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Research paper

Cellulose-lignin interactions during fast pyrolysis with different temperatures and mixing methods

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ABSTRACT

In this work, interactions between cellulose and lignin during fast pyrolysis were studied to identify the impact of sample preparation on the light-products distribution. Cellulose-lignin interactions were investigated by Py-GC-MS with different temperatures (500, 600, and 700 °C), mixing ratios (mass ratio 1:1, and 2.1:1), and mixing methods (physical mixture and native mixture). Generally, cellulose-lignin co-pyrolysis could promote low weight molecular products (esters, aldehydes, ketones, and cyclic ketones) form cellulose and lignin-derived products (phenols, guaiacols, and syringols), while inhibit formation of anhydrosugars, especially the formation of levoglucosan. The native cellulose-lignin mixture had the most dramatic impact on the product distribution between the mixing methods studied. Finally, a statistic method-correlation coefficient R has been introduced to evaluate the interaction strength under different conditions, finding that mixing method played the most significant role on interaction, followed by temperature, and mixing ratio was the least significant.

1. Introduction

Nowadays, with the fast development of biomass utilization, pyrolysis has been regarded as a promising technology for converting biomass into liquid fuel and valuable chemicals [1]. Meanwhile, the decomposition mechanism of biomass during pyrolysis has also been researched in detail, a recently published work of Lin et al. pointed out that biomass pyrolysis products are affected by its composition of three main components (cellulose, hemicellulose and lignin), secondary reactions caused by inorganic components, and interactions between the primary components [2]. However, though there are a number of articles about interactions between three main components, there is no definite conclusion on whether there is interaction and how it works. Table 1 shows some researchers' work on the three main components interactions with different experimental apparatuses and conditions. It is really interesting to find that with same experiment apparatuses and similar experiment conditions, they drew different conclusions. The reasons for this situation could be concluded as follows: (1) at the outset of the interaction research, the attentions are paid on the establishment of generalized biomass pyrolysis models based on the three main components, under this condition, the effects of interaction on thermogravimetric curves are not remarkable, so people tend to neglect the interactions between the three main components; (2) at the initial stage of utilization of biomass, usually, syngas, bio-oil and bio-char are produced from biomass, so when compared the yields of these three products, as there are no change of H:C:O ratios, it is really difficult to come to the conclusion with interaction. However, as the development of biomass application, biomass are transferred into liquid fuels and valuable platform chemicals, which needs detailed information about the compounds in bio-oil and biomass decomposition mechanism, under this condition, the importance of interaction has been evolved.

When the importance of interaction on biomass product distribution had been realized, a series of literature have been published to elucidate the interaction between the three components (Table 1). Hosoya et al. investigated the cellulose-hemicellulose and cellulose-lignin interactions in wood pyrolysis at 800 °C, reporting that significant interactions were observed in cellulose-lignin pyrolysis with comparatively weak interactions were also observed in cellulose-hemicellulose pyrolysis; what's more, they also concluded that lignin inhibited the thermal polymerization of levoglucosan and enhanced the formation of the low molecular

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Table 1
The study of interactions between the three main components under pyrolysis conditions.

Authors	Apparatus	Experiment conditions	
Conclusion: no interaction			
Yoon et al.	TG-GC	Air/steam atmosphere, 10 °C/min, 140–900 °C	[3]
Skreiberg et al.	TG and macro-TG	Air atmosphere, 5, 20, and 100 °C/min, 60–900 °C	[4]
Qu et al.	Tube furnace	350–600 °C	[5]
Wang et al.	TG	Hydrogen/syngas atmosphere, 5、10、15、20 °C/min, 30–600 °C	[6]
Gani et al.	TG	Nitrogen/air atmosphere, 20 °C/min, 25–900 °C	[7]
Yang et al.	TG	Nitrogen atmosphere, 10 °C/min, 105–900 °C	[8]
Biagini et al.	TG-FTIR	Nitrogen atmosphere, 20 °C/min, 105–1000 °C	[9]
Svenson et al.	Single particle reactor	Argon atmosphere, 225–650 °C	[10]
Miller et al.	Kinetic analysis		[11]
Raveendran et al.	TG	Nitrogen atmosphere, 50 °C/min, 20–1000 °C	[12]
	Packed-bed reactor	Nitrogen atmosphere, 500 °C	
Alen et al.	Py-GC/MSD	Nitrogen atmosphere, 300–1000 °C	[13]
Conclusion: with interaction			
Wang et al.	TG-FTIR,	Nitrogen atmosphere, 20 °C/min, 30–800 °C	[14]
Liu et al.	TG-FTIR	Nitrogen atmosphere, 60 °C/min, 30–800 °C	[15]
Hosoya et al.	Ampoule reactor	Nitrogen atmosphere, 600 °C, 40–80 s residence time	[16]
Hosoya et al.	Glass tube reactor	Nitrogen atmosphere, 800 °C, 30s	[17]
Fushimi et al.	Cross-flow moving bed	Steam atmosphere, 400 °C	[18,19]
Couhert et al.	Entrained flow reactor	Nitrogen atmosphere, 950 °C	[20,21]
Caballero et al.	Py-FID-TCD	Helium atmosphere, 700–900 °C	[22]
	TG	Nitrogen atmosphere, 5、10、25 °C/min, 20–1000 °C	
Wu et al.	TG-FTIR	Nitrogen atmosphere, 10,20 and 30 °C/min, 20–800 °C	[23]
J.Hilbers et al.	TGA and Py-GC-MS	TGA: Nitrogen atmosphere, 10 and 50 °C/min Py-GC-MS: 350 °C and 500 °C	[24]
P. Giudicianni et al.	Steam pyrolysis reactor	Steam atmosphere, 600 °C	[25–27]
Zhang et al.	Py-GC-MS	Helium atmosphere, 500 °C	[28]

weight products form cellulose with reduced yield of char formation, meanwhile, cellulose enhanced the formation of some lignin-derived products including guaiacol, 4-methylguaiacol and 4-vinylguaiacol [17]. In a following study, they also proposed a possible interaction mechanism, in this mechanism the cellulose-derived volatiles act as H-donors while the lignin-derived volatiles (radicals) act as H-acceptors [16]. Fushimi et al.'s works pointed out the evolution of tar from the lignin component of biomass is enhanced [18,19]. Couhert et al. used two types of mixing (simple mixing and intimate mixing) to show that interactions occur between the components during flash pyrolysis [20,21]. Wu et al. checked intensive interaction region between lignin and cellulose during co-pyrolysis, suggesting that cellulose-lignin complex connected by hydrogen bond may be the possible interaction mechanism [23]. Zhang et al. has pointed out that the interaction could be influenced by sample sources, as interaction between herbaceous cellulose-lignin mixture was much stronger than woody cellulose-lignin mixture [28].

Among these studies, there are some important aspects need to be figured out. The first vital issue is the mixing method for the three main components mixture resemble to natural biomass. Normally, commercial cellulose, hemicellulose (actually, xylan was used as hemicellulose surrogate), and lignin were used to mix up to make mixture samples. However, Couhert et al. has pointed out different mixing method will cause different interaction in different ways and phases [20,21]. In their research, along with the direct mixture, a tightly bound mixture has also been prepared by agglomerating fine three main components with a press. They found by simple mixing, interactions were only favored in gas phase, but by intimate mixing, the thin elements of the components were in contact inside a given particle, so interactions between the components could also occurred inside the particles. Both mixing methods are physical mixing processes, so they could just represent interactions during the pyrolysis process as depicted in Fig. 1. Nevertheless, for a real biomass, cellulose is wrapped up by lignin with hemicellulose between them, and covalent linkages connect these three main components, this structure strongly suggests that the morphology and covalent linkages will also influence the pyrolysis for a real biomass. But these two influence factors can't be studied by physical mixture. In order to deal with this problem, Zhang et al. used chemical method (hot water treatment) to remove hemicellulose form biomass samples to make native cellulose-lignin mixtures, reporting that the interactions for native mixtures were much stronger than physical mixtures [28].

Another important problems is the interaction evaluation method. The common method was using yield ratio to compare the experiment yield to the predicted yield (addition law without interaction) of a certain compound. By this method, the effect of interaction on a certain compound could be seen, but this method can't depict a whole vision about the influence of interaction on the product distribution. Thus an evaluation method for interaction on whole product distribution should be introduced.

Finally, the mechanism for interaction still needs more attention. Hosoya et al. attributed H-transfer mechanism as an explanation, regarding that cellulose-derived volatiles act as H-donors while lignin-derived volatiles act as H-acceptors [16]. Wu et al. considered that cellulose-lignin complex connected by hydrogen bond could account for the influence of interaction [23]. While Zhang et al. suggested that covalent linkages played an important role during cellulose-lignin co-pyrolysis [28]. Meanwhile, Asri Gani et al. reported that morphology of mixtures also act as a significant factor for cellulose-lignin interaction [7]. Generally, the mechanism of interaction is really a controversial topic.

Before, TG-FTIR has been used to elucidate the intensive interaction region during cellulose-lignin co-pyrolysis [23]. In this article, cellulose-lignin interaction has been checked by Py-GC-MS at pyrolysis conditions. Both direct and native mixture has been used to shed a light on the influence on mixing methods. The cellulose-lignin mixtures has been pyrolyzed at 500, 600, and 700 °C to reveal the influence of pyrolysis temperatures. What's more, the effect of mixing ratio has also been investigated. Finally, an evaluation method for judging the intense of interaction has