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Synergistic effects, gaseous products, and evolutions of NO_x precursors during (co-)pyrolysis of textile dyeing sludge and bamboo residues



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GRAPHICAL ABSTRACT



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ABSTRACT

This study aimed to investigate the synergistic influences of the textile dyeing sludge (TDS) and bamboo residues (BR) co-pyrolysis, and its effects on the formation mechanisms of NH_3 and HCN. The mass loss rate was lower for TDS than BR, with the co-pyrolysis with 50% BR exerting the strongest synergistic effect. The pyrolysis stages 1 (< 400 °C) and 2 (400 – 800 °C) were best described using the diffusion and third-order reaction mechanisms, respectively. Activation energy and frequency factor were lower for the pyrolysis of TDS than BR. The addition of no less than 50% BR significantly increased the emissions of CO_2 , CO, CH_4 , C=O, and C–O and reduced the aromatic compounds. The thermal stability of N-A structure was lower in TDS than BR. The co-pyrolysis with 50% BR significantly inhibited the formations of NH_3 and HCN and improved the aromaticity of biochar. This may due to the weakened hydrogenation reaction at N sites, the enhanced conversion of NH_3 , the inhibition of the ring cleavage in the char-secondary cracking, and the formation of more quaternary-N. Our results provide insights into the co-treatment of TDS and BR, and controls over NO_x precursors for a cleaner energy production.

1. Introduction

The rapid economic and industrial growth has resulted in a large

amount of industrial wastes that need to be treated as a feedstock in a circular economy. Textile dyeing sludge (TDS) is such a waste stream generated by the wastewater treatment plants of the textile industries.

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Since TDS contains toxic components such as dyes, pathogens, additives, and heavy metals (Huang et al., 2018), its improper disposal and treatment pose a serious hazard to the natural environment and public health. 10 tons of TDS with the water content of 80% can be produced per 1000 tons of textile dyeing wastewater (Zhang et al., 2018a). About 21 million tons of TDS are generated annually in China alone (Liu et al., 2018). Its traditional disposal methods such as landfill and incineration are being scrutinized increasingly due to their unpredictable land pollution risks and toxic incineration smoke emissions (Dou et al., 2017). Meanwhile, the non-renewability and adverse environmental impacts of fossil fuels have driven countries to seek the clean and renewable energy technologies (Chen et al., 2020). The pyrolysis process has come to the forefront as a more economically and environmentally efficient way to achieve the second-generation bioenergy conversion (Navas-Anguita et al., 2019), and thus, stands as a promising alternative management option to avoid the serious environmental issues associated with the TDS disposal (Xia et al., 2020). Not only can the TDS pyrolysis break down potential organic pollutants and pathogens but also helps to recover high value-added syngas, biooils (Sun et al., 2019a; Raheem et al., 2018), and biochar products with environmental application value (Cho et al., 2019). Thus, the TDS pyrolysis treatment is relatively cleaner and more eco-friendly than are the traditional disposal methods (Ran et al., 2019).

However, the inherent defects of high moisture and ash contents in TDS restrict its pyrolysis performance including the generation of high quality products (Chen et al., 2018a). Not only can the addition of second-generation feedstocks with the higher volatiles and carbon contents such as agricultural and forestry residues offset the short-comings of the TDS pyrolysis alone (Wang et al., 2016a), but also the second-generation feedstocks are carbon-neutral and do not compete with land and food resources (Yang et al., 2019a). Bamboo residues (BR) are one such feedstock since bamboo forests grow extremely fast and are globally abundant covering 31.5 million hectares of land (Yuen et al., 2017). Bamboo stalks have many industrial uses, while BR such as leaves and branches have not been tapped for industrial applications and are discarded in large quantities. Therefore, the combined treatment of BR and TDS is expected to be economically feasible and environmentally benign so as to jointly eliminate two waste streams.

In the related literature, synergy between some feedstocks was verified for the co-pyrolysis. For example, Wang et al. (2016a) reported that the co-pyrolysis of sewage sludge and wheat straw accelerated the reaction process and improved the gas and liquid yields. Hu et al. (2017) showed that adding petroleum sludge to sawdust increased the heating value of pyrolysis oil. null[pointed out that the addition of sludge had a catalytic effect on the pyrolytic products of bagasse. nullU found that the co-pyrolysis of corn straw and sewage sludge reduced NO emission. The co-pyrolysis of red mud and lignin was reported to have enhanced the production of H₂ and CO, with its resultant biochar had excellent environmental application potential (Cho et al., 2019). In simple terms this means that co-pyrolysis of TDS and BR can not only effectively compensate for the inherent defects of sludge itself, but also may have interaction to affect the pyrolysis process. However, no qualitative research exists as to synergistic interactions between TDS and BR in terms of the co-pyrolysis performance and products including pollutant emission. For example, the NO_x precursors (mainly NH_3 and HCN) from the pyrolysis of sludge with a relatively high N content have always been concerning (Zhan et al., 2018a) since they lead to acid depositions and photochemical smog, thus adversely affecting the human and ecosystem health (Seo et al., 2020). Previous studies focused on the individual materials in terms of the pathways of the conversion of N in sewage sludge or biomass to NO_x precursors (Zhan et al., 2019; Tian et al., 2014; Chen et al., 2017). To what extent and how the co-pyrolysis of BR and TDS may exert a positive or negative impact on the formation of NO_x precursors still remain to be explored in detail. Filling the aforementioned knowledge gaps may pave the way for understanding and controlling interactions for the cleaner bioenergy production.

In terms of elucidating the pyrolysis process, thermogravimetric (TG) analysis is an effective method to monitor the real-time mass loss, decomposition characteristics, and kinetic parameters as a function of the operational conditions such as temperature and blend ratio (Zou et al., 2019). Principal component analysis (PCA) can be used for dimensionality reduction and clustering of numerous data for further analysis. TG coupled to Fourier transform infrared spectroscopy (FTIR) can detect the evolution of gaseous substances and functional groups (Zhang et al., 2018b). Since the pyrolysis of sludge produces a large amount of chars (Raheem et al., 2018), X-ray photoelectron spectroscopy (XPS) is used to characterize their N structures (Wang et al., 2017) to better clarify the influence mechanism of the co-pyrolysis on the formation of NO_x precursors. Therefore, using the above analysis techniques, the objective of this experimental study was three-fold: to characterize and quantify (1) the synergistic and kinetic mechanisms of the (co-)pyrolysis of TDS and BR; (2) the formation and emission characteristics of their gaseous products; and (3) the effects of the evolutions of the char-N structures on the NH₃ and HCN formations.

2. Materials and methods

2.1. Sample preparation and physicochemical characterization

TDS was sampled from a textile printing and dyeing plant in the Guangdong province, China, while BR was gathered from a bamboo forest of the Henan province, China. The obtained samples were sundried, ground to a size of less than 74 μ m using a grinder and stored in a sealed bag for subsequent tests. The five blended samples of TDS and BR were prepared using the TDS:BR ratios (wt.%) of 9:1, 7:3, 5:5, 3:7, and 1:9 coded as 0.9TDS, 0.7TDS, 0.5TDS, 0.3TDS, and 0.1TDS, respectively. The basic physicochemical characteristics of TDS and BR are presented in Table 1.

2.2. TG-FTIR experiments and their data processing

The TG-FTIR (TG209 F1, Netzsch, Germany/iS50 FT-IR, Thermo, America) experiments were performed in the N₂ atmosphere. The heating program was set to heat from room temperature to 1000 °C at a heating rate of 20 °C/min. The other experimental conditions can be found in our previous research (Hu et al., 2020). FTIR analysis was performed using OMNIC software.

Table 1

Physicochemical properties of textile dyeing sludge (TDS) and bamboo residue (BR) samples.

Sample	Proximate analysis (wt.%) ^a				Ultimate analysis (wt.%) ^b					HHV (MJ/kg) ^c
	М	v	А	FC	С	Н	Ν	S	0	
TDS BR ^d	9.03 6.94	48.24 66.98	34.23 12.40	8.50 13.67	24.68 40.51	5.00 5.72	3.00 1.30	3.50 0.13	20.56 33.01	10.59 16.79

^a The moisture (M), volatiles (V), ash (A) and fixed carbon (FC) contents of TDS were analyzed according to GB/T.212-2008.

^b Tested using an elemental analyzer (vario EL cube, Elementar, Germany).

^c The higher heating value (HHV) was tested using a microcomputer calorimeter (WZR-1T-CII, Bente, China); and ^d Data from a previous study (Hu et al., 2020).

In order to further determine the dominant factors of the co-pyrolysis, principal component analysis was applied to derivative TG (DTG) data of all samples using SPSS 19.0. The standardization of the DTG data for all the samples was realized. Factor analysis in the dimensionality reduction function was performed on all the standardized DTG data. The principal component was selected using the extraction method. The number of extraction factors was set to 2. The rotation method was based on the orthogonal approach with Kaiser standardization. Finally, two principal components (PC1 and PC2) were extracted.

2.3. Kinetic analyses

The reaction rate of a heterogeneous solid-state reaction is usually described thus (Cao et al., 2019):

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{1}$$

where *t* is the reaction time (min); $f(\alpha)$ is the reaction mechanism; and α is the conversion rate of the material:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \tag{2}$$

where m_i , m_t and m_f are the initial, real-time at time *t* and final masses of the sample, respectively.

At a linear heating rate where $\beta = dT/dt$, Eq. (1) can be transformed into Eq. (2) according to the Arrhenius equation as follows (Wang et al., 2016b):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha)$$
(3)

where *A* is the frequency factor; s^{-1} ; *R* is the universal gas constant, 8.314 J/(mol·K); E_{α} is the apparent activation energy, kJ/mol; and *T* is the absolute temperature, K.

Integrating both sides of Eq. (3) yields Eq. (4) below (Liu et al., 2017):

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE_a}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx = \frac{AE_a}{\beta R} \cdot p(x)$$
(4)

 $G(\alpha)$ is the integral form of $1/f(\alpha)$, while p(x) has no exact solution. According to the Coats-Redfern approximate expression, Eq. (4) is transformed into the following (Song et al., 2020):

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_{\alpha}}\left(1 - \frac{2RT}{E_{\alpha}}\right)\right] - \frac{E_{\alpha}}{RT}$$
(5)

By plotting $\ln \left[\frac{G(\alpha)}{T^2}\right]$ versus $\frac{1}{T}$, and fitting the best-fit line with the highest coefficient of determination (R^2), E_α can be estimated from the slopes $\left(-\frac{E_\alpha}{R}\right)$ of this fit. In general, if $E_\alpha \gg 2RT$ ($1 - \frac{2RT}{E_\alpha} = 1$), then A can be estimated using the intercept $\left(\ln \frac{AR}{BE_\alpha}\right)$.

2.4. Biochar preparation

A tube electric furnace (SK-G06123K, Zhonghuan, China) was used in the pyrolysis experiments to prepare the biochar samples. The reactor was a quartz tube, while the sample carrier was a ceramic crucible. One end of the air inlet was connected to the gas cylinder (N₂ of 99.99% purity), while the flow was controlled at 200 mL/min, and the air outlet was connected to an exhaust gas treatment device. About 5 g of the sample were weighed for each experiment and placed in a constant temperature zone. The sample was heated from room temperature to the specified temperature at the same heating rate as with TG-FTIR analysis (20 °C/min) and held for 30 min. The heating program was closed once the experiment was completed. During the period of (co-) pyrolysis experiments until the sample was cooled to room temperature, the device was kept sealed and filled with N₂. Finally, biochar was weighed to estimate its yield and vacuumed for preservation. The experiment was performed in triplicate, with the average value being taken as the experimental result.

2.5. Characterization of char-N structures

X-ray photoelectron spectroscopy (Escalab 250Xi, Thermo Fisher, America) was used to determine the morphology of C and N elements in the control (TDS and BR) and biochar samples. The vacuum in the analysis chamber was higher than 5.0 \times 10⁻¹⁰ mBar. During the analysis, the beam spot of the X-ray source (Al Ka) was 650 um, while the electron emission angle was 90° . The voltage and current were set to 15 kV and 15 mA, respectively. The analyzer mode was CAE, with a passing energy of 100.0 eV and an energy step size of 1.000 eV. The XPS tests of all the samples were performed under the same conditions. For the elemental signal of each sample, the maximum peak with C1s binding energy corresponds to 284.6 eV (C-C bond) as the calibration reference, and the smart-type background was subtracted. The binding energies assigned to different N structures were (Zhan et al. (2018b)): (1) N-A: including amine-N, amino-N, and protein-N/amide-N, 399.8 (± 0.3) eV; (2) N-6: pyridinic-N, 398.8 (± 0.2) eV; (3) N-5: pyrrolic-N, 400.4 (\pm 0.2) eV; (4) N-Q : quaternary-N/inorganic-N, 401.4 (\pm 0.2) eV; and (5) N-X: oxide-N, 402.0-405.0 eV. All the analysis was conducted using Avantage software.

3. Results and discussion

3.1. (Co-)pyrolysis behaviors and synergistic effects

The (co-)pyrolysis behaviors of TDS and BR are shown in Fig. 1a and b. The mass loss during the pyrolysis was more for BR than TDS. The maximum mass loss rate of BR (336 °C, -15.75 %/min) was 4.62 times that of TDS (355 °C, -3.41 %/min) indicating that BR had a better devolatilization performance. With the increased BR addition, the (D)TG curves showed a regular change, while the maximum mass loss rate gradually increased from 4.52 to 14.62 %/min. To capture the individually complex pyrolysis behaviors of TDS and BR, Gaussian functions in Peakfit 4.0 software were used to deconvolve their DTG curves to clarify the overlapping sub-reactions (Fig. 1c). The pyrolysis process of TDS was mainly divided into the following three stages (Lin et al., 2017): (1) dehydration (up to 200 °C) mainly eliminating cells and externally bound water and corresponding to the separated peak 1, with a mass loss of 7.41%; (2) the main pyrolysis reaction stage (200-800 °C) corresponding to the separated peaks 2 (200-260 °C, the decomposition of light components), 3 (260-410 °C, the decomposition of medium molecular weight components), and 4 (410-800 °C, the decomposition of heavy carbon substances), with a total mass loss of 43.37%; and (3) the decomposition of inorganic and carbonaceous substances (800-1000 °C), with a mass loss of 2.62%. The pyrolysis of BR exhibited a similar reaction pattern, but the temperature of its main pyrolysis reaction stage ranged from 200 to 600 °C, which mainly involved the thermal degradation of hemicellulose (peak 2), cellulose (peak 3), and lignin (peak 4) (Chen et al., 2015a), with a mass loss of 62.57%.

For the blends, the main co-pyrolysis stages involved were more complicated. PCA analysis was used to reduce the dimensionality of these numerous DTG data in order to facilitate the observation and analysis of the dominant reactions (Cai et al., 2019). The rotation was converged after the three iterations, and thus, the two principal components (PC1 and PC2) accounted for 58.20% and 41.45% of the total variance, respectively. The sum of the cumulative squared loads of the two components met a typical threshold of 80% (Xie et al., 2018). According to the PCA score chart (Fig. 1d) with PC1 and PC2 as the definition axes, PC1 and PC2 represented BR and TDS, respectively. With the increased BR ratio, the blend gradually dispersed and pointed to PC1 (Fig. 1d). The difference between the PC2 fractions of TDS and



Fig. 1. (Co-)pyrolysis characteristics of TDS and BR: (a) TG curves, (b) DTG curves, (c) deconvolution of DTG curves for TDS and BR, (d) principal components in a rotating space, (e) factor scores of principal components, and (f) deviation with blend ratio.

0.9TDS was not by more than 0.1, while BR, 0.1TDS, and 0.3TDS were clustered together (the difference was also not by greater than 0.1). These more aggregated samples illustrated their similar pyrolysis characteristics. The pyrolysis behaviors of 0.5TDS and 0.7TDS most differed from those of the control samples, thus it was difficult to distinguish the contribution degree of TDS and BR in a certain temperature range, the thermodynamic modes of PC1 and PC2 were used to illustrate the pyrolysis processes of these samples (Fig. 1e).

In Fig. 1e, the factor scores indirectly mapped the mass loss rates of the components, thus indicating whether PC1 or PC2 contributed more to the mass loss rate in a certain temperature range. The five peaks identified in Fig. 1e were peak 1 at below 200 °C due to the water evaporation, peaks 2, 3 and 4 in the range of 200 - 400 °C, and peak 5 at above 400 °C. In the range of 200 - 265 °C (peak 2, 215 °C), the decomposition of light organic volatiles in TDS dominated (Chen et al., 2015b). PC1 dominated the pyrolysis reaction (peak 3, 334 °C) from

265 to 352 °C due to the rapid decomposition of (hemi)celluloses in BR. In the narrow range of 352 – 400 °C, PC1 began to gradually approach zero, while PC2 became the main reaction (peak 4, 368 °C). At a later higher temperature (> 400 °C), only the mass loss peak (peak 5, 458 °C) of PC2 was observed. Overall, PCA analysis determined the dominant reaction in the complex pyrolysis process of the blends. The pyrolysis of the blends in the range of 200 – 400 °C (stage 1) involved the most complex reactions, and the reactions that dominated this stage were thus: decomposition of light organic volatiles in TDS → volatilization and cracking of (hemi) cellulose in BR → decomposition of medium molecular weight components in TDS. The co-pyrolysis of the blends in the range of 400 – 800 °C (stage 2) was basically dominated by the decomposition of heavy carbon substances in TDS, which may involve the pyrolysis of some protein units and the secondary cracking of chars/ tars (Lin et al., 2017).

In order to better determine the interaction strengths, the deviations of experimental (TG_{exp}) and theoretical TG (TG_{cal}) were compared. TG_{cal} was estimated as follows (Zhang et al., 2020):

$$TG_{cal} = x \cdot TG_{TDS} + (1 - x) \cdot TG_{BR}$$
(6)

where *x* is the TDS fractions of the blends; and TG_{TDS} and TG_{BR} represent the experimental TG curves of TDS and BR, respectively. The deviation formula to measure the strength of interactions was as follows (Liu et al., 2019):

$$Deviation(\%) = \left(\frac{\mathrm{TG}_{\mathrm{exp}} - \mathrm{TG}_{\mathrm{cal}}}{\mathrm{TG}_{\mathrm{cal}}}\right) \times 100\%$$
(7)

The larger the deviation was as a function of the blend ratio and temperature, the stronger the interaction was (Fig. 1f). The positive deviations represented the less mass loss given the theoretical values, while the negative deviations showed the more substance escapes. With 0.9TDS, the zone of 100-250 °C was dominated by the enhanced volatilization of its water and light organics. With the increased BR ratio, the interaction was concentrated basically in the range of 250-500 °C. At this stage, the release of volatiles from the co-pyrolysis appeared to be suppressed. The strongest interaction occurred in the range of 260-350 °C. Combined with PCA analysis, it was found that the strongest interaction range was consistent with the temperature range of PC1 as the main reaction, which indicated that the co-pyrolysis exerted the greatest influence on (hemi)cellulose in BR. Among all the samples, the largest deviation occurred with 0.5TDS. PCA analysis also showed that the co-pyrolysis behavior at this blend ratio significantly differed from the pyrolysis behavior of TDS or BR. Thus, it can be inferred that the addition of 50% BR may exerted the greatest synergistic effect on the co-pyrolysis.

3.2. Co-pyrolysis kinetics

In the range of stages 1 and 2, the kinetic triplets were estimated (α \in [0.1, 0.9] at an interval of 0.05). The data were fitted to the 15 common reaction models (details were shown in the supplementary materials) whose results with the highest R^2 are shown in Table 2. All the samples in stage 1 were best described using the diffusion mechanism (the D3 model), except for 0.7TDS best described by the D4 model. In other words, heat or gas diffusion plays a major role in the (co-)pyrolysis reaction in the range of 200-400 °C (Mallick et al., 2018), where the escape of volatiles, and the formation of biochar dominated. The best-fit model for the reaction of the samples in stage 2 belonged to the third-order reaction model, the random nucleation of three nuclei on a single particle (Zhang et al., 2019). Regardless of the stage, the activation energy value of the TDS pyrolysis was lower than that of the BR pyrolysis based on the CR method. The activation energy estimate is usually proportional to the thermochemical stability of the material (Qu et al., 2019). The structural units were thermally degraded more easily in TDS (proteins, lipids, and carbohydrates) than BR (hemicellulose, cellulose, and lignin), thus requiring less energy to break the chemical bonds. With the increased BR ratio, the activation energy gradually increased from 78.61 to 155.86 kJ/mol in stage 1. In stage 2, the increased addition of BR grew the activation energy from 118.71 to 133.01 kJ/mol. For the solid-state heterogeneous reactions, a higher frequency factor usually means that the material has more reaction sites (Liu et al., 2017). The addition of BR increased the frequency factor (Table 2) and provided more reaction sites for the copyrolysis, which improved the collision strength between the reactive molecules (Li et al., 2019).

3.3. Evolution characteristics of gaseous products

The IR bands are summarized in Table 3 for the eight key gaseous products of NH_3 , HCN, CO_2 , CO, CH_4 , C=O, C–O, and aromatic compounds. The real-time evolution characteristics of the gaseous products during the (co-)pyrolysis are shown as a function of the temperature and the blend ratio in Fig. 2.

3.3.1. Emission characteristics of major C-containing substances

CO₂ was the gas product with the highest absorbance during the (co-)pyrolysis of all the samples. All the samples reached the maximum release strength of CO₂ at about 340 °C. The CO₂ emission occurred in a wide range of 100 – 800 °C from the TDS pyrolysis, and in a range of 150 – 500 °C from the BR pyrolysis due to the cleavage and reformation of some thermally unstable functional groups such as carboxy (–COOH), carbonyl (CO=), and ether bonds (R–OR–) (Mehmood et al., 2019). In the range of 600 – 700 °C, the CO₂ release from the BR pyrolysis reappeared probably due to the decomposition of CaCO₃ (CaCO₃ → CaO + CO₂). The maximum CO₂ absorption peak intensity of TDS was about 5.5 times as low as that of BR. With the addition of BR, the CO₂ release from the co-pyrolysis gradually increased (Fig. 2a).

The CO emission (Fig. 2b) was attributed to the breaking of ether bond and carbonyl at below 800 °C. The Boudouard reaction (CO₂ + C → 2CO) between char and CO₂ at above 800 °C was the main contributor to the CO emission (Fang et al., 2017). The CO emission was lower from TDS than BR at below 800 °C. This may be since TDS contained less volatiles than did BR, or TDS contained fewer ether bonds and carbonyl groups than did BR. However, TDS released more CO at above 800 °C. This suggested that the Boudouard reaction of TDS at above 800 °C was more advantageous. The CH₄ release intensity of TDS was slightly lower than that of BR (Fig. 2c). At below 500 °C, the side chain fracture was the main source of CH₄. The demethylation of methoxy group (O−CH₃) may also generate CH₄ at above 400 °C (Mehmood et al., 2019). Overall, the co-pyrolysis emitted more CO and CH₄ than did TDS; however, the BR ratios of below 30% exerted a less impact on CO and CH₄ (Fig. 2b−c).

The absorption peaks of C=O (in carboxylic acids, ketone, aldehyde, and ester) and C-O (in alcohols, phenols, and ethers) are usually the condensable parts of the pyrolytic products (Tahir et al., 2019). There was only one peak of C=O and CO- released by all the samples, with their release range occurring between 200 and 600 °C (Fig. 2d and e). The decomposition of amino acids, carbohydrates and lipids in TDS produced the C=O groups, while the decomposition of lipids also produced the C-O groups (Chen et al., 2018b). The C=O and CO- absorption peaks produced were higher with the BR than TDS pyrolysis due to the pyrolysis products of (hemi)celluloses and lignin. This in turn showed that BR produced more CO than did TDS at below 800 °C. Fig. 1d and e showed that the addition of BR improved the yields of C=O and CO- which in turn increased acid, ketone, aldehyde, ester, alcohol, phenol, and ether.

The aromatic compounds emitted from the individual pyrolysis of TDS and BR had the two peaks, with the release ranges of 200-600 °C for TDS and 200-800 °C for BR (Fig. 2f). The release intensity of the aromatic compounds was higher from the TDS than BR pyrolysis. For the first peak of TDS at about 360 °C, protein was initially decomposed

Table 2				
Kinetic parameters	of the (co-)pyrolysis	of TDS	and	BR.

Stage	Sample	Reaction model	<i>f</i> (α)	E_{α} (kJ/mol)	$A (s^{-1})$	R^2
1 (200–400 °C)	TDS 0 9TDS	Diffusional Diffusional	$\frac{[(3/2)(1-\alpha)^{2/3}]}{[1-(1-\alpha)^{1/3}]}$	78.61 87.57	2.28×10^{2} 1 40 × 10 ³	0.9938
	0.7TDS	Diffusional	$\frac{[(3/2)(1-\alpha)^{1/3}]}{[(3/2)(1-\alpha)^{1/3}]/[1-(1-\alpha)^{1/3}]}$	99.28	1.21×10^4	0.9965
	0.5TDS 0.3TDS	Diffusional	$\frac{[(3/2)(1-\alpha)^{2/3}]}{[(3/2)(1-\alpha)^{2/3}]/[1-(1-\alpha)^{1/3}]}$	132.77 151.33	1.65×10^{6} 7.86 × 10 ⁸	0.9973
	0.1TDS BR	Diffusional Diffusional	$[(3/2)(1-\alpha)^{2/3}]/[1-(1-\alpha)^{1/3}]$ $[(3/2)(1-\alpha)^{2/3}]/[1-(1-\alpha)^{1/3}]$	157.91 155.86	3.21×10^9 2.29×10^9	0.9993 0.9990
2 (400-800 °C)	TDS	Reaction order	$(1-\alpha)^3$	118.71	8.71×10^4	0.9927
	0.9TDS 0.7TDS	Reaction order Reaction order	$\frac{(1-\alpha)^3}{(1-\alpha)^3}$	120.63 123.34	1.26×10^{5} 2.18×10^{5}	0.9942 0.9953
	0.5TDS	Reaction order	$(1-\alpha)^3$	125.32	3.37×10^{5}	0.9947
	0.3TDS 0.1TDS	Reaction order Reaction order	$(1-\alpha)^3$ $(1-\alpha)^3$	130.75 133.01	9.76×10^{3} 1.69×10^{6}	0.9938 0.9897
	BR	Reaction order	$(1-\alpha)^3$	136.82	3.75×10^{6}	0.9866

Table 3

IR bands assigned to gaseous substances and functional groups for the (co-) pyrolysis (Lin et al., 2017; Chen et al., 2018b).

Species	Wavenumber (cm^{-1})	Peak (cm ⁻¹)
NH ₃ HCN CO ₂ CO CH ₄ =CO (Carboxylic acids, ketone, aldehyde, ester) -CO (Alcohols, phenols, ethers)	966 714 2400-2240 2240-2060 3000-2700 1850-1600 1300-950	- 2334 2185 2968 1739 1122
Aromatic compounds	3015	-

to produce the aromatic compounds such as phenol, indole, and pyrrole (Lin et al., 2017). The aromatization of cellulose in BR and the initial decomposition of lignin led to the first absorption peak of its aromatic compounds at about 340 °C. At about 470 °C, the further cleavage of proteins in TDS produced the second release peak of the aromatic compounds. The second absorption peak of BR at about 500 °C was due to the secondary cleavage of lignin. It was observed that BR ratios above 50% significantly reduced the yield of the co-pyrolyzed aromatic compounds (Fig. 2f).

3.3.2. Emission characteristics of NO_x precursors

NH₃ and HCN are the precursors of the NO_x formation (Yang et al., 2015) as well as the most important N-containing gas pollutants during the co-pyrolysis of sludge and biomass (Zhan et al., 2018a; Xiao et al., 2019). The maximum release intensity of NH₃ produced by the individual TDS and BR pyrolysis was similar (Fig. 2g), mainly concentrated at below 600 °C and derived from the decomposition of inorganic-N (such as ammonium and nitrate) and proteins (Yang et al., 2015). NH₃ was released earlier by the BR than TDS pyrolysis, with the release range of 220-800 °C and the maximum release intensity at about 330 °C. The NH₃ emission from TDS was in the range of 250-800 °C, with its maximum release intensity at 350 °C. The NH₃ emission from the BR pyrolysis decreased rapidly after reaching the maximum release intensity. At above 340 °C, the NH₃ emission was significantly more from TDS than BR.

For the HCN emission from the TDS pyrolysis, the two obvious peaks were observed (Fig. 2h). The first peak in the range of 250-500 °C was due to the direct decomposition of heterocyclic-N (such as pyridine-N and pyrrole-N) in TDS (Tian et al., 2014). At above 500 °C, the re-cracking of nitrile-N and heterocyclic-N (produced by the dehydrogenation and polymerization of amine-N) formed in char/tar contributed to the second peak of HCN (Zhan et al., 2019). Although the HCN generation mechanisms of the individual BR and TDS pyrolysis were similar, HCN was generated more from the BR than TDS pyrolysis

at below 500 $^\circ C$ and more from the TDS than BR pyrolysis at above 500 $^\circ C.$

It can be theoretically inferred that the maximum release intensity of NH₃ of the co-pyrolysis at below 400 °C would be equivalent to that of the TDS pyrolysis, while the amount of NH₃ and HCN produced at the re-cracking stage of char/tar at above 400 °C would be slightly lower than that of the TDS pyrolysis. However, in the actual experiments, it was found that NH₃ and HCN produced by the co-pyrolysis did not amount to the theoretical sum of the two individual feedstocks. The maximum release intensity of NH₃ fell, while very little HCN release was observed in the range of 400-800 °C with 0.5TDS and 0.7TDS (Fig. 2g–h). The reduced NH₃ and HCN emissions can be attributed to the synergistic effect of the co-pyrolysis whose mechanism is further explored in the next section.

3.4. Evolution of biochar-N structures during co-pyrolysis

The co-pyrolysis led to the obvious synergistic effects, in particular, with the addition of 50% BR achieving the optimal outcome. Therefore, 0.5TDS was selected as the representative blend ratio to explore its synergetic effect on the evolution of N in the biochar products. Based on our analysis in Section 3.2, 400, 600 and 800 °C were selected as the temperatures of the biochar preparation since the range of 400 - 800 °C was the thermal cracking stage of the biochar. The biochars prepared for TDS, BR, and 0.5TDS were named TDS400, BR400, and 0.5TDS400 at 400 °C and the like at the other temperatures.

3.4.1. Characteristics of biochars

Our results of the key organic elements in biochars (Fig. 3a) showed that the (co-)pyrolysis temperature rise decreased the H and N contents of the solid products. Regardless of the temperature, the C contents of the BR biochars (50.83-52.28%) were more than twice those of the TDS biochars (23.06-23.95%). Likewise, the yields of the TDS biochars (43.13-57.21%) were higher than those of the BR biochars (28.13-39.44%) (Fig. 3b). The atomic H/C ratio can indirectly reflect the aromaticity of biochars, while the H/C value of biochar less than 0.3 indicates its highly condensed structure (Yang et al., 2019b). This kind of biochar with the lower H/C value has the potential to be used as stable soil agents for carbon sequestration (Zhao et al., 2020). With the elevated temperature, the H/C ratios of the TDS and BR biochars decreased from 0.1169 to 0.0426 and from 0.0746 to 0.0286, respectively, which indicated the higher aromatization degree of the BR biochar. The H/C ratio of the 0.5TDS biochar fell from 0.0891 to 0.0284 with the temperature rise and was lower than that of the TDS biochar, or even BR800. In other words, not only did the addition of BR increase the carbon content of the co-pyrolytic biochar but also enhanced the cyclization and polymerization reactions as well as the aromatization degree and stability of the co-pyrolytic biochar.



Fig. 2. IR absorbance as a function of temperature and blend ratio during the (co-)pyrolysis: (a) CO₂, (b) CO, (c) CH₄, (d) C=O, (e) C–O, (f) aromatic compounds, (g) NH₃ and (h) NCH.

3.4.2. Structures of N in raw materials

XPS can effectively detect the chemical structures of the N functional groups in the complex organic samples (Zhan et al., 2018c). Fig. 4 shows the distribution of each N structure, and its normalized relative content in the N1s spectra of TDS and BR. The N-A, N-5, N-6 and N-Q peaks were observed in the control samples (TDS and BR). The N-A type structures were in the highest proportion in the control samples accounting for more than 60% of the total N content. The N-A type mainly represents the N structures in proteins and their hydrolysates (Zhan et al., 2019) including amino-N, amine-N, protein-N, and amide-N (Fig. 4). The structures of pyrrole-N and pyridine-N represented by N-5 and N-6 are derived from the decomposition products of nucleic acids (Tian et al., 2014). The binding energy of pyridine and its isomer is close to that of pyrrole-N (Wang et al., 2017), which is also classified as N-5. The N-5 and N-6 types accounted for about 30% of the control samples. The N-Q type had the lowest content of less than 7%. N-Q represents the structures of quaternary-N and inorganic-N (Fig. 4). The binding energy of these two structures was too similar to be distinguished, while N-Q in the control samples was more likely to be inorganic-N (Zhan et al., 2018c). Overall, the content order of each N structure was thus: N-A (63.70%) > N-5 (16.40%) > N-6(13.16%) > N-O(6.74%) for TDS; and N-A (62.59%) > N-6

(16.61%) > N-5 (14.72%) > N-Q (6.09%) for BR.

3.4.3. Evolution of N structures in chars

The N structure in the prepared biochars was characterized to clarify the synergetic effect of the co-pyrolysis on the formation pathways of NH3 and HCN. The N1s spectral analysis results of the char products at 400, 600 and 800 °C for TDS, BR and 0.5TDS are illustrated in Fig. 5. The full width at half-maximum (FWHM) of each N functionality is 1.4 ± 0.1 eV (Gao et al., 2020). The evolutions of N in the TDS and BR chars differed clearly at 400 °C. Having gone through the devolatilization phase, N-A in TDS and BR fell, while heterocyclic-N (N-5, N-6, and N-Q) rose (Fig. 5a and d). Since inorganic-N is easily decomposed to produce NH₃ at a low temperature (Chen et al., 2017), N-Q at this stage was more likely to be quaternary-N. N-5 and N-6 are converted from N-A by either the cyclization of some long-chain amino acids with the polar side chains (Gao et al., 2020) or the dimerization of aliphatic amino acids (Zhan et al., 2018b). The transitions from N-A to N-5 and N-6 appeared to be accompanied by the dehydration, dehydrogenation, decarboxylation or deamination processes resulting in the large releases of H₂O, CO₂, and NH₃. However, the N-A structure was easier to convert in TDS than BR (Fig. 5a and d). In order to clarify the transformation degree of the N structures during the (co-)pyrolysis, its



Fig. 2. (continued)



Fig. 3. Characteristics of biochars as a function of three temperatures and blend ratios: (a) elemental analysis, and (b) H/C ratio and yield.



Fig. 4. Chemical structures of the N functional groups in the control TDS and BR samples.

quantification was performed using the following equations:

$$Yield_{\rm N \, structure} = Yield_{\rm Char} \cdot N_{\rm Char} \cdot \frac{A_{\rm N \, structure}}{\sum A_{\rm N \, structure}}$$
(8)

$$N_{\text{Retention rate}} = \frac{Yield_{\text{Char}} \cdot N_{\text{Char}}}{N_{\text{Original sample}}}$$
(9)

Yield _{N structure} represents the yield of each N structure in the original samples, %; *N*_{Retention rate} is the retention rate of N in the original samples, %; *Yield* _{Char} is the yield of char; *N*_{Original sample} and *N*_{Char} are the N content in the control samples and chars, respectively; and *A*_{Nstructure} is the peak area of each N structure obtained via XPS analysis.

N-A accounted for only 27.91% of TDS400 and 48.32% of BR400 (Fig. 6). N-A in TDS400 was most converted to N-5 (36.84%) followed by N-6 (23.23%) and N–Q content (12.02%). The N-A conversion patterns of 0.5TDS400 and TDS400 were similar. 0.5TDS400 had a higher N retention rate than did TDS and BR (Fig. 6b). The synergistic influence of the co-pyrolysis enhanced the N retention in the biochar. This in turn verified the results of the reduced NH₃ and HCN emissions discussed in Section 3.3.1.

At 600 °C, the N-6 peak further declined, while the peak of heterocycle-N became dominant (Fig. 5b, e and h), and the proportions of N-5 and N-6 reached more than 60% (Fig. 6a). The increased temperature promoted the formation of the more stable heterocyclic-N structures in unstable N-A (Zhan et al., 2019). However, the outputs of all the structures fell, with the N retention rates of TDS, BR, and 0.5TDS dropping to 27.77, 31.43, and 34.82%, respectively (Fig. 6b). At 800 °C, the N-A peak disappeared and was replaced by N-5, N-6, N-Q and a very small amount of N-X, which was pyridine-N oxides (Wang et al., 2017) (Fig. 5c, f and i). The loss of N in the range of 600 – 800 °C was not so high (Fig. 6a), while N-5 was the main structure at 800 °C.

Overall, the evolution patterns of N-A towards heterocyclic-N in TDS, BR and 0.5TDS significantly differed in the range of 400 - 800 °C.

N-A in TDS was more easily decomposed to form heterocyclic-N. Although it tended to form N-5, a considerable part of it was still converted to N-6. N-6 formed more stable N-Q through the ring condensation, or the H radical adsorption reaction (Zhang et al., 2013a). N-A in BR was more inclined to form N-5, while the less content of N-6 (not more than 20%) reduced the N-Q production in BR. During the evolutions of N-6 and N-5 with the temperature rise, the active N-sites formed NH₃ by adsorbing the H radicals (hydrogenation reaction) (Tian et al., 2014). The structure of N-6 was more stable than that of N-5, while N-5 was more prone to the ring-opening reactions to form HCN (Zhang et al., 2013b). This showed that the N structure was transformed into a stable structure at a lower temperature in TDS than BR. The addition of BR led to more N-5 and less N-6 in the N structure in the 0.5TDS biochar and did not decrease the N-Q structure.

The N retention rate of 0.5TDS did not simply amount to the sum of the N retention rates of TDS and BR and was higher. This is why the total N yields of 0.5TDS and TDS were similar at any temperature (Fig. 6a) although the addition of BR diluted the N content of TDS. The yield of N-5 was higher in the 0.5TDS biochar (0.2619%) than the TDS char (0.2272%) at 800 °C, whereas the yield of N-6 was lower (Fig. 6a). This suggested that when the secondary cracking of the biochar reached the range of 600 - 800 °C, the co-pyrolysis inhibited the decomposition of N-5, retained it and enhanced the transformation of N-6 into more stable N-Q.

3.4.4. Evolution of char-N structures, and its influence mechanism on NH_3 and HCN emissions

The evolutions of the char-N structures can explain the emission characteristics of NH_3 and HCN to a certain extent. The evolutions of the char-N structures, and the formation pathways of NH_3 and HCN are illustrated in Fig. 7. The conversion of N in the feedstocks to NH_3 and HCN is generally classified as the preliminary pyrolysis and secondary reactions (Zhan et al., 2019). The preliminary pyrolysis (< 400 °C) is



Fig. 5. The N1s spectrum analyses of prepared biochars during the (co-)pyrolysis of BR, TDS and 0.5TDS at three temperatures.

indicated in the left half of Fig. 7. The direct decomposition of inorganic-N and the deamination of a large amount of the N-A structure in the raw materials are the main pathways for the formation of NH_3 . The hydrogenation of the pyrrole and pyridine structures also produces some NH_3 . This is why the peak NH_3 emissions from TDS and BR occurred at below 400 °C. The higher HCN emission from the preliminary pyrolysis of BR may indicate that the ring-opening reaction of heterocyclic-N in the original BR was more sensitive to temperature. The secondary pyrolysis (400 – 800 °C) of the feedstocks is shown in the right half of Fig. 7. TDS released more NH_3 and HCN than did BR at this stage, thus indicating that the hydrogenation, ring breakage and further deamination reactions in the TDS char were more intense. Char-N formed a more stable N (C) structure during the secondary reaction, thus terminating the NH_3 and HCN emissions. Overall, TDS was more



Fig. 6. (a) Yield of each N structure based on XPS analysis, and (b) N retention rate as a function of three temperatures and blend ratios.



Fig. 7. Schematic diagram of the char-N evolution during the co-pyrolysis process, and its effect mechanism on the formation of NO_x precursors.

prone to the deamination during the preliminary pyrolysis, while BR emitted a large amount of NH_3 and HCN. The hydrogenation and ringopening reactions were more intense for TDS than BR during the secondary cracking.

The reductions of NH₃ and HCN by 0.5TDS can be considered a synergistic effect on their formations. For example, the reduction of NH3 may be due to the weakening deamination and hydrogenation, or the catalyzing effect of ash. First, the addition of BR may have increased the C=O and CO- releases as the highly active oxygen-containing functional groups to compete with the active N-sites for H radicals, weakened the hydrogenation of the N-sites, and affected the formation of NH₃. Second, Fe_2O_3 and CaO may have contributed to convert the fuel-N to N₂ (Fe₂O₃/CaO + Char-N \rightarrow xFe/CaC_x + N₂) (Xiao et al., 2019), while Fe acted as a catalyst to promote the conversion of NH_3 to N_2 (2NH₃ + 8Fe \rightarrow 2Fe₄N + 3H₂, 2Fe₄N \rightarrow 8Fe + N_2) (Sun et al., 2019b). The Fe content of the TDS ash was more than that of the BR ash, while the Ca content of the BR ash was more which improved the Fe-Ca content of the blend (details are shown in the supplementary materials). The most likely way to influence the reduced HCN release at the high temperature was to reduce the ring-opening reaction in the secondary cracking. As described in Section 3.4.3, the co-pyrolysis retained more N-5 structures. This may be because the abundant K and Ca contents of the BR ash inhibited the cleavage of heterocyclic-N (Ren and Zhao, 2013) which in turn hindered the formation of HCN (details are shown in the supplementary materials). Finally, the higher N retention of 0.5TDS may be attributed to the enhanced transition of N at the edge of the molecular structure to a more stable N-Q structure (Fig. 7).

Overall, the elucidation of the different evolutions of char-N of TDS and BR can provide valuable insights into controls over their respective NO_x precursors during the cleaner energy generation. The co-pyrolysis effectively inhibited the releases of NH_3 and HCN and formed a more stable char(-N) structure. This pointed to the prospects of the co-pyrolysis for the cleaner energy production. Simultaneously, the synergistic effect of the co-pyrolysis enabled the resultant biochar to better perform such as higher aromaticity, C content, and N-5 structure. The abundant N-containing functional groups (including N-5, N-6, N-Q, and N-X) in the biochar were the basic active groups that can effectively adsorb the acid gases or provide the catalytic sites (Chen et al., 2020). The high ash content of TDS contributed abundant metal elements (such as aluminum) to the co-pyrolytic biochar, which provided the adsorption sites for the pollutant removal. This suggests that the copyrolytic biochar may present great potential for the environmental applications, and thus, enhances the feasibility of the co-pyrolysis of TDS and BR. Future studies are still needed to quantify the effect of the co-pyrolysis on the production of bio-oils as well as to detect the functional groups, surface metal morphology, and heavy metal content of the co-pyrolytic biochars in terms of their environmental applications such as adsorbents.

4. Conclusion

The TDS pyrolysis had a lower mass loss rate than did the BR pyrolysis. The main pyrolysis reaction stage occurred between 200 and 800 °C for TDS and between 200 and 600 °C for BR. The sequential decompositions of light organic volatiles in TDS, (hemi)celluloses in BR, medium molecular weight components in TDS, and heavy carbon substances in TDS dominated the co-pyrolysis, with 0.5TDS exerting the strongest interaction. All the (co-)pyrolysis processes exhibited a transition from a diffusion mechanism (200-400 °C) to a third-order reaction mechanism (400-800 °C). The addition of 50% BR significantly increased the CO2, CO, CH4, C=O and C-O emissions, reduced the aromatic compounds, and improved the aromaticity and stability of the char products. At below 400 °C, the fuel-N was dominated by the N-A structure, while the thermal stability of N-A was lower in TDS than BR. At this stage, the maximum NH3 release intensity of TDS and BR was similar, but the HCN emission was higher from BR than TDS. In the secondary reaction stage (400-800 °C), TDS was more prone to the deamination, hydrogenation and ring-opening reactions, and thus, led to the higher NH₃ and HCN release intensity than did BR. However, the synergistic effect of the co-pyrolysis inhibited the formations of NH₃ and HCN. Its possible mechanism involved the enhanced conversion of NH_3 to $\mathrm{N}_2,$ the weakened hydrogenation reaction, the inhibition of the ring-opening reaction in the char-secondary cracking, and the formation of more stable quaternary-N.

CRediT authorship contribution statement

Jinwen Hu: Methodology, Software, Validation, Formal analysis,

Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. Yueyao Song: Formal analysis, Investigation, Writing - review & editing. Jingyong Liu: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition. Fatih Evrendilek: Writing - review & editing, Software. Musa Buyukada: Formal analysis, Writing - review & editing. Youping Yan: Formal analysis, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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