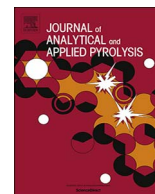




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The emission of gaseous nitrogen compounds during pyrolysis of meat and bone meal

Yuheng Feng*, Lu Wan, Shengjie Wang, Tianchi Yu, Dezhen Chen

Thermal & Environmental Engineering Institute, Tongji University, Shanghai, 200092, China

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ABSTRACT

Pyrolysis is a clean and economical method to dispose meat and bone meal (MBM) from animal carcasses. However, the large quantity of nitrogen from the animal protein will lead to the formation of gaseous-N compounds such as NH_3 and HCN, which are the precursors of NO_x . In this study, the release behavior of these gaseous-N compounds during the pyrolysis of MBM was investigated using a temperature-programmed tube reactor combined with an FTIR analyzer. Moreover, the formation mechanism of them was elucidated by examining the evolution of solid and liquid N-products with temperature. The result showed that 31.0% of the MBM was released as gaseous N including NH_3 , HCN and HNCO, among which NH_3 accounted for 76.2% while HNCO was a minor product. NH_3 was mainly released below 300 °C from the decomposition of ammonium and the polymerization of liable protein. On the other side, the nitriles and heterocyclic N-compounds identified in tar and char were the precursors of HCN and HNCO. The results provided basic data for the inhibition and removal of gaseous N-compounds during the pyrolysis of animal biomass.

1. Introduction

In March 2013, more than 16 000 dead pigs were found floating on Shanghai Huangpu River. This event drew public attention to the safe disposal of dead livestock in China. If not treated properly, the carcasses would be a source of diseases and endanger the health of the residents [1]. Producing meat and bone meal (MBM) is an effective method to destroy the caustic bacteria and virus in livestock remains [2]. During the production process, the carcasses are heated in the pressurized inert or steam atmosphere in a batch reactor operated over 100 °C. Then the lipid produced is separated and MBM is left as the solid product. The MBM was widely used as animal feed since the high content of protein. Yet this has been gradually forbidden in European and other countries because of the potential risk of bovine spongiform encephalopathy [2]. Using it as a secondary fuel of the combustor such as fluidized bed is an alternative in Europe [3]. However, the promotion of waste incineration has met some difficulties in China due to the public concern for the risk of excessive discharge of dioxin and other pollutants [4].

Pyrolysis is an economical and cleaner treatment of MBM disposal compared with incineration [5–7] due to the less pollutant discharge and higher utilization value of the products. The char produced contains a large fraction of hydroxyapatite (HAP) from the bones and heavy metals such as Pb, Zn, and Cd, are known to form stable minerals and complexes with hydroxyapatite [8,9] in acidic and neutral water.

Accordingly, Betts [10] tried to absorb Zn in waste water using MBM biochar and the result showed a high absorption capacity. Meanwhile, the high calorific value of the volatiles allows them to be combusted and provide heat for pyrolysis reactor. In addition, the oil produced could also be used as bio-diesel after further processing [11].

The high content of N in MBM from the proteins will be converted the gaseous-N products such as NH_3 and HCN during pyrolysis [6,7,12]. These N compounds, if not removed, will not only cause the corrosion of the gas pipeline, but also led to the high emission of NO_x during combustion of pyrolysis gas. Some studies focused on the emission of nitrogen from the pyrolysis of plant biomass and the model N compounds. Hansson [13,14] found that the HCN/ NH_3 ratio increases with temperature for different biomasses. Becidan [15] indicated that tar and volatile cracking are important contributors to the overall formation of HCN. Ren [16] investigated the role of the main constituents of plant biomass on N emission during the pyrolysis and the result showed that N- NH_3 conversion is inhibited by while promoted by lignin. However, N-compounds are not released independently from the rest components of the biomass [15]. Therefore, it's necessary to study the emission of gaseous N compounds from pyrolysis of MBM to provide basic data for the inhibition or the removal of them.

This study focused on the formation of gaseous-N products during pyrolysis of MBM. The emission of NH_3 , HCN and HNCO along with the temperature in inert atmosphere was quantified by a temperature-

* Corresponding author.

E-mail address: fengyh@tongji.edu.cn (Y. Feng).<https://doi.org/10.1016/j.jaap.2017.12.017>Received 4 September 2016; Received in revised form 17 December 2017; Accepted 26 December 2017
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Table 1
Proximate and ultimate analysis of the MBM sample (wt%).

Proximate analysis ^a				Ultimate analysis ^b				
Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	O
24.32	12.14	59.65	3.89	58.44	8.69	9.83	0.92	22.12

^a as received basis.

^b dry and ash-free basis.

programming tube furnace combined with an FTIR analyzer. To reveal the pathway from MBM-N to the gaseous-N during pyrolysis, the N compounds in tar collected in different temperature range was semi-quantified by a GC–MS analyzer. In addition, the evolution of N functionalities in char with pyrolysis temperature was investigated by XPS and FTIR analysis.

2. Materials and methods

2.1. Material

The MBM sample made from pig carcasses was provided by an energy company in Shanghai. The batch reactor was operated at 130 °C and 0.4 MPa and the residence time for the carcass was 30 min. The ultimate and proximate analysis of the MBM was listed in Table 1. The sample used in this study was dried in the oven at 105 °C for 12 h and grounded into powder with the size smaller than 0.5 mm. Amino acids in the MBM were quantified by an amino acid analyzer (L-8900, HITACHI, Japan) and listed in Table 2. It could be found that the total fraction of amino acids represented 49.97% of the dried sample, which was close to the reported data [17]. N in amino acids accounted for 86.51% of the MBM-N.

2.2. TG experiment

The weight loss behavior of the MBM was studied by TG analysis on a WRT-3P thermal balance (Shanghai Precise Scientific Instrument LTD, China). During the TG experiment, the crucible containing around 6 mg of the sample was placed on the balance and heated from 50 °C to 800 °C at 10 °C/min with N₂ as the carrier gas.

Table 2
Contents of different amino acids in MBM sample (wt%, dried base).

Name	Proportion
Aspartic acid	4.05
Threonine	1.86
Serine	1.90
Glutamic acid	6.83
Glycine	5.49
Alanine	3.68
Cystine	0.51
Valine	2.40
Methionine	0.98
Isoleucine	1.76
Leucine	3.50
Tyrosine	1.25
Phenylalanine	2.23
Lysine	3.01
Histidine	1.15
Arginine	3.18
Proline	3.49
Hydroxy-Proline	1.97
Total of amino acids	49.97

2.3. Analysis of the gaseous-N compounds

As in Fig. 1, the pyrolysis reactor was a tube furnace. A ceramic boat containing 0.3 g of the MBM sample was placed in the middle of the furnace. A portable Fourier transform infrared spectrometer gas analyzer GASMET Dx-4000 (Temet Instrument Oy, Finland) was used to quantify the N compounds in pyrolysis gas. In the experiment, the sample was heated from 100 °C to 800 °C at 10 °C/min and kept at 800 °C for 40 min to ensure the complete emission of the pyrolysis gas. Ar was passed into the tube as the carrier gas at the flow rate 4L/min. NH₃, HCN, HCNO, NO, N₂O and NO₂ were set as possible N products while only NH₃, HCN and HNCO were identified in the FTIR spectrum. The wavenumber regions in 918–980 cm⁻¹ and 2190–2300 cm⁻¹ were used to quantify NH₃ and HNCO. The highest band of HCN is in 3172–3419 cm⁻¹, but the stretching of NH₂ is around 3335 cm⁻¹. Therefore, 3172–3300 cm⁻¹ was used to quantify HCN. To avoid the condensation of water, the pipe connecting the reactor and the analyzer was heated to 140 °C during the experiment.

2.4. Analysis of N functionalities in solid product

X-ray photoelectron spectroscopy (XPS) analysis of the MBM and its pyrolysis chars produced at different temperatures was performed on an ESCALAB 250 Xi spectrometer with an Al K α X-ray source (20 kV and 10 mA). The spectrometer was operated under pass energy 20 eV for the survey spectra and 100 eV for the single element spectra. All samples were analyzed under identical conditions and referenced to the C 1s peak at 284.6 eV. Least-squares curves fitting of the spectra were performed using Gauss-Lorentzian shapes. N-functionalities in different samples were semi-quantified from dividing the corresponding peak area value by the total peak area of N in the raw sludge.

In the FTIR analysis of the chars, the sample was thoroughly mixed with KBr (FTIR grade, from Merck) in the mass ratio 1:100 and then made into pellets. The analyses were performed using an EQUINOXSS/HYPER, Bruker Vertex 70 spectrometer (Bruker Co., Germany) in the region 4000–400 cm⁻¹ at the resolution 0.5 cm⁻¹.

2.5. Analysis of N compounds in liquid product

To collect the oil sample over the heating process, the same tube furnace pyrolysis system as in Fig. 1 was connected to an ice bath. 20 g of the sample was placed into the furnace, while other parameters were set as the same in the analysis of gaseous-N compounds. The pyrolysis liquid in the temperature range 250–350 °C, 350–450 °C, 450–550 °C, 550–650 °C and 650–800 °C was collected. The final temperature was kept for 10 min at the end of each range to ensure the complete emission of the volatiles. The organic phase was extracted by dichloromethane and analyzed in a gas chromatograph-mass spectrometric (GC–MS) analyzer Shimadzu GCMS-QP2010SE (Shimadzu Corporation, Kyoto, Japan), using an Rtx-5MS capillary column, 60m \times 0.25 mm i.d., film thickness 0.25 μ m). The heating program of GC was set as 35 °C for 5 min, 35–300 °C at 6 °C/min and 300 °C for 3 min. The identification was performed by comparing the mass spectrum of the separated compound with the NIST mass spectra library. To study the variation of the concentration of nitrogen compounds with different temperature range, the compounds was semi-quantified by normalization, which divide the peak area of the individual compound by the total peak area in the total ionization chromatograph (TIC).

3. Results and discussions

3.1. TG analysis and pyrolysis liquid formation

The TG and DTG curves of the pyrolysis of MBM are displayed in Fig. 2. According to the peaks in the DTG curve, the pyrolysis process could be divided into three stages. The first stage was from 50 °C to

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