolysis of xylan, cellulose, and lignin in Macro-TGA.

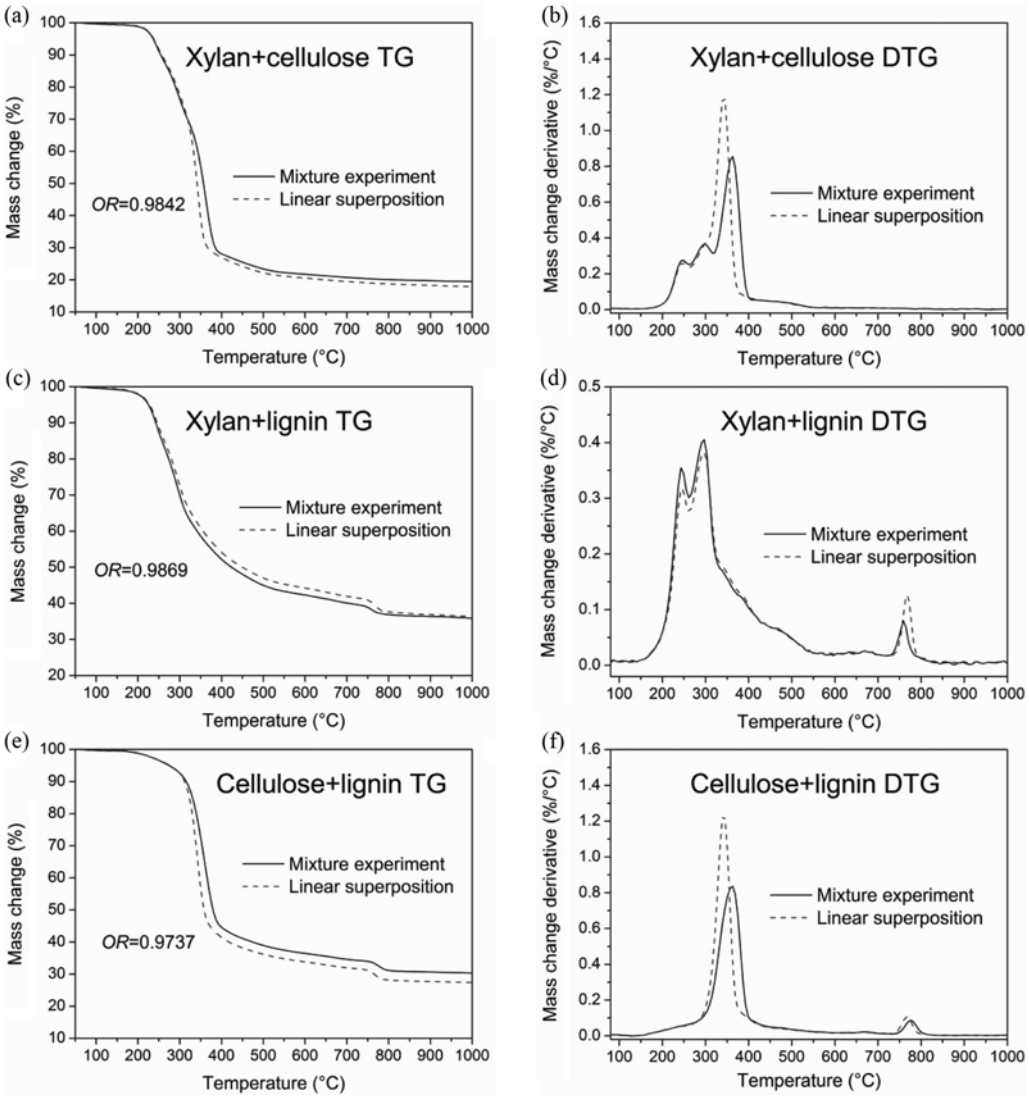

Fig. 4. The comparison of mixture experiments and linear superposition of pyrolysis in TGA.

For every TG curve, N sets of data were exported and the OR could be calculated from Eq. (3). In this paper, N was chosen as 16000, which was large enough to keep the error acceptable.

$$OR = 1 - \frac{(t_e - t_s)\lim_{N\to\infty}\frac{\sum|\Delta m(t)|}{N}}{(t_e - t_s)(m_s - m_e)} = 1 - \lim_{N\to\infty}\frac{\sum|\Delta m(t)|}{N} \quad (3)$$

2-1. Interactions of Biomass Components During Co-pyrolysis in TGA

As shown in Fig. 4(a) and (b), the OR of experimental and calculation results of xylan and cellulose is 0.9842. The DTG curves from experiments differ widely from calculated results. The peak of xylan is not affected significantly, while the interactions make the peak of cellulose occur later (from 342 to 362 °C) and shorter. Stefanidis et al. also reported that the experimental and calculated TG curves agreed quite well for co-pyrolysis of xylan and cellulose, but there were obvious differences in the DTG curves [14].

The OR of experimental and calculated results of xylan and lignin is as high as 0.9869. The DTG curves from experimental result and calculated result are almost coincident, as shown in Fig. 4(c). The residue content at 1,000 °C is similar for experimental and calculated results, which is consistent with the result of steam gasification [3]. Wang et al. investigated the interaction of xylan and lignin in TGA, and found that they did not present significant interactions during co-pyrolysis process, which is consistent with the results in this paper [17].

By contrast, the interaction between cellulose and lignin is strong, with the OR 0.9737. As shown in Fig. 4(e), the interactions between cellulose and lignin have inhibition effect on pyrolysis, and the residue is increased. Worasuwannarak et al. investigated the interactions of cellulose and lignin in TGA at 10 °C min^{-1}; the interactions increased the char yield, which is consistent with the result in Fig. 4(e) [18]. It can also be concluded that the mechanisms of interaction of xylan and cellulose may be similar with that of cellulose and lignin, as shown in Fig. 4(b) and (f).

Considering the results in Fig. 4(b) and (d), the pyrolysis of xylan was not affected by cellulose or lignin significantly, with the peaks

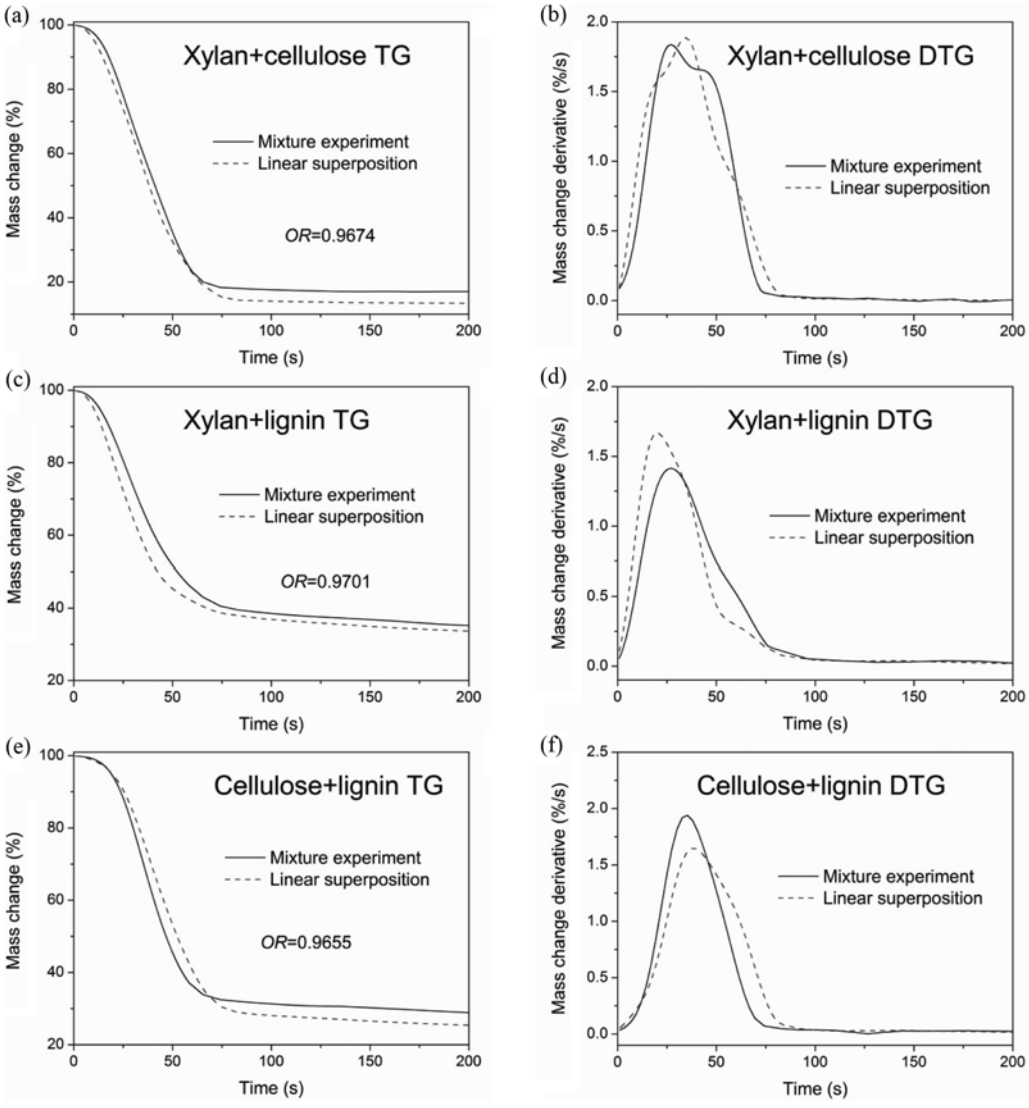

Fig. 5. The comparison of mixture experiments and linear superposition of pyrolysis in Macro-TGA.

below 300 °C being similar for both experimental results and calculation results. However, considering the results in Fig. 4(b) and (f), the pyrolysis of cellulose was inhibited by xylan or lignin. The reason might be that the pyrolysis xylan or lignin started at a low temperature, and the char formed inhibited the heat transfer and mass transfer process of unreacted cellulose. Hosoya et al. and Wang et al. delineated the effect of mass transfer [31,32], while Stefanidis et al. emphasized that the effect of heat transfer was also very considerable [14].

The effect of ash in the pyrolysis of biomass has been extensively studied previously, and a common conclusion is that the ash will catalyze the pyrolysis of biomass, resulting in the DTG peaks shift to a lower temperature [33]. In Fig. 4, the catalytic effect of ash in xylan and lignin on the decomposition of cellulose cannot be proved. The reason might be that the mechanical mixture of ash and cellulose was not enough for the catalytic effect of ash. In fact, the interactions between two solid samples were expected to be very limited. The study of Couhert et al. also indicated that ash only slightly affected pyrolysis behavior when simple mixing with biomass was applied [34].

2-2. Interactions of Biomass Components During Co-pyrolysis in Marco-TGA

Fig. 5 shows the comparison of experimental and calculated results of pyrolysis in Macro-TGA. The interactions between xylan and cellulose produce more residue content, which is consistent with the results of Stefanidis et al. during the co-pyrolysis of xylan and cellulose in a fixed bed reactor [14].

In TGA, xylan and lignin did not interact with each other significantly, while the situation is different in Macro-TGA. The interactions inhibit the co-pyrolysis, as shown in Fig. 5(c). The DTG peak of mixture experiment is lower than that of calculated results, as shown in Fig. 5(d).

The interactions of cellulose and lignin are very intensive, with the OR 0.9655, as shown in Fig. 5(e). The interactions promote pyrolysis at low temperature and inhibit pyrolysis when the temperature is elevated. Mixture experiment generates more final resi-

due than linear superposition, which is consistent with the result in TGA. Stefanidis et al. also reported that during co-pyrolysis of cellulose and lignin, the interactions were significant due to the rapid heat transfer rates and quick removal of the pyrolysis vapors [14].

Based on the results in Fig. 4 and 5, the interactions of biomass component in Macro-TGA are more significant than that in TGA. In TGA, the inhibition of pyrolysis was attributed to the effect of heat transfer and mass transfer. This was well supported by the results in Macro-TGA. In Macro-TGA, with much higher heating rate and much more sample, the poor heat and mass transfer conditions were expected to have a stronger inhibition effect on co-pyrolysis. The results proved that mixture experiments had much higher residue yields than superposition results.

CONCLUSIONS

The interactions among three biomass components (hemicellulose, cellulose, and lignin) during pyrolysis were studied in TGA and a self-designed Macro-TGA. Binary mixture experiments (1 : 1) were performed to compare with the linear superposition results of single components. In TGA, the pyrolysis of xylan was not significantly affected by cellulose, whereas the pyrolysis of cellulose was affected by xylan considerably. The co-pyrolysis of xylan and lignin in TGA did not present remarkable interactions, whereas the interactions between cellulose and lignin were strong, which inhibited pyrolysis.

In Marco-TGA, the interactions of xylan and cellulose inhibited the co-pyrolysis. For the co-pyrolysis of xylan and lignin, the DTG peak of the mixture experiment was lower than that of calculation results. Co-pyrolysis was promoted at low temperature and inhibited at high temperature by the interactions of cellulose and lignin. In Macro-TGA, with much higher heating rate and much more sample, the heat and mass transfer conditions had a stronger inhibition effect on co-pyrolysis than in TGA.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Interactions among biomass components during co-pyrolysis in (macro)thermogravimetric analyzers

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EXPLANATION OF TG CURVES OVERLAP RATIO (OR)

There are two TG curves for the comparison of experimental results and calculated results. Therefore, overlap ratio (OR) of TG curves was proposed to quantitatively evaluate the interactions between components, which was defined as Eq. (S1). From the geometrical perspective, OR was the area sandwiched by two curves divided by the total area; from the algebraic perspective, OR was the absolute-value norm of the difference of two sets of data.

$$OR = 1 - \frac{\text{The area sandwiched by two curves}}{\text{The total area}} = 1 - \frac{\int_{t_s}^{t_e} |\Delta m(t)| dt}{(t_e - t_s)(m_s - m_e)} \quad \text{(S1)}$$

In Eq. (S1), represents the absolute value of mass difference of two TG curves at the same temperature; t_s and t_e represent start temperature and end temperature, respectively; m_s and m_e represent start mass (100%) and residue mass, respectively.

"The area sandwiched by two curves" is shown as the black area in Fig. S1. "The total area" was be calculated as "$(t_e - t_s)(m_s - m_e)$", which was actually constant for every cases. It was introduced to make the overlap ratio a dimensionless number. Considering the limiting case, when one curve is the blue one (Curve A) and the other curve is the red one (Curve B) in the figure, the overlap ratio is 0. This means the characteristics of these two curves have the greatest difference.

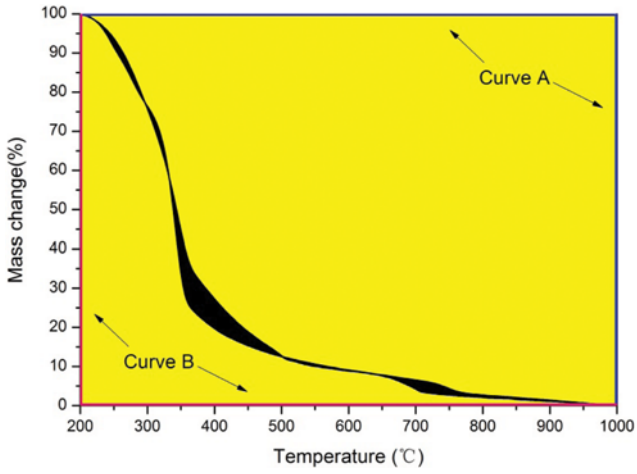

Fig. S1. Examples of overlap ratios.