THERMOCHEMICAL BEHAVIOUR OF SEWAGE SLUDGE DURING ITS SLOW PYROLYSIS

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Abstract- Processing of sewage sludge waste is a major concern in modern societies, and pyrolysis is one of the technological options that can convert sewage sludge into useful energy and biofuels. The aim of this study was to investigate the thermochemical behaviour of sewage sludge during its slow pyrolysis from room temperature to 1000°C at a heating rate of 10°C/min. Thermogravimetric analysis showed that the pyrolysis process of sewage sludge consisted of three main steps in the respective temperature zones of <180°C, 180–600°C, and >600°C. The most intense mass loss rate occurred between 210 and 550°C with a maximum peak value of 0.21wt%/°C at 328°C. Computer aided thermal analysis was applied to determine the specific heat and the reaction heats during pyrolysis of the sewage sludge. Three main reaction peaks were identified. Gas chromatography results indicated that CO_2 and CO were the primary gas species evolved in the low (<500°C) and high (500–1000°C) temperature ranges, respectively. The yields of solid, liquid and gas products at 500 °C were 55.7, 35.6, and 8.7wt%, respectively. Understanding of the thermochemical behaviour of sewage sludge will facilitate more elaborate control of sewage sludge pyrolysis to produce energy and biofuels.

IndexTerms- sewage sludge, thermogravimetric analysis, specific heat, pyrolysis

I. INTRODUCTION

The increasing global material and energy demands combined with other factors, such as more stringent regulations on pollution control and carbon emissions, accelerate the exploitation of renewable sources, including biomass and domestic wastes. As the main waste from the treatment of municipal wastewater, sewage sludge is a complex blend of organic compounds (e.g., cellulose, proteins, lips, and carbohydrates), inorganic materials (e.g., silicates and metals), water and other components (e.g., pathogenic microorganisms) [1,2].

Besides the use as feedstock to produce industrial materials, e.g., fertilisers and building materials[2], sewage sludge has also found applications for energy and biofuel production via thermochemical conversions, such as combustion, hydrothermal carbonization [3] and gasification [4].

Pyrolysis of biomass is now a well recognised technology that processes the feedstock at 400-1000°C (preferable 450-550°C) under inert atmosphere, which results in decomposition products of solid bio-char, liquid bio-oil (or called bio-tar) and gas [5]. Bio-chars derived from sewage sludge pyrolysis have promising potential applications as catalysts. For example, the bio-char obtained at 900°C in nitrogen has high catalytic activity for oxygen reduction reaction with an optimum power density of approximate 500 mWm^{-2} which was close to the Pt cathode [6], due to the substantial content of transiton metals supported on the carbon substance. The sludge bio-oil is a dark brown liquid with a large amount of water (usually 20-70 wt%), some ash, and hundreds of organic compounds, such as furans, acids, aromatic hydrocarbons, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, alkenes, nitrogen compounds and miscellaneous oxygenates [7]. Its heating value ranges from 22 to 40 MJ kg^{-1}, which is half or nearly comparable to those of commercial liquid fuels (45-46 $MJkg^{-1}$) [7-9]. Thus, the sludge bio-oil has been considered as a potential source for production of liquid fuels or chemicals. The gas product may be used to generate heat through combustion or to synthesise chemicals and transportation fuels.

In this work, dried sewage sludge was subject to low pyrolysis from room temperature to 1000°C at a heating rate of 10°C/min via technologies of thermogravimetric analysis and computer aided thermal analysis. The volatiles released were also monitored. The objective of this work was to evaluate the thermochemical behaviour of sewage sludge during its slow pyrolysis to provide reference information to the energy and bio-fuel production process from sewage sludge pyrolysis.

II. EXPERIMENTAL

A. Feedstock
Dried sewage sludge sample with mixed particles of different sizes was collected from an Australian wastewater treatment plant. The sample was dried at 80°C for 4 h in a vacuum oven and then crushed into fine powder (<212 µm) and subject to proximate and ultimate analyses. The moisture content was tested by the mass difference between the sample of ~ 1 g as received and after heating at 105 °C in N_2 for 16 h [10]. The volatile matter (VM) content was determined by the mass difference between the sample of ~ 1 g as received excluding the moisture content and the sample mass after heating at 900 °C in N_2 for 7 min [11]. The ash content was analysed according to ASTM D-1102. The ultimate analysis

was conducted as per AS1038 Part 5. The results are shown in Table 1.

Table 1. Proximate and ultimate analyses of dried sewage sludge feedstock.

Proximate analysis / wt.%		Ultimate Analysis / wt.% (daf[a])	
Moisture	7.65	C	58.5
Volatiles	51.66	H	5.8
Ash	35.02	N	0.53
Fixed carbon	5.67	S	1.43
Calorific value (MJ/kg)	13.16	O[b]	33.74

[a] Dry-ash-free basis.
[b] By difference.

B. Mass change during pyrolysis:thermogravimetricanalysis (TGA)
A thermogravimetricanalyser (TGA/DSC 1 STAR[e] System, Mettler Toledo Ltd.) was used to measure the mass loss of the sewage sludge sample during heatingfrom room temperature to 1000°C under a heating rate of 10°C/min with nitrogen at 20 ml/min as the carrier gas. A differential thermogravimetric (DTG, in units of wt.%/°C) curve was also obtained by differentiating the thermogravimetric (TG, in units of wt.%) curve.

C. Heat change during pyrolysis:computer aided thermal analysis (CATA)
Specific heat of the sewage sludge sample during pyrolysis was analysed in a CATA apparatus as described in previous studies [12-14]. The sample was packed at 2.86g in 2.65cm^3 and heated in argon at a heating rate of 10°C/min from room temperature to 1000°C. The controlling temperature as well as the temperatures of the sample surface and centre was logged to calculate the specific heat of the sample. The calculation principle and process has been previously outlined in detail. [12].

D. Gas release during pyrolysis: Gas Chromatography (GC) analysis
Volatiles released during the sludge pyrolysis mainly consisted of CO_2, CO, H_2 and light hydrocarbons (C_xH_y, x ≤ 4) which were analysed by a micro gas chromatograph (GC model: M200, MTI Analytical Instruments) with thermal conductivity detectors and using a carrier gas of ultra-high purity helium. H_2 and CO were determined by a molecular sieve 5A column at 60°C, and CO_2, CH_4, C_2H_4, and C_2H_6 were analysed by a Poraplot U column at 40°C. The evolution rate of each gas species was defined as the gas mass percent of the initial sample per minute.

III. RESULTS AND DISCUSSION

A. Mass change of sludge during pyrolysis
The TG and DTG curves of the sewage sludge at a heating rate of 10°C/min are shown in Figure 1.
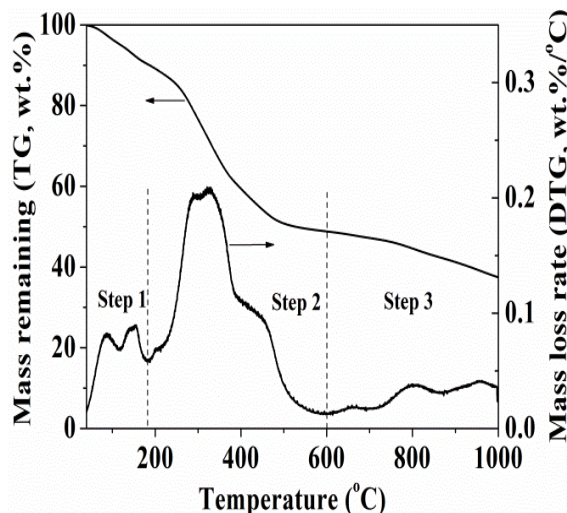
Figure 1. TG and DTG curves of sewage sludge at a heating rate of 10 °C/min.

As shown in the TG curve, 37.5wt.% of the initial sample remained as solid bio-char after heating to 1000°C in N_2. It could be concluded that the residual bio-char was mostly inorganic ash component with a small amount of carbonaceous matter considering that about 35wt.% of the initial sample was ash. According to the DTG curve, the overall pyrolysis process was comprised of three main steps. The first step ranged from room temperature to around 180°C, which was responsible for the mass loss of around 10% of the initial sample. The double peaks corresponded to the evaporation of water remaining after sample drying [15] and the decomposition of the bonded hydrated compounds [16].
The second step involved the primary pyrolysis reactions, starting from 180°C to approximately 600°C, which was in accordance with previous studies [17,18].
Several peaks overlapped, indicating the co-occurrence and complexity of reactions. The main peak between 210°C and 380°C was most likely due to the depolymerization reactions of biodegradable matter while the lower shoulder peak locating at 380-550°C should be ascribed to the degradation reactions of non-biodegradable organic matter [18,19].
The maximum mass loss rate of 0.21 wt.%/°Coccurred at 328°C. This second step resulted in a mass loss of 41.5% of the initial sample. The pyrolysis process moved into the third step after 600°C, during which the residual carbonaceous material and ash experienced the mass loss at slow rates.
B. Heat change of sludge during pyrolysis
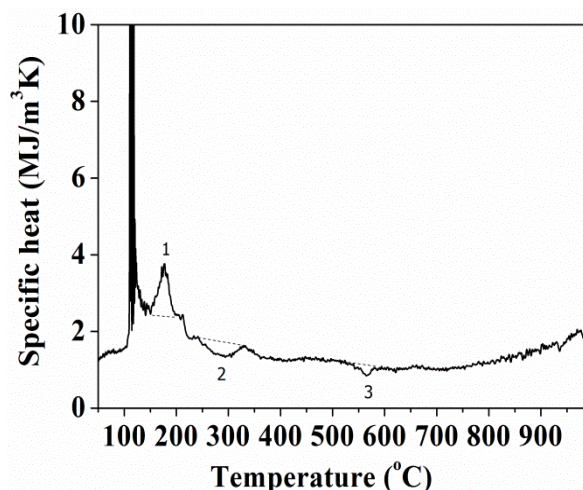The specific heat (C_p) of the sewage sludge during heating is shown in Figure 2.

Figure 2. Specific heat (Cp) of sewage sludge with temperature during pyrolysis at a heating rate of 10 °C/min.

The positive peaks represent endothermic energy changes while the negative peaks indicate exothermic changes. The extremely sharp positive peaks before 150°C were attributed to the latent heat of water content vaporisation.The volumetric heat of reaction (ΔH_v) was quantified through integration of each peak in the C_p curve.The ΔH_v results are shown in Table 2.

The specific heat of the sewage sludge was in the range of 1–4 MJ/m³K. The endothermic reaction between 150 and 200°C (Reaction number 1) corresponded to the DTG curve peak at around 120–180°C in Figure 1 and was ascribed to water release from the decomposition of the bonded hydrated compounds[16]. The heat of this reaction was 28.5 MJ/m³.

Table 2. Heats of reactions of sewage sludge pyrolysis at a heating rate of 10 °C/min.

Reaction number	Energy change direction	Reaction heats	
		Temperatu-re range (°C)	ΔHv (MJ/m³)
1	Endothermic	150–200	28.5
2	Exothermic	210–332	-21.2
3	Exothermic	531–598	-5.3

The following negative trough ranging from around 210 to 332°C, an indication of an exothermic reaction (Reaction number 2), was also observed. This phenomenon was also found in previous studies on sludge and algae [5,20]. A reaction heat of -21.2MJ/m³ was determined for this temperature region. This reaction corresponded to the major peak in the DTG curve, which might be due to the decomposition of proteins and the carboxyl groups as well as the cracking of carbon-containing structures,

such as saturated aliphatic chains, N-alkyl long chains and aromatic ring [21].

As the temperature continued to rise, an exothermic trough at 531–598°C was observed in the C_p curve (Reaction number 3). The reaction heat was calculated to be -5.3MJ/m³, as presented in Table 2. It may arise from the charring reaction [5].

C. Gas release during pyrolysis

The evolution rates of the main volatiles (i.e., H_2, CO, CO_2, CH_4, C_2H_4, and C_2H_6) from sewage sludge pyrolysis are presented Figure 3.

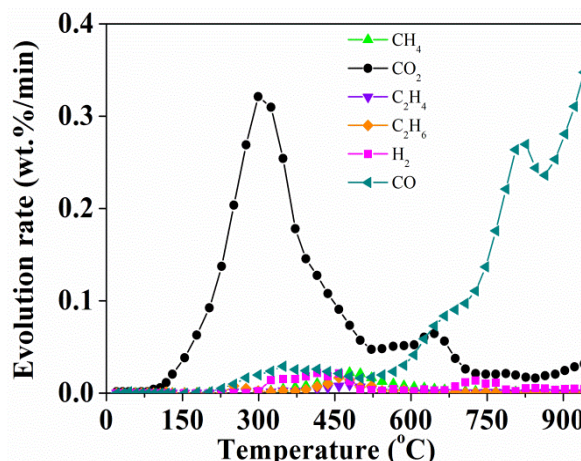**Figure 3. Evolution rates (wt %/min) of individual volatiles from sewage sludge pyrolysis with the temperature at a heating rate of 10 °C/min.**

CO_2 and CO were the dominant volatile products. CO_2 started to evolve at about 100°C and its evolution rate reached maximum value of 0.32 wt.%/minat around 300°C. The evolution rate of CO_2 then declined and rose again, forming a smaller side peak with summit of 0.064wt.%/minat around 650°C.CO was released after 230°C, and formed a low but wide peak at 230–500°C with the highest evolution rate of 0.03wt.%/min at 350°C. After 500°C, evolution rate of COincreased steadily and a much higher peak formed at around 830°C. The general decrease of CO_2 accompanied by the increase of CO after 500°C may be partly due to the reaction of $C + CO_2 = 2CO$ [20].

Negligible amounts of H_2, CH_4, C_2H_4, and C_2H_6 were also observed during the pyrolysis process. While CO_2 and CO are the main volatile products of primary decarboxylation and decarbonylationreactions, H_2, CH_4, C_2H_4, and C_2H_6 are most likely results from the secondary thermal cracking and/or reformation of the high temperature organic vapours[22-24].

D. Product distribution

Generally, the optimum liquid product yield is obtained at the pyrolysis temperature of around 500°C. In this work, the sewage sludge was heated to 500°Cat a heating rate of 10°C/min. The residual solid bio-char and liquid was collected and then weighted. The gas amount was obtained from the total evolution rate of all gas species in Figure 3. The

result of product distribution (yields)is shown in Table 3.

Table3.Product distribution for sewage sludge pyrolysis at a heating rate of 10°C/min to 500°C.

Products yields (wt.%)			Total yield (wt.%)
Solid	Liquid	Gas	
55.7	35.6	8.7	100

The solid bio-char was the major product with a yield of 55.7 wt.%, which was mainly due to the high ash content and the slow heating rate. The liquid and gas yields were 35.6 wt.% and 8.7 wt.%, respectively.

CONLUSION

In this study, the thermochemical behaviour of sewage sludge during slow pyrolysis at the heating rate of 10°C/min was characterised by thermogravimetric analysis, computer aided thermal analysis and gas chromatography. Results showed that the sewage sludge experienced a major mass loss between 210°C and 550°C with a maximum mass loss rate of 0.21wt.%/°C at 328°C. The specific heat result indicated one main endothermic and two exothermic reactions with the reaction heats of 28.5, -21.2, and -5.3MJ/m^3, respectively. CO_2 and CO were the dominant volatile products in the low (<500°C) and high 500–1000°C) temperature ranges, respectively. Negligible amounts of H_2, CH_4, C_2H_4, and C_2H_6 were also detected.Results also showed that the solid bio-char (yield of 55.7 wt.%) was the primary product with the respective liquid and gas yields of 35.6 wt.% and 8.7 wt.%.

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