Quantification of Total Organic Carbon in Ashes from Smoldering Combustion of Sewage Sludge via a Thermal Treatment—TGA Method

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1. INTRODUCTION

Sewage sludge of high moisture content (>80 wt %) is a major byproduct from wastewater treatment plants, the high annual production of which poses great challenges for its proper disposal or use.1–4 Sewage sludge is mainly applied to land for agricultural purposes, disposed via landfilling, and/or incinerated for energy recovery,5,6 which are expensive because of high energy inputs and long transportation distance, necessitating the development of novel alternative technologies. One of the promising technologies is smoldering combustion that has been extensively investigated from a safety perspective.7,8 It is a self-sustaining smoldering combustion, which requires low energy inputs, has been successfully employed to destroy liquid and solid organic wastes, such as coal tar, feces, and sewage sludge (or biosolids).6,9–19 These previous studies have been focused on mapping process conditions, under which self-sustaining smoldering combustion is achieved, and exploring the effects of key process parameters (e.g., moisture content, sand-to-fuel ratio, and air flow rate) on the propagation of smoldering front.

Despite significant progress made from the aforementioned studies, it has been done to systematically characterize the properties of ashes from smoldering combustion of sewage sludge, which is of critical importance because these ashes have to be eventually disposed or used. Our recent study investigated the occurrence forms and leachability of major inorganic elements and heavy metals in sewage sludge.19 Little work has been done to systematically characterize the properties of ashes from smoldering combustion of sewage sludge, which is of critical importance because these ashes have to be eventually disposed or used. The results suggest that the residue ashes have potential to recover nutrients and are safe for landfilling. Another important ash property is the content of total organic carbon (TOC) that consists of both volatile carbonaceous
Table 1. Review of Some Studies That Applied Smoldering Combustion for the Destruction of Organic Waste Materials

| no. | organic waste | reactor type | reaction conditions | key findings | references |
|-----|---------------|--------------|---------------------|--------------|------------|
| 1   | nonaqueous phase liquids (NAPLs, e.g., coal tar) | fixed bed column reactor | mass ratios of coal tar/sand: 0.014−0.28 g/g; Darcy air fluxes: 4.25−5.31 cm/s | smoldering combustion has been proved to be an effective approach to treat soils contaminated by a range of organic liquids | Switzer et al.9 |
| 2   | coal tar and field-obtained mixed oil waste | fixed bed column, drum, and bin reactors | mass ratios of organic liquid-to-sand (or soil): 0.028−0.142 g/g; Darcy air fluxes: 0.5−9.15 cm/s | self-sustaining smoldering remediation of soils contaminated with organic liquid was successful in pilot field conditions | Switzer et al.10 |
| 3   | coal tar | field test cells (3.0 and 7.9 m below the ground surface) | air flow rates range from 10 to 340 m³/h; pressure varies from 3.4 to 275 kPa | smoldering combustion can successfully treat the soil contaminated with coal tar in the field | Scholes et al.11 |
| 4   | coal tar and crude oil | fixed bed column reactor | mass ratios of coal tar (or crude oil)-to-sand: 0.0142−0.014 g/g; Darcy air fluxes: 0.5−9.15 cm/s | propagation velocity was dependent on air injection rate and the yields of bio-oil were up to 7 wt % (dry basis) during smoldering combustion of feces | Pironti et al.12 |
| 5   | coal tar | a steel box reactor | mass ratios of coal tar-to-sand: 0.071 g/g; Darcy air fluxes: 0.98−64.38 cm/s | self-sustaining smoldering combustion was achieved for moisture contents of ≤50 wt %, air flow rate of 10−100 g/min, and wet sand-to-feces ratio of ≥3.25 | Haan et al.13 |
| 6   | organic liquid | fixed bed column reactor | mass ratios of organic liquid/sand: 0.06 g/g; Darcy air fluxes: 1.25−6.25 cm/s | downward organic liquid mobilization can occur under certain experimental conditions, which impacts smoldering behavior | Kinsman et al.14 |
| 7   | surrogate feces | fixed bed column reactor | moisture content: 0−75 wt %; sand-to-feces ratio: 2.75−11.9 g/g; air flow rate: 7−108 g/min | about 3700 and 860 kg of coal tar were destroyed over 12 and 11 days, respectively | Yerman et al.15 |
| 8   | surrogate feces | fixed bed column reactor | moisture content: 50−72 wt %; sand-to-feces ratio: 4−24 g/g; air Darcy fluxes: 3.0−46.7 cm/min; sand grain size: 0.3−4.5 mm; ignition temperature: ≤400 °C | self-sustaining smoldering combustion was achieved for moisture contents of ≤50 wt %, air flow rate of 10−100 g/min, and wet sand-to-feces ratio of ≥3.25 | Yerman et al.16 |
| 9   | surrogate feces | fixed bed column reactor | moisture content: 0−40 wt %; sand-to-feces ratio: 15−25 g/g; air flow rate: 30−50 L/min | the yields of bio-oil were up to 7 wt % (dry basis) during smoldering combustion of feces | Yerman et al.17 |
| 10  | surrogate feces | fixed bed column reactor | moisture content: 33−50 wt %; fuel-to-sand ratio: 0.036−0.25 g/g; air flow rate: 4−80 L/min | fuel consumption rate increases with the increasing fuel concentration and air flow rate, but is irrelevant to the fuel’s original moisture content | Yerman et al.18 |
| 11  | surrogate feces | column reactor operated under continuous mode | moisture content: 53 wt %; sand-to-fuel ratio: 24 g/g; air Darcy fluxes: 1.85−7.4 cm/s | continuous smoldering of feces was realized at various trigger heights | Fabris et al.19 |
| 12  | biosolids | fixed bed column reactor | moisture content: 74−85 wt %; sand-to-fuel ratio: 1.5−25 g/g; air Darcy fluxes: 1.6−8.1 cm/s | self-sustaining reaction was achieved at a moisture content up to 80 wt % | Rashwan et al.20 |
| 13  | anaerobic digestate | fixed bed column reactor | moisture content: 70−85 wt %; sand-to-fuel ratio: 0−1 g/g; air Darcy fluxes: 5−50 cm/s | smoldering combustion could be a new promising technology for biosolids management | Serrano et al.21 |

"Some other NAPLs (e.g., crude oil, mineral oil, and vegetable oil) and field-contaminated samples were also tested in the study. "Mixture of canola oil and viscosity index improver at a ratio of 1:1."
matter and unburned carbon because it not only reflects combustion efficiency but also leads to adverse impacts on ash disposal or utilization. For instance, in the context of landfill, the EU Council decision (2003) requires the concentrations of TOC to be <6% for hazardous waste, <5% for nonhazardous waste, and <3% for inert waste.

To quantify unburned carbon (or TOC in the absence of volatile carbonaceous matter) in ash residues from coal and/or biomass combustion, methods based on thermogravimetric analysis (TGA) have been established in addition to the simple but less accurate loss-on-ignition method. However, the applicability of these TGA-based methods to the ashes from smoldering combustion of sewage sludge is questionable for at least two reasons. One is the drastic discrepancies in the fuel properties of sewage sludge and other solid fuels such as coal and biomass. The other reason is that the temperatures experienced by sewage sludge particles during smoldering combustion are much lower than that during other conventional flame combustion processes, leading to the presence of volatile carbonaceous matter in ashes.

Therefore, this study aims to develop a two-step thermal treatment—TGA method for quantifying TOC in the ashes from the self-sustaining smoldering combustion of sewage sludge. The first step was to thermally treat the ashes at 500 °C in nitrogen (N₂) for removing volatile matter. Carbon released during thermal treatment was quantified by ultimate analysis of the raw and thermally treated ashes, considering the solid yields after treatment. The second step was nonisothermal TGA for the thermally treated ashes, following a temperature program that was able to identify the contribution of organic carbon oxidation to the weight loss. The two-step method was validated by a purposely designed method that involves acid washing of the thermally treated ashes, elemental analysis of the acid-washed ashes, and TOC analysis of the leachates.

## 2. RESULTS AND DISCUSSION

### 2.1. Self-Sustaining Smoldering Combustion of Sewage Sludge

Figure 1 shows typical temperature profiles monitored by 13 thermocouples (TCs) for the smoldering combustion of sewage sludge [moisture content: 50 wt %; sand-to-fuel (rewetted) mass ratio: 5.4 g/g; and Darcy air flux: 5.7 cm/s] in the presence and absence of the stainless steel meshes (detailed in Section 4), with three important findings. First, the close agreement on the temperature profiles with and without the stainless steel meshes indicates that loading the meshes has no obvious impact on the propagation and extinction of the smoldering combustion process. Therefore, employing these meshes allows us to collect ashes at different locations/zones, which can represent the ashes from smoldering combustion of sewage sludge under conventional reactor configuration, that is, without the meshes.

Second, the self-sustaining smoldering combustion of sewage sludge has been achieved under the experimental conditions. Specifically, taking Figure 1a as an example, water evaporation for the region 2 cm above the heater (TC1) was completed at ∼29 min. When the temperature of TC1 reached 200 °C, air was injected into the smoldering reactor. Once TC1 reached the peak temperature of 786 °C, the heater was turned off. The temperature readings for the first five TCs were higher than those for the rest because of the excess energy...
provided by the heater. However, the peak temperatures of TCs 6−11 were nearly equal, indicating a typical self-sustaining smoldering combustion process had taken place.

Third and last, as calculated from the peak temperatures of TCs 6−11, the average peak temperatures were ∼554 and ∼544 °C for the experiments with and without the steel meshes, respectively, with corresponding average front velocities being ∼0.50 and ∼0.54 cm/min. These average peak temperatures and smoldering front velocities are in broad agreement with those reported in a previous study.6 Importantly, the close agreements on the average peak temperatures and front velocities for the experiments with and without the steel meshes further confirm their negligible impact on the smoldering combustion process and thereby the properties of the resulting ashes.

2.2. Thermal Behavior of Ashes from Smoldering Combustion of Sewage Sludge. Figure 2a depicts the thermal behavior of the raw ashes of >200 μm (ground to <75 μm prior to TGA) collected from the three zones in air. One immediate finding is that the DTG curves at temperatures >700 °C of the raw ashes collected from the three zones are similar, with a peak at ∼850 °C. This can be attributed to the thermal behavior of inorganic materials such as evaporation of alkali salts.21 However, the thermal behavior of these ashes at temperatures <700 °C is drastically different, with no distinguished individual peaks observed. Using the raw ashes collected from zone III as an example, their DTG curve in air at temperatures <700 °C was fitted with three Gaussian peaks and compared with that in nitrogen (N2), the data of which are presented in Figure 2b.

Clearly, the fitted curves for both DTG curves are peaked at ∼550, ∼422−430, and ∼311−330 °C. The peaks at ∼550 °C for the DTG curves under both air and N2 atmospheres are largely overlapped, implying that the peaks are most likely caused by the decomposition of inorganic matter rather than the combustion of organic materials. Identifying the exact reasons that result in the peaks at ∼550 °C requires further investigation but is out of the scope of this study. Even under an inert atmosphere (N2), the two peaks at ∼422−430 and ∼311−330 °C still exist, demonstrating the presence of volatile organic matter in the raw ashes. This hinders the use of the single TGA-based method21 for accurate quantification of TOC in the raw ashes from sewage sludge smoldering combustion because the DTG peaks associated with TOC combustion cannot be distinguished under air and N2 atmospheres. Therefore, thermal treatment of the raw ashes, prior to nonisothermal TGA, is necessary to quantify TOC.

2.3. Two-Step Thermal Treatment—TGA Method for Quantifying TOC in the Raw Ashes. 2.3.1. Method Overview. Figure 3 illustrates the proposed method for quantifying TOC in the raw ashes from sewage sludge smoldering combustion, which consists of two steps. The first step is the thermal treatment of the raw ashes at 500 °C under N2 for 1 h, which is sufficient because no further weight loss is observed when further increasing the holding time. The temperature of 500 °C is also carefully chosen to completely remove residue volatiles in the raw ashes and avoid decomposition of carbonates (if any). It has been reported that decomposition of carbonates can start from temperatures as low as 530 °C.21 This step yields thermally treated ashes, which (together with the raw ashes) are then subjected to ultimate analysis for carbon quantification. The content of carbon that is released during thermal treatment (TOC1, see Figure 3) can then be determined, considering sample weight loss during thermal treatment. It should be noted that the calculation of TOC1 is essential because direct ultimate analysis of the raw ashes cannot rule out the contribution of carbonate decomposition. The second step is nonisothermal TGA of the thermally treated ashes. It identifies a temperature range, at which the weight loss is caused by organic carbon oxidation. Then, the weight loss occurred in this temperature range is used to calculate the content of carbon retained in the
thermally treated ashes (TOC₂, see Figure 3). Finally, the sum of TOC₁ and TOC₂ represents the content of TOC in the raw ashes from sewage sludge smoldering combustion.

2.3.2. Quantification of Carbon Released during Thermal Treatment (TOC₁). Figure 4 shows the weight losses of the raw ashes after thermal treatment at 500 °C in N₂ for 1 h.

![Figure 4. Weight losses of the raw ashes after thermal treatment at 500 °C in N₂ for 1 h.](image)

...are required to characterize these ashes. From sewage sludge smoldering combustion, implying that some homogeneous pretreatment (e.g., sieving) would be required to characterize these ashes.

2.3.3. Quantification of Carbon Retained in Thermally Treated Ashes (TOC₂) via TGA. The thermally treated ashes were subjected to nonisothermal TGA in air, with the DTG curves shown in Figure 6, in comparison with those of their corresponding raw ashes. As expected, thermal treatment leads to drastic decreases in the rates of weight loss at temperatures <600 °C, indicating the removal of volatile organic carbon. In addition, the weight losses for the thermally treated ashes commence at ~310 °C, considerably higher than the starting temperatures (~210–235 °C) for the raw ashes. On the other hand, thermal treatment results in little changes in the DTG curves at temperatures >600 °C, indicating that the weight loss in this temperature range is caused by thermal behavior of inorganic matter (stable at the treatment temperature of 500 °C). This is further confirmed by the fact that acid washing of the thermally treated ash leads to the disappearance of the DTG peak at ~780–900 °C (see Figure 7).

To identify the temperature range, at which the weight losses of the thermally treated ashes are caused by organic carbon oxidation, the selected thermally treated ashes were subjected to TGA in N₂ and TGA–mass spectrometry (MS) analysis in air. A set of example data are presented in Figure 8, with other samples following identical behavior (the data are not shown here). The weight loss of the thermally treated ash in air starts at 310 °C, but that in N₂ only takes place at temperatures >500 °C (Figure 8a). Furthermore, Figure 8b demonstrates that, during the oxidation of the thermally treated ash in air, the only CO₂ signal peak is observed between 310 and 500 °C, consistent with the only exothermal peak (shown by the differential scanning calorimetry curve) observed in the same temperature range. Therefore, it is plausible to conclude that the weight loss for the thermally treated ashes at 310–500 °C is due to the oxidation of organic carbon.

The weight losses of the thermally treated ashes at 310–500 °C in air were then taken to calculate the contents of carbon retained in these ashes. Such data, along with the contents of TOC in the raw ashes, are also illustrated in Figure 5. Unlike the size variation observed for the contents of carbon released during thermal treatment, those of carbon retained in the thermally treated ashes do not vary considerably with the particle size of the ashes. However, the contents of carbon retained in the thermally treated ashes from zone III are considerably higher than those in the ashes from zones I and II. Overall, the TOC contents are ~0.85–1.22, ~1.16–2.06, and ~4.55–6.52 wt % (db) of the raw ashes collected from zones I, II, and III, respectively, depending on their particle sizes.

2.3.4. Method Validation and Further Discussion. The validation of the two-step method is focused on that of the second step (determination of carbon retained in the thermally treated ashes via TGA) because the first step (thermal treatment and ultimate analysis) is based on the well-established experimental method and instrumentation. To do this, another set of ultimate analysis for the thermally treated ashes was conducted. Briefly, the thermally treated ashes were washed with 1.0 M HCl acid solution for 24 h at a solid/liquid ratio of 1/250 g/mL to remove any potential carbonates, yielding leachates and acid-washed ashes. The leachates were subjected to TOC analysis, the results of which indicate the...
absence of organic carbon for all the samples. The acid-washed ashes were dried, weighed (with the solid yield recorded after washing, data not shown here), and subjected to ultimate analysis for carbon. The carbon contents in the acid-washed ashes were then converted back to those in the thermally treated ashes, considering the weight losses during acid washing. Figure 9 compares TOC in the raw ashes quantified by the ultimate analysis-based method and the two-step method. Clearly, a close agreement on the contents of TOC in the raw ashes determined by the two methods validates the two-step thermal treatment—TGA method.

Compared with the ultimate analysis-based method, which requires acid washing for the removal of carbonates and subsequent TOC analysis of the resulted leachates, the two-step method only requires a thermogravimetric (TG) analyzer, a tube furnace (essentially can be replaced by the TG analyzer), and an elemental analyzer, which are commonly available in most chemistry/chemical engineering laboratories. Oppositely, the ultimate analysis-based method requires a TOC analyzer, the availability of which could be limited, and involves tedious wet treatment (acid washing). The other advantage is that TGA of the raw and thermally treated ashes can provide comprehensive information on their thermal behavior, which is an important property to be considered when exploring technologies for the utilization or disposal of ashes from sewage sludge smoldering combustion. In this regard, quantification of TOC in the raw ashes can be considered as a “byproduct”. The proposed two-step thermal treatment—TGA method can be applied to the ashes that contain considerable amount of volatile organic matter.

3. CONCLUSIONS

This study develops a two-step thermal treatment—TGA method for quantifying TOC in the ashes from self-sustaining smoldering combustion of sewage sludge. The first step involves thermal treatment of the raw ashes at 500 °C in N2 for 1 h, followed by ultimate analysis of both the raw ashes and the thermally treated ashes. In this step, carbon released during thermal treatment is quantified. The second step is non-isothermal TGA of the thermally treated ashes. The weight losses at 310−500 °C for the TGA in air are confirmed to be caused by oxidation of organic carbon, enabling us to determine the contents of carbon retained in the thermally treated ashes. The sums of the two portions of carbon represent the contents of TOC in the raw ashes, which are ∼0.85−1.22, ∼1.16−2.06, and ∼4.55−6.52 wt % (db), for the raw ashes collected from zones I, II, and III, respectively. The two-step method is validated via a purposely designed method that consists of acid washing of the thermally treated ashes, elemental analysis of the acid-washed ashes, and TOC analysis of the leachates. The results also highlight the heterogeneous nature of the contents of TOC in the raw ashes collected from different zones/locations and of different particle sizes.

4. MATERIALS AND METHODS

4.1. Preparation of Ashes from Self-Sustaining Smoldering Combustion of Sewage Sludge. Sewage sludge was collected from a local municipal wastewater treatment plant in Wuhan, China. The sewage sludge was dried at 105 °C in an oven for 24 h to reduce the moisture content to <1.0 wt %, manually crushed and sieved to a size fraction of <0.5 mm, packed in sealed plastic containers, and then stored at 4 °C in a freezer, before being used for smoldering combustion experiments. The smoldering combustion experiments were conducted using a column reactor, as depicted in Figure 10. The reactor consists of two parts, a cylindrical reaction column and a base, both of which are made of 316 stainless steel. The reaction column (height: 100 cm and inner diameter: 15 cm) is placed over the base that houses an air diffuser and a coiled resistive heater (1000 W and 220
V). The air diffuser is a 316 stainless steel disc, which is homogeneously drilled with 160 holes and covered with coarse

Figure 8. Comparison of DTG curves of ashes collected from zone III (particle size: >200 μm) heated in air and N₂ (a) and data for TGA–MS analysis for the same ash (b).

Figure 9. Comparison of TOC contents of the raw ashes measured by the two-step thermal treatment—TGA method and ultimate analysis-based method.

Figure 10. Schematic diagram of the smoldering column reactor.
gravel (50−70 mm) and fine sand (0.8–1 mm) to ensure uniform air flow. The heater is placed above the upper fine sand layer. The propagation of smoldering combustion of sewage sludge is monitored by 13 TCs, which are inserted horizontally into the central axis of the reaction column at intervals of 2 cm for the first 5 TCs and 4 cm for the rest.

Two types of experiments, without and with stainless steel meshes, were conducted. For a typical experiment without the stainless steel meshes, the sewage sludge was rewetted into ∼50 wt % moisture content and mechanically mixed with clean sand (grain size = 0.8−1 mm) using a food mixer at a sand-to-fuel (rewetted) ratio of 5.4 g/g. The clean sand was prepared by washing the raw sand with 1.0 M HCl acid solution, flushing with ultrapure water, and drying at 105 °C in an oven overnight. After thorough mixing, the mixture of rewetted sewage sludge and sand was packed into the reaction column at a height of 38 cm and then covered by clean sand (∼3 mm thick). To start smoldering combustion, the heater was first switched on to preheat the fuel-sand mixture, without air flow, until the temperature of the first TC (TC1), located 2 cm above the heater, reached 200 °C. Smoldering combustion was then initiated by injecting air into the reaction column through the base at a flow rate of 60 L/min and an equivalent Darcy air flux of 5.7 cm/s. Once the temperature of TC1 peaked, the heater was turned off and subsequent combustion was sustained by the heat released from the smoldering combustion of sewage sludge.

Our preliminary experiments demonstrated that the ashes after sewage sludge smoldering combustion are highly heterogeneous in terms of particle size and color, particularly from the edge of the combustion column to its centerline, because of a considerable temperature gradient. Although we did not measure this temperature gradient, it has been reported that the temperature at the reactor centerline is ∼105 °C higher than that at the near-wall edge during the smoldering combustion of simulated feces. To collect ashes at different locations, the second type of smoldering combustion experiments was conducted via packing the fuel-sand mixture in the smoldering column using six stainless steel meshes, with other conditions identical to those employed for the first type of experiments. After smoldering combustion, the meshes loaded with the mixture of sand and ashes were taken out from the reaction column layer-by-layer using two hooks. The sand-ash mixture collected on each layer was then divided into three zones (I−III, as illustrated in Figure 10) based on its color. Because no apparent difference was visually observed for the ashes collected at different layers, ashes of identical zones in the 6 layers were mixed together and screened with a sieve of 300 μm mesh screen to separate the ashes from sand. The ashes were sieved into four size fractions using a mechanical shaker with mesh screens of 75, 125, and 200 μm to further improve their homogeneity. These size-narrowed ashes collected from the three zones, termed as “raw ashes” hereafter, were subjected to TOC analysis.

4.2. Thermal Treatment of the Ashes and TGA Programs. The TGA-based method developed by Zhao et al. for quantifying unburned carbon in biomass ashes stems from the fact that distinct thermal behavior was observed for the ashes under air and N2 atmospheres at temperatures lower than 530 °C. Specifically, whereas no obvious weight loss was observed for the ashes at temperatures <530 °C under N2, considerable weight loss was observed at the same temperature range under air, which was attributed to the combustion of unburned carbon. To assess whether this method is applicable to the ashes from sewage sludge smoldering combustion, the raw ashes (particle size: >200 μm) collected from zone III were subjected to TGA using a TG analyzer (NETZSCH, STA449F3) under both air and N2 atmospheres. Briefly, ∼10 mg of the raw ashes was loaded in a TGA crucible, heated to 105 °C, held for 30 min to remove moisture, and then heated to 900 °C at 10 °C/min under air or N2 (flow rate: 40 mL/min). The results demonstrated that considerable weight loss occurred for the raw ashes under N2 at temperatures even lower than 500 °C. This indicated that the TGA-based method developed for biomass ashes is not suitable for quantifying TOC in the ashes from the self-sustaining smoldering combustion of sewage sludge because of the presence of unstable and volatile carbon compounds.

To remove these carbon-containing compounds, the raw ashes were thermally treated at 500 °C under N2 (flow rate: 1 L/min) using a horizontal tubular furnace (model: SK2-2-12, manufactured by Yingshan County Jiani Electric Furnace Manufacturing Co., Ltd.). Specifically, the raw ashes were loaded into a ceramic boat, heated from room temperature to 500 °C/min in the tube furnace, and then held for 1 h. TGA of the raw ashes indicated that a holding time of 1 h is sufficient to get a stabilized mass of the thermally treated ashes. It should be noted that a modest thermal treatment temperature of 500 °C was chosen to avoid thermal decomposition of carbonates, which can start at temperatures as low as 530 °C.

The thermally treated ashes were manually crushed into <75 μm and then subjected to nonisothermal TGA, using the same TG analyzer employed for the raw ashes. Specifically, ∼10 mg of thermally treated ashes was loaded in a TGA crucible, heated from room temperature to 105 °C, held for 30 min to remove moisture, and further heated to 900 °C at 10 °C/min under air. The same TGA temperature program was also applied for selected thermally treated ashes under N2. The flow rates of both air and N2 were 40 mL/min. To distinguish the contribution of organic carbon oxidation to the weight loss, selected thermally treated ash samples were washed with 1.0 M HCl acid solution to remove carbonates (if any) and water-soluble salts. The acid-washed samples were analyzed via TGA in air, following the same temperature program used for the thermally treated ashes. In addition, TGA (NETZSCH, STA449F3)−MS (AMETEK) was employed for the thermally treated ash (>200 μm) collected from zone III, following the same temperature program, to further verify the contribution of organic carbon oxidation to the weight loss.

4.3. Sample Analysis and Characterization. Proximate analysis of the sewage sludge was conducted using the same aforementioned TG analyzer according to ASTM E870-82. Ultimate analysis for the contents of carbon (C), hydrogen

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Table 2. Proximate and Ultimate Analyses of the Sewage Sludge

|                  | proximate analysis (wt %, dry basis) | ultimate analysis (wt %, dry-ash-free basis) |
|------------------|-------------------------------------|---------------------------------------------|
|                  | ash  | volatile matter | fixed carbon | C     | H     | N     | S     | O (by difference) |
|                  | 50.7 | 42.1           | 7.2          | 44.7  | 7.8   | 8.59  | 1.51  | 37.4             |

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(H), nitrogen (N), and sulfur (S) was determined using a Vario Micro cube elemental analyzer, with the content of oxygen (O) calculated by difference. These properties of the sewage sludge are presented in Table 2. Both the raw and thermally treated ashes were subjected to ultimate analysis, using the same elemental analyzer, to quantify carbon released into volatiles during thermal treatment, considering the yields of ashes after the treatment. The contents of inorganic elements in the raw ashes were determined by a combination of X-ray fluorescence (XRF) spectrometer (EAGLE III, EDAX) and inductively coupled plasma MS (ICP—MS, ELAN DRC-e, PerkinElmer). Briefly, the contents of Al and Si were measured by the XRF. To determine the contents of other elements, ~1 mg of ash was digested by ~10 mL of digestion reagent, a mixture of hydrogen peroxide (H₂O₂, 30 wt %), hydrofluoric acid (40 wt %), and nitric acid (HNO₃, 68 wt %), at 180 °C for 2 h, followed by ICP—MS analysis. The contents of inorganic elements are given in Table 3. Clearly, the raw ashes contain predominantly Si, Al, and Fe, followed by Ca, K, Mg, and Na in a decreasing order.

| elements | zone I | zone II | zone III |
|----------|--------|---------|----------|
| Na⁺      | 0.243  | 0.275   | 0.282    |
| K⁺       | 1.337  | 1.519   | 1.566    |
| Mg²⁺     | 0.467  | 0.532   | 0.459    |
| Ca²⁺     | 1.684  | 1.914   | 1.971    |
| Fe³⁺     | 4.034  | 4.582   | 4.722    |
| Si⁴⁺     | 21.324 | 21.162  | 20.823   |
| Al³⁺     | 10.323 | 9.045   | 9.504    |

*“Analyzed by ICP—MS. *²Analyzed by the XRF spectrometer.

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Notes

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**REFERENCES**

(1) Yui, K.; Kuramochi, H.; Osako, M. Understanding the Behavior of Radioactive Cesium during the Incineration of Contaminated Municipal Solid Waste and Sewage Sludge by Thermodynamic Equilibrium Calculation. ACS Omega 2018, 3, 15086–15099.

(2) Gong, W.; Zhou, Z.; Liu, Y.; Wang, Q.; Guo, L. Catalytic Gasification of Sewage Sludge in Supercritical Water: Influence of K₂CO₃ and H₂O₂ on Hydrogen Production and Phosphorus Yield. ACS Omega 2020, 5, 3389–3396.

(3) Li, Y.; Fang, Z.; Teng, W.; Shen, S.; Li, R. Comprehensive Evaluation of the Control Efficiency of Heavy-Metal Emissions during Two-Step Thermal Treatment of Sewage Sludge. ACS Omega 2020, 5, 24467–24476.

(4) Wang, Y.; Li, D.; Zhao, D.; Fan, Y.; Bi, J.; Shan, R.; Yang, J.; Luo, B.; Yuan, H.; Ling, X.; Huhe, T.; Chen, Y. Calcium-Loaded Municipal Sludge-Biochar as an Efficient and Stable Catalyst for Biodiesel Production from Vegetable Oil. ACS Omega 2020, 5, 17471–17478.

(5) Liaw, S. B.; Rahim, M. U.; Wu, H. Trace Elements Release and Particulate Matter Emission during the Combustion of Char and Volatiles from In Situ Biosolid Fast Pyrolysis. Energy Fuels 2016, 30, 5766–5771.

(6) Rashwan, T. L.; Gerhard, J. I.; Grant, G. P. Application of self-sustaining smoldering combustion for the destruction of wastewater biosolids. Waste Manage. 2016, 50, 201–212.

(7) Wang, H.; van Eyk, P. J.; Medwell, P. R.; Birzer, C. H.; Tian, Z. F.; Possell, M. Identification and Quantitative Analysis of Smoldering and Flaming Combustion of Radiata Pine. Energy Fuels 2016, 30, 7666–7677.

(8) Wang, H.; van Eyk, P. J.; Medwel, P. R.; Birzer, C. H.; Tian, Z. F.; Possell, M. Effects of Oxygen Concentration on Radiation-Aided and Self-sustained Smoldering Combustion of Radiata Pine. Energy Fuels 2017, 31, 8619–8630.

(9) Switzer, C.; Pironi, P.; Gerhard, J. I.; Rein, G.; Torero, J. L. Self-Sustaining Smoldering Combustion: A Novel Remediation Process for Non-Aqueous-Phase Liquids in Porous Media. Environ. Sci. Technol. 2009, 43, 5871–5877.

(10) Switzer, C.; Pironi, P.; Gerhard, J. I.; Rein, G.; Torero, J. L. Volumetric scale-up of smoldering remediation of contaminated materials. J. Hazard. Mater. 2014, 268, 51–60.

(11) Scholes, G. C.; Gerhard, J. I.; Grant, G. P.; Major, D. W.; Vidumsky, J. E.; Switzer, C.; Torero, J. L. Smoldering Remediation of Coal Tar Contaminated Soil: Pilot Field Tests of STAR. Environ. Sci. Technol. 2015, 49, 14334.

(12) Pironi, P.; Switzer, C.; Gerhard, J. I.; Rein, G.; Torero, J. L. Self-Sustaining Smoldering Combustion for NAPL Remediation: Laboratory Evaluation of Process Sensitivity to Key Parameters. Environ. Sci. Technol. 2011, 45, 2980–2986.

(13) Hasan, T.; Gerhard, J. I.; Hadden, R.; Rein, G. Self-sustaining smoldering combustion of coal tar for the remediation of contaminated sand: Two-dimensional experiments and computational simulations. Fuel 2015, 150, 288–297.

(14) Kinsman, L.; Torero, J. L.; Gerhard, J. L. Organic liquid mobility induced by smoldering remediation. J. Hazard. Mater. 2017, 325, 101–112.

(15) Yermán, L.; Hadden, R. M.; Carrascal, J.; Fabris, L.; Cormier, D.; Torero, J. L.; Gerhard, J. I.; Krajcovic, M.; Pironi, P.; Cheng, Y.-L.
Smouldering combustion as a treatment technology for faeces: Exploring the parameter space. *Fuel* 2015, 147, 108–116.

(16) Yerma, L.; Wall, H.; Torero, J.; Gerhard, J.; Cheng, Y. L. Smoldering combustion as a treatment technology for faeces: Sensitivity to key parameters. *Combust. Sci. Technol.* 2016, 188, 968–981.

(17) Yerma, L.; Cormier, D.; Fabris, I.; Carrascal, J.; Torero, J. L.; Gerhard, J. I.; Cheng, Y. L. Potential Bio-oil Production from Smouldering Combustion of Faeces. *Waste Biomass Valorization* 2017, 8, 329–338.

(18) Yerma, L.; Wall, H.; Torero, J. L. Experimental investigation on the destruction rates of organic waste with high moisture content by means of self-sustained smoldering combustion. *Proc. Combust. Inst.* 2017, 36, 4419–4426.

(19) Fabris, I.; Cormier, D.; Gerhard, J. I.; Bartczak, T.; Kortschot, M.; Torero, J. L.; Cheng, Y.-L. Continuous, self-sustaining smouldering destruction of simulated faeces. *Fuel* 2017, 190, 58–66.

(20) Feng, C.; Cheng, M.; Gao, X.; Qiao, Y.; Xu, M. Occurrence forms and leachability of inorganic species in ash residues from self-sustaining smouldering combustion of sewage sludge. *Proc. Combust. Inst.* 2020, DOI: 10.1016/j.proci.2020.06.008.

(21) Zhao, M.; Han, Z.; Sheng, C.; Wu, H. Characterization of Residual Carbon in Fly Ashes from Power Plants Firing Biomass. *Energy Fuels* 2013, 27, 898–907.

(22) Kumpiene, J.; Robinson, R.; Brännvall, E.; Nordmark, D.; Bjurström, H.; Andreas, L.; Lagerkvist, A.; Ecke, H. Carbon speciation in ash, residual waste and contaminated soil by thermal and chemical analyses. *Waste Manage.* 2011, 31, 18–25.

(23) Bjurström, H.; Lind, B. B.; Lagerkvist, A. Unburned carbon in combustion residues from solid biofuels. *Fuel* 2014, 117, 890–899.

(24) Burris, S. C.; Li, D.; Riley, J. T. Comparison of Heating Losses and Macro Thermogravimetric Analysis Procedures for Estimating Unburned Carbon in Combustion Residues. *Energy Fuels* 2005, 19, 1493–1502.

(25) Fan, M.; Brown, R. C. Comparison of the Loss-on-Ignition and Thermogravimetric Analysis Techniques in Measuring Unburned Carbon in Coal Fly Ash. *Energy Fuels* 2001, 15, 1414–1417.

(26) ASTM D7348-13, “Standard Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues”; ASTM International: West Conshohocken, PA, 2013, DOI: 10.1520/D7348, www.astm.org.

(27) Folgueras, M. B.; Díaz, R. M.; Xiberta, J.; Prieto, I. Thermogravimetric analysis of the co-burning of coal and sewage sludge. *Fuel* 2003, 82, 2051–2055.

(28) Lv, D.; Xu, M.; Liu, X.; Zhan, Z.; Li, Z.; Yao, H. Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification. *Fuel Process. Technol.* 2010, 91, 903–909.

(29) Sheng, C.; Li, Y. Experimental study of ash formation during pulverized coal combustion in O2/CO2 mixtures. *Fuel* 2008, 87, 1297–1305.

(30) Chen, C.; Wang, J.; Liu, W.; Zhang, S.; Yin, J.; Luo, G.; Yao, H. Effect of pyrolysis conditions on the char gasification with mixtures of CO2 and H2O. *Proc. Combust. Inst.* 2013, 34, 2453–2460.

(31) Huang, J.; Wang, Z.; Qiao, Y.; Wang, B.; Yu, Y.; Xu, M. Transformation of nitrogen during hydrothermal carbonization of sewage sludge: Effects of temperature and Na/Na acetates addition. *Proc. Combust. Inst.* 2020, DOI: 10.1016/j.proci.2020.06.075.

(32) Wang, B.; Huang, J.; Gao, X.; Qiao, Y. Effects of Secondary Vapor-Phase Reactions on the Distribution of Chlorine Released from the Pyrolysis of KCl-Loaded Wood. *Energy Fuels* 2020, 34, 11717–11721.

(33) Winter, F.; Prah, M. E.; Hofbauer, H. Temperatures in a fuel particle burning in a fluidized bed: The effect of drying, devolatilization, and char combustion. *Combust. Flame* 1997, 108, 302–314.

(34) Serrano, A.; Wyn, H.; Dupont, L.; Villa-Gomez, D. K.; Yerma, L. Self-sustaining treatment as a novel alternative for the stabilization of anaerobic digestate. *J. Environ. Manage.* 2020, 264, 110544.