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INVESTIGATION ON CO-PYROLYSIS OF SEWAGE SLUDGE WITH COAL

Co-pyrolysis characteristics of sludge with coal and sludge briquetted with coal were studied by the TG-FTIR method. From TG data, weight loss of sludge briquetted was higher than that of sludge and sludge and coal which means that thermal reaction effect of sludge briquetted is better than those of other two materials. Gas products of pyrolysis were CO, CO_2, H_2O, alcohol, ketone, acid, hydrocarbon, amine and azine from the FTIR analysis. At last, evolving patterns of the pyrolyses and the yields of their gas products have been recorded, providing extremely important data on the mechanism of the process.

1. INTRODUCTION

With the rapid development of sewage disposal in China, sewage sludge becomes an extrusive environmental problem. The incineration of sludge briquetted prepared from the mixing compression molding of sludge and coal is underdeveloped in China, which can be referred as co-pyrolysis or co-incineration processes. Among the sludge heat treatment technologies, co-incineration sludge with coal has been widely used because this technology (1) significantly decreases the volume of sludge, (2) destroys pathogens and hazardous organics, (3) renders the sludge to become into building materials from incineration ash and (4) produces energy. It seems that the technology of sludge co-incineration will be used more and more in China [1]. Co-incineration is based on pyrolysis, gasification, and combustion. To reveal the mechanism of co-

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incineration of sludge briquetted, it is necessary to know the pyrolysis process as well as the corresponding products for the sludge briquetted.

Thermogravimetry (TG) has been widely used in thermal analysis and kinetics parameter studies under both air and nitrogen atmospheres [2–4]. For the pyrolysis process, the heating rates are needed in order to develop the kinetic model. Using TG, the oxygen contents and the heating rates can be determined. Meanwhile, Fourier transform infrared spectroscopy (FTIR) can be used to detect the functional groups and identify species [5–7], and it has been used to identify the composition of gaseous mixture, for example, the composition of CO_2, CO, CH_4, HCN, NH_3 and some organic compounds [8, 9].

When TG is combined with FTIR, the gas products and the sample weight loss can be continuously recorded. This TG-FTIR technology provides a useful tool to study the pyrolysis process, and it has been widely used to study the waste and biomass pyrolysis [10–13], coal pyrolysis [14–16] and thermal degradation of polymers [17, 18]. However, reports on the sludge co-pyrolysis by using TG-FTIR is very limited.

In this work, TG-FTIR was used to detect the weight loss of samples and pyrolysis of gaseous products. To minimize the amount of gaseous products generated from the secondary reactions, gaseous products of pyrolysis were swiftly carried into gas cell by carrier-gas. From the measured parameters, the process of the co-pyrolysis for sludge briquetted was analyzed.

2. EXPERIMENTAL

The coal for experiments was taken from the Shanxi province in China. The sludge was collected from a sewage disposal plant in Guangdong province in China. Sludge briquettes were prepared by compression molding of the mixture of coal and sludge in the following procedure: 100 g of sewage sludge which contained 79 g of water was blended with 300 g of dry coal. The mixture of sludge and coal containing 20% of moisture was molded into briquettes by hydraulic pressure molding machine under the pressure of 20 MPa. The briquettes were air dried for 7 days at 30 °C in the oven to obtain constant weight and very low moisture content. The shape and the size of sludge briquettes are shown in Fig. 1.

The sample of sludge with coal was the mixture of coal and sludge with the ratio of dry sludge to coal the same as that for sludge briquettes but it was not briquetted. In the experiment, sludge and sludge with coal samples were used as references for the samples briquetted. The results of proximate and ultimate analyses of coal and sludge are shown in Table 1.

The apparatus for thermogravimetry (TG) coupled with Fourier transform infrared spectrometer (FTIR) was used to detect the weight loss of the samples and to analyze gaseous products as well as their distributions. Nitrogen was used as purge gas for the FTIR. Resolution in FTIR was set to be 4 cm^{-1}, the number of scans per spectrum was 20 min^{-1}, and the spectral region analyzed ranged from 4000 to 400 cm^{-1}.

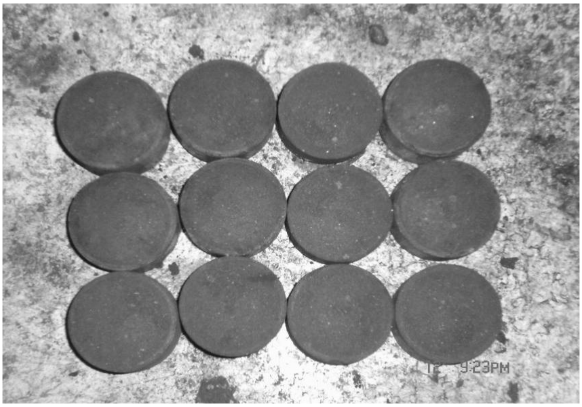

Fig. 1. Shape and size of sludge briquettes; diameter 30 mm, height 20 mm

Table 1

Results of proximate and ultimate analyses of materials [wt. %]

Material	Proximate analysis				Ultimate analysis					Q [kJ/kg]
	Moisture[a]	Volatiles[d]	Ash[d]	Fixed carbon[d]	C	H	O	N	S	
Sludge	81.00	36.09	57.05	6.86	22.20	3.34	70.38	3.33	0.73	8880
Coal	6.00	37.31	10.89	51.80	66.56	5.10	26.77	0.59	0.96	24542

[a]As-received basis.
[d]Dry basis.

The optimized experimental conditions were as follows: nitrogen atmosphere with the flow rate of 35 cm^3/min, heating rate of 10 °C /min, and temperature from 25 °C to 910 °C. The flow rate of purge gas was also 35 cm^3 /min. A quarter of a block of the sludge briquetted, sludge and sludge with coal samples were placed in a reaction big crucible, and then TG-FTIR experiment was carried out

3. RESULTS AND DISCUSSION

3.1. TG AND DTG ANALYSES

TG and DTG curves are shown in Fig. 2. It shows that TG curves are similar and no more information can be provided. However, from the DTG curves which were

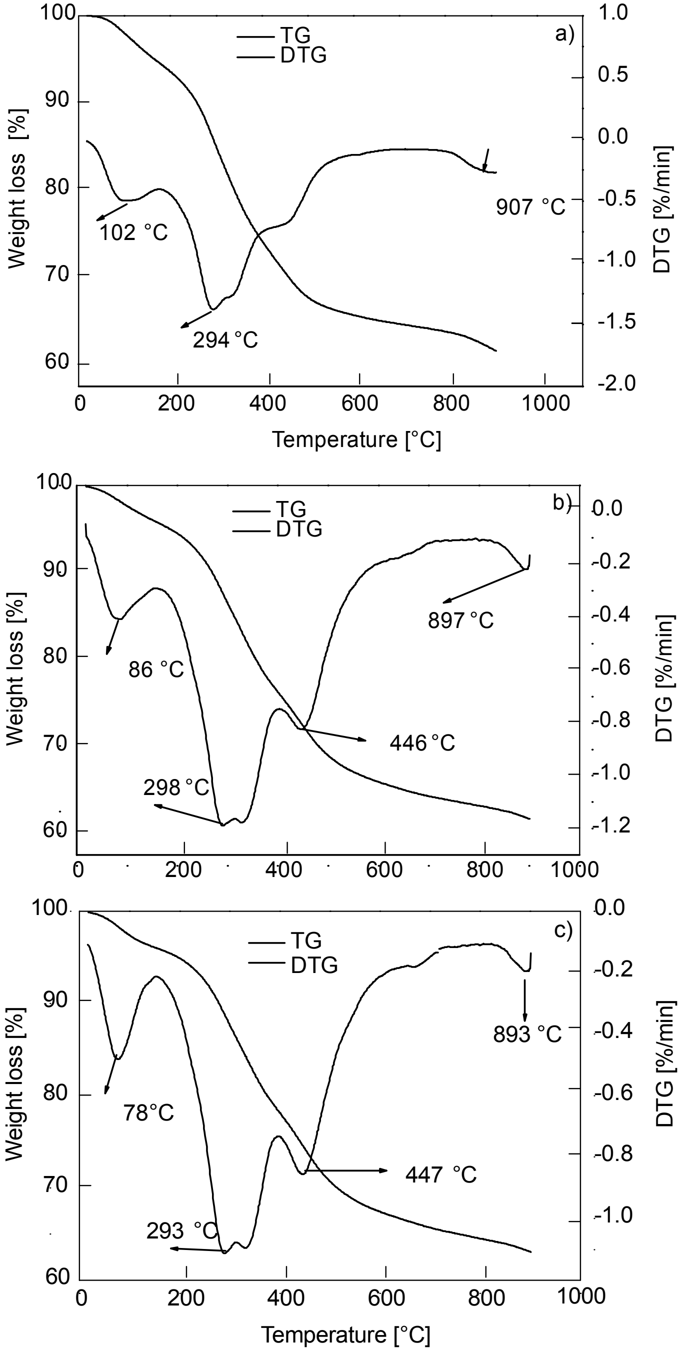

Fig. 2. Results of TG and DTG for the samples: a) sludge, b) sludge and coal, c) sludge briquettes (heating rate – 10 °C/min, N_2 flow rate – 35 cm^3/min)

obtained from the TG data, it is obvious that in the investigated temperature range, the pyrolysis processes are different. For the sample of sludge, DTG curve shows three peaks of weight loss at 102, 294 and 907 °C, respectively. For the sample of sludge with coal, there are four pyrolysis peaks at 86, 290, 446 and 897 °C. For the sample of sludge briquetted with the same sludge to coal ratio as in previous sample, the pyrolysis process also displayed four peaks, and the corresponding DTG peak temperatures are 78, 293, 447 and 893 °C.

The temperature corresponding to the first weight loss peak of sludge briquetted is lower than that of sludge with coal and sludge alone. For the sample of sludge, the temperature of the first stage of weight loss ranges from normal temperature to 183 °C. For the sludge with coal, its range is from normal temperature to 155 °C, while for sludge briquetted from normal temperature to 154 °C. It may be concluded that the first stage of change temperature for the sample of sludge with coal is similar to that for sludge briquetted. In addition, the first weight loss peak temperature of sludge briquetted is the lowest among three samples, which indicates that the reaction activity of sludge briquetted is the highest.

The stage of second weight loss from 155 °C to 400 °C is the most important part of the pyrolysis. The weight loss peak of sludge briquetted lies still at the lowest temperature of 293 °C. The stage of third weight loss ranges from 400 °C to 600 °C, while the last one from 850 °C to 910 °C for all the samples.

3.2. FTIR ANALYSIS

Infrared spectrum is often used to identify various inorganic and organic products of pyrolysis at various temperatures. From the 3D infrared spectrum, time dependence of absorbance reflects the trend of TG results. For sludge, three peaks have been identified, while for sludge with coal and sludge briquetted, four peaks have been found.

3.2.1. GAS COMPOSITION ANALYSIS

After the pyrolysis, gases were swept into a gas cell in order to make FTIR analyses. At fixed time, absorbance measured at various wavenumbers provides information on gas composition at this moment. At wavenumber fixed, time dependence of absorbance enables tracing concentrations of one compound during pyrolysis. Modes characteristic of main functional groups are listed in Table 2.

Here we analyzed the second DTG peak of sludge briquetted as an example because most gaseous products of pyrolysis were produced at this time. Combined with the 3D spectrum, the main pyrolysis products were identified from this peak, which is CO, CO_2, H_2O, alcohol (glycerin), ketone (2-butanone), acid (cycloheptane-acetic acid and acetic acid), hydrocarbon (hexane), amine (butyl amine), and azine (hydrazine). The absorbance of alcohol, ketone, acid and hydrocarbon was strong.

Table 2

Identification of molecule configuration

Range [cm^{-1}]	Peak [cm^{-1}]	Functional group	Mode	Product
2060–2402	2360 2170	C=O C–O	stretching	CO, CO_2
3500–3756 1275–1875	3568 1508	O–H H–O–H	stretch bending	H_2O
3500–3756	3628	O–H	stretching	alcohol
1500–1928	1616	C=O		ketone
1500–1928 895–1300 3500–3756	1808 1116 3576	C=O C–O O–H		acid
2760–3101	2916	C–H		hydrocarbon
1020–1433	1380	C–N		amine
873–1111	964	N–N		azine

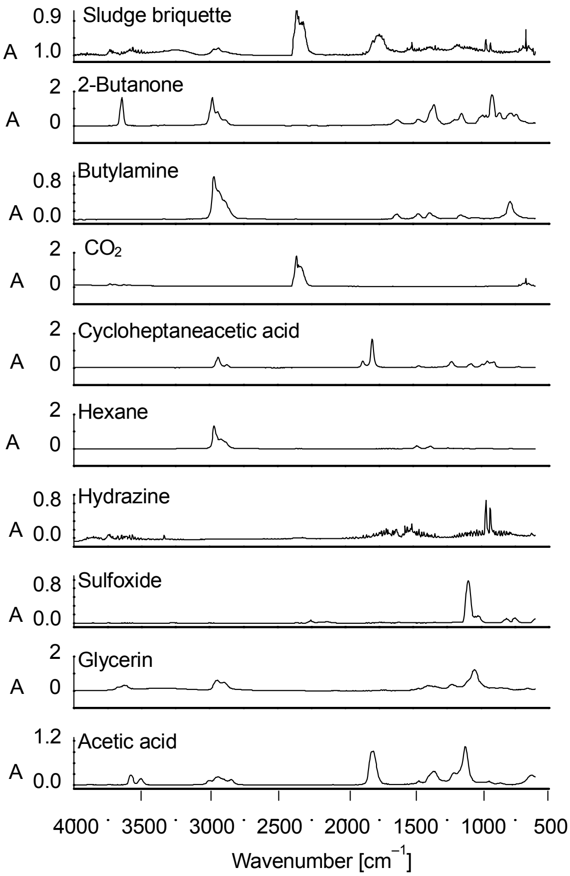

Fig. 3. Identification of pyrolysis of sludge briquettes at the second DTG peak (290 °C); A – absorbance

Owing to the low sulfur proportion (Table 1) and vibrations of its functional groups at 1500–1000 cm^{-1} overlapping with C–O, C–H, and H–O–H stretching vibrations, S products could not be identified. N occurs in considerable proportion as listed in Table 1, and the N products absorbing at 1020–1433 cm^{-1}, 873–1111 cm^{-1} were obviously found, which indicates the existence of amine and azine, especially for the clear azine absorbance. There was no obvious absorbance at 3400–3200 cm^{-1} and 800–600 cm^{-1}, which indicates that very small amount or no NH_3 was generated. Meanwhile, there was no absorbance at 3400–3200 cm^{-1}, thus no N–H configuration existed in N products. In addition, gaseous H_2, N_2 and O_2 could not be detected by means of FTIR due to their nonpolar character despite the fact that CO and CO_2 were present in a large quantity. The evolving volatile products of pyrolysis of sludge, sludge with coal, and sludge briquetted at 290 °C are shown in Fig. 3.

3.2.2. GAS EVOLUTION

Once the composition of pyrolysis products was identified, the time dependence of each product against time could be recorded. From the heating rate (10 °C/min), we could obtain the distribution of each product against temperature. Analysis of evolution patterns of TG-FTIR for pyrolysis products of the samples of sludge, sludge with coal and sludge briquetted leads to the following observations:

- The evolution of CO and CO_2 includes three stages corresponding to three peaks. The first stage is the most important to CO and CO_2 productions for three kinds of samples, and the release intensity of sludge briquetted is the highest one. It is reason that the sludge briquetted is better to operate than the two others. In terms of thermal efficiency, and pyrolysis efficiency the samples may be ordered as follows: sludge briquetted > sludge with coal > sludge.
- H_2O shows two releasing peaks, one at about 100 °C, corresponding to the physical release H_2O in the sludge, and the other at about 300 °C which is corresponding to the chemical decomposition of water..
- H_2O, alcohol, ketone and amine are released from the beginning of pyrolysis at normal temperature and the weight of samples decreases (Fig. 2).
- In all the samples, alcohol, small amount of ketone, H_2O and small amount of amine were produced in the first stage of weight loss around 100 °C. CO, CO_2, acid, most of ketone, most of amine and azine were produced in the second weight loss stage around 290 °C. A small amount of CO, CO_2 and hydrocarbon were produced in the third weight loss stage around 450 °C, and only CO_2 was released in the last stage around 900 °C as a product of carbonate decomposing at high temperatures.
- The samples of sludge with coal and sludge briquetted have a higher hydrocarbon peak than that for the sample of sludge.

In Figure 4, the yields of all pyrolysis products based on TG-FTIR are shown. From the figures the following conclusions may be drawn:

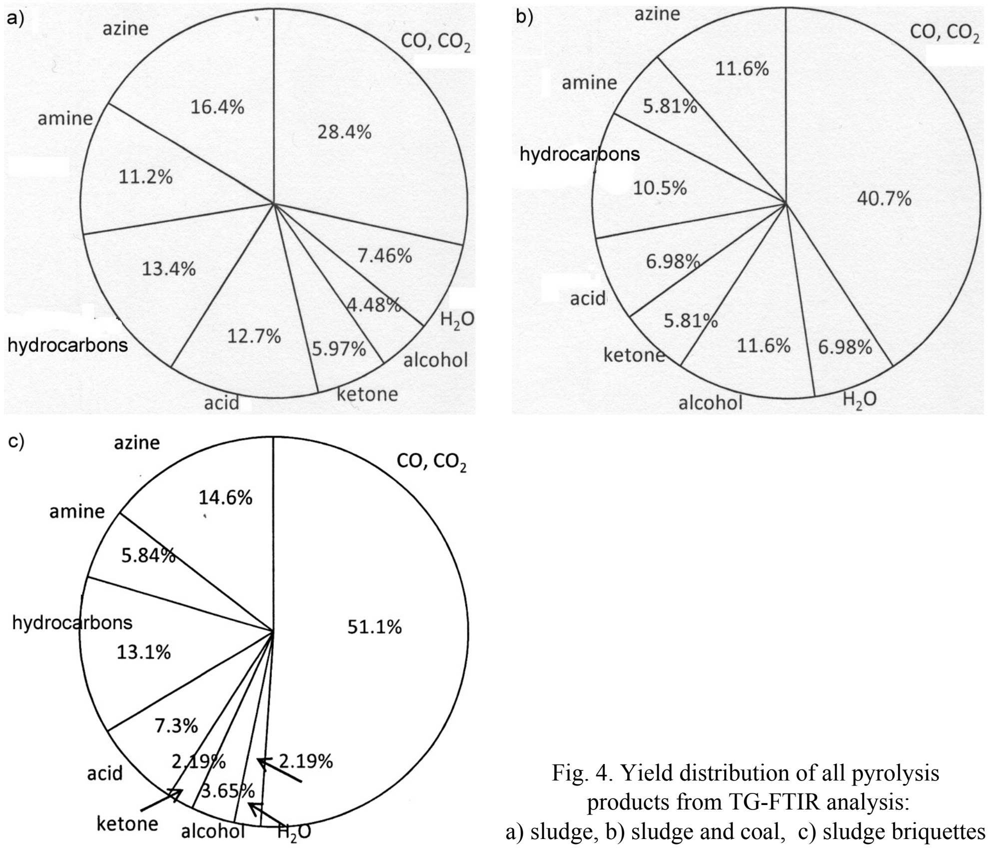

Fig. 4. Yield distribution of all pyrolysis products from TG-FTIR analysis:
a) sludge, b) sludge and coal, c) sludge briquettes

- The contents of CO and CO_2 as well as that of hydrocarbons in products of pyrolysis of sludge briquetted are higher than those for other samples.
- The content of acid, ketone, amine and azine in products from sludge is the highest among three samples, while the alcohol content in products from sludge with coal is the highest among three samples.

4. CONCLUSION

Process of pyrolysis and gas products of sludge briquetted have been successfully analyzed by using TG-FTIR. TG and DTG results showed that sludge briquetted is the easiest way pyrolyzed compared to sludge and sludge with coal. Main gas products were identified as follows: CO, CO_2, H_2O, alcohol, ketone, acid, hydrocarbon, amine, and azine. Evolving pattern and yield ratio have also been obtained. Further studies on mechanism and pyrolysis models of sludge briquetted pyrolysis have already been planned. First, TG-FTIR pyrolysis experiments will be performed at several heating rates in order to determine kinetic parameters for the pyrolysis model which is based on parallel, independent, first order reactions with Gaussian distribution of activation energy [19]. Then the model will be used to determine the rate and yield of evolution for individual pyrolysis products with given kinetic parameters from the TG-FTIR analyses. The rates obtain may be used as the input parameters in CHEMKIN simulations. At last, the understanding of evolution of volatile species during the pyrolysis and CHEMKIN simulations may be important in understanding and improving the incineration of sludge briquetted.

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