# **RSC Advances**



# PAPER



Cite this: RSC Adv., 2015, 5, 82227

# Drying behavior and thermo-gravimetrical kinetic analysis of foam-pretreated sewage sludge

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An innovative pretreatment technology, in which CaO was jointly added with NaOH followed by appropriate mechanical whipping, was investigated for the foaming and drying of sewage sludge (SS). Foaming efficiency, appropriate density of the best drying performance and drying temperature were examined. Considering high foaming efficiency and low energy consumption, the optimal mixture was found to be 1.0 wt% NaOH with 1.0 wt% CaO, which takes only 50% of the foaming time to reach the appropriate density (0.6 g mL<sup>-1</sup>) compared to that with 2.0 wt% CaO. When compared with SS, the optimal mixture also saved 20%–26% drying time to reach 40% moisture content. Non-linear regression techniques (Nonlinear Curve Fit (Dose Resp)) were applied to simulate the drying process of S<sub>2:2</sub>. The kinetics of sludge was studied by thermogravimetry analysis using the Starink method with three heating rates (10, 20 and 50 K min<sup>-1</sup>). Different trends in apparent activation energy support the conclusion that differences appear in the chemical compositions of sludge samples that have different ratios of additives. Moreover, the TG analysis results provide referable combustion data for the sludge samples in this research.

Received 16th June 2015 Accepted 7th September 2015 DOI: 10.1039/c5ra11479a

www.rsc.org/advances

# 1. Introduction

With the fast development of the urbanization process, sewage sludge (SS), which is a byproduct of wastewater treatment with a moisture content of about 80 wt%, has been increasing with the construction and expansion of wastewater treatment plants. The sludge treatment and disposal technologies applied in China currently, such as incinerations and landfills, require more stringently a low moisture content of sludge itself. The disposal of sewage sludge cannot be achieved directly with a moisture content of about 80 wt%. To some degree, the continuous production of large amounts of sewage sludge is becoming a serious environmental problem. The high moisture content and presence of organic components, which are mainly bacterial cells and extracellular polymeric substances (EPS), in the sludge make its treatment and disposal difficult.<sup>1,2</sup> In general, about 50% of the total cost of a whole wastewater treatment plant is attributed to the sludge treatment.<sup>3,4</sup> It is well established in previous researches that the separation of water after dewatering is essential, which can obviously reduce the mass and volume of waste, hence cutting down the cost for storage, handling and transportation. Moreover, the removal of water content increases the calorific value, thus transforming the sludge into an acceptable combustible.5-7

Sludge contains unbound and bound water: unbound water is relatively easy to remove using mechanical techniques, whereas bound water is the most challenging to remove, which typically requires extended thermal drying techniques.<sup>8,9</sup> Due to the distinct characteristics of mixed sludge such as its stickiness and relatively low heating values, the application of many drying technologies can be technically and economically challenging.<sup>10,11</sup> The existing direct heat drying process for organic sludge is not straight forward due to unpleasant odors, the contamination of pathogenic microorganisms, expensive treatment costs, and high energy consumption.<sup>12</sup>

Since dewatered sludge is highly sticky and viscous, in our previous research,<sup>13</sup> a novel approach for improving the drying behavior of sewage sludge was established. The addition of CaO (at 2.0 wt%) followed by the appropriate treatment of mechanical whipping was employed for the foaming of dewatered sewage sludge. Moreover, in the convective drying process, the foamed sludge at 0.70 g mL<sup>-1</sup> had the best drying performance at any given temperature, which saved 35%-41% drying time to reach 20% moisture content when compared with non-foamed sludge. Mat drying followed by proper pretreatment of foaming cuts down energy consumption and reduces environmental pollution. However, the previous research is confined to a low foaming efficiency, which is an obstacle in the large-scale application of the novel technology.

Researchers found that the sludge foaming was mainly derived from the decreased surface tension due to the surfactants and the promoted foam persistence due to the protein derived compounds. The addition of CaO in dewatered sludge

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could disrupt micro-organism cells and release the inner organic materials of sludge, which can result in changes among the major components.14,15 The addition of NaOH is shown to be more effective in deriving protein compounds, which results in a fast speed in sludge foaming, but the foam persistence is too weak to support the thermal drying of sludge samples and no advantages in water evaporation were gained. Thus, in this study, an economical pretreatment method has been realized, CaO added with NaOH followed by appropriate mechanical whipping, which not only promoted the foaming efficiency extensively, but also achieves cost reduction during the waste disposal. To investigate the differences in the chemical and physical properties of pretreated sludge samples, the knowledge of pyrolysis kinetics is also needed, which is usually determined by thermogravimetric (TG) analysis. TG analysis is able to provide a rapid assessment of the fuel value and the temperatures at which combustion starts and ends and other characteristics such as maximum reactivity temperature or total combustion time.16,17 For biomass resources, the pyrolysis process is considered to be an independent process, which is the initial step in all thermal conversions and production of various chemicals and fuels. Differences in chemical and physical properties between sludge samples lead to different thermal behaviors such as reactivity and char yield.18,19 Combustion or co-combustion also contributes to the biological stabilization of SS due to its volume reduction and the decrease in the need for fossil fuels for power production.<sup>20</sup>

Taking into consideration the facts mentioned above, the aims of the present work are (1) investigate the optimum operation of foaming pretreatment for sewage sludge; (2) evaluate the conditions of best drying performance for the foamed sludge; (3) determine the suitable mathematical modeling of the drying curve for the ideal pretreatment sludge sample; and (4) use thermo-gravimetric analysis to give a novel appraisal to the sludge samples and thus verify the changes in the composition of sludge samples due to mixed additions.

### 2. Methods

#### 2.1 Properties of sewage sludge

The dewatered SS sample was obtained from a municipal wastewater treatment plant in Changsha, Hunan Province. The sludge was stored below 4 °C and used directly after the collection. The moisture content of the dewatered sludge was about 80%–85%. The elemental compositions of SS were analyzed by an elemental analyzer (Vario EL III, German). The calorific value was measured using an oxygen bomb calorimeter (KSLR-4000, Kesheng, China). The amounts of combustibles and ash in the SS were analyzed by burning it at 600 °C for 30 min. The physicochemical characteristics of the dewatered sludge are listed in Table 1.

#### 2.2 Pretreatment of sludge

To accelerate foam formation, the dewatered sludge was premixed with different dosages of CaO and NaOH in a portable cement mixer (JS140, JISHUN, China) at a rotation speed of 20 rpm. Based on the addition of 2.0 wt% in previous research,

Table 1 Physicochemical characteristics of the sewage sludge

Proximate analysis <sup>a</sup>		Ultimate analysis <sup>a</sup>					Calorific value		
(wt%)		(wt%)					(kJ kg <sup>-1</sup> )		
Combustibles	Ash	C	Н	N	S	O <sup>b</sup>	12 153		
62.85	37.15	31.79	4.43	4.77	1.52	20.34			
<sup><i>a</i></sup> On a dry basis. <sup><i>b</i></sup> By difference, $O = 100 - C - N - S - ash.$									

three different dosage ratios were created: 1 : 3 (sewage sludge with 0.5 wt% NaOH and 1.5 wt% CaO); 2 : 2 (sewage sludge with 1.0 wt% NaOH and 1.0 wt% CaO); and 3 : 1 (sewage sludge with 1.5 wt% NaOH and 0.5 wt% CaO). The texture of the dewatered sludge then changed from a block mass to a slurry flow with more homogeneous properties. The foam formation was conducted by whipping the premixed sludge using a cement mortar mixer (JJ-5, JIANYI, China) at a rotation speed of 140  $\pm$  5 rpm. The densities of the sludge foam was determined using a plastic measuring cylinder (range of 0–100 mL) every 5 min.

#### 2.3 Foam mat drying process

During the drying experiments, a Petri dish (35 mm diameter and 10 mm height) was covered with 5.00 g pretreated sludge sample. The different thicknesses of the sludge foam mat were neglected. The dishes were placed in a drying oven (FED-115, Binder, German) at different air temperatures of 40 °C or 50 °C, with a superficial air velocity of 0.3 m s<sup>-1</sup> and a relative humidity of 20%. The drying oven was pre-stabilized by passing hot air at the pre-set temperature for 30 min. The moisture loss of the samples was determined using an electronic balance (±0.01) outside the drying oven every 20 min. The dimensionless moisture content was calculated using eqn (1):

Moisture content (%) = 
$$\frac{m_t - m_0}{m_t}$$
 (1)

where  $m_t$  and  $m_0$  are the mass at a given time and the mass at a total dry base, respectively.



Fig. 1 Effects of whipping time and joint additions on the foam-ability of sludge.

#### 2.4 TG experiments

2.4.1 Thermal analysis. The combustion characteristics of the samples under non-isothermal conditions were determined in a thermo-gravimetric (TG) analyzer (TG/DTA 7300, Seiko SII Nano, Japan). To simulate the combustion process, an oxidizing atmosphere of synthetic air ( $21 \pm 1\%$  O<sub>2</sub> and N<sub>2</sub> balance; purity  $\geq$ 99.9994%) was used with a flow rate of 100 mL min<sup>-1</sup>. Samples weighing 6–8 mg were placed in an aluminum oxide crucible. The reaction temperature range was 40–1000 °C and the heating rate test, a separate blank run was carried out for baseline correction using an empty pan. Several repeated runs were conducted to ensure the reproducibility of each run, and the results revealed that the reproducibility was good, with deviations mainly occurring at low temperatures (<525 K) and generally being below 1.0%.<sup>21</sup>

**2.4.2 Kinetic models and data processing.** As a typical type of heterogeneous solid-state reaction, the primary pyrolysis process of biomass is represented by the following reaction scheme:

Biomass 
$$\rightarrow$$
 char + (volatiles + gases)<sup>22</sup>

In general, the rate of solid-state reactions can be described by eqn (2):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{1}{\beta} \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{\beta} A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{2}$$

where  $\alpha$  is the conversion degree of the combustible material,  $\beta$  is the heating rate ( $\beta = dT/dt$ ), A is the Arrhenius parameter, E is the activation energy, T is the absolute temperature, R is the universal gas constant (8.314 J mol<sup>-1</sup>·k<sup>-1</sup>), and t is time. In addition,  $f(\alpha)$  is the reaction model function, which is generally described as  $f(\alpha) = (1 - \alpha)^n$ , and n is the order of the reaction.

The Flynn–Wall–Ozawa (FWO) method and Kissinger–Akahira–Sunose (KAS) method are the two most common modelfree methods to determine kinetic parameters. The Flynn– Wall–Ozawa (FWO) equation is as follows:<sup>23</sup>

$$\ln\beta_i = \ln\left[\frac{AE}{RG(\alpha)}\right] - 2.315 - 0.4567\frac{E}{RT} = C_0 - 0.4567\frac{E}{RT}$$
(3)

and the Kissinger–Akahira–Sunose (KAS) equation is as follows:<sup>24</sup>

$$\ln\left(\frac{\beta_{i}}{T_{pi}^{2}}\right) = \ln\left(\frac{A_{k}R}{E_{k}}\right) - \frac{E_{k}}{RT_{pi}} = C_{k} - \frac{E_{k}}{RT_{pi}} \quad [i = 1, 2, 3, 4, 5, 6]$$
(4)



Fig. 2 Drying curves of sludge at different densities and drying temperatures:  $S_{1:3}$  at 40 °C (a) and 50 °C (b), 0.5–0.9 g mL<sup>-1</sup> are foamed sludges; (a<sub>1</sub>) and (b<sub>1</sub>), the evaporation rates, respectively.

According to the Starink method,<sup>25</sup> the approximate expression of the FWO method and KAS method can both be transformed into the same general formula as follows:

$$\ln\left(\frac{\beta}{T^S}\right) = C_S - \frac{BE}{RT} \tag{5}$$

For the FWO method (eqn (3)), s = 0, B = 0.4567; for the KAS method (eqn (4)), s = 2, B = 1. After a further exact analysis by Starink, the parameters of *s* and *B* were adjusted to s = 1.8 and B = 1.0037, respectively. Hence the Starink method can be described as follows:

$$\ln\left(\frac{\beta}{T^{1.8}}\right) = C_S - 1.0037 \frac{E}{RT} \tag{6}$$

With a given conversion fraction, a, the points of  $\ln(\beta/T^{1.8})$ *versus* 1/T at different temperature heating rates can be fitted to a straight line, and the slope of the line corresponds to 1.0037E/R. Hence, the apparent activation energy, *E*, can be calculated from the slope of the straight line.<sup>26</sup>

# 3. Results and discussion

#### 3.1 The foaming process of sludge

As reported by Jing Huang et al.,<sup>13</sup> it takes about 40 minutes for a sewage sludge sample with 2.0 wt% CaO added to it to reach the best drying performance density  $(0.70 \text{ g mL}^{-1})$ . However, to improve the foaming efficiency, new additions of CaO jointly added with NaOH have been found to be effective. Fig. 1 shows the effects of whipping time and joint addition on the foam-ability of sludge. The density of the  $S_{1:3}$  sample was observed to be almost 0.9 g mL<sup>-1</sup> after 5 min and a lower density of about 0.7 g mL<sup>-1</sup> for S<sub>2:2</sub> and S<sub>3:1</sub>. With a mechanical whipping of about 40 minutes, the density of these three types of samples reached 0.45-0.5 g mL<sup>-1</sup>. As mentioned in previous literature, sludge foaming is mainly derived from the decreased surface tension by surfactants. NaOH jointly added with CaO contributed to a faster decrease in surface tension than CaO added alone. The new mixed additives significantly shortened the foaming time, which indicates that the energy consumption was cut off. However, the optimal mixed additives and the appropriate best drying density performance are required, which are determined from drying experiments.



Fig. 3 Drying curves of sludge at different densities and drying temperatures:  $S_{2:2}$  at 40 °C (a) and 50 °C (b), 0.5–0.9 g mL<sup>-1</sup> are foamed sludges; (a<sub>1</sub>) and (b<sub>1</sub>), the evaporation rates, respectively.



Fig. 4 Drying curves of sludge at different densities and drying temperatures:  $S_{3:1}$  at 40 °C (a) and 50 °C (b), 0.5–0.9 g mL<sup>-1</sup> are foamed sludges; (a<sub>1</sub>) and (b<sub>1</sub>), the evaporation rates, respectively.

Table 2The time for samples to achieve the ideal moisture content(40%)

Sample	Density of best drying performance (g mL <sup><math>-1</math></sup> )	Drying time at 40 °C (min)	Drying time at 50 °C (min)
S1.2	0.7	100	75
S <sub>2·2</sub>	0.6	100	80
S <sub>3:1</sub>	0.6	125	95
SS	_	135	100
S <sub>CaO</sub>	0.7	100	80

#### 3.2 Drying performance of sludge samples

**3.2.1 Drying curves.** The influence of sludge foam density, convective drying temperature and drying time on the decrease of moisture content was studied in this research. Fig. 2–4 show the changes of moisture content *versus* drying time at various temperatures (40 °C and 50 °C). The short drying time of the pretreated samples primarily resulted from the larger surface area exposed to the drying space. However, the lower thermal conductivity of foams seemed to have a negative effect on the heat transfer compared to liquids. Thus, the drying performance of sludge will not be improved by foaming pretreatment infinitely.

The drying time taken for the S1:3 sample to reach the moisture content of 40% at 40 °C was about 100 min with the best drying performance density of 0.7 g mL<sup>-1</sup> (Fig. 2a). At 50 °C, the drying time required was 75 min, which also had the best drying performance density of 0.7 g mL<sup>-1</sup> (Fig. 2b). The same sample performed discriminately at different temperatures. Moreover, with the temperature increasing from 40 °C to 50 °C, the gaps of moisture content (%) between the sludge of different densities (0.5, 0.6, 0.7, 0.8, 0.9 g mL<sup>-1</sup>) appear to be more distinct. Driving temperature accelerated the evaporation of water in the pretreated samples, which is in satisfactory agreement with the previous research.<sup>27,28</sup> When compared with the drying temperature of 40 °C, about 25% less drying time was needed to achieve the ideal moisture content (40%) at 50 °C. Fig.  $2a_1$  and  $b_1$  show the evaporation rates of three typical drying curves, and the area below the curves represents the amount of moisture loss. This area expanded when the temperature changed from 40 °C to 50 °C, which indicates a larger amount of moisture loss. However, it is implied that more energy was inputted to the system with a higher drying temperature.

As shown in Fig. 3a and b, with the best drying performance density of 0.6 g mL<sup>-1</sup>, the drying time was about 100 min (at 40 °C) and 80 min (at 50 °C) for the  $S_{2:2}$  sample to reach the moisture content of 40% and more 20 min were spent at a lower



Fig. 5 The moisture variation of samples at 50 °C with the density of their best drying performance.

temperature. Moreover, with the increase in temperature, the moisture content (%) gaps between the sludge of different densities (0.5, 0.6, 0.7, 0.8, 0.9 g mL<sup>-1</sup>) appear to be more distinct. The results shown in Fig.  $3a_1$  or  $b_1$  are consistent with these findings.

The drying time required for  $S_{3:1}$  to achieve the ideal moisture content (40%) was 125 min (or 90 min) at 40 °C (or 50 °C) (Fig. 4a and b). With the increase in temperature, the moisture content (%) gaps between the sludge of different densities (0.5, 0.6, 0.7, 0.8, 0.9 g mL<sup>-1</sup>) occur at the same time (Fig. 4a<sub>1</sub> and b<sub>1</sub>), but is shown to be not that much obvious than the other two samples (S<sub>1:3</sub> and S<sub>2:2</sub>).

It is clearly shown in Fig. 2–4 that the addition of more NaOH can shorten the foaming time, and hence improve the efficiency of foam mat drying. However, the drying time to achieve the ideal moisture content (40%) increased under the same drying conditions (Table 2). Results showed that  $S_{2:2}$  appears to be the optimal mixed sludge sample and the appropriate best drying performance density is 0.6 g mL<sup>-1</sup>. The drying temperature and economic cost budget should be investigated for the further large-scale use of the technology.

Fig. 5a shows the moisture variation of the original sewage sludge and samples after foaming over time. All the samples were dried at 50 °C and each at their best drying performance density. Compared with the sewage sludge, the ideal drying time was reduced regardless if CaO was added alone or together with NaOH. As shown in Fig. 5b, between the 80% and 70% period of moisture content, the evaporation rate of S<sub>CaO</sub> prevails. This may due to the water imbibition characteristics of NaOH. However, after this period of time, the moisture loss rate of the mixed samples is shown to be far more than S<sub>CaO</sub>, especially for S1:3 and S2:2. This may due to the proper ratio additions of NaOH and CaO, which reduced the degree of bubble bursting during the thermal drying. The mixed additives delayed the maximum moisture evaporation efficiency, but the total amount of the moisture loss is still higher than SS or S<sub>CaO</sub>. A final moisture content below 10% was achieved in the case of 50 °C (Fig. 5a). Thus, the mixed additives contribute to the pace of foaming and better drying performance.

**3.2.2** Mathematical modeling of drying curves. An efficient modeling of drying curves could be used to perform an accurate estimate of the moisture content (%) of the foamed sludge at any time during the whole drying process.<sup>29,30</sup> In this research, the results of moisture content (%) *versus* drying time were fitted to adequate empirical and semi-theoretical models, which are widely used to describe the kinetics in the drying process. Finally, non-linear regression techniques (Nonlinear Curve Fit (Dose Resp)) were successfully applied to simulate the whole drying process of S<sub>2:2</sub> at the ideal density of 0.6 mg L<sup>-1</sup>, using the Origin Pro 8.0 software based on the Levenberg–Marquardt method (nonlinear least square method). The results of the statistical computing are summarized in Fig. 6. The  $R^2$  value is over 0.99, which indicates that the fitting result was successful.

#### 3.3 TG analysis

**3.3.1 Thermal decomposition characteristics.** Fig. 7 shows the thermo-gravimetric (TG) curves of the four samples under the atmosphere of synthetic air at different heating rates of 10, 20, and 50 K min<sup>-1</sup>. It can be observed that the TG curves for the



Fig. 6 Results of the statistical computing for  $S_{2:2}$ .



Fig. 7 TG/DTG curves for the pyrolysis of  $S_{1:3}(a)$ ,  $S_{2:2}(b)$ ,  $S_{3:1}(c)$  and SS(d) at heating rates of 10, 20, 50 K min<sup>-1</sup>.

four samples were similar, which involve mainly two stages during the pyrolysis process.

To describe the properties of the pyrolysis of the four samples under the effects of varied heating rates, some

characteristic parameters calculated from the TG-DTG curves are listed in Table 3, where  $T_i$ : the initial thermal decomposition temperature at any stage,  $^{\circ}$ C;  $T_{p}$ : the corresponding temperature of the peak rate of weight loss, °C;  $T_{f}$ : the final thermal

Sample	Stage I				Stage II					
	$T_{\rm i}$ (°C)	$T_{\rm f} \left(^{\circ} { m C} \right)$	$T_{\rm p}$ (°C)	DTG <sub>max</sub>	ML (%)	$T_{\rm i}$ (°C)	$T_{\rm f} \left(^{\circ} { m C}\right)$	$T_{\rm p}$ (°C)	DTG <sub>max</sub>	ML (%)
S <sub>1:3</sub>										
10	40	345	282	0.018	22.57	425	580	506	0.069	19.35
20	40	358	290	0.043	23.06	460	573	507	0.112	17.43
50	40	390	306	0.113	23.77	485	620	525	0.126	17.14
S <sub>2:2</sub>										
10	40	338	261	0.016	23.09	446	517	493	0.027	9.42
20	40	372	278	0.037	24.37	474	647	521	0.049	18.11
50	40	382	296	0.13	25.09	509	654	586	0.1	17.02
S <sub>3:1</sub>										
10	40	349	271	0.021	23.99	425	529	499	0.025	12.53
20	40	372	287	0.037	23.88	472	560	522	0.037	12.29
50	40	380	293	0.128	23.62	494	635	545	0.127	18.2
SS										
10	40	371	250	0.022	35.13	415	580	501	0.057	22.13
20	40	393	276	0.043	34.6	458	573	538	0.095	19.55
50	40	423	290	0.13	38.02	490	631	558	0.113	18.24

Table 3	Characteristic	parameters of	f S <sub>1:3</sub> , S <sub>2:2</sub> ,	S <sub>3:1</sub> and S	S during the	e pyrolysis	process
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Fig. 8 Regression lines to apparent activation energy proposed using the Starink method for  $S_{1:3}(a)$ ,  $S_{2:2}(b)$ ,  $S_{3:1}(c)$  and SS(d) at heating rates of 10, 20, 50 K min<sup>-1</sup>.

decomposition temperature at any stage,  $^{\circ}C$ ;  $DTG_{max}$ : the maximum weight loss rate at any stage,  $^{\circ}C^{-1}$ ; and ML: the total mass loss at any stage, %.

It can be seen from Table 3 that the entire decomposition process was shifted to a higher temperature zone as the temperature heating rate increased from 10 to 50 K min<sup>-1</sup>. During stage I, the value of  $T_{\rm p}$  increased from 250 °C (SS), 282 °C (S1:3), 261  $^{\circ}C$  (S2:2) and 271  $^{\circ}C$  (S3:1) to 290  $^{\circ}C$ , 306  $^{\circ}C$ , 296  $^{\circ}C$  and 293 °C, respectively. As for stage II of weight loss, the corresponding value of  $T_p$  was increased from 501 °C (SS), 506 °C (S1:3), 493 °C (S2:2) and 499 °C (S3:1) to 558 °C, 525 °C, 586 °C and 545 °C, respectively. Table 3 also shows that the ML data for the four samples display a fluctuation with different heating rates. Jeguirim *et al.*<sup>31</sup> reported that the total mass loss is mainly determined by the essential component of the tested samples and the heating rate. In addition,  $T_{\rm f}$  and  $\rm DTG_{max}$  had higher values throughout the whole thermal decomposition process of the four samples. This may be due to the fact that the time consumed in reaching the settled final temperature is less with the increase of heating rate. Consequently, the heat transferred from the heating furnace within the thermo-gravimetric instrument to the tested sample is limited, which may bring about a discrepancy between the recorded temperature and the actual sample temperature.26

3.3.2 Variation of apparent activation energy (E). To evaluate the dependence of apparent activation energy on the

conversion fraction during the major pyrolysis process, several levels of conversion fractions, ranging from 10% to 50%, were employed at different heating rates of 10, 20 and 50 K min<sup>-1</sup>. Based on the model-free iso-conversional Starink method, the regression lines of the four samples are illustrated in Fig. 8. The deduced slope value, correlation coefficient ( $R^2$ ), standard deviation (SD) and apparent activation energy (*E*) are summarized in Table 4.

It can be seen from Fig. 8 and Table 4 that the Starink method is suitable to determine the kinetic parameter of apparent activation energy based on the high value of  $R^2$  and low calculated SD value. The apparent activation energies of the four samples varied from each other to some degree, which correspond to the differences of TG-DTG curves for the four samples. This may due to the adoption of different proportions of alkaline substances, including CaO and NaOH, which could disrupt micro-organism cells and release the inner organic materials of sludge.

As shown in Fig. 9, during the initial stage of combustion (conversion between 10% and 25%), the four samples maintain a quite stable trend with a small gap among the *E* values, which indicates  $S_{2:2} > S_{1:3} > S_{3:1} > SS$ . However, the adoption of CaO and NaOH can improve the value of *E* during the main combustion stage (conversion between 25% and 35%). These findings support the conclusions that differences appear in their chemical compositions after the pretreatment, and the



Fig. 9 Relationships between the apparent activation energy (*E*,  $kJ \text{ mol}^{-1}$ ) and the conversion (*a*, %).

**Table 4** Slope, apparent activation energy (*E*) and correlation coefficient ( $r^2$ ) deduced from Starink method for S<sub>1:3</sub>, S<sub>2:2</sub>, S<sub>3:1</sub> and SS

Sample	Conversion (%)	Slope	E (kJ mol <sup>-1</sup> )	$r^2$	SD
S <sub>1.3</sub>	10	-19.284	159.736	0.995	0.002
1.5	20	-19.182	158.891	0.974	0.008
	30	-33.740	279.480	0.938	0.005
	40	-21.986	182.118	0.991	0.007
	50	-28.433	235.521	0.953	0.013
S <sub>2:2</sub>	10	-20.053	166.106	0.984	0.003
	20	-21.981	182.076	0.932	0.006
	30	-34.570	286.356	0.947	0.005
	40	-21.230	175.856	0.979	0.004
	50	-31.405	260.139	0.893	0.008
S <sub>3:1</sub>	10	-16.420	136.013	0.999	0.003
	20	-17.262	142.987	0.978	0.005
	30	-19.340	160.200	0.923	0.009
	40	-15.251	126.329	0.982	0.007
	50	-6.536	54.140	0.996	0.010
SS	10	-15.023	124.441	0.978	0.012
	20	-17.795	147.402	0.944	0.009
	30	-9.200	76.207	0.997	0.005
	40	-24.978	206.902	0.983	0.003

joint additives result in changes among the major components.<sup>13,32</sup> The peak E of the non-pretreatment sludge appears near the conversion of 40%, which is shown to be the last. The combustion process of the samples was advanced by the pretreatment.

## 4. Conclusion

The new addition, 1.0 wt% CaO together with 1.0 wt% NaOH, shows a superior performance with high foaming efficiency and low energy consumption. The addition of NaOH contributes to a quicker decrease in surface tension than CaO added alone. Moreover, CaO assisted by NaOH can reduce the degree bubble bursting during thermal drying. Non-linear regression techniques (Nonlinear Curve Fit (Dose Resp)) were successfully applied to simulate the whole drying process of  $S_{2:2}$  at the best drying performance density of 0.6 mg L<sup>-1</sup>, thus providing an accurate estimate of the moisture content (%) of the foamed sludge at any time.

The thermal behavior of the four sludge samples was investigated using a TG analyser. The Starink method was found to be suitable to determine the kinetic parameter of apparent activation energy based on the high value of  $R^2$  and low value of SD calculated. The apparent activation energy (*E*) of the samples improved slightly during the main combustion stage (conversion between 25% and 35%), whereas peak E of the non-pretreatment sludge appears lower and later (near a conversion of 40%), which supports the conclusion that differences appear in their chemical compositions after pretreatment.

# Acknowledgements

We are grateful for the financial support of the National Natural Science Foundation of China (51378189).

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