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Combination of combustion with pyrolysis for studying the stabilization process of sludge in landfill

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Abstract

Study on the stabilization processes is important to follow the landfill process and evaluate quality of organic matters. However, a simple, yet reliable and widely acceptable analytical tool to evaluate the degree of stability remains to be found. Temperature programmed combustion and pyrolysis tests were carried out to investigate the stabilization degree of sludges and demonstrate applicability of thermal methods in waste management. By the combination of combustion and pyrolysis, we can get more information of the sludges and reaction happened in the programmed heating process than combustion only.

TG/DTG analysis of sludge combustion helps us to know about the variation of different kinds of organic matters and the degradation degree of the anaerobic stabilization process. The decreasing tendency of DSC peaks reveals the stabilization process is still ongoing.

Keywords: Thermogravimetry (TG); Differential thermogravimetry (DTG); Differential scanning calorimetry (DSC); Stabilization; Sewage sludge; Pyrolysis

1. Introduction

Wastewater treatment entails the generation of a by-product, sewage sludge, which is difficult to dispose of, owing to both increased production and more restrictive policies concerning re-use. The production of dried sewage sludge corresponding to China is around 300,000 tons per year. The general technologies for the treatment of these large amounts are the direct use, composition with fertilizer for as product, disposal in landfills, dumping into the sea and thermal treatments [1]. Considering the environmental effects and economy, landfill should be a good option in China.

It is necessary to follow the landfill process with suitable parameters able to evaluate stabilization and the quality of its organic components. Many parameters have been proposed for the evaluation of waste materials stability, with varying degrees of reliability and technical complication, including chemical tests, microbiological assays and the determination of the humified organic matter; but the analytical determination of all these parameters was often complicated [2,3]. Despite the widespread use of sludge stabilization processes, there is still no simple, reliable and universally acceptable analytical method for assessing the stability. One of the approaches with the most scientific basis is that proposed by Hartenstein [4], whereby sludge could be said to be stable when the original solid residues have been converted into non-putrefying odorless humic matter with very slight and very slow degradation. Then, and bearing in mind the basis of stabilization, a parameter for the characterization of stability should be related to the principal stabilization process taking place.

Degradation and stabilization are manifested by changing energy content. This fact leads to consider thermal methods as promising techniques through the control of the energy content of the sludges and the loss of organic matter by oxidation/ignition. They are based on a programmed heating of the samples in controlled atmosphere, which finally provides qualitative and quantitative information regarding the organic matter. In addition the entire sample can be analyzed avoiding chemical extraction steps that very often affect the nature and the ambience of organic matter. For complex samples this approach proves advantageous and provides additional information.

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To study the thermal degradation of wastes, many thermal analysis techniques have been used [5–7]. Different stages of compost maturity have been studied using differential scanning calorimetry (DSC) and thermogravimetry (TG) [8,9]. The stabilization progress of sewage sludge was monitored by means of differential thermogravimetry [10]. However, most studies have focused on the materials using compost technology. The study on the stabilization process of sewage sludge in landfill using thermal method has not been reported by now.

However, deriving knowledge of the thermal degradation process from TG mass loss data is rather complicated owing to generally complex kinetics [11]. In this regard, mass spectrometry is a useful tool for the investigation of thermal decomposition of wastes. The combination of MS and a thermogravimetric analysis system offers several advantages in thermal gas emission determination such as real-time analysis and qualitative and quantitative analysis [12]. Different stages of compost have been characterized using pyrolysis field-ionization mass spectrometry [13,14].

Some papers have been published about the pyrolysis of sewage sludge. Caballero et al. [15] analyzed the formation of primary and secondary products in the pyrolysis of sewage sludge considering the formation of hydrocarbons and carbon oxides. Conesa et al. [16] studied the evolution of some gases and volatiles in the pyrolysis of different sewage sludge samples. However, there is little study on the stabilization process of sewage sludge using pyrolysis technology. No studies have also been found considering pyrolysis and combustion of the same sludges in the stabilization process.

The aim of this work was to give a contribution to a deeper knowledge of the landfill process and to demonstrate the applicability of thermal analysis to assess stability of sewage sludge by analyzing TG-DTG, DSC of combustion and corresponding pyrolysis of sludge with different stabilization degree. In the absence of mass spectrometry, the combination of combustion and pyrolysis provide more detailed information than combustion only to define sludge quality and stability. Therefore, the study carried out in this work is important and novel with respect to other papers.

2. Materials and methods

Sewage sludge employed in this study came from the Bailonggang wastewater treatment plants in Shanghai. The sludge was landfilled at Shanghai Refuse landfill. A total weight of 1800 tons of sewage sludge was placed in the landfill unit. The top and bottom area of the unit was 1024 m^2 (32 m × 32 m) and 100 m^2 (10 m × 10 m), respectively. The total height of the unit was 6 m and it was divided into three layers in average by the ladder shape of the landfill slope. During the positioning of every layer, tri-planer geocomposites were laid to accelerate the drainage and concretion.

The samples were taken from the same sampling points for an interval from weeks to months. For thermal analyses five samples (0, 60, 90, 150, 300 days) were selected from the samples during the landfill process (0 day represents the sludge used for landfill) .The sludge was air dried at room temperature for about 24 h, ground in an agate mill, screened through 0.63 mm, and milled with an agate mortar.

Thermal analyses were performed with an SDT Q600 (TA) that enables the recording of thermograms and DSC curves, all samples were combusted with synthetic air (gas flow: 100 ml min^{-1} composition 21 ± 1% O_2 and 79 ± 1% N_2; purity ≥ 99.9994%) and pyrolyzed with N_2 (purity ≥ 99.9994%). The sample (of 10 mg) was subjected to a heating rate of 10 °C min^{-1} from 50 to 900 °C. A total calibration with indium/zinc, followed by a check DSC exo-indium, was performed before the analysis.

Water-soluble extract 1:10 (w/v) for shaking one hour was made to measure pH using pH meter and soluble total organic carbon (STOC) after filtration with 0.45 μm membrane using TOC—VCPN (SHIMADZU) analyzer. The total content of volatile matter (VM) was determined by incineration at 550 °C. Total carbon (TC) and total inorganic carbon (TIC) was analyzed by combustion in a VCPN (SHIMADZU) analyzer. Total organic carbon (TOC) was calculated by the difference between TC and TIC. Dehydrogenase activity (DHA) was measured using INT-DHA methods [17].

3. Results and discussion

3.1. Physical, chemical and biological parameters

During different periods, some parameters of the sludge were analyzed to make sure that we can follow the stabilization process. Table 1 shows the variation of these parameters. It can be observed that pH decreases in the former 60 days and then shows an increasing tendency. This indicates that the anaerobic process entered the stage of methane production after finishing acid stage. The decrease of VM and TOC along the stabilization process indicates degradation of the total organic matters. Moreover, the degradation rate of the former 60d is faster than that of later stages.

Microorganism activity can change during biodegradation of organic compounds under anaerobic conditions. DHA concentration was used to indicate microorganism activity in this study. There is relative high DHA content in 60d and 90d. This is related to the acid stage of anaerobic process. In these two stages, the microorganism activity is higher than that in later methane production stage. STOC can reflect the content of soluble organic matters already directly degradated. There is good correlation relationship between STOC content and DHA content, and the degradation ability of microorganisms can be determined by measuring DHA content.

Table 1
Changes of parameters during landfill process

Parameters	0d	60d	90d	150d	300d
pH	7.34	7.04	7.25	7.44	7.93
VM (%/dry basis)	44.7	38.6	36.3	35.1	32.2
TOC (%/dry basis)	23.5	19.8	18.6	18.0	17.1
DHA (mg TF/g 6 h)	6.72	13.6	13.8	12.0	11.4
STOC (mg/L)	469	747	758	673	651

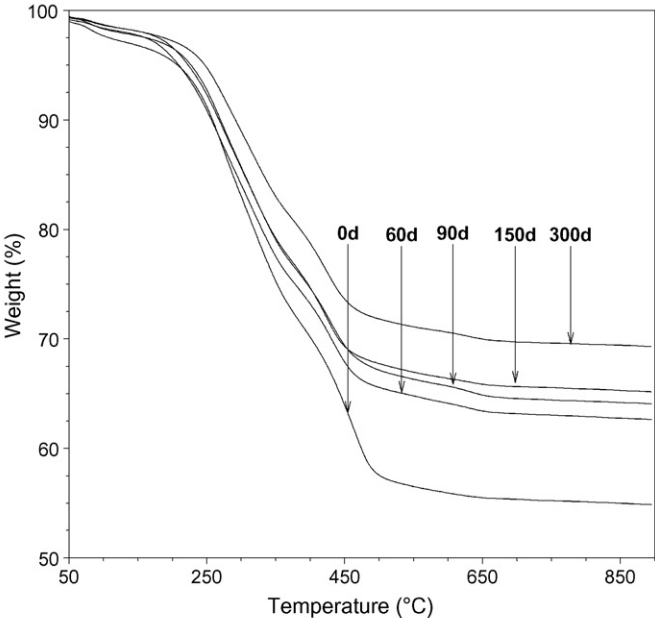

Fig. 1. TG combustion curves of sludges at different stages in the landfill process.

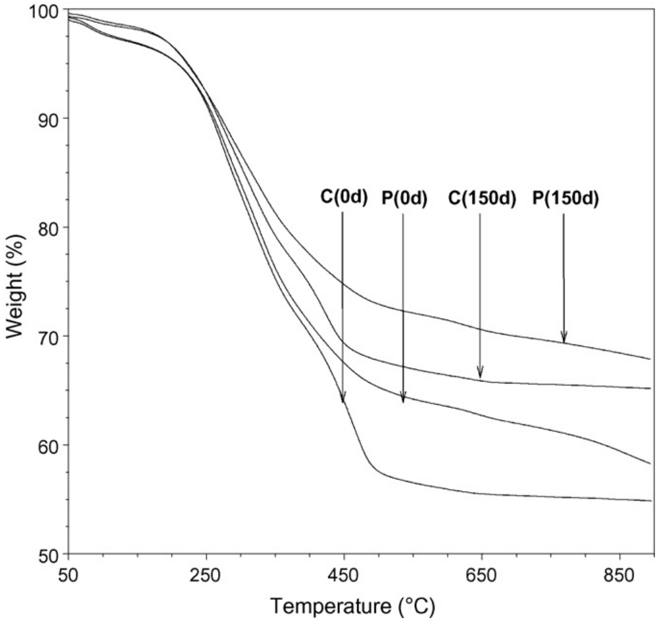

Fig. 2. Comparison of TG combustion and pyrolysis curves of sludges at different stages in the landfill process.

3.2. TG Analysis and comparison of combustion and pyrolysis

Fig. 1 shows the TG combustion curves of the sludges in different landfill periods. It can be observed that there is a general tendency of decomposition. Owing to the mineralization process taking place during stabilization treatment, sewage sludge residues from temperature programmed combustion increase as stabilization progresses. The residual weight fraction at 900 °C varies between 55.6 and 67.8%.

Considering the undistinguishable characters of so many TG combustion curves and the corresponding pyrolysis curves, only combustion curves and corresponding pyrolysis curves of two landfill periods are listed in Fig. 2 for comparison. C and P is representative of combustion and pyrolysis process, respectively.

From Fig. 2 we can see that 0d and 150d sludge have a combustion curve that is coincident or close to the corresponding pyrolysis curve in the 50–400 and 50–260 °C temperature range, respectively (the first part) and then shows decay till 900 °C (the second part). Font et al. [18] and Francisca et al. [19] had the same finding in analyzing the pyrolysis and combustion of sewage sludge by TG. This phenomenon indicates that the weight loss of the first part is mainly caused by the thermal separation of volatiles. The decrease of volatiles due to degradation in landfill makes the first part of C150d curve end earlier than that of 0d. With the temperature rises, in the second part, the oxygen accelerates the decomposition rate in comparison to the pyrolysis, organic matters start to combust and as a consequence of the char formation there is a final sharp decay of the curve due to the combustion of the char. So combustion process is faster than pyrolysis process. We can see that there is almost equilibrium for combustion at the time when the temperature of the furnace reaches 900 °C, but this does not seem to be the case for pyrolysis. In this part, the C150d curve is closer to the corresponding pyrolysis curve than that of 0d. This can be attributed to the degradation of 150d sludge, and the char formation is also less than that of 0d sludge.

Here, we should note that the degradation of organic materials in the second part may increase the amount of volatiles at the same time, because volatile matter is usually the easiest to be digested by microorganisms and it has been the first to disappear along the landfill process. The amount of volatiles produced in the second part is less than that of degraded in the first part, so the temperature at which combustion starts for most of materials in 150d sludge is still lower than that of 0d sludge.

So we can conclude that the TG combustion curve and corresponding pyrolysis curve of landfill sludge in different degradation stages can not only give us some information about the weight variation of the sludge in certain temperature, but also let us to know about the degradation of simple and complex organic matters generally.

3.3. DTG analysis

3.3.1. DTG comparison of combustion and pyrolysis

Fig. 3 shows changes undergone by the DTG combustion and pyrolysis profiles corresponding to sludges along the stabilization process. In accordance with the shape of the curves, the combustion sludge curves can be divided into four obvious phases, while only three obvious phases can be detected in the pyrolysis curves. For both of these kinds of curves, a slight weight loss within the temperature range from 50 to 130 °C, is mainly caused by the dehydration reactions. The water content of The DTG combustion curve of this phase is almost coincident with the corresponding pyrolysis curve. The loss of residual water within this temperature range was also reported by Dell'Abate et al. [9] and Melis and Castaldi [20]. We also determined the water content of air dried samples, and they are

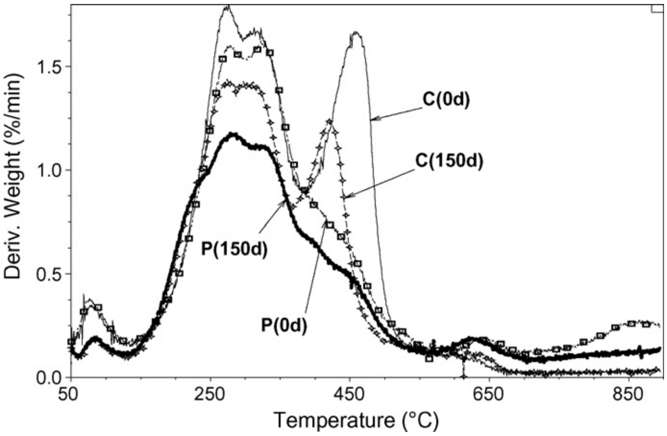

Fig. 3. Comparison of DTG combustion and pyrolysis curves of sludges at different stages in the landfill process.

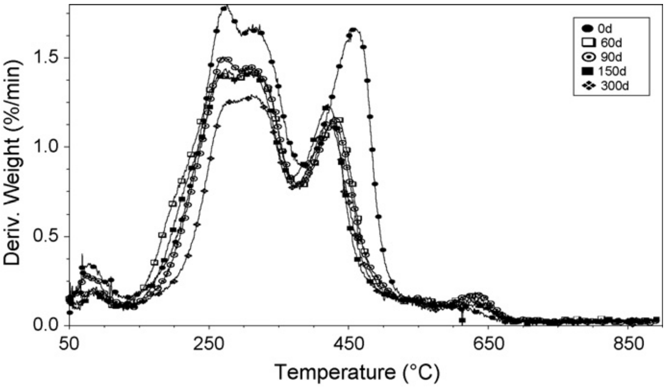

Fig. 4. DTG combustion curves of progressive stages in the landfill process.

1.7%, 1.5%, 1.4%, 1.3%, and 1.1% for 0d, 60d, 90d, 150d, and 300d sludges, respectively. This further confirms the dehydration reactions at this temperature.

Two obvious peaks (between 130 and 375 °C, and 375 and 590 °C, respectively) are observed in the DTG combustion curve. While for the pyrolysis curve only the first peak can be differentiated, as the second one does not take place. It shows us that the first peak is mainly caused by the thermal decomposition and loss of volatiles. The first peak has the maximum mass loss compared with the other stages. By comparison, we can see that the combustion curve is a little higher than the corresponding pyrolysis curve, which can be attributed to the combustion of a small amount of organic materials with shorter hydrocarbon chains. According to the disappearance of the second peak of the pyrolysis curve, we know that the second peak of the combustion curve is mainly caused by the combustion of organic matters with longer hydrocarbon chains.

From 590 to 900 °C, the rate of mass loss has become small, and there is a small peak between 590 and 670 °C. The rate of mass loss for the pyrolysis curve is higher than that of the combustion curve in this phase. Several factors, including thermal decomposition of residual organic materials and the mineral materials, the char combustion and oxidation of metals in the presence of oxygen, etc., may contribute to the results mentioned above.

Accordingly, we can further analyse and discuss about the main materials and reactions happening under different temperature by comparing DTG curves of combustion and pyrolysis.

3.3.2. DTG analysis of sludge combustion

DTG combustion curves of different landfill periods are presented in Fig. 4. Owing to the dehydration and solidification process of sludge, the water content decreases and the intensity of the first peak shows a little decrease along the stabilization process. In the 130–375 °C range, corresponding mainly to the loss of volatiles and a little to the combustion of organic matters, the weight loss rate decreased as the landfill process proceeded. This indicates the degradation of organic matters during landfill. Intensities of the third peak are also affected by the degradation process. Moreover, more metabolic products, which have different chemical structure and are preferentially combusted, were produced with the stability of organic matters. This influences the peak positions and the shift towards lower temperatures. From the decrease tendency of this peak, we know that the stabilization process is still ongoing. Otero [10] also found the decrease of the second peak intensity as the sludges become more stable. However, he found the peak at around 475 °C increased in intensity with stabilization at first to then decrease and shifted to higher temperatures later, which is contrary to the results we obtained. The reason may be related to the different stabilization processes. In the anaerobic process we studied, the third peak of DTG combustion curve is mainly caused by the combustion of organic matters. The peak intensities are mainly affected by the degradation process. On the contrary, in the aerobic process reported in the literature, the peak at around 475 °C can be attributed to scarcely degradable molecules that are enriched during stabilization process. So it is easy to see that the peak intensities at this temperature by aerobic stabilization process are less affected by the degradation process than by anaerobic stabilization process. Between 590 and 900 °C, the weight loss rate of different stabilization periods has no big variation. Consequently, DTG analysis of sludge combustion helps us to know about the variation of different kinds of organic matters and the degree of the anaerobic stabilization process.

From results in Table 1 and especially from TOC and VM reduction it may be observed that the most evident progress towards stabilization takes place in the first 60 days of anaerobic process. This is in agreement with weight loss results and DTG profiles. Therefore, we can acquire the general information about the degradation degree according to these characterization parameters.

3.4. DSC analysis

3.4.1. DSC comparison of combustion and pyrolysis

Fig. 5 presents the heat flow values of combustion and pyrolysis for 10mg samples. DSC combustion curves show two distinct exothermic peaks while the pyrolysis curves do not show evident exothermic behavior. In general, the sludge combustion has

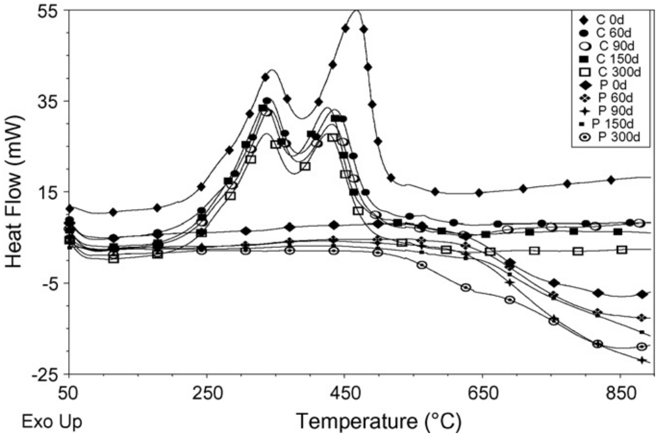

Fig. 5. DSC combustion and pyrolysis curves of progressive stages in the landfill process.

more energy release than the corresponding pyrolysis. Both DSC combustion curves and corresponding pyrolysis curves present a little endothermic peak at low temperature, which is caused by the dehydration reactions. By comparing two distinct exothermic peaks, we find that the area of the first peak is bigger than that of the second peak for DTG combustion curves. On the contrary, the area of the first peak is smaller than or almost the same as that of the second peak for DSC combustion curves. The reason is that devolatilization as well as combustion contributes to the first peaks whereas only combustion to the second peaks. Endothermic reaction for devolatilization leads to the reduction of the first peaks intensities for DSC combustion curves. The energy for DSC pyrolysis curves are almost in a balanced state at 100–650 °C. This confirms that the energy release for the products of organic matters thermal decomposition react with some components of sludge is equal with the energy needed for pyrolysis. At 650–900°C, DSC pyrolysis curves present endothermic tendency, which is the result of pyrolysis of some inorganic matters.

It is noteworthy that the temperature of the two distinct DTG peaks does not correspond exactly with the two peaks maximum of the heat flow in the aged samples, especially the first peak. This is mainly because of the thermal inertia of the heat flux sensor (delay on signal).

3.4.2. DSC analysis of sludge combustion

According to the declining energy content, the energy release is higher in the undecomposed material than in the degraded one. The decrease of organic compounds results in a reduction of DSC peak intensities. As the landfill process advanced, because of preference combustion of the degradated organic matters during landfill, energy release of the second peak begins at lower temperature.

The declining tendency of heat flow indicates that stabilization of sludge is still ongoing. This finding is confirmed by conventional parameters. Smidt and Lechner [21] pointed out that a constant level for the peak intensities and peak shift indicate stabilization Therefore, the DSC curves analysis, according to other authors [2,10,20], could be used to evaluate the stability of the sludge.

4. Conclusions

Thermal methods have proved to be a faster and complementary way for the assessment of the stage of degradation and stabilization in waste materials. They have proved to be advantageous in the management of complex materials and only require a simple procedure for data interpretation. In the absence of mass spectrometry and other complementary methods, thermal analysis of combustion are not so effective in distinguishing the materials and reactions going on in the programmed heating process, while the combination of combustion with pyrolysis analysis can give us more information to estimate them.

Due to the mineralization process taking place during stabilization treatment, sewage sludge residues from temperature programmed combustion increase as stabilization progresses. According to the combustion DTG, the volatiles and easy degradable organic matters are the main fraction consumed first by microorganisms at different landfill periods. A small amount of complicated organic materials are also degraded. The decreasing intensity and shift toward lower temperatures of DTG/DSC peaks reveals that the stabilization process is still ongoing.

The influence of aerobic and anaerobic disposal technologies on stabilization efficiency, thermal behavior, and exothermic reactions still remains to be properly investigated.

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