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Key intermediates in nitrogen transformation during microwave pyrolysis of sewage sludge: A protein model compound study

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HIGHLIGHTS

- A novel Microwave Heating Reactor was designed to introduce microwave heating in the pyrolysis.
- The evolution of nitrogenated compounds in the char, tar and gas fractions were investigated.
- Three key intermediate compounds was identified in the pyrolysis tars during the pyrolysis.
- The gas products were formed with comparable activation energies from the same reactive species.
- The nitrogen transformation pathways in relation to NH_3 and HCN formation were proposed.

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ABSTRACT

The nitrogen transformations with attention to NH_3 and HCN were investigated at temperatures of 300–800 °C during microwave pyrolysis of a protein model compound. The evolution of nitrogenated compounds in the char, tar and gas products were conducted. The amine-N, heterocyclic-N and nitrile-N compounds were identified as three important intermediates during the pyrolysis. NH_3 and HCN were formed with comparable activation energies competed to consume the same reactive substances at temperatures of 300–800 °C. The deamination and dehydrogenation of amine-N compounds from protein cracking contributed to the formation of NH_3 (about 8.9% of Soy-N) and HCN (6.6%) from 300 to 500 °C. The cracking of nitrile-N and heterocyclic-N compounds from the dehydrogenation and polymerization of amine-N generated HCN (13.4%) and NH_3 (31.3%) between 500 and 800 °C. It might be able to reduce the HCN and NH_3 emissions through controlling the intermediates production at temperatures of 500–800 °C.

1. Introduction

One of the major environmental problems is the disposal of the huge amount of sewage sludge produced in the wastewater treatment plants (Wei et al., 2003). For the recovery of maximum energy from sewage sludge, pyrolysis has been receiving increasing attentions in recent years (Sanchez et al., 2009; Butler et al., 2011; Swain et al., 2011; Xu et al., 2011). It has been reported that a hydrogen rich bio-gas product is obtained at high temperatures above 500 °C during the sludge pyrolysis, which could be used as a clean alternative to fossil fuels in power generation (Menendez et al., 2004; Dominguez et al., 2006, 2007, 2008; Fernandez and Menendez, 2011). Although pyrolysis indeed enjoys many obvious advantages, it should be noted that the relative higher nitrogen contents in sewage sludge result in the release of nitrogen-containing gases. The nitrogen-containing gases might be converted into NO_x compounds, contributing to the severe photochemical smog and acid rain pollution (Tian et al., 2002; Chen et al., 2011).

Many efforts have been conducted to study the nitrogen-containing species in the tar and gas products during the pyrolysis of sewage sludge (Fullana et al., 2003; Cao et al., 2010, 2013; Yuan et al., 2011). It is reported that the cyano-N and heterocyclic-N compounds are identified as the major nitrogenated compounds in the tars during the pyrolysis of sewage sludge (Sanchez et al., 2009; Tsai et al., 2009; Chen et al., 2011). HCN and NH_3 are believed to be the major gaseous nitrogen products during the sludge pyrolysis (Tian et al., 2002; Cao et al., 2013). It should be noted that previous studies regarding the nitrogen-containing species mainly focus on the production and characterization of nitrogeneous gas and tar products from the sludge pyrolysis process (Chen et al., 2011). The conversion of the nitrogen-containing compounds in the gas and tar fractions is not fully understood during the pyrolysis of sewage sludge

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(Cao et al., 2013). This may be attributed to the complex molecular structure of sewage sludge. From this point of view, the substitution of the sewage sludge nitrogen (SS-N) by model compounds bears some advantages on increasing insight into the nitrogen transformations in the products during pyrolysis.

In our previous studies, a novel Microwave Heating Reactor (MHR) was designed to introduce microwave heating in the sewage sludge pyrolysis and bio-gas with high hydrogen contents (40%) was obtained in few minutes successfully (Zuo et al., 2011). Our works were focused on the nitrogen conversions in the tar and gas products during the microwave pyrolysis of a protein model compound: (1) characterization of sewage sludge nitrogen for model compound selection; (2) identifying the key intermediates through investigating the evolution of nitrogen-containing compounds in the char, tar and gas products; (3) proposing the nitrogen transformations of the protein model compound to provide possible strategies for minimization of HCN and NH_3 emissions during the pyrolysis.

2. Methods

2.1. Materials

Sewage sludge samples used in this study were obtained from a wastewater treatment plant in Harbin, China. The samples were dried at 106 °C for 24 h and then stored in airtight containers until they were cooled to room temperature. After cooling, the samples were sieved to obtain a particle size of 106–150 μm. The properties of the sludge samples were given in Table 1. The soybean protein used in the experiments was delivered by Sigma–Aldrich Inc. The protein was free from moisture and had a nitrogen content of 13.6%.

2.2. Microwave pyrolysis

The schematic apparatus for microwave pyrolysis of SS-N model compound (soybean protein) was shown in Fig. 1, mainly consisting of a microwave magnetron of 2450 MHz, a multiple mode cavity and the temperature controlling system. An infrared optical pyrometer was employed to measure the temperatures of the samples during the experiments. The constant temperature mode of microwave magnetron was employed in this study.

The samples were placed in a quartz reactor inside the microwave cavity. Soybean protein has a high transparency to microwave. It was necessary to mix it with an appropriate microwave receptor to reach the high temperatures required to produce gas products. Thus, activated carbon (1 mm × 1 mm) was selected as microwave receptor and its optimal dosage in the protein was also determined. In each experiment, the activated carbon (ca. 2.4 g) was homogenously mixed with 20 g protein before microwave heating. Activated carbon in solid residue of protein pyrolysis could be recovered due to different grain sizes. Argon (Ar) was injected into the system with the constant flow rate of 1.4 L/min to purge out air. The evolution of temperature and volatile contents in solid were determined in previous experiments. Temperature got to the maximum value at 8 min and remained more or less stable thereafter. No significant volatile matter was observed in the solid residue after 8 min. Therefore, the samples subjected to microwave radiation were controlled within 10 min to ensure reaction completed in all the microwave experiments.

2.3. Quantification method

In this study, the tar collection lines were connected to the NH_3 and HCN sampling lines. The negligible influence of the tar adsorption system on the gaseous-N compounds was observed by our previous experiments. The volatile substances evolved from the pyrolysis passed through a number of ice-cooled dichloromethane-containing condensers. Then the pyrolysis gases were carried out from the tar trap to the bubbling solutions by the carrier gas. HCN and NH_3 in the pyrolysis gas were collected by bubbling through NaOH (0.2 mol/L) and H_2SO_4 (0.1 mol/L) solutions, respectively. When the reaction completed, the microwave generator was turned off. The tar products would be recovered from the condensers by evaporating the dichloromethane solvent in a water-bath at 60 °C for 24 h. The elemental compositions (C, H, N, and S) of raw sludge and tar samples were measured in an Elemental Analyzer (Americas Vario EL III). HCN and NH_3 absorbed in the solutions were quantified with a Dionex 500 ion chromatograph equipped with an ED 40 electrochemical detector. All of the experiments were triplicate to take an average as final results.

2.4. Characterization of sewage sludge nitrogen (SS-N)

2.4.1. XPS analysis

XPS was used to investigate the nitrogen functional forms in the raw sewage sludge and the chars produced from soybean protein pyrolysis. The experiment was performed on a PHI5700ESCA spectrometer equipped with Al Kα radiation (12.5 kV and 16 mA) at a base pressure of 5×10^{-7} Pa. The sludge samples were referenced to the C 1s peak at 284.6 eV. The areas of peaks reflected the relative contents of different components for the semi-quantitative analysis.

2.4.2. Protein hydrolysis for amino acids analysis

The main procedures for the extraction of protein from sewage sludge were specified according to the literatures (Chen et al., 2007; Liu et al., 2009). 40 ml distilled water together with 25 g raw sewage sludge (80% moisture) was mechanically stirred for 10 min. The slurry pH (1.2) was adjusted with 2 M HCl solution, then poured into the hydrolysis reactor and heated at 121 °C for 5 h. After the slurry hydrolysis, the protein solutions were collected by centrifugal separation (5000g for 10 min).

Microwave-assisted extraction (MAE) was performed for the extraction of amino acids from the protein solutions. 4 ml protein solution and 8 ml HCl solution (6 M) were added into the vessels. The extraction vessels were covered with pressure resistant holders introducing into the microwave cavity and preheated for

Table 1
Characteristics of raw sewage sludge.

Proximate analysis (wt.%)				Ultimate analysis (wt.%, daf)					
M	A_d	V_d	FC_d	C	H	N	O		
80	42	55	3	30.94	4.773	4.61	20.56		
Ash analysis (expressed as wt.% of metal oxides)									
SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	CaO	K_2O	TiO_2	ZnO	CuO	SrO
26.402	8.64	8.298	6.13	5.115	1.621	0.654	0.14	0.03	0.027

M, moisture content; A, ash content; V, volatile content; FC, fixed carbon; d, dried basis; daf, dried and ash-free basis.