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Characterization of herb residue and high ash-containing paper sludge blends from fixed bed pyrolysis

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ABSTRACT

High ash-containing paper sludge which is rich in various metal oxides is employed in herb residue pyrolysis to enhance the yield of fuel gas and reduce tar yield in a drop tube fixed bed reactor. Effects of heat treatment temperature and blending ratio of paper sludge on the yields and composition of pyrolysis products (gas, tar and char) were investigated. Results indicate that paper sludge shows a significantly catalytic effect during the pyrolysis processes of herb residue, accelerating the pyrolysis reactions. The catalytic effect resulted in an increase in gas yield but a decrease in tar yield. The catalytic effect degree is affected by the paper sludge proportions, and the strongest catalytic effect of paper sludge is noted at its blending ratio of 50%. At temperature lower than 900 °C, the catalytic effect of paper sludge in the pyrolysis of herb residue promotes the formation of H_2 and CO_2, inhibits the formation of CH_4, but shows slight influence on the formations of CO, while the formation of the four gas components was all promoted at 900 °C. SEM results of residue char show that ash particles from paper sludge adhere to the surface of the herb residue char after pyrolysis, which may promote the pyrolysis process of herb residue for more gas releasing. FT-IR results indicate that most functional groups disappear after pyrolysis. The addition of paper sludge promotes deoxidisation and aromatization reactions of hetero atoms tars, forming heavier polycyclic aromatic hydrocarbons and leading to tar yield decrease.

1. Introduction

China is the largest producer and consumer of herbal medicine in the world. After the extraction of medical ingredients from natural plants, more than 15 million tons of solid waste, named Herb Residue (HR), is produced annually by over 1500 pharmaceutical companies (Wang et al., 2010; Guo et al., 2013). The traditional way of HR treatment mainly relies on the direct landfill which causes serious contamination to the environment and groundwater, and pungent gas is also generated because of the drug residue. However, HR represents a kind of concentrated industrial biomass resource and direct landfill of HR is a waste of resource (Guo et al., 2014). The reuse and recycling of this value-added biomass resource in a clean and efficient way is of great necessary. Paper Sludge (PS) is one of the main by-products from papermaking industry. It generally contains water, fiber, organic compound, inorganic salt and inorganic filler (Maschio et al., 2009). PS generally has high content of ash which contains high amounts of Ca, Mg, Na, Al and other metals. PS also requires the development of new and alternative valorization technologies due to the risks for health and environment associated with the current disposal methods, such as agricultural reuse or landfill (Samolada and Zabaniotou, 2014; Lou et al., 2012; Ridout et al., 2015).

In this scenario, thermochemical processes for energy recovery, such as pyrolysis or gasification, attract wide attention, as the products can be used as bio-fuels or source of chemicals. In addition, these processes would help to meet the current requirements for replacing fossil fuels by renewable and alternative raw materials. The gasification characteristics of HR were investigated by Guo et al. (2014) in a pilot-scale circulating fluidized bed, and the calorific value of the product gas exceeded 4.0 MJ/N·m^3 using air as gasification agent. Using similar herb residue as raw material, a two-stage gasification process was conducted by Zeng et al. (2016) on an externally heated laboratory two-stage gasification setup and an industrial demonstration plant, finding that the produced fuel gas had a higher heating value of around 5.0 MJ/Nm^3 with tar content as low as 400 mg/Nm^3. Herb residue, from a pharmaceutical factory in Tianjin, was investigated by Wang et al. (2010) in a fixed-bed to produce bio-oil through pyrolysis. They found that the catalytic treatment provided enhancement in the production of target components. Based upon these results, herb residue can be converted into combustible gas or bio-oil through pyrolysis or gasification, while the quality of the product need to

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Nomenclature

HR	herb residue
PS	paper sludge
TG	thermal gravity
DTG	differential thermal gravity
m/z	mass-to-charge ratio
Y_{Char}	the yield of char, mg/g
Y_{Tar}	the yield of tar, mg/g
Y_{Gas}	the volume yield of gas, ml/g
M_{Char}	the mass of dry char, g
M_{Tar}	the mass of tar, g
M_F	the mass of dry feed, g
Y_H	the individual yield of herb residue
Y_P	the individual yield of paper sludge
Y_{Cal}	the calculation values of the product yields
υ_P	the mass ratio of paper sludge, %

be improved for better industrial application. Toward this problem, catalytic treatment is the most effective method at present in the production of these products, and effective and low-cost catalysts are required.

Thermochemical methods are seen as promising alternatives for sludge disposal as well and researches also have been conducted on its conversion into char, gas and oil via pyrolysis/gasification for energy and material utilization (Jayaraman and Gökalp, 2015). Experimental gasification tests of sewage sludge were carried out by Freda et al. (2018) in a bench scale rotary kiln, showing that gasification of sewage sludge is a feasible process as it produces a relatively clean raw gas. The properties of recycled paper sludge during pyrolysis were investigated by Strezov and Evans (2009), finding that the bio-gas compounds produced at 500 °C contained 24% of the sludge weight and had calorific value only slightly higher than the energy required to pyrolyse. Morgano et al. (2018) reported that sewage sludge can be used as material to produce particle-free vapors and gases in a screw reactor and the metals and the other minerals were completely retained in the char. However, compared with the other solid fuels, the single pyrolysis of sludge can hardly produce high quality fuels due to high moisture and ash contents (Shao et al., 2007).

Co-pyrolysis of sludge and another biomass feedstock could provide several advantages, such as enhanced reaction performance and increased calorific values of biochar (Manara and Zabaniotou, 2012). Thomsen et al. (2017) gasified straw and/or municipal sewage sludge using a low temperature circulating fluidized bed. Mixing municipal sewage sludge with straw was found to be an effective way to reduce the accumulation rate of large amounts of inorganic material from the fuel in the bed. Huang et al. (2015) observed that the addition of rice straw increased the performance of microwave heating during the co-pyrolysis of sludge, and they proposed that the results could be attributed to the synergetic effect. Wang et al. (2016) reported that synergetic effect of sewage sludge and wheat straw in the course of the co-pyrolysis processes can be clearly observed in a fixed-bed reactor, which results in an increase in the gas and liquid yields and a decrease in the solid residue yield. Similar synergetic effect was also observed in the study of Xu et al. (2017) in the co-pyrolysis of municipal sewage sludge and hazelnut shell. These findings above prove that interaction may exist in co-pyrolysis process of sewage sludge and biomass, which would help to find a more effective way for the reuse of biomass and sludge together.

This work deals with the paper sludge from a paper mill in China which has low volatile matters content but high ash content around 60%. To the best our knowledge, there has not been much report on recovering and utilizing energy from this type of sludge because of their compositions and characteristics. However, this problem may be solved by blending biomass feedstocks for co-pyrolysis, as the metals and the other minerals may serve as a catalyst during biomass pyrolysis (Guo et al., 2016a). Furthermore, significant interactions are expected in the course of the co-pyrolysis due to the high ash content of paper sludge, which can catalyze secondary reactions involving bio-oil components, such as dehydration and cracking (Ren, 2013; Ding and Jiang, 2013), and therefore the bio-oil yield would be considerably reduced and lead to more gas production (Zuo et al., 2014). Comprehensively, in order to reuse herb reside and high ash containing paper sludge by pyrolysis/gasification technologies, detailed study is needed to investigate the products distribution during the co-pyrolysis of these two materials.

With the aim at clarifying the practicability and optimal conditions for the co-pyrolysis process of herb reside and high ash containing paper sludge, this work investigated the products yield characteristics in a drop tube fixed-bed reactor with varied temperatures and blending ratios. The catalytic effect of high ash containing paper sludge on the pyrolysis characteristics of herb residue in terms of product distributions and gas compositions was described by comparing the pyrolytic experiments of herb residue, paper sludge and their blends. The variation of the tar composition and char structure was also analyzed for further study on the interactions between herb residue and paper sludge during co-pyrolysis.

2. Materials and methods

2.1. Materials

HR and PS were used as feedstock in this study. HR was obtained from the production of a kind of Chinese medicine in Henan Wanxi Pharmaceutical Co., Ltd, which located in the southwest of Henan province, China. PS was obtained from a paper mill in Rizhao city, Shandong province, China. Both HR and PS were dried at 105 °C for 24 h, and then ground and sieved to 0.2–0.45 mm and <0.125 mm, respectively. These two materials were mixed at HR to PS ratio of 1:0, 3:1, 2:1, 1:1, 0:1 prior to each experiment.

The ultimate analysis of HR and PS was carried out using an elemental analyzer (Vario MACRO cube, Elementar, German) and the proximate analysis was conducted according to GB/T28731-2012 standard using a muffle furnace (SX2-2.5-12A, China), and these results were summarized in Table 1. As observed, HR has higher volatile content, while PS shows high ash content. Given the impact this ash in the PS has on the pyrolysis process, the chemical composition has been determined by the X-ray Fluorescence (XRF-1800, SHIMADZU, Japan), and the relative content of these elements were also listed in Table 1. The results show that PS is rich in metals, particularly alkaline-earth metals, which have been proved having catalytic effect on biomass pyrolysis as well as tar cracking (Jiang et al., 2015).

2.2. Thermogravimetric analysis (TGA)

Non-isothermal pyrolysis characteristics of HR and PS were determined using a thermogravimetric analyzer (TGA, Labsys Evo STA, France) under pure N_2 (99.999%) flow rate of 60 ml/min. Samples with particle size range of 0.054–0.125 mm were dried first to