Releases of NO and its precursors from coal combustion in a fixed bed

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Abstract

Experiments have been carried out to investigate the emissions of nitrogen species including NO and its precursors during temperature-programmed coal combustion by TG/EGA method. Experimental results show that the conversion ratio of fuel nitrogen to NO is the highest, followed by that of fuel nitrogen to HCN and the conversion ratio to NH₃ is negligibly small. Nitrogen is retained in the char and released mainly as NO at the later stages of coal combustion. HCN and NO are both primary products from coal char oxidation. Coal rank, heating rate, indigenous minerals and external additives are the major influential factors of the nitrogen species release. Higher rank coals with higher fuel ratio have higher NO releases. HCN release decreases as fuel ratio increases for most coals. The fuel nitrogen conversion to NO increases and the fuel nitrogen conversion to HCN decreases with the increase of heating rate, which may imply that the char nitrogen prefers to react with oxygen to form NO instead of HCN while coal char is combusted at higher temperatures. Different metallic additives show different effects on nitrogen species emission and the effects of indigenous minerals on nitrogen release can be qualitatively estimated by ash analyses.

Keywords: Nitrogen release; TG/EGA; Coal rank; Heating rate; Metallic additive; Mineral

1. Introduction

NOₓ can cause serious environmental problems such as acid rain and photochemical fog. If no further controls were taken, NOₓ emissions would increase by 350% during the period of 1990–2020 in Asia [1]. The combustion of fossil fuel such as coal in industry is a major source of NOₓ emission. Conceivably, the comprehensive understanding of the evolution mechanism of nitrogen species during coal combustion would be of great help to minimize the emission of NOₓ.

As well known to all, NOₓ is formed during coal combustion by three distinct mechanisms: thermal NOₓ, prompt NOₓ and fuel NOₓ, of which fuel NOₓ is the most significant [2]. It has been generally accepted that nitrogen mainly exists in the heterocyclic ring structures of coal, and that there are several forms of fuel-type nitrogen species in coal, including pyridinic-N, pyrrolic-N and quaternary-N, among which the pyrrolic-N may be the predominant one. Some investigators found that there is a relationship between NOₓ and nitrogen functionalities in coal and put forward an equation between them [3]. On the contrary, many investigators argue that the distribution of nitrogen in char does not exert any significant influence on the formation of nitrogen oxides during the char combustion [4,5].

TG-MS has been widely used to investigate nitrogen release from coals, chars and model compounds during combustion process [5–16]. Generally, the coal nitrogen is distributed between the volatiles and the solid char matrix during the initial stage of coal combustion, and the resulting char-N and volatile-N undergo different oxidation mechanisms to form nitrogen oxides during the subsequent combustion [2,17–19]. NO can also be reduced by the char. Therefore, the final emission of NO is governed by the balance of NO-formation and NO-reduction reactions. However, some contributions from light hydrocarbons to m/z signals of nitrogen containing species ions cannot be excluded because most of the m/z signals can be assigned to more than one fragmented ion.

It has been known that the minerals in coal have catalytic effects on coal gasification [20]. The indigenous minerals in coal or external metallic additives may also affect the nitrogen release during coal combustion. Therefore, it is necessary to clarify the effects of minerals on nitrogen evolution during coal combustion.
In this paper, the evolution of gaseous species during coal devolatilization is monitored and measured by using TG coupled with evolved gas analysis (EGA) during temperature-programmed combustion. The influential factors including coal rank, heating rate, indigenous minerals and external additives have been examined. The results will be helpful to elucidate the nitrogen release mechanism during coal combustion.

2. Experimental

2.1. Sample preparation

Seven coals ranging from high volatile bituminous to high rank anthracite are selected for present study. Coal samples are air-dried, ground, and sieved to size <280 μm.

The ultimate and proximate analyses of coals are listed in Table 1. The elements in the coal are measured with PE2400-II elemental analyzer. In order to investigate the effects of indigenous minerals on the nitrogen release, SM and YB coal are demineralized by HCl and HF leaching and dried at 50 °C. The ash analyses of SM and YB are listed in Table 2 and the ultimate and proximate analyses of demineralized coal. The ash analyses of SM and YB are listed in Table 1. The elements in the coal are measured with PE2400-II elemental analyzer. In order to investigate the effects of indigenous minerals on the nitrogen release, SM and YB coal are demineralized by HCl and HF leaching and dried at 50 °C. The prefix ‘D’ is added to the code name to denote the demineralized coal. The ash analyses of SM and YB are listed in Table 2 and the ultimate and proximate analyses of demineralized coal samples are listed in Table 3.

Three types of metallic compounds are added to the parent SM coal. The additives used are NaCl, CaCO3, and Fe(C5H5)2, which are dried and ground into fine particles less than 40 μm in advance. Each additive is mixed directly with the SM coal which are dried and ground into fine particles less than 40 μm, then mixed well, dried at 105 °C and load rate is 5% by weight. Each mixture (sample) is stirred well, dried at 105 °C and kept airproof in a glass container overnight at room temperature before being combusted.

2.2. Temperature-programmed combustion and evolved gas analysis

Thermogravimetry coupled with EGA is used in the experiments, as shown in Fig. 1. About 20 mg of coal sample is loaded into an alumina container, which is then placed on the NETZSCH STA 409 PC Luxx thermobalance. All the experiments are carried out at a constant heating rate of 10 or 20 °C/min with a temperature range of 20–1000 °C at a 20% O2–He gas flow rate of 100 ml/min.

Different from TG-MS, the EGA is performed by the following method. An on-line flue gas analyzer is used to monitor the released gases, including NO, NO2 and CO, at the gas exit of the thermobalance continuously at 10-s intervals. NO2 cannot be detected in present experiment. The errors of NO, NO2 and CO measurements determined by repeated runs are within ±5%.

NH3 and HCN evolutions are measured during the whole course of combustion in present investigation as follows. The product gases pass through a pair of bubblers containing an absorption solution for the collection of NH3 or HCN separately at preset temperature (time) intervals. The HCN and NH3 release rates are averaged values in each interval. NH3 is collected in bubblers containing 0.005 M H2SO4 solution. HCN is collected in a separate experiment in bubblers containing an aqueous solution of 0.1 M NaOH. Prior experiments with more bubblers in series containing the same solutions confirm that NH3 or HCN collected in extra bubblers are negligible.

HCN and NH3 absorbed in the solutions are quantified with a UV-754N spectrophotometer. HCN is quantified with isonicotinic acid–pyrazolone spectrophotometry at 638 nm [21]. The calibration of CN– is performed with standard solutions purchased from Fluka Company. The quantification of NH3 is carried out with spectrophotometric method with salicylic acid at 697 nm [22].

3. Results and discussions

3.1. Profiles of nitrogen release rate

In Fig. 2, the data of NO, HCN, NH3 and CO emissions and X (coal conversion ratio) versus temperature from the parent SM coal show the activity distinctions between coal nitrogen and carbon. CO is the dominant product among these species and there is a peak at 478 °C, corresponding to the temperature at which coal char is burnt severely. The curve for NO has a single peak with a small plateau in the range of 554–574 °C, and remarkable NO cannot be detected until the temperature is over 448 °C, which indicates that nitrogen in coal is more difficult to be released than carbon in coal.

Different from NO, HCN can be detected at the temperature as low as 300 °C, and HCN evolution stops at the temperature at which NO evolution starts, which suggests that HCN be formed in the in situ char combustion process as well as in the
devolatilize process. Nevertheless, less NH$_3$ is released, compared to HCN and NO. In the literature [7] significant amounts of HCN (10–15%) were also detected during gasification for some of the coals. However, in the literature [23], an indirect evidence proved that HCN is not released during char oxidation since the time for devolatilization does not affect the amount of the char-bound nitrogen converted to NO or N$_2$O. The difference in experimental method may cause the difference between the conclusions in the literatures and in this investigation.

Approximately combustion occurs below 650 °C in this investigation. According to Wargadalam et al. [24], the NO$_x$ precursors can be directly released because they do not react with O$_2$ or NO in such a combustion temperature range. HCN is a primary product formed via heterogeneous oxidation and not via slow or secondary devolatilization [25].

As can be seen in Fig. 2, NO is released mainly in the later stage of combustion, which implies that nitrogen in coal may be retained in the partially oxidized coal char and released at the very late stage of char combustion, which can be confirmed by direct measurement of the nitrogen yield of partially combusted parent SM char samples at different temperatures, as shown in Fig. 3.

Differential curve of char-N yield is also presented in Fig. 3. Char-N starts to release considerably at about 450 °C, and above 600 °C, nitrogen is nearly completely released, which means that nitrogen cannot be retained in the minerals after the coal is burnt off and all the nitrogen in coal is released into flue gas. By comparing Figs. 2 and 3, it can be seen that when char-N release rate reaches its maximum, the corresponding temperature is close to NO peak temperature. Therefore, nitrogen in coal char is the main source of NO, and the NO is the primary product of char nitrogen oxidation [5,11,15,26,27] as in Eq. (1).

$$C(N) + O_2 \rightarrow NO + C(O)$$  \hspace{1cm} (1)
where C(N) and C(O) denote nitrogen and oxygen species, respectively, on the char surface.

The NO formed may subsequently be readsorbed on the char surface by a dissociative chemisorption to produce C(N) as in Eq. (2), then reacts with another NO to produce $N_2$ as in Eq. (3) [26,28].

\[
\text{NO} + 2C \rightarrow \text{C(N)} + \text{C(O)} \quad (2)
\]

\[
\text{C(N)} + \text{NO} \rightarrow \text{N}_2 + \text{C(O)} \quad (3)
\]

As mentioned in the Introduction, the amount of nitric oxide detected during combustion is a balance between its production and reduction in present experiment.

The low-temperature oxidation conditions employed in this work reveal another interesting feature in Fig. 3, namely, nitrogen is preferentially retained in the char as the carbon is oxidized. It can be explained as follows: as the remaining char is consumed, NO escapes from the bed without being converted to $N_2$.

### 3.2. Effect of coal rank on nitrogen release

Fig. 4 gives the profiles of NO and HCN emissions of different rank coals. Because of the low emission of $NH_3$, the profiles of $NH_3$ release are not presented. NO and HCN release profiles change greatly with the coal rank. As can be seen in Fig. 4, the peak temperatures of NO release profiles are in the following order: $FS < HL < SM < PDS < TC < YB < JZ$, while the peak temperatures of HCN are in the following order: $FS < HL < SM < PDS < TC < YB < JZ$. Because reactivity of coal decreases as the coal rank increases, the ignition point of the coal and peak temperature of nitrogen release increases with the coal rank.

Gaseous evolutions during the temperature-programmed combustion are integrated. The conversion $X$ is the ratio of nitrogen converted to each nitrogen species to the nitrogen contained in the coal during the combustion process:

\[
X_{\text{NO}} = \frac{m_{\text{NO}} \times 14/30}{m_{\text{Fuel-N}}} \times 100(\%)
\]

\[
X_{\text{HCN}} = \frac{m_{\text{HCN}} \times 14/27}{m_{\text{Fuel-N}}} \times 100(\%)
\]

\[
X_{\text{NH}_3} = \frac{m_{\text{NH}_3} \times 14/17}{m_{\text{Fuel-N}}} \times 100(\%)
\]

Fig. 5 shows the effect of coal rank on conversion of fuel nitrogen to NO, HCN and $NH_3$. Clearly, NO emission increases with the increase of fuel ratio (FC/VM). For most part, HCN decreases as fuel ratio increases, but for the JZ coal with very high fuel ratio, HCN can be quite high, as an exception. HCN can be scarcely released at low temperatures during pyrolysis.
runs for anthracites such as YB and JZ coals. Nevertheless, as shown in Fig. 5, HCN can be detected for YB coal, and a relative large amount of HCN is formed as well as NO for high rank JZ coal during temperature-programmed combustion. It may be concluded that heterocyclic nitrogen in coal matrix becomes unstable because of the O2 attack. Two reasons were given in the study by Orikasa and Tomita [29]. One reason is that the C(N) surface species is activated due to the O2 attack on the char skeleton. The other for the formation of HCN at lower temperatures would be that more active hydrogen species are available during the char oxidation reaction, more hydrogen radicals and/or activated surface species on the char are essential for HCN formation. In addition, the oxidation of coal at low temperatures may lead to the formation of HCN as well as NH3 due to the enhanced formation of (H) radicals [30].

3.3. Effect of heating rate on nitrogen release

To investigate the effect of heating rate on nitrogen release, three coals were combusted at 10 and 20 °C/min, respectively. Fig. 6 shows the NO and HCN release profiles at two heating rates for parent SM coal. Obviously, the peak values of NO and HCN emissions become higher and lower, respectively, and the corresponding peak temperatures shift to higher values, as the heating rate increases. The reason for this may be that ignition point and the maximum combustion rate increase as the heating rate increases.

Data in Table 4 show that nitrogen conversion to NO is enhanced after the heating rate increases from 10 to 20 °C/min. On the contrary, fuel nitrogen conversion to HCN is decreased, while the conversion to NH3 does not change much. This
finding seems to show that the char nitrogen prefers to react with oxygen to form the primary product NO when coal char is combusted at a higher temperature. On the contrary, HCN release decreases at higher heating rates.

3.4. Effects of additives on nitrogen release

Some metal additives can reduce char-N release and increase N\textsubscript{2} emission during coal pyrolysis process [31–33]. The influence of the metal additives on nitrogen release during combustion process is studied in this paper. The effects of metal additives on NO and HCN release profiles are illustrated in Fig. 7. Obviously, with the addition of metal additives into the parent SM coal, the peak temperatures of NO profiles shift to lower temperatures due to the catalysis of metal additives on the activity of coal. For ferrocene-added SM coal, the initial NO release temperature of NO profile shifts to a lower temperature, but the end temperature of NO emission does not change much, which indicates that ferrocene may promote the NO release in the initial stage of char combustion. HCN release profile is changed significantly in the presence of ferrocene. In detail, there is a shoulder at about 400°C, which suggests that ferrocene catalyze the macromolecule cleavage at low temperatures to release more HCN. Compared to the effect of ferrocene, CaCO\textsubscript{3} and NaCl show slight effects on NO and HCN release profiles. CaCO\textsubscript{3} can increase the peak values of both NO and HCN, while NaCl can decrease the peak values of both NO and HCN greatly.

Fig. 8 gives the effects of additives on nitrogen conversions to NO, HCN and NH\textsubscript{3}. Obviously, the total conversions of nitrogen to NO, HCN and NH\textsubscript{3} decrease in the presence of NaCl, but increase in the presence of CaCO\textsubscript{3} or ferrocene. With the NaCl addition, fuel nitrogen conversions to NO, HCN and NH\textsubscript{3} decrease from 20.8%, 14.5% and 1.59% to 17.8%, 13.0% and 1.3%, respectively. The addition of CaCO\textsubscript{3} into parent SM coal increases the conversions to NO and HCN to 23.6% and 18.7%, but reduces the conversion to NH\textsubscript{3} to 1.08%. Similar to the effect of CaCO\textsubscript{3}, the addition of ferrocene into parent SM coal increases NO and HCN to 24.4% and 22.4%, but decreased NH\textsubscript{3} to 0.91%. This observation implies that NO and HCN be suppressed by the catalytic reaction of Na, and be promoted by the catalytic reaction of Fe and Ca.

The final effect of an additive on nitrogen species emission depends on the competition between the catalytic effect on char-N oxidation and the catalytic effect on NO-char reaction during the combustion. As described above, sodium chloride can decrease three nitrogen species in coal combustion. Therefore, the catalysis of sodium on NO reduction may be dominant over the catalysis of sodium on fuel-N oxidation.

The present research shows that Fe addition can give rise to an increase of NO emission, which is consistent with the report by Zhu et al. [26]. It has been elucidated by Illan-Gomez et al. [34] that the presence of iron particles on the carbon surface can catalyze the reduction of NO. Therefore, it can be concluded that iron catalyzes the fuel-N oxidation more effectively than it catalyzes NO–char reaction. Based on the oxygen-transfer mechanism, Zhu et al. [26] proposed that iron catalyst enriches the concentration of oxygen surface species on the carbon surface, especially in the vicinity of catalyst.
particles during combustion. This higher concentration of oxygen surface complex on the carbon surface may promote the fuel-N oxidation. Ca may play the same role as Fe in the nitrogen release process.

### 3.5. Effect of demineralization on nitrogen release

Fig. 9 shows the influence of demineralization on NO and HCN profiles of NO emission during the combustion of SM and YB coals under temperature-programmed heating conditions. It can be seen that the NO and HCN emission behaviors of parent coal chars are significantly different from those of their corresponding deashed coal chars. In general, the NO evolution of the DSM sample starts and ends at the same temperatures as that of parent SM coal, while NO evolution of the DYB sample starts and ends at lower temperatures compared to that of parent YB coal. When HCl/HF treatments are performed, the peak value of NO becomes higher for bituminous coal, while the peak value of NO emission becomes lower and the corresponding peak temperature shifts to a lower value for high rank coals. Fig. 9 also shows the HCN evolution profiles of the examined coal samples. Obviously, the HCN peak value of demineralized coals is higher than that of parent coal, which suggests that nitrogen should be liable to be released as HCN after coal is demineralized.

Table 5 gives the influence of demineralization on nitrogen conversion for SM and YB coals. It can be seen that after demineralization, fuel conversion to NO increases for SM coal, but decreases for YB coal, which indicates that the indigenous minerals in these two coals have different effects on NO formation, which may be induced by the catalytic effect of different metals present in coal minerals. The Na/Fe (molar ratio) in the minerals of SM is much larger than that of YB. Because of the influence of additives on NO formation discussed above, the catalytic effect of Fe on NO formation should be greater than that of Na for YB. Therefore, after demineralization, conversion to NO is reduced and a reverse change happens for SM coal.

On the other hand, the conversion to HCN increases after demineralization regardless of coal rank. The reason for this may be that the removal of clay minerals in the raw coal after HCl/HF treatment will cause the coal to be more porous and lead to the enhancement of the mass and/or heat transport and the catalysis of metal components is suppressed. This hypothesis needs to be verified by further work.

### 4. Conclusions

The releases of the nitrogen species including NO, HCN and NH₃ from the temperature-programmed combustion of coal have been investigated, the influential factors such as coal rank, heating rates, metal additives and demineralization,
have been examined using TG/EGA method, and the following conclusions can be drawn:

1. The conversion ratio of coal nitrogen to NO is the highest, followed by that of HCN, and the conversion ratio to NH₃ is the lowest. During the combustion process, nitrogen tends to be retained in the char at the initial stages and released mainly as NO at the later stages of coal combustion. HCN and NO are both primary products from coal char oxidation.

2. The fuel conversion to NO is related to coal rank, higher rank coals with higher fuel ratio have more release of NO, while HCN exhibits a different trend. For most part, HCN decreases as fuel ratio increases, but for the coal with very high fuel ratio, HCN can be quite high, as an exception.

3. The fuel conversion to NO increases and conversion to HCN decreases with the increase of heating rate. This observation indicates that the char nitrogen prefers to react with oxygen to form NO instead of HCN when coal char was combusted at higher temperatures.

4. Different metallic additives show different effects on nitrogen species emission. The effects of indigenous minerals on nitrogen release can be qualitatively estimated via ash analyses, although some interactions among metal composites in fuel may exist. The minerals with high content of Na or sodium additive can suppress the nitrogen species release. Nevertheless, Fe and Ca in minerals or corresponding additives can induce an increase of nitrogen species.

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