Combustion Behavior of Hydrochar Derived from Poultry Manure

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Abstract

This study has the objective to investigate the combustion behavior of hydrochar derived from poultry manure that was prepared under varying temperatures and compare it with combustion of raw manure, biochar (produced by slow pyrolysis of manure) and commercial sub-bituminous coal. For this purpose, poultry manure was collected from a broiler farm, and a subsample was wet to 1:3 solid water content and hydrothermally carbonized to hydrochar at temperatures of 200, 220 and 250 °C. Another subsample was dried and went through slow pyrolysis (at 450 °C) to biochar. The produced chars were characterized in terms of its chemical composition, and behavior during combustion by thermogravimetric analysis. The hydrothermal carbonization treatment resulted in an increase in carbon content, and consequently an increase in caloric value of the hydrochar. The chemical composition of hydrochar produced at 250 °C and biochar resembled sub-bituminous coal. The combustion profile of the hydrochar was also significantly affected by the treatment. An increase in treatment temperature resulted in an increase in ignition, peak and burnout temperatures. These results indicate that the combustion of hydrochar produced at 250 °C can be safer, more efficient, and less pollutant than manure combustion. Moreover, the combustion behavior of 250 °C hydrochar is similar to biochar and coal. Still, hydrochar has an advantage over the more common biochar since its production is more energy efficient. Therefore, this study has shown that hydrothermal carbonization is capable to transform poultry manure into an energy-dense fuel which resembles sub-bituminous coal not only in its composition, but also in its combustion behavior. Therefore, hydrochar could replace coal commonly used in electricity production and reduce our dependency on fossil fuels.

Keywords: Hydrochar, Thermogravimetric analysis, Combustion, Coal.

1. Introduction

Biomass is presently the largest renewable energy source worldwide (1), however crops grown for energy production, place a burden on land, water and fertilizer resources (2). Yet, biomass from waste, such as animal manure, could be an ideal source for renewable energy production as it potentially converts waste that is often an environmental and economic burden into a resource. Moreover, with a growing world population that is consuming more animal protein, the production of manure will continue to increase (3).

Manure is often reused by spreading on land as a source of fertilizer, or for energy production by anaerobic digestion or direct combustion (4,5). Unfortunately these practices can result in pollution of water, air and soil, and are physically and energetically inefficient (4,5). Upgrading manure into biochar through slow pyrolysis has been proposed as method to produce renewable energy more efficiently (6). Biochar has a higher energy content than the original material and is more reactive (6), making it a better fuel. However, given the high moisture content of manure, the slow pyrolysis process of heating the feedstock to 450 °C is very energy demanding. This inefficiency could be prevented by maintaining the moisture in a liquid state throughout the procedure by hydrothermal carbonization (HTC). In HTC the wet biomass is heated to 180–250 °C under autogenous pressures (7), and the solids are converted by hydrolysis, dehydration and decarboxylation reactions into a carbon rich hydrochar (8).

Manure-derived hydrochar appears to be a promising renewable energy source, yet little is known about its combustion behavior, how it is influenced by production conditions, as well as how it compares with "close" alternatives such as biomass, biochar, and coal. Moreover, to the best of our knowledge, there are no studies that focused on hydrochar derived from poultry manure. Poultry manure is of specific interest due to the rapid growth rate of poultry farming (9), and the difficulties in using this type of manure due to high N concentration (4).

Therefore, this study had the objective to investigate the combustion behavior of hydrochar derived from poultry manure that was prepared under varying temperatures and compare it with combustion of raw manure, biochar (produced by slow pyrolysis of manure) and commercial sub-bituminous coal.

2. Material and methods

Poultry manure from a broiler farm in the Negev region of Israel was used as the feedstock. Manure at a solid-to-water ratio of 1:3 was placed inside 50-mL stainless-steel reactors. The reactors were heated by immersion in preheated Paratherm (Conshohocken, PA) HR heat-transfer fluid. The carbonization experiments were conducted in triplicates at temperatures of 200, 220, and 250 °C, for a duration of 60 min. The treatment time did not include the time required to reach the desired temperature, which lasted up to 20 min. When the treatment was completed, the reactors were placed in an ice bath to quench the reaction.

The reactors were opened and the produced hydrochar was separated from the liquid phase by vacuum filtration. Hydrochar from each reactor was dried at 105 °C for 24h prior to characterization. Hydrochar ash content was determined after combustion at 450 °C for 6h. Hydrochar was characterized in terms of elemental composition of C, H, N, and S with a FlashEA™1112 CHNS-O Analyser (Thermo Fisher Scientific Inc., UK). O composition was calculated as the remaining fraction after subtraction of C, H, N, S, and ashes. Hydrochar higher heating values

(HHV) were calculated based on the chemical composition (in %) following the correlation established by Channiwala (14):

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211Ashes \text{ (MJ/Kg)}.$$

Biochar was produced from the same poultry manure through slow pyrolysis to compare this more common method with hydrothermal carbonization. Biochar was created by heating poultry litter to 450°C.

The combustion behavior of hydrochar, biochar, and untreated poultry manure was investigated in the TGA apparatus. Combustion was conducted at a dry air-like gas flow mixture of N_2 and O_2 at a flow rate of 90 ml/min. Samples of 20-30 mg were heated up to 1000 °C at a rate of 10 °C/min. The normalized weight loss (TG) and the weight loss rate (DTG) were analyzed to determine key combustion parameters. Ignition temperature and burnout temperature were calculated using the intersection method (15). In brief, ignition temperature is the intersection point in the TG graph of the line tangent to the point where the DTG peak occurs (maximum weight loss rate) and the line tangent to the point of initial devolatilization after the sample was dried (Figure 1). Burnout temperature is the intersection point in the TG graph of the line tangent to the point where the DTG peak occurs and the line tangent to the point where the weight loss becomes steady. If two major peaks were present in the DTG the burnout temperature was determined by the second peak (26). The peak temperature is the temperature where the DTG peak occurs (Figure 1).

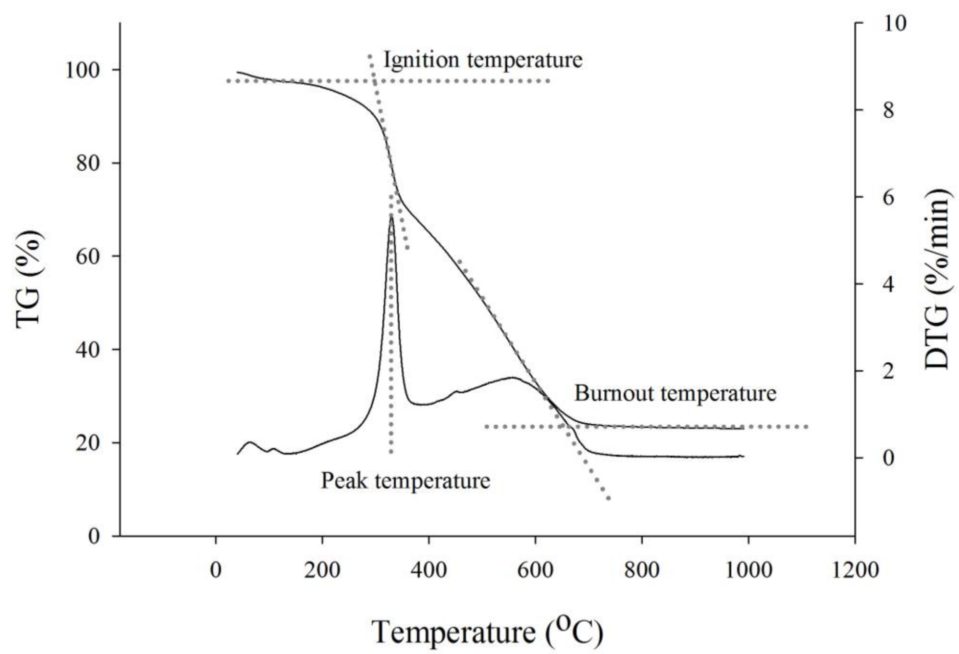

Figure 1. Normalized weight loss (TG) and normalized weight loss rate (DTG) of hydrochar showing intersection method for the calculation of ignition, peak and burnout temperatures

3. Results and discussion

3.1 Fuel properties

Poultry manure, biochar and hydrochar were characterized in terms of elemental composition and caloric value. Poultry manure had originally a carbon concentration of 37.8 %, energy content 15.1 MJ/kg (Table 1), and the atomic ratios of H:C and O:C were typical of biomass (Figure 2) (12). The carbon content of biochar and hydrochar significantly increased after treatment, and as a result, the caloric value per unit of weight increased as well. The HTC process increased the carbon content to 57.6 % at 250 °C which resulted in a higher energy content of 24.4 MJ/kg (Table 1), and the atomic ratios of H:C and O:C became similar to coal (Figure 2). Overall, hydrochar produced at 250 °C resembled sub-bituminous coal (12). The carbon content of biochar was similar to hydrochar prepared at 250 °C. The H:C and O:C ratios are also similar to coal, though biochar displayed a H:C ratio lower than hydrochar produced at 250 °C (Figure 2). Despite similar C content, the calculated caloric value of biochar was significantly lower ($p<0.005$) than in hydrochar (Table 1). One explanation for this disparity can be the lower H content and higher N and S content in the hydrochar (14). This higher caloric value indicates that HTC leads to a more energy-dense fuel than slow pyrolysis is able to achieve. The energy efficiency of these two processes can be further characterized through the energy yield, or in other words, the energy fraction originally present in the manure that is retained in the final char. It was calculated based on the caloric value of the char in comparison to the raw poultry manure, and the mass of char produced in relation to the initial dry mass of poultry manure. The energy yield of biochar is significantly lower than of hydrochar, averaging 51% versus 75% respectively (Table 1). This is due to the low production of biochar, where only 37.5% (by weight) of poultry manure on average became biochar (Table 1), and the rest was transformed into bio-oil and gases. In comparison, hydrochar yield was much higher, ranging from 46.1 to 60.7%. This indicates that the production of hydrochar is more energy efficient than biochar even when only considering dry weights.

Table 1. Physicochemical parameters of poultry litter, hydrochar and biochar. Data are based on dry weights. Standard error is shown. Statistical differences are indicated by different superscript letters. Data from poultry litter and hydrochar are based on previous work by Mau et al. (12).

Parameters	Poultry manure	Hydrochar			Biochar
		200 °C	220 °C	250 °C	
Ultimate analysis					
H (%)	4.8	4.7 ± 0.05^{a}	4.4 ± 0.05^{a}	4.6 ± 0.05^{a}	2.5 ± 0.06^{b}
C (%)	37.8	46.6 ± 1.67^{a}	45.0 ± 1.46^{a}	57.6 ± 0.72^{b}	54.1 ± 0.77^{b}
O (%)	31.0	21.3 ± 1.07^{ab}	17.6 ± 0.43^{b}	4.0 ± 1.05^{c}	4.6 ± 1.33^{c}
N (%)	1.9	2.1 ± 0.04^{b}	2.4 ± 0.03^{a}	3.1 ± 0.01^{c}	5.1 ± 0.07^{d}
S (%)	0.1	0.1 ± 0.01^{a}	0.2 ± 0.01^{a}	0.3 ± 0.01^{b}	0.0 ± 0.00^{c}
Proximate analysis					
Ash (%)	24.4	25.2 ± 1.03^{a}	30.4 ± 1.05^{b}	30.4 ± 0.28^{b}	33.7 ± 0.71^{b}
HHV (MJ/Kg)	15.1	19.0 ± 0.64^{ab}	18.5 ± 0.53^{a}	24.4 ± 0.40^{c}	20.6 ± 0.32^{b}
Mass yield (%)[1]		60.7 ± 0.11^{b}	58.1 ± 0.18^{c}	46.1 ± 0.19^{d}	37.5 ± 0.32^{e}
Energy yield (%)[2]		76.4 ± 2.56^{b}	71.1 ± 2.11^{b}	74.6 ± 1.52^{b}	51.1 ± 1.23^{c}

[1](mass of dry char/mass of initial dry litter)*100; [2](mass of dry char*HHV char)/(mass of initial dry litter*HHV litter)*100.

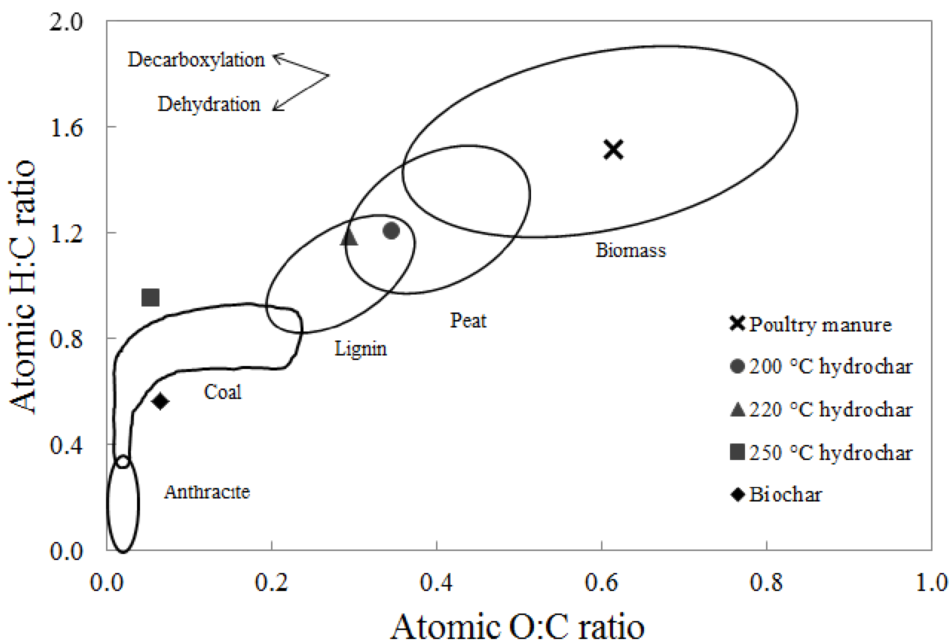

Figure 2. H:C and O:C ratios of poultry manure, hydrochar and biochar. Data from poultry manure and hydrochar are based on previous work by Mau et al. (12).

3.2 Combustion properties

From the TGA analysis the combustion profile of the poultry manure, hydrochar, and biochar were obtained (Figure 3 and 4). The burning characteristics are important to properly compare the reactivity and combustion behavior of the fuels and infer on their performance when used in combustors (16,17). All fuels possess a small peak at temperatures below 200 °C. This peak is associated with weight loss due to evaporation of the moisture present in the fuel. In the combustion profile region above 200 °C, poultry manure, 200 and 220 °C hydrochars presented two peaks, the first associated with volatile matter combustion, and the second with char combustion (5,18–20). This is typical combustion behavior of biomass, where the volatile matter quickly volatilizes and is combusted at low temperatures, leaving the char behind to be combusted at much higher temperatures (15,19–21). Meanwhile, 250 °C hydrochar and biochar display one peak at a wide temperature range and elevated temperatures (Figure 4). The presence of only one peak is probably due to the concurrent combustion of volatile matter and char (18,22). This behavior is typically observed in the combustion of coal, as the profile of sub-bituminous coal obtained by Idris et al. (21) indicates (Figure 4). In general, the combustion profile of hydrochar produced at 250 °C and biochar are more similar to sub-bituminous coal than the raw poultry manure.

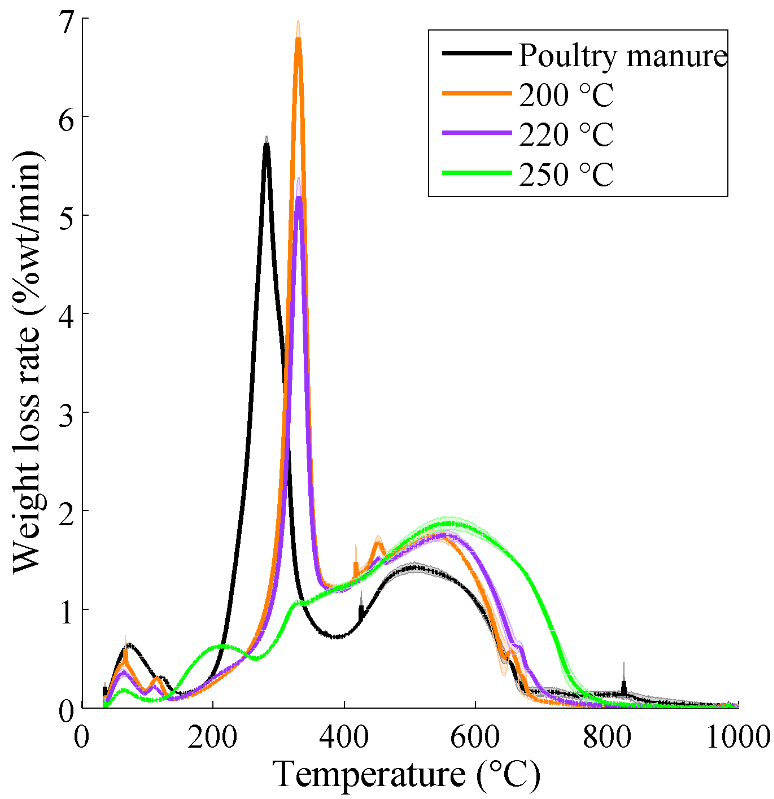

Figure 3. Combustion profile of poultry manure, and hydrochar produced at 200, 220, and 250 °C.

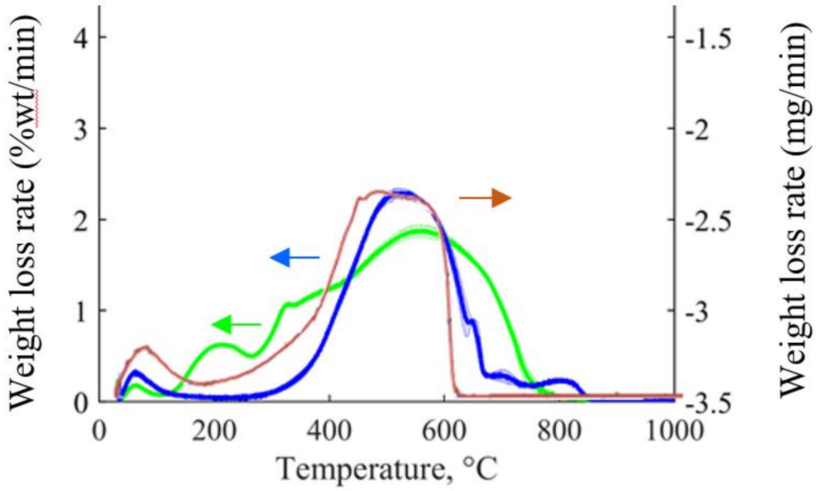

Figure 4. Combustion profile of hydrochar produced at 250 °C, biochar, and sub-bituminous coal. The latter was determined by Idris et al. (21).

These general differences can be quantified through the key combustion parameters (Table 2). There is a significant ($p<0.005$) increase in ignition temperature with increased hydrochar production temperature. Moreover, the ignition temperature of biochar is higher than 250 °C hydrochar. The higher ignition temperature of biochar could be due to the higher N content, which retards ignition of volatiles and reactions at the material surface (5). A high ignition temperature is desirable as it minimizes the risk of spontaneous ignition, making fuel storage and transportation safer (15). An increase in hydrochar production temperature also results in an increased peak temperature, set when the maximum weight loss occurred. Peak temperature can be used to assess the reactivity of the fuel, with higher temperatures indicating lower reactivity (23,24). In other words, as the hydrochar production temperature increases, higher combustion temperatures are necessary to burn the fuel. Lastly, a significant increase in burnout temperature was observed for the 250 °C hydrochar.

Table 2. Key combustion parameters of poultry manure, hydrochar and biochar. Standard error is shown. Statistical differences are indicated by different superscript letters.

Sample	Ignition temperature (°C)	Peak temperature (°C)	Burnout temperature (°C)
Poultry manure	249 ± 0.4^{a}	281 ± 0.4^{a}	637 ± 6.1^{a}
Hydrochar 200 °C	301 ± 1.0^{b}	329 ± 0.5^{b}	631 ± 8.2^{a}
Hydrochar 220 °C	300 ± 0.2^{b}	330 ± 0.6^{b}	648 ± 1.8^{a}
Hydrochar 250 °C	330 ± 2.2^{c}	558 ± 7.6^{c}	700 ± 5.1^{b}
Biochar	417 ± 0.5^{d}	526 ± 6.6^{d}	645 ± 4.8^{a}

With the objective to replace coal with a renewable energy source, the similarity to coal in terms of combustion behavior is important. Contrarily to coal, poultry manure and hydrochar generated at low temperatures ignite and combust rapidly, which influences the combustion efficiency in coal combustors. Coal combustors may not ensure complete combustion of volatiles, leading to energy losses and pollutant emissions (26,28). On the other hand, 250 °C hydrochar and biochar resemble coal in terms of ignition temperature, temperature range of combustion, and weight loss during the combustion process. Similar behavior in TGA analysis indicates that these fuels would behave similarly in industrial combustors (17). In addition, it has been shown that hydrochar possesses caloric value similar to sub-bituminous coal, which is commonly used in electricity production (12). Still, HTC is preferred over slow pyrolysis as a manure conversion method since it results in higher energy yields. Therefore, manure-derived hydrochar produced at 250 °C is a suitable fuel for renewable energy production replacing coal combustion.

Conclusion

Poultry manure is an ideal candidate for renewable energy production since it is considered as an abundant waste, and requires treatment before it can be disposed. This research has determined that hydrothermal carbonization is a technology capable of transforming poultry manure into an energy-dense fuel which resembles sub-bituminous coal not only in its composition, but also in its combustion behavior. Moreover, the conversion process of poultry manure into an energy-dense solid fuel is more efficient by HTC than by the more common method of slow pyrolysis. Thus, hydrochar could replace coal commonly used in electricity production and reduce our dependency on fossil fuels.

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