

NO_x and N₂O precursors from co-pyrolysis of biomass and sludge

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Abstract Biomass is an effective substitute for fossil fuels and has a substantial impact on CO₂ reduction. Meanwhile, alkali metal-related problem is a major barrier in biomass combustion. Sludge is a waste with low heating value, high water, sulfur, and nitrogen contents, as well as high phosphorus content, which makes the sludge a potential choice to inhibit the alkali metal-related problems during biomass combustion. The nitrogen behavior and the emissions of NO_x and N₂O are one of the key problems when sewage sludge is co-fired with biomass. Thus, nitrogen transformation during co-pyrolysis of cotton stalk and sludge at different heating rates were studied. The results show that HCN and HNCO are the major nitrogen-containing species for petrochemical sludge. The addition of petrochemical sludge changes the path of the conversion of fuel nitrogen and the presence of cotton stalk in the mixture promotes NH₃ and HCN formation.

Keywords NO_x and N₂O precursor · Sludge · Biomass · Pyrolysis

Introduction

There is currently a considerable interest in the efficient use of sludge as energy source. Incineration has gradually taken as major disposal measures for recovering energy from sludge [1–4]. However, incineration of sludge brings serious environmental problems, such as the emissions of

NO_x, N₂O, SO₂, HCl, heavy metal, and dioxins [5, 6]. Therefore, it is necessary to explore cleaner techniques for sludge recycling.

Petrochemical sludge is the solid waste generated in the petrochemical production process; with the vigorous development of China's petrochemical industry, the amount of sludge generated is also growing. According to statistics, the annual sludge scum of the national petrochemical plant was over 30 million tons. The disposal of the petrochemical sludge has been attracting much attention.

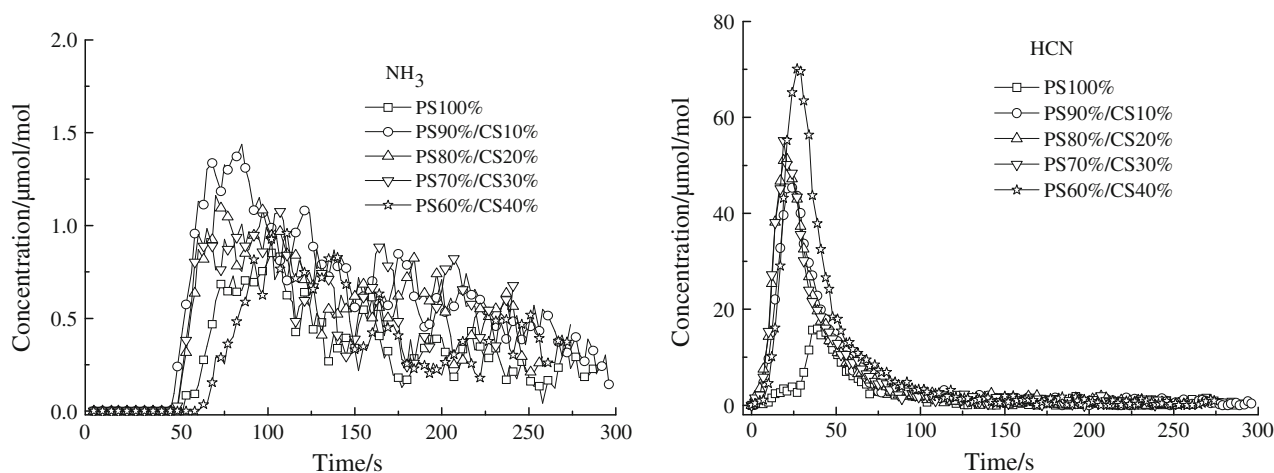
The high moisture content was one of the major drawbacks for the incineration of petrochemical sludge. Biomass was abundant, renewable, and low cost. Agricultural straw was the main biomass resource in China. Compared with sludge, straw contained high contents of volatile matter and fixed carbon, but low ash and moisture contents. The addition of straw to wet sludge in appropriate proportion could adjust the moisture content of the blends. Moreover, we have found that sludge which is rich in sulfur, nitrogen, and phosphorus is a potential choice to inhibit the alkali metal related problems during biomass combustion [7, 8]. Co-combustion of agricultural residues with sludge is a promising area in the global cleaner energy strategy.

Both petrochemical sludge and biomass have certain nitrogen contents, and NO_x and N₂O emission during co-combustion of the blends is an environmental concern. Cao et al. [9] investigated nitrogen transformation during pyrolysis of sludge, however, the nitrogen behavior during co-pyrolysis of biomass and straw is rarely reported. The objective of this research was to investigate the nitrogen behavior during co-pyrolysis of petrochemical sludge and straw at a high heating rate and a low heating rate.

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Table 1 The proximate and ultimate analyses of cotton stalk and sludge samples

Sample	Proximate analysis			Ultimate analysis (dry ash free basis)				
	Fixed carbon ^a	Ash ^b	Volatile ^a	C	H	S	O ^c	N
Sludge	6.05	14.58	24.10	19.10	2.79	0.73	11.04	1.41
Cotton stalk	24.34	1.75	75.66	48.56	6.12	0.13	44.89	0.30

^a Dry ash free basis^b Dry basis^c By difference**Fig. 1** HCN and NH₃ release curves during fast pyrolysis of cotton stalk and petrochemical sludge**Table 2** The yield and conversion of HCN and NH₃ during co-pyrolysis of cotton stalk and petrochemical sludge

Sample	Yield/μmol		Conversion/%		HCN/NH ₃
	N_{NH_3}	N_{HCN}	X_{NH_3}	X_{HCN}	
Cotton stalk	0.638	1.218	11.760	22.439	1.909
Petrochemical sludge	0.166	1.212	1.643	12.029	7.301
90 %PS/10 %CS	0.329	3.032	3.426	31.559	9.216
80 %PS/20 %CS	0.248	3.137	2.713	34.311	12.649
70 %PS/30 %CS	0.237	3.186	2.735	36.709	13.443
60 %PS/40 %CS	0.178	4.100	2.169	49.919	23.034

PS petrochemical sludge, CS cotton stalk

Materials and methods

Material

The petrochemical sludge used in the experiments was collected from refinery, chemical plants, and sewage plants of Fushun Petrochemical Corp. in Liaoning, China. For each experiment, the sludge was dried at 105 °C in an electric oven. After sieving, the powder of dried sewage sludge in the size range of 0–0.3 mm was used as the samples.

Cotton stalk, a representative agricultural biomass in China, was used as the biomass sample. The stalk sample was ground into particles less than 0.1 mm in diameter. The proximate and ultimate analyses of cotton stalk and sludge samples have been listed in Table 1.

Apparatus and product analysis

The fast pyrolysis experiments were performed in a horizontal fixed-bed tubular reactor (40-mm i.d., 60-mm o.d., and 400-mm long). The pyrolysis temperature was 800 °C.

The mass of each sample was 10 ± 0.01 mg. Samples were introduced into the center of the preheated reactor with a porcelain boat. Argon with purity of 99.999 % was used as the carrier gas to provide an inert atmosphere for pyrolysis which can eliminate the influence of atmosphere on the formation of N-containing species and to remove the gaseous and condensable products. The argon flow rate was $1,500 \text{ mL min}^{-1}$ ($20 \text{ }^\circ\text{C}$, 1 atm). HCN and NH₃ emitted from pyrolysis were continuously measured using Gasetm Dx-4000 Fourier transform infrared (FT-IR) Gas Analyzer which was composed of two units: the sampling unit for gases sampling and cleaning and the measuring unit for continuous analysis using Bruker Vector 22 Fourier transform infrared (FT-IR) analyzer. The resolution of the collected spectra was set to 1 cm^{-1} . No quantification of HNCO was available due to the lack of calibration spectra for this species. The measurement time interval of FTIR is set to 5 s. The analyzer detects concentrations exceeding approximately 1 ppm for each of these species under the experimental conditions. Infrared spectra obtained were processed by means of Calmet Software 2005. Detailed information about the product analysis method can be referred to [10].

The slow co-pyrolysis of sludge with stalk was performed using a TG analyzer in argon atmosphere. Experiments were carried out from room temperature to $800 \text{ }^\circ\text{C}$ at $40 \text{ }^\circ\text{C min}^{-1}$. The total mass of each mixture was around 10 mg. Evolved gases from TG were connected to and detected online using a FTIR spectrometer. The concentration of each gaseous product was determined based on the integral value of the release curves under specific IR absorptions. Detailed information about the TG-FTIR apparatus and product analysis method can be referred to [11, 12].

Results and discussion

Nitrogen behavior during fast pyrolysis

Three repeated tests were carried out on the tubular reactor to find out the uncertainty quantification of the experimental results, and the relative standard deviation was 2.27 %. Thus, the results reported are quite reproducible.

Figure 1 shows NH₃ and HCN release curves during fast pyrolysis of cotton stalk and petrochemical sludge. Higher HCN yield than NH₃ is formed during co-pyrolysis of cotton stalk and petrochemical sludge. According to our previous study [10–12], the formation pathway of NH₃ from biomass pyrolysis can be summarized as follows. The first one is that proteins and amino acids may release in the form of NH₃ in the temperature range of $300\text{--}500 \text{ }^\circ\text{C}$. The second one is thermal cracking reactions of tar and char by

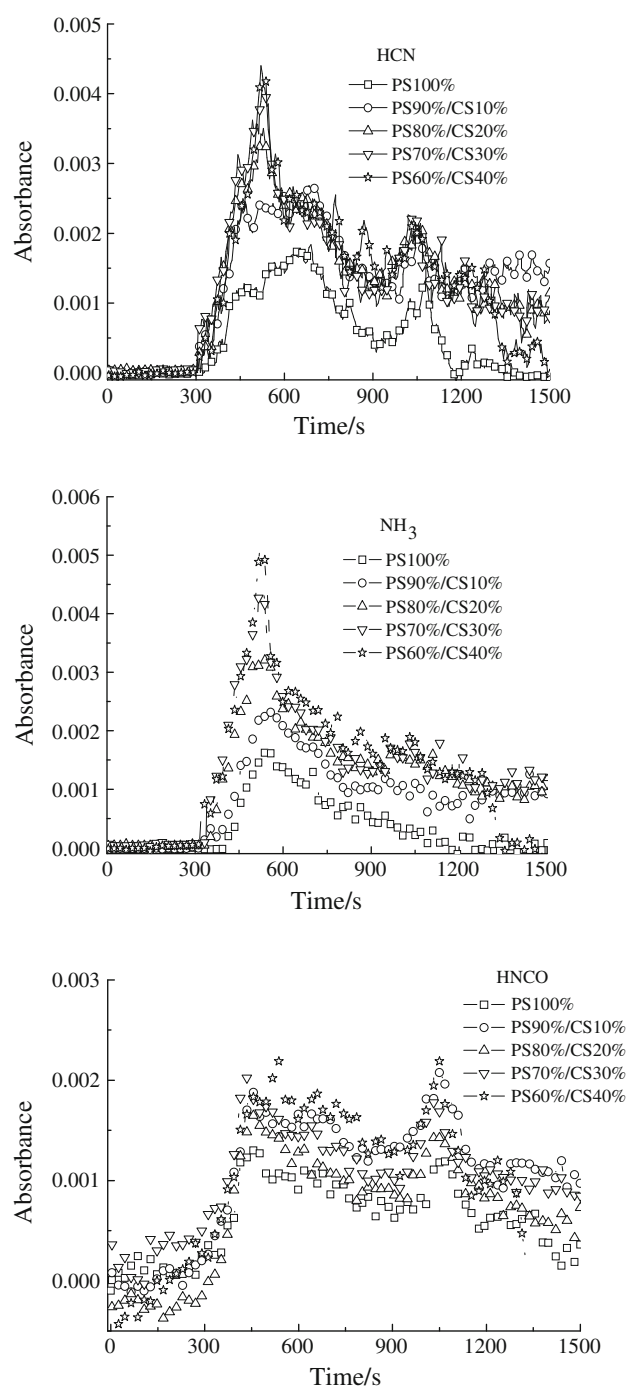


Fig. 2 HCN, NH₃, and HNCO release curves during slow pyrolysis of cotton stalk and petrochemical sludge

undergoing secondary reactions. Tar components from amino acids are 2,5-diketopiperazine (DKP), which is cyclic amide. The last one is hydrogenation and hydrolysis of HCN on the surface of the char. As for HCN production, the protein first leads to the release of volatile cyclic amides and then cracks the cyclic amides into HCN. The decomposition of dipeptide and polypeptides at high

Table 3 Yield of nitrogen-containing species during co-pyrolysis of cotton stalk and petrochemical sludge

Sample	Integral value of gas release curve/a.u.			N-conversion selectivity	
	HCN	NH ₃	HNCO	HCN/NH ₃	HNCO/HCN
PS100 %	0.801	0.538	0.948	1.489	0.020
PS90 %/CS10 %	1.947	1.322	1.596	1.473	0.014
PS80 %/CS20 %	1.960	1.810	1.066	1.083	0.009
PS70 %/CS30 %	1.984	2.056	1.548	0.965	0.013
PS60 %/CS40 %	1.922	1.986	1.283	0.968	0.011
CS100 %	2.449	2.662	0.900	0.920	0.370

PS petrochemical sludge, CS cotton stalk

temperature produce DKP. Both the decomposition reaction of primary amines and the bimolecular reactions between imine and amine can produce NH₃. Another reaction may be thermal decomposition of tar, which competes with the aforementioned reaction that some part of HCN addition into light aromatic compounds forms cyano aromatic compounds in tar at the same time. However, at higher temperature, ring scission becomes prevalent, resulting in HCN production. The intermediacy of 2,5-piperazinedione (DKP) provides an attractive explanation for the formation of HNCO and HCN [13–17].

During co-pyrolysis of cotton stalk and petrochemical sludge, small NH₃ formation is found, and HCN starts to release at lower temperature than NH₃; NH₃ mainly releases at the mid-late stage of the pyrolysis stage. With the cotton stalk share increase, the peak value of HCN release curve increases and the corresponding time occurs in advance. The yield and conversion of HCN and NH₃ are shown in Table 2. PS and CS in Table 2 represent petrochemical sludge and cotton stalk, respectively.

HCN is the main nitrogen-containing species in the pyrolysis process of cotton stalk or petrochemical sludge. As for petrochemical sludge, NH₃ yield increases with the addition of cotton stalk. The increasing release of NH₃ from the blends should be related to the high protein content in the cotton stalk. The straw fuel nitrogen conversion to HCN and NH₃ is higher than that of petrochemical sludge, which is 35.8 and 13.6 %, respectively. With cotton stalk share increases, the yields and conversion of NH₃ and HCN increase. The high volatile and mineral matter contents in straw may promote the formation of nitrogen-containing species. Another possible explanation is that the cellulose, hemicellulose, and lignin have also positive effects on nitrogen conversion pathway of amino acid [10].

The results show that concerted reaction occurs during co-pyrolysis of cotton stalk and petrochemical sludge. The addition of petrochemical sludge changes the path of the conversion of fuel nitrogen and significantly increases the conversion of N–HCN. The possible explanation is that

sulfur content in the sludge is high; the presence of SO₂ restrains NH₃ formation due to the rapid consumption of O radicals, and OH radicals by SO₂ through the following reactions [18–23].



Nitrogen behavior during slow pyrolysis

The TG experiment showed good reproducibility of the peak absorbance between the consecutive runs. The mean run-to-run variability was estimated by the relative standard deviations (RSD) by averaging the relative analytic peak area calculated from three runs by area normalization method. For the N-containing compounds, the RSD was within good limits. The average RSD was 2.8 %.

It is well known that ammonia (NH₃), hydrogen cyanide (HCN), isocyanic acid (HNCO), and organics are the precursors of nitrogen oxides (NO_x and N₂O). HNCO is believed to be a precursor to N₂O [24]. The formation of HNCO during slow pyrolysis was analyzed.

Figure 2 shows the formation curves of NO_x precursors for petrochemical sludge, cotton stalk, and their blends. HCN, NH₃, and HNCO start to release at lower temperature and sustain a wide temperature range with the increase of cotton stalk share. HCN curves for petrochemical sludge or the mixture have an evident peak at the late period of pyrolysis process. The peak absorbance of HCN curve for the mixture is significantly higher than that of the sludge and the peak occurs in advance. NH₃ release curve from cotton stalk and the blends have only one peak. The peak absorbance of NH₃ for the mixture is bigger than that of the sludge. Few HCN and NH₃ are formed for sludge at the late period of pyrolysis process. However, there are still certain HCN and NH₃ formation for the mixture. Co-pyrolysis of

petrochemical sludge and cotton stalk prefers to HNCO formation.

Table 3 shows the yield of nitrogen-containing species during co-pyrolysis of cotton stalk and petrochemical sludge. Contrary to higher heating rate experiments, NH₃ becomes the major N-containing species for the two samples. Slow heating rate pyrolysis generates lower N-conversion, N-retention in char is increasing, and the secondary thermal cracking reaction of tar and char is weak. As can be seen from the table, the total amount of nitrogen-containing species from the mixture is bigger than that from sludge. Cotton stalk has high volatile content, and the fuel nitrogen is mainly released in the form of volatile-N. HCN yield increases when stalk share increases to 10 %, with the stalk share continues to increase, HCN yield remain basically unchanged. NH₃ yield has an obvious increase when stalk share increases to 30 % and then does not change a lot with the stalk share continues to increase. HNCO yield from the mixture is higher than that from sludge. It is clear that the variation in the nitrogen species formation is affected by added stalk.

In order to better understand the N-selectivity of the mixtures, the correlation between N-selectivity to NH₃, HCN, and HNCO and the mass proportion of stalk was studied. As the cotton stalk share increases, HCN/NH₃ molar ratio first decreases, and when the cotton stalk share is bigger than 30 %, HCN/NH₃ molar ratio does not change sharply. HNCO/HCN molar ratios for the mixtures are smaller than that of cotton stalk or petrochemical sludge.

As seen from Table 3, HCN and HNCO are the major nitrogen-containing species for petrochemical sludge, with the increased cotton stalk share, NH₃ share increases significantly, when the cotton stalk share is 40 %, NH₃ share increases to 38.3 %. HCN share first increases and then decreases gradually to remain stable; HNCO share significantly reduced. NH₃ and HCN gradually increase and become the main nitrogen-containing species for the mixture.

Conclusions

The study shows N-behavior characteristics during co-pyrolysis of petrochemical sludge and cotton stalk, and several interesting findings are obtained. The addition of petrochemical sludge changes the path of the conversion of fuel nitrogen. HCN and HNCO are the major nitrogen-containing species for petrochemical sludge. The presence of cotton stalk in the mixture promotes NH₃ and HCN formation. The results provide valuable basis for optimizing combustion of biomass and sludge to effectively control NO_x emission.

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