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Polycyclic aromatic hydrocarbon formation during the gasification of sewage sludge in sub- and supercritical water: Effect of reaction parameters and reaction pathways

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ABSTRACT

The formation of polycyclic aromatic hydrocarbon is a widespread issue during the supercritical water gasification of sewage sludge, which directly reduces the gasification efficiency and restricts the technology practical application. The changes of the concentrations and forms as well as the synthesis rate of polycyclic aromatic hydrocarbons in the residues from supercritical water gasification of dewatered sewage sludge were investigated to understand influence factors and the reaction pathways. Results showed that the increase of reaction temperature during the heating period favours directly concentration of polycyclic aromatic hydrocarbon (especially higher-molecular-weight), especially when it raise above 300 °C. Lower heating and cooling rate essentially extend the total reaction time. Higher polycyclic aromatic hydrocarbon concentration and higher number of rings were generally promoted by lower heating and cooling rate, longer reaction time and higher reaction temperature. The lower-molecular-weight polycyclic aromatic hydrocarbons can be directly generated through the decomposition of aromatic-containing compounds in sewage sludge, as well as 3-ring and 4-ring polycyclic aromatic hydrocarbons can be formed by aromatization of steroids. Possible mechanisms of reaction pathways of supercritical water gasification of sewage sludge were also proposed.

1. Introduction

Sewage sludge is the end-product of the wastewater treatment process, which is especially produced increasingly every year in China. Total sewage sludge production had an average annual growth of 13% from 2007 to 2016, and 7.34 million tons dry solids were produced in 2016. More than 80% of sewage sludge are disposed by improper dumping, which raised significant concerns in China (Yang et al., 2015). Dewatered sewage sludge (DSS) has higher organic matter (OM) content, accounting for approximately 50% on a dry basis, has high potential value for bio-energy use. Therefore, the utilization of DSS has been a continuous hot research topic among scholars in recent years (He et al., 2014; Methling et al., 2014; Qian et al., 2015; Rulkens, 2007). Supercritical water gasification (SCWG) of sewage sludge is considered as an economically and environmentally promising technology, which can transform the OM in sewage sludge into clean energy source like hydrogen without expensive pre-drying (Guo et al., 2015; He et al., 2014; Qian et al., 2016). However, except potential OM, sewage sludge also contains a variety of organic pollutants, such as halogenated hydrocarbons and aromatic compounds (Hua et al., 2008; Zeng et al., 2014; Zhang et al., 2014). Thus, the environmental safety of the gasified products needs be clarified.

However, in our previous studies, phenols, polycyclic aromatic hydrocarbons (PAHs) and other undesired organic pollutants were found during the SCWG of DSS (Gong et al., 2014a; Xu et al., 2013). Similar results were also revealed by other researchers. Zhang et al. (2010) treated secondary pulp/paper-mill sludge and sewage sludge in supercritical water (SCW) and detected a lot of phenols and 2-ring PAHs produced in the heavy oil products. Mo et al. (2015) investigated the reactions of saturated and unsaturated fatty acids in supercritical water over the zeolite catalyst, and found that high yields of single-ring aromatics (toluene and xylenes) were generated in the liquid products (up to 42 wt%). Qian et al. (2015) treated sewage sludge in SCW and detected high

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proportion of refractory intermediates such as phenols and pyridines in the liquid products. Brown et al. (2010) converted microalgae into biocrude products via hydrothermal processing, results showed that PAHs and their alkylated derivatives were found in all bio-oils at 300 °C and above, and turned to be the dominant species in the bio-oils at 500 °C. Similarly, Guan et al. (2012) analyzed the intermediates in liquid products from SCWG of the algae, and found benzenes, phenols and indoles has produced at longer reaction times (30 min). Besides, the benzenes and phenols also considered as precursor molecules of PAHs and char, which is more refractory and higher toxicity (Huelsman and Savage, 2012). Thus, the formation of persistent organic pollutants is a widespread issue during the SCWG of biomass, especially of waste biomass which self-contained organic pollutants. In order to address this issue, these problems are the driving force of the deep investigation to understand the influence factors of the organic pollutants' formation and reaction pathways during the SCWG of sewage sludge, here PAHs were used as a typical representative of persistent organic pollutants.

To our knowledge, very less research focus on the formation of PAHs during the SCWG reaction process, and heating periods during SCWG were very similar in pyrolysis. Therefore, the mechanism of PAHs generation during the pyrolysis process were referred to explain the formation of PAHs in SCWG process in our previous study (Xu et al., 2013). Diels–Alder reaction, which is a cycloaddition reaction between dienes and alkenes to form a cyclohexene, is widely accepted as the explanation for the PAHs formation. Then formed monocyclic aromatic hydrocarbons can go through hydrogen abstraction acetylene addition (HACA) reaction route to increase the number of rings and produced high-ringed PAHs (Richter and Howard, 2000; Zhou et al., 2015). In addition, some researchers have proposed another PAHs formation mechanism based on the free radicals (Comandini et al., 2012; Guo et al., 2013; Ledesma et al., 2005). Benzyl radicals can add to benzene to form diphenylmethane and then further react to form fluorene (3-ring PAH), the recombination of two benzyl radicals lead to bibenzyl and then to form phenanthrene (4-ring PAH). Also naphthalene can react with cyclopentadienyl radical to form phenanthrene and chrysene (Xu et al., 2013). Meanwhile, the reaction parameters such as reaction temperature and time had effects on the formation of PAHs (Ledesma et al., 2005; Xu et al., 2013). Higher reaction temperature and longer reaction time could promote the production of PAHs. Kruse also pointed out that Diels–Alder reaction typically enhanced by increased pressure (Kruse and Dinjus, 2007).

Current researchers mainly concerned the optimal of hydrogen production, and lack of attention has raised on the formation of persistent organic pollutants during the SCWG of biomass. Although more and more researchers have reported that the presence of organic pollutants synthesized in the SCWG of biomass, but still lacks of systematically study. In this study, the changes of the PAH concentrations and forms in the residues from the SCWG of DSS during the heating period were firstly investigated. The effects of heating rate (3–20 °C/min), cooling rate (18–50 °C/min), resistance time (0–120 min) and reaction temperature (400–500 °C) on changes in the PAH concentrations and forms, as well as the PAHs synthesis rate were examined. Based on the GC/MS qualitative analysis of solid residues during the heating period, the proposed reaction pathways of SCWG of sewage sludge were also discussed.

All the experiment carries out in this study were based on laboratory-scale batch reactor and were used as scientific theoretical studies. The SCWG of sewage sludge is indeed a great gap from industrial applications. There are many issues need to be addressed before the practical application. The main concerned problem for this study is one of them. Currently, there are practical examples of pilot plant scale application in supercritical water oxidation/-gasification of sewage sludge (Boukis et al., 2017; Guo et al., 2015; Xu et al., 2012a; Yan, 2017). This indicated that the high-temperature and high-pressure reactor manufacturing technology is feasible, also shows that the SCWG technology is expected to achieve further industrial applications. The SCWG of sewage sludge focuses on the treatment and disposal of sludge, to achieve some resource utilization on the other hand. For hazardous waste sewage sludge, SCWG technology may well be competitive due to the revenues associated with the disposal of sewage sludge as a waste product and by disinterring byproduct utilization value (Gasafi et al., 2008; Xu et al., 2012a). We believe that SCWG will be more favorable to deal with hazardous waste like sewage sludge as environment protection requirements become much stricter day by day.

2. Materials and methods

2.1. Materials

The sewage sludge produced in the Jianxinzhou sewage treatment plant located in Nanjing, China was dewatered by filter press and then collected as original material and stored in the preservation box of a refrigerator at a temperature below 4 °C. The properties of the sludge are displayed in Table 1. The moisture content of sludge on an air-dried basis was 77.05 wt%, and the sample contained 27.84 wt% volatile matter and a relatively high ash content. The sample also contained some heavy metals, such as iron, zinc, and copper. The content and composition of the 16 US EPA priority controlled PAHs are also shown in Table 1. The total PAHs concentration of raw sludge is 7.24 μg/g and was dominated by 3-ring and 4-ring PAHs.

2.2. Experimental apparatus and procedure

The SCWG of DSS was performed in a 316L stainless steel batch reactor obtained from the Songling Chemical Instrument Co., Yantai, Shandong, China. The schematic of the reactor has been described in detail previously (Gong et al., 2014a). Our experimental records showed that the reactor pressure was above 22.1 MPa at 400 °C with 33 mL of water in the reactor. Therefore, the mass of DSS added into the reactor was calculated from the required water volume (i.e., 33 mL) divided the moisture content of the DSS.

In a typical experiment, 43 g of wet sewage sludge was placed in the reactor, which was then sealed and placed in a salt-bath furnace kept at 400 °C. When the pre-set temperature (400 °C) was reached, it was maintained for a pre-determined residence time (60 min). After that, the reactor was moved from the salt-bath and rapidly cooled to room temperature by water and fans. After cooling, the procedures for sample collection and separation were described in detail in a previous paper (Xu et al., 2012b).

In addition, in order to investigate the changes of PAH concentrations and forms in the liquid and solid residues during the heating period, the heating period was divided into five temperature stages. Namely, 200, 275, 325, 375, and 400 °C, as shown in Fig. 1. When the pre-set temperature was reached the reactor was then immediately removed from the salt-bath furnace, and the residence time is 0 min. The different cooling rate was controlled by using different cooling ways, from slow to fast by nature cooling, cooled by fans, cooled by water, cooled by water and fans, respectively.

2.3. Product analysis

The methods of extraction, concentration, and purification of PAHs have been described in detail previously (Gong et al., 2016;