Characterization of NO Emission in Combustion of Hydrothermally Treated Antibiotic Mycelial Residue

Dachao Ma², Guangyi Zhang^{1*}, Chinnathan Areeprasert², Chunxing Li¹, Yafei Shen², Kunio

Yoshikawa^{2*} and Guangwen Xu^{1*}

¹ State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

² Department of Environmental Science and Technology, Tokyo Institute of Technology, G5-8, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa, 226-850, Japan

*Corresponding authors:

Guangyi Zhang: Tel.: +86 10 82544905; fax: +86 10 82629912; Email: gyzhang@ipe.ac.cn.

Kunio Yoshikawa: Tel.: +81 45 9245507; fax: +81-45-924-5518; Email: yoshikawa.k.aa@m.titech.ac.jp.

Guangwen Xu: Tel.: +86 10 82544905; fax: +86 10 82629912; Email: gwxu@ipe.ac.cn.

Abstract: The NO emission characteristics from both conventional and air-staged combustions of antibiotic mycelial residue were investigated in the temperature range of 1073 ~ 1273 K. The effect of hydrothermal treatment (HTT) prior to combustion on the NO emission was clarified. In conventional combustion, the NO emission from combustion of the hydrothermally pretreated antibiotic mycelial residue (HTT-AMR) was 20~30% lower than that from combustion of the directly dried antibiotic mycelial residue (Dried-AMR). By air-staged combustion, the NO emission of HTT-AMR was reduced by about 45% at 1273 K, compared to that by conventional combustion. As a

result, the NO emission was largely reduced by 57% by air-staged combustion of HTT-AMR at 1273K in comparison with conventional combustion of Dried-AMR, showing a significant combining effect of HTT and air-staged combustion on the NO emission. Results of thermogravimetric analysis and X-ray photoelectron spectroscopy revealed that the AMR based fuels have only volatile matters which consist of light and heavy volatiles. Deconvoluting the NO emission curves demonstrated that the reduction in NO emission via HTT mainly resulted from the removal of the nitrogen in the light volatile as the form(s) of amino acid or/and ammonia, while the reduction via air-staged combustion was because air-staged combustion suppressed the formation of NO from the heavy volatile.

Keywords: Hydrothermal treatment; Antibiotic mycelial residue; High-nitrogen solid biofuel; NO emission; Air-staged combustion.

1. Introduction

The amount of residues from antibiotic pharmaceutical processes keeps increasing with the development of this industry. As the dominant country producing antibiotics, China discharged about 0.3 million tons of antibiotic mycelial residue (AMR) in 2012 [1]. Because AMR retains approximately 0.6 wt.% of antibiotic chemicals, it would unavoidably arouse serious environmental problems that have been widely recognized [2, 3]. The usage of AMR as animal feedstock or fertilizer has been rigidly forbidden in many countries due to its residual antibiotics [4]. As the residues come from the fermentation processes, they are usually rich in moisture

existing mostly as bond water or water inside the mycelial cells [5, 6]. Therefore, the incineration of AMR after efficient removal of moisture is anticipated to be the most feasible way for its innocent treatment and safe utilization [5, 7-10].

Numerous previous studies have showed that the hydrothermal treatment (HTT) is an applicable technology to prepare clean solid fuel from high moisture biomass wastes including municipal solid waste [11-14], various sludge [15-17] and so on. HTT enables efficiently dewatering and upgrading of biomass wastes [18]. We have also verified that HTT can degrade the residual antibiotics in AMR and improve the dewaterability of AMR to allow its safe disposal and efficient production of solid biofuel [5, 7, 9, 10]. Although HTT can partially remove nitrogen present in AMR [8], there is yet little understanding about the NO emission characteristics of burning the AMR-based solid fuels obtained after HTT. The nitrogen content in the hydrothermally treated AMR was shown as high as 5.8 wt.% [5], and it would be highly necessary to control the NO emission from its combustion [19-21].

Because HTT has been widely applied to prepare solid biofuel from high-moisture and high-nitrogen biomass wastes [18], the effect of HTT on NO emission from the combustion of the biofuel is indeed a kind of important knowledge that necessary to be understood. However, there is rare study on this topic. Zhao et al. [22] have given some primary information about the effect of HTT on NO emission from sludge combustion, but it is still unclear that how HTT affects the NO formation and emission. Additionally, the effect of HTT on NO emission should also be related with the properties of fuels from different sources [23]. In that literature, there is

almost not systematic work on the combustion characteristic and the NO emission characteristics of hydrothermally pretreated AMR (HTT-AMR).

In this article, AMR before and after HTT are combusted via both conventional and air-staged combustion modes to investigate the corresponding NO emission characteristics, whereby clarifying the effect of HTT on NO emission and the mechanism about the NO emission reduction due to HTT. For these research objectives, pyrolysis of AMR before and after HTT at 1273 K were also performed in the study. The X-ray photoelectron spectroscopy (XPS) and thermo gravimetric (TG) analyses of both the dried raw AMR (Dried-AMR) and HTT-AMR are conducted to understand the transfer of nitrogenous components in the pyrolysis and combustion.

2. Material and Methodology

2.1. Fuel characterization

The raw antibiotic mycelial residue (AMR) tested in this study was from the fermentation process in cephalosporin C production, and the HTT-AMR used for combustion tests was made via the optimized condition HTT at 200 °C for 30 min [5, 8]. A sub-bituminous coal was also tested for comparison. Table 1 shows the properties of all the tested fuels. Prior to the combustion test, all fuels were dried at 102 °C for 24 h in an atmospheric air oven, then milled and sieved to size of 0.3~0.4 mm to minimize the influence of particle size. Different from the tested coal, both the raw AMR and HTT-AMR (AMR-based biofuels) have no fixed carbon, and their combustible matters are volatiles only. HTT-AMR and the tested coal have similar ash

contents of about 15 wt.% (dry basis). The AMR-based biofuels have high nitrogen contents, reaching 7.7 wt.% and 5.8 wt.% (dry ash-free basis) for Dried-AMR and HTT-AMR, respectively. The reason for nitrogen reduction should be due to hydrolysis of nitrogenous substances like protein, amino acid and the like in AMR during HTT [8, 24]. All the tested fuels have similar sulfur content and relatively high higher heating value (HHV) of about 20 MJ/kg.

Fig. 1 and 2 show the analysis results from pyrolyzing and combusting the three tested fuels in TGA (SHIMADZU D50). The pyrolysis and combustion were respectively conducted in the atmospheres of pure Ar and a mixture of Ar + 21 vol.% O₂. The temperature was increased from room temperature to about 1173K at a heating rate of 50 K/min. Fig. 1 shows that there is no steady char formation stage for Dried-AMR and HTT-AM, verifying further no fixed carbon in them. The weight loss curves for both of them, however, exhibit two distinctive stages of devolatilization (see before and after dotted vertical lines). By contrast, for the tested coal, its pyrolysis curve can be also divided into two stages - the first one representing the releasing of volatile and the second stage corresponding to the carbonization to form char. Because there is no formation of char for the two AMR-based fuels, we distinguished their two devolatilization stages as the releases of light and heavy volatiles, respectively. As shown in Fig. 1, ones can see that the demarcation of the two stages for AMR-based fuels occurred roughly at the time of 500 s or the temperature of 800 K. Clearly, the light volatiles were released quickly while the release of heavy volatiles was very slow, possibly through a kind of cracking reactions

strongly depending on temperature. Fig. 1 further confirms that the fuel Dried-AMR has the lower ash and higher light-volatile contents than the HTT-AMR does. Carefully examining the TGA curves for both the AMR-based fuels, it can be figured out that the heavy volatile respectively takes about 15 wt.% and 20 wt.% for the Dried-AMR and HTT-AMR.

The TGA and DTG curves shown in Fig. 2 for the combustion of the AMR-base fuels further verified the preceding analysis about two types of volatiles. In Fig. 2, the AMR-based fuels take on two distinctive DTG peaks, while also an inflection point appears on their respective TGA curves. For each fuel, its inflection area just corresponds to the transition period in its DTG curve between two big DTG peaks. The second DTG peak starts at about 370 s and 430 s for Dried-AMR and HTT-AMR, respectively. It is obvious in Fig. 2 that HTT lowered the combustion rate so that the HTT-AMR fuel shifted its two DTG peaks to the right to make the first peak have a lower intensity and a wider time span. The obviously delayed second DTG peak for HTT-AMR indicates a reduced combustion activity. Furthermore, the first big peak for both Dried-AMR and HTT-AMR consists of two fractional peaks, indicating that their light volatiles would rather be divided into two slightly different types of volatiles (needed to be further studied for better understanding the difference). By matching with the pyrolysis data in Fig. 1, one can reasonably suppose that the second DTG peaks for Dried-AMR and HTT-AMR mainly correspond to the combustion of their heavy volatiles. For the tested coal there was only one big DTG peak at the left corner of the area to indicate the combustion of the volatile. Then, its flatten DTG

peak area, till the peak end, of the DTG curve should correspond to the combustion of coal char.

The study also characterized the tested fuels using X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi). For the analysis, a sample was, in succession, dried in a vacuum dryer, degased at 10^{-7} Pa for 3 h and neutralized by Ar-ion sputtering. Monochromatic Al K Alpha (350W, $h\nu = 1486.8\text{eV}$) X-ray was used to excite the fuel sample. All spectra were obtained at 20 eV of pass energy in the fixed transmission mode. The resolution and analysis area were 0.05 eV and 0.8 mm^2 , respectively. The analysis was automatically performed at 3 ~ 5 different positions on the surface to obtain the high-quality N 1s spectra.

2.2. Combustion and pyrolysis tests

All combustion and pyrolysis experiments were conducted in an electrically heated fixed bed reactor, which is schematically shown in Fig. 3. It mainly consists of a gas supply section, an online flue gas cleaning and analysis section and the fixed bed reactor. The reactor is made of quartz glass and divided into three parts, an outer tube, an inner tube and a top cover having a primary gas inlet. The outer tube has a flue gas outlet on its top and a secondary gas inlet at its bottom. The two gas inlets enable the reactor to simulate various combustion modes (will be shown later). A sintered quartz porous plate at the middle height of the inner tube supported the tested fuel sample. A gas mixture of argon and oxygen at a volumetric ratio (Ar/O_2) of 79:21 was adopted as the oxidant to avoid any thermal NO emission. An online flue gas analyzer (Testo 350XL, Japan) monitored and recorded the composition of the flue

gas from the reactor. The measured NO_2 was invariably low in all experiments [21], thus only NO was considered in this study when analyzing the NO_x emission.

For all combustion tests, 0.25 g fuel sample was mixed with 5 g silica sand to maintain a certain bed height for enhancing the gas-solid interaction and also preventing the possible ash agglomeration at plate during combustion. The modes of conventional combustion (CC) and air-staged combustion (ASC) were performed, considering ASC is one general technology for lowering NO emission. When conducting CC, the fuel sample was placed in the inner tube and the oxidant gas was injected from the primary gas inlet at the top cover (through valve 1) at a flow rate of 2 L/min. For ASC, the oxidant gas was injected through the primary and secondary gas inlets with the flow rates of 1.5 L/min and 0.5 L/min, respectively. We then can assume that all the combustions in this study are conducted under the same fuel to air ratio, while 25% of the total oxygen was sent as the secondary oxygen in ASC. Inside the inner tube, the sample was firstly pyrolyzed and then preliminarily burned in O_2 -deficient condition. The pyrolysis gas flowed down and was fully burned out through interacting with the sufficient O_2 supply from the secondary gas inlet in the interstice between inner and outer tubes. For all tests, the flue gas was online monitored and recorded by a Testo flue gas analyzer to get the instantaneous NO concentration (in ppm). The combustion temperature was varied in 1073~1273 K.

With the instantaneous NO concentration (ppm) given by the Testo gas analyzer, the total amount of NO emitted (mg/g) in a testing period was calculated by

$$\text{NO emission} = \frac{40}{22.4 * \text{Mass of fuel}} * \sum_0^n \left(\frac{\text{Gas flow rate}}{60} * \frac{\text{NO concentration}}{10^4} * \Delta t \right) \quad (1)$$

where, the mass of fuel is 0.25 g, $\sum$ indicates the calculation period of fuel combustion, gas (flue gas) flow rate is 2 L/min, Δt means the time period between two adjacent data points which is 1 s in this study. The fuel-N conversion to NO was defined as the percent of nitrogen converted into NO from fuel-N:

$$\text{Fuel - N conversion to NO} = \frac{14 * \text{NO emission}}{30 * \text{Fuel - N}} * 100\% \quad (2)$$

Where, 14 and 30 respectively represent the molar weight ratios of N in NO, NO emission is adopted from Eq. (1), and fuel-N is the nitrogen mass in 1 gram of fuel (mg/g) from Table 1.

For understanding the mechanism about reduction in NO emission in fuels combustions, all solid fuels were pyrolyzed in the same reactor at 1273 K to measure the released NH_3 , one of the main NO precursors. The NH_3 released from pyrolysis was determined with the standard method of JIS K0099-2004. Firstly, NH_3 in the pyrolyzing gas was fully absorbed using 200 mL 0.1N sulfate acid. The resulting solution was in turn measured by a Thermos 9512 ammonia analyzer to obtain the NH_4^+ concentration. Finally, the total released NH_3 was calculated by multiplying the NH_4^+ concentration and the volume of the absorption solution.

3. Results and discussion

3.1. NO emission characteristics

Fig. 4 shows the absolute NO emission per gram of solid fuel calculated by Eq (1)

and corresponding Fuel-N conversion from Eq. (2) for all the tested fuels in the CC mode at different combustion temperatures. Similar to many other studies [20, 21, 25], NO emission and fuel-N conversion increased with increasing temperature from 1073 to 1273 K. For the biomass fuels like Dried-AMR and HTT-AMR, the quicker release of volatile N by raising temperature would be also a main reason for increasing NO emission and fuel-N conversion, except that higher temperatures enhanced reaction kinetics between N species and O₂. In this case (fuel without fixed carbon), the volatile N is the only precursor of NO formation [26, 27].

The absolute NO emission for Dried-AMR, HTT-AMR and coal followed the same order as that of their N contents (see Table 1). Nonetheless, the Fuel-N conversion was the highest for coal but the lowest for Dried-AMR (see Fig. 4). For Dried-AMR and HTT-AMR, the difference in their fuel-N conversion was insignificant (always < 2 percentages) and slightly bigger at high combustion temperatures. At 1073 K there was almost no difference in the fuel-N conversion for Dried-AMR and HTT-AMR. Figure 1 has shown that the devolatilization rate is the same for the two AMR-based fuels. Also, all the tests used same amounts of fuel and O₂. Considering the higher ash content of HTT-AMR than Dried-AMR (Table 1), the carbon amount in unit weight of fuel should be lower for HTT-AMR, thus the actual oxygen excess ratio is slightly higher, which would be the one reason for the slightly higher fuel-N conversion of HTT-AMR. Additionally, compared to HTT-AMR with less volatile, Dried-AMR must release more instantaneous volatile which has strong NO reduction capability. Therefore, Dried-AMR had a lower fuel-N conversion [19].

The highest fuel-N conversion for coal would be due to the lowest volatile content in it and thus the least reducing matter present in its combustion atmosphere for NO reduction [28].

The NO emission from burning HTT-AMR is lower than that from burning Dried-AMR, even though HTT-AMR had a higher oxygen excess ratio as indicated above. This means that HTT obviously reduced the NO emission of AMR-based fuels combustion. For an example, the combustion at 1073 K had the NO emissions of 6.5 mg/g for HTT-AMR but 9 mg/g for Dried-AMR. This effect of HTT on NO emission from burning its resulting fuel is similar to that observed in burning sewage sludge after HTT (Zhao. al. [22]) and can be attributed to removal of some nitrogenous species by HTT for fuel production, as shown in Table 1.

Figure 5 shows the NO emission and fuel-N conversion into NO from burning Dried-AMR and HTT-AMR in the ASC mode. Different from the results for the CC mode in Fig. 4, the NO emission and fuel-N conversion peaked at 1173 K and then decreased reversely at the tested highest temperature of 1273 K. The increase in the NO emission and the fuel-N conversion from 1073 K to 1173 K can be similarly understood as the data in Fig. 4, that is, higher temperatures increased NO formation kinetics and quickened release of volatile nitrogen precursors. However, compared to the CC, the ASC has the potential to reduce NO remission at because it can suppress NO formation in the primary combustion zone under oxygen-deficient condition [28, 29]. In our tests, the O₂ amounts fed into the primary and secondary combustion zones are fixed. Generally, a higher temperature is apt to lead to rapider release of more

volatile from AMR-based fuels (without fixed carbon), and will in turn make the combustion in the primary zone oxygen-deficient to form much less NO or even leave more reducing volatiles in the primary exhaust gas. Through the secondary combustion zone, at which 25% of the total oxygen was supplied, when all fuel volatiles were fully combusted the NO formation was much inhibited due to the relatively less O₂ amount. Therefore, the NO emission and fuel-N conversion into NO were reduced at the highest temperature of 1273 K here, as shown in Fig. 5. This result possibly implies that, with 25% as the secondary O₂ supply (75% as the primary), the primary combustion of Dried-AMR and HTT-AMR may be under oxygen-lean conditions when the temperature was 1173 K or below but under oxygen-deficient conditions when the temperature was above 1273 K.

As given in Fig. 5, the fuel-N conversion into NO was always higher for HTT-AMR than for the Dried-AMR regardless of combustion temperature. Similar to the above explanation, this should be mainly attributed to the slightly higher oxygen excess ratio for burning HTT-AMR. Nonetheless, the NO emission from burning HTT-AMR was lower (by 1.5 ~ 2 mg/g) than that from Dried-AMR at all the tested temperatures. This was supposed to mainly result from the lower N content of HTT-AMR than that of Dried-AMR, especially after considering the higher fuel-N conversion into NO for the former compared to that for the latter.

3.2. NO emission reduction by HTT and ASC

Both Dried-AMR and HTT-AMR were combusted with different modes to

clarify the potential of reducing NO emission via HTT, ASC and their combination.

Fig. 6 compares the results based on the following benchmarked tests (with the former as the control test) - Dried-AMR in CC *vs.* HTT-AMR in CC, HTT-AMR in CC *vs.* HTT-AMR in ASC and Dried-AMR in CC *vs.* HTT-AMR in ASC.

In the CC mode the reduction in NO emission for HTT-AMR against Dried-AMR, which naturally corresponded to the effect of HTT, reached 30% at 1073K and decreased to about 20% at 1173 K and 1273 K. Since the conversion of fuel-N into NO was similar at 1073 K for both HTT-AMR and Dried-AMR (Fig. 4), the reduction of 30% in NO emission was mainly subject to the difference (25%) in the N content between the two biofuels (that was, 5.8 wt% for HTT-AMR *vs.* 7.7 wt.% for Dried-AMR, see Table 1). By contrast, the lower reductions (20% or so) in NO emission for the two higher temperatures (1173 K and 1273 K) could be partially attributed to the approximately bigger conversion of fuel-N into NO for HTT-AMR (refer to Fig. 4).

For HTT-AMR, the reduction in NO emission resulting from ASC (HTT-AMR in CC *vs.* HTT-AMR in ASC) increased with raising the temperature, say, from about 16% at 1073K to about 45% at 1273K. Similar to the explanation employed for Fig. 5, in ASC the speeded release of volatiles including nitrogenous species for AMR-based fuels at higher temperatures probably represented better abilities to lower NO emission. This is because at high temperatures the rapidly generated reducing volatiles in the primary combustion zone decreased the oxygen excess ratio and even formed O₂-deficient conditions, so as to considerably reduce the NO formation [29].

The volatiles including nitrogenous species (NH_3 , HCN , etc.) can also further reduce NO before they flow into the secondary combustion zone. Therefore, with respect to ASC, the higher the combustion temperature, the larger the reduction in NO emission, as it is shown in Fig. 6 by combusting the same HTT-AMR via CC and ASC modes.

Based on the actual results for such the two cases as CC of Dried-AMR and ASC of HTT-AMR the comparison was made for the specific NO emission per gram of fuel, and the combined effect of HTT and ASC is thus revealed in Fig. 6. That is, at 1073 and 1173 K the NO emission from ASC of HTT-AMR was about 40% lower than that from CC of Dried-AMR. This reduction further increased to 57% at 1273 K. Noting that the fuel amount of HTT-AMR should be lower than that of Dried-AMR, it can be induced that combination of HTT of AMR with ASC of the HTT-produced solid fuel indeed greatly reduced the absolute NO emission by, for example, over 50% in comparison with the case of Dried-AMR in CC. This result is consistent with the report made for combining HTT of sewage sludge and then combustion of its produced solid fuel [20].

3.3. Time-series variation in NO emission

The variation of NO concentration in flue gas with burning time was investigated to understand more about the effect of HTT and combustion mode on NO emission, as was previously done in decoupling combustion [21, 30, 31]. Fig. 7 shows real-time NO concentration (ppm) in CC of coal and Dried-AMR at 1273 K. The curves with experimental data represent the actual measurement, while the fractional curves

shown with dash lines refer to the deconvolution fitting according to the Guass curve fitting function. The two deconvoluted fractional curves can be suggested to represent two types of NO sources. For coal (top plot), the two deconvoluted fractional curves are considered to be from volatile-N (left) and char-N (right) [27, 32], respectively. While for AMR-based fuels (see Figs. 1 and 2, here Dried-AMR), they are supposed to correspond to the nitrogen released respectively from the light and heavy volatiles (denoted herein as LV-N (left) and HV-N (right) in the lower-side plot of Fig. 7). Based on the deconvolution approach, comparing the different cases varying with the fuel type and combustion mode will allow the identification of what type of nitrogen is dominant in forming NO or in realizing the NO reduction. From the upper-side plots for coal in Fig. 7, it can be seen that the integrated areas of the left and right deconvolution curves are equivalent, indicating that both volatile-N and char-N are important to the NO emission of coal combustion, as has been verified by many studies [26, 27]. With regard to the lower plots for Dried-AMR, the area of left curve is much smaller than that of the right curve, indicating that the overall NO emission should be mainly from the HV-N. In other words, this means that the converted HV-N is much more than the converted LV-N, although a further justification is needed.

Fig. 8 compares the time-series NO concentration and its deconvolution fitting for combusting both Dried-AMR and HTT-AMR in CC and ASC modes at 1273 K. Surprisingly, we found from Fig. 8 that the experimental time-series NO concentration curve exhibited two obvious peaks for the fuel HTT-AMR (Fig. 8(b)) and the ASC mode (Fig. 8(c), 8(d)). This actually further confirmed that there should be two types

of volatile nitrogen for the AMR-based fuels. Figure 8 also shows that, for all the cases, the right deconvolution curve have a much bigger area than the left deconvolution curve, verifying that the NO formation of AMR-based fuels should be mainly due to the conversion of the HV-N. Based on the curve heights and widths (flue gas flow rate being basically equal), it can be easily indicated that the curves in the second row for ASC mode corresponded to lower NO emissions than the first row for CC mode, whilst Fig. 8 (b) implies also the lower NO emission for HTT-AMR than Fig. 8 (a) does for Dried-AMR. These indications just comply with the results clarified from Figs. 4 to 6 in terms of the actually measured NO emission and fuel-N conversion. Consequently, it is quite reasonable to use the areas of deconvoluted curves to analyze the relative contribution of each kind of nitrogen.

Table 2 summarizes the integrated areas (equivalent to the NO emission) of all deconvoluted curves in Fig. 8 and the estimated variation ratio of HV-N to LV-N in curve area, to analyze the relative NO reduction caused by HTT or ASC. The ratio of HV-N to LV-N shows that the NO emission contributed from HV-N is ca. 1.8 - 8.4 times that from LV-N, where it is 8.4 for CC of HTT-AMR and 1.8 for ASC of Dried-AMR. For the same combustion mode the HTT-AMR has the higher ratio of HV-N to LV-N than Dried-AMR does (that is, for CC 8.4 with HTT-AMR > 3.6 with Dried-AMR, for ASC 4.0 with HTT-AMR > 1.8 with Dried-AMR), while for the same fuel the ASC mode has the lower ratio than CC does (that is, for Dried-AMR 1.8 with ASC < 3.6 with CC, for HTT-AMR 4.0 with ASC < 8.4 with CC). Comparing the reduction in NO emission from Dried-AMR with that from HTT-AMR for the same

modes (CC or ASC) further reveals that the relative decrease in NO emission (also area in Fig. 8) for LV-N (56-60%) is much higher than for HV-N (2-8%) (see Table 2). Actually, the absolute decrease in area of LV-N is also higher (over 10000 for LV-N against 1000-5000 for HV-N) (refer to Table 2 again). As a result, the dominant reason for the reduction in NO emission caused by HTT is that HTT decreased NO formation from LV-N. This shows plausibly that HTT removed mainly LV-N which is easier to be removed than HV-N. Consequently, the NO emission from HTT-AMR was more dependent with HV-N, especially for CC having no potential for NO reduction. As given in Table 2, comparison of the CC with ASC modes for a given fuel clarifies that the HV-N dominates the relative (54-57%) and absolute (30000) decrease in the curve area. Therefore, the reduction in NO emission due to adopting ASC is dominantly due to the decreased conversion of HV-N into NO, accounting for above 90% of total NO reduction for HTT-AMR (53.8% vs. 57%). It is worthy to note that when ASC was adopted for combusting Dried-AMR, the reduction in NO emission (56.0%) from the HV-N surpassed the total NO reduction (53.6%). These paradox results implied that ASC tended to exhibit a positive effect on reducing NO from HV-N rather than on reducing NO from LV-N. Further, slow release of volatile nitrogen probably facilitated the performance of ASC in term of NO reduction.

3.4. Effects of HTT on NO emission

As our previous studies clarified [8], the nitrogen in AMR mainly consist of protein and amino acid. The HTT can hydrolyze these solid substances into liquid phase. Consequently, some part of nitrogen could be removed by HTT, which is

consistent with the above inference that HTT removed certain nitrogenous components from AMR via hydrolysis (see Table 1). As a result, the HTT itself has a potential to reduce the NO emission from combusting HTT-AMR (Figs. 4 to 6). The above analyses also show that there are two types of volatile nitrogen in AMR- light volatile N (LV-N) and heavy volatile N (HV-N). The removed nitrogen via HTT should be mainly LV-N (Table 2). Herein, to insight into the effect of HTT on the migration of various nitrogen species existing in the fuels, all fuels are tested with XPS and their XPS spectra compared; and further the NH_3 amount released in fuel pyrolysis is measured to clarify how the release of the volatile nitrogen was affected by HTT and how HTT was combined with combustion for NO reduction.

Fig. 9 shows the XPS spectra of all tested fuels, and the dash-line plots are the deconvoluted curves representing different types of nitrogen species. Literatures have reported that, in coal, some specific heteroaromatic rings are the main nitrogenous functionalities with the pyridine, pyrrole and quaternary-N as the representative ones [23, 33]. The three deconvoluted curves of coal XPS spectra In Fig. 9 are just at binding energies (BEs) of 398.7 eV for pyridine-N, 400.1 eV for pyrrole-N and 401.1 eV for quaternary-N. This, on one hand ratifies the approach, and on the other hand, provides a comparison with the deconvolution for the tested AMR-based fuels. For the latter, two fitting curves are obtained at BEs of 399.8 eV and 401.5 eV to respectively represent the N-C bond in amide or amine and N-H bonds in ammonia or protonated amine [22, 34]. A slight difference in BEs for such two curves from those reported in the previous study [24] could be attributed to the different natures of fuels

from AMR and sewage sludge.

Comparing the XPS spectra of Dried-AMR and HTT-AMR in Fig. 9, one can see that HTT of AMR dramatically weakened the deconvoluted curve at BE of 401.5 eV representing amino acid or ammonia, while it correspondingly increased the intensity of amide or amine. This decrease in amino acid or ammonia is presumed to accord with the removal of some related volatile matters, thus justifying the above analysis that the NO reduction by HTT mainly resulted from the lowered LV-N content of HTT-AMR.

Fig. 10 shows that the amount of released NH_3 (mg/g) and its corresponding conversion against the total fuel nitrogen measured in pyrolysis of the tested fuels at 1273 K. Distinctly, the released NH_3 amount is different for the three fuels by following an order of Dried-AMR $\gg$ HTT-AMR $\gg$ coal. The conversion ratio of fuel-N into NH_3 was not that different for all the fuels, but it was only 13% for HTT-AMR, compared to about 20% for both Dried-AMR and coal. Meanwhile considering the preceding XPS spectra, it can be reasonably deduced that the higher content of amino acid or/and ammonia in Dried-AMR lead to the release of more NH_3 during pyrolysis. The removal of these nitrogenous species via HTT [8], thus lowered NH_3 release as well as the lower conversion of fuel-N into NH_3 from HTT-AMR. The lowered NH_3 release naturally caused the worse capability of the volatile product from HTT-AMR to reduce NO. This thus contributes more or less to the higher fuel-N conversion into NO clarified in Figs. 3 and 4 when compared with the burning of Dried-AMR.

4. Conclusions

The NO emission characteristics of the combustion of antibiotic mycelial residue (AMR) before or after hydrothermal treatment (HTT) were investigated by employ a batch-type fixed bed reactor. Analyses of the fuel nitrogen functionalities and deconvoluting the NO emission curves clarified the mechanism on how HTT and combustion mode affected the NO emission. Compared to combustion of directly dried AMR (Dried-AMR), the NO emission of hydrothermally treated AMR (HTT-AMR) was 20~30% lower. This HTT-induced reduction in NO emission mainly resulted from the removal of amino acid or/and ammonia form of nitrogen that exist in the light volatile matters (LV-N) of AMR. Through burning HTT-AMR in air-staged combustion (ASC), it was found that the reduction in NO emission, in comparison with the conventional combustion (CC), increased with raising the combustion temperature, and reached about 45% at 1273K. Deconvoluting the time-series NO emission curves revealed that ASC reduced NO emission mainly by suppressing NO formation from the nitrogen existing in the heavy volatile (HV-N). In comparison with CC of Dried-AMR, it was found that, via ASC of HTT-AMR, the reduction in NO emission increased from 40 to 57% with raising the combustion temperature from 1073 to 1273 K. HTT and ASC exhibited an integrated effect on reducing NO emission. Consequently, combination of HTT with ASC provides an effective way to control NO emission when recovering biomass with high contents of moisture and nitrogen into energy.

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Table 1 Properties from proximate and ultimate analyses of tested fuels.

Fuel sample	Proximate analysis (wt.%, dry)				HHV (MJ/kg)	Ultimate analysis (wt.%, daf)				
	M	Ash	VM	FC		C	H	S	N	O
Dried-AMR	5.8	8.4	91.6	0	19.3	43.5	6.7	0.8	7.7	41.3
HTT-AMR	2.4	14.8	85.2	0	24.6	53.3	6.6	0.9	5.8	33.4
Coal	1.9	15.1	37.3	47.6	22.7	75.3	4.2	0.7	1.1	18.7

Table 2 Deconvoluted information for NO emission curves of Fig.8.

Fuel and combustion mode	Emission or curve area		Ratio of HV-N to LV-N	Reduction by HTT (%) ^a		Reduction by ASC (%) ^b	
	LV-N	HV-N		LV-N	HV-N	LV-N	HV-N
Dried-AMR by CC	18748	68191	3.64				
HTT-AMR by CC	7532	63137	8.38	59.8	7.4		
Dried-AMR by ASC	16569	30014	1.81			11.6	56.0
HTT-AMR by ASC	7270	29174	4.01	56.1	2.8	3.5	53.8

a: Against the case of Dried-AMR for the same combustion mode.

b: Against the case of CC mode for the same fuel.

Figure 1. Pyrolysis tests in TGA under Ar atmosphere for the tested solid fuels.

Figure 2. Combustion tests in TGA and Ar+O₂ atmosphere of all solid fuels.

Figure 3 A schematic diagram of the fixed bed combustor.

Figure 4. NO emission and fuel-N conversion in burning fuels via CC mode at various temperatures.

Figure 5. NO emission and fuel-N conversion in burning AMR-based fuels via ACS mode.

Figure 6. Percentage of NO reduction by HTT or/and ASC.

Figure 7. Time-series NO concentration and its curve deconvolution for burning coal and Dried-AMR at 1273 K.

Figure 8. Time-series NO concentration and its curve deconvolution for burning Dried-AMR and HTT-AMR via both CC and ASC modes at 1273 K.

Figure 9. Spectra of XPS for N 1s of all tested fuels

Figure 10. Ammonia released in pyrolysis of the tested fuels and its corresponding conversion against total fuel-N.