Carbon-containing gaseous pollutants emission characteristics during municipal sewage sludge combustion and pyrolysis with TG-MS technique

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Abstract. In this study, the carbon-containing gaseous pollutants emission characteristics during municipal sewage sludge combustion and pyrolysis were investigated by using simultaneous thermogravimetry-mass spectrometry (TG-MS) method. The results indicated that the sewage sludge possesses different devolatilization characteristics in the terms of mass loss and gas evolution. The main decomposition of sewage sludge during the combustion process was divided into four stages, and only first three ones existed during sludge pyrolysis. The evolved carbon-containing gaseous products (CO_2 and light hydrocarbons) emission behaviours during combustion and pyrolysis were different. This research provided basic data support and background knowledge for municipal sewage sludge thermal disposal and fuel gas treatment, which could help to control the gaseous pollutants during sewage sludge thermal treatment.

1. Introduction

Municipal sewage sludge (MSS) originates from urban waste water treatment plant and is being produced in increasingly higher volumes due to ever greater establishment of wastewater treatment plants[1]. With the increasing rigor of national environmental regulations and the growing demand for environmental quality, finding an economic, efficient and safe sewage sludge treatment and disposal method has become one of the major environmental issues of particular concern[2]. Due to the relatively high quantity of high calorific value which similar to that of brown coal[3], MSS could be considered as an alternative type of fuel. Several thermal technologies, such as gasification, combustion and pyrolysis processes were applied because of the outstanding advantages of large reduction in volume, the thermal destruction of toxic organics and the recovery of energy[4,5]. Among them, combustion and pyrolysis are the most promising options.

Nowdays, thermal decomposition characteristics of MSS during combustion and pyrolysis have been widely investigated by thermal analytical techniques. The influence of reaction atmosphere and temperature has been studied[6], mechanisms and kinetics of combustion or pyrolysis processes has been performed[7]. However, there is barely any report on the comprehensive thermal analysis of MSS in thermal decomposition processes including the effects of both reaction atmosphere and stages on emission characteristics of gaseous pollutants so far. Therefore in this study, emission characteristics of carbon-containing gaseous pollutants during MSS combustion and pyrolysis were compared by

using thermogravimetry-mass spectrometry (TG-MS), which provided basic data support and background knowledge for MMS thermal disposal and fuel gas treatment.

2. Materials and methods

2.1. Materials preparation
MMS sample used in this study was collected from a wastewater treatment plant in Guangzhou, China. Dewatered sewage sludge with about 80% moisture content was taken from the plant during its normal operation. After dried and milled, the sludge was stored at 20 ºC and 60% RH for at least 3 days before use. The characteristics of raw material are shown in Table 1. The moisture(M), ash(A), volatile matter(V) and fixed carbon(FC) contents were measured according to the Chinese standards(GB/T212-2008). The ultimate analysis was carried out in an elemental analyzer (EuroVector Instrument, EA3000). Metals contents was analyzed by a XPS (Escalab 250Xi, Thermo, America), with C1s(284.6 eV) peak as the internal calibration. High heat value(HHV) was determined with a PARR adiabatic calorimeter.

Table 1. Characteristics of sewage sludge sample.

Proximate analysis (wt.%, adb)				Ultimate analysis(wt.%, db)				
M	A	V	FC[a]	C	H	N	S	O
3.60	56.84	37.50	1.06	21.11	3.42	2.84	1.13	9.39
Metals contents(wt.%, db)							HHV (MJ/kg, db)	
K	Ca	Na	Mg	Al	Fe	Si		
0.61	0.73	0.30	0.56	5.13	0.16	7.05	9.80	

Notes: adb-air dry basis; db-dry basis; [a] Calculated by difference.

2.2. TG-MS analysis
The thermogravimetric (TG), derivative thermogravimetric (DTG) and differential scanning calorimetry (DSC) analysis were run in a synchronous thermal analyzer (Netzsch, SAT449C). Evolved gas was identified on line by mass spectrometer (MS) (Netzsch, QMS 403). The thermobalance furnace was connected with an ionization chamber of the mass spectrometer by means of a fused silica capillary heated at 200 ºC. The mass spectrometer was operated with an electron ionizer (70 eV) and the selected intensities of m/z ranging from 2 to 100 were monitored.

In combustion and pyrolysis process, synthetic air (80% helium and 20% oxygen) and 100% helium were used as simulated gas respectively. In both process, 40 ± 0.5 mg of MSS sample with the particle size less than 75 μm was placed into alumina crucibles without lids and heated up from room temperature (about 25 ºC) to 1200 ºC under simulated gas flowing around the sample with the rate of 40 ml/min. The constant heating rate was 10 ºC/min ensured the heat transfer limitation can be ignored. Data of TG, DTG and DSC were obtained by computer automatically during each experiment.

About 1% of the effluent gas from the synchronous thermal analyzer was allowed to pass the MS through the capillary. The mass-charge ratio (m/z) was 1 to 300 (atomic mass unit) with the scan rate of 0.2-60 s/u. Gaseous products identified by characteristic ions were monitored together with the TG, DTG and DSC data at different times, every weight loss peak means a detected peak of molecular ions and fragment ions were detected on the MS curve[8].

3. Results and discussions

3.1. Behaviours of MSS during thermal decomposition
The TG, DTG and DSC curves obtained from the combustion process of MSS were displayed in Figure 1. As shown in Figure 1, MSS combustion process could be divided into four stages, which including dehydration (start-190 ºC), 1st devolatilization (190-580 ºC), 2nd devolatilization (580-850

ºC) and inorganic decomposing (850 ºC-end). While during the pyrolysis, only three mass loss peaks were detectable, and the temperature ranges of the three stages were close to the first three ones of combustion. During the water evaporation stage, a mass loss peak appeared on the DTG and a small endothermic peak was detected on the DSC curve, the mass loss ratio of sewage sludge pyrolysis at this stage was 3.27%, which was similar to that of the first mass loss peak during sludge combustion. Different from coal, the content of fixed carbon in MSS can be ignored (<1.5 wt.%), then the mass loss at the temperature range of 190 ºC to 850 ºC was mainly caused by the decomposition of volatile and can be divided into two sections: 190-580 ºC and 580-850 ºC. The first volatile decomposing stage during sewage combustion was exothermic, while the summit of DSC curve took place earlier than that of DTG at this temperature range, it can be inferred that this mass loss was mainly caused by the volatilization and decomposition of volatile matter in the sludge, as volatile released at relatively low temperature first, and then reacted with the oxygen and decomposed. Compared with the behaviours during sludge combustion, the mass loss ratio during sludge pyrolysis was smaller and no endothermic or exothermic peak existed on the DSC curve. The reason could be interpreted as that: the volatile matter began to absorb heat in the temperature range of 190-580 ºC, the pyrolysis of small molecules was exothermic, and the heat values of the two were synchronous and equal, so there was no obvious peak on the DSC curve at this stage. As the temperature increased to 650 ºC, the volatile matter in MSS which thermally decomposed in this temperature range began to react, the peak positions of the two processes were close, and both have an obvious exothermic peak on the DSC at this stage, while the mass loss ratio and releasing heat during MSS pyrolysis was bigger than that of combustion, which was opposite to the previous stage. When the temperature reached 850 ºC, a small endothermic mass loss peak appeared on the DTG curve. As combustible matter in MSS decomposed almost completely, the mass loss at this stage was caused by the decomposition of the inorganic salts. Based on the fact that no mass loss occurred with the absence of oxygen, it could be presumed that the reaction atmosphere played an important role in inorganic matter decomposition. The total mass loss during MSS combustion was 40.30%, which was similar to that of pyrolysis, both had no distinctly difference from the proximate analysis results.
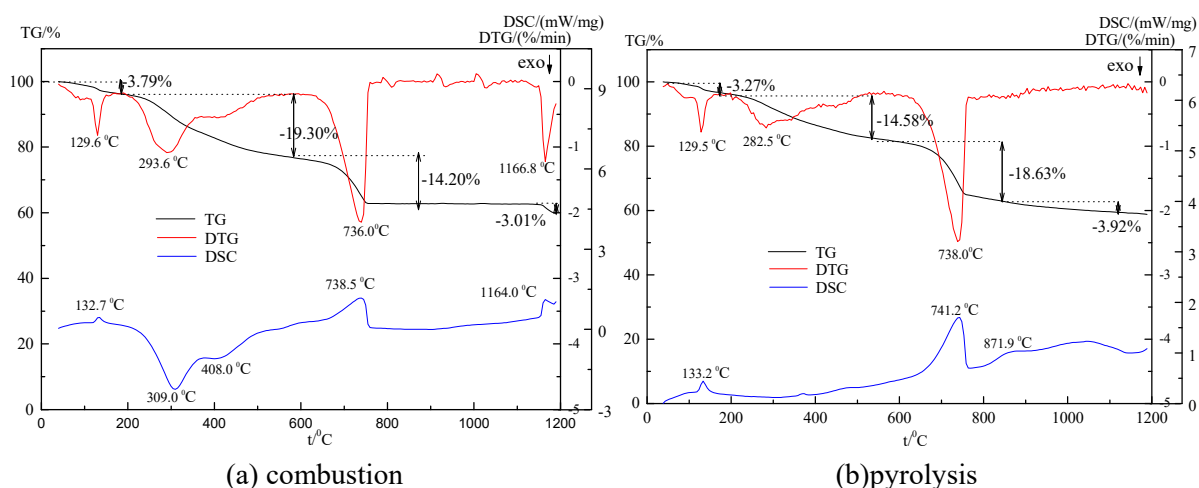

Figure 1. Behaviour and characteristics during MSS thermal decomposition.

3.2. Release characteristics of gaseous pollutants

It is believed that the organic matter in MSS mainly consisted of protein, fat, carbohydrate and cellulose[9]. During combustion and pyrolysis, MSS thermally decomposed and evolved gases are evolved by series of thermal decomposition reactions and gaseous components such as H_2O, CO_2, SO_2, NOx and light hydrocarbons were formed. Figure 2 and Figure 3 display the on-line MS curves of carbon-containing gas evolution as described in Section 2.2, and the results are shown below:

3.2.1 Carbon dioxide (CO₂). When the temperature increased to 200 ºC, unstable C=O of macromolecular organic matters began to break and generated CO_2 (m/z 44). The emission of CO_2 mainly focused on the second and third mass loss stages of MSS decomposition. The first CO_2 emission stage took place between 200 ºC and 550 ºC. Compared the CO_2 emission patterns between MSS combustion and pyrolysis at 200-600 ºC, it can be found that there was a strong peak detected during combustion, while no CO_2 detectable at this temperature range. As the decomposition of carboxyl functional group was mainly concentrated at the range of 400-500 ºC[10], the source of CO_2 at this stage was presumed to be the decomposition and oxidation of carboxyl group. Despite CO_2 released at 600-800 ºC and reached its summit near 740 ºC in both processes, the relative amounts were different. The weight loss ratio and endothermic value in pyrolysis process were larger than those of combustion, which indicated the weight loss was mainly caused by the fracture of oxygen-containing heterocyclic ring of the volatile components with higher precipitation temperature and the decomposition of carbonate minerals[11], and anaerobic conditions were more favourable for this reaction.
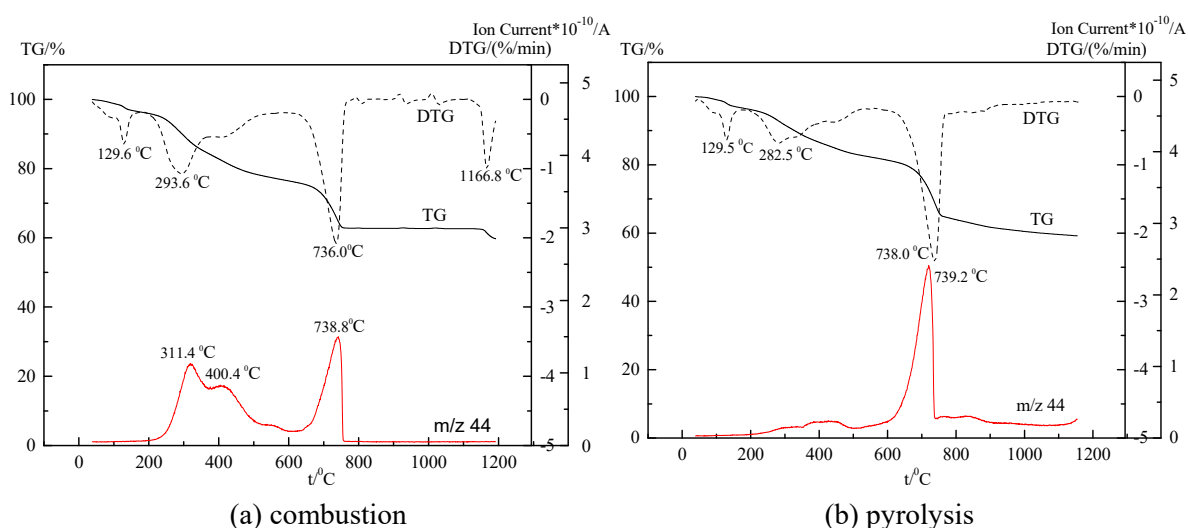

Figure 2. Release characteristics of CO_2 during MSS combustion and pyrolysis.

3.2.2 Light hydrocarbon (HC). During MSS decomposing, the C-C bond could be easily broken. Because the bond energy of C-C (246.9 kJ/mol) is lower than that of the C-H bond (413.8kJ/mol)[12], and the free radicals formed can mutually combine freely with hydrogen atoms[13], some light hydrocarbon were formed. Despite the differences between peak intensity, m/z 39, 41, 42 and m/z 43, 45 curves (shown in Figure 3) were in good similarity and consistency respectively. For m/z 39, 41 and 42 curves, only one peak was detectable and reached the peak at 292 ºC, corresponding to the decomposition of volatile which resolved at 200-500 ºC in the combustion process, while no obvious peak but emission interval was detected at the same temperature range during pyrolysis. Comparing the peak area of each curves, it can be seen that the emission intensity of m/z 39, 41 and 42 during pyrolysis were bigger than that of combustion. As no obvious heat absorption or heat release peaks were found at this temperature range, the products were low molecular weight organic compounds which produced by incomplete combustion of organic matter with lower volatilization temperature, while the structure of macromolecule was relatively stable. For curves of m/z 43 and 45, peaks were both observed at the second and third mass loss steps which corresponded to the decomposition of volatile at both 200-500 ºC and 600-800 ºC. Under aerobic condition, the emission of light hydrocarbon (m/z 43) mainly centered between 200-600 ºC, which corresponding to the volatile matter of lower decomposition temperature in the sludge, so as m/z 45. While under anaerobic conditions, the formation of light hydrocarbons (m/z 45) was mainly concentrated around 730 ºC, and light hydrocarbons (m/z 43) existed both in lower reaction temperature range and the higher one. The light hydrocarbons produced in the higher temperature range mainly came from the pyrolysis of macromolecular organic compounds, and the aerobic conditions were more favourable for the

formation of products with lower mass-to-charge ratio. Substances with relatively high mass-to-charge ratio were more likely to generate during pyrolysis, and the types of products were related to the composition of the sludge itself and the reaction atmosphere.
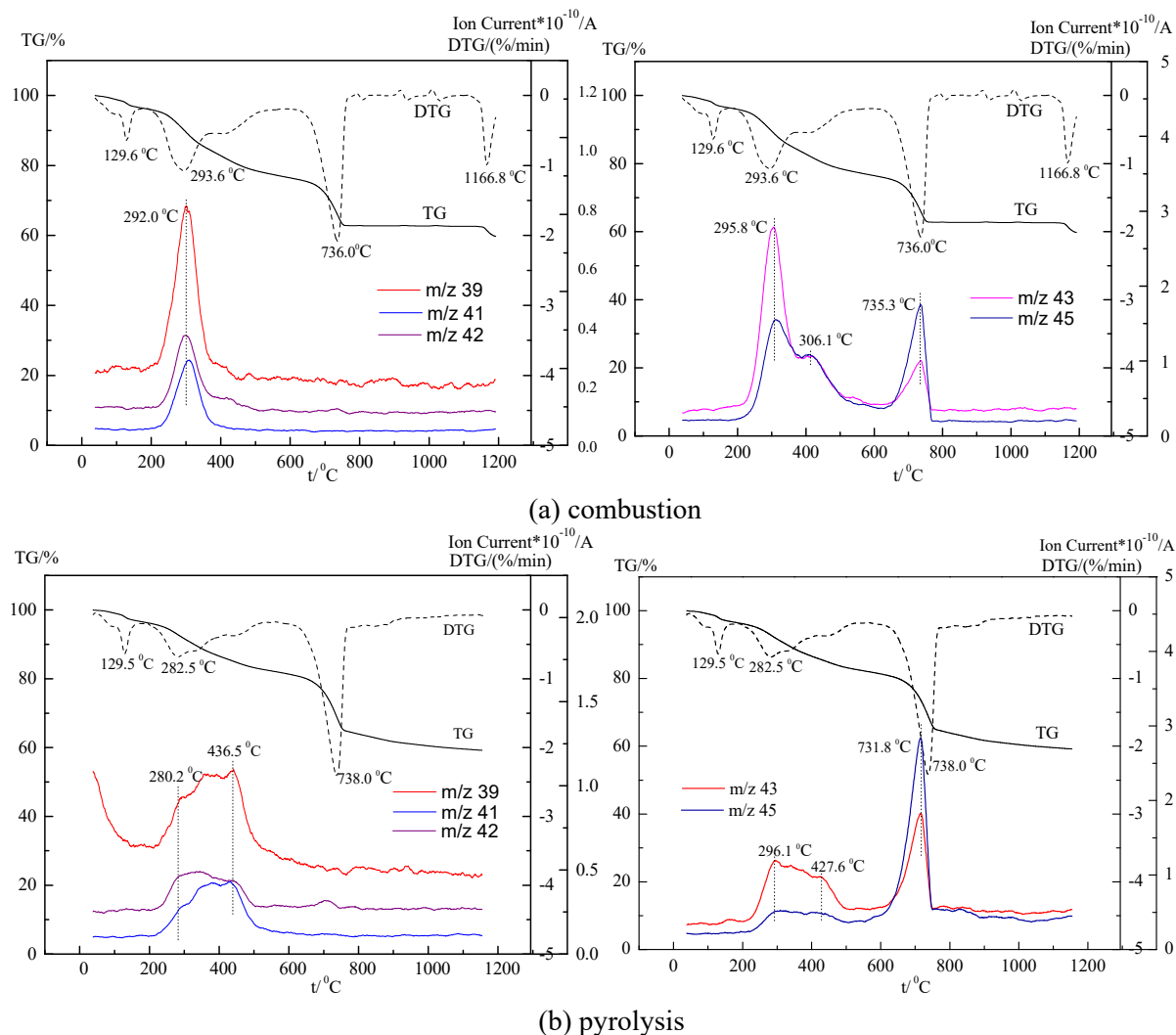

(a) combustion

(b) pyrolysis

Figure 3. Release characteristics of light hydrocarbon during MSS combustion and pyrolysis.

According to this research, TG-MS method can be used to distinguish the emission characteristics of gaseous products during MSS combustion and pyrolysis, which will help to control the reaction temperature and atmosphere to adjust the release of gaseous pollutants.

4. Conclusions

Based on the TG-MS results of carbon-containing gaseous pollutants emission characteristics during MSS combustion and pyrolysis, the following conclusions can be drawn:

(1) There were four main weight loss peaks in the sludge combustion process, which were the emission of water, the decomposition of low volatile matter, the decomposition of high volatile matter and the decomposition of inorganic salts. Except for the decomposition of volatile matter with low precipitation temperature was exothermic, all the rest three stages were endothermic. In the pyrolysis process, only three peaks existed, and the whole process was endothermic.

(2) As for the production of CO_2, under aerobic condition, it mainly came from the decomposition of carbonate and oxygen-containing groups in the sludge and the combustion of organic carbon; while

under anaerobic conditions, it mainly came from the pyrolysis of volatile compounds with higher precipitation temperature.

(3) The main organics generated during the sludge combustion and pyrolysis was light hydrocarbon (m/z 39-45), aerobic conditions were more favourable for the formation of products with lower mass-to-charge ratio, while substances with relatively high mass-to-charge ratio were more likely to be produced in an anaerobic atmosphere, the types of products were related to the composition of the sludge itself and the reaction atmosphere at which it was decomposed.

Acknowledgements

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