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Fast microwave-assisted catalytic pyrolysis of sewage sludge for bio-oil production

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HIGHLIGHTS

- A microwave-assisted system for catalytic pyrolysis of sewage sludge was developed.
- The optimal temperature and catalyst to feed ratio were determined.
- Mineral elements were concentrated in the bio-char after pyrolysis.
- HZSM-5 catalyst had good stability against deactivation during the pyrolysis process.

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ABSTRACT

In this study, fast microwave-assisted catalytic pyrolysis of sewage sludge was investigated for bio-oil production, with HZSM-5 as the catalyst. Pyrolysis temperature and catalyst to feed ratio were examined for their effects on bio-oil yield and composition. Experimental results showed that microwave is an effective heating method for sewage sludge pyrolysis. Temperature has great influence on the pyrolysis process. The maximum bio-oil yield and the lowest proportions of oxygen- and nitrogen-containing compounds in the bio-oil were obtained at 550 °C. The oil yield decreased when catalyst was used, but the proportions of oxygen- and nitrogen-containing compounds were significantly reduced when the catalyst to feed ratio increased from 1:1 to 2:1. Essential mineral elements were concentrated in the bio-char after pyrolysis, which could be used as a soil amendment in place of fertilizer. Results of XRD analyses demonstrated that HZSM-5 catalyst exhibited good stability during the microwave-assisted pyrolysis of sewage sludge.

1. Introduction

Sewage sludge from municipal and industrial wastewater treatment plants is a great issue risking the environment and human health, and has raised growing concern recently (Fytili and Zabaniotou, 2008; Laturnus et al., 2007). Nowadays, the most common methods for treatment and disposal of sewage sludge include landfill, agricultural application and incineration (Fonts et al., 2012). However, they all have drawbacks and have become less acceptable (Houillon and Jolliet, 2005; Rio et al., 2006; Werther and Ogada, 1999). An alternative management technique is pyrolysis which could achieve 50% reduction in waste volume (Inguanzo et al., 2002), the stabilization of organic matter, as well as the production of fuels. Elements such as Na and Mg will be concentrated in the pyrolysis char, which can then be used as the soil amendment or be upgraded to become an adsorbent (Bridle and Pritchard, 2004; Smith et al., 2009). The produced gas and oil can be either directly burned as a fuel to provide heat and electricity, or further converted to other chemicals through subsequent processes (Domínguez et al., 2006; Park et al., 2008).

Fonts et al. (2008) conducted pyrolysis of sewage sludge in a fluidized bed and obtained the maximum liquid yield of about 33 wt.% at the temperature of 540 °C with a solid feed rate of 3.0 g/min and nitrogen flow rate of 4.5 L/min. By using a quartz reactor, Sánchez et al. (2009) examined the effect of temperature increase from 350 to 950 °C on the composition of the oils obtained from sewage sludge pyrolysis and observed an increase in the

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concentration of mono-aromatic hydrocarbons and a strong decrease in the concentration of phenol and its alkyl derivatives. In order to improve the yield and quality of the bio-oil, many researchers used different catalysts in the pyrolysis of sewage sludge. Kim and Parker (2008) investigated the effect of zeolite on the product distribution from pyrolysis of different types of sewage sludges and concluded that zeolite did not improve oil and char yields due to the increased conversion of volatile matter to gas. However, Park et al. (2010) found that metal oxide catalysts (CaO and La_2O_3) contributed to a slight decrease in bio-oil yield but were significantly effective in removal of chlorine from the bio-oil.

Microwave based technology is an alternative heating method and has already been successfully used in biomass pyrolysis for biofuels production (Bu et al., 2012; Du et al., 2011; Wang et al., 2012). Microwave assisted heating has many advantages over conventional processes, which include: (1) Microwave can provide uniform internal heating for material particles since the electromagnetic energy is directly converted into heat at the molecular level (Sobhy and Chaouki, 2010). (2) Microwave heating is easier to control due to its instantaneous response for rapid start-up and shut-down. (3) The set-up of microwave system is simple, which facilitates its adaption to currently available large-scale industrial technologies. (4) It does not require high degree of feedstock grinding and can be used to handle large chuck of feedstock. (5) Microwave heating is a mature technology and the development of microwave heating system is of low cost. Despite many advantages of microwave heating over conventional heating methods and some progress made in biomass pyrolysis, only a few studies have been conducted on sewage sludge pyrolysis using microwave technology and the effects of catalyst on the pyrolysis process were not examined in their research (Domínguez et al., 2006; Menéndez et al., 2002).

In this study, microwave-assisted catalytic pyrolysis of sewage sludge was carried out with HZSM-5 as the catalyst for bio-oil production under different conditions. The effects of pyrolysis temperature and catalyst to feed ratio were investigated on product distribution and bio-oil composition. X-ray Diffraction (XRD) analyses of catalyst before and after reaction were conducted to examine its stability during pyrolysis process. In addition, characterization of bio-char was conducted using elemental analysis and ICP-OES multi-element determination.

2. Methods

2.1. Materials and catalysts

The sewage sludge used as the raw material for this study was obtained from the Metropolitan Wastewater Treatment Plant, Saint Paul, Minnesota. The sewage sludge was a mixture of primary and secondary sludge. The basic physico-chemical characteristics of the sewage sludge including proximate analysis, elemental analysis and mineral elements determination are shown in Table 1. According to the elemental analysis, the simplified chemical formula of the raw material that derives is $CH_{1.67}N_{0.10}O_{0.47}$. The higher heating value (HHV) observed for sewage sludge is similar to that of other conventional and non-conventional fuels such as paper, wood, black liquor or low rank coal (Perry, 1984). It is reported that the presence of inorganic matter can influence the thermal decomposition process (Mohan et al., 2006; Oasmaa et al., 2010; Richards and Zheng, 1991). It can be seen from Table 1 that there are considerable amounts of P, Ca and K in the sewage sludge, whereas other metals such as Co, Ni, Cu and Zn are in lower proportions. Prior to use, the sewage sludge samples were ground using a rotary cutting mill and then screened to limit the particle size smaller than 2 mm. These ground samples were then dried for 72 h at 80 ± 1 °C.

A commercial zeolite, namely ZSM-5 (Si/Al = 30, surface area = 405 m^2/g), in the ammonium form purchased from Zeolyst International (Conshohocken, PA) was used as the catalyst in the present study. Prior to use, the catalyst was calcined at 550 °C in air for 5 h to its active hydrogen form HZSM-5.

2.2. Apparatus

The tests of catalytic pyrolysis of sewage sludge were performed in a microwave oven (MAX, CEM Corporation), with the power of 750 W at a frequency of 2450 MHz. The schematic diagram of experimental apparatus is shown in Fig. 1. The system is composed of: (1) biomass feeder; (2) inlet quartz connector; (3) microwave oven; (4) quartz reactor; (5) microwave absorbent bed; (6) thermocouple (K-type) to measure the temperature of cavity; (7) thermocouple (K-type) to measure the temperature of bed particles; (8) outlet quartz connectors; (9) liquid fraction collectors; (10) condensers; (11) connection for vacuum pump. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage.

In this study, SiC particles with particle size of 30-grit were used as the microwave adsorbent bed, whose temperature could be increased very quickly with the microwave absorbed. Five hundred grams of SiC particles were first put in a quartz reactor, which was then placed in the cavity of the microwave oven. In order to maintain an inert atmosphere within the quartz reactor during pyrolysis, the system was vacuumed at 170 mm Hg for 10 min prior to the commencement of the microwave heating, with the vacuum being maintained during the entire heating process. The microwave oven was then turned on for heating process. For each experiment, the sample was prepared by physically mixing 15 g sewage

Table 1
Characteristics of sewage sludge.

Proximate analysis (wt.%)				Elemental analysis[a,b] (wt.%)				HHV[d] (MJ/kg)		NHV[e] (MJ/kg)
M	A[a]	V[a]	FC[a,c]	C	H	N	O[c]			
4.53	15.01	68.57	16.42	53.24	7.39	6.12	33.25	24.42		21.77
Mineral elements[a] (mg/L)										
Al	As	B	Be	Ca	Cd	Co	Cr	Cu	Fe	K
4188.5	6.2	22.4	0.36	20737.2	0.96	3.8	44.9	315.4	5108.5	6298.6
Li	P	Mg	Mn	Mo	Na	Ni	Pb	Ti	V	Zn
2.2	25641.3	5526.4	1153.0	5.0	1161.8	30.8	32.3	111.2	2.0	596.0

M: moisture content; A: ash content; V: volatile matter content; FC: fixed carbon.
[a] Dry basis.
[b] Ash free basis.
[c] Calculated by difference, FC (%) = 100 − A − V, O (%) = 100 − C − H – N.
[d] Higher heating value, calculated using the equation (Vallios et al., 2009) HHV (MJ/kg) = 34.1 C + 123.9 H − 9.85 O + 6.3 N + 19.1 S.
[e] Net heating value, calculated using the equation (Vallios et al., 2009) NHV (MJ/kg) = (HHV − 21.92 H) (1 − MCWB/100) − 0.02452 MCWB, where MCWB is the moisture content on a wet basis of biomass.