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Conference Title

Effect of Heating Rate on the Municipal Sewage Sludge Pyrolysis Character

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Abstract

In this paper, the TG and DTG curve of sewage sludge from Xi'an Business Water Limited Corporation were derived from tests of thermogravimetric analyzer. Pyrolysis characteristics and kinetics of dried sludge were investigated using thermalanalysis. The result showed that there are three temperature ranges in which the sludge lost weight in the process of pyrogenation. Kinetic fitting equation of the second pyrolysis reaction stage were founded and the kinetic parameters of pyrolysis reaction were calculated respectively by Coats-Redfern integration method, and the effect of heating rate on the sludge pyrolysis characteristics was discussed.

Keywords: sewage sludge; thermogravimetric analysis; pyrolysis kinetics

Sludge are main by-products from municipal sewage treatment plant, and the yield of sludge are ever-increasing due to the rapid urbanization and higher environmental protection criteria implemented in recent decades. How to dispose of tremendous sewage sludge to eliminate the potential hazardous effect on environment has become an important issue of environmental protection. Pyrolysis is receiving more attention as an economical efficiency and environmental friendly route to waste treatment. Pyrolysis of sewage sludge is a promising thermal conversion technology aiming at sludge reduction, stabilization, hazard-free treatment and reclamation. In this paper, the pyrolysis characteristics of sewage sludge sample from Xi'an Business Water Limited Corporation was studied with thermogravimetry.

1. Thermalanalysis experiment

1.1 Basic characteristic of sludge

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Raw municipal sewage sludge were dried in the air, then pulverizing and sieving to 60 mesh, vacuum drying under 105℃ till constant weight. The basic properties of dried sludge sample has been done (see table 1). Table 1 shows that the sludge is a fuel which has high content of volatile, low content of fixed carbon and low quantity of heat .

Table.1 Characteristic analysis of sludge sample

Proximate analysis /%				Quantity of heat（*MJ/kg*）	Ultimate analysis /%			
M_d	A_d	V_d	FC_d	$Q_{net,v,d}$	C_d	H_d	N_d	S_d
5.72	42.58	46.04	5.66	8.12	33.59	5.03	5.65	1.20

1.2 TG experiment results and analysis

The pyrolysis characteristics of dry sewage sludge sample was studied with Q600SDTX thermogravimetry which was made from America TA Instrument. Pyrolysis experiment was carried out in N_2 atmosphere, the flow of N_2 was 30mL/min. Thermalanalysis experiment was made at diferent heating rate which were 10℃/min、20℃/min and 30℃/min separately from room temperature to 800℃. As well as, every experiment got a set of TG and TGA curve which was showed in figure 1.

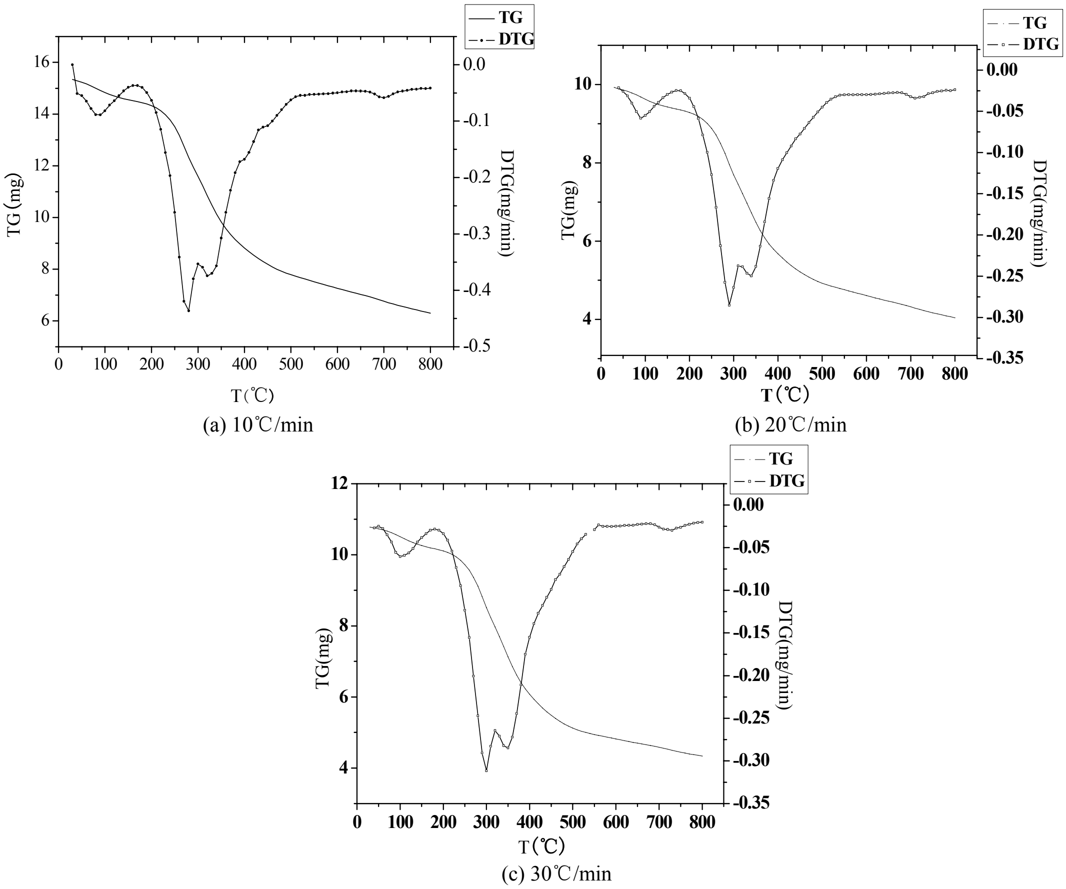

Fig.1 TG-DTG curves of sludge sample at different heating rate

TG and TGA curves in Figure 1(a)～(c) show that the pyrolytic reaction of sewage sludge consist of three stages, that is, dehydration, devolatilization and the phase of fixed carbon burning. The characteristic of each stage is as follows.

The first weight loss phase of DTG curve is the phase of moisture release, the temperature range and peak value of the phase are in relation to experiment conditions. The weight loss of the first stage result from evaporation of free moisture and bound moisture consist in sludge.

The second weight loss phase of DTG curve is the phase of devolatilization. The second stage have two obvious radiative apexes which temperature range and peak value of the phase are in relation to experiment conditions, but have less difference. The weight loss of the second stage mainly due to C-C bond of carbon-containing compounds in sludge broken and then produced tar, CO_2 and CO. The first exothermic peak is because of aliphatic compound decomposed, the second exothermic peak is because of carbohydrates and protein decomposition. [1] In this stage, a majority of volatile components, so it has the most gas generation and weight loss.

The third weak weight loss phase of DTG curve is the phase of fixed carbon burning. In this stage, high boiling compounds consist in sludge were decomposed , then produced char and ash content finally. In the pyrolysis experiment, sludge burning reaction rate is mainly up to mixed condition of released volatile components and oxygen. When heating to the certain temperature, there are abundant volatile components released and formed a gas film layer, combustion carried on mostly in mixed diffusion region of gas film layer outside surface and oxygen, the gas film layer burning would consume oxygen, fixed carbon could meet with oxygen and burn after the gas film layer break only when volatile components combustion to certain degree, so obvious fixed carbon burning region only appeared at higher temperarure phase of DTG curve. Because this experiment carried out under N_2 atmosphere, therefore, the burning region was not obviously.

Figure 1 show that the sludge pyrolysis TG and DTG curves have the same variation trend under different experimental conditions. The laws of the coke combustion, moisture and volatile volatilize were same basically. In each stage, the starting temperature, final temperature and temperature of maximum reaction rate increased in different degree with the increase of heating rate, while the main reaction region decreased. These were because of in order to reach the same temperature, the heating rate more quick, the sample reaction time more short , thereby the reaction degree more lower. At the same time, heating rate affected heat-transfer temperature difference and temperature gradient between survey point and sample as well as sample's outer layer and interior, with the result that the curves moved to high temperature accompanied by obvious heat-transfer hysteresis phenomenon.

Initial pyrolysis temperature of each pyrolysis stage increased and DTG curve moved to higher temperature along with heating rate increased. The quickly heating delayed pyrolysis reaction because medium diffusion and heat transmission need some time. In addition, the same particle size sludge samples had same total weight loss at different heating rate condition which showed that heating rate had little influence on organics conversion rate. Moisture weight loss, ash weight loss and volatiles weight loss of sludge sample obtained by TG experiment were true to sludge proximate analysis data which showed that thermalanalysis experiments were reasonable.

2. Sludge pyrolysis reaction kinetic parameters calculate

By means of Coats-Redfern method[4], the kinetic parameters, the pre-exponential factor A and the activation energy E, were calculated to obtain the kinetic equation. The theoretical data fit the experimental data verywell.

The second stage was the primary pyprolysis reaction stage because a majority of organic matters were thermal decomposed in the second pyprolysis stage which had maximum weight loss, so the paper would focus on analysing the sludge pyrolysis characteristics of the second stage. The foundation and solving process of pyrolysis reaction kinetic equation refer to literature [5], the calculate results show in table 2.

Table.2 The fitting results of pyrolytic kinetics equation（60 mesh）

Heating rate ℃/min	Reaction stage number	Fitting equation Y=a+bX	Correlation coefficient
10	1	Y = -522.61X – 10.964	0.9821
	2	Y = -633.53X – 10.445	0.9856
	2.5	Y = -692.06X – 10.172	0.9857
	3	Y = -752.61X – 9.8901	0.9852
20	1	Y = -531.21X – 11.0422	0.9664
	2	Y = -634.12X – 10.563	0.9642
	2.5	Y = -688.23X – 10.312	0.9626
	3	Y = -744.08X – 10.0541	0.9607
30	1	Y = -530.7X – 11.109	0.9483
	2	Y = -628.5X – 10.655	0.9449
	2.5	Y = -679.8X – 10.418	0.9428
	3	Y= -732.69X – 10.174	0.9406

Table 2 data showed that under the coditions of the same particle size and reaction stage number, slope of fitting straight line changed less along with heating rate increased or decreased, the activation energy changed not obviously by the equation $E = -bR$. We can get that heating rate had little effect on sludge pyrolysis activation energy. It also showed that constant a of fitting straight line decreased along with heating rate increased under the coditions of the same particle size and reaction stage number, so pre-exponential factor augmented, and then reaction rate constant augmented. We can also get that sludge pyrolysis reaction rate increased along with heating rate increased.

On the basis of table 2 data, we have obtained the optimum kinetic fitting equation and reaction stage number of the phases of volatiles released during sludge pyrolysis, the activation energy and the pre-exponential factor have obtained too in different heating rate condition, all results were showed in table 3.

Table.3 The best fitting kinetic equation and the solving results of kinetic parameters

Heating rate ℃/min	Fitting equation Y=a+bX	Reaction stage number	Correlation coefficient	Activation energy /kJ/mol	Pre-exponential factor /min^{-1}
10	Y = -692.06X – 10.172	2.5	0.9857	5.75	0.26
20	Y= -531.21X -11.0422	1	0.9664	4.42	0.41
30	Y= -530.7X – 11.109	1	0.9483	4.41	0.61

3. Conclusion

（1）There are three temperature ranges in which the sludge lost weight. The TG and DTG curve of sludge pyrolysis have the same variation trend, the laws of the coke combustion, moisture and volatiles released were alike basically. In each stage, the starting temperature, final temperature and temperature of maximum reaction rate increased along with the increase of heating rate, while the main reaction region decreased.

（2）Heating rate have little effect on sludge pyrolysis reaction activation energy and in proportion to reaction rate.

（3）When the heating rate was 10℃/ min, the reaction stage number of optimum kinetic fitting equation for sludge were 2.5. When the heating rate was 20℃/ min or 30℃/ min , the reaction stage number of optimum kinetic fitting equation for sludge were 1.

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