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Two-step gasification of cattle manure for hydrogen-rich gas production: Effect of biochar preparation temperature and gasification temperature

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ABSTRACT

Two-step gasification process was proposed to dispose cattle manure for hydrogen rich gas production. The effect of temperature on product distribution and biochar properties were first studied in the pyrolysis-carbonization process. The steam gasification of biochar derived from different pyrolysis-carbonization temperatures was then performed at 750 °C and 850 °C. The biochar from the pyrolysis-carbonization temperatures of 500 °C had high carbon content and low volatiles content. According to the results of gasification stage, the pyrolysis-carbonization temperature of 500 °C and the gasification temperature of 850 °C were identified as the suitable conditions for hydrogen production. We obtained 1.61 m^3/kg of syngas production, 0.93 m^3/kg of hydrogen yield and 57.58% of hydrogen concentration. This study shows that two-step gasification is an efficient waste-to-hydrogen energy process.

1. Introduction

Approximately 1200 million dry tons of cattle manure are produced annually in the world from about 964 million head of cattle (USDA Economic Research Service, 2015). Cattle manure can lead to environmental pollutions if not handled properly (De Vries et al., 2012; Larney et al., 2014). Cattle manure contains abundant cellulose, hemicellulose, and lignin, which has great potential for the production of value-added products, such as biogas, hydrogen rich gas, and bioethanol (Yue et al., 2011). Thermochemical conversion technology is considered as one of the most promising waste treatment practices, in which both energy recovery and pollution control can be achieved (Fernandez-Lopez et al., 2015; Parthasarathy and Narayanan, 2014; Cao et al., 2016).

There are two major thermochemical reaction pathways: pyrolysis and gasification. Pyrolysis process is the thermal decomposition in the absence of oxygen with a relatively low temperature (450–600 °C). The main products of pyrolysis are biochar, liquid biofuels, and gaseous fuel (Díaz-Rey et al., 2015). Gasification is a well-known thermochemical technology that can convert carbonaceous material into syngas by adding a gasifying agent. It is classified depending on the gasifying agent into air, steam, and air-steam, etc. (Lv et al., 2004). Compared with biomass air gasification, the steam-gasification process can produce high heating value hydrogen rich gas with high H_2 content (30–60 vol.%) Parthasarathy and Narayanan, 2014; Udomsirichakorn and Salam, 2014; Acar and Dincer, 2014.

For the conventional steam gasification process, all biomass materials need to undergo a drying process before gasification. The high moisture biomass, such as cattle manure, would require a high-energy consumption. Thus, some researchers studied the in-situ gasification of wet biomass for hydrogen production (Guoxin and Hao, 2009; Peng et al., 2012; Zhang et al., 2011). However, during in-situ gasification process, it is difficult to control and optimize different steps in one-gasifier due to overlapping of drying, pyrolysis, and gasification. Moreover, the volatile-char interactions had an inhibitory effect on the gasification of biochar (Kajitani et al., 2013). Therefore, to develop sustainable energy treatment of high moisture feedstocks, an important challenge is to regulate the reaction mechanism during gasification.

In light of the above considerations, two-step gasification, including pyrolysis-carbonization and gasification steps, is here proposed to process cattle manure (Fig. 1). After drying, cattle manure is pyrolyzed/carbonized into biochar and volatile products (condensable and non-condensable gases). Then, the biochar is gasified for hydrogen rich gas production by introducing steam, produced in the drying process. Moreover, the pyrolysis-carbonization process can produce bio-oil and combustible gas.

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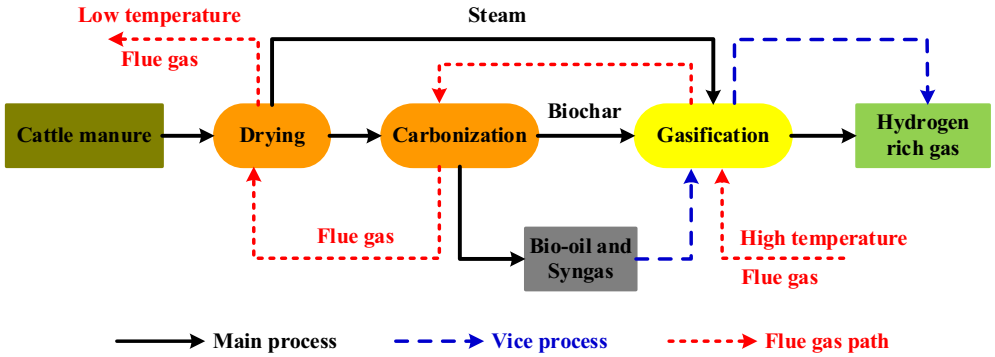

Fig. 1. Illustration of two-step gasification process of cattle manure.

The bio-oil and gas can be used as feedstock to produce hydrogen rich gas by gasification. Moreover, the bio-oil can be used as a liquid fuel or chemical feedstock in various applications. In addition, the flue gas recycle route in the whole process can make full use of the energy of flue gas.

At present, some studies have reported the gasification properties of biochar from different biomass materials. Sattar et al. (2014) studied the steam gasification of biochar derived from rapeseed, wood, sewage sludge and miscanthus, and obtained high-quality syngas. Salleh et al. (2010) investigated the air gasification characteristics of biochar from empty fruit bunches, optimized the hydrogen rich gas production, and observed that biochar of empty fruit bunches has a great potential to replace coal as a gasification agent in power plants. However, the effect of manure biochar derived from different carbonization temperatures on hydrogen rich gas production during biochar gasification process has not been reported.

This study aims to enhance the hydrogen rich gas production of cattle manure biochar derived from different pyrolysis-carbonization temperatures through a two-step gasification process. The products distribution and biochar properties from different pyrolysis-carbonization temperatures were studied in the pyrolysis-carbonization process. Furthermore, the effect of biochar preparation temperatures and gasification temperature on hydrogen production was investigated.

2. Materials and methods

2.1. Cattle manure

Cattle manure used in this study was collected from the Dongzheng feedlot located in Jiangxia District, Wuhan City, Hubei Province, PR China. The moisture content of fresh cattle manure was 85.12 ± 1.5 wt%. The cattle manure samples were dried, crushed and screened to 60 mesh (0.250 mm) size particles. The cattle manure sample was stored in air-tight containers.

2.2. Biochars preparation

Cattle manure (dry basis) was pyrolyzed/carbonized at temperatures of 300, 350, 400, 500 and 600 °C, holding time of 30, 60, 90 and 120 min. Pyrolysis-carbonization was carried out in a laboratory-scale fixed bed reaction system, which was from SHENGLI Test Instruments Co. Ltd (SLG1200-100, Shanghai, China). The fixed bed system consisted of an electric furnace heater and a quartz tube reactor (1000 mm length and 90 mm inner diameter). Prior to starting the reaction system, the gas phase in the quartz tube reactor was flushed with 99.99% nitrogen for 0.5 h to ensure that the reactor has inert atmosphere. The reactor was then heated to the desired temperature. For each run, 10.00 g sample (dried basis) was loaded onto a porcelain boat and placed in the reactor at desired temperature. When the run was completed, the reactor was flushed with nitrogen to maintain anoxic conditions. After being cooled to room temperature, the produced biochar was taken out and weighed to calculate the biochar yield. Finally, the biochar was ground to pass through a 100 mesh sieve and stored in air-tight containers for further use.

2.3. Steam gasification of biochar

The biochar derived from different carbonization temperatures (300, 350, 400, 500 and 600 °C) with a holding time of 30 min was used as feedstock for steam gasification. The biochar samples from 300 to 600 °C were named BC-300, BC-350, BC-400, BC-500, and BC-600, respectively. Steam gasification experiments were also carried out in the fixed bed reactor described in Section 2.2. For each run, 5.00 g of biochar was gasified at the desired temperatures (750 °C, 850 °C) for 30 min. Steam used in gasification was produced by a steam generator (Suzhou Richtreatment Environment Technologies, Inc.), and introduced into the reactor with a flow rate of 1.66 g/min. The produced syngas was condensed using a ball condenser, washed, and analyzed by gas chromatography. To minimize the effect of random errors, each run was duplicated and the average data was reported.

2.4. Analytical methods

The elemental compositions (C, H, N and O) of samples were determined by an elemental analyzer (V Vario Micro cube CHNS Analyzer, Germany). The O content was calculated by difference. The volatiles content of samples was determined in thermal analyzer (SDT Q600). Ash content was measured using the Laboratory Analytical Procedure (LAP) developed by the National Renewable Energy Laboratory (NREL) Sluiter et al., 2008. The fixed carbon (FC) content of the test samples was calculated by difference. Thermogravimetric (TG) analysis of the samples was performed by a simultaneous thermal analyzer (TA SDT Q600) under atmospheric pressure. Samples were heated in the TA apparatus from ambient temperature to 1000 °C with a constant heating rate (10 °C/min). The carrier gas was ultrahigh pure nitrogen (99.99%), which was supplied with a constant flow rate of 100 ml/min, to maintain an inert atmosphere and purge the volatiles generated from sample pyrolysis. The surface morphology of the biochar was analyzed using a scanning electron microscope (JSM-6390LV, NTC, Japan). The functional group analyses of the biochar were achieved using a FT-IR spectrometer (VERTEX70, Germany) in the range of 600–4000 cm^{-1} wavenumbers.

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