ARTICLE IN PRESS

Waste Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Supercritical water pyrolysis of sewage sludge

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ARTICLE INFO

Article history:
Received 7 March 2016
Revised 26 October 2016
Accepted 31 October 2016
Available online xxxx

Keywords:
Supercritical water
Pyrolysis
Sewage sludge
Bio-oil
Bio-char

ABSTRACT

Municipal sewage sludge (SS) from wastewater treatment plant containing high water content (>85 wt.%), lead to the difficulty of co-combustion with MSW or coal due to the high cost of drying. This study explores an alternative method by supercritical water (SCW) pyrolysis of sewage sludge (SS) in a high pressure reaction vessel. The effects of temperature and moisture content of SS on yield and composition of the products (bio-oil, bio char and non-condensable gas) were studied. A temperature of 385 °C and moisture content of 85 wt.% were found to be the optimum conditions for the maximum bio-oil production of 37.23 wt.%, with a higher heating value of 31.08 MJ/kg. In the optimum condition, the yields of aliphatic hydrocarbon and phenols were about 29.23 wt.% and 12.51 wt.%, respectively. The physical and chemical properties of bio-char were analyzed by using XRF and BET. Results of GC analyses of NCG showed that it has the maximum HHV of 13.39 MJ/m^3 at 445 °C and moisture content of 85 wt.%. The reaction path from SS to bio-oil through SCW pyrolysis was given. Moreover, carbon balance was calculated for the optimal condition, and finding out that 64.27 wt.% of the carbon content was transferred from SS to bio-oil. Finally, this work demonstrates that the SCW pyrolysis is a promising disposal method for SS.

1. Introduction

Sewage sludge (SS) with 85 wt.% moisture content is frequently being discharged by municipal wastewater treatment plants in China and has amounted to 28 million tons since 2015 (China Statistical Yearbook, 2016). The discharging of SS has drawn much attention due to the ecological problems associated as well as the health hazards to human resulting from their complex heterogeneous mixture of microorganisms, undigested organics and heavy metals.

The most traditional treatment and disposal methods of SS are: agricultural application, landfill and incineration. However, landfill and incineration becomes less acceptable due to land limitations and stringent environmental regulations (Huang et al., 2014). Nowadays, with the advantage of waste utilization, pyrolysis has gained much support in SS treatment. Pyrolysis is a thermochemical conversion process which includes heating SS in an oxygen-deficient atmosphere or in the absence of air, producing non-condensable gas (NCG), bio-oil, and bio-char (Lin et al., 2012). Bio-oil is the most valorized product since it has high heating value and can be used as an alternative liquid fuel.

To obtain the maximum yield and high-quality, bio-oil has been produced under fast pyrolysis, microwave heating pyrolysis, supercritical water pyrolysis and hydrothermal liquefaction, etc. Park et al. (2010) investigated the effect of temperature on the yield and chemical composition by fast pyrolysis of SS in a fluidized bed reactor and a catalyst bed reactor. The bio-oil yield reached a maximum of 42.6 wt.% at 450 °C. Lin et al. (2012) researched microwave heating process for the production of bio-oil from SS. It was found that a higher heating rate can not only increase the yield of bio-oil, but also improved the quality of bio-oil according to the elemental composition and calorific values. The maximum bio-oil yield was 30.4 wt.%, obtained from the pyrolysis of 3.5 kg dried SS at a microwave radiation power of 8.8 kW and final pyrolysis temperature of 500 °C. By using a high pressure batch reaction vessel, Wang et al. (2013) studied the bio-oil production from SS by a supercritical conversion using temperature from 350 to 500 °C and reaction residence time of 0.30–60 min. In supercritical conversion, the maximum bio-oil yield achieved is 39.73 wt.%, which was performed at 375 °C and 0 min.

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http://dx.doi.org/10.1016/j.wasman.2016.10.053
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Supercritical water (SCW) pyrolysis of SS is an attractive approach, due to its tolerance to high moisture content of 85 wt.%. SCW is a state where the pressure and temperature are increased to or over the critical point (22.1 MPa and 374.3 °C). At these conditions, water is neither gas nor liquid, but shares properties from both phases, making it appropriate as a solvent. As a reaction medium, SCW is featured as having a high diffusivity, a low viscosity, and high solvating ability for organic compounds (Acelas et al., 2014; Guo et al., 2015).

Although pyrolysis of SS and reaction processes has been intensively studied, there are very few researches in SCW pyrolysis of SS that were reported. In this work, SS pyrolysis in SCW was studied focusing on the effects of temperature and moisture content on products distribution and bio-oil composition. The characteristics of bio-char and NCG products at the optimal condition were also investigated.

2. Experimental

2.1. Materials

The SS used in this experiment was obtained from Jizhuangzi Wastewater Treatment Plant, Tianjin, China. The SS was mechanically dewatered in the municipal wastewater treatment plant until the moisture content of 85 wt.% was achieved. Table 1 lists the main properties of SS.

The SS sample was placed in a muffle furnace to be dried at 105 °C for 24 h until a constant weight was obtained. Then, the dewatered SS was grinded by a ball grinding mill and then passed through mesh. 90 g of particles size less than 0.45 mm, was dissolved in distilled water in the reactor to simulate different moisture contents of SS.

2.2. Experimental procedure and separation

The experiment was performed in a 316 L stainless steel alloy batch autoclave reactor with an internal volume of 2 L. It was designed for a maximum temperature of 550 °C and maximum pressure of 35 MPa. The experimental system diagram is shown in Fig. 1.

Table 1
Characteristics of SS and bio-char (dry basis).

	SS	Bio-char[a]
Ultimate analysis (wt.%)		
C	40.50	15.62
H	4.51	1.93
O[*]	48.50	81.07
S	1.01	0.34
N	5.48	1.05
H/C	0.11	0.12
HHV (MJ/kg)	13.64	3.86
Proximate analysis (wt.%)		
Moisture	3.59	1.49
Ash	36.25	82.71
Volatile	53.93	11.30
Fixed carbon[*]	6.23	4.50
Organic components analysis (wt.%)		
Protein	26.29	
Oxy-compound	4.03	
Cellulose	14.65	
Semi-cellulose	2.37	
Lignin	5.86	
Aliphatic compound	27.26	

[a] Bio-char: produced at 385 °C, moisture content of 85 wt.%.
[*] Calculated by difference.

The experimental system mainly consist of nitrogen cylinder, high-pressure batch reaction vessel installed with thermo detector and pressure gage, control panel (CP), cooling pipe, condenser and devices for products separation and collection. Firstly, the sample was placed in the high-pressure batch reaction vessel and swept it with high purity nitrogen to remove air. Temperature and residence time of the reaction were controlled by CP. Reaction vessel was heated by an electrical heating socket to a specified temperature (name the temperature) and held for 10 min. The extension of dwell time at final temperature did not led to the considerable increase of bio-oil, especially at the higher final pyrolysis temperature (Lin et al., 2012). With the temperature increasing to the specified temperature (355–505 °C), water evaporated quickly leading to an increase in the final pressure from 17.5 to 27.2 MPa. When the temperature reached state here the temperature the reaction was ran for 10 min, then the heating process was stopped. The reactor was allowed to cool down to the room temperature and pressure. The experiment was repeated three times, and the average results and error bars were calculated as shown in the results section.

The experimental procedure is shown in Fig. 2. 90 g dewatered SS with a certain quantity of water was pyrolyzed in supercritical state. The NCG was sampled and analyzed with GC. The mixed products of liquid and solid phase were then separated through vacuum filtration to obtain the liquid product and bio-char. The liquid product was separated into the organic phase and water by methylene chloride. Finally the bio-oil was extracted by rotary evaporator. The bio-oil was analyzed by a Vario MACRO Cube Elemental analyzer, the thermos-gravimetric analyzer (EXSTAR 6000), microcomputer automatic heat meter (WZR-1T) and GC-MS. The bio-char was analyzed by a Vario MACRO Cube Elemental analyzer, the thermos-gravimetric analyzer (EXSTAR 6000), microcomputer automatic heat meter (WZR-1T), XRF and BET.

The yield distribution of bio-oil, bio-char and NCG were calculated by the following equations:

$$\text{Yield distribution of } bio_{oil}(bio_{char})(wt.\%) = \frac{\text{the total mass of } bio_{oil}(bio_{char}) \text{ product}}{\text{the mass of SS (dry basis) in feedstock}} \times 100\% \quad (1)$$

$$\text{Yield distribution of } bio_{gas}\ (wt.\%) = \frac{\text{the mass of SS (dry basis) in feedstock} - \text{the total mass of } bio_{oil} \text{ and } bio_{char}}{\text{the mass of SS (dry basis) in feedstock}} \times 100\% \quad (2)$$

2.3. Product analysis

The elemental compositions (C, H, N, and S) of SS, bio-oil and bio-char were measured by a Vario MACRO Cube Elemental analyzer. The proximate analysis of SS and bio-char were carried out by the thermos-gravimetric analyzer (EXSTAR 6000). The higher heating value (HHV) of the SS, the bio-oil and the bio-char were executed by microcomputer automatic heat meter (WZR-1T).

The composition of bio-oil was determined using GCMS-QP 2010 plus with an Rtx-5MS (30 × 0.25 mm × 0.25 μm) capillary column. Helium was used as the carrier gas at a flow rate of 2 mL/min. The injection size was 1 μL with a split ratio of 1:30. The oven temperature was initially 50 °C held for 3 min and was then increased to 280 °C at a rate of 6 °C/min, and held at 280 °C for 5 min. The operating conditions were: ion source temperature of 200 °C, ionization energy of 70Ev, the scan per second over mass range electron (m/z = 25–550). Using methanol as dilution solvent and the dilution rate was 1:10. The compounds were identified by comparing their mass spectra with those from the National Institute of Standards and Technology (NIST) mass spectral data library.

Please cite this article in press as: Ma, W., et al. Supercritical water pyrolysis of sewage sludge. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.10.053