Effect of Mixed Fe/Ca Additives on Nitrogen Transformation during Protein and Amino Acid Pyrolysis

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ABSTRACT: Considerable amounts of NOx are generated from the thermal utilization of solid wastes. To control NOx emission, we investigated the influence of mixed Fe/Ca additives on the formation of NOx precursors (HCN and NH3) during pyrolysis at 873, 1073, and 1273 K. Protein, proline, and phenylalanine were selected as model compounds to represent the primary nitrogen forms in typical solid wastes, as biomass and sludge. According to the results, the iron effect is a remarkable property that enables the obvious reduction of NH3. This was most likely because NH3 was consumed by iron compounds to generate FeN. Iron compounds facilitated thermal cracking of heterocyclic N with the release of HCN. Ca(OH)2 promoted the conversion of HCN to NH3 and fixed HCN to form CaC2N5 simultaneously. These intermediates (FeN3 and CaC2N5) play important roles in the reduction of NOx precursors. A lower emission of NOx precursors was observed with mixed Fe/Ca additives than with either Fe or Ca individually. This is because the generation of CaFe2O5 enhanced the transformation of intermediates to N2. The transformation of intermediates to N2 was enhanced at elevated temperatures, which allows for the lowest emission of precursors (NH3 and HCN) at 1273 K with a higher ratio of CaFe2O5 in char.

1. INTRODUCTION

Recently, thermal utilization has become a promising treatment and disposal technology for solid wastes, owing to the valuable products generated.1 However, it should be noted that large amounts of NOx emitted from this process, originating from the high nitrogen content in solid wastes, cause acid rain and photochemical smog.2−4 The content of nitrogen in sludge is as high as 6−9%,5,6 and the nitrogen content in agricultural residues and aquatic plants is as high as 3−7%.7−9 Moreover, several studies10−12 have shown that fuel N is the main source of NOx, especially during the combustion of N-rich solid wastes, such as biomass and sludge. Studies have shown that the N species in solid wastes mainly exist as organic N in protein and amino acids.5,9,11,12

It is well-accepted that fast pyrolysis plays a crucial role in the formation of NOx,13−15 HCN and NH3 are the main NOx precursors formed during pyrolysis for biomass.10,16,17 However, owing to the diversity and complex compositions of solid wastes, it is hard to achieve a deeper understanding of the release of NOx precursors from different kinds of solid wastes.15,18−20

Furthermore, nitrogen conversion varies with different nitrogen species in solid wastes during pyrolysis.21,22 The decomposition of protein N and amine N compounds occurs easily at lower temperatures, whereas the thermal cracking of nitrile N and heterocyclic N compounds was observed at higher temperatures, ranging from 773 to 1073 K.2 The contents of NH3 and HCN generated during the thermal cracking of these N species were also different from each other.23−26 The variety and interactions of amino acids influence HCN and NH3 yields during pyrolysis to varying degrees.25,27 Consequently, the release of NOx precursors is associated with the thermal decomposition of nitrogen bound to protein and amino acids.28−30

To minimize the emission of NOx precursors, some minerals, such as calcium salts and iron salts, were applied during pyrolysis.3,28 The total amount of NH3 and HCN decreased from 105 to 55 μmol/g at 1173 K with the presence of metallic iron.29 Ca(OH)2 additives also suppressed NH3 and HCN emissions from 627 to 873 K.30 It was further indicated that the addition of iron and calcium compounds could significantly improve the conversion of biomass N to N2 (from 8 to 31%) and decrease the amount of char N from 18 to 4%.30 According to our previous study,31−33 the inhibition of sludge N to NOx precursor conversion via synergistic catalysis of Fenton−CaO was more effective than that of single Fenton or CaO catalyst. Owing to the complexity of solid waste compositions, there is thereby an urgent need but still a significant challenge to evaluate the effects of mixed Fe/Ca additives on nitrogen evolution during pyrolysis.

To gain more insight, many researchers34,35 have used pyridine N and pyrrole N compounds as coal N models to study the transformation during pyrolysis. This method simplifies chemical components and nitrogen functionalities, which helps to pinpoint the reactivity of different nitrogen functionalities. As mentioned above, N-containing compounds in typical solid wastes largely exist as protein and amino acids. Therefore, three highly representative model compounds (protein, proline, and phenylalanine) were used in this study to gain a better understanding of the mechanism of nitrogen conversion with mixed Fe/Ca additives during pyrolysis.

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Table 1. Characteristics of Model Amino Acids and Protein

<table>
<thead>
<tr>
<th>Samples</th>
<th>Purity</th>
<th>Molecular Formula</th>
<th>Structural Formula</th>
</tr>
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<tbody>
<tr>
<td>Proline</td>
<td>99%</td>
<td>C$_3$H$_2$NO</td>
<td></td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>99%</td>
<td>C$<em>3$H$</em>{11}$NO$_2$</td>
<td></td>
</tr>
<tr>
<td>Protein (BSA)</td>
<td>96%, low salt</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

2. EXPERIMENTAL SECTION

2.1. Materials. On the basis of several representative structures of the amino acids (amine N and heterocyclic N) and protein (protein N) in solid wastes, three samples (phenylalanine, proline, and protein) were chosen as N-containing model compounds in this study. Characteristics of these three compounds are shown in Table 1.

2.2. Additive Preparation. Iron and calcium mainly exist as ferric salt and Ca(OH)$_2$ in solid wastes. Several studies have shown that Fe$_2$(SO$_4$)$_3$ and Ca(OH)$_2$ are known to be inexpensive and widely available and have advantageous catalytic properties. Fe$_2$(SO$_4$)$_3$ (99.95%, metal basis, Aladdin) and Ca(OH)$_2$ (≥95%, ACS grade, Aladdin) were used as additives. To elucidate the complete reaction with minerals, the additives were thoroughly and physically mixed with sample (mass ratio = 1:1 or 1:1:1). The amount of raw sample was 0.3 g. The samples were labeled as RS, S–Fe$_2$(SO$_4$)$_3$, S–Ca(OH)$_2$, and S–Fe$_2$(SO$_4$)$_3$–Ca(OH)$_2$, where S denotes the three different samples.

2.3. Catalytic Pyrolysis. Pyrolysis was performed on a quartz fixed-bed reactor and electric furnace at 873, 1073, and 1273 K. The system temperature was monitored using a thermocouple. Argon (purity of 99.999%) was the carrier gas and was supplied into the reactor at 100 mL min$^{-1}$. Bubbling solutions (0.2 mol L$^{-1}$ NaOH and 0.1 mol L$^{-1}$ H$_2$SO$_4$) were used to absorb HCN and NH$_3$, and helical condenser pipes were used as tar traps (ice–water bath). The apparatus is illustrated in Figure 1. The system was heated to the desired temperature. To ensure an inert atmosphere, a 2 min equilibration time was implemented to remove air after placing the quartz boat in the water condenser and filling in the plug. Then, the quartz boat was pushed into the reactor. After a 10 min reaction time, the quartz boat was pushed back into the water condenser for 10 min in an inert atmosphere to adequately collect NH$_3$ and HCN. To collect tar as accurately as possible, liquid nitrogen was used as a coolant instead of ice.

2.4. Product Analysis. When the quartz boat, containing residues of samples, was cooled to room temperature, the char, solutions, and tar were collected. The solutions that absorbed HCN and NH$_3$ were analyzed by an ion chromatograph (IC-2010, TOSOH) equipped with an electrochemical detector (896 Professional Detector, Metrohm) to determine the amount of NH$_4^+$ and CN$^-$ present. Gas chromatography–mass spectrometry (GC–MS) analysis of pyrolysis tar was conducted by Agilent 7890 A/5975 C. This method can provide nitrogen distributions and species in tar. X-ray diffraction (XRD) was used to investigate the forms of Fe and Ca in char and N-containing compounds in the residues produced from pyrolysis.

The conversion ratio of NO$_x$ precursors (HCN and NH$_3$) during pyrolysis was calculated with the following equation:

$$\text{conversion ratio (N-HCN)} = \frac{M(N-HCN)}{M(N-S)}$$

$$\text{conversion ratio (N-NH}_3\text{)} = \frac{M(N-NH}_3\text{)}{M(N-S)}$$

where M(N-NH$_3$) is the weight of nitrogen in NH$_3$ (g), M(N-HCN) is the weight of nitrogen in HCN (g), and M(N–S) is the weight of nitrogen in samples (s).

3. RESULTS AND DISCUSSION

3.1. Gas Phase. Figures 2 and 3 depict the NH$_3$ and HCN yields during pyrolysis of three representative N-containing compounds at different temperatures. The units of NH$_3$ and HCN produced (mL/g) in Figures 2 and 3 mean the amount of HCN or NH$_3$ produced per gram of material. The results indicate that the species of nitrogen affected nitrogen transformation significantly during pyrolysis. For phenylalanine, NH$_3$ was the main N-containing gas, arising from the deamination and hydrogenation of amine N compounds. The amount of NH$_3$ with free catalysts was similar across different temperatures, indicating that the decomposition of amine N compounds was nearly complete below 873 K. On the contrary, it was not until the temperature reached 1073 K that a certain amount of HCN had been detected when the catalyst is not added. One possible explanation is that heterocyclic or nitrile compounds are more thermally stable.

In the presence of Fe$_2$(SO$_4$)$_3$ additives, the NH$_3$ yield was noticeably reduced, while the amount of HCN became higher, especially at...
1273 K. The reason could be that iron can enhance the secondary thermal cracking of char N and tar N, releasing HCN at higher temperatures. At a high temperature, iron minerals can be converted to metallic iron.\textsuperscript{29} Then, iron metal might further react with NH\textsubscript{3} to form N\textsubscript{2}, as described in eqs 4 and 5.\textsuperscript{35,39} On the contrary, calcium can promote NH\textsubscript{3} formation up to 10.73 mL/g at 873 K and suppress HCN emission. In the presence of both Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} and Ca(OH)\textsubscript{2}, the synergistic effects show the catalytic properties of calcium at lower temperatures. The increase of NH\textsubscript{3} promoted by mixed Ca/Fe additives was more substantial than that of single Ca-based additives. Above 1073 K, the catalytic behavior of iron began to appear, as indicated by the suppression of NH\textsubscript{3}, NH\textsubscript{3} and HCN emissions both decreased at 1073 K, and the conversion ratio of nitrogen in NO\textsubscript{x} precursors (NH\textsubscript{3} and HCN) to total nitrogen in substrate was the lowest at 1273 K (as shown in Figure 4). Therefore, it was deduced that the mixed Ca/Fe additives exhibit better synergistic effects on the reduction of NO\textsubscript{x} precursors for amine N compounds at a higher temperature.

In the proline pyrolysis experiments (Figures 2b and 3b), the emission of NH\textsubscript{3} was unchanged for 10 mL/g at different temperatures and the formation of HCN was negligible at 873 and 1073 K. However, at 1273 K, the formation of HCN rapidly increased from 1.30 to 24.33 mL/g. The difference between proline and phenylalanine indicates that amine N compounds.
Compounds are the main source of NH₃ at lower temperatures. The thermal decomposition of heterocyclic N compounds to form HCN may start at a higher temperature as a result of their stable structures. In the case of single additives, a similar trend was observed for Fe₂(SO₄)₃ and Ca(OH)₂ additives but iron enhanced HCN emission during heterocyclic N compound pyrolysis when compared to amine N compounds. This suggests that iron compounds lowered the deconjugation temperature of heterocyclic N, and subsequently, a significant amount of HCN was released at 873 K. In comparison to phenylalanine pyrolysis, the inhibition effect of calcium was more pronounced for proline pyrolysis. The synergistic effects of Fe₂(SO₄)₃ and Ca(OH)₂ on suppressing the emission of HCN and NH₃ were also observed above 873 K. It was noted that HCN and NH₃ formations were simultaneously reduced at a relatively high temperature (1273 K).

Proteins have a relatively high nitrogen content. As seen from Figures 2c and 3c, the amount of NOₓ precursors was remarkably higher than that of two other non-catalyzed samples. It is should be noted that the release of HCN and NH₃ gases increased from 873 to 1073 K, probably as a result of the secondary thermal cracking of intermediate compounds. Notably, little NH₃ was released under single Fe₂(SO₄)₃ conditions. Iron contributed to a slight reduction in HCN at 873 and 1073 K, whereas HCN increases at 1273 K. Accordingly, Ca(OH)₂ may thermally decompose to form CaO and H₂O, which can also facilitate the evolution of NH₃ by reacting with intermediate CaCₓNᵧ (eqs 1–3). Complete details of the above inference will be discussed further below. Similarly, the removal efficiency of NOₓ precursors (HCN and NH₃) with mixed Fe/Ca additives was the highest at 1073 and 1273 K, as shown in Figure 4.

\[
\text{HCN} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}
\] (1)

\[
\text{CaO} + 2\text{HCN} \rightarrow \text{CaCN}_2 + \text{CO} + \text{H}_2
\] (2)

\[
\text{CaCN}_2 + 2\text{H}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{NH}_3 + 2\text{CO}
\] (3)

\[
\text{CaO} + \text{char} - \text{N} \rightarrow \text{CaC}_x\text{N}_y + \text{CO}
\] (4)

\[
2\text{Fe} + 2\text{NH}_3 \rightarrow 2\text{FeN} + 3\text{H}_2
\] (5)

\[
2\text{Fe}_2\text{N} \rightarrow 2\text{Fe} + \text{N}_2
\] (6)

The proportion of nitrogen from HCN and NH₃ in the sample is shown in Figure 4. It has been discussed that the main NOₓ precursor of protein N and amine N compounds is NH₃, and Fe₂(SO₄)₃ effectively catalyzed the conversion of NH₃ to N₂. Consequently, this might result in the lowest emission of HCN and NH₃, as shown in Figure 4. Thus, for solid wastes containing protein N and amine N, the Fe-containing additives could be more suitable catalysts to control NOₓ precursors at temperatures ranging from 873 to 1073 K. However, iron will cause sintering problems, which were observed during the experiment. The mixed Fe/Ca additives can effectively prevent the sintering of iron during pyrolysis and, at the same time, achieve the highest removal efficiency of HCN and NH₃ at 1273 K.

On the basis of the above results, it can be concluded that calcium can promote NH₃ formation and suppress HCN emission. On the contrary, iron increases the HCN yield and strongly hampers the NH₃ yield. The synergistic effects of mixed Fe/Ca additives enhanced the removal of HCN and NH₃. The effects of Ca-based additives dominated catalysis at a lower temperature, whereas Fe₂(SO₄)₃ played an important role between 1073 and 1273 K. Furthermore, the variation in the NH₃ yield was generally not equal to that of HCN, suggesting that a portion of gas N was generated from tar N and char N. In the following sections, we compare the catalytic effects of the mixed Fe/Ca additives and single additives on tar N and char N in detail. The nitrogen balance during this pyrolysis is within 80–110%, which is acceptable, indicating that the data are valid.

Figure 4. Conversion ratio of nitrogen in NOₓ precursors to total nitrogen: (a) phenylalanine, (b) proline, and (c) protein.
3.2. Solid Phase. To further clarify the effects of minerals on nitrogen transformation. The XRD patterns of different char obtained from pyrolysis at 873, 1073, and 1273 K are shown in Figure 5. It is inferred that nitrogen was almost not integrated with char at 873 K. At 1073 K, the strongest peak identified was CaC$_3$N$_6$ in the XRD patterns of char with a single addition of Ca(OH)$_2$. The typical CaC$_3$N$_6$ phase abruptly vanished at a higher temperature (1273 K) and was replaced by high-intensity Ca(OH)$_2$ peaks. It was found that CaC$_3$N$_6$ was transformed to N$_2$ when the temperature exceeded 973 K.\textsuperscript{40,41} According to the above results, the NH$_3$ and HCN emissions and tar N formation were almost all reduced, indicating that CaC$_3$N$_6$ decomposed into N$_2$ and CaO/Ca(OH)$_2$ above 1073 K.

Furthermore, with the presence of the mixed Fe/Ca additives, it is important to highlight the disappearance of CaC$_3$N$_6$ and iron-containing compounds as well as the generation of Ca$_2$Fe$_2$O$_5$ and CaS. This could be because the strong interactions between Fe and Ca formed stable Ca$_2$Fe$_2$O$_5$. Zamboni et al.\textsuperscript{42} reported that the Ca$_2$Fe$_2$O$_5$ phase was the dominant phase of iron, which is in accordance with the XRD peaks of char catalyzed by mixed Fe/Ca at 1073 and 1273 K, shown in Figure 5. This probably means that the suppression of NH$_3$ at higher temperatures could be attributed to the formation of Ca$_2$Fe$_2$O$_5$ in char. Sun et al.\textsuperscript{43} reported the reduction of Ca$_2$Fe$_2$O$_5$ by temperature-programmed reduction of hydrogen (H$_2$-TPR) at temperatures ranging from 903 to 1023 K. Thus, the presence of Ca$_2$Fe$_2$O$_5$ would have enhanced the oxidation of HCN to N$_2$. Moreover, the species observed in the XRD patterns at 1273 K was simpler than that at a lower temperature, and the intensity of the Ca$_2$Fe$_2$O$_5$ peaks was significantly stronger. This indicates a good agreement between the increased generation of Ca$_2$Fe$_2$O$_5$ with the obvious reduction of NO$_x$ precursors at 1273 K. Previous studies report that the oxidation of Fe$^{3+}$ is predominant in the catalysis of Ca$_2$Fe$_2$O$_5$\textsuperscript{42} which supports Fe$_2$(SO$_4$)$_3$ as the major influence at a higher temperature, as mentioned earlier. Besides, it is confirmed that it is not just the interaction between Fe$_2$O$_3$ and Ca(OH)$_2$ to directly generate Ca$_2$Fe$_2$O$_5$ in this condition. Instead, the generation of Ca$_2$Fe$_2$O$_5$ indeed has a close relationship with the catalysis of metals on the nitrogen conversion during pyrolysis.

3.3. Liquid Phase. The GC−MS analysis was performed to investigate the effects of additives on the distribution of tar N and other functional groups in tar. To clarify the changes in composition and yield of oxygen functionalities, the general catalytic effects on oxygenated functional groups and hydrocarbon in tar were analyzed and the results are qualitatively depicted in Figure 6. In comparison to the blank results, the structures and kinds of compositions became comparatively simpler. The minimum number of oxygen-containing groups was observed in the presence of calcium compounds. The dehydroxylation of phenolic compounds contributed to the deoxygenation process. Thus, the deoxygenation process in tar initially produced a large amount of OH and O radicals, which

![Figure 5. XRD patterns of the char sample for pyrolysis of proline at (a) 873, (b) 1073, and (c) 1273 K.](image-url)

![Figure 6. Variation of oxygenated functional groups with additives.](image-url)
reacted with CaC_3N_2 in char to produce CaO/Ca(OH)_2 and N_2. Regenerated CaO/Ca(OH)_2 also had the ability to fix HCN. Consequently, this illustrated that the deoxygenation process can enhance the conversion of HCN to N_2 with CaO/Ca(OH)_2. The amount of H_2 releasing increased in the presence of Ca(OH)_2 and Fe_2(SO_4)_3. On the basis of the above discussion, the evolution of a single Ca(OH)_2 additive during pyrolysis is illustrated in Figure 7.

For different N-containing species, the effects of added minerals on the ratio of hydrocarbon and oxygen groups in tar at 1073 K are shown in Figure 8. On the basis of the catalytic role of metals, the large molecular substances can break down into smaller molecules, such as phenolic compounds, nitrogen-containing functional groups, and smaller hydrocarbons. The hydrocarbon production for non-catalyzed phenylalanine pyrolysis was up to 50% in tar, as shown in Figure 8. Fe_2(SO_4)_3 and Ca(OH)_2 can encourage the decomposition of hydrocarbons. However, the hydrocarbons generated in tar from proline and protein were relatively few, illustrating that amino N compounds are the main sources of hydrocarbon in tar during fuel pyrolysis. It has been reported that the generation of hydrocarbons is in accordance with the reduction of ketones, aldehydes, and acids. Thus, the increase of hydrocarbons can cause less OH or O radicals, which might be somewhat detrimental to the removal of HCN for CaO/Ca(OH)_2. This also explains the low HCN removal efficiency from amine N compounds catalyzed by Ca(OH)_2, because relatively less oxygenated radicals are generated.

The distribution of N species in tar at 873 K can be seen in Table 2, and the unit of data in Table 2 is the relative content (%) of components in tar. For tar derived from protein, the amount of heterocyclic N (19.55%) was the largest without additives, followed by the amount of amine N. The reduction of these three kinds of nitrogen functional groups was observed in the case of iron catalysis, in which tar N compounds thermally decompose to HCN and NH_3. However, Fe might catalyze the conversion of NH_3 to N_2 and H_2 at high temperatures (eqs 4 and 5), causing the NH_3 emission to decrease and the HCN emission to increase. Instead, the content of nitrile N increased in tar in the presence of Ca(OH)_2, and HCN production was higher at 1073 K.

According to the proline pyrolysis results depicted in Table 2, the ring-opening reactions were conducted with considerably higher energy. Thus, the removal of heterocyclic N was approximately 87.7% at a relatively low temperature (873 K). However, the added minerals enhanced the reduction of heterocyclic N to at least 55.98%. Ca(OH)_2 and Fe_2(SO_4)_3 significantly improved the thermal cracking of heterocyclic N, probably because these additives can lower the ring-opening temperature of tar. Interestingly, for phenylalanine (amine N), both Fe_2(SO_4)_3 and Ca(OH)_2 remarkably enhanced the conversion of amine N compounds to intermediate nitrile N. As we known, nitrile N was the predominant source of HCN during pyrolysis. Ultimately, less HCN was emitted because more nitrogen was fixed in tar as nitrile N. Conclusively, mixed Fe/Ca additives are more effective than separate catalysts for the pyrolysis of N-containing model compounds.

From the above discussions, it can be concluded that Fe_2(SO_4)_3 can promote ring-opening reactions and Ca(OH)_2 can promote the conversion of amine N to intermediate nitrile compounds in tar and NH_3 emission. Thus, the effects of mixed Fe/Ca catalysts on the transformation of nitrogen species are illustrated in Figure 9.

![Figure 7](image-url)  
Figure 7. Nitrogen conversion routes affected by mixed Fe/Ca additives during pyrolysis.

![Figure 8](image-url)  
Figure 8. Effects of additives on the ratio of hydrocarbon and oxygen groups in tar at 1073 K for three samples.

![Figure 9](image-url)  
Figure 9. Effects of a mixed Fe/Ca additive on the transformation of nitrogen species.

### Table 2. GC–MS Analysis of Tar Samples

<table>
<thead>
<tr>
<th></th>
<th>proline</th>
<th>phenylalanine</th>
<th>protein</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>amine N</td>
<td>nitrile N</td>
<td>heterocyclic N</td>
</tr>
<tr>
<td>RS</td>
<td>2.26</td>
<td>0.28</td>
<td>87.68</td>
</tr>
<tr>
<td>S–Fe_2(SO_4)_3</td>
<td>3.33</td>
<td>0</td>
<td>63.76</td>
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<tr>
<td>S–Ca(OH)_2</td>
<td>0.63</td>
<td>2.19</td>
<td>58.98</td>
</tr>
<tr>
<td>S–Ca(OH)_2–Fe_2(SO_4)_3</td>
<td>2.68</td>
<td>0.92</td>
<td>60.32</td>
</tr>
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</table>
4. CONCLUSION

Three representative N model compounds were mixed with Fe$_2$(SO$_4$)$_3$ and Ca(OH)$_2$ and pyrolyzed at 873−1273 K to investigate the effect of mixed Fe/Ca additives on nitrogen evolution. The main conclusions are summarized as follows: (1) The mixed Fe/Ca additives showed more advantageous effects of iron and calcium on NH$_3$ and HCN emissions. Fe$_2$(SO$_4$)$_3$ improved the transformation of NH$_3$ to N$_2$ and Ca(OH)$_2$ consumed HCN simultaneously. Especially for protein, the nitrogen conversion ratio of (HCN + NH$_3$) emission with the addition of mixed Fe/Ca was reduced to half the value of non-catalyzed pyrolysis (from 39.59 to 19.44%). (2) Ca$_3$Fe$_2$O$_6$ was formed in char at temperatures above 873 K, which improved the transformation of CaC$_3$N$_2$ and FeN$_2$ to N$_2$. With an increasing temperature, Ca$_3$Fe$_2$O$_6$ became the predominant mineral compound and the ratio of Ca$_3$Fe$_2$O$_6$ was higher in char. (3) Fe$_2$(SO$_4$)$_3$ and Ca(OH)$_2$ additives promoted ring-opening reactions and enhanced the conversion of amine N to intermediate nitrile N in tar. Additives facilitated the decomposition of phenolic functional groups in tar to produce more O and OH radicals, resulting in higher reactivity of the conversion of CaC$_3$N$_2$ to N$_2$.

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Notes
The authors declare no competing financial interest.

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