Research on Thermal Behaviors and NO\textsubscript{x} Release Properties during Combustion of Sewage Sludge, Sawdust, and Their Blends

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ABSTRACT: To investigate the thermal behaviors and NO\textsubscript{x} emission properties during combustion of sewage sludge (SS), sawdust (SD), and their blends (SS5SD5, SS3SD7, and SS1SD9 with SD proportions of 50, 70, and 90 wt %, respectively), tests were conducted using thermogravimetry–mass spectrometry (TG-MS), Fourier transform infrared spectroscopy (FTIR), and a tube furnace in this study. Results indicated that hydrogen in the fuel was mainly released during volatile combustion, and carbon conversion proceeded during the whole combustion process. With the SD proportion increasing, samples exhibited better combustion characteristics. Compared to SD, SS emitted more NO\textsubscript{x} due to its higher nitrogen content but showed lower conversion ratios from fuel nitrogen to NO\textsubscript{x}, and the NO\textsubscript{x} yields decreased significantly with the increase in SD proportion. NO\textsubscript{x} emissions of higher volatile samples were more sensitive to temperature, and NO\textsubscript{x} yields of SD and SS1SD9 continued to decrease from 800 to 1000 °C, whereas NO\textsubscript{x} yields of SS, SS5SD5, and SS3SD7 changed slightly from 800 to 900 °C and decreased significantly from 900 to 1000 °C. Synergistic effects of cocombustion on NO\textsubscript{x} emission varied with the blending ratio and temperature. SS5SD5 and SS3SD7 always presented a positive NO\textsubscript{x} reduction performance, and SS1SD9 exhibited opposite NO\textsubscript{x} reduction effects at different temperatures. Synthetically considering the SS disposal capacity, combustion characteristic, and NO\textsubscript{x} yield, an SS proportion of around 30% in blends is more recommended in practical applications.

1. INTRODUCTION

Sewage sludge (SS) is an inevitable byproduct of wastewater treatment. The amount of SS has increased steadily worldwide with the rapid expansion of urban cities and wastewater treatment capacities over the past decades.\textsuperscript{1,2} Lots of undesirable substances in SS, such as viruses, bacteria, parasites, and heavy metals, pose a constant threat to the environment and human health.\textsuperscript{3,4} The common disposal methods of SS include landfill, agricultural application, composting, and incineration, but the practical application of each method varies all over the world.\textsuperscript{5–7} Nonstandard or irregular treatments do much harm to the environment and human health. Incineration is an efficient and convenient method to achieve sludge reduction and reutilization, and the abundant numbers of studies on the combustion of solid fuels provide rich research methods and utilization experiences for sewage sludge combustion.\textsuperscript{8–11} Considering the poor fuel properties of SS due to its high ash content and low calorific value, a practical way to achieve efficient utilization of SS is cocombustion with some other high-quality fuels such as most agricultural and forestry wastes, which can also make remarkable contributions to the reduction of CO\textsubscript{2} emission.

Considering the high nitrogen content of most SS, the investigation of both thermal behaviors and NO\textsubscript{x} release properties is of great significance for the application of cocombustion. Thermogravimetric analysis (TG) has been
widely used to assess thermal behaviors and kinetics of cocombustion of SS and various fuels. The release of typical gas species during pyrolysis of SS and biomass was also investigated by thermogravimetry−mass spectrometry (TG-MS) and thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR),12,13 which contributed to the better NO\textsubscript{x} emission control. The results of TG-MS analysis during cocombustion of straw and SS suggested an SS proportion of less than 30% in blend fuels.14 The synergistic effect on NO\textsubscript{x} and SO\textsubscript{2} reduction was observed during the cocombustion of SS and three kinds of biomasses.15 Meanwhile, the study on volatile-N and char-N during pulverized coal combustion in the O\textsubscript{2}/CO\textsubscript{2} atmosphere at a high temperature16 helped obtain the fuel nitrogen conversion mechanism. Previous research on NO\textsubscript{x} emission mainly focused on the total yield of NO\textsubscript{x} during combustion, whereas the relevance between NO\textsubscript{x} release and combustion process has not been discussed in detail. The NO\textsubscript{x} release properties versus time make sense, but it is insufficient to assess the NO\textsubscript{x} emission during actual combustion due to the uncertainty of burnout time, fuel amount, and airflow velocity. However, the carbon conversion proceeds throughout the entire combustion process and represents the combustion status to a great extent. The carbon conversion ratio always ranges from 0 to 100%, which makes the carbon conversion ratio become an excellent medium for connecting actual combustion with bench-scale tests. Therefore, the NO\textsubscript{x} emission versus time and carbon conversion process is indispensable to a better understanding of NO\textsubscript{x} emission performance during combustion, which also contributes to more effective and accurate measures for initial NO\textsubscript{x} control during combustion.

The mass loss, residue evolution, and NO\textsubscript{x} emission properties during combustion were of great importance to the study on combustion of SS and SD and have been discussed in this paper. The mass loss and gas release properties of SS, SD, and their blends in different proportions were investigated by TG-MS analysis under nonisothermal conditions. FTIR analysis was used to investigate the residue evolution characteristics of SS and SD during the heating process in an air atmosphere. Isothermal experiments in a tube furnace were also performed to study NO\textsubscript{x} emission properties with the process of time and carbon conversion during combustion. Therefore, a clear understanding of the cocombustion process was obtained, which contributed to evaluating the feasibility of cocombustion of SS and SD, achieving initial NO\textsubscript{x} control and eventually finding a practical, secure, and optimized utilization method for these two resources. This study will also provide an important reference for industrial applications of SS and biomass.

2. MATERIALS AND METHODS

2.1. Materials. SS and SD were obtained from a municipal wastewater treatment plant in Yantai (Shandong Province, China) and a poplar wood plant in Hanzhong (Shaanxi Province, China), respectively.

Table 1. Proximate and Ultimate Analyses and Lower Heating Values (LHVs)\textsuperscript{a}

| samples   | \(M_{ad}\) | \(A_{ad}\) | \(V_{ad}\) | \(C_{ad}\) | \(H_{ad}\) | \(O_{ad}\) | \(N_{ad}\) | \(S_{ad}\) | LHV (MJ/kg) |
|-----------|------------|------------|------------|------------|------------|------------|------------|------------|--------------|
| SS        | 7.2        | 47.1       | 40.5       | 22.9       | 3.5        | 14.1       | 4.2        | 0.97       | 9.8          |
| SS5SD5    | 5.2        | 24.6       | 59.6       | 34.3       | 5.1        | 27.6       | 2.5        | 0.64       | 13.5         |
| SS3SD7    | 4.4        | 15.7       | 67.2       | 38.9       | 5.7        | 33.0       | 1.8        | 0.50       | 15.0         |
| SS1SD9    | 3.6        | 6.8        | 74.8       | 43.4       | 6.3        | 38.4       | 1.1        | 0.36       | 16.5         |
| SD        | 3.2        | 2.3        | 78.6       | 45.7       | 6.7        | 41.1       | 0.8        | 0.30       | 17.2         |

\textsuperscript{a}Notes: ad is air-dried basis; M is moisture; A is ash; V is volatile matter; FC is fixed carbon.

Table 2. Ash Compositions of Samples at 550 °C (wt %)

| samples   | Ca     | K      | Na     | Mg     | Fe     | Al     | Zn     | Si     | P     | S     | C     | O     |
|-----------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|-------|-------|
| SS        | 16.21  | 1.54   | 1.21   | 5.11   | 6.60   | 5.72   | 0.72   | 5.84   | 3.49  | 1.89  | 3.10  | 48.3  |
| SS5SD5    | 16.09  | 2.61   | 1.20   | 4.97   | 6.31   | 5.47   | 0.69   | 5.61   | 3.39  | 1.83  | 3.05  | 48.5  |
| SS3SD7    | 15.95  | 3.90   | 1.19   | 4.81   | 5.97   | 5.17   | 0.65   | 5.34   | 3.27  | 1.76  | 2.99  | 48.7  |
| SS1SD9    | 15.44  | 8.58   | 1.16   | 4.22   | 4.71   | 4.08   | 0.53   | 4.34   | 2.82  | 1.50  | 2.76  | 49.5  |
| SD        | 13.72  | 24.61  | 1.03   | 2.23   | 0.42   | 0.34   | 0.11   | 0.93   | 1.31  | 0.63  | 1.99  | 52.3  |

Figure 1. Schematic diagram of the experimental system.
Province, China), respectively. Both SS and SD were dried at 105 °C for 24 h in an oven. The dried SS and SD were milled and sieved into 75−147 μm in diameter, and samples for each test were well ground evenly in a mortar by definite mass proportions. Three types of mixtures with SD mass proportions of 50, 70, and 90 wt % were named as SS5SD5, SS3SD7, and SS1SD9, respectively.

The proximate (GB/T 28731-2012) and ultimate (GB/T 28728-2012, GB/T 28732-2012, and GB/T 28734-2012) analysis results and lower heating values (LHVs, GB/T 30727-2014) of samples are presented in Table 1. As shown in Table 1, there were distinct differences between the compositions of SS and SD. With the increase in SD proportion, the average combustible material content increased, the average ash content and nitrogen content decreased, and the fuel properties were remarkably affected. The XRF results of ash at 550 °C are shown in Table 2. SS ash showed remarkable Ca and Fe contents, and the K and Ca were the significant components in SD ash. All three blends presented similar ash compositions to SS due to the much higher ash content of SS than SD.

2.2. Experimental Apparatus and Procedure. In this study, TG-MS tests, FTIR analysis, and tube furnace experiments were conducted, and the schematic diagram of the experimental system is shown in Figure 1.

TG-MS tests of SS, SD, and their blends were conducted by the Thermo Mass Photo instrument. For each test, 5 mg of sample was put into an Al2O3 crucible and heated in the TG-MS apparatus at a heating rate of 10 °C/min from room temperature to 1000 °C with a 21 vol % O2/79 vol % He flow rate of 100 mL/min. The mass loss characteristics were obtained by the TG results, and the release properties of gas products were obtained by the corresponding ion current intensity signals from MS.

To obtain SS and SD residues at specified temperatures, SS and SD were put into a tube furnace (GSL 1200X) with an airflow rate of 1 L/min, and then, the temperature increased from room temperature to preset temperatures (200, 300, 400, 500, 600, 700, 800, and 900 °C) at a heating rate of 10 °C/min. Residues were taken out and cooled with liquid nitrogen immediately when the tube furnace reached the target temperatures. SS, SD, and their residues were analyzed using a Fourier transform infrared spectrometer (Nicolet iS50 FTIR). In addition, to study the NOx emission properties of SS, SD, and their blends at various combustion temperatures, 0.1 g of samples was put into the tube furnace, which was preheated to 800, 900, and 1000 °C, respectively. Air with a flow rate of 1 L/min was injected into the furnace to provide the necessary oxygen for combustion. A flue gas analyzer (GA-21plus) was used to monitor the O2, CO2, CO, NO, and NO2 concentrations during the whole combustion process. This study was focused on the NOx yields and the correlation between NOx release and carbon conversion.

To investigate potential interactions during cocombustion of SS and SD, the experimental and theoretical values for specific parameters, such as TG, NOx yield, and the ratio of fuel nitrogen to NOx, were also compared in this study.

3. RESULTS AND DISCUSSION

3.1. Combustion Characteristics of SS and SD.

3.1.1. TG-MS Analysis. The TG, DTG, and DSC curves of
SS and SD at a heating rate of 10 °C/min under a 21 vol % O2/79 vol % He atmosphere are presented in Figure 2. According to the MS results, strong ion intensity signals of m/z of 18 (H2O+), 28 (CO+), and 44 (CO2+)) were detected during the heating process. The DTG curves and main gas release curves of SS and SD during the heating process are demonstrated in Figure 3.

As exhibited in Figures 2a and 3a, after a slight weight loss of 7.35% between 40 and 180 °C by the removal of moisture, SS mainly experienced three weight-loss stages during the heating process. A dramatic weight loss of 31.40% between 180 and 400 °C (Stage I) was visible along with the distinct evolution of H2O, CO2, and CO corresponding to the devolatilization and combustion of most volatiles. During Stage I, the release of H2O was mainly related to thermal decomposition reactions (mainly dehydration) and the oxidation of hydrogen in fuel; the CO evolution was mainly caused by the decomposition of labile compositions like alkyl aryl ethers and the oxidization of light hydrocarbyl groups. CO2 was mainly released from the decomposition of carboxyl and carboxylate groups, as well as the oxidization of carbon-containing compounds. Then, there was a weight loss of 12.81% between 400 and 650 °C (Stage II) with remarkable CO2 evolution, which mainly resulted from the combustion of residual organics with low reactivity and fixed carbon. Meanwhile, the slight CO yield during Stage II mainly resulted from the incomplete oxidization of carbon. The high ash content of SS decelerated the devolatilization, resulting in a much higher weight loss during Stage II (12.81%) than the fixed carbon content (5.2%) in Table 1. Finally, calcium carbonate decomposition resulted in a weight loss of 9.42% between 650 and 750 °C (Stage III) with abundant CO2 yield. SS presented a lower final residual mass fraction (mR) of 38.33% than the ash content of 47.1% (Table 1) mainly due to carbonate decomposition of Stage III.

As shown in Figures 2b and 3b, SD experienced a slight weight loss of 2.33% between 40 and 160 °C with a slight H2O release peak by the removal of moisture; a sharp weight loss of 74.62% between 220 and 400 °C (Stage I) with remarkable evolution of H2O, CO2, and CO corresponding to the devolatilization and combustion of most volatiles; and finally an apparent weight loss of 20.21% between 400 and 500 °C (Stage II), mainly due to the combustion of fixed carbon along with a significant CO2 yield. The mR of SD (1.93%) was slightly lower than the corresponding ash content (2.3%) shown in Table 1 due to ash transformation at high temperatures.

The positive and negative values of DSC in Figure 2 represent endothermic and exothermic conditions, respectively. For both SS and SD, the removal of moisture below 180 °C was an endothermic process, and the combustion of volatiles and char corresponded to the distinct exothermic peaks of Stage I and Stage II, respectively. Additionally, the decomposition of CaCO3 during Stage III of SS was an endothermic process. With the temperature further increasing, both SS and SD presented an endothermic process, indicating the existence of mineral transformation in ash. During the whole combustion process, the heat release of SS was 52% less than that of SD, which was consistent with the different calorific values as shown in Table 1. In addition, SS presented a higher heat release ratio of Stage I/Stage II (2.09) than SD (0.90), which mainly resulted from the higher fixed carbon/volatile ratio of SD.

SS and SD presented similar gas evolution properties during Stage I and Stage II. During Stage I, the evolution of H2O, CO, and CO2 of SD was mainly caused by the degradation and combustion of hemicellulose, cellulose, and lignin, and the release of H2O, CO, and CO2 of SS was mainly due to the decomposition and combustion of lipid, protein, and carbohydrate. SD presented a stronger intensity of H2O and CO during Stage I than SS due to its higher volatile and hydration contents, suggesting a stronger local reducing atmosphere during devolatilization. During Stage II, the evolution of CO and CO2 of both SD and SS was mainly due to the combustion of fixed carbon (C-rich materials by aromatic cyclization and graphitization). However, the complex compositions and high ash content in SS resulted in a wider temperature zone of decomposition and higher char combustion temperatures. In addition, for both SS and SD, the conversion of hydrogen to H2O mainly took place during Stage I, whereas the conversion of carbon to CO2/CO took place throughout the whole combustion process, which made it reasonable to evaluate the combustion status by the conversion ratio of carbon.

3.1.2. FTIR Analysis. To study the residue evolution properties of SS and SD, FTIR analyses of SS, SD, and their residues at various temperatures were conducted. The mid-infrared spectra of the original SS and SD are shown in Figure 4, and the mid-infrared spectra of residues at multiple temperatures are illustrated in Figure 5. The characteristic
absorption bands observed in Figures 4 and 5 are presented in Table 3.19–22

Table 3. Characteristic Absorption Bands Observed in the Mid-Infrared Spectra

| Band (cm⁻¹) | Assignments                      |
|------------|----------------------------------|
| 3600–3000  | O–H stretching of hydroxyl groups or water |
| 3000–2800  | C–H stretching of aliphatic methylene or alkyl |
| 2280–2210  | C≡C stretching, C≡N stretching |
| 1750–1700  | C≡O stretching of aldehydes, carboxylates, esters, ketones |
| 1680–1640  | C≡O stretching of carboxylates (amide I band) |
| 1597, 1509, 1375 | C≡C stretching of aromatic rings, alkenes |
| 1570–1540  | N–H in-plane (amide II band) |
| 1510–1390  | CO₃²⁻ stretching of carbonates |
| 1470–1350  | C–H deformation of aliphatic compounds |
| 1335–1240  | C–O stretching of carboxylates, phenols, ethers |
| 1160       | C–O stretching of esters |
| 1100–1000  | C–OH stretching of carbohydrates |
| 1080       | Si–O stretching of silicates |
| 1058       | C–O stretching, glycosidic linkages between sugar units |
| 1035       | Si–O stretching of silicates |
| 898        | C–O–C stretching of glucose ring (cellulose) |
| 872        | CO₃²⁻ out-of-plane bending of carbonates |
| 712        | CO₃²⁻ in-plane bending of carbonates |
| 668        | O–H out-of-plane bending in C–OH alcoholic groups |
| 462        | Fe₂O₃ |

Figures 4 and 5. Mid-infrared spectra of (a) SS residues and (b) SD residues.

From the SS spectrum presented in Figure 4, there were abundant O–H (3600–3000 cm⁻¹) and C–H (2800–3000 cm⁻¹) bonds in SS, indicating the presence of considerable alcohol and aliphatic compounds. The distinct absorption peak at 1650 cm⁻¹ (C=O stretching) corresponded to carboxylates in lipid and protein. The peak at 1543 cm⁻¹ corresponded to the overlap of the C=C stretching vibration and the N–H in-plane bending vibration (amides II band). These amide structures mainly originated from abundant DNA and RNA of animal and plant cells and microorganisms in SS. In addition, the high ash content of SS resulted in the distinct band overlap of organic functional groups and inorganic components.22 The intense peaks at 1456 and 1417 cm⁻¹ were mainly owing to the combination of the CO₃²⁻ stretching vibration and the C–H deformation vibration, and the peaks at 1080 and 1035 cm⁻¹ corresponded to the combination of the Si–O stretching vibration and the C–O stretching vibration. The SS spectrum indicated the main organic components of lipid, protein, and carbohydrate22 and the main inorganic components of silica oxides (1080 and 1035 cm⁻¹), carbonates (1456, 1417, 872, and 712 cm⁻¹), and iron oxides (462 cm⁻¹).

From Figure 5a, SS mainly experienced organic evolution from 200 to 600 °C and inorganic evolution from 600 to 800 °C. The desorption of external water mainly occurred below 200 °C. With the temperature increasing from 200 to 400 °C, the quantities of O–H, C–H, and C–O decreased significantly by bond breaking23 with the release of H₂O, CO₂, and CO, as shown in Figure 3a, and the cleavage of intramolecular H-bonds, the subsequent dehydration, and complex condensation reactions led to the structure rearrangement of carbon (aromatic cyclization and graphitization),24 which resulted in the stronger absorption of C≡C stretching (1597 cm⁻¹) and the absorption of C≡C and C≡N stretchings (2215 cm⁻¹) at 400 °C. When the temperature reached 600 °C, most amounts of C≡C (1597 cm⁻¹) and C≡O (1650 cm⁻¹) bonds were consumed by oxidation with the release of CO₂ and the residue presented significant features of ash. Then, carbonates (1453, 1417, 872, and 712 cm⁻¹; mainly CaCO₃) decomposed between 600 and 800 °C. The relative amounts of carbonates increased with the consumption of organics in SS and then decreased by decomposition.

From the SD spectrum in Figure 4, the intense absorption bands of O–H stretching (3600–3000 cm⁻¹), C–H stretching (2800–3000 cm⁻¹), and C≡O stretching (1750–1640 cm⁻¹) were visible, indicating the presence of alcohol, aliphatic compounds, ketones, or short-chain carboxylic acids in SD. Peaks at 1597, 1509, and 1375 cm⁻¹ (C–C stretching vibration) corresponded to aromatic rings from lignin compounds. Peaks between 1470 and 1350 cm⁻¹ were due to the C–H deformation vibration of cellulose and lignin. Peaks between 1300 and 1100 cm⁻¹ resulted from the C–O stretching vibration of carboxylic acids, phenols, or ethers. Peaks between 1100 and 1000 cm⁻¹ (C–O stretching vibration) indicated the presence of carbohydrates like cellulose and hemicellulose. SD was also characterized by the peaks at 1058 and 898 cm⁻¹ corresponding to O-glycosidic linkages between sugar units and glucose rings. The FTIR results verified the three main components of hemicellulose, lignin, and cellulose of SD.25

From Figure 5b, SD mainly experienced similar residue evolution properties to SS, including the organic evolution
from 200 to 500 °C and inorganic evolution from 500 to 800 °C. After the removal of external moisture below 200 °C, the amounts of O−H, C−H, and C−O−C of the glucose ring and O-glycosidic linkages between sugar units gradually decreased by decomposition and oxidization;23 meanwhile, complex condensation and rearrangement reactions took place below 400 °C with the generation of C-rich compounds and the release of H2O and CO2, as shown in Figure 3b, resulting in the stronger C=C vibration (1597 cm−1) and C=O vibration (2215 cm−1) at 400 °C. Compared to SS, SD exhibited a lower burnout temperature of about 500 °C, during which C=C (1597 cm−1) and C=O (1737 cm−1) got nearly exhausted, and strong inorganic peaks (Si−O stretching at 1088 and 1035 cm−1, C O3 2− vibration at 1450 and 872 cm−1) became visible. The carbonates (mainly CaCO3 and K2CO3) gradually decomposed with the further increase in temperature from 600 to 800 °C.

3.2. Combustion Characteristics of Blends. The TG, DTG, and DSC curves of all samples as well as the experimental and theoretical TG curves of blends are shown in Figure 6.

Table 4. Weight-Loss Stages of SS, SD, and Blends during the Heating Process

| samples     | stage I | stage II | stage III |
|-------------|---------|----------|-----------|
|             | T (°C)  | TG (%)   | DSC (%)   | T (°C)  | TG (%)   | DSC (%)   | T (°C)  | TG (%)   |
| SS          | 180−400 | 31.40    | 67.59     | 400−650 | 12.81    | 32.43     | 650−750 | 9.42     |
| SS5SD5      | 200−400 | 49.72    | 57.12     | 400−620 | 18.93    | 42.94     | 620−750 | 5.45     |
| SS3SD7      | 200−400 | 60.11    | 53.80     | 400−600 | 20.63    | 46.22     | 600−750 | 3.85     |
| SS1SD9      | 220−400 | 68.15    | 50.11     | 400−600 | 19.32    | 49.91     | 600−750 | 1.64     |
| SD          | 220−400 | 74.62    | 47.49     | 400−500 | 20.21    | 52.50     |         |          |

Table 5. Combustion Characteristic Parameters of SS, SD, and Their Blends

| samples     | Ti (°C) | Tb (°C) | mb (%) | T1 (°C) | DTG1 (%/min) | T2 (°C) | DTG2 (%/min) | T3 (°C) | DTG3 (%/min) | DTGmean (%/min) | S × 10−8 (K−3·min−2) |
|-------------|---------|---------|--------|---------|--------------|---------|--------------|---------|--------------|-----------------|---------------------|
| SS          | 246     | 734     | 38.33  | 332     | 6.55         | 395     | 1.07         | 717     | 1.63         | 1.14             | 2.75                |
| SS5SD5      | 247     | 716     | 21.51  | 340     | 15.05        | 449     | 1.42         | 696     | 0.95         | 1.55             | 8.72                |
| SS3SD7      | 254     | 701     | 14.21  | 340     | 21.54        | 457     | 1.79         | 690     | 0.58         | 1.81             | 14.44               |
| SS1SD9      | 262     | 547     | 6.15   | 343     | 25.06        | 480     | 2.39         | 670     | 0.35         | 3.05             | 32.60               |
| SD          | 267     | 505     | 1.93   | 341     | 30.67        | 468     | 3.40         |         |              | 3.71             | 50.15               |

Notes: Ti, Tb, and T3 are the temperatures according to DTG peaks of Stage I, Stage II, and Stage III, respectively. DTG1, DTG2, DTG3 are the DTG values at Ti, Tb, and T3, respectively. DTGmean is the average mass loss rate during the whole mass loss process.

from 200 to 500 °C and inorganic evolution from 500 to 800 °C. After the removal of external moisture below 200 °C, the amounts of O−H, C−H, and C−O−C of the glucose ring and O-glycosidic linkages between sugar units gradually decreased by decomposition and oxidization;23 meanwhile, complex condensation and rearrangement reactions took place below 400 °C with the generation of C-rich compounds and the release of H2O and CO2, as shown in Figure 3b, resulting in the stronger C=C vibration (1597 cm−1) and C=O vibration (2215 cm−1) at 400 °C. Compared to SS, SD exhibited a lower burnout temperature of about 500 °C, during which C=C (1597 cm−1) and C=O (1737 cm−1) got nearly exhausted, and strong inorganic peaks (Si−O stretching at 1088 and 1035 cm−1, CO3 2− vibration at 1450 and 872 cm−1) became visible. The carbonates (mainly CaCO3 and K2CO3) gradually decomposed with the further increase in temperature from 600 to 800 °C.

3.2. Combustion Characteristics of Blends. The TG, DTG, and DSC curves of all samples as well as the experimental and theoretical TG curves of blends are shown in Figure 6.
in Figure 6. The TG, DTG, and DSC curves of blends exhibited a significant correlation with the blending ratio.

Blends presented three main weight-loss stages during the heating process: Stage I (devolatilization and combustion of most volatiles), Stage II (combustion of fixed carbon and residual volatiles), and Stage III (decomposition of carbonates), and the details are shown in Table 4. Blends presented higher initial temperatures of Stage I and lower final temperatures of Stage II than SS due to the addition of SD. With the SD proportion increasing, the weight loss of Stage I increased significantly, whereas the heat release ratio of Stage I/Stage II decreased, which was mainly due to the remarkable increase in the calorie-rich fixed carbon. Meanwhile, blends with higher SD proportions presented lower weight-loss ratios of Stage III due to the lower carbonate contents, and the increased heat release during combustion resulted in the earlier decomposition of carbonates during Stage III.

The combustion parameters were also calculated by the TG-DTG curves and are presented in Table 5. $T_{\text{max}}$ is the temperature with the maximum mass loss rate; the ignition temperature ($T_{i}$) is defined as the intersection of the tangent at $T_{\text{max}}$ and the horizontal curve at the temperature starting to lose weight concerning the TG curve; and the burnout temperature ($T_{b}$) is the temperature where the mass loss of samples reached 98% of the total mass loss. The combustibility index $S$ is used as a criterion for fuel combustion characteristics. A bigger $S$ indicates a better combustion characteristic, and $S$ is defined as follows:\(^\text{26}\)

$$S = \frac{\text{DTG}_{\text{max}} \times \text{DTG}_{\text{mean}}}{T_{i} \times T_{b}}$$  \hspace{1cm} (1)

where DTG$_{\text{max}}$ denotes the maximum mass loss rate (%/min), DTG$_{\text{mean}}$ is the average mass loss rate (%/min), $T_{i}$ is the ignition temperature (K), and $T_{b}$ is the burnout temperature (K).

As shown in Table 5, SS exhibited a lower $T_{i}$ but much higher $T_{b}$ and $m_{b}$ than SD, and the DTG$_{1}$ and DTG$_{\text{mean}}$ of SS were much smaller than those of SD due to their different components. The index $S$ of SS ($2.75 \times 10^{-6} \text{K}^{-3} \cdot \text{min}^{-2}$) was much smaller than that of SD ($5.015 \times 10^{-7} \text{K}^{-3} \cdot \text{min}^{-2}$), which indicated that SD had better combustion characteristics than SS.

With the increase in SD proportion, $m_{b}$ of blends decreased proportionally, and both DTG$_{1}$ and DTG$_{\text{mean}}$ increased due to the increasing volatile content and combustible material content. Meanwhile, $T_{i}$ increased slightly and $T_{b}$ decreased significantly due to the higher $T_{i}$ and lower $T_{b}$ of SD. The increasing $S$ indicated that blends with higher SD proportions exhibited better combustion properties.

In addition, the comparison of experimental and theoretical TG curves of blends is shown in Figure 6d. The theoretical values are calculated as follows

$$T_{G_{T}} = p_{SD} \cdot T_{G_{SD}} + p_{SS} \cdot T_{G_{SS}}$$  \hspace{1cm} (2)

where TG$_{SD}$ and TG$_{SS}$ are the experimental TG values of SD and SS, respectively, and $p_{SD}$ and $p_{SS}$ are the mass proportions of SD and SS in blends, respectively.

The experimental TG curves before 340 °C were in good agreement with theoretical curves, which suggested that the decomposition of labile compounds was barely influenced by cocombustion. Nonetheless, the experimental weight-loss ratios were smaller than the theoretical values between 350 and 500 °C for all blends, especially for SS/SD. During cocombustion, SS ash slowed down the devolatilization and char combustion of SD by decelerating heat transfer and oxygen diffusion, and therefore, more time or a higher
temperature was required for the combustion process, which was undesirable in practical applications. In addition, blends presented higher burnout ratios than theoretically, and the experimental values of SS5SD5, SS3SD7, and SS1SD9 were higher than the calculated values by 1.23, 1.38, and 0.56%, respectively. During co-combustion, volatiles in SD were released rapidly to generate loose structures with abundant pores in char, which promoted the oxygen diffusion in SS char and contributed to the higher burnout ratios of blends. In addition, the higher calorific value of SD increased the interior temperature of residues, which also promoted burnout and ash decomposition. On the whole, co-combustion of SS and SD showed positive effects on improving fuel properties, and SS3SD7 exhibited optimum interactions during combustion.

The gas release curves of blends during the heating process are demonstrated in Figure 7. Three blends presented similar evolution properties of H2O, CO, and CO2 to individual SS and SD. Most H2O was released during Stage I, while CO and CO2 presented considerable release yields during both Stage I and Stage II, which suggested that the conversion of hydrogen of blends mainly took place during Stage I and the conversion of carbon took place throughout the whole combustion process. In addition, the intensity of both H2O and CO2 got stronger with the SS proportion increasing.

The carbon in the fuel was continuously converted to flue gas during the whole combustion process, and the carbon conversion ratios of SS, SD, and blends during different weight-loss stages are calculated as follows and illustrated in Table 6

\[
\alpha_i = \frac{m_i}{m_C} \times 100\% \quad i = 1, 2, 3
\]

Table 6. Carbon Conversion Ratios of Samples during Different Weight-Loss Stages

| samples | SS | SS5SD5 | SS3SD7 | SS1SD9 | SD |
|---------|----|--------|--------|--------|----|
| \( \alpha_{C1} \)% | 55.9 | 50.7 | 49.2 | 48.3 | 46.9 |
| \( \alpha_{C2} \)% | 34.4 | 43.7 | 48.7 | 51.1 | 53.1 |
| \( \alpha_{C3} \)% | 9.7 | 4.3 | 2.1 | 0.6 | |
| \( \alpha_{C2}/(\alpha_{C1}+\alpha_{C2}) \) | 0.381 | 0.457 | 0.497 | 0.514 | 0.531 |
| \( \text{FC}_{ad}/C_{ad} \) | 0.227 | 0.309 | 0.326 | 0.341 | 0.348 |

where \( \alpha_{C1}, \alpha_{C2}, \) and \( \alpha_{C3} \) denote the carbon conversion ratio during Stages I, II, and III, respectively; \( m_{C1}, m_{C2}, \) and \( m_{C3} \) denote the relative carbon amounts in both CO and CO2 released during Stages I, II, and III, respectively; and \( m_C \) denotes the total relative carbon amount in both CO and CO2 released during the whole heating process. The relative carbon amount in CO and CO2 is obtained by the line integral of CO and CO2 release curves versus time.

With the increase in SD proportion, \( \alpha_{C1} \) and \( \alpha_{C2} \) gradually increased, which was mainly due to the increasing volatile contents and fixed carbon contents in samples. The \( \alpha_{C2}/(\alpha_{C1}+\alpha_{C2}) \) ratios were higher than the \( \text{FC}_{ad}/C_{ad} \) ratios for all samples, which demonstrated that there was a distinct overlap between the combustion of volatiles and fixed carbon. In addition, samples with higher SD proportions presented a much lower \( \alpha_{C3} \) due to the much lower carbonates in blends.

3.3. NOx Emission Properties. The NOx emission during combustion mainly resulted from three sources: fuel NOx, thermal NOx, and prompt NOx \(^{27} \) but the thermal NOx and prompt NOx were mainly generated above 1500 °C. Therefore, the NOx in this study was considered as fuel NOx, which came from nitrogen in the fuel. A flue gas analyzer was used to monitor the concentrations of O2, CO2, CO, NO, and NO2 during the isothermal combustion in a tube furnace, and NOx concentration \((c(\text{NOx}))\) was considered as the total concentration of NO and NO2. According to the monitoring results, the CO concentration was maintained below 50 mg/m³ during the whole combustion process, indicating the complete combustion of samples.

During volatile combustion, fuel nitrogen was partly transformed to NOx or N2 by complex oxidation–reduction reactions and generated heterocyclic-N, amine-N, and nitrile-N compounds, \(^{28} \) which were further released during char combustion. The NOx could be roughly divided into volatile-NOx released during the combustion of volatile and char-NOx released during char combustion. \(^{10} \) To obtain the correlation between NOx release and the combustion process, the conversion ratio of carbon in fuel to CO2 (\( \alpha_C \)) was studied, and \( \alpha_C \) as a function of time \( t \) is calculated as follows

\[
\alpha_C = \frac{m_t(CO_2)/m_0(CO_2)}{100}\%
\]

where \( m_t(CO_2) \) denotes the amount of CO2 released before time \( t \), and \( m_0(CO_2) \) denotes the total amount of CO2 released during the whole combustion process. The amount of CO2 is obtained by the line integral of CO2 release curves versus time.

3.3.1. NOx Emission Properties of SS and SD. The \( c(\text{NOx}) \) and \( \alpha_C \) as a function of time during the combustion of SS and SD at 800, 900, and 1000 °C are demonstrated in Figure 8. With the process of time, the carbon conversion proceeded accompanied by the successive release of volatile-NOx and

Figure 8. NOx release curves and \( \alpha_C \)-change curves during combustion of (a) SS and (b) SD.
char-NOx. With the temperature increasing, the carbon conversion of both SS and SD was accelerated, and the acceleration effect on SS was stronger than that on SD. SS always presented a much higher volatile-NOx peak value than SD at different temperatures due to its high nitrogen content, and both SS and SD presented a much stronger volatile-NOx release peak and a less distinct char-NOx release peak, indicating the much higher amounts of volatile-NOx than char-NOx. With the temperature increasing from 800 to 1000 °C, the enhanced devolatilization contributed to an earlier volatile-NOx peak with a higher peak value, and the release of char-NOx also took place much earlier due to the acceleration of char combustion. The boundary between volatile-NOx and char-NOx became weak due to the stronger overlap of devolatilization and char combustion at higher temperatures.

To investigate the specific correlation between NOx emission and the combustion process, the absolute NOx yield per gram of sample (m(NOx), mg/g) as a function of αc and its derivative with respect to αc (dm(NOx)/dαc, mg/g, representing the NOx release amount per unit carbon conversion) are illustrated in Figure 9. Particularly, the total carbon could be divided into volatile carbon and fixed carbon according to Table 1, which contributed to the definition of an imaginary boundary (the dotted lines in Figure 9) between volatile-NOx and char-NOx.

As shown in Figure 9a, the dm(NOx)/dαc of SS presented a declining trend during volatile combustion (the αc range of 0–70%) for all temperatures, indicating that more volatile nitrogen released during the earlier carbon conversion stage, whereas the dm(NOx)/dαc of SD in Figure 9b changed slightly during volatile combustion (the αc range of 0–65%) for all temperatures, indicating that the volatile-NOx of SD was released more uniformly. The nitrogen-containing materials in SS became more independent during the wastewater treatment process and were more likely to decompose with the temperature rising, while nitrogen in SD was mainly uniformly distributed in certain forms and tended to release accompanied by the consumption of volatiles.

The volatile-NOx release properties varied with temperature. SS presented similar volatile-NOx yields at 800 and 900 °C but exhibited dramatically lower volatile-NOx yields at 1000 °C, whereas the volatile-NOx yields of SD continued to decrease with the increase in temperature. The increasing temperature enhanced the reducing atmospheres of CO2, H2, and hydrocarbys by the acceleration of devolatilization, which significantly promoted the conversion from fuel nitrogen to N2 and contributed to volatile-NOx reduction. In addition, the high volatile content enhanced the effects of temperature on devolatilization, and therefore, SD presented a wider volatile-NOx-related temperature range.

Temperature also had impacts on char-NOx of both SS and SD. There was a significant increase in dm(NOx)/dαc during the char combustion of SS at both 800 and 900 °C, whereas the corresponding dm(NOx)/dαc at 1000 °C exhibited a declining trend and presented much lower values than that at 800 and 900 °C. SS presented similar and considerable char-NOx yields at 800 and 900 °C but showed a much lower char-NOx amount at 1000 °C. The abundant metal oxides in SD such as CaO and Fe2O3, as shown in Table 2, had positive effects on the reduction of NOx precursors by generating FeN4 and CaC2N2, and the transformation of fuel nitrogen to N2 was also enhanced by Ca,Fe2O5, especially at higher temperatures.29,30 High temperature also accelerated the generation of NOx by carbonate decomposition and contributed to NOx reduction. Meanwhile, SS ash with a high slagging potential31,32 enhanced the fixing of nitrogen in char with the fusion of eutectic mixtures33 at 1000 °C. Therefore, combustion at 1000 °C presented much less char-NOx yield.

Nonetheless, temperature had different impacts on char-NOx of SD. The corresponding dm(NOx)/dαc of char-NOx increased moderately during the whole char combustion process at 800 °C but rose sharply during the last char combustion stage after moderate increases at 900 and 1000 °C. The char-NOx during the last 10% carbon conversion process increased remarkably with the temperature increasing, and SD presented higher char-NOx yields at 900 and 1000 °C than at 800 °C. The increasing temperature enhanced the condensation process of combustible materials in SD and probably promoted the transfer of fuel nitrogen into char, which increased the char-NOx release of SD.

The total NOx yield and the conversion ratio of fuel nitrogen to NOx (αN) of SS and SD at different temperatures are shown in Figure 10, and αN is calculated as follows

\[
\alpha_N = \frac{m_N}{m_{NOx}} \times 100\%
\]

where \(m_N\) denotes the nitrogen amount in NOx released during the whole combustion process and \(m_{NOx}\) denotes the total nitrogen amount in the fuel.

The higher nitrogen content of SS as shown in Table 1 led to the higher NOx yields of SS to a great extent, and the NOx yields of SD at 800, 900, and 1000 °C were 27.0, 24.9, and 26.4% of that of SS, respectively. Nonetheless, the αN values of SS at 800, 900, and 1000 °C were smaller than those of SD by 2.29, 1.72, and 1.70%, respectively. The high ash content of SS

![Figure 9](http://pubs.acs.org/journal/acsodf)
slowed down the oxygen diffusion and provided abundant metal oxides with positive nitrogen reduction effects, both of which contributed to the smaller $\alpha_N$ of SS. Furthermore, the ash slagging of SS at high temperatures also fixed more nitrogen in ash. In addition, the total NO$_x$ yield of SD continued to decrease from 800 to 1000 °C, whereas the total NO$_x$ yield of SS experienced a tiny increase from 800 to 900 °C and a remarkable decrease from 900 to 1000 °C, which suggested that the NO$_x$ emission of higher volatile fuels was more sensitive to temperature.

3.3.2. NO$_x$ Emission Properties of Blends. The composition of samples changed with the blending ratio, which had important impacts on NO$_x$ emission properties during combustion. The NO$_x$ release curves versus time, and NO$_x$ yield and $dm$(NO$_x$)/$d\alpha_C$ curves versus carbon conversion ratio at 800, 900, and 1000 °C are demonstrated in Figure 11.

The NO$_x$ emission varied remarkably with the blending ratio. As shown in Figure 11, with the SD proportion increasing, the volatile-NO$_x$ concentration reduced significantly, and the total NO$_x$ yield decreased for all temperatures owing to the decreasing nitrogen content. However, the blending ratio exhibited uncertain effects on char-NO$_x$ at different temperatures.

Blends with higher SD proportions presented lower $dm$(NO$_x$)/$d\alpha_C$ during char combustion and released less char-NO$_x$ at both 800 and 900 °C. The char-NO$_x$ peaks were visible at 800 °C for all blends as shown in Figure 11c, indicating the existence of a concentrated char-NO$_x$ release process, whereas all blends exhibited relatively steady char-NO$_x$ release during the whole char combustion process at 900 °C as shown in Figure 11f. In addition, at 1000 °C, the $dm$(NO$_x$)/$d\alpha_C$ during the early and middle stages of char combustion (the $\alpha_C$ range of 60–85%) decreased with the SD proportion increasing, but blends with higher SD proportions presented higher $dm$(NO$_x$)/$d\alpha_C$ during the last char combustion process (the $\alpha_C$ range of 90–100%), as shown in Figure 11i, because the char-NO$_x$ of SD tended to release during the last char combustion stage at 1000 °C.

Furthermore, to investigate the effects of temperature on NO$_x$ emission for a specific blend, the NO$_x$ yields and emissions were studied. Figure 11 demonstrates the NO$_x$ release curves and NO$_x$ yields versus $\alpha_C$ of blends: (a), (b), and (c) at 800 °C; (d), (e), and (f) at 900 °C; (g), (h), and (i) at 1000 °C.
Both SS5SD5 and SS3SD7 presented similar volatile-NO\textsubscript{x} changing rules with temperature to SS, and SS1SD9 exhibited similar volatile-NO\textsubscript{x} changing properties with temperature to SD. The $\frac{\text{dm(NO}}{\text{d} \alpha C}$ during volatile combustion of SS5SD5 and SS3SD7 decreased slightly from 800 to 900 °C and then decreased significantly from 900 to 1000 °C. However, the volatile-NO\textsubscript{x} of SS1SD9 continued to decrease dramatically from 800 to 1000 °C. The increase in volatile content strengthened the effects of temperature increase on volatile-NO\textsubscript{x} release due to the enhanced local reducing atmosphere.

With the increase in temperature, the release of char-NO\textsubscript{x} of three blends tended to move toward the earlier carbon conversion process, suggesting that the nitrogen in char was more sensitive to temperature than fixed carbon and the release of char-NO\textsubscript{x} proceeded earlier than char combustion. The char-NO\textsubscript{x} amount of SS5SD5 changed slightly from 800 to 900 °C and then decreased from 900 to 1000 °C, presenting similar properties to SS. The decrease of char-NO\textsubscript{x} from 900 to 1000 °C was mainly due to the severer fusion of eutectic mixtures and the relatively stronger reduction effects of metal oxides in SS at 1000 °C. However, the char-NO\textsubscript{x} yields of SS1SD9 continued to increase from 800 to 1000 °C, presenting similar properties to those of SD due to its high SD proportion, and the char-NO\textsubscript{x} yield of SS3SD7 increased from 800 to 900 °C and changed slightly from 900 to 1000 °C, which was affected by both SS and SD.

3.3.3. Synergistic Effects on NO\textsubscript{x} Emission. To evaluate the synergistic effects of co-combustion, the experimental and theoretical values of the total NO\textsubscript{x} yield and $\alpha_N$ of three blends at different temperatures are compared in Figure 13.
theoretical NO\textsubscript{x} yield \( (m(\text{NO}_\text{x})_T) \) during cocombustion is calculated as follows

\[
m(\text{NO}_\text{x})_T = p_{\text{SD}} m(\text{NO}_\text{x})_{\text{SD}} + p_{\text{SS}} m(\text{NO}_\text{x})_{\text{SS}}
\]

(6)

where \( m(\text{NO}_\text{x})_{\text{SD}} \) and \( m(\text{NO}_\text{x})_{\text{SS}} \) are the experimental values of \( m(\text{NO}_\text{x}) \) for SD and SS, respectively; and \( p_{\text{SD}} \) and \( p_{\text{SS}} \) are the mass proportions of SD and SS in blends, respectively. The theoretical \( \alpha_N \) is calculated by eq 5 using the theoretical \( m_N \) corresponding to \( m(\text{NO}_\text{x})_T \).

Compared to theoretical values, the \( \text{NO}_\text{x} \) yield of SS5SD5 decreased by 4.9, 7.7, and 5.5% at 800, 900, and 1000 °C, respectively, and the corresponding \( \alpha_N \) decreased by 0.29, 0.34, and 0.26% at 800, 900, and 1000 °C, respectively. Cocombustion influenced the local atmosphere during devolatilization and had positive impacts on reducing volatile-\( \text{NO}_\text{x} \) from SS but negative impacts on volatile-\( \text{NO}_\text{x} \) reduction from SD. The \( \text{NO}_\text{x} \) from SS took up the vast majority of the total \( \text{NO}_\text{x} \) of SS5SD5, and therefore SS5SD5 presented an overall volatile-\( \text{NO}_\text{x} \) reduction effect. Meanwhile, compared to individual SS, the more fixed carbon (mainly from SD) strengthened the reducibility of char, and the SS ash in SS5SD5 decelerated the char combustion of SD and lengthened the lifetime of fixed carbon, both of which contributed to the reduction of \( \text{NO}_\text{x} \) from SS. In addition, the abundant metal oxides in SS ash promoted the reduction of \( \text{NO}_\text{x} \) from SD.

The \( \text{NO}_\text{x} \) yield of SS3SD7 decreased by 3.7, 4.2, and 4.8% compared to the theoretical values at 800, 900, and 1000 °C, respectively, and the \( \alpha_N \) decreased by 0.23, 0.26, and 0.24% at 800, 900, and 1000 °C, respectively. During the combustion of SS3SD7, the \( \text{NO}_\text{x} \) from SS and SD presented approximate amounts. Compared to individual SS, the higher volatile content of SS3SD7 generated a stronger reducing atmosphere and promoted volatile-\( \text{NO}_\text{x} \) reduction from SS; the fixed carbon from SD and the considerable SS ash also contributed to \( \text{NO}_\text{x} \) reduction; meanwhile, the high SD proportion of SS3SD7 led to a much looser char structure, which enhanced oxygen diffusion and promoted NO\textsubscript{x} emission. With the comprehensive effects of various factors, SS3SD7 presented a positive \( \text{NO}_\text{x} \) reduction performance but the synergistic effects were slightly weaker than those of SS5SD5.

Compared to theoretical values, the \( \text{NO}_\text{x} \) yield of SS1SD9 increased by 5.1% at 800 °C and decreased by 3.7% and 6.7% at 900 and 1000 °C, respectively, and \( \alpha_N \) presented an increase of 0.36% at 800 °C but decreased by 0.25 and 0.38% at 900 and 1000 °C, respectively. During the combustion of SS1SD9, the \( \text{NO}_\text{x} \) from SD took up the majority of the total \( \text{NO}_\text{x} \). SS1SD9 presented a much looser structure than SS during combustion, which promoted the oxidation of fuel nitrogen, although SS1SD9 presented a much stronger reducing atmosphere during devolatilization than individual SS. Meanwhile, the small amount of SS ash played little role in \( \text{NO}_\text{x} \) reduction. Therefore, SS1SD9 presented negative \( \text{NO}_\text{x} \) reduction effects at 800 °C. Nonetheless, the effects of reducing atmosphere on volatile-\( \text{NO}_\text{x} \) reduction became enhanced with an increase in temperature, and SS1SD9 showed a positive \( \text{NO}_\text{x} \) reduction performance at 900 and 1000 °C.

In conclusion, the synergistic effects on \( \text{NO}_\text{x} \) emission during cocombustion were complex and influenced by various factors. In this study, the \( \text{NO}_\text{x} \) reduction effects of SS1SD9 were highly dependent on combustion temperature, and SS5SD5 showed better \( \text{NO}_\text{x} \) reduction performances than SS3SD7 at all temperatures. Nonetheless, the \( \text{NO}_\text{x} \) yield of SS5SD5 remained high and the application of SS5SD5 was also severely restricted by the low calorific value and worse combustion characteristics. Synthetically considering the SS disposal capacity, combustion characteristic, and \( \text{NO}_\text{x} \) yield, SS3SD7 is more recommended in practical applications.

4. CONCLUSIONS

The thermal behaviors and \( \text{NO}_\text{x} \) release properties during combustion of SS, SD, and their blends were studied, and the main conclusions are summarized as follows.

1. All samples experienced dehydration, volatile combustion, char combustion, and ash transformation during the heating process. The conversion of hydrogen to \( \text{H}_2\text{O} \) mainly occurred during volatile combustion, whereas the conversion of carbon to \( \text{CO}_2/\text{CO} \) proceeded during the whole combustion process.

2. SD exhibited better combustion characteristics than SS, and with the SD proportion increasing, blends exhibited better combustion performances. Compared to theoretical conditions, the burnout ratio increased due to the looser structure of SD, but the combustion of char (mainly from SD) was decelerated by SS ash during cocombustion.

3. SS emitted more \( \text{NO}_\text{x} \) mainly due to its high nitrogen content than SD but showed a lower \( \alpha_N \) owing to its high ash content and high metal oxide content like \( \text{CaO} \) and \( \text{Fe}_2\text{O}_3 \). Volatile nitrogen in SS existed in less stable forms than that in SD, and the volatile-\( \text{NO}_\text{x} \) release rate versus carbon conversion ratio presented a declining trend for SS but remained relatively stable for SD.

4. Samples with higher SD proportions released less \( \text{NO}_\text{x} \) due to the lower nitrogen contents. The increase in temperature was more likely to influence the \( \text{NO}_\text{x} \) emission of higher volatile samples. The \( \text{NO}_\text{x} \) yields of SD and SS1SD9 continued to decrease from 800 to 1000 °C, whereas the \( \text{NO}_\text{x} \) yields of SS, SS5SD5, and SS3SD7 changed slightly from 800 to 900 °C and decreased remarkably from 900 to 1000 °C.

5. Cocombustion exhibited synergistic effects on \( \text{NO}_\text{x} \) emission according to the difference between experimental and theoretical \( \text{NO}_\text{x} \) yields. The blending ratio and temperature affected the synergistic effects by affecting the local atmosphere during devolatilization, oxygen diffusion rate, and the reducivity of char. SS5SD5 and SS3SD7 always presented a positive \( \text{NO}_\text{x} \) reduction performance, and SS1SD9 had opposite \( \text{NO}_\text{x} \) reduction effects at different temperatures. SS5SD5 showed better overall \( \text{NO}_\text{x} \) reduction effects, but its \( \text{NO}_\text{x} \) yields remained high due to its high nitrogen content.

Synthetically considering the SS disposal capacity, combustion characteristic, and \( \text{NO}_\text{x} \) yield, an SS proportion around 30% in blends is more recommended in practical applications, and a study on the correlation between \( \text{NO}_\text{x} \) release and carbon conversion can lay the foundation for efficient initial \( \text{NO}_\text{x} \) control methods during combustion. In addition, due to the differences between bench-scale tests and complicated industrial situations, it is suggested to conduct some relevant actual field tests in the future to obtain a more comprehensive correlation between \( \text{NO}_\text{x} \) release and fuel status.
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Notes
The authors declare no competing financial interest.

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