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High quality syngas produced from the co-pyrolysis of wet sewage sludge with sawdust

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ABSTRACT

A method for wet sewage sludge (WS) direct pyrolysis with sawdust (SD) at high temperature for syngas production in a screw moving bed reactor was proposed to solve the issue of direct WS utilization. Meanwhile, the co-pyrolysis characteristics of WS with SD at 900 °C was investigated by TG, Py-GC/MS analysis. The TG analysis showed that significant interactive effects, including inhibition and acceleration occurred when the ratio of SD increased from 20 to 80 wt%. According to Py-GC/MS and co-pyrolysis experiment results, lowest yields of O-containing compounds, aromatic hydrocarbons and the liquid were found under 40 wt% SD addition ratio. Meanwhile, synergetic effects — effects of acceleration as well as moisture on syngas, became more distinct in the same addition ratio. The catalytic in-situ steam, which performed as an oxidizer, promoted steam reforming reaction and secondary cracking of macromolecular. Under the optimum SD addition ratio (40 wt%), the quality of syngas was improved, e.g. H_2+CO content increased about 10.19%, H_2/CO increased about 0.14, syngas heat produced from 1 kg raw material increased about 4.04 MJ/kg and carbon conversion increased about 12.75%, respectively.

Introduction

In recent years, a large number of sewage sludge has been produced from the wastewater treatment plants [1]. Except organic matters, sewage sludge contains high moisture and many harmful and toxic substances, such as heavy metals [2], viruses, dead bacteria and a vast amount of microorganisms. Thus, the treatment of sewage sludge has caused more and more attention in terms of economic, environment and reuse. There are some conventional methods (including landfills, compost and incineration [3]) for the reduction and recycling of sewage sludge. However, these ways easily lead to secondary pollution. Among the various management options, pyrolysis is a kind of effective and potential method for treatment and utilization of sewage sludge as it produces gas, bio-oil and char while avoids the formation of toxic organic compounds [4,5].

Currently, wet sewage sludge from wastewater treatment plants need to be dewatered before pyrolysis or gasification due to high moisture content (about 80 wt% water) [4,6]. From the view of energy consumption, however, the pre-drying process is illogical and increase the cost of disposal considerably. According to previous researches [6–12] on the direct pyrolysis of wet sewage sludge, it has been proved that the steam, especially in-situ steam, could act as an oxidizer to enhance the contents of H_2 and CO and promote the secondary cracking reaction of tar. Thus, it is meaningful to investigate pyrolysis characteristics of wet sewage sludge. However, the quality of the products from single pyrolysis of wet sewage

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sludge is not high because of high moisture and ash contents [6,12,15,16].

In contrast, due to high volatile matters and low ash content, biomass can be seen as a valuable renewable energy resource [13,14]. Thus, to obtain high quality syngas, an effective method, wet sewage sludge direct pyrolysis with biomass at high temperature, was proposed. In this case, the moisture content and the ratio of C, H and O in mixture samples could be controlled and adjusted. During co-pyrolysis, there were some interactions between sewage sludge and biomass to accelerate or inhibit the thermal decomposition process. For example, some synergetic effect occurred in the co-pyrolysis process of sewage sludge with wheat straw [17–19], poplar sawdust [20] and microalgae [21], and this effect was strongly affected by biomass adding ratio according to TG analysis and the fixed bed experiment results. On the contrary, no significant accelerated effect was found in sewage sludge co-pyrolysis with pine sawdust [22] or manure [23] based on the TG analysis results. Additionally, it was proved that there was no interactive effect in co-pyrolysis process if the biomass has similar thermogravimetric characteristics with sewage sludge [24]. Besides, there were both inhibition and acceleration during co-pyrolysis of sewage sludge with hazelnut shell, and the interactive effect would transform from inhibition to acceleration as the temperature increasing from 260 to 900 °C [5]. From current studies, it can be seen that there is still no clear conclusion on the interactive effect in co-pyrolysis of sewage sludge with biomass due to different pyrolysis conditions, biomass types and reactors. Therefore, it is important to investigate the interaction mechanism during wet sewage sludge and sawdust co-pyrolysis process.

Considering that thermogravimetric analysis is frequently used to study the thermal events [4,11], but it has little benefit to investigate the volatile evolution process. The pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) is proven to be a fast instrument for separating and identifying the volatile products yield from the decomposition process [25]. Brebu et al. [26] showed that the compounds produced from Py-GC/MS were strongly related to the structure of lignins and the majority of them were distributed in the n-C_{10} to n-C_{17}. Zhou et al. [27] used Py-GC/MS to study the nitrogen transformation during pyrolysis of sewage sludge in different temperature range. Fang et al. [25] reported that the acid was the main product during the co-pyrolysis between combustible solid waste and paper mill sludge. Due to the uncertainty of interactions mechanism of sewage sludge and biomass co-pyrolysis as well as the diversity and complexity of volatile products, although there were many researches for biomass by Py-GC/MS, the paper on co-pyrolysis sewage sludge and sawdust was less found. Thus, in our paper, TG and Py-GC/MS were combined to investigate the evolution process of volatile and the interactions during the co-pyrolysis of sewage sludge and sawdust.

In current studies [4,17–23], the fixed bed reactor was main lab-scale reactor to obtain three-phase products and gas compositions. From the point of industrial implementation, reactors need to be able to work continuously and may treat jointly different types of irregular materials. The screw moving bed has been proven to be a practical way for the thermochemical conversion of different lignocellulosic biomass [28] and sewage sludge [29] due to the robustness and stability as well as excellent reproducibility of the results [30]. However, the paper on wet sewage sludge direct pyrolysis by moving bed was less found. Thus, a screw moving bed reactor was designed to further investigate the co-pyrolysis characteristics of WS and SD and the effect of moisture in WS. In addition, by adjusting motor frequency, the screw moving bed can be applied well to intermediate pyrolysis [31], which combines high heating rates in fast pyrolysis and long residence time in slow pyrolysis to promote the increase of gases fraction. In this method, the high heating rates contributes to the production of macromolecule substances with the reduction of char, and long residence time is beneficial to the secondary tar cracking, accompanied by the decrease of oil. As a result, the quality of syngas can be improved.

The aim of this work is to find a practical solution for wet sewage sludge direct thermochemical conversion to obtain high quality syngas. In this work, co-pyrolysis experiments of wet sewage sludge and sawdust were carried out by TG, Py-GC/MS analysis and a screw moving bed reactor to study the interactive effects and determine the optimal sawdust addition ratio, according to the investigation of thermogravimetric characteristics, volatile evolution process, three-phase products distribution and gas compositions. Meanwhile, the performance of catalytic in-situ steam on wet sewage sludge co-pyrolysis with sawdust was discussed.

Materials and methods

Materials

The wet sewage sludge (WS) used in this study was provided by Nanjing urban wastewater treatment plant in Nanjing, Jiangsu province, China. The sawdust (SD) was collected from a furniture factory in Nanjing. WS and SD prepared for TG and Py-GC/MS analysis were dried at 105 °C for 12 h in the oven to ensure that their weight was constant. The wet sewage sludge in mixture samples used for the co-pyrolysis experiment in the moving bed reactor contained 80 wt% water. The proximate analysis was tested according to GB/T 212-2008, and the ultimate analysis was measured by Vario EL cube element analyzer, in which the selected mode was CHNS/O. The contents of C, H, N and S were obtained through combustion method, and the O level was calculated by difference ($O\% = 100\% - Ash\% - C\% - H\% - N\% - S\%$) according to GB/T 476-2001. Then, the proximate and ultimate analysis was displayed in Table 1. The dried samples were milled into 0.5–1 mm in particle size. Then sewage sludge and sawdust were blended well in several proportions (WS/SD 20:80, 40:60, 60:40, 80:20 wt% respectively).

TG analysis

The thermogravimetric (TG) and the derivative thermogravimetric (DTG) analysis on the co-pyrolysis of WS and SD were conducted in a STA449 F1 thermal analyzer (NETZSCH, German). In each experiment, the sample (15 mg) was placed into an Al_2O_3 crucible, and then was heated from ambient