Applied Energy xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Energy

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

# Energy conversion and gas emissions from production and combustion of poultry-litter-derived hydrochar and biochar

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## HIGHLIGHTS

- 250 °C hydrochar has combustion behavior similar to sub-bituminous coal.
- HTC results in 24% more net energy generated than slow pyrolysis.
- Pollutant emissions decreased as HTC production temperature increased.
- Hydrochar from poultry litter can replace 10% of electricity generated by coal.

## ARTICLE INFO

*Keywords:*
Hydrothermal carbonization
Slow pyrolysis
Poultry litter
Combustion
Greenhouse gases

## ABSTRACT

Growing amounts of poultry litter call for improved treatment solutions. Its conversion to renewable energy can offer a solution while concomitantly reducing environmental impact and reliance on fossil fuels. We compared the production and combustion of biochar by slow pyrolysis to that of hydrochar by hydrothermal carbonization (HTC) in terms of char behavior, energetics, and gas emissions. Poultry litter is significantly different from other feedstocks when treated by slow pyrolysis and HTC, and requires a detailed study of its combustion behavior before it can be utilized in large-scale energy generation. Poultry litter was converted to biochar at 450 °C, and to hydrochar at 180, 200, 220 and 250 °C. Their chemical composition, combustion behavior and gaseous emissions were characterized by TGA–FTIR analysis. Hydrochar produced at 250 °C was more energy-dense than biochar, resulting in 24% higher net energy generation. Combustion behavior of hydrochar produced at 180, 200 and 220 °C was similar to that of the original litter, which is typical of biomass. On the other hand, hydrochar produced at 250 °C and biochar were more similar to coal. The main gaseous emissions during char production were $CO_2$, $CH_4$ and $H_2S$. During the combustion step, NO and $SO_2$ emissions were higher for hydrochar than biochar. Increasing HTC production temperature decreased emissions of $CH_4$ and $NH_3$ during hydrochar combustion. Biochar's emissions were more significant during the production step than during combustion, whereas the opposite held true for hydrochar. Thus, HTC was seen to convert poultry litter more efficiently into a solid fuel that can potentially replace 10% of coal in the generation of electricity, thereby significantly reducing greenhouse gas emissions associated with electricity generation and agricultural waste.

## 1. Introduction

Biomass accounts for 72.8% of renewable energy production worldwide [1]; however, crops grown for energy production place a burden on land, water, and fertilizer resources [2]. Less resource-intensive renewable energy production can potentially be achieved through biomass considered as "waste", such as animal manure. Manure production is on the rise due to a growing world population that is consuming more animal protein [3]. In fact, manure reuse is common practice, mainly via land application as a source of fertilizer (directly or after treatment) [4], or for energy production by anaerobic digestion or direct combustion [5]. Unfortunately, these practices still face technological difficulties leading to high inefficiencies, and result in significant environmental impact, such as emission of greenhouse gases (GHGs), spread of pathogens and micropollutants, and runoff of nutrients into water bodies [4–6].

In recent years, the use of manure as an energy source has been suggested by performing slow pyrolysis [7,8] and hydrothermal carbonization (HTC) [9,10] to produce biochar and hydrochar respectively. During slow pyrolysis, the biomass is converted by heating to approximately 300–600 °C at a rate ranging from 1–30 °C/min in the absence of $O_2$, under atmospheric pressure [11]. In HTC, the biomass is

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https://doi.org/10.1016/j.apenergy.2017.11.033
Received 17 August 2017; Received in revised form 30 October 2017; Accepted 3 November 2017

heated to 180–250 °C in the presence of water, under autogenous pressure [9]. The advantages of these processes are sterilization of pathogens, reduction of pollutants, reduction of waste volumes, and production of an energy source similar in quality to sub-bituminous coal [12,13].

Manure produced by poultry is usually referred to as poultry litter because it is mixed with bedding materials, feathers, and spilled feed. Considering an annual worldwide poultry litter production of 625–938 Mton [14,15], its continuing growth [16], and approximately 38% C content [12], poultry litter is an ideal candidate for renewable energy production. Poultry litter is also of particular interest as it contains high N concentrations which might be converted to potent GHGs during production and following combustion of hydrochar and biochar.

The slow pyrolysis of poultry litter has been investigated, focusing on a large range of final temperatures of 300–800 °C considering various applications [11,13,17–24]. In general, slow pyrolysis of poultry litter results in biochar yields (char mass relative to the initial litter mass) ranging from 32–54% [13,24], and gas yields of 20–24% [18,24]. This is a significant divergence from experiments performed with many other feedstocks, where typical yields are of 35, 30 and 35% for biochar, bio-oil and gases, respectively [25]. This indicates that poultry litter pyrolysis is different from other feedstocks and requires individual analysis. Based on the available literature, the potential for efficient use of biochar derived from poultry litter as a fuel is not clear due to the large span of caloric values (12–20 MJ/kg) and energy yields (36–68%). Recently, it has been shown that hydrochar produced by HTC of poultry litter has the potential to be used as fuel [12,20,26]. In HTC treatment it is also evident that poultry litter behaves differently from other feedstocks [27,28]. Despite the available knowledge, the combustion properties and gaseous emissions of slow pyrolysis and HTC have not been thoroughly studied [19,29–35]. Moreover, this information is essential for any future application of these chars as energy source.

Despite being described as a fuel source, few studies have actually investigated biochar and hydrochar behavior during combustion [8,29–34,36,37]. Moreover, to the best of our knowledge, only a few studies have addressed the combustion of poultry-litter-derived biochar [19,38], and none have addressed the derived hydrochar. Fuel combustion properties are commonly investigated by thermogravimetry analysis (TGA), generating a combustion profile (weight-loss rate versus temperature) [8,33,39]. The combustion profiles of biochar and hydrochar generated from various feedstocks display one peak in a wide range of elevated temperatures due to reduced volatile matter content [34,40], whereas biomass generates two peaks due to differences in reactivity between volatile matter and the resulting char [34]. He et al. [29] and Liu et al. [31] found that increasing the time and temperature of the HTC reaction results in increased ignition, peak and burnout temperatures. These combustion properties have not been properly compared to those of biochar or coal. Such comparisons are of particular importance because they can demonstrate a preference for hydrochar or biochar, as well as the ease of the transition from energy production from coal to renewable energy production from these chars.

The gas emissions during the combustion process are crucial to establishing the environmental footprint of these energy sources. HTC life-cycle analysis covering hydrochar production until combustion has demonstrated that the combustion step is one of the most important stages in terms of impact on climate change [41]. Nevertheless, to the best of our knowledge, the gaseous emissions during the combustion of litter-derived hydrochar have not been investigated. During biomass combustion process, several gases are emitted, including $CO_2$, CO, $CH_4$, $SO_2$, NO, and $NH_3$ [39,42]. Generally, $CO_2$ is emitted at the greatest magnitude, while the magnitudes of $SO_2$, NO, and $NH_3$ emission vary greatly, depending on the material combusted and the initial concentration of S and N [39,42]. More research is needed to establish the gas emissions from litter-derived biochar and hydrochar, and to determine how they are influenced by the production temperature.

Therefore, the objectives of this study were to: (a) compare the production of biochar by slow pyrolysis to hydrochar by HTC in terms of char quality, energetics, and gas emissions; (b) explore the combustion properties of hydrochar produced under different temperatures in comparison to raw litter and biochar derived from the same poultry litter; (c) compare gas emission during the combustion of hydrochar and biochar derived from poultry litter, and that from the untreated litter.

The analysis of these issues is essential in understanding the potential benefits of HTC as a technology to produce renewable energy from animal litter. This study investigated for the first time the gaseous emissions from hydrochar combustion as a function of HTC production temperature. It also compared for the first time the entire process of treating poultry litter to produce a solid fuel by slow pyrolysis and HTC. Poultry litter deserves this dedicated consideration since it has been shown that it behaves differently from other feedstocks under the considered treatments. Moreover, the high and growing availability of poultry litter represent a great potential in renewable energy generation. This investigation is essential in bridging the gap from a theoretical potential energy source to the development of an alternative renewable fuel.

## 2. Experimental

### 2.1. Litter source

Poultry litter was collected from a broiler farm in the Negev region of Israel. The litter contained mainly broiler excretions mixed with some bedding material and feathers. The feedstock was dried at 105 °C for 24 h, and aggregates were crushed with a mortar and pestle and then sieved through a No. 8 mesh. The dried and homogenized feedstock was stored in a desiccator prior to HTC and slow pyrolysis experiments.

### 2.2. HTC apparatus and procedure

HTC was conducted as previously described by Mau et al. [12]. Briefly, the litter was mixed with double-distilled water at a solid-to-water ratio of 1:3. HTC was carried out in a set of 50-mL stainless-steel tubular cylinders rated to withstand the anticipated temperatures and pressures. The reactors were heated by immersion in preheated Paratherm (Conshohocken, PA) HR heat-transfer fluid. The carbonization was conducted at 180 °C, 200 °C, 220 °C, and 250 °C for 60 min. The reaction time did not include the 12- to 20-min period required for the reactors to reach the desired temperature. To ensure replicability, all experiments were conducted in triplicate; averages values and standard errors are presented. The hydrochar was separated from the aqueous phase by vacuum filtration, then oven-dried at 105 °C for 24 h. Once dried, it was crushed with a mortar and pestle.

Gas emission was investigated according to the procedure described by Mau et al. [12]. Briefly, gas samples were collected into sampling bags (SKC Inc., Eighty Four, PA) and subsamples were transferred to 20-mL glass vials sealed with a butyl valve and septum and stored for further analysis within days after collection. Immediately after collection in the bags, $NH_3$ and $H_2S$ concentrations were measured using a Kitagawa Gas Detector Tube System (Komyo Rikagaku Kogyo K.K., Japan) with a detection limit of 0.5 ppm and 100 ppm, respectively. $N_2O$, $CH_4$ and $CO_2$ gases were analyzed using a CP-3800 gas chromatograph (Varian, Walnut Creek, CA) with a 0.53 mm × 30 m Rt-Q-Bond column (Restec, Bellefonte, PA). $N_2O$ was measured using an electron-capture detector with He as the carrier gas (10 mL/min) and $N_2$ as the makeup gas (20 mL/min). Temperatures of the injector, column, and detector were 220 °C, 40 °C, and 300 °C, respectively. $CH_4$ and $CO_2$ were analyzed with a thermal conductivity detector using He as the carrier gas (7 mL/min). Temperatures of the injector, column, and detector were 225 °C, 30 °C, and 225 °C, respectively.