Bioresource Technology 238 (2017) 78–85

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Hydrothermal carbonisation of poultry litter: Effects of initial pH on yields and chemical properties of hydrochars

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HIGHLIGHTS

- Hydrothermal treatment of PL was performed at varying pH.
- pH value was varied using CH_3COOH or H_2SO_4.
- Influences of pH on carbonisation were evaluated.
- Structures and chemical compositions of hydrochars were evaluated.

ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form 5 April 2017
Accepted 6 April 2017
Available online 9 April 2017

Keywords:
Hydrothermal carbonisation
Hydrochar
Poultry litter
Acetic acid
Sulphuric acid

ABSTRACT

In this study, hydrothermal carbonisation (HTC) of poultry litter (PL) was carried out to evaluate the impact of initial pH using acetic acid (CH_3COOH) or sulfuric acid (H_2SO_4) on the yields and properties of hydrochar (HC). The PL samples were treated by HTC at various initial pH and at 250 °C for 2 h. The HCs produced were characterized by ultimate, proximate and fibre analyses as well as heating value and surface area measurements. The results indicated that undertaking HTC in the presence of acids (CH_3COOH, H_2SO_4) significantly affects the yields and properties of HC. The C content and HHV of the HC increased with decreasing initial pH. In the presence of H_2SO_4, the hydrochar yield (HY) increased while the ash content was significantly reduced. The lowest ash content and the highest HY were measured in the HC produced from the suspension with an initial pH of 2 using H_2SO_4.

1. Introduction

Poultry litter (PL) is a heterogeneous feedstock consisting of bedding material, faeces, urine, feathers and waste feed, and is the most suitable manure feedstock for thermal conversion processes (Ghanim et al., 2016). PL has been described as a complex mixture of alkyl moieties, sugars, aromatic systems, and acidic functionalities (Di Gregorio et al., 2014; Lynch et al., 2013). Notwithstanding, the advantages of PL for increasing soil fertility, there are environmental concerns about its over application on agricultural sites which may result in human and animal health risks through leaching of nitrates and other pollutants into groundwater (Lynch et al., 2013). These risks have been alleviated to some extent by legislation such as the Nitrates Directive, nevertheless conversion of PL is attractive to stabilise the PL, reduce its volume, weight and its risk, and to potentially produce valuable products.

Developing environmentally beneficial uses for animal by-products for application to land would help to alleviate problems associated with their management. Disposal technology for bio-waste has clearly indicated that thermochemical conversion processes have the capability to covert animal by-products into combustible gases, bio-oils and solid products which can be used as a soil amendment/fertiliser (Pandey et al., 2016; Taupe et al., 2016). Accordingly, thermal conversion technologies, including pyrolysis, gasification, combustion and hydrothermal carbonisation (HTC), are being used to convert biomass and/or biowaste into useful products while addressing compliance with environmental emission norms. Unlike pyrolysis, gasification or combustion which require relatively dry feedstocks, HTC typically is performed in water at moderate temperatures between 180 and 260 °C and with residence times from 5 min to several hours under self-generated pressures above 1 MPa (Bach and Skreiberg, 2016; Ghanim et al., 2016; Reza et al., 2016b;

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http://dx.doi.org/10.1016/j.biortech.2017.04.025

Wikberg et al., 2015). The HTC process is regarded as an environmentally friendly thermochemical process suitable for wet biomass and/or biowaste. There are several terminologies such as wet torrefaction and hot compressed water treatment sometimes used to describe HTC in the literature. The main advantages of the HTC process are the ability to convert wet biomass and/or biowaste into a sterile material, a significant reduction in weight and volume, and the facility to recover large amounts of heat (Libra et al., 2011). During HTC processing, the wet biomass and/or biowaste undergoes a number of complex chemical reactions including hydrolysis, dehydration, decarboxylation, aromatization and recondensation reactions (Acharya et al., 2015; Kambo and Dutta, 2015; Libra et al., 2011; Wikberg et al., 2015). As a result, a solid residue (hydrochar), a liquid by-product and some gaseous products are formed.

One the main aims of the HTC process and the point-of-interest for this study is to produce a hydrochar (HC) with better chemical, physical and fuel properties compared with the raw biomass/biowaste (Bach and Skreiberg, 2016). The HC, which has been proposed as a soil amendment and as a substrate for environmental remediation, is carbon and energy-dense (Wikberg et al., 2015). The quality and yields of the HC depend on the composition and conditions of the process such as treatment temperature, residence time, pH, etc. In addition to treatment temperature and residence time, the formation and quality of the products can be affected significantly by the composition of the process reagents such as feedstock type, raw material/water ratio, and initial pH (Ghanim et al., 2016), etc.

Even though the utilization of PL as raw material for HTC has been studied by Ekpo et al. (2016b), Heilmann et al. (2014), Oliveira et al., (2013) and Sun et al. (2011) relatively few investigations focus on the effects of the process parameters on the HC properties and quality (Ghanim et al., 2016; Mau et al., 2016). Understanding the effect of the process parameters on the HC properties is crucial to address its agricultural and environmental uses and to allow meaningful application quality assessments. Ghanim et al. (2016) addressed the effects of treatment temperature and residence time on HC produced from PL and concluded that treatment temperature was the most significant variable in changing the HC qualities. They also found that the optimum process conditions for obtaining high HY from PL with high C and low ash content in the HCs were 250 °C for 120 min.

As well as investigating the effects of treatment temperature and residence time, a number of studies have undertaken HTC of biomass and biowaste at different initial pH's using a variety of acids and bases. Other studies in this field have focused on the effect of various salts on HTC. The investigations have found that the addition of acids, bases and salts can have a significant effect on the degree of carbonisation, and have been recommended to extract certain elements, in order to improve the physicochemical properties of the HTC products and to reduce the reaction pressure and temperature (Ekpo et al., 2016a; Latham et al., 2014; Lynam et al., 2011; Xu et al., 2010). Various acids have been used in these HTC experiments with a significant impact on product characteristics being observed. The most frequently reported organic acids were acetic and citric acid (Hu et al., 2008; Lynam et al., 2011; Reza et al., 2015), while the equivalent mineral acids were hydrochloric and sulfuric acid (Latham et al., 2014; Lu et al., 2014; Wikberg et al., 2015; Yang et al., 2015). However, the role of the initial pH in the overall distribution and composition of reaction products from the HTC of PL remains unclear which provides the motivation for this study. Moreover, the potential to enhancing the hydrothermal reaction rate using catalysts is becoming an essential option because it can help lower the treatment temperature and residence time of the processes, which can reduce both the energy consumption and the operating pressure.

2. Materials and methods

2.1. Materials

PL samples with straw as the bed material were collected from a farm located near Limerick, Ireland. The collected samples were transferred to the laboratory and prepared according to BS EN 14780:2011. The samples were kept in sealed polyethylene bags and stored in the freezer until required. The stored samples used for the experiments were on an as received basis (ar) however prior to analysis the PL was crushed and sieved to a particle size < 0.75 mm and dried in an oven at 105 °C for 24 h. Sulfuric acid (H_2SO_4) 95.0–97.0 w/w% and acetic acid (CH_3COOH) $\geq$ 99.8 w/w% were purchased from Sigma–Aldrich.

2.2. HTC experimental procedure

HCs were produced following a typical HTC process. Briefly, the experiments were carried out using an 8.0 litre Parr stirred pressure reactor fitted with a removable glass liner. An electric heater was used to supply the heat to maintain the temperature of the reactor. The heating and cooling rates were the same for each experiment as the same reactor was used for all experiments. The PL(ar) with a moisture content of 37.26 ± 0.51% was loaded into the glass liner with one litre of distilled water. The suspension was thoroughly mixed for 30 min and then the pH value was measured as 9.21 ± 0.18, following which concentrated CH_3COOH or H_2SO_4 was added to achieve the desired pH. For comparison a control experiment (CE) was conducted with no acid added. After the glass liner containing the suspension was placed into the stainless steel reactor, it was purged with N_2 and the stirring was started. The reactor was then heated to the desired treatment temperature (250 °C) set using a PID controller, however, the reactor pressure was not controlled but was monitored during the experiments. When the desired temperature was reached inside the reactor, the 2 h residence time was initiated. After the target residence time was achieved, the heating was turned off and the reactor was rapidly cooled to room temperature by immersion in a cold water bath. A more detailed description of the experimental conditions for each experiment can be found in the Supplementary material.

The reactor was vented of gases at ambient temperature and the HCs were recovered as a solid residue by vacuum filtration, followed by drying at 105 °C overnight. The HCs were powdered to <0.75 mm, homogenised and stored in an airtight container at room temperature for analysis. Each experiment was carried out in duplicate and the HC's were mixed prior to analysis. The HC samples were designated as SA-pH and AA-pH where the SA, AA and pH are sulfuric acid, acetic acid and initial pH respectively.

2.3. Characterization methods of PL and HC

Characterisation of PL and HCs was conducted on a dry basis (db) using suitable standard methods, with all measurements performed in triplicate and the mean values with standard deviation (SD) reported. Moisture content was determined by the mass loss of the sample at 105 °C according to I.S. EN 14774-3:2009, whereas ash and volatile matter (VM) were measured according to BS EN 14775:2009 (550 °C) and I.S. EN 15148:2009 (900 °C) respectively. Fixed carbon (FC) content was calculated by subtracting the ash and VM contents from 100%. The elemental composition (C, H, N, S) was determined using a Vario EL cube elemental analyser with oxygen calculated by difference. The higher heating value (HHV) was measured using an Isoperibol Calorimeter 6200 (Parr Instrument) according to I.S. EN 14918:2009. The liquid samples gener-