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Hydrogen production from supercritical water gasification of chicken manure

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ABSTRACT

The gasification characteristics of chicken manure in supercritical water (SCW) were investigated in a fluidized-bed reactor. Effects of reaction parameters such as reaction temperatures, manure concentrations and catalytic effect of activated carbon on the gasification were studied. The results showed that the temperature play a key role in the formation of gaseous products. Chicken manure was almost completely gasified at 620°C without addition of catalyst and the carbon gasification efficiency can reach up to 99.2%. The liquid and solid products were characterized by COD, SPE-GC/MS, SEM, EDX and FTIR. The main compositions of liquid products were phenol and substituted phenols, N-heterocyclics, benzene and substituted benzenes, carbocyclics. The types of organic compounds in liquid products decreased quickly with the increase of temperature. The FTIR spectra of solid products showed a lower content of carbohydrates and higher content of aromatic structures compared to the initial chicken manure. N-heterocyclic compounds had been detected in both solid and liquid products. Activated carbon as a catalyst could improve the hydrogen yield significantly and promote carbon gasification efficiency at a lower temperature. The maximum hydrogen production of 25.2 mol/kg was achieved at 600°C with activated carbon loading of 6 wt%. Besides, activated carbon showed a good removal ability of inorganic species, specifically the metal cations in chicken manure.

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Introduction

Chicken manure (CM) is a waste of chicken breeding that contains various organic and inorganic matters and needs to be disposed of responsibly. Nowadays, disposal of this waste meets more challenges due to the raising consumption of chicken and eggs around the world. Chicken manure, containing >70 wt% water, is unattractive feedstock for further utilization due to the high transport cost, energy consumptive thermal separation prior to further processing (combustion), and also environmental considerations. Moreover the malodorous chicken manure always contains heavy metal element such as Cu, Hg and As, and large numbers of pathogens including bacteria, viruses and parasites [1]. The traditional treatment approaches of chicken manure include landfill, composting as fertilizer, incineration and methane fermentation. When used as fertilizer, the malodor released by chicken manure is a significant threat to local air quality and human health [2]. Additionally, the excess N, P in chicken will cause eutrophication during landfill and composting [3]. Incineration is not a wise choice due to the high moisture content of chicken manure. Methane fermentation is a good alternative for other animal manure, but the high nitrogen content of chicken manure is not appropriate to fermentation.

In this work, supercritical water gasification (SCWG) of chicken manure was assessed as an alternative method for manure disposal and hydrogen production. The supercritical water is the water beyond the critical point (374°C, 22.1 MPa) has special physical and has chemical properties such as low viscosity, high diffusivity and low dielectric constant. These properties make SCW an excellent solvent for the both organic substances and gases, providing a homogenous condition for gasification of organics with short residence time and high-efficiency [4–8]. Thus the SCWG technology has been proposed as an alternative to conventional waste treatment technologies, especially due to their great ability to process high moisture content biomass waste, allowing improvements in energy and economic advantages. Meanwhile, supercritical water has additional advantages such as COD removal, odor and pathogen elimination when treating chicken manure. Moreover, relatively low temperature of SCW conversion of chicken manure impedes the formation of NO_x and SO_x although it contains a high content of N and S.

Adding catalysts is an efficient way to enhance the gasification in SCWG process. Activated carbons produced from different sources are found to be catalytically effective for SCWG reactions. Xu et al. [9] used carbon-based catalysts, including coal activated carbon, coconut shell activated carbon, macadamia shell charcoal and spruce wood charcoal, for organic compounds gasification in SCW. Antal et al. [10] completely gasified high-concentration biomass at the temperature above 650°C with carbon-based catalyst in SCW. Both reports demonstrated that the activated carbons are efficient catalysts to promote the organics decomposition in SCW. Consequently, we anticipated that activated carbons could also be effective catalyst for the manure gasification.

A wide range of biomass wastes has been treated by the SCWG process, including tannery waste [11], sewage sludge [12,13], black liquor from pulp mill [14,15], etc. There are also a few studies reported on hydrothermal or supercritical water gasification of chicken manure. Ekpo et al. [16] studied the product yields and behavior of inorganic content in processing chicken manure during the thermal hydrolysis and hydrothermal process. Bircan et al. [17] analyzed the compounds in liquid and solid phase for detection of dioxins after hydrothermal gasification of chicken manure and found that the total toxic equivalent quantities of dioxins produced were much lower than regulation levels in Japan. They also studied the behavior of heteroatom compounds in the hydrothermal gasification (400°C) of chicken manure for hydrogen production and found that the formation of pollutants was suppressed [18]. Minowa et al. [19,20] investigated the SCWG of catalyst-suspended chicken manure in an experimental pilot plant and obtained an efficiency ratio of 70% by a detailed calculation of the energy balance. Their results showed that chicken manure feedstock of 10 wt % with 5 wt% of activated carbon could be completely gasified at 600°C. However, experiments on SCWG of chicken manure are still limited and only one report [20] assessed the suitability of catalyst for the application and hydrogen production from the SCWG of chicken manure. Moreover, there are also no reports on reaction mechanism about the SCWG of chicken manure. In order to obtain more information and further determine the feasibility of manure gasification in SCW, studies on the chicken manure gasification in SCW with a continuous flow fluidized bed reactor were carried out and the activated carbon catalyst was used in these experiments. Firstly, pyrolysis of chicken manure under steam atmosphere was investigated by a thermogravimetric analyzer (TGA) to study the thermodynamic property of chicken manure. Then, the effects of temperature, manure concentration and activated carbon catalyst on gasification were studied to show that the SCWG for chicken manure is a promising method. Finally, characterizations of gaseous, solid and liquid products were carried out to deeply understand the reaction mechanism.

Experimental section

Materials

The chicken manure was obtained from the Luoman chicken farm in Shannxi province. The sample contains the excrements of the birds, together with urines, undigested food, feathers, egg shell and even sand. Sample was pretreated by passing a strainer to remove those feathers, shells and sand that may cause plugging in reactor system. Table 1 lists the main composition of chicken manure. The analysis of manure was carried out by a vario MACRO cube Elemental analyzer.

In addition, the pyrolysis of chicken manure under steam atmosphere was investigated by a thermogravimetric analyzer. Fig. 1 presents the weight loss curves and the differential thermogravimetric graves (DTG) for chicken manure at a heating rate of 10°C/min and a water vapor flow of 20 mL/min. The DTG curve presents three main peaks of reaction at 282°C, 430°C and 703°C, indicating that the first peak represents the cellulosic components the undigested food in the manure; the second peak at 430°C is most probably from the decomposition of lipid and proteins according to Kebelmann