Ex-situ catalytic pyrolysis of wastewater sewage sludge – A micro-pyrolysis study

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H I G H L I G H T S

- *Ex-situ* catalytic pyrolysis of sewage sludge with HZSM-5 was investigated.
- Full recovery of most inorganic elements in sludge were found in the char.
- Formation of NH_3 suggests potential of nitrogen recycle from catalytic pyrolysis.

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A B S T R A C T

Concerns over increasing amounts of sewage sludge and unsustainability of current disposal methods have led to development of alternative routes for sludge management. The large amount of organics in sewage sludge makes it potential feedstock for energy or fuel production via thermochemical pathways. In this study, *ex-situ* catalytic pyrolysis using HZSM-5 catalyst was explored for the production of olefinic and aromatic hydrocarbons and nutrient-rich char from sewage sludge. The optimal pyrolysis and catalysis temperatures were found to be 500 °C and 600 °C, respectively. Carbon yields of hydrocarbons from sewage sludge were higher than for lignocellulose; yield differences were attributed to the high extractives content in the sludge. Full recovery of most inorganic elements were found in the char, which suggests that catalyst deactivation maybe alleviated through *ex-situ* catalytic pyrolysis. Most of the nitrogen was retained in the char while 31.80% was released as ammonia, which suggests a potential for nitrogen recycling.

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1. Introduction

Sewage sludge is an inevitable waste derived from municipal wastewater treatment facilities. On the basis of demographic projections and improving living standards, the amount of sewage sludge is expected to continue increasing worldwide (Fonts et al., 2012; Kinney et al., 2008). Inappropriate management of sewage sludge has several negative environmental and economic impacts (Manara and Zabaniotou, 2012). Sewage sludge is primarily organic material, although also containing significant inorganic materials, some of which have potential value as agricultural nutrients (Fonts et al., 2012; Manara and Zabaniotou, 2012). To date, sewage sludge has been largely used as fertilizer for land application (Fonts et al., 2012). Unfortunately, sewage sludge also contains potentially hazardous materials including heavy metals, patho-

gens, and organic pollutants, which make agricultural applications controversial (Fonts et al., 2012; Manara and Zabaniotou, 2012; Samolada and Zabaniotou, 2014; Velghe et al., 2013). Disposal by landfill is another route for sewage sludge management, however, rising processing costs and diminishing land resources limit this option (Fonts et al., 2012). Alternatives that are sustainable and economically favorable are of great interest.

Thermochemical processing technologies, including combustion, gasification, and pyrolysis, have been investigated for energy-recovery alternatives to current sewage sludge disposal routes (Fonts et al., 2012; Manara and Zabaniotou, 2012). Among thermochemical technologies, pyrolysis is attractive for its potential to produce liquid biofuel and nutrient-rich biochar for soil application (Chen et al., 2015; Fonts et al., 2012; Manara and Zabaniotou, 2012; Méndez et al., 2013; Samolada and Zabaniotou, 2014). Pyrolysis studies have been conducted on various types of reactors using both raw and digested sludge (Manara and Zabaniotou, 2012; Velghe et al., 2013). High contents of oxy-

gen, nitrogen, and even sulfur have typically been reported for sewage sludge-derived bio-oil (Fonts et al., 2012), which must be removed from the final product if it is to serve as transportation fuel.

Recently, considerable effort has been devoted to catalytic pyrolysis, in which pyrolysis vapors are upgraded over catalysts to improve bio-oil quality (Du et al., 2016; French and Czernik, 2010; Wang et al., 2016; Zhang et al., 2014; Zheng et al., 2016). Previous studies with lignocellulosic biomass have shown that HZSM-5 catalysts outperformed others due to their ability to produce value-added aromatics and olefins (Carlson et al., 2011; Cheng et al., 2012). Based on the configuration of feedstock and catalyst, catalytic pyrolysis can be classified as either *in-situ* and *ex-situ* (Gamliel et al., 2015; Iisa et al., 2016; Luo and Resende, 2016). *In-situ* catalytic pyrolysis is a one-pot process: pyrolysis and catalysis occur in the same reactor. For *ex-situ* catalytic pyrolysis, catalytic upgrading of pyrolysis vapors occurs in a separate reactor downstream of the pyrolysis reactor.

Only a limited number of studies have explored catalytic pyrolysis for sewage sludge management and those studies used *in-situ* processes. Park et al. (2010) conducted *in-situ* catalytic pyrolysis of sewage sludge using CaO and La$_2$O$_3$ as catalysts in a fluidized bed reactor. They reported that the presence of catalyst reduced yield of organic liquid compared to fast pyrolysis. However, the composition of the liquid and gaseous products was not detailed (Park et al., 2010). Another study claimed zeolites enhanced yield of non-condensable gases from sludge while the yield of bio-oil was unaffected by changes in the sludge-to-zeolite ratio (Kim and Parker, 2008). Shao et al. (2010) used a thermogravimetric analyzer to develop reaction kinetics for sewage sludge conversion in the presence of metal oxide catalysts, which accelerated the decomposition process. A study on microwave-assisted catalytic pyrolysis of sewage sludge reported reductions in oxygen and nitrogen heteroatoms in the bio-oil in the presence of zeolite catalyst (Xie et al., 2014). More recently, Liu et al. (2016) reported enhanced production of aromatics and olefins from acid-pretreated sewage sludge in a micro-pyrolyzer.

In this study, *ex-situ* catalytic pyrolysis of sewage sludge with HZSM-5 catalyst was explored with aim of producing higher-value chemicals, specifically olefins and aromatics, and nutrient-rich biochar. The advantages of *ex-situ* pyrolysis include: independent control of pyrolysis and catalysis reaction conditions, and minimization of catalysts deactivation by inorganic materials from the feedstock (Mullen and Boateng, 2013). Study parameters targeted the effects of pyrolysis temperature and catalysis temperature on product distribution. The transformation of inorganic elements in the sewage sludge during catalytic pyrolysis was also studied.

2. Materials and methods

2.1. Materials

Digested sewage sludge was collected from a local waste water treatment plant (Ames, IA, USA). Sewage sludge paste, with over 90% moisture content, was dried in an oven at 105 °C for 48 h. The oven-dried material was ground and sieved to less than 200 mesh (<75 μm) prior to experiments. It is noteworthy that raw sewage sludge contains a significant amount of water which much be removed to make the sludge suitable for catalytic fast pyrolysis. Developing energy-efficient and cost-effective dewatering and drying processes will be critical to the commercialization of sewage sludge management via a pyrolysis pathway. Extractives in the sewage sludge were measured using the Soxhlet extraction method (Manirakiza et al., 2001). Protein content was approxi-

mated by multiplying elemental N concentrations by a factor of 6.25. Commercial ZSM-5 catalyst (CBV2314 with SiO$_2$/Al$_2$O$_3$ ratio of 23, Zeolyst, USA) was calcined in a muffle furnace at 600 °C for 5 h. Calcined catalyst was pelletized and sieved to 50–70 mesh (212–300 μm) size before catalysis experiments.

2.2. Catalytic pyrolysis and products characterization

Catalytic pyrolysis experiments were conducted in a tandem micro-reactor system (Rx-3050 TR, Frontier Laboratories, Japan) as illustrated in Fig. 1. Helium (90 ml/min) was used as the carrier gas to sweep the vapor products into a 7890A gas chromatograph (GC) (Agilent Technologies, USA) for analysis. Approximately 0.5 mg of feedstock was placed into a deactivated stainless steel sample cup, which was then dropped into the preheated pyrolysis reactor. Pyrolysis vapors were transported through a downstream catalyst bed that was packed with 10 mg of the prepared HZSM-5 catalyst. Final products, including non-condensable gases and condensable vapors, were qualitatively analyzed by a mass spectrometer detector (MSD), and quantitatively analyzed by a thermal conductivity detector (TCD) and a flame ionization detector (FID). A detailed description of the system and GC settings can be found in a previous paper (Wang et al., 2014).

Micropyrolysis experiments were also conducted without the GC for the purpose of analyzing ammonia (NH$_3$), hydrogen cyanide (HCN), and biochar. For the NH$_3$ test, pyrolysis vapors were vented into a solution of hydrochloric acid (100 mmol L^{-1}, 20 ml) to convert NH$_3$ into ammonium ion (NH$_4^+$). The concentration of NH$_4^+$ was analyzed using an ammonium ion selective electrode (Fisher Scientific, USA). HCN was collected in a sodium hydroxide solution and CN$^-$ content was quantitatively analyzed using ion chromatography (IC; Dionex, USA) with an IonPac AS15 column (Dionex, USA). The thermally-derived solid product collected in the pyrolysis reactor was designated as char. The mass yield of char was calculated by the weight change of the sample recorded by a microbalance. Coke was defined as the carbonaceous material deposited on the zeolite catalyst in the catalytic reactor. Carbon in the char and coke were quantified by combustion analysis in an elemental analyzer (Vario MICRO cube, Elementar, USA). Ultimate analysis of the feedstock was also conducted using the elemental analyzer. Oxygen content was calculated by difference. Proximate analysis was performed using a thermogravimetric analyzer (TGA; Mettler, Toledo, USA) (Ottaway, 1982).
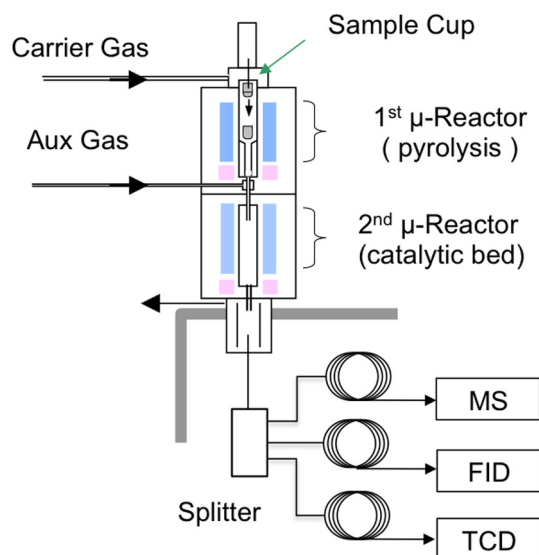

Fig. 1. Schematic of a tandem micro-reactor system used in this study.