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Release Mechanism of Fuel-N into NO_x and N₂O Precursors during Pyrolysis of Rice Straw

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Abstract: Rice straw, which is a typical agricultural residue in China, was pyrolyzed in a horizontal tube reactor connected with a Fourier transform infrared (FTIR) analyzer at temperatures ranging from 500 to 900 °C to research the release mechanism of fuel-N into NO_x and N₂O precursors. The concentrations of gaseous nitrogen components were monitored online. NH₃, HCN, HNCO, as well as NO were identified components. A high dependency between the gaseous products and temperature was found. NH₃ and HNCO preferred to be formed at lower temperatures and HCN tended to form at higher temperatures. It is worth noting that NO was also an important product. X-ray photoelectron spectroscopy (XPS) was performed to analyze the nitrogen species in rice straw. The result showed that amino-N (N-A) was the main form of nitrogen which accounted for 88.85%. Pyrrolic-N (N-5) was also identified and occupied the rest. Then nitrogen modeling compounds, glycine and pyrrole, were appropriately selected based on the results of XPS to well understand the nitrogen release mechanism during pyrolysis of rice straw. The formation routes of all the nitrogen gaseous components were confirmed. NH₃, HNCO and NO were originated from the decomposition of amino-N. While both amino-N and pyrrolic-N produced HCN. NO was not detected during the pyrolysis of pyrrole and a little NO was found during the pyrolysis of glycine. Hence, it can be deduced that the large amount of NO formed during the pyrolysis of rice straw was due to the direct oxidation reaction of –NH and –OH, the latter is abundant in the raw material. In order to provide evidence for this deduction, cellulose was added to increase the amount of –OH and co-pyrolysis of cellulose and glycine was conducted. The effect of –OH on the formation of NO was confirmed. Then, the release mechanism of fuel-N into NO_x and N₂O precursors during rice straw pyrolysis was concluded based on the experimental results.

Keywords: nitrogen; biomass; amino acid; pyrrole; NO_x; pyrolysis

1. Introduction

Biomass is considered as one of the most promising alternative energy because of its renewability and carbon-neutrality [1–8]. About 300 million tons of straw wastes, as well as the same amount of forestry wastes, are generated in China [9]. Direct combustion power generation is the major technology for large scale utilization of biomass [10]. Rice straw, which is abundant in southern China, dominates the amount of straw wastes, and is widely used as a fuel for biomass power plants. NO_x and N₂O, which can lead to environmental pollution [11], are the main gaseous pollutants during biomass combustion although the nitrogen content in most biomass is lower than that of coal. It is well known that pyrolysis is the first step of combustion, during which, part of the nitrogen in biomass is converted into NO_x and N₂O precursors (that is, NH₃, HCN, HNCO, et al.). These precursors will produce NO_x and N₂O via subsequent combustion. It was reported that about 80% of the nitrogen in

biomass is released into gaseous precursors during pyrolysis at temperatures above 850–900 K [12]. It means that most of NO_x and N_2O originate from the combustion of volatile-N. Hence, it is necessary to understand the release mechanism of nitrogen during pyrolysis well, so that the emission of NO_x can be reduced by appropriate in-furnace low-nitrogen combustion measures.

Researches have been conducted to investigate the nitrogen release during biomass pyrolysis. It was reported that the gaseous components generally contain NH_3 , HCN , HNCO , and NO [13–15]. Two approaches, chemical method and thermogravimetry infrared spectrum (TG-FTIR) method, were frequently used to research the conversion of fuel-N into gaseous nitrogen components.

Chemical method was carried out by many researches [13,14,16–22]. In those studies, NH_3 and HCN were absorbed by acid and alkaline solutions to form NH_4^+ and CN^- , respectively. The total yields of NH_3 and HCN could be confirmed based on the ion concentrations of NH_4^+ and CN^- in the solutions. However, the yield of NH_3 was actually the sum of NH_3 and HNCO . HNCO , the precursor of N_2O [23], could not be investigated due to the reaction $\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2$ [10,15–17]. The yield of NO was also not measured. Additionally, only the yields of NH_3 and HCN could be measured by chemical method, rather than the dynamic variation of concentrations for the precursors.

The nitrogen release was also studied by TG-FTIR [15,24–27], during which, the temperature of the sample was heated from ambient temperature to a higher temperature at a certain heating rate. However, the temperature of the sample was instantly heated up in an industrial combustor. For this reason, the results obtained from those researches could not accurately represent the nitrogen conversion in industrial combustors.

Rice straw is a typical agricultural residue and contains a higher nitrogen content, therefore, it was employed to investigate the release of fuel-N into NO_x and N_2O precursors during pyrolysis. The conversion of fuel-N into gaseous components during rice straw pyrolysis was researched in a few previous studies [17,28]. Yuan et al. [14] investigated the fuel-N conversion characteristic during rapid pyrolysis of rice straw at temperatures ranging from 600 to 1200 °C using a high frequency furnace. The yields of NH_3 and HCN were measured by chemical method. The results showed that HCN was the main nitrogen product while little NH_3 was found. Ren et al. [28] researched the formation of NO_x precursors during rice straw pyrolysis using TG-FTIR. They found that HCN and HNCO were the main nitrogen products. However, the results obtained from previous studies were based on TG-FTIR or chemical method, the shortcomings of which were discussed above.

A review of literatures shows that researches on nitrogen release during the pyrolysis of rice straw are rare and the release mechanism is still not well understood. Therefore, pyrolysis experiments of rice straw were conducted in a horizontal tube furnace in this study, and the concentrations of NH_3 , HCN , HNCO , and NO were accurately and dynamically monitored by a FTIR gas analyzer (Gasmeter DX4000, Gasmeter Technologies Inc., Helsinki, Finland) during the whole reaction process at temperatures ranging from 500 to 900 °C. Compared with previous studies, in which chemical method was employed, the concentrations of gaseous nitrogen products were on-line monitored, not only the yields. HNCO was also measured in current work. Besides, different from TG, the temperature of the sample could be heated up to the set value instantly so that the pyrolysis process could be more similar to that of an industrial combustor.

It was reported that the nitrogen conversion mechanism of biomass could be explained by nitrogen modeling compounds to some extent [23,29–33], while X-ray photoelectron spectroscopy (XPS) was reliable to investigate the nitrogen occurrence form in biomass [12,34–36]. Therefore, in order to further understand the fuel-N release mechanism during pyrolysis, XPS was performed to analyze the occurrence form in rice straw, and the appropriate nitrogen modeling compounds were selected according to the XPS result.

2. Materials and Methods

2.1. Materials

Rice straw, a widely available biomass raw material in China, was employed. The samples were first dried for 2 h at 105 °C and then pulverized. The particle size was between 0.15 and 0.25 mm. Proximate analysis of the sample was performed using an Automatic Industrial Analyzer (5E-MAG6700, Kaiyuan Instruments Co., Changsha, China). Ultimate analysis was conducted with an elemental analyzer (LECO-CHNS932, LECO Co., St. Joseph, MI, USA). The results are shown in Table 1.

Table 1. Proximate (ar, wt. %) and ultimate analysis (ad, wt. %) of rice straw.

Proximate Analysis				Ultimate Analysis				
M ^a	A ^a	V ^a	FC ^a	C	H	N	S	O
1.51	11.31	69.09	18.09	42.66	5.68	0.64	0.44	39.10

^a M, A, V, FC represent moisture, ash, volatile and fixed carbon, respectively.

The occurrence form of nitrogen in rice straw was characterized using XPS (Escalab 250Xi, Thermo Fisher Scientific, Waltham, MA, USA), equipped with Al K α radiation source. The constant analyzer energy (CAE) mode with 30 eV pass energy was used for survey spectra and 20 eV was used for high resolution spectra. To calibrate the binding energy, the C1s peak was set to 284.8 eV and the Shirley background was subtracted from the spectra. The N1s peaks were fitted using Gaussian (80%)–Lorentzian (20%) and established with XPSpeak. According to the result of XPS, as shown in Figure 1, the main peak at 399.9 eV was assigned to amino-A and the other peak at 400.5 eV was assigned to pyrrolic-N. Thus, the nitrogen in rice straw was composed of 11.15% pyrrolic-N (N-5) and 88.85% amino-N (N-A). Therefore, Pyrrole and glycine, commercial reagents with high purity of 98% or more, were chosen as the modeling compounds for mechanism research. Cellulose, with a purity of 99%, was also purchased as an additive to research the effect of –OH on NO formation. All of the modeling compounds were purchased from Sigma-Aldrich (St. Louis, MO, USA).

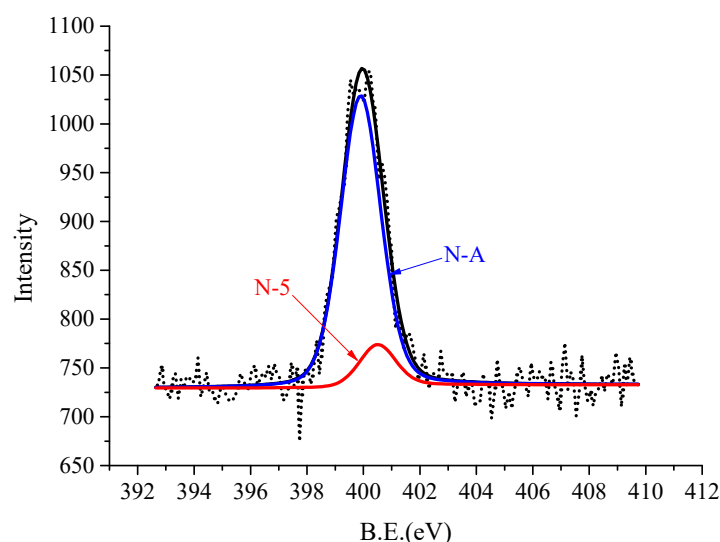


Figure 1. Nitrogen species in rice straw.

2.2. Experimental Methods

Experiments were conducted in a horizontal tube furnace reactor system, as shown in Figure 2. The furnace was 800 mm long and the inner diameter was 60 mm. The quartz tube was 1000 mm long and the inner diameter was 36 mm. The temperature of the reaction zone was controlled by a thermocouple connected to a temperature controller. The monitoring point of the thermocouple was set inside the quartz tube where the solid materials were placed to ensure an accurate temperature control. During experiments, 20 mg samples (rice straw or modeling compounds) were employed and were placed in a quartz boat (with length of 100 mm, width of 25 mm, and thickness of 1 mm). The reactor was heated by an electric furnace up to the given temperature ranging from 500 to 900 °C and maintained for 15 min. Then, the quartz boat that contained the sample was quickly pushed into the reaction zone. The carrier gas was argon (Ar) with a high purity of 99.999%. The gas flow rate was controlled at 4 L/min by mass flow meters. The volatiles released during pyrolysis were removed out from the reactor immediately by the carrier gas to keep a short residence time (less than 1.5 s) and to avoid the secondary reactions. Gasmet DX4000 (Gasmet DX 4000, Gasmet Technologies Inc., Helsinki, Finland), a kind of Fourier transform infrared gas analyzer, was employed to measure the concentrations of nitrogen containing components (NH₃, HCN, HNCO, and NO) on line. A sampling line was connected between the reactor and the gas analyzer, the temperature of which was maintained at 180 °C to avoid secondary pyrolysis and components condensing. The measurement time interval of the analyzer was set to be 3 s. Each test was repeated for three times to make sure that the relative standard deviations were less than 5%.

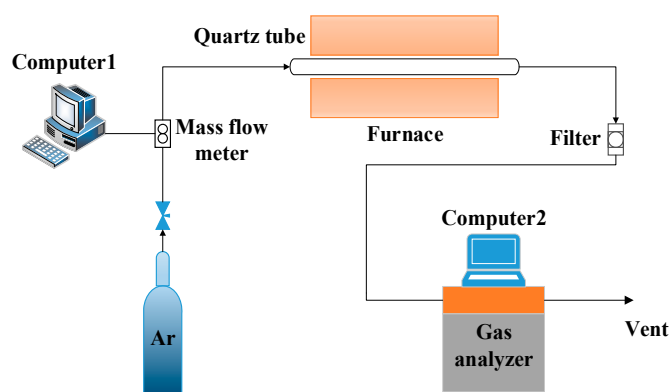


Figure 2. Schematic diagram of the horizontal tube furnace reactor system.

The convert ratios of fuel-N to gaseous nitrogen containing products (NH₃, HCN, HNCO, and NO) were calculated by Equation (1):

$$R_{\text{gas-N}} = \frac{\int c dt \times Q}{22.4 \times 10^6 \times 60} \times \frac{M_N}{m \times N_{\text{pc}}} \times 100\% \quad (1)$$

where $R_{\text{gas-N}}$ is the convert ratio of fuel-N to gaseous nitrogen components (%), c is the concentration of gaseous species (mg/Nm³), t is the measuring time (s), Q is the flow rate of flue gas (L/min), M_N is the molar mass of nitrogen (g/mol), and m is the weight of initial rice straw sample (g).

3. Results and Discussion

3.1. Nitrogen Release during Pyrolysis of Rice Straw

NH₃, HCN, HNCO, and NO were all found during the pyrolysis experiments of rice straw. Their concentrations were measured by a FTIR gas analyzer and recorded online. Figure 3 shows the release behavior of these gaseous products at temperatures ranging from 500 to 900 °C.

As shown in Figure 3, the peaks of the concentration curves of all the species appeared earlier as the temperature increased. This means that the chemical bond was broken more easily and that the reaction was more drastic at higher temperatures. NH_3 was detected at lower temperatures. Its concentration decreased with increasing temperature and totally disappeared at temperatures higher than 700°C . HNCO also decreased with rising temperature, and was disappeared at 800°C . On the contrary, HCN was first detected at 600°C and the concentration increased with an increasing temperature. It should be noted that NO was also a very important product, the concentration of which firstly increased with temperature and reached its maximum at 800°C and then decreased.

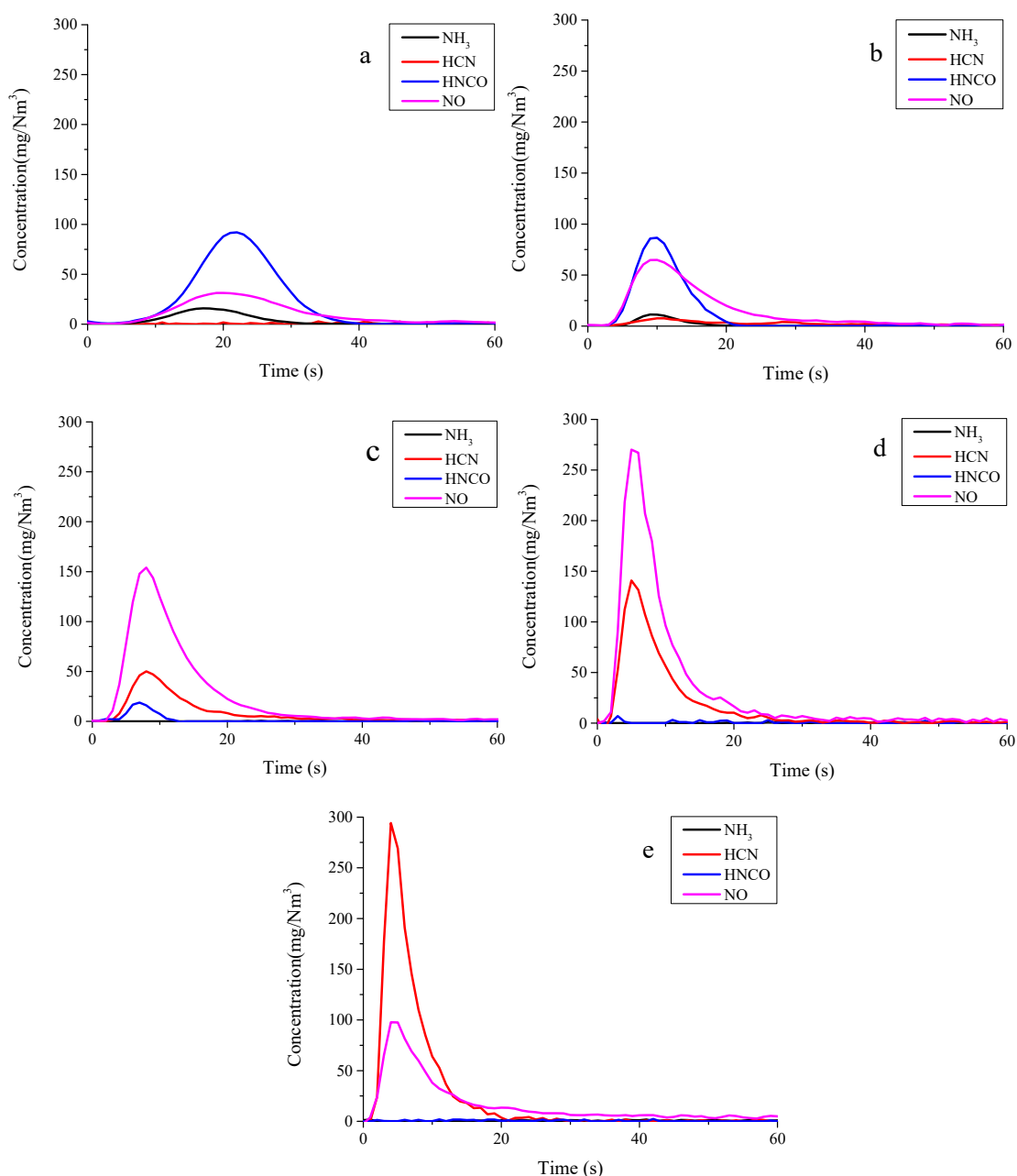


Figure 3. Release behaviors of nitrogen gaseous products during rice straw pyrolysis. (a) 500°C , (b) 600°C , (c) 700°C , (d) 800°C , (e) 900°C .

The convert ratios of fuel-N to gaseous products are shown in Figure 4. The convert ratios of fuel-N to NH_3 and HNCO decreased, while that of HCN increased with the increasing temperature.

Previous researchers also reported that HCN is preferentially formed at a higher temperature or at a higher heating rate, and that NH_3 is formed at a lower temperature or a lower heating rate [4,17,23,24]. Nitrogen release during rice straw pyrolysis was also studied by other researchers [17,28]. They also reported that HCN was the main product and little NH_3 was found. These results are in accordance with the result of the current study. The convert ratio of fuel-N to NO, a very important product, firstly increased and reached its maximum yield at 800 °C, and then decreased.

It is well known that the nitrogen species in biomass is mostly composed of amino acids [2,10,23,28]. The primary decomposition step of amino acid during pyrolysis contains decarboxylation, dehydration and deamination [32,33,37]. In present experiments, NH_3 was produced at temperatures lower than 700 °C, while at higher temperatures, NH_3 thoroughly disappeared. It was reported that amino acid could be converted into heterocyclic nitrogen compounds during thermal treatment [2], which would then lead to the decrease of amino acid. Due to this, the convert ratio of fuel-N to NH_3 decreased with the increase of temperature.

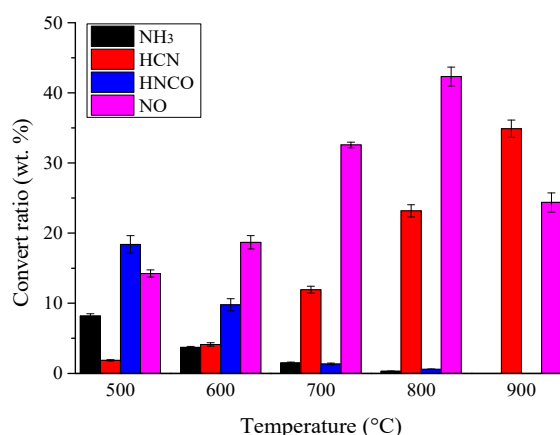


Figure 4. Convert ratios of fuel-N to gaseous products during pyrolysis of rice straw.

Cyclic amide, which was produced by dehydration, could be decomposed into HNCO and HCN further [15,23,32]. The convert ratio of fuel-N to HNCO decreased with the increase of temperature, while the reverse of HCN was observed. This corresponded with a previous study [38]. Therefore, the decomposition of cyclic amide has a high selectivity [15,23]. At lower temperatures, the convert ratio of fuel-N to HNCO was larger than that of HCN, while HCN was the main product at the higher temperatures. Hansson [38] pointed out that the activation energy for the formation of HNCO was lower than that of HCN during the decomposition of all cyclic amides. Besides, HNCO could be decomposed into HCN at high temperatures via the following reaction [24,32]:



which also led to the decrease of HNCO.

The peaks of NO concentration curves appeared simultaneously with that of other products at the same temperature, even a little earlier at lower temperatures. Hence, NO was definitely attributed to the direct oxidization reaction of N-sites with $-\text{OH}$, which is abundant in rice straw. The convert ratio of fuel-N to NO firstly increased with the increase of temperature and decreased at 900 °C. It was probably caused by the reduction reaction of NO and CO, which was catalyzed by inorganic impurities and even the chars at high temperatures [12,39]. CO was largely generated during pyrolysis and the reduction reaction easily occurred at higher temperatures. The concentration of CO was also tested by the gas analyzer in the experiments, as shown in Figure 5, which was powerful evidence for this explanation.

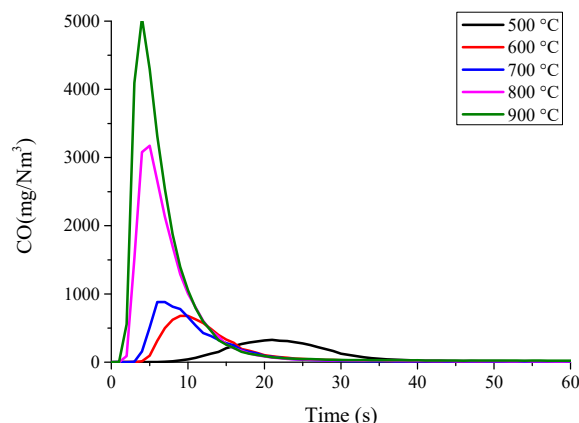


Figure 5. Variation of CO concentration with temperature.

3.2. Nitrogen Release during Pyrolysis of Nitrogen Modeling Compounds

Nitrogen in rice straw consisted of N-5 and N-A, as shown in Figure 1. It was reported that glycine is one of the major amino acids in agricultural straw [40]. Therefore, glycine and pyrrole were employed as modeling compounds to provide evidence for the release mechanism of fuel-N into gaseous components proposed above.

3.2.1. Pyrolysis of Glycine

Figure 6 shows the nitrogen release behavior during glycine pyrolysis at different temperatures. The concentrations of gaseous nitrogen containing products were much higher than that of rice straw. This was attributed to the high purity of glycine as well as its higher nitrogen content of 18.7%. The peaks of the concentration curves also appeared much earlier with the increasing temperature. The concentrations of HCN and NH_3 increased with the rising temperature, while the concentrations of other products firstly increased, and reached their maximum at 800 °C, then decreased.

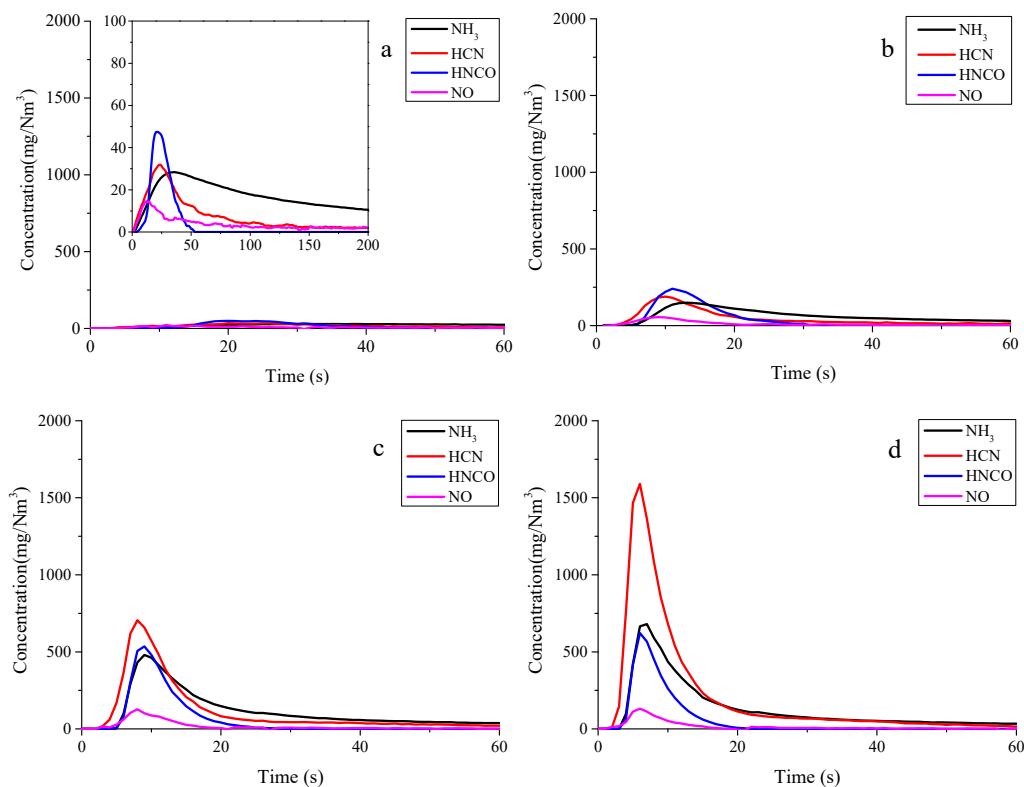


Figure 6. Cont.

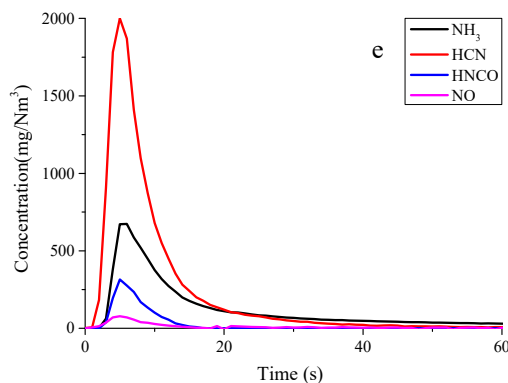


Figure 6. Release behavior of nitrogen gaseous products during glycine pyrolysis. (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C.

The convert ratios of fuel-N into gaseous nitrogen containing products are shown in Figure 7. Different from the pyrolysis of rice straw, the convert ratios of fuel-N to NH_3 and HNCO firstly increased, and reached their maximum at 800 °C, then decreased. In particular, the proportion of NO was much smaller than that of rice straw.

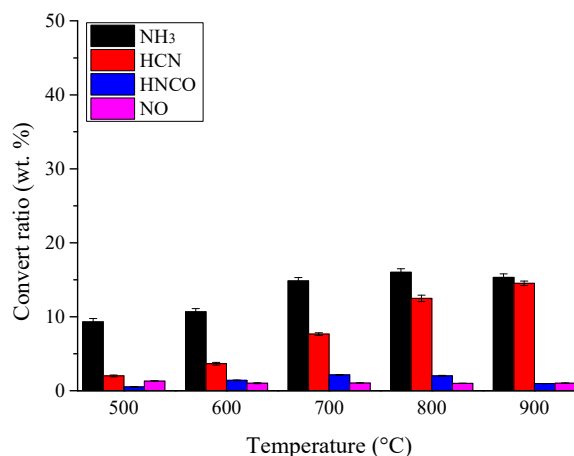
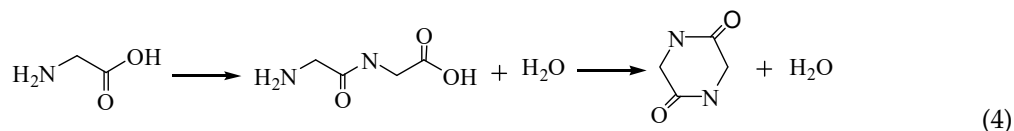
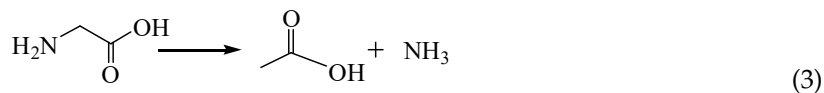
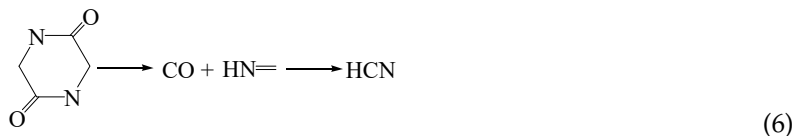


Figure 7. Convert ratios of fuel-N to gaseous nitrogen containing products during pyrolysis of glycine.

It was reported that during the pyrolysis of glycine, the main primary decomposition reactions are deamination and dehydration [33]. NH_3 and HNCO were formed via Equations (3) and (4). Additionally, the decomposition reaction of primary amines, as well as the bimolecular reactions between imine and amine, could also produce NH_3 [41].



HNCO was produced by the decomposition of cyclic amino, which was formed by the dehydration reaction, as shown in Equation (5). Meanwhile, the cracking of cyclic amino also produced HCN (see Equation (6)). HNCO could be further decomposed into HCN and CO at higher temperatures, and then the reduction of HNCO could be explained.



The peaks of NO concentration curves appeared a little earlier than that of other products at the same temperature. Hence, it is undoubted that NO was formed by the direct oxidation reaction of $-\text{NH}$ with $-\text{OH}$. The less convert ratio of NO might be caused by the lack of $-\text{OH}$ in glycine when compared to that rice straw.

3.2.2. Pyrolysis of Pyrrole

HCN was found to be the only product and was detected at temperatures higher than 700 °C during the pyrolysis of pyrrole, as shown in Figure 8. The concentration of HCN at higher temperatures was much higher than that of rice straw. It was caused by the high purity of pyrrole and the high nitrogen content of 20.90%.

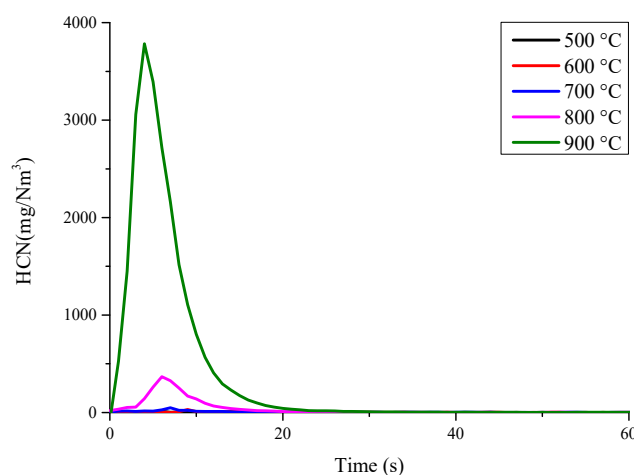
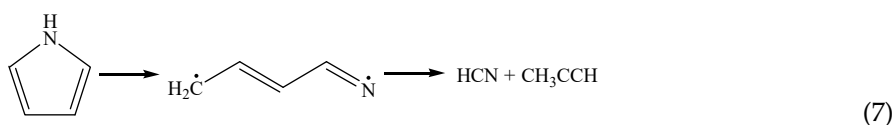


Figure 8. Variation of HCN concentration with temperature during pyrrole pyrolysis.

As it was reported in previous researches in regard to pyrrole pyrolysis [41–43], C–N was broken to generate an intermediate that decomposed into HCN and $\dot{\text{C}}\text{H}_2\text{--CH=}\dot{\text{C}}\text{H}$ subsequently, as shown in Equation (7). The formation of HCN tended to occur at temperatures higher than 700 °C [17,44]. This highly corresponded with the current study.



3.2.3. Effect of $-\text{OH}$ on the Formation of NO

NO was a major product during rice straw pyrolysis, however, it was not detected during the pyrolysis of pyrrole and little was formed during the pyrolysis of glycine. Therefore, it can be deduced that the large amount of NO formed during pyrolysis of rice straw was due the direct oxidation reaction of $-\text{NH}$ and $-\text{OH}$, which is abundant in rice straw.

Cellulose is the major component in lignocellulosic biomass, which accounts for 32–47% [45,46]. The percentage of cellulose in rice straw is 35% [46]. In order to prove the deduction of NO formation, cellulose was mixed into glycine to increase the amount of –OH and co-pyrolysis of glycine and cellulose was conducted. The mass ratio of cellulose to glycine was 1:4. The convert ratios of fuel-N to NO are shown in Figure 9. It is obvious that the convert ratio of NO increased with the addition of –OH. Furthermore, the ratio of –OH to amino acid in rice straw is much higher than in the mixed samples. Therefore, the larger amount of NO that is produced during pyrolysis of rice straw than model amino acid could be explained.

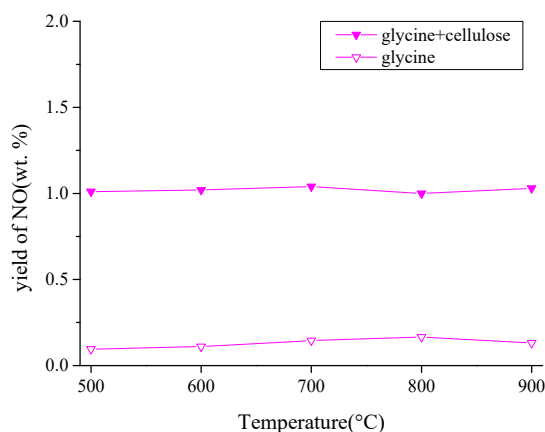


Figure 9. Convert ratios of fuel-N to NO during pyrolysis of glycine and co-pyrolysis of glycine and cellulose.

3.3. Mechanism of Nitrogen Release during Rice Straw Pyrolysis

As discussed above, NH_3 and HNCO were derived from the pyrolysis of amino acid. HCN was produced by pyrolysis of both amino acid and pyrrole. NO was an important product during rice straw pyrolysis, while a small amount of NO was found during amino acid pyrolysis, and it was not detected during pyrrole pyrolysis. Therefore, the formation of NO was attributed to the oxidation reaction of –NH and –OH, which is abundant in rice straw. This was proved by the co-pyrolysis of glycine and cellulose.

The nitrogen in rice straw was more complex than the model compounds of glycine and pyrrole. The transformation of nitrogen was reported to be affected by mineral matters [28,29,47] and the three major components of raw material, that is, cellulose, hemicellulose, and lignin [10,30,40] during pyrolysis of biomass. However, the research on modeling compounds could explain the nitrogen release route during pyrolysis due to the definite nitrogen occurrence forms in rice straw analyzed by XPS. Thus, the release mechanism of fuel-N into NO_x and N_2O precursors during rice straw pyrolysis was concluded in Figure 10.

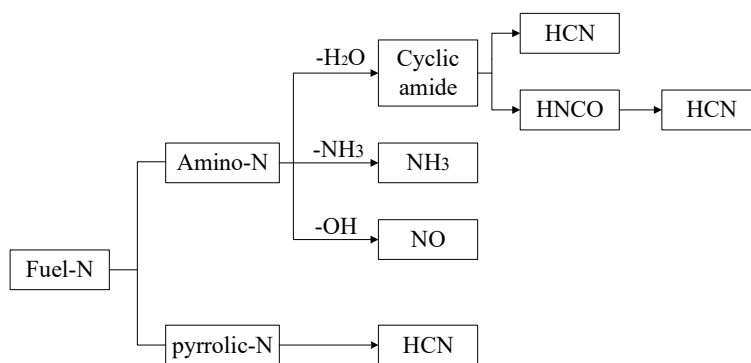


Figure 10. Release mechanism of fuel-N during rice straw pyrolysis.

4. Conclusions

Pyrolysis of rice straw was conducted to research the release mechanism of fuel-N into NO_x and N_2O precursors. The concentration variations of gaseous nitrogen components, i.e., NH_3 , HCN , HNCO , and NO were dynamically monitored. The formation of gaseous nitrogen components was found to be highly dependent on temperature. NH_3 and HNCO preferred to be formed at lower temperatures and HCN tended to form at higher temperatures. It is worth noting that NO was also an important product.

The nitrogen occurrence form in rice straw was analyzed by XPS. Amino-N and pyrrolic-N were identified. Therefore, glycine, as well as pyrrole, were chosen as the nitrogen modeling compounds based on the results of XPS to understand the release mechanism of nitrogen during rice straw pyrolysis well. The formation routes of all nitrogen gaseous components were confirmed. NH_3 , HNCO , and NO originated from the decomposition of amino acid. HCN was formed by the decomposition of both amino acid and pyrrole. NO was not detected during pyrolysis of pyrrole, and a little NO was found during amino acid pyrolysis. Therefore, a considerable proportion of NO formed during the pyrolysis of rice straw was due to the direct oxidization reaction of $-\text{NH}$ and $-\text{OH}$ in the raw material. To provide evidence for this proposal, cellulose was selected as an additive to increase the amount of $-\text{OH}$ and co-pyrolysis of glycine and cellulose was conducted. Then, the release mechanism of fuel-N into NO_x and N_2O precursors during rice straw pyrolysis was proposed based on the experimental results. In future research, various biomass materials with different nitrogen occurrence forms would be employed to investigate the effect of fuel type on nitrogen release.

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Author Contributions: Zhongyang Luo and Chunjiang Yu conceived and designed the experiments; Xiaorui Liu performed the experiments; Xiaorui Liu analyzed the data; Hanchao Tu and Bitao Jin contributed reagents/materials/analysis tools; Xiaorui Liu wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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