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## Nitrogen transformations during fast pyrolysis of sewage sludge

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#### ABSTRACT

Fast pyrolysis of a sewage sludge sample, which contains a high content of nitrogen, was investigated to understand the effects of pyrolysis temperature and sweeping gas flow rate on the yields of pyrolysis products and the distributions of carbon and nitrogen. The maximum oil yield of ca. 48.7% (daf) was achieved at a pyrolysis temperature of 500 °C and a sweeping gas flow rate of 600 cm<sup>3</sup>/min. NH<sub>3</sub> was found to be the predominant nitrogenous gas under all the conditions, and its yield increased with raising pyrolysis temperature and decreasing sweeping gas flow rate. The significant release of NH<sub>3</sub> at temperatures lower than 500 °C should be related to the high protein content in the sludge. The N yield in HCN was lower than 2% during pyrolysis below 550 °C, and sharply increased to 5.8% at 700 °C due to thermal cracking of volatile matter. Water-insoluble nitrogen- and carbon-containing species were significantly decomposed to water-soluble ones during secondary reactions. At high temperatures, heavy hydrocarbons were mainly cracked to gaseous products, while the nitrogen-containing species tended to form water-soluble species. This study provides a basic insight into the nitrogen transformations during fast pyrolysis of sludge, which would benefit the clean utilization of sludge as an energy source.

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#### 1. Introduction

Sewage sludge is the major byproduct of wastewater treatment plants worldwide. It becomes a growing problem as a potential source of heavy metal- and pathogen-containing wastes with increasing production [1]. Annual production in Japan increased from 1.63 Mt in 1994 to 2.17 Mt (dry basis) in 2004 and was estimated to continuously increase in the future [2]. Agricultural application, landfill and incineration were the most common disposal processes, whereas the traditional disposal routes are facing more and more pressure, due to land limitations and stringent regulations [2,3]. Thus, finding a cost-effective and environmental friendly solution is an urgent subject.

Sewage sludge is rich in volatile matter and thereby recognized as a potential bioresource for heating or perhaps as liquid fuel and chemicals [1]. Pyrolysis is considered as a promising alternative technology that converts sludge waste into useful products of gas, oil and solid char. Recently, fast pyrolysis in an oxygen-free atmosphere at relatively low temperature, rapid heating rate and short gas residence time to maximize oil product for fuel and chemical use has attracted significant interest [2,4,5]. However, conversion of sewage sludge into either fuel or chemicals by pyrolysis is limited by its low environmental feasibility. The nitrogen content in ligneous biomass is normally lower than 1 wt.% (daf) [6,7]. In contrast, nitrogen in sewage sludge accounts for up to 9 wt.% (daf) [3,4], resulting in much higher nitrogen content in pyrolytic oil from fast pyrolysis of sewage sludge than that from ligneous biomass [8,9]. In order to develop pyrolysis processes for reducing the formation of nitrogen-containing products, it is significant to understand the distribution and the structures of the nitrogen-containing species (NCSs) formed from the fast pyrolysis. Many researches investigated the pyrolysis mechanism [10] and the effects of operating parameters [4,5] on product distribution using different pyrolysis reactors and by characterizing the gases [8], oils [11,12] and solid char [12], but to our knowledge, few reports, if any, were issued on the nitrogen transformations during fast pyrolysis of sewage sludge.

In this work, we investigate the effects of reaction temperature and sweeping gas flow rate (SGFR) on product yields and the distribution of NCSs formed from fast pyrolysis of a sewage sludge. Prior to the pyrolysis experiment, the organic composition and pyrolysis characteristic of the starting sludge sample were first studied in this work. In addition, pyrolysis parameters on carbon and nitrogen distributions were compared and the possible formation routes of NCSs were presented.

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#### 2. Experimental

#### 2.1. Sewage sludge sample

A dehydrated anaerobically digested sludge was collected from sewerage management centre in Ako, Hyogo, Japan. It was pulverized to pass through a 60-mesh sieve ( $<250 \mu$ m) followed by drying at 107 °C for 24 h and then stored in an airtight container before use. Ultimate analysis was conducted with a Leco CHN-2000 elemental determinator and a Leco SC-432 sulfur determinator and the higher calorific value (HCV) was obtained with a Shimadzu CA-4PJ auto-calculating bomb calorimeter. The contents of major components in ash obtained at 815 °C for 1 h were determined with a Shimadzu EDX-700 energy dispersive X-ray spectrometer. Table 1 summarizes the main characteristics of the sludge sample (Ako sludge sample, ASS).

#### 2.2. Infrared spectral analysis

A mixture (1:10 w/w) of ASS with spectroscopic grade KBr was prepared and ground finely in an agate mortar. Then it was transferred into a sample cup (13 mm i.d.) to overflowing and a spatula was scraped across the top of the cup to remove excess powder and smoothed the sample surface in order to maintain uniform distribution of particle size. The process was then repeated with pure KBr in a separated sample cup. The sample cup was then loaded into a Nicolet Magna-II 550 spectrometer equipped with Spectra-Tech diffuse reflectance accessory, IR source, KBr beam splitter and a deuterated triglycerine sulfate/KBr detector. Diffuse reflectance infrared Fourier transformed spectrometry (DRIFTS) spectrum was collected 128 scans at a resolution of 4 cm<sup>-1</sup> in reflectance mode with measuring regions of 4000–400 cm<sup>-1</sup>. The pure KBr background spectrum was subtracted from the sample spectrum.

#### 2.3. Thermogravimetric analysis

A thermogravimetric analyzer (TGD 9600S, ULVAC-RIKO) was used to determine the pyrolysis behaviors of ASS. About 50 mg of ASS was placed in a pottery crucible and heated at 5, 10 and 20 °C/min from ambient temperature to 700 °C under the dry argon (Ar) flow of 500 cm<sup>3</sup>/min. The thermogravimetry (TG) and derivative thermogravimetry (DTG) were obtained using the software of the analyzer.

#### 2.4. Pyrolysis

As shown in Fig. 1, the fast pyrolysis experiments were performed at a prescribed temperature between 400 and 700 °C and an indicated SGFR between 150 and 1200  $\text{cm}^3/\text{min}$  in a drop tube quartz reactor (10 mm i.d. and 500 mm long) heated by electrical furnace and Ar was used as a sweeping gas. During the experiments, temperature measurements were taken above the quartz

## Table 1 Characteristics of ASS



Fig. 1. Schematic diagram of the fast pyrolysis process.

frit, with a K-type thermocouple in the middle of the tubular reactor. For each experiment, the reactor was heated up to the selected final temperature and then 2 g ASS was fed continuously dropped to the frit at a rate of approximate 0.1 g/min. After the sample was fed, the temperature was held for 10 min until no significant release of gas was observed. The liquid products were collected in a tar trap series with methanol cooled with an ice-water bath while the noncondensable gases were collected in a gas bag for GC analysis. After the experiments, methanol was removed with a rotary evaporator and the residual liquid was weighed as the liquid product. The residual solid remained above the frit was transferred and weighed as char.

In order to determine the amounts of HCN and NH<sub>3</sub> formed, other experiments were carried out using deionized water (DIW) as the absorption solvent in the same manner as above. The oil product dissolved in DIW is denoted as water-soluble oil (WSO) and the undissolved part as water-insoluble oil (WISO).

All the product yields are average from at least two repeated experiments and were calculated on daf basis.

#### 2.5. Characterization

Total carbon and nitrogen contents in char recovered were determined with the Leco-2000 elemental determinator.  $H_2$  and  $N_2$  in gaseous products were analyzed with a GC/TCD (GC/14B, Shimadzu), but the accuracy of  $N_2$  was somewhat low due to its low concentration as well as low sensitivity of the detector. The

Proximate analysis (wt.%)				Ultimate analysis (wt.%, daf)				<i>S</i> <sub>t</sub> (wt.%, d)	H/C	HCV (MJ/kg, d)
M <sub>ar</sub>	Ad	V <sub>d</sub>	$FC_d^a$	С	Н	Ν	O <sup>a</sup>			
12.29	28.74	60.05	11.21	50.72	7.70	8.69	31.30	1.59	1.82	16.24
Ash analysis (expressed as wt.% of metal oxides)										
CaO	$P_2O_5$	SiO	2	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	TiO <sub>2</sub>	CuO	Zı	nO SrO
28.93	19.95	19.6	58	13.54	4.43	2.80	2.16	1.14	0.	91 0.65

M, moisture content; A, ash content; V, volatile content; FC, fixed carbon; ar, as received basis; d, dried basis; daf, dried and ash-free basis. <sup>a</sup> Calculated by difference. Download English Version:

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