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Effects of inorganic and organic acid pretreatments on the hydrothermal liquefaction of municipal secondary sludge

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ABSTRACT

In this study, the effects of inorganic (HCl, HNO_3 and H_2SO_4) and organic (HCOOH, CH_3COOH and HOOCCOOH) acid pretreatments on the hydrothermal liquefaction (HTL) of municipal secondary sludge (MSS) were investigated. The results showed that all acid pretreatments could increase bio-oil yield by changing the proportion of organic matters and ash content in feedstock and thus facilitating the conversion of water soluble product to bio-oil. A maximum bio-oil yield of 26.75 wt% was obtained from the HCl pretreatment which increased 7.5 wt% compared to the blank experiment. Moreover, the inorganic acid pretreatments showed a better performance in terms of enhancing bio-oil quality as their higher heating values (HHVs, 31.83–36.04 MJ/kg) were much higher than that from organic acid pretreatments (24.57–29.22 MJ/kg). The characterization analysis of bio-oil indicated that the HCl pretreatment was most beneficial for the formation of light fraction and increment of hydrocarbon.

1. Introduction

Sewage sludge, as a by-product from municipal wastewater treatment, has become an inevitable environmental risk when taking into account its high toxicity, extensive sources and enormous amount [1]. However, sewage sludge contains massive organic matters such as protein, lipid, carbohydrate, lignin, cellulose and hemicellulose, so it is also considered as a potential biomass that can be transformed into high-quality bio-oil for replacing traditional fuels [2–4]. Recently, to realize harmlessness, reduction, and resource utilization for sewage sludge, a number of researches have been carried out [5,6]. In particular, thermochemical processes including gasification, pyrolysis, hydrothermal liquefaction (HTL), hydrogenation, and direct combustion attracted wide attention due to shorter reaction time and cleaner process compared to traditional sludge utilization methods [3,7,8]. Among them, HTL seems to be an attractive option for sewage sludge as it eliminates dewatering step that demands high-energy consumption [9].

HTL is a process where organic compounds in sludge can be converted into bio-oil, gas, solid residue and water soluble product at higher temperatures (250–374 °C) and pressures (4–22 MPa) [10]. The obtained bio-oil has the potential to become alternative fuel due to its high HHVs of 30–40 MJ/kg. So far, several operating parameters such as reaction temperature, residence time, and water content have been explored during the HTL of sewage sludge to enhance the bio-oil yield and quality [11]. Wang et al. investigated the liquefaction of sewage sludge at a temperature of 350–500 °C and residence time of 0–60 min and found that the highest bio-oil yield of 39.73% was obtained at 375 °C and 0 min [12]. Zhang et al. studied the effect of reaction temperature (400–550 °C) and residence time (20–120 min) on the liquefaction of secondary pulp/paper-mill sludge (SPP) and sewage sludge [9]. The results showed that lower temperature and short residence time were helpful for the formation of heavy oil. It turned out that adjusting these reaction conditions caused a positive effect on the reaction process leading to higher bio-oil yield or better quality [13]. However, results were not always economic which sometimes required a severe reaction environment and consume expensive catalysts [14]. Thus, another approach – biomass pretreatment – was suggested as alternative to reduce the severity of reaction conditions and promote the reaction efficiency [15]. For example, Shi et al. liquefied rice husk via ultrasonic pretreatment in subcritical water and found that the structures of rice husk were remarkably changed and the bio-oil yield increased [16]. Hu et al. reported that a pre-cooled NaOH/urea solution which applied in microalgae HTL could result in better quality of bio-oil with denitrification and deoxidization effects [17]. Kapusta

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investigated the effect of ultrasound pretreatment on the HTL of municipal sewage sludge and found it was beneficial for the bio-oil production at different temperatures, which a maximum increase of 19 wt % was achieved at 320 °C [18]. From the respective of mechanism, the pretreatments could change the physical and chemical structures of biomass and break down cell wall efficiently so that exert a positive effect on liquefaction behavior.

Previous studies showed that sewage sludge contained various metal elements (i.e. Na, K, Mg, Ca, Mn, Fe, Cr, Ni, Cu, Zn, Cd and Pb) at different levels [4,19], and the bio-oil yield are relatively low compared to other biomass [20]. Moreover, the shift of trace amount of heavy metals from ash into bio-oil lowered the quality of bio-oil and caused a hindrance to subsequent refining [2]. To solve these two problems, the acid pretreatment might be a fit. On the one hand, the acid pretreatment can dissolve those alkali metals in sewage sludge and improve organic matter contents, resulting in higher bio-oil yields. On the other hand, it prevents metals from transferring into bio-oil phase and obviously improves bio-oil quality.

In this study, three inorganic acids (HCl, HNO_3, and H_2SO_4) and three organic acids (HCOOH, CH_3COOH, and HOOCCOOH) were adopted to pretreat municipal secondary sludge (MSS). All pretreated samples were converted into bio-oil via HTL process at 300 °C for 30 min. The effects of the acid pretreatments on the ash content of municipal secondary sludge, the yield, and quality of bio-oil were investigated. The characterization of bio-oils was analyzed by elemental analysis, Gas Chromatography-Mass Spectrometry (GC–MS), Fourier Transform Infrared (FT-IR), and Thermo-gravimetric analysis (TGA). This work might be helpful for developing an efficient pretreatment method to HTL of sludge.

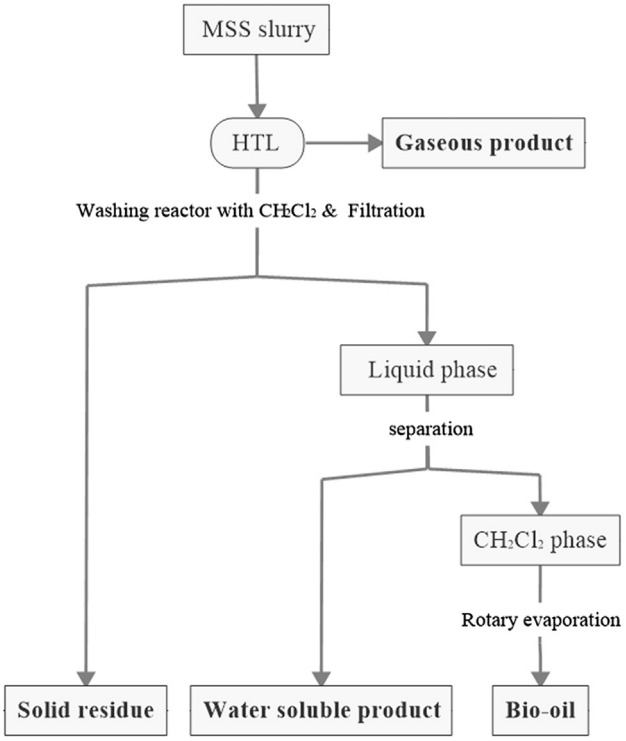

Fig. 1. Schematic of hydrothermal liquefaction and separation procedure.

2. Materials and methods

2.1. Materials

The raw material used in this study was municipal secondary sludge obtained from Qinghe wastewater treatment plant, located in Haidian District, Beijing, China. In order to remove the contained water, the MSS was dried in an oven at 105 °C for 24 h. After dehydration, the dried MSS was ground in a ball mill and then sieved into fraction of particle diameter below 80 meshes. The results of proximate and ultimate analysis of un-pretreated MSS were given in Table 1. All chemical reagents were purchased from Beijing Chemical Works in analytical reagent grade and directly used as received.

2.2. Acid pretreatment

Prior to the acid pretreatment of MSS, the concentration of the HCl, HNO_3, HCOOH and CH_3COOH solutions was prepared to 0.6 mol/L while that of H_2SO_4 and HOOCCOOH to 0.3 mol/L. The MSS powder (60 g) was evenly divided into three parts and added into three same triangle flasks (500 mL) and mixed with acid solution (200 mL) in the ratio of 1:10. Then, three triangle flakes were placed together in a constant temperature water bath oscillator to keep at 25 °C. After oscillating 2 h, the slurry was poured out, filtered using a Büchner funnel, and rinsed with deionized water until its pH reached neutral. Finally, the pretreated MSS was scraped down to a glass dish and placed in an oven at 105 °C for 12 h to remove water. The dried pretreated MSS was used as a raw material for HTL.

2.3. Hydrothermal liquefaction and separation procedure

Liquefaction processes were conducted using a 1 L reactor made of stainless 316 steel, which the maximum temperature and pressure are 400 °C and 20 MPa, respectively. The process and separation procedure was presented in Fig. 1. In each run, 20 g of MSS powder and 160 mL of deionized water were loaded into the reactor and sealed. Then the reactor was purged with nitrogen to remove the residue air. Finally, the reactor was heated to a designed temperature (300 °C) and then maintained for 30 min. The maximum pressure could achieve up to 8.5 MPa. All the experiments were carried out with a magnetic stirrer at 200 rpm.

Upon the completion of the reaction, the reactor was rapidly cooled down to ambient temperature through the internal circulating water.

Table 1
Proximate and ultimate analysis of un-pretreated MSS.

Proximate analysis (wt%)[a]		Ultimate analysis (wt%)[a]					HHV (MJ/kg)
Organic matter	Ash	C	H	N	S	O[b]	
53.52	46.48	44.69	7.55	7.12	1.01	39.63	21.33

Content of inorganic elements in the ash (wt%)															
Na	Mg	Al	Si	P	K	Ca	Ti	Cr	Mn	Fe	Ni	Zn	Rb	Sr	Ba
0.46	1.55	14.05	14.09	6.49	1.69	5.43	0.51	0.04	0.12	5.66	0.016	0.27	0.004	0.13	0.14

[a] On the dry basis.
[b] O = 100 − (C + H + N + S).