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Research article

A two-step process for sewage sludge treatment: Hydrothermal treatment of sludge and catalytic hydrothermal gasification of its derived liquid

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ABSTRACT

The worldwide increase in amount of sewage sludge has recently attracted considerable interest in developing an efficient and economical sludge disposal method. A sewage sludge treatment process combining the hydrothermal treatment (HT) of sludge and the catalytic hydrothermal gasification (CHTG) of its derived liquid (HT&CHTG-Process) is proposed in this paper. Liquid hourly space velocity (LHSV) value of 25–100 h^{-1} and liquid flow rate of 10–40 mL/min were employed with a self-designed CHTG experimental setup. During the first stage of the HT-Process, approximately 56% of the carbon in the sludge was transferred into the derived liquid at 300 °C. During the second stage of the CHTG-Process, the derived liquid was gasified into CH_4, H_2, and CO_2 using a Ni/carbon catalyst, and the carbon conversion reached 88% at 350 °C and 20 MPa with a LHSV of 25 h^{-1}. Using the integrated HT&CHGT-Process, approximately 0.78 Nm^3 of CH_4, 0.62 Nm^3 of H_2 and 0.31 Nm^3 of CO_2 were generated from 1 kg of carbon in the sewage sludge. The combined process was expected to be an efficient method for sewage sludge treatment due to its mild conditions (≤350 °C and ≤20 MPa) and high yield of fuel gases.

1. Introduction

With the acceleration of global industrialization and urbanization, the amount of sewage sludge produced annually from municipal and industrial wastewater treatment plants (WWTPs) is increasing dramatically [1–3]. Sewage sludge has a high moisture content (up to approximately 98 wt%) and potentially contains heavy metals and pathogens [4–8]. Thus, how to treat sewage sludge in an efficient and economical manner has attracted wide interest recently, and is expected to remain a research focus in the coming decades.

Current sewage sludge disposal methods include agricultural application, landfilling and incineration [9–13]. However, all of these processes require a sludge moisture content below 60 wt% [14]. Therefore, dewatering is the first essential step in almost any disposal process. Mechanically dewatered sludge still has a moisture content of almost 80 wt%, and it is necessary to further dewater the sludge [14,15]. The conventional thermal drying process is effective in removing water from sludge [16,17]; however, the evaporation of water during the process consumes a significant amount of energy [18]. Therefore, the development of a cost-effective dewatering process is desired and challenging for the treatment of sludge.

As a non-evaporative method, hydrothermal (HT) treatment is perceived to be a promising method for dewatering since the water is removed as a liquid, and the latent heat of vaporization can be saved [19–21]. It is preferable to use a higher temperature to achieve a higher efficiency; however, more organic compounds are leached out from the sludge into the derived liquid, causing the energy loss and the liquid treatment issue. Supercritical water gasification (SCWG, above 374 °C and 22.1 MPa) of organic compounds has received a great deal of attention because it can convert the organic compounds to fuel gases such as CH_4 and H_2 [22]. Xu et al. [23] gasified a mixture of sewage sludge and corn starch using an activated carbon catalyst in SCW at 650 °C and 28 MPa to produce H_2, CH_4 and CO_2. Yamamura et al. [24] gasified sewage sludge in the presence of RuO_2 in SCW and found that a total gas yield of 11% based on carbon was achieved at 450 °C and 47.1 MPa with a reaction time of 120 min. Schmieder et al. [25] succeeded in using KOH and K_2CO_3 as catalysts for the SCW gasification of several organic compounds including biomass at 600 °C and 25 MPa. However, the experimental conditions in these studies were rather severe and the costs of its large-scale application were slightly higher.

Only a small number of studies have been carried out under relatively mild conditions. Elliott et al. [26–28] succeeded in using a Ni/Al_2O_3 catalyst to gasify p-cresol (10 wt%) completely at 350 °C and 20 MPa with a liquid hourly space velocity (LHSV, volume flow rate of liquid feed/catalyst volume) of 1–3 h^{-1}. Morimoto et al. [29] studied the hydrothermal extraction of an Australian brown coal and catalytic

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hydrothermal gasification of the extract at 350 °C and 18 MPa with a LHSV of 3.5 h^{-1} and a wastewater flow rate of 1 mL/min. Nakagawa et al. [30] studied the hydrothermal dewatering of brown coal and catalytic hydrothermal gasification of the wastewater at 200–350 °C and 20 MPa with a LHSV of 10–50 h^{-1}. The concentration of total organic carbon (TOC) in wastewater was 2000 mg/l and the liquid flow rate was 0.2–1.0 mL/min.

To provide a possible solution for the sewage sludge treatment, a process combining the hydrothermal treatment of sludge and the catalytic hydrothermal gasification of its derived liquid (HT&CHTG-Process) is proposed in this paper. During the first stage of the HT-Process, the sludge was hydrothermally dewatered at a temperature of 150–350 °C, and the organic compounds in sludge were transferred from solid phase into liquid phase as much as possible. Then, during the second stage of the CHTG-Process, the wastewater generated form HT process was hydrothermally gasified at 250–350 °C and 20 MPa using a Ni/carbon catalyst to produce fuel gases, such as H_2 and CH_4. Additionally, a LHSV value of 25–100 h^{-1} and a liquid flow rate of 10–40 mL/min were employed with a self-designed CHTG experimental setup. Furthermore, the integrated HT&CHTG-Process was carried out under mild conditions ($\leq$350 °C and $\leq$20 MPa) in order to obtain an optimized working conditions both concerning the efficiency and avoiding the strict operation conditions. Systematic experiments were performed to verify the feasibility of the proposed process in this study.

2. Experimental

2.1. Sample preparation

A municipal sludge from Tangxun Lake sewage treatment plant in Wuhan, China (WH sludge) was used in this study. The moisture content of this sewage was approximately 97%. The primary sludge was dried at 40 °C for 24 h before it was ground to pass through an 80-mesh sieve (< 180 μm); then, it was dried at 105 °C for 2 h and stored in a desiccator before use. The proximate analysis was performed using a TGA2000 instrument (Las Navas Corp., Spain), and the ultimate analysis was determined using a Vario Micro Cube analyzer (Elementar Corp., Germany). The ash composition of sludge was analysed using X-ray Fluorescence (XRF) technology (EDX-8000, Shimadzu Corp., Japan). The surface morphology of sludge was analysed by scanning electron microscopy (SEM, Sigma 300, Carl Zeiss Corp., Germany).

2.2. HT-Process

The HT-Process was conducted in a 0.5 L cylindrical autoclave (CJF-0.5, Dalian Tongda Corp., China) and more details about the autoclave can be found in the Supporting Information (Fig. S1). For each run, 5 g of WH sludge (dried basis) and 200 mL of deionized water were added into the reactor to obtain a simulated raw sewage with 2.4 wt% solid content. The reactor was purged several times with 3 MPa of N_2 to remove air residues. Then, the sample was heated at a rate of 5 °C/min from room temperature to a pre-set temperature of 150–350 °C using a holding time of 0.5 h and a stirring rate of 300 r/min. Finally, the autoclave was cooled naturally to room temperature. The produced gas was collected in a gasbag for gas chromatography (GC) analysis (Micro GC3000, NFICON Corp., USA). The derived liquid (named L150, L200, etc.) containing the organic compounds was filtered for the TOC analysis (Multi N/C 3100, Jena Corp., Germany). The treated sludge (named HT150, HT200, etc.) was leached out using a vacuum pump, and then was dried at 105 °C for 2 h before the calculation of solid recovery yield, the proximate and ultimate analyses, XRF analysis and SEM analysis by the procedure stated above (see Section 2.1). The solid recovery yield of sludge was calculated according to Eqs. (1):

$$\text{Yield}\ (\%) = \frac{m_x}{m_0} \quad (1)$$

where m_0 and m_x are the weight of dried sludge before and after the HT-Process respectively.

2.3. Catalyst preparation

A methacrylic acid type ion exchange resin (Mitsubishi Chemical, WK-10) which has carboxyl acid groups as ion exchange sites was used as the starting material [22,29,30]. Approximately 20 g of WK10 was dissolved in 300 mL of an ammonia solution containing 52 g of $NiSO_4{\cdot}6H_2O$ for 24 h. Then, the treated resin was washed with deionized water and dried at 70 °C for 24 h in a vacuum oven. Finally, the dried resin was heated up to 500 °C at a rate of 10 °C/min in a N_2 atmosphere to prepare the Ni/carbon catalyst. The surface morphology and the elemental distribution of this catalyst were analysed by scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX, Quanta 200, FEI Corp., Netherlands). Fig. S2 in the Supporting Information shows a SEM image of this prepared catalyst. The catalyst behaves like a hard particle with a regular spherical shape in a diameter of 0.3–0.4 mm. The EDX analysis shows that the catalyst has 30.80 wt% of Ni, 66.31 wt% of C and 2.89 wt% of O. This prepared catalyst was expected to be effective for gasifying the organic compounds in the derived liquid during the CHTG-Process.

2.4. CHTG-Process

The self-designed CHTG experimental setup is shown in Fig. 1. The reactor is divided into two sections: the preheating tube to preheat the derived liquid and the catalytic tube above where approximately 50 g of the prepared catalyst was loaded to gasify the derived liquid. The reactor was heated up to the reaction temperature (250, 300, and 350 °C) with a backpressure of 20 MPa. Then, the derived liquid obtained in the HT-Process was continuously supplied to the preheating tube by a fluid pump at a flow rate of 10–40 mL/min, which corresponded to 25–100 h^{-1} of LHSV. Finally, the gas–liquid product was separated for the GC and TOC analyses by the procedure stated above (see Section 2.2).

2.5. Determination of metal elements contents

Approximately 0.10 g of each solid sludge sample (or 10 mL of liquid product) was mixed with 10 mL of HNO_3, 4 mL of HF and 2 mL of H_2O_2, and then heated at a rate of 10 °C/min from room temperature to 180 °C and maintained at 180 °C for 1 h using a microwave digestion system (ETHOS-E, Milestone Corp., Italian). After cooling to room temperature, the digestion solution was diluted into 100 mL with deionized water. Then the contents of metal elements were determined using an inductively coupled plasma mass spectrometer (ICP-MS, ELAN DRC-e, PerkinElmer Corp., America). Every experiment was repeated three times and the blank sample was also compared to correct the results.

3. Results and discussion

3.1. HT-Process analysis

3.1.1. Sludge characterization

Table 1 shows the proximate and ultimate analyses of the sludge before and after the HT-Process. WH sludge was characterized by high ash content, high volatile matter content and low carbon content. With increasing HT temperature, the ash content increased from 55.55% in WH sludge to 85.45% in HT300 and reached 87.48% in HT350. The volatile matter content dropped from 37.74% in WH sludge to 10.90% in HT350. In addition, it is apparent that the contents of C, H, O, N and S in the dry sludge significantly decreased as temperature increased. The main elements C, H, O, N and S, composing the organic compounds, were released from the solid phase of sludge to the water phase