Release Profile of Nitrogen During Thermal Treatment of Waste Wood Packaging Materials

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Abstract: Wood packaging waste with a high recycling value is one of the main components of packaging waste. However, most research has been focused on natural wood, and less is known about the recycling of wood-based panel waste commonly used in packaging. This paper examined the pyrolysis of common urea-formaldehyde (UF) resin particleboard, including the decomposition characteristics of its nitrogen-containing adhesives, the product types, and how they are generated. The samples and pyrolysis products were analyzed by infrared spectroscopy. The results showed that the UF resin was the main contributor to the release of ammonia (NH₃) and hydrogen cyanide (HCN). At low temperatures, more NH₃ was released than the HCN, and at high temperatures, the reverse was true. A high heating rate promoted the release of the NH₃ and HCN. The UF resin and wood in the particleboard interacted and caused the release of the NH₃ and HCN. These results provide a reference for further study of the thermochemical regeneration of wood-based packaging waste.

Keywords: wood; particleboard; urea-formaldehyde (UF); release profile; packaging materials; thermal treatment


1 Introduction

Packaging is an integral part of most commodities. In particular, it plays an important role in the storage, transportation, and marketing of goods. Nowadays, with continuous improvement to living standards comes a rapid increase in the production of garbage and waste materials (Yu et al., 2000; He, 2014), which in turn means that packaging materials should be studied. Wood has been widely used in packaging engineering for a long time. Most packaging is simply thrown away after use, which results in large volumes of wood waste (Gou et al., 2012; Wang et al., 2013; Wang et al., 2016).

More research has studied the use of wood-based panel waste as a resource. Waste wood-based panels can be used in recycling, however, some renewable particleboards (PBs) suffer from serious degradation that leads to poor performance, and their adhesive content is a further drawback. Many studies have been focused on the use of wood-based panel waste as initial material for recycled particleboard (PB) (Yu et al., 1998; Huang et al., 2004; Huang et al., 2005; Su et al., 2012; Zhang, 2016). However, there are few studies on the use of this waste to generate energy, which is mainly because wood-based panels contain a variety of adhesives that have a great impact on the technology and equipment currently used in plants that generate energy from waste (Li et al., 2017).

Research on the characteristics of slow pyrolysis and the properties of the products from woody materials is relatively extensive, but there are few studies that have specifically covered waste wood-based panels. The existing research has been mainly focused on pyrolysis behavior, pyrolysis kinetics, and the characteristics of the released products (Yi et al., 2017). The main components of waste wood-based panels are wood materials. The eigenvalues and pyrolysis temperature range of waste wood-based panels are similar to those of wood materials (Hussain et al., 2017), but the adhesives these panels contain strongly influence the pyrolysis behavior and resulting products (Gou et al., 2015; Liu et al., 2016) and the products or byproducts will result in air or water pollution.

In this paper, the pyrolysis of three different types of material was studied, specifically urea-formaldehyde (UF) resin, natural wood, and PB. In particular, the effects of the temperature and heating rate (HR) on the production rate of ammonia (NH₃) and hydrogen cyanide (HCN) were studied. Additionally, how the nitrogen content influenced the pyrolysis of woody material was considered. An in-depth analysis of the PB and its components was performed, and the mechanism of the release of nitrogen from this material during pyrolysis was inve-
stigated, including the interactive influence of individual components.

2 Materials and Methods

2.1 Materials

The materials were selected from those commonly used in the packaging industry. These materials were UF resin, natural wood (larch and poplar), and two types of the PB, one of which was made from larch (PBL) and the other from poplar (PBP). The 30-year-old larch timber and 10-year-old poplar timber both came from the Da Hinggan Mountains (Inner Mongolia, China). The UF adhesive was provided by Beijing Chemical Co. The ratio of formaldehyde to urea was 1.1:1.0 and the solid content was 53%. The PB samples were made in the authors’ laboratory with 5%, 10% and 20% UF resin respectively. The condition to prepare the PB is controlled precisely to ensure the resin cured. The results of an elemental analysis of the experimental materials are shown in Table 1. The data was obtained from air-drying tests, and the oxygen content was determined by subtraction. The component analysis results of the two timbers are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Elemental analysis of samples (%)</th>
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<tbody>
<tr>
<td>Sample</td>
<td>C</td>
</tr>
<tr>
<td>Larch wood</td>
<td>46.15</td>
</tr>
<tr>
<td>Poplar wood</td>
<td>45.24</td>
</tr>
<tr>
<td>UF</td>
<td>33.45</td>
</tr>
<tr>
<td>PBL</td>
<td>44.15</td>
</tr>
<tr>
<td>PBP</td>
<td>43.35</td>
</tr>
</tbody>
</table>

Notes: element analyzer was used to analyzing C, H and N. O% was calculated by subtraction method.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Component analysis of samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Larch wood</td>
<td>42.76</td>
</tr>
<tr>
<td>Poplar wood</td>
<td>45.87</td>
</tr>
</tbody>
</table>

2.2 Equipments

The pyrolysis experiment was performed using a pre-programmed temperature ramp on coupled thermal gravimetric-Fourier transform infrared (TG-FT-IR) instruments. Nitrogen did not react under the chosen experimental conditions, and therefore the use of nitrogen as a carrier gas had no effect on the experimental nitrogen production results.

The coupled TG-FT-IR experimental devices included a NETZSCH STA449F3 simultaneous thermal gravimetric analyzer (NETZSCH, Germany) and Bruker TENSOR 27 Type FT-IR spectroscopy (Bruker, Germany). The dedicated connector and tubing connecting the TG analyzer to the infrared spectrometer and the piping connection interface were insulated to maintain a maximum constant temperature of 350 °C, which would enable a slow online real-time analysis of the pyrolysis products.

2.3 Methods

The slow preset temperature-program experiments were conducted in the following manner. The sample was placed in an aluminum oxide (Al₂O₃) crucible and compacted. Once the crucible was positioned in the experimental setup, the environment was purged with nitrogen to obtain an inert atmosphere. The HR was then set, though the temperature range for pyrolysis was automatically controlled. The products from pyrolysis were carried with the carrier gas into the FT-IR spectroscopy, which was connected to the thermal analyzer for online real-time detection.

A computer-controlled linear heating mode was used to control the HR (10 °C/min, 20 °C/min, and 40 °C/min), sample size (10–25 mg), pyrolysis temperature (25 °C–1000 °C), and pyrolysis residence time (10 min). High-purity nitrogen (99.999%) was used during the experiments to ensure an inert atmosphere within the reaction system, and the carrier gas flow rate was 50 mL/min. This flow effectively ensured an adequate residence time and served to prevent secondary cracking of the small port and connecting pipe. The IR spectrometer and TG analyses were conducted at 180 °C, which prevented the condensation of tar and absorption of NH₃. After completion of each experiment, a blank was read to correct for the phenomenon of virtual thermogravimetric weight-gain and to eliminate any systematic errors. The real pyrolysis curve for each set of experimental conditions was then obtained by subtracting the blank curve. The FT-IR wavenumber range was 500–4000 cm⁻¹, and the scanning frequency was 4 s⁻¹ with a resolution of 1 cm⁻¹.

2.4 Detection of nitrogen-containing compounds

The initial slow-pyrolysis nitrogen compound products are mainly gaseous nitrogen, carbon nitrogen, and tar nitrogen (Chen et al., 2017). Because this study was limited to the FT-IR analysis, only the gaseous nitrogen was analyzed. The initial slow-pyrolysis products of gaseous nitrogen are mainly NH₃, HCN, and HNCO compounds. Most studies reported that the NH₃ and HCN are representative materials of gaseous nitrogen (Becidan et al. 2007; Wang et al., 2016). However, there is some controversy over HNCO. While its formation during the
heat treatment process is expected, there are some uncertainties in the literature over its detection and manner of generation. The main reasons for this uncertainty are the unreliability of the test method and inaccuracy of the HNCO analysis. Many researchers have used solution absorption to detect the nitrogen compounds, but when HNCO is released during an experiment, ammonium (NH$_4^+$) will form during hydrolysis; therefore, the HNCO can not be measured by this method. Some studies have discussed the presence and release characteristics of the HNCO when using FT-IR technology to analyze nitrogen compounds in the product (Dejong et al., 2003; Hansson, 2003; Girods et al. 2008a, 2008b; Wang et al., 2011; Ren et al., 2012). However, researchers thought that the use of the HNCO line detection methods, such as FT-IR, is not viable because the biomass pyrolysis process is bound to generate a little amount of water. Additionally, hydroxyl ions generated during pyrolysis would instantly react with any generated HNCO, which would produce NH$_3$. In view of this, it was assumed in this study that the slow pyrolysis of the PB waste and its components generated only two gaseous nitrogen compounds, NH$_3$ and HCN, and that these compounds alone were detected by the FT-IR analysis.

Figures 1 and 2 are the standard spectra for the NH$_3$ and HCN, respectively, from the US National Institute of Standards and Technology (NIST). Referring the previous literatures, the NH$_3$ and HCN windows were determined (Dejong et al., 2007; Peng et al., 2009; di Nola et al., 2009, 2010; Giuntoli et al., 2009).

3 Results and Discussion

3.1 The UF resin pyrolysis

3.1.1 Release profile of NH$_3$ and HCN during waste wood pyrolysis

The IR spectra of the products from the UF resin pyrolysis at four different temperatures (240°C, 271°C, 323°C, and 384°C) are shown in Fig. 3. The NH$_3$ peaks appeared at 966 cm$^{-1}$ and 930 cm$^{-1}$, and the HCN peaks appeared at 3330 cm$^{-1}$ and 710 cm$^{-1}$. The strength of these signals indicated that the main nitrogen products from the pyrolysis of the UF resin as the temperature increased were the NH$_3$ and HCN.

Fig. 1 The FT-IR spectrum of NH$_3$

Fig. 2 The FT-IR spectrum of HCN

3.1.2 Effect of temperature on HCN and NH$_3$ release characteristics

The release of the NH$_3$ and HCN during the UF resin pyrolysis is shown in Fig. 4. A HR of 40°C/min was used. Figure 4 shows that the release of the NH$_3$ and HCN was basically consistent with the decomposition of the sample during the temperature-programmed process, which indicated that the small molecular gases generated during the pyrolysis of the UF resin were NH$_3$-based. The release of these two gaseous nitrogen compounds during pyrolysis is discussed below.

The NH$_3$ was produced initially at 200°C, and reached a maximum release rate at 270°C. The maximum weight loss corresponded to the loss rate. As pyrolysis progressed after the shoulder at 320°C, the release rate of the NH$_3$ was gradually reduced until the end of the experiment. An increase in the release rate was observed at 550°C, but was not obvious. This showed that at 550°C the UF-resin
underwent a carbonization stage with a cleavage reaction. When di Nola et al. (2009) studied chicken litter, they found that the release of the NH₃ had several stages, and the reason was that this material contains not only protein, but also nitrogen in the form of urea. Hence, the release of both amide nitrogen and amino nitrogen from the UF resin present in the initial material was consistent with the release of the NH₃ during pyrolysis.

The HCN was released from the beginning of pyrolysis, although at a very low level. As the temperature increased, the release rate slowly increased and reached a maximum at 350 °C, which was nearly 100 °C higher than the maximum peaks of the pyrolysis weight loss and NH₃ release rate. Furthermore, as the temperature continued to increase above 400 °C, the HCN release rate became relatively stable and greater than the NH₃ release rate. Figure 4 illustrates that the UF resin pyrolysis products were mainly the NH₃ in the low temperature region and the HCN in the high temperature region.

3.1.3 Effect of HR on release characteristics of NH₃ and HCN

The release of the NH₃ and HCN during the UF pyrolysis for different HRs is shown in Fig. 5. The results indicated that the product release rate did not vary to any great extent with the HR, although it was consistent with the differential thermogravimetric (DTG) curve. With a low HR, the pyrolysis peak (i.e., the DTG graph) was bimodal and the corresponding product graphs were also bimodal, which indicated that the reaction type during pyrolysis did not depend on the HR. Moreover, the pyrolysis process and subsequent release of products showed a dependency upon a single component. As the HR increased, there was a delay in the heat transfer to the initial materials, and so the product curve was shifted towards higher temperatures with higher HRs.

3.2 Wood pyrolysis

The FT-IR spectra of the products from larch wood pyrolysis are shown in Fig. 6. A HR of 40 °C/min was applied to four different temperature maxima (225 °C, 332 °C, 394 °C, and 433 °C). The major products observed were CO₂, CO, H₂O, and CH₄. Only a few nitrogen compounds were observed, and were mainly at the wavenumbers of 966 cm⁻¹ and 930 cm⁻¹ for NH₃, and 3330 cm⁻¹ and 710 cm⁻¹ for HCN. These peaks are clearly observed in the inset sections of the 394 °C spectrum (Fig. 6, top left and right).
3.2.1 Effect of temperature on release characteristics of NH$_3$ and HCN
The release of nitrogen products during the pyrolysis of larch and poplar wood with a HR of 40°C/min is shown in Fig. 7 and Fig. 8, respectively. The nitrogen content in the wood samples was low, and correspondingly the release of the NH$_3$ and HCN was low. The HCN in particular had almost no obvious peak value.

![Fig. 7](release_profile_larch.png)

![Fig. 8](release_profile_poplar.png)

The emission of the NH$_3$ at 320°C appeared as a small shoulder, and increased to a maximum peak at 380°C. This was consistent with other studies that have investigated the nitrogen release characteristics of products from different thermal biomass gasification phases (Tian et al., 2005; Dejong et al., 2007; Ren et al., 2011; Ren et al., 2013; Yang, 2016).

The NH$_3$ released from poplar wood pyrolysis as measured by the first peak was much greater than that from larch. This difference could have been because of the higher content of hemicellulose in poplar compared with larch. A considerable amount of decomposition occurred at 320°C, which increased the porosity of the paralytic carbon and caused a greater release of the NH$_3$ (Hansson et al. 2004).

Throughout the pyrolysis process, the emission of the HCN was little. Only at the most extreme pyrolysis temperature did a peak appear, and even this was very small, which indicated that if lower temperatures (< 800°C) are chosen for pyrolysis, and the nitrogen from natural wood would mainly be the NH$_3$. The low amount of the HCN also reflected the low nitrogen content in the feedstock.

While the amount of the NH$_3$ released from larch and poplar was similar, the amount of the HCN differed. Given that the nitrogen content of the two kinds of wood was similar, the lower amount of the HCN from poplar pyrolysis compared with that from larch pyrolysis may have been caused by a lower lignin content in the poplar. Thus, suggesting that lignin may promote the formation of the HCN.

3.2.2 Effect of HR on release characteristics of NH$_3$ and HCN
The release of nitrogen compounds over the full temperature range for pyrolysis with different HRs is shown for poplar and larch in Fig. 9 and Fig. 10, respectively. As the...
HR increased, the degree of pyrolysis increased, the release of products was more intense, and the release interval was longer. The graphs showed a close relationship between the NH$_3$ and DTG peaks, which indicated that the NH$_3$ had come mainly from the sample. However, the peak for the HCN showed a displacement towards lower temperatures, which suggested that the HCN production was affected by secondary reactions as pyrolysis occurred. For example, as primary HCN formed, there was possibly some decomposition caused by hydrogen radicals. As the HR increased, primary coke formation of the pyrolysis product from the sample occurred, so that more HCN was generated by the HCN or it reacted with hydrogen radicals to generate the HCN. This resulted in the advancement of the HCN peak. This phenomenon was more obvious for larch than for poplar due to the higher lignin content in larch. The pyrolysis of lignin increased with the HR and was greater at high temperatures, which indicated the release of the HCN. Therefore, the final release of the HCN from larch at a lower temperature had lower intensity than that from poplar.

3.3 Discarded PB pyrolysis

3.3.1 Effect of temperature on release characteristics of NH$_3$ and HCN

The release of nitrogen compounds from the pyrolysis of the PBL and PBP is shown in Fig. 11 and Fig. 12, respectively. In each of the figures, the data were similar to those from the pyrolysis of the UF resin and natural wood. Because the nitrogen in the PBs was mainly from the UF resin, it was observed that the release of nitrogen-containing products from the pyrolysis of the PBs was similar to that of the UF resin. The wood component had little effect on the release.

Three peaks were apparent at 270°C, 320°C, and 380°C in both NH$_3$ graphs. The first two peaks were due to the pyrolysis of lignin increased with the HR and was greater at high temperatures, which indicated the release of the HCN. Therefore, the final release of the HCN from larch at a lower temperature had lower intensity than that from poplar.
release of the HCN played a catalytic role during the introduction of lignin.

3.3.2 Effect of HR on release characteristics of NH$_3$ and HCN

The release of the NH$_3$ and HCN during the pyrolysis of the PBL with different HRs is shown in Fig. 13. As the HR increased, the peaks for both gases tended to move to higher temperatures, as was shown for the wood. When the HR was low, individual peaks in the graphs were obvious, which suggested that the release of each gas was independent of the others. When the HR was 10°C/min, the first pyrolysis peak reflected the characteristics of the UF resin pyrolyzed at a lower HR. The wood pores filled with the UF resin required more time to be pyrolyzed. This also proved the conclusions drawn from the analysis of the nitrogen release mechanism of the pyrolysis process.

3.3.3 Interaction of waste PB components on release of nitrogen

To study the interaction of each product released during the pyrolysis of the PBs, the experimental and calculated values of the products were compared. The results for the PBL and PBP pyrolysis are shown in Fig. 14 and Fig. 15, respectively. If no interaction occurred between the products during the experiments, the measured values should be equal to the calculated values. In contrast, difference between the experimental and calculated values would suggest some sort of interaction between the pyrolysis products.

The figures show that the NH$_3$ released during both the PBL and PBP pyrolysis not only had three peaks, but also that the experimental and calculated peaks occurred at different temperatures. The experimental value of the first peak was lower than the calculated value. A possible reason for this was that the UF resin component of the PBs affected the pore structure of the wood component, which led to a delay in the release of the NH$_3$ and its full release occurred at higher temperatures. The experimental value of the second release peak was higher than the calculated value. However, the experimental value of the third peak was much lower than the calculated value. A possible reason for this was that not only was the UF resin

Fig. 11 Release of NH$_3$ (a) and HCN (b) during PBL pyrolysis

Fig. 12 Release of NH$_3$ (a) and HCN (b) during PBP pyrolysis
present physically in the wood because of the process of hot pressing, but the resin also formed cross-links (i.e., chemical bonds) with the wood components. During the carbonization phase of pyrolysis, paralytic carbon was generated from the UF resin, which had a higher density than the carbon generated from wood pyrolysis, and remained within the pore structure to a greater extent. This affected the breakdown of some of the UF resin, and thus hindered the release of nitrogen from the wood particles. Therefore, the value of third release peak of the NH$_3$ at 380°C in the experimental setup was remarkably lower than the calculated value.
The results of Fig. 14 show that the experimental HCN values from the PBL pyrolysis were higher than the calculated values, which indicated that the presence of lignin in the PBL may have promoted the release of the HCN during the UF resin pyrolysis, as had been discussed previously. However, while the graphs of the calculated and experimental release of the NH$_3$ were similar for the pyrolysis of the PBL and PBP, the experimental data for the PBP were much lower than the calculated values in the case of the HCN. This difference may have been due to the mechanized high fiber lignin content of the PBP, which meant a relatively high porosity of the paralytic carbon. It in turn led to a relatively low-temperature transformation phase that would produce more NH$_3$. In contrast, during the high-temperature phase, residual nitrogen was relatively lower, which led to a decrease in the amount of the HCN. As was discussed during the earlier analysis of the release of the HCN from the pyrolysis of poplar wood, and the higher ash content in poplar compared with larch also inhibited the release of the HCN via the pyrolysis of the UF resin.

The experimental and calculated values for the release of the NH$_3$ and HCN from the pyrolysis of the PBL containing different amount of the UF resin (contents of 5%, 10% and 20%) are shown in Fig. 16. As the resin content increased in the experimental setup, so did the interaction between the pyrolysis products. It resulted in increased emissions of the NH$_3$ and HCN.

The results presented in this study can be used to design
a fast pyrolysis process for waste UF resin-based man-made boards. In particular, the data implied that a two-step pyrolysis process would be advantageous for the removal of nitrogen from the initial material and the preparation of fast pyrolysis oil. The first step in the process should be a low-temperature slow pyrolysis, which would ensure that most of the nitrogen in the initial material is removed. The second step should be a medium-temperature fast pyrolysis, during which pyrolysis oil can be extracted for use in the manufacture of high-value chemical products or fuel.

4 Conclusions

The release of the NH₃ and HCN during the slow pyrolysis of the UF resin, natural wood (larch and poplar), and PBs (PBL and PBP) were studied by using TG–FTIR spectroscopy. The results showed that the UF resin was the main contributor to the formation of the NH₃ and HCN during the pyrolysis of the PBL and PBP. The amount of the NH₃ released from the pyrolysis of the UF resin was higher than that of the HCN at lower pyrolysis temperatures, and the amount of the HCN released was higher than that of the NH₃ at higher temperatures. Increasing the HR enhanced the release of the NH₃ and HCN for all of the studied materials. The UF resin and wood in the PBs obviously interacted to release the NH₃ and HCN. At low temperatures, the interaction led to greater releases of these gases, while at high temperatures, the reverse was true.

References


