

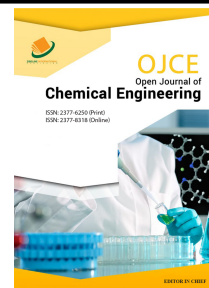


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KINETIC EXPERIMENT STUDY ON DRYING AND COMBUSTION OF SEWAGE SLUDGE

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ABSTRACT

Thermo gravimetric (TG) experiments of sludge can reflect the drying and combustion characteristics of material for exactly obtaining the mechanism of drying and combustion processes. The weight loss process of wet sludge includes three stages: drying stage, flammable stage and non-flammable stage. The Paper conducts thermo gravimetric test and kinetic parameter calculation for these three stages. The weight loss and drying process of sludge consists of five stages: preheating stage, rapid weight loss stage, constant-rate weight loss stage, decelerating weight loss stage I and decelerating weight loss stage. This Study carried out more detailed division of multi-stages than the previous on drying and combustion process to Chinese southern municipal sludge. The kinetic process for the drying and for the combustion of sewage sludge should be expressed by phase interface reaction mechanism function $g(a)=1-(1-a)^n$ and chemical reaction equation $f(a)=(1-a)^n$ respectively. Kinetic parameters reveal that activation energy decreases in the sequence of non-flammable stage, flammable stage and drying stage, and when changing the heating rate, the activation energy changes significantly in flammable stage while nearly remains unchanged in non-flammable stage.

KEYWORDS

Sewage sludge, thermo gravimetric (TG) experiment, drying, combustion, kinetics

1. INTRODUCTION

TG experiments of sludge can reflect the drying and combustion characteristics of material under specific heating conditions and can be applied to exactly analyze the mechanism of drying and combustion processes of sludge. During recent years, many scholars at home and abroad researched the drying, pyrolysis-combustion characteristics of sludge via TG experiments. A group of researchers investigated the combustion characteristics of wet sludge in a fluidized bed via TG experiments; studied the ignition characteristics of paper-mill sludge particulates by conducting TG experiments with sewage sludge particulates of same granularity; reported the effects of volatilization on sludge via TG experiments [1-4]. In China, a group of scholars examined pyrolysis-combustion characteristics of paper-mill sludge under oxygen-enriched combustion conditions, explored the isothermal drying characteristics of dewatered sludge and the combustion characteristics and kinetic characteristics of urban sewage sludge with thermo gravimetric/differential thermal analyzer (TG DTA) [5-7]. TG curve shows that the pyrolytic reaction of sewage sludge consists of three stages, 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. Based on a study, heating rate have little effect on sludge pyrolysis reaction activation energy and in proportion to reaction rate [8]. This Study carried out more detailed division of multi-stages than the previous on drying and combustion process to Chinese southern municipal sludge.

2. TG EXPERIMENTS OF SLUDGE

In this study, German Netzsch Simultaneous Thermal Analyzer STA 409 PC Luxx was adopted to perform TG experiments. The sewage sludge used in the experiment is 42 mg, with water content of about 84%, and made

into s sample and put into a small crucible of the analyzer, with the testing conditions as follows: oxygen flow 21 mL/min, nitrogen flow 79 mL/min, and heating rate respectively 10 K/min, 20 K/min and 30 K/min.

2.1 Drying Experiments and Characteristics Analysis at Different Heating Rates

In TG experiments, heated sludge underwent drying stage and combustion stage in order. Figure 1 respectively shows the TG (Thermo Gravimetric) and DTG (Differential Thermo Gravimetric) curves of drying process at heating rates of 10 K/min, 20 K/min and 30 K/min. It can be found by comparing three DTG curves that, the curve representing high heating rate has higher weight loss rate than that representing low heating rate across the whole drying course. By analyzing DTG curves, five stages of variable-temperature drying process of sludge can be discovered, i.e. preheating state, rapid weight loss stage, constant-rate weight loss stage, decelerating weight loss stage I and decelerating weight loss stage II. In the preheating stage, the temperature of moisture contained in sludge was increased, with a small amount of free water on the sludge surface be removed by drying. As shown in Table 1, the weight loss rate started to change when the ambient temperature reaches 100-105°C and some surface water is vaporized when heated to 100°C. Then comes the rapid weight loss stage, when free water was separated. The weight loss rate is lowered gradually along with the decrease in the moisture content of sludge, leading to the constant-rate weight loss stage, when interstitial water is removed. In this stage, the internal and external temperatures of sludge are uniformly distributed, and the heat transferred from the crucible wall and heated air to sludge is equivalent to the latent heat required for gasification of water on the sludge surface, thus the weight loss rate changes little and remains almost constant. Then the drying process

enters the decelerating weight loss stage I, when capillary water and internal water is removed, which is hard to remove, resulting in a rapid slowdown of weight loss process. Finally, the drying process enters the decelerating weight loss stage II, since the internal water in sludge is bound with solid particles via chemical forces, making it difficult to remove.

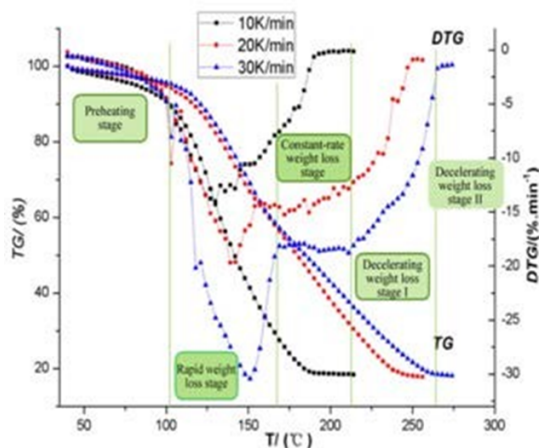


Figure 1: Curves of weight loss ratio and weight loss rate against temperature change in drying stage.

The point at which the drying process enters the rapid weight loss stage and the weight loss rate fluctuates quickly is defined as the weight loss rate fluctuation point z; the inflection point at which the drying process enters the decelerating weight loss stage II is defined as the weight loss rate decelerating point x. As can be seen from Table 1, the temperature, duration and weight loss rate at point z all decrease along with the increase of heating rate. In the constant-rate weight loss stage, as the heating rate went up, the start and end points of temperature range are both raised, the temperature interval is widened, the time intervals are 0.9 min, 1.4 min and 1.1 min respectively, and the weight loss rate increases. At the decelerating point x, the temperature increases with the increase of heating rate, while the duration is shortened and the weight loss rate increases.

Table 1: Characteristic stages and characteristic points for drying at different heating rates.

K/min Heating Rate of Sewage sludge (K/min)	Weight Loss Rate Fluctuation Point z			Constant-rate Weight Loss Stage			Weight Loss Rate Decelerating Point x		
	Temperature (°C)	min Duration (min)	Weight Loss Rate (%/min)	Temperature Range (°C)	Duration (min)	Weight Loss Rate (%/min)	Temperature (°C)	min Duration (min)	Weight Loss Rate (%/min)
10	104	7.2	-5.5	133-144	0.9	-12.58	190.8	14.8	-0.5
20	101.5	4.4	-4.9	155-190	1.4	-14.29	250.6	10.5	-0.68
30	100	3.4	-4.66	169-213	1.1	-18.14	265.7	7.7	-1.51

2.2 Combustion Experiments and Characteristics Analysis at Different Heating Rates

Figure 2 is the curve of weight loss ratio and weight loss rate against temperature in the combustion stage. As shown in the figure, each DTG curve has two peaks, one at about the range of 200-380°C and the other at about the range of 380-580°C. At the same temperature, the weight loss rate at higher heating rate is larger than that at lower heating rate while the weight loss ratio is in contract, with the rule similar with the water drying rule. During the combustion process, the material is heterogeneously ignited at high heating rate, and the components with higher activity react first, and flammable phase and non-flammable phase are observed when the heat released from the reaction is insufficient to ignite the components with lower activity. The increase of heating rate may intensify the heating of material and lengthen the flammable phase.

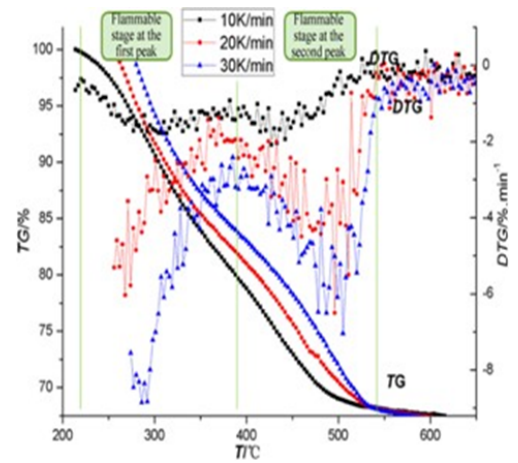


Figure 2: Curves of weight loss ratio and weight loss rate against temperature in combustion stage.

By comparing three weight loss rate curves, two obvious weight loss peaks can be found at the heating rates of 20 K/min and 30 K/min respectively, while no obvious weight loss peak can be found at the heating rate of 10 K/min, exhibiting a much higher weight loss rate than the former two curves. The reason is that when the temperature reaches 200°C, the drying time for lower heating rate is longer than that for higher heating rate. Moreover, the evaporation rate of volatiles is lower at lower heating rate, resulting in poor ignition and combustion performances. However, at high heating rate, it took less time to go up to the same drying temperature, and volatiles are separated before complete drying of moisture. There might be a period when water evaporation coexists with volatiles vaporization in the temperature range of 200-250°C. Meanwhile, at high heating rate, volatiles of sludge are built up to a high concentration in a short time, leading to improved ignition and combustion performance of sludge. As the concentration and temperature of volatiles both increase to a certain level, severe combustion reaction occurs, and the flammable stage begins. When fixed carbon is burnt at the later combustion stage of volatiles, another weight loss peak at lower combustion rate is observed, forming the non-inflammable stage.

3. NONLINEAR KINETIC MODELS AT DIFFERENT HEATING RATES AND ANALYSIS

$\frac{d\alpha}{dt} = Kf(\alpha) = Ae^{-E/(RT)}f(\alpha)$ Though sewage sludge has a complex composition, its pyrolysis-combustion reaction can be considered as composed of a series of parallel and continuous reactions. DTG curves of sewage sludge can depict its pyrolysis-combustion reaction with simple mathematical models, and the impacts of temperature and oxygen concentration on the drying and oxidization-combustion of sludge can be expressed by Arrhenius equation and power law [9-12].

$$\frac{d\alpha}{dt} = Kf(\alpha) = Ae^{-E/(RT)}f(\alpha)$$

Select an appropriate mechanism integral function $f(\alpha)$, where α denotes conversion rate; and consider pre-exponential factor A , activation energy E and mechanism function reaction order n as parametric variables. Then, perform iterative operations by continuously attempting to change parametric variables A , E and n to get optimal correlation coefficient R and SSD (Sum of Square Difference), and the optimal A , E and n can be solved. SSD can be expressed as:

$$SSD = \sum_{i=1}^n (a_{c_i} - a_{e_i})^2 \quad (1)$$

Many mechanism functions are substituted for the fitting calculation in the study to compare the calculation results, and the above equation is recognized as the optimal mechanism function.

3.1 Kinetic Models of Drying Process and Analysis

Table 2 shows the calculation results of kinetic parameters for the moisture drying process using selected mechanism functions at different heating rates. It can be known that, if the entire drying process is deemed as a drying reaction at phase interface, the activation energy and pre-exponential factor decrease while the reaction order increases progressively with the increase of the heating rate. The average temperature of the entire drying process was elevated by relatively higher heating rate, which in turn reduces the apparent activation energy of moisture. As shown in Table 1, the total heat

Table 2: Calculation results of kinetic parameters for drying process using phase interface mechanism function $g(a) = 1 - (1-a)^n$.

Heating Rate (K/min)	Temperature Interval (°C)	Reaction Order n	Activation Energy E (kJ/mol)	Pre-exponential Factor A (min ⁻¹)	Correlation Coefficient R	SSD
10	40-214	0.00031	49.223	148.57	0.9983	0.01496
20	40-257	0.00678	33.223	16.7	0.997	0.02786
30	40-274	0.00998	30.558	14.48	0.9932	0.06976

3.2 Kinetic Models of Combustion Process and Analysis

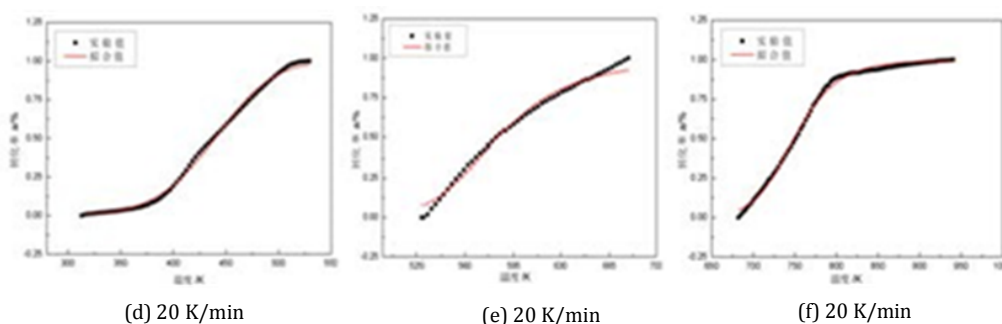
Table 3 shows the calculation results of nonlinear kinetic parameters of sludge for the flammable stage and non-flammable stage under different environment conditions. The flammable stage is the first peak and the non-flammable stage is the second peak of the weight loss rate curve. The chemical reaction mechanism function $f(a) = (1-a)^n$ was employed for the combustion process. Figure 3 (b) and (c) show the curves of experimental values and fitting values of the flammable and non-flammable stages under different environment conditions.

Table 3 lists the kinetic parameters of the flammable stage and non-flammable stage for sludge pyrolysis-combustion at different heating rates. As suggested in the table, for the flammable stage of the first peak,

the reaction order n , activation energy E and pre-exponential factor A all increase with the increase of heating rate. This may be attributable to the wider temperature interval of the first peak at high heating rate. In contrast, for the non-flammable stage of the second peak, the reaction order did not exhibit any obvious change rule and the calculated values of activation energy change little or even remain constant. In the temperature interval of the flammable stage at the first peak, mainly due to the control of chemical reaction, the activation energy was on the rise. While in the temperature interval of the non-flammable stage at the second peak, it is mainly controlled by diffusion reaction. The changes of heating rate are mainly controlled by chemical reaction factors; thus, the heating rate factors impose little impact to the reaction degree of the non-flammable stage of the second peak, with small changes of values of activation energy.

Table 3: Kinetic parameters for combustion of sludge at different heating rates.

Heating Rate (K/min)		Temperature Interval (°C)	Reaction Order n	Activation Energy E (kJ/mol)	Pre-exponential Factor A (min ⁻¹)	Correlation Coefficient R	SSD
Flammable stage at the first peak	10	216-382	1.716	81.76	6.87×106	0.9961	0.02243
	20	258-406	2.823	121.198	8.225×1010	0.9881	0.04924
	30	275-428	3.602	151.414	4.778×1013	0.9859	0.05451
Non-flammable stage at the second peak	10	385-565	2.26	186.18	2.1×1013	0.9976	0.0148
	20	407-667	2.278	185.83	8.13×1012	0.9972	0.02516
	30	429-673	2.205	185.33	6.21×1012	0.9942	0.04477

**Figure 3:** Comparison of experimental values and fitting values of conversion rates for all phases at different heating rates.

At all heating rates, higher activation energy was observed in the non-flammable stage of the second peak than in the flammable stage of the first peak. The reasons include: 1) high temperatures in the temperature interval of the non-flammable stage intensifies the reaction degree, so the old active centre is destroyed quickly while new active centre fail to be generated; 2) the ash content of sewage sludge takes up around 55% of dry basis, and a considerable portion of volatiles is released in the flammable stage. In a high-ash material, large resistances need to be overcome for the precipitation of residual volatiles and fixed carbon and the penetration of oxygen into the material, so the diffusion control factor of oxygen and flammables instead of temperature control factor becomes the dominant factor.

4. CONCLUSIONS

The weight loss process if wet sludge can be divided into drying stage, flammable stage and non-flammable stage for the calculation of kinetic parameters. The moisture weight loss process at a constant sludge heating

rate substantially consists of five stages: preheating stage, rapid weight loss stage, constant-rate weight loss stage, decelerating weight loss stage I and decelerating weight loss stage II. The weight loss rate starts to fluctuate when the sewage sludge temperature reaches about 100°C, followed by the rapid weight loss stage. The temperature range of the constant-rate weight loss stage is widened with the increase of heating rate. There exists a stage when water evaporation coexists with volatiles vaporization at higher heating rate; and in this stage, when combustion reaction takes place, the weight loss rate of sludge moisture decreases sharply. Moreover, the initial mass of material directly influences the weight loss rate of moisture in drying. Calculation results indicate that, phase interface reaction mechanism function $g(a) = 1 - (1-a)^n$ should be adopted for moisture drying stage, the heat absorbed during drying process, the activation energy and pre-exponential factor all decrease with the increase of heating rate, and the reaction order also increases. The pyrolysis-combustion reactions of sludge should be expressed by the chemical reaction equation $f(a) = (1-a)^n$. Calculation results reveal that, the activation energy decreases in the

sequence of the non-flammable stage, flammable stage and drying stage; and the activation energy changes significantly in the flammable stage while remain substantially constant in the non-flammable stage when changing heating rates; the activation energy remains substantially unchanged in the flammable stage but changes significantly in the non-flammable stage when changing oxygen concentrations; therefore, it can be inferred that the flammable stage is mainly controlled by chemical reaction factors while the non-flammable stage by diffusion reaction factors.

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