

THE INFLUENCE OF UREA FORMALDEHYDE RESINS ON PYROLYSIS CHARACTERISTICS AND PRODUCTS OF WOOD-BASED PANELS

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In China each year, large amounts of wood-based panels are consumed and abandoned. These are huge resources for energy recovery and materials reuse. In order to study the influence of urea formaldehyde resin (UF) resin on waste wood-based panels during pyrolysis, thermobalance experiments together with the evolution of main gaseous products of wood, wood-based panels, and UF resins were carried out and analyzed by TG-FTIR. Elementary and GC-MS analyses were also done to study the characteristics of solid and liquid products. Results from TG and DTG analyses indicated that UF resin used in wood-based panels accelerated the degradation rate of wood-based panels at lower temperature; however the resin inhibited the degradation of wood-based panels over the later stage at higher temperatures. Compared with solid wood, the higher intensity and earlier releasing time of H₂CO and NH₃ in wood board revealed that the release of nitric gases is mainly due to the presence of UF resin, especially between 180 °C and 320 °C. Mass loss of hydrogen is significantly inhibited by UF resin, and nitrogen is quite stable in the char. The influence of UF resin on pyrolysis liquids of wood-based panels is mainly on nitrogen compounds and ketones rather than aldehydes and esters, which is probably due to the chemical reactions of UF resin with lignin constituent in wood.

Keywords: GC-MS; Pyrolysis; TG-FTIR; Urea formaldehyde resin; Wood-based panel

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INTRODUCTION

Considering energy and resources, major conventional fossil energy resources are non-renewable and face the problem of gradually becoming extinct (Goyal *et al.* 2008). Biomass as a renewable resource has been explored as the substitute for conventional energy and chemical resources. The collection and logistics of biomass sometimes make its cost unacceptable, especially in China.

Waste wood-based panels are a kind of lignocellulosic bioresource and show great potential to provide raw materials for the production of renewable fuels and chemical feedstocks. The developing rate of wood-based panels in China is over 20% year by year, and the production of wood-based panels first exceeded 100 million m³ in 2009 (Qian 2010). The large consumption makes nearly 10% of wood-based panels and their relevant products abandoned each year, and these are huge energy resources for recycle and reuse (He *et al.* 2008).

Nowadays, the main energy reuse of waste wood-based panels is through incineration (Girods *et al.* 2009a). This is an effective way to convert waste wood-based panels into energy. However, because waste wood-based panels contain formaldehyde-based adhesives, the release of hazardous nitric gases in the course of combustion is unavoidable and can do great harm to the environment.

Thermochemical conversion, including gasification and pyrolysis, has proven to be a highly efficient process to utilize bioresources, including waste wood-based panels. The products of pyrolysis or gasification can be classified into gases, char, and bio-oil, which are distributed, flexible, and may be developed stage-wise (Windt and Meier 2010). Gases can be used as syngas to provide energy. Bio-oil can be upgraded into fuel or used as value-added chemicals (Liu *et al.* 2012). Even tar has been shown to have resistance to fungi (Mazela 2007). Char can be burnt for energy recovery or for the feedstock of activated carbon.

Pyrolysis of adhesives and waste wood-based panels has already been studied by some researchers, and many positive results have been obtained (Girods *et al.* 2008a-c). Studies on pyrolysis of UF and melamine formaldehyde (MF) resins have suggested that there are three reactions involved in the pyrolysis: initiation reactions, reactions splitting off volatile fragments, and reactions forming stabilized structures (Hirata *et al.* 1991).

Comparison of UF resin during the pyrolysis and combustion process was studied using TG-FTIR, and conclusions suggested that UF residues should be pyrolyzed at low temperatures to remove the initial nitrogen. In terms of poisonous nitric gases, the gaseous products during pyrolysis should be burnt in a high temperature furnace under oxygen-rich conditions for control of pollutants (Jiang *et al.* 2010). Because of the presence of UF resins, the characteristics and products of pyrolysis of wood-based panels are much different from those of common bioresources, and the influence of resins should be clarified.

Studies of pyrolysis of wood-based panels show that the degradation temperature of UF resin is lower than that of wood, indicating selective pyrolysis between UF resin and wood. Waste wood-based panels could be pre-treated to eliminate hazardous nitric compounds so that “clean” feedstock could be prepared for the later energy recovery. A two-step thermochemical process could thus be determined. Staged degasification has also been studied (Zhang *et al.* 2007 and 2008; Wild *et al.* 2009) and results show positive effects. Activated carbons prepared from particleboard wastes show a stronger ability in absorbing acid gases and phenolic compounds because of their nitrogen-containing surface groups (Girods *et al.* 2009b). Bio-oil prepared from low temperature pyrolysis of UF-contained wood-based composites and high temperature pyrolysis of PF-contained wood-based composites show excellent resistance to the fungi (Nakai *et al.* 2007).

Apart from research studies discussed above, published studies have seldom paid attention to the influence of UF resin on waste wood-based panels during the pyrolysis process. The purpose of the present study was to cast some light on the mechanism and the influence of UF resin on thermal degradation of waste wood-based panels.

EXPERIMENTAL

TG-FTIR Analysis

Samples used in this experiment were provided by Beijing Wood Factory. The materials of study included particleboard (PB), medium density fiber board (MDF), wood, and UF resin with the molar ratio F/U 1.08. Samples were crushed into a size smaller than 0.2 mm and dried in an oven at 103 °C for 3 h before the experiments. Figure 1 shows the typical UF resin unit and linkages in UF resin.

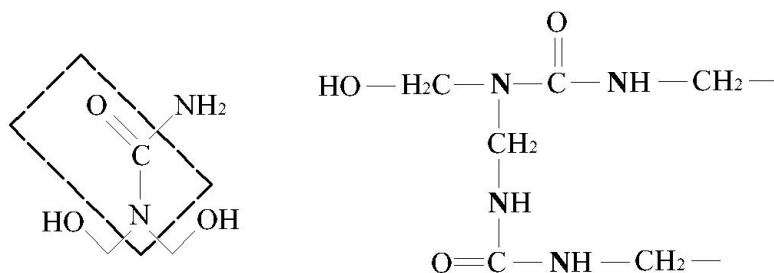


Fig. 1. Typical linkages in the structure of UF resin

The experiment was carried out with a Netzsch TG209 F1 thermo analyzer coupled with a Nicolet 6700 FTIR device. The experiment was done at a linear heating rate of 20 °C min⁻¹ from the ambient to 800 °C. The carrier gas was nitrogen set at 60 mL min⁻¹ in order to achieve an inert atmosphere. The tube and FTIR gas cell were maintained at 200 °C in order to avoid any condensation of volatiles. The weight of sample was around 5 mg for each experiment.

The spectrum scope of FTIR was in the range of 700 to 4000 cm⁻¹ with the resolution of 4 cm⁻¹, and each spectrum corresponded to the average of 20 scans. The FTIR spectrometer recorded one spectrum during each 10 seconds. The characteristic frequencies used for the qualitative and quantitative analysis were 2300 to 2400 cm⁻¹ for carbon dioxide (CO₂), 2000 to 2250 cm⁻¹ for carbon monoxide (CO), 800 to 1200 cm⁻¹ for ammonia (NH₃), and 2200 to 2300 cm⁻¹ for isocyanic acid (HNCO). Gas analysis was also done by matching the spectra against those from the spectrum library Nicolet TGA Vapor Phase of the software Ominic together with the methods reported by literature (Liu *et al.* 2008; Girods *et al.* 2008). According to the Lambert-Beer law (Liu *et al.* 2008), the absorbance is linearly dependant on gas concentration. As a result, the tendency of the product yield of each gas species was expressed and compared in the form of absorbance at specific wavenumbers.

Pyrolysis Reactor

Samples (around 500 g) were pyrolyzed in a laboratory-scale furnace. Heating temperature was set from ambient to 500 °C in 2 h and maintained for 1 h. Pyrolysis liquids were collected by using cold water to trap the condensable products. Thermocouples were used to detect the internal temperature of samples during the pyrolysis process, as shown in Fig. 2.

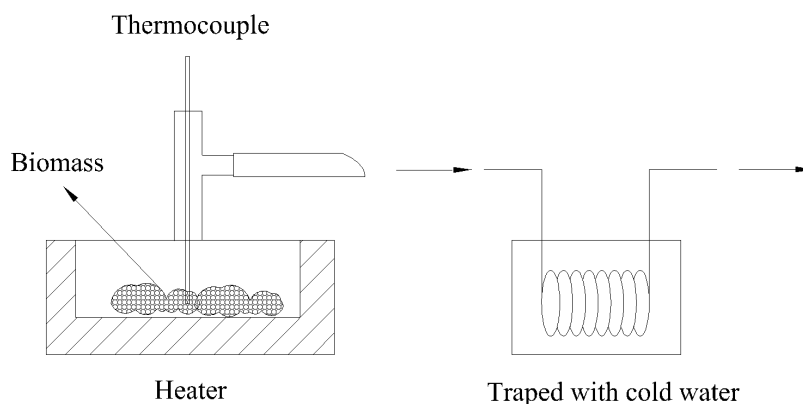


Fig. 2. Pyrolysis method used in our experiment

Elemental Analysis

In order to further explore the influence of UF resin on the pyrolysis of wood-based panels, particleboards with different content of UF resins were made in our laboratory, including particleboard with 6% UF resin (6%PB), particleboard with 9% UF resin (9%PB), particleboard with 12% UF resin (12%PB), and particleboard with 15% UF resin (15%PB). The particleboard samples were pyrolyzed in the static bed with the temperature of 500 °C in 2h. Char and pyrolysis liquids were obtained for later analysis.

Samples used in this part included both virgin samples and the char of wood, 6%PB, 9%PB, 12%PB, 15%PB, and UF resin. Elemental analysis was done by Elementar Vario EL III. Contents of C, H, and N were calculated by the mean value of two tests. Content of O was obtained by the difference.

GC-MS Analysis

Pyrolysis liquids were obtained from pyrolysis of wood, 6%PB, 9%PB, 12%PB, 15%PB, and UF resin by static bed. The components of the pyrolysis liquids were analyzed by GC-MS (Shimadzu 2010). The RTX-5 column (30 m × 0.32 mm × 0.5μm) was maintained at 50 °C for 2 min, then the temperature was raised to 250 °C at the heating rate of 10 °C /min, and held at 250 °C for 5 min. Helium was used as the carrier gas. The injection was performed at 250 °C in the split mode of (30:1). The mass spectrometer was operated in the electron ionization (EI) mode with ionization energy of 70eV. The interface temperature was 250 °C. The scan interval was 0.5 s and the scan range for m/z was 33 to 500.

RESULTS AND DISCUSSION

Pyrolysis Characteristics of Wood-based Panels by Thermobalance Analysis

The TG and DTG curves obtained from different materials are displayed in Figs. 3 and 4. Wood, as the main component in the wood-based panels, resulted in the similarity in TG and DTG curves between wood and wood-based panels, while still some

differences should not be neglected because of the presence of UF resin. Figures 3 and 4 show that the pyrolysis process could be divided into three main stages: from room temperature to 200 °C for the first stage, 200 to 400 °C for the second stage, and 400 to 800 °C for the third stage.

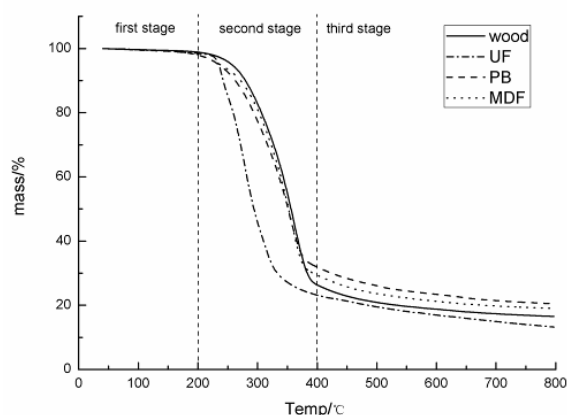


Fig. 3. TG curves of different samples

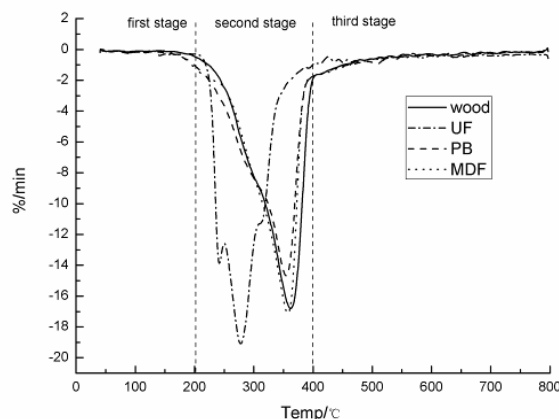


Fig. 4. DTG curves of different samples

Little weight loss could be found in the TG curves in the first stage, because samples were pre-dried before thermal analysis. The second stage is the most significant degradation stage during the whole process, with the weight loss of nearly 75% of the total weight for all the samples. The temperature range extended from 200 °C to 400 °C, where we could distinguish two peaks for UF resin and a small shoulder peak for wood, PB, and MDF in DTG curves. The DTG curve of UF resin was generally in accordance with the data of the literature (Jiang *et al.* 2010). According to Fig. 4, the two peaks of UF resin were probably attributable to the two crucial reactions during the thermal degradation of UF resin. Higher temperature enables the possibility of reactions involving chain rupture in the UF molecule. The shoulder peak of wood and wood-based panels might correlate to the decomposition of hemicellulose (Lee and Fasina 2009).

DTG curves reveal that the degradation of wood-based panels occurs at 175 °C, while no significant weight loss was found for wood and UF resin at this temperature. The degradation rates of PB and MDF gradually became slower than wood until 308 °C and 361 °C, respectively. TG curves also show that the mass residue of wood-based panels was less than wood until 380 °C. Conclusions could be made that the pyrolysis of wood-based panels is not the independent decomposition of wood and UF resins, which is in accordance with the literature (Peng *et al.* 2011). UF resin is more likely to accelerate the chemical reactions of wood-based panels at a lower temperature; however it inhibited the degradation of solid residue of wood-based panels at a higher temperature during the global pyrolysis process.

The terminal mass residue for wood was 16.6%, PB was 20.5%, MDF was 19.1%, and UF was 13.2%. At higher temperatures, the mass loss rate of wood was higher than that of wood-based panels, resulting in less terminal mass residue of wood. The thermal

stability of UF resin is weaker than wood, however it enhanced the thermal stability of wood-based panels, which confirms former conclusions.

FTIR Analysis of Gaseous Products and the Formation Mechanism

The gaseous products of different samples during the thermal process were detected on-line by FTIR. Because of this device, we could first distinguish main gaseous products from the FTIR spectrum and then observe the evolution patterns of each gas from the absorbance intensity curve. Figure 5 shows representative FTIR spectra of the four samples when the total released gas reached its highest intensity value. From the characteristic peak in the spectrum, main gaseous products and functional groups could be determined. Characteristic peaks related to main gases of CO, CO₂, HNCO, and NH₃ could be easily distinguished in all the FTIR spectra. However, an evident absorbance peak in wood at 1700 to 1800 cm⁻¹ and 2750 to 3000 cm⁻¹ appears in our experiment, which could not be found in the literature. In comparison with the spectrum library, these peaks are most likely responsible for the carboxyl and carbonyl absorbances. Such specific peaks could also be found in PB and MDF, but are not so obvious. Absorbance peaks in the range 3450 to 3600 cm⁻¹ in the spectrum of UF resin represents the release of HCN. Very little HCN was found in other samples, especially at low temperatures. It is concluded that the degradation of urea function in UF resin generates HNCO and a precursor of HCN, which will crack into HCN under 650 °C (Girods *et al.* 2009a). HCN is therefore much more difficult to be detected during the pyrolysis process.

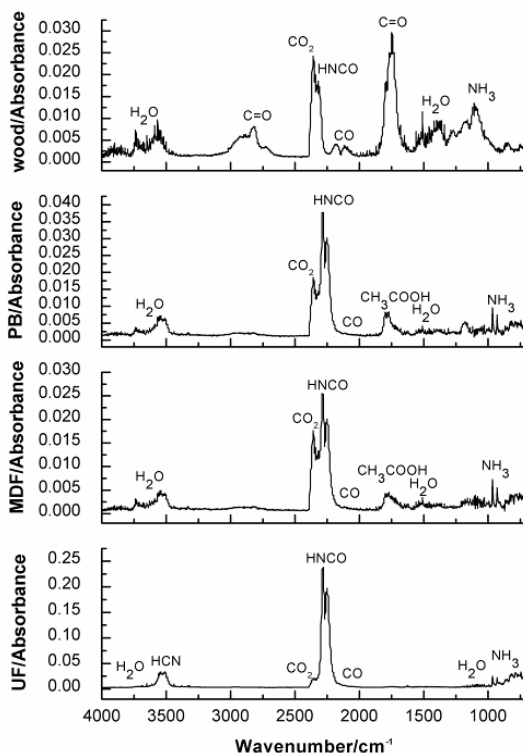


Fig. 5. Spectra of gases released at the highest intensity value for each sample

In the first stage, the absorbance at 3500 to 4000 cm^{-1} shows the release of water, which is mainly attributable to hygroscopic water and chemical water in solid wood. With the temperature rising in the first stage, some complex compounds including aliphatic hydroxyl groups are going to crack to generate smaller chemical compounds. From the absorbance curves of main gaseous products (see Figs. 6 to 9), small amounts of CO and CO₂ could also be detected gradually, which is primarily due to the breakdown of oxygen-contained groups and aliphatic hydrocarbons in the lateral chains. According to the literature (Rowell 1988), it is assumed that CO₂ and CO are formed by decarboxylation and decarbonylation, respectively.

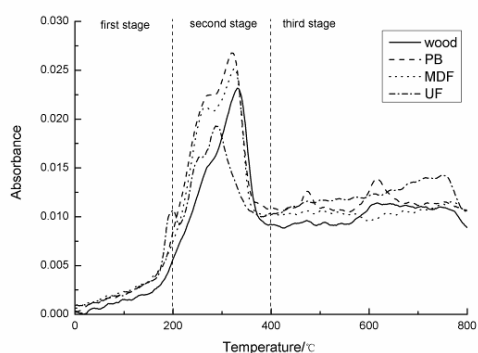


Fig. 6. Evolution patterns of CO₂

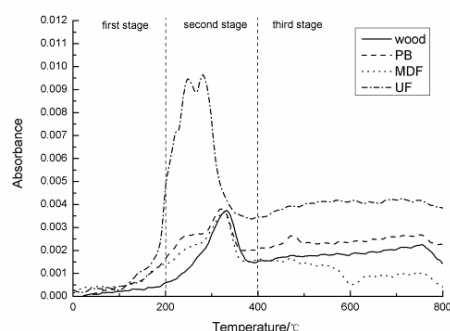


Fig. 7. Evolution patterns of CO

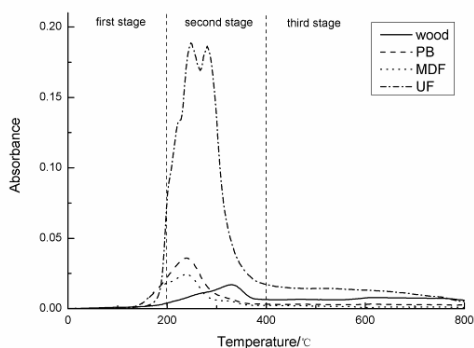


Fig. 8. Evolution patterns of HNCO

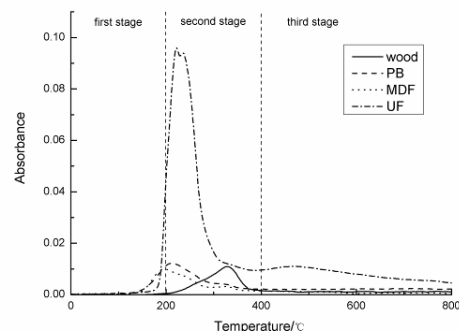


Fig. 9. Evolution patterns of NH₃

When the second stage, which is the primary and most important stage, takes place during the thermal process, almost all the gaseous products reached their highest intensity values. Generally, the thermal degradation range for hemicellulose is between 200 and $300\text{ }^{\circ}\text{C}$, cellulose between 300 and $400\text{ }^{\circ}\text{C}$, and lignin between 250 and $500\text{ }^{\circ}\text{C}$ (Wild *et al.* 2009). The breakage of carboxyl in the lateral chains in furfural acid results in the release of CO₂. The less stable carbonyl in volatiles is more likely to be the

precursor of CO. The formation of CO is also largely influenced by secondary cracking of volatiles during thermal process (Li *et al.* 2009).

Figure 6 shows that the evolution patterns of CO₂ created by different samples were similar to each other. The shoulder peak of the curve is in accordance with the results obtained from DTG, which suggests the maximum degradation rate of hemicellulose. The peak at around 300 °C reveals that the mass loss rate of hemicellulose, cellulose, and lignin as a whole reached its highest value. Because CO₂ originates mainly from carboxyl and there is little carboxyl in UF resin, the influence of UF resin on CO₂ yield of wood-based panels could thus be neglected. Figure 7 shows that the evolution patterns of CO were much different from that of CO₂. The carbonyl in UF resin led to a large amount of CO during thermal process.

The two peaks of UF resin between 200 °C and 300°C in the curve correspond to that of the DTG curve. Carbonyl groups in UF resin go through reforming, rearrangement, and isomerization at high temperature, resulting in the elimination of unstable double bonds and carbonyl groups. More stable molecular structure is rapidly formed during this process with the release of CO at the same time, resulting in the first peak that could be observed in the curve (Li *et al.* 2009). The two peaks of UF resin here may be attributed to the two crucial reactions during the thermal degradation, which is in agreement with former DTG results. During this temperature range, the CO intensity of PB and MDF was higher than that of wood for the reason of the existence of UF resin in the wood-based panels.

As for one of the nitric gases HNCO shown in Fig. 8, it is interesting that the evolution pattern of HNCO was similar to that of CO. Under thermal treatment, the breakdown of the unstable azyl and methylol in UF resin would make chemical groups in the circle in Fig. 1 an active group. Combined with an active hydrogen, large quantities of HNCO would then be formed, reaching its highest intensity at 240°C. In regards to NH₃, Fig. 9 shows that there is mainly one peak, which is much higher than wood and wood-based panels; conclusions could be made that the fragmentation of UF resin unit directly leads to the formation of azyl functions within the narrow temperature range between 180 °C and 320 °C and then the formation of large quantities of NH₃ with the highest intensity at 210 °C.

During the third pyrolysis stage in the high temperature range between 400 and 800°C, the intensity of almost all the gases was relatively low and varied very little. Lignin degradation plays an important role in this stage. Functional groups in the lateral chains of phenyl propane are still cracking, and volatiles undergo further secondary reactions. The higher CO release intensity in UF resin is due to the more carbonyl bonds and the breakdown of C-N single bonds in UF resin, compared with wood and wood-based panels.

The influence of UF resin on wood-based panels could be found mainly in the release of nitric gases during the second stage. Intensity peaks of nitric gases of wood-based panels are higher and occur earlier than that of wood. Together with the results of evolution patterns of CO₂ and CO, we could draw a conclusion that UF resin is the main factor contributing to the nitric gases of the pyrolysis of waste wood-based panels, while the influence on the CO₂ was not obvious. Measures must be taken to deal with the hazardous nitric gases especially in the temperature range between 180 and 320 °C.

Influence of UF Resin on the Elemental Distribution of Solid Samples

The four main elemental components contained in the wood and PB are C, H, N, and O. The elements C and O, with highest elemental content, account for 40.30wt% and 43.30wt% on average. Wood contains very little N, only 0.14wt%, while UF resin contains 33.4 wt%.

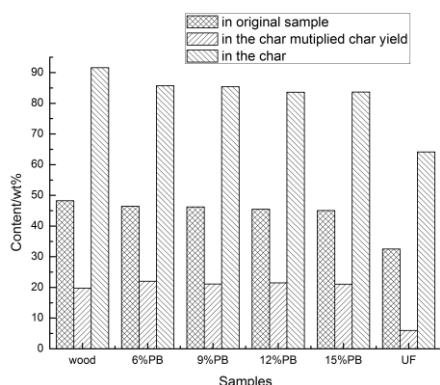


Fig. 10. Content of C in the original sample and char

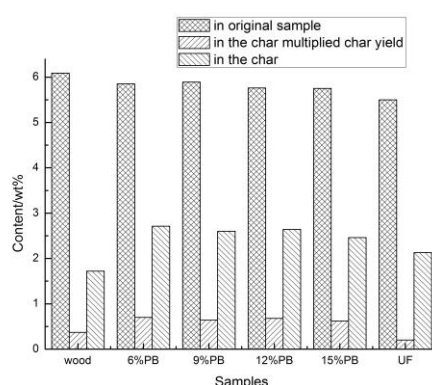


Fig. 11. Content of H in the original sample and char

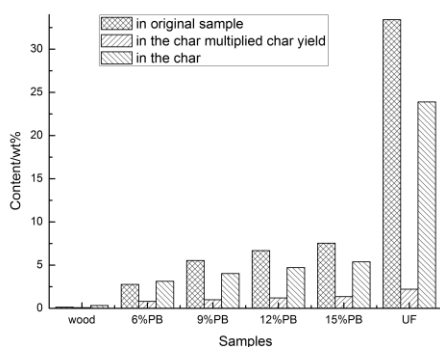


Fig. 12. Content of N in the original sample and char

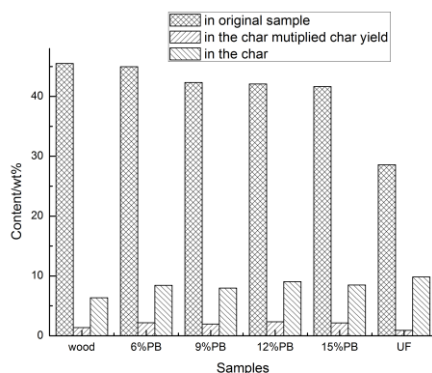


Fig. 13. Content of O in the original sample and char

Figures 10 to 13 show the content of C, H, N, and O of different samples before and after pyrolysis. The comparison of element content in the original sample and in the char multiplied char yield could show the loss of the element.

The contents of C, H, and O in UF resin was the lowest of all samples, which makes the content of C, H, and O in PB lower than that in wood. The content ratio of C in each sample was relatively stable both before and after pyrolysis. Although large amounts of C were lost, C was still the main element in the char, accounting for 91.59wt% in wood char and around 79.72 wt% in PB char. The influence of UF resin on C was therefore not significant. The tendency of O is quite similar to that of C. The

content ratio of O in wood and PB are not obviously influenced by different content of UF resin. However, the mass loss of O is the largest one, probably fixed in the form of oxygenated compounds in pyrolysis liquids and CO and CO₂ in gases during pyrolysis process.

With the increase of UF resin contained in PB, the tendency of H content is much different from that of C and O. In contrast to the content in original samples, the content of H in the char of PB is notably higher than that of wood and UF. It could be concluded that UF resin in PB inhibited the loss of H the most during pyrolysis; however concerning the loss of H, no apparent relationships with different resin content could be found in PB. N contained in PB with different UF resin content is mainly due to the UF resin, and the content steadily increases by the increase of UF resin both before pyrolysis (from 2.76% to 7.53%) and after pyrolysis (from 3.12% to 5.39%) with little changes for each sample. This indicates that N stays stable even after high temperature thermal treatment, which is in accordance with the literature (Girods *et al.* 2009a).

From elemental analysis results, it could be concluded that the main elements in wood and PB are C and O, and the main elements in UF resin are N, C, and O. The tendency of C and O distribution are similar to each other with little influence of UF resin, while the mass loss of O is the most significant one of all elements. UF resin inhibited mass loss of H in PB the most, while the most stable element is N contained in all samples.

Influence of UF Resin on the Components of Pyrolysis Liquids of PB

The main components of all the samples from GC-MS results are shown in Table 1, from which it can be found that almost all the compounds contain oxygen, which meets the results from elemental analysis that the largest mass loss is oxygen. Because the amount of acetic acid and formic acid were too high compared with other components and these acids contained no nitrogen compounds, the peaks of such acids were removed from the total ion current chromatograms in order to specifically clarify the influence of UF resin on nitric compounds in pyrolysis liquids.

The influence of UF resin is mainly on the nitrogen compounds. Almost no nitric compounds were detected in pyrolysis liquids of wood, but various types of amides were found in pyrolysis liquids of PB and UF resin. The formation of nitric compounds in pyrolysis liquids of PB is mainly through the conversion of urea in UF resins as applied in wood-based panels.

The two most abundant components in pyrolysis liquids of UF resin were methyl-urea and N, N'-dimethyl-urea, but in PB with 12% and 15% UF resin content the most abundant compound was acetamide, indicating that the transformation of nitrogen-containing compounds is influenced by the interactions between UF resins and wood constituents.

Different resin content did not make a linear increase in relative abundance of nitric compounds in pyrolysis liquids of PB, which is probably attributable to the intricate structures in wood-based panels. Such specific characteristics of pyrolysis liquids of PB might enable the multi-uses as new feedstock materials.

Table 1. Main Components of Pyrolysis Liquids of Different Samples

No.	Name	Elementary composition	Group	Peak area/%					
				Wood	6%PB	9%PB	12%PB	15%PB	UF
1	Phenol	C ₆ H ₆ O	Phenol	15.11	/	1.58	0.52	1.19	1.24
2	2-methoxy- Phenol	C ₇ H ₈ O ₂	Phenol	8.63	/	0.81	1.09	2.73	/
3	2-methoxy-4-methyl-Phenol	C ₈ H ₁₀ O ₂	Phenol	2.98	1.71	0.58	3.14	/	0.31
4	2,6-dimethoxy-Phenol	C ₈ H ₁₀ O ₃	Phenol	4.08	5.23	7.68	6.23	0.95	0.68
5	3-Pyridinol	C ₅ H ₅ NO	Phenol	/	9.64	6.05	6.84	5.10	/
6	2,6-dimethoxy-4-(2-propenyl)- Phenol	C ₁₁ H ₁₄ O ₃	Phenol	/	0.99	1.01	0.15	0.08	/
7	2,3-Pentanedione	C ₅ H ₈ O ₂	Ketone	9.67	/	/	/	/	/
8	1-(acetyloxy)- 2-Propanone	C ₅ H ₈ O ₃	Ketone	2.68	0.47	0.43	/	/	/
9	2-Cyclopenten-1-one	C ₆ H ₈ O	Ketone	0.91	0.44	/	0.59	0.39	/
10	3-methyl-2-Cyclopenten-1-one	C ₆ H ₈ O	Ketone	0.35	0.52	1.39	0.82	0.49	/
11	3-methyl-1,2-Cyclopentanedione	C ₆ H ₈ O ₂	Ketone	6.70	2.97	3.28	/	/	/
12	1,3,5-Triazine-2,4,6(1H,3H,5H)-trione	C ₆ H ₉ N ₃ O ₃	Ketone	/	1.34	/	/	/	0.33
13	2,2'-Carbonylbis(4-methyl-1,2,4-oxadiazolidine-3,5-dione)	C ₇ H ₆ N ₄ O ₇	Ketone	/	/	/	/	/	9.82
14	Furfural	C ₅ H ₄ O ₂	Aldehyde	7.20	/	/	/	/	/
15	Pentanal	C ₅ H ₁₀ O	Aldehyde	7.78	/	6.44	/	/	/
16	3-Hexanol	C ₆ H ₁₄ O	Alcohol	/	7.71	/	/	/	/
17	Cyclopropyl carbinol	C ₄ H ₈ O	Alcohol	7.78	/	/	7.18	7.51	/
18	Butyrolactone	C ₄ H ₆ O ₂	Ester	/	6.43	0.18	/	2.89	/
19	2-Pentenoic acid, 3-ethyl- methyl ester	C ₈ H ₁₄ O ₂	Ester	/	0.44	0.26	0.25	/	/
20	N,N-dimethyl-Acetamide	C ₃ H ₇ NO	N-compound	/	5.13	8.77	/	/	3.36
21	N-methyl- Acetamide	C ₃ H ₇ NO	N-compound	/	2.92	2.14	4.17	3.57	/
22	N,N-diethyl-3-oxo-Butanamide	C ₈ H ₁₅ NO ₂	N-compound	/	1.57	1.33	/	/	5.78
23	N-methyl- Formamide	C ₂ H ₅ NO	N-compound	/	/	2.98	/	2.21	1.78
24	N,N-dimethyl-Acetamide	C ₄ H ₉ NO	N-compound	/	/	3.53	6.95	4.82	/
25	Acetamide	C ₂ H ₅ NO	N-compound	/	/	/	13.79	13.36	/
26	methyl-Urea	C ₂ H ₆ N ₂ O	N-compound	/	/	/	/	/	18.30
27	N,N'-dimethyl-Urea	C ₃ H ₈ N ₂ O	N-compound	/	/	/	/	/	13.57
28	1,4:3,6-Dianhydro-α-D-glucopyranose	C ₆ H ₈ O ₄	Sugar	/	/	5.48	4.84	5.44	/

Various kinds of ketones were detected in pyrolysis liquids of PB with different UF resin content, which are probably formed by decarboxylation with active chemical properties. Ketones are quite likely to have originated from the large amount of carbonyls in levoglucosan degraded from cellulose in wood. Some pyridone, as well as imidazolone

in the form of nitrogen heterocyclic compounds, are found in pyrolysis liquids of PB, but little are found in UF resin, suggesting that nitrogen from UF resin is reformed and fixed with chemical groups degraded from wood in the form of ketones in the pyrolysis liquids.

Phenol is the most abundant compound in pyrolysis liquids of wood, while phenol, 2-methoxy-phenol, and 2,6-dimethoxy-phenol could be detected in almost all the pyrolysis liquids. Phenolic compounds in pyrolysis liquids of PB mainly originated from lignocelluloses; however, their structures might be influenced by UF resin in terms of nitrogen during the thermal conversion process, resulting in a small amount of phenol (peak area around 1.5%) in PB despite the large amount (peak area over 15%) detected in pyrolysis liquids of wood. The influence of UF resin on other components including aldehydes, alcohols, and esters is not significant, since these compounds are not the main components in pyrolysis liquids of PB and not detected in pyrolysis liquids of UF resin.

As the main constituent in wood, cellulose will go through dehydration reactions during pyrolysis process, forming levoglucosan and glycolaldehyde. Glucosyl groups will then crack into smaller structures at high temperature. However, in our experiment, 1,4:3,6-dianhydro- α -D-glucopyranose was only detected in PB with resin content over 9%. The research showed that acids could catalyze the dehydration reactions (Wang *et al.* 2006), while UF resin introduces alkaline atmosphere during the pyrolysis, which inhibits further cracking of glucosyl groups. Compared with cellulose, hemicelluloses are inhomogeneous glycan species with weaker thermal stability. The pyrolysis of xylan in hemicelluloses releases acid and aldehyde products, which are not significantly influenced by UF resin. Lignin is the only aromatic constituent in wood with very complicate structures, while in UF resin most structures are linear and network linkages. However many detected nitrogen compounds show aromatic properties, such as pyridine and pyrimidine. It could be concluded that concerted reactions between UF resin and lignin occur in the pyrolysis process so that lignin is probably the mostly influenced constituent by UF resin in wood.

CONCLUSIONS

1. Based on wood, wood-based panels, UF resin, and particleboards with different UF resin content, the influence of UF resin on wood-based panels in pyrolysis was studied by thermobalance, with elementary and components analysis. There are three stages, with the second stage being the most rapid stage between the temperature range of 200 to 400 °C for wood and wood-based panels. From TG and DTG results it is found that UF resin in wood-based panels make them easier to degrade at the beginning of thermal treatment, but that the presence of UF resin inhibits the degradation of wood-based panels during the second and third stage.
2. For the pyrolysis solid products, the mass loss of O is the largest one; however it is not significantly influenced by UF resin, while the mass loss of H is obviously inhibited by UF resin during the pyrolysis process. There are around 3wt% of N element in the char of wood-based panels, making the char of wood-based panels different from that of biomass. The loss of the element could directly influence the properties of pyrolysis gases and liquids.

3. The influence of UF resin on pyrolysis gases during the pyrolysis process of wood-based panels is mainly on the release of H₂CO and NH₃ within a narrower temperature range than CO and CO₂ between 180 °C and 320 °C corresponding to the second stage in TG results.
4. For the pyrolysis liquids, the influence of UF resin is mainly on the nitrogen compounds. Structures in phenols and ketones are also influenced by nitrogen in UF resin; however influences of UF resin on aldehydes, alcohols, and esters were not obvious. Based on the results of the influence of UF resin on the pyrolysis of wood-based panels, further study is still needed to make clear the interactions of UF resin with constituents of cellulose, hemicelluloses, and lignin in wood.

ACKNOWLEDGMENTS

This study was funded by the National Natural Science Foundation of China (31170533).

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Article submitted: May 29, 2012; Peer review completed: July 15, 2012; Revised version received and accepted: July 30, 2012; Published: August 8, 2012.