Effect of Hydrothermal Carbonization on the Fuel Properties of Chicken Manure Hydrochar

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Abstract Recently, the use of chicken manure (CM) for energy has drawn particular attention as a solution for the proper management of this waste. This study aims to determine the impact of hydrothermal carbonization on hydrochar's fuel properties. The statistical study revealed that temperature was the key factor that most strongly influenced variations in the higher heating value (HHV) and mass yield. The residence time (30-120 min) had a greater impact at lower temperatures (180 °C) than at higher temperatures. The hydrochar with the best balance between mass yield (50.13%) and HHV (19.37 MJ/kg) was produced at 180 °C for 120 minutes. Characterization findings showed that hydrochar could lead to reduced H/C and O/C ratios, resulting in an HHV in the sub-bituminous coal region. According to its HHV, fuel ratio, and energy densification ratio, CM's HTC is a promising method to produce solid fuel and is a waste-to-energy opportunity for energy recovery.

Keywords: Hydrothermal carbonization, Chicken manure, Hydrochar, Fuel properties

1. Introduction

In recent years, thermochemical treatments like pyrolysis, gasification, and hydrothermal carbonization (HTC) have become more popular because biochemical methods like anaerobic digestion (AD) can't handle complex wastes like lignin-rich waste [1]. HTC is a potential conversion method that turns wet solid waste, like animal manure, into a solid byproduct (hydrochar) and a liquid byproduct (process water). Compared to pyrolysis and gasification, this method has advantages since it does not require a drying pre-treatment stage, which consumes a significant amount of energy. According to Kumar and Ankaram [2], CM seems to be an appropriate raw material for HTC with a moisture content of between 75 wt. % and 90 wt. %.

Numerous studies have explored the use of HTC for poultry litter conversion [3]–[6]. Although poultry litter mainly contains CM it has different characteristics due to the litter material. Therefore, controlling the solid/water ratio in HTC conversion, taking into account the moisture content in the raw material, is needed. Few studies examine HTC's CM conversion, requiring detailed investigation for comprehensive understanding. Hejna et al. [7] examined the fuel qualities of the hydrochar produced by HTC of CM at 180 °C, 240 °C, and 300 °C for 30, 90, and 180 min, stirring at 120 rpm. Li et al. [8] studied the effects of co-HTC of CM and swine manure (in mass ratios of 2:1, 1:1, and 1:2) at 240 °C for 10 h on the properties of the liquid and the hydrochar resulting from possible cross-interaction of both feedstocks. The two factors that have the most influence on the HTC process are temperature and time [3], [4], [7], [8].

Even though the mechanism of decomposition of lignocellulosic materials explains most of the HTC process of biomass, the high protein content of CM makes it more complex when organic waste is involved [9]. In order to valorize this waste more effectively, additional knowledge is therefore required regarding how temperature and time affect the HTC process of CM and the fuel characteristics of CM-derived hydrochar. The aims of this study is to determine the effect of hydrothermal carbonization on the fuel properties of chicken manure hydrochar.

2. Materials and Methods

The samples of CM used in this study were collected from mechanized laying hen farms in Belgium's Aalter municipality (51°05′N 03°27′E). A laboratory freezer set to -24°C was used to keep the samples after they were stored in sterile plastic bags.

The autoclave configuration (Parr®, 4560 series) had a 450 mL stainless steel reactor that was heated electrically using a ceramic fiber heater. The needed mixing speed (250 rpm) and primary temperatures were adjusted for the experiments by a reactor controller (Parr®, 4848 model). To lower the TS content in the reactor to 15%, distilled water (1:2, biomass: water) was combined with a sample of 100 g (TS 57.64 wt%, d.b.) of wet CM. The reaction times did not take into account the 30 to 60 minutes it took for the reactor to reach the proper temperature. Vacuum filtering was used to separate the hydrochar from the liquid fraction. The hydrochar was dried in an oven (AX oven Carbolite Gero) for 24 hours at 105 °C. A 0.025 mm mesh screen was then used to homogenize the dry and placed in plastic bags at room temperature.

Using a modified version of Singh et al.'s [10] method, moisture, volatile matter (VM), and ash mass fraction in CM and their equivalent hydrochars produced under different operating conditions was measured in technical triplicates. For the elemental analysis, a 5-Bis(5-tert-butyl-benzoxazol-2-yl) thiophene (BBOT) standard reference was used to calculate the mass fractions of C, H, N, and S using a Flash 2000 Elemental Analyzer Thermo Fisher Scientific (Waltham, Massachusetts, USA). The mass fraction of O was estimated by the difference between the elemental analysis and the ash mass fraction. Based on elemental compositions and ash mass fraction, the HHV was estimated using the correlation from Channiwala and Parikh [11].

The fuel ratio was calculated using Eq. (1). Where FC is fixed Carbon (in wt.%) and VM is the volatile matter content (in wt.%). The mass yield was calculated using Eq. (2). Where mf and mi are the final dry mass of hydrochar and the initial dry mass of raw material, respectively (in g). The energy densification ratio (EDr) was determined using Eq. (3), where HHVf and HHVi are the higher heating values (in MJ/kg) of the hydrochar and the raw material, respectively. Energy yield was calculated using Eq. (4).

$$fuel\ ratio\ (wt.\%)\ = \frac{FC}{VM} \tag{1}$$

$$mass\ yield(wt.\%) = 100 \times \frac{m_f}{m_i} \tag{2}$$

$$EDr\ (\%) = 100 \times \frac{HHV_f}{HHV_i} \tag{3}$$

$$energy\ yield\ (\%) = mass\ yield \times EDr \tag{4}$$

One-way ANOVA (analysis of variance) was used to test for significant differences in mean values for CM characteristics of this work compared to others, and between CM and CM-hydrochar response variables. The means between pairs were statistically compared using a test of multiple ranks (Duncan's test). The datasets were analyzed using Statgraphics Centurion (v.19) with a confidence interval of 95%.

3. Results and Discussion
3.1. Raw material characterization

The CM used as feedstock contains 42.36 ± 2.61 wt.% moisture, despite being close to 50 wt.%, the addition of extra water was necessary for the HTC experiments. Table 1 shows the results of the physicochemical characteristics of raw CM as well as the properties of the hydrochars generated at different temperatures and times. For the VM content in the feedstock (65.72 ± 1.29 wt.%), there were no significant differences ($p > 0.05$) from what was reported by other authors [7], [12]. Ash content varies ($p < 0.05$), but similarities with other studies were found (Table 1). The mass fraction of ash can vary depending on meteorological factors and rearing procedures [13]. The FC content in the CM of the present study, 23.93 ± 1.31 wt%, is within the range (8.53 - 43.47 wt%) of the FC content in the CM of other studies ([7], [12]). The mass fractions of C and H did not differ significantly from those reported in the literature ($p > 0.05$). The N mass fraction of the CM differed significantly ($p < 0.05$) from previous results in the literature. The low N mass fraction in the raw material studied (less than 4 wt%) may be due to NH_3 and N_2O losses during storage, as well as the

fact that the sample was dried at 105 degrees to prepare it for elemental analysis. The absence of S and the low mass fraction of N are considered beneficial for the carbonization process. When N and S are present in biomass used for energy production, unwanted emissions such as NOx and SOx are released into the atmosphere [14].

3.2. Hydrochar characterization

The results of the proximate and elemental analyses of CM-hydrochar produced at various temperatures and times are also shown in Table 1. As the thermal intensity (higher temperature and/or longer duration) of the HTC process increased, the FC content increased, but the TS and VM content decreased. Up to 22% of the volatile mass fraction was released in the initial CM purchased with the hydrochar generated in the most extreme conditions. Similar results were obtained by Mau et al. [3], which can be explained by the fact that a reduction of organic matter occurs as a result of chemical processes including dehydration and decarboxylation that shift organic compounds to the aqueous and gas phases. According to Kambo et al. [15], polymerization and cross-linking favour the development of more stable solid molecules, which is observed in an increased FC in hydrochar. The ash mass fraction in the hydrochar increased from 28.67 wt.% (180 °C) to 40.23 wt.% (260 °C), both at 30 min, as a result of the loss of VM in the feedstock. Marin-Batista et. al [16] observed similar results when using cow dung as feedstock for an HTC conversion. They found that increasing the HTC temperature resulted in VM loss, which increased the ash mass fraction. The elemental composition of the raw material was changed by the carbonization process (Table 2). The carbonization process significantly ($p < 0.05$) increased the C mass fraction as a function of increasing process temperature and/or reaction time, from 31.82 wt.% in the initial CM to 48.57 wt.% in hydrochar produced after 120 min at 260 ºC. The O mass removal of 87% was higher than found in other studies [7], which may be the reason behind the increase in the C mass fraction. These changes could be explained through the van Krevelen diagram (Fig. 1).
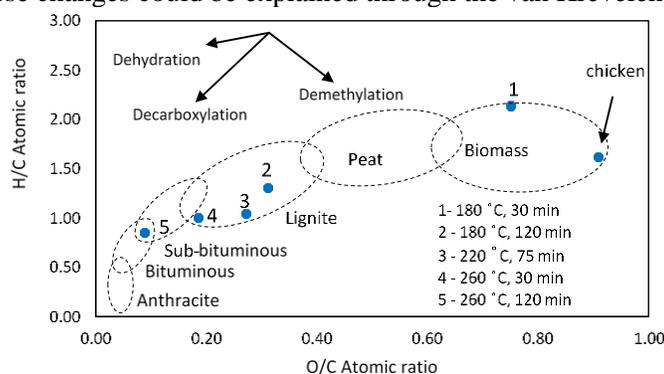
Fig. 1: van Krevelen's diagram of raw chicken manure and derived hydrochar at different temperatures and times.

With an increase in process temperature, the atomic ratios of H/C and O/C decreased. In the Van Krevelen diagram, the hydrochar positions acquired at the lowest thermal process intensity (180 °C and 30 min, point nr. 1) were close to biomass, whereas the hydrochars formed at higher thermally intense conditions (points nr. 2, 3, and 4) were closer to lignite. The most carbonized hydrochar with qualities like sub-bituminous coal was produced at the highest temperature and longest testing period (260 °C and 120 min, point no. 5). The fuel ratio ascended steadily from 0.14 to 0.40 as a result of the rise in FC content and the rising trend in VM loss as HTC temperature and/or time increased. Given that none of the hydrochars that were obtained had a fuel ratio greater than 2.5 (Table 2), their combustion characteristics are suitable for use as fuel [17]. The HHV in the hydrochar produced at 260 °C for 120 min was enhanced by increasing the fuel ratio, going from 15.26 MJ/kg (feedstock) to 20.16 MJ/kg.

Table 1: Physical-chemical properties, mass, and energy yield of raw chicken manure (CM) and hydrochar produced at a solid-to-water ratio of 1:2. Means ± standard error (n = 3); Duncan's multiple range test; statistical differences are denoted by various superscript letters at a probability of *p < 0.05*.

parameters	CM (this study)	180 30 min	180 120 min	220 75 min	260 30 min	260 120 min
TS (*wt*.%, d.b.)	57.64 ± 2.61^a	17.31 ± 0.28^b	26.77 ± 0.81^c	27.53 ± 1.27^c	27.81 ± 3.82^d	27.73 ± 2.94^d
moisture (*wt*.%, w.b.)	42.36 ± 2.61^a	82.69 ± 0.28^b	73.23 ± 0.81^c	72.46 ± 1.04^c	66.24 ± 3.82^d	61.69 ± 2.94^d
VM (*wt*.%, d.b.)	65.72 ± 1.29^a	63.17 ± 0.93^b	60.49 ± 0.18^c	55.22 ± 0.54^c	49.50 ± 0.35^e	43.39 ± 0.29^{ee}
ash (*wt*.%, d.b.)	23.93 ± 1.31^a	28.67 ± 1.16^b	32.53 ± 0.95^c	36.75 ± 0.56^d	40.23 ± 0.02^e	39.45 ± 0.97^{de}
FC (*wt*.%, d.b.)	9.67 ± 0.61^a	8.16 ± 0.27^b	6.98 ± 0.89^b	8.02 ± 0.36^b	10.27 ± 0.34^a	17.16 ± 0.69^c
fuel ratio	0.14 ± 0.01^a	0.13 ± 0.00^{ab}	0.12 ± 0.01^b	0.15 ± 0.01^a	0.21 ± 0.01^e	0.40 ± 0.01^f
N (*wt*.%, d.b.)	3.47 ± 0.22^a	3.64 ± 0.24^a	3.27 ± 0.39^a	2.75 ± 0.14^b	2.76 ± 0.13^b	2.68 ± 0.07^b
C (*wt*.%, d.b.)	31.82 ± 0.63^a	30.20 ± 1.21^a	42.15 ± 0.58^b	41.75 ± 1.49^b	42.87 ± 0.58^b	48.57 ± 0.56^c
H (*wt*.%, d.b.)	3.99 ± 0.09^a	5.38 ± 0.07^b	4.58 ± 0.28^c	3.62 ± 0.38^d	3.59 ± 0.24^{ad}	3.46 ± 0.25^d
O (*wt*.%, d.b.)	36.76 ± 0.93^a	30.17 ± 1.01^b	17.48 ± 1.14^c	15.09 ± 1.85^c	10.55 ± 0.28^d	5.84 ± 0.34^e
HHV (MJ/kg)	15.26 ± 0.32^a	16.18 ± 0.35^b	19.37 ± 0.25^c	17.71 ± 0.55^c	18.30 ± 0.14^d	20.16 ± 0.11^e
mass yield (wt.%)	-	75.01 ± 0.89^a	50.13 ± 2.89^b	58.08 ± 0.73^c	48.38 ± 0.34^d	41.76 ± 0.07^e
EDr	-	1.06 ± 0.03^a	1.27 ± 0.02^b	1.16 ± 0.01^c	1.20 ± 0.01^{bc}	1.39 ± 0.01^d
energy yield (%)	-	79.84 ± 1.18^a	63.66 ± 4.5^b	67.48 ± 0.90^b	58.03 ± 0.02^c	55.18 ± 0.25^c

*TS: Total Solid, VM: Volatile Matter, FC: Fixed Carbon, HHV: High Heating Value, EDr: Energy Densification radio

The HHV ranged from 16.18 to 18.30 MJ/kg when temperatures increased from 180 to 260 °C for 30 min. In other words, an increase in temperature and/or reaction time greatly enhanced the HHV. The lowest HHV (16.18 MJ/kg) was observed at 180 °C for 30 min while the highest value of 20.16 MJ/kg was obtained at 260 °C. In general, all HHVs showed significant differences, with an increase in temperature having a beneficial effect. Hemicellulose, cellulose, and lignin are all discomposed when the temperature is elevated (in that sequence), and the product is hydrochar with a higher HHV. The HHV rise with reaction temperature during the HTC process is also explained by the C enrichment as well as the depletion of O mass fraction. Because of the rise in FC, hydrochar's fuel qualities get better at higher temperatures [4], [5], [16], [18].

3.3. Influence temperature and time on hydrochar properties

The results indicated that temperature had a greater negative impact on hydrochar yield than time. This behaviour was expected since, according to Murillo et al. [18], temperature is the main factor favouring hydrothermal carbonization processes. When the process temperature was raised from 180 to 260 °C for 30 minutes, the hydrochar mass yield decreased substantially (p 0.05) by 29%, while at 120 minutes, it only decreased by 11% (Table 1). As expected, HTC at 180 °C for 30 minutes, the mildest conditions tested, had the highest mass yield (75.01 wt.%). This is due to the change that takes place in the biomass during HTC conversion [9]. To create pentose and hexose monomers, cellulose and hemicellulose must first be hydrolyzed. This is followed by dehydration, which produces intermediate compounds such as furfurans and organic acids. When lignin is hydrolyzed, phenols and catechol are produced. Aromatic oligomers, which are converted to hydrochar, are produced by the final stage of polymerization and cross-linking. Similar patterns have been observed by other researchers, especially in feedstocks with high lignocellulosic content, such as chicken litter [3], loblolly pine [19], oat hulls [18], and cow dung [16]. However, CM is a complex residue full of organic components and nutrients (N and P) compared to lignocellulosic materials. Biomass degradation is complicated by organic materials produced by microorganisms, such as lipids, proteins, nucleic acids, and carbohydrates [9]. The amino

acid content, the hydrothermal conditions used, and the pH of the solution are just a few examples of factors that can affect the protein breakdown process. Compared to the 1,4- and 1,6-glycosidic bonds found in cellulose and starch, the peptide bond of proteins has a higher degree of stability, which makes the depolymerization process slower [20].

Although the residence time was not as important as the reaction temperature, it did have a detrimental effect on the mass yield, especially at low temperatures. When the temperature was increased from 30 to 120 minutes, it was observed that the mass yield decreased faster at 180 °C (29%) than at 260 °C (14%). Because pH has an effect on the HTC reaction, organic acidic compounds made when hemicellulose breaks down can speed up the breakdown of cellulose even at temperatures below 200 °C [21]. Reza et. al [19] states that for HTC at 200 °C and 230 °C, the mass yield decreased with longer residence times to around 54%; however, at higher reaction temperatures (260 °C), the mass yield varies less intensely with longer residence times. On the other hand, over a longer period, amino acids form a Maillard reaction with sugar breakdown products (containing carbonyl groups) to create N-ring molecules [22]. Since CM contains a significant amount of proteins, it can be inferred that prolonged residence time causes charring as a result of the degradation of the protein and amino acid species that are part of its composition.

The range of the hydrochar's EDr was 1.16-1.39. Temperature and time both caused the values to rise significantly ($p < 0.05$) (Table 1). Due to the reduced lignin content of its feedstock compared to other types of biomass like woody biomass, which results in a lower HHV before and after the HTC process, the EDr of CM-hydrochar was lower than other hydrochars generated under comparable conditions.

The best energy yield was achieved from hydrochar produced at 180 °C for 30 min, which is comparable to that found in CM-hydrochar produced at 240 °C for 30 min, as reported by Hejna et. al [7]. Since the decreased mass yield greatly lowers energy yield, the HTC conditions with the highest mass yield values are those with the highest energy yield [3]. On the other hand, it is expected that at low temperatures the degree of carbonization is lower and therefore the energy value is closer to that of untreated biomass, which is why a compromise must be found between mass yield and energy yield. At 180 degrees for 120 minutes, a hydrochar with high HHV (19.37 MJ/kg) and a reasonable mass yield (around 50 %) is produced. Since an important issue in industrial processes is energy self-sufficiency, future CM-HTC studies should focus on optimizing the conditions to achieve a hydrochar with high a HHV and reasonable mass yield.

4. Conclusion

The temperature was the most influential factor on the fuel properties of CM hydrochar, while the residence time had a prominent influence at lower temperatures (180°C). The most carbonized hydrochar, like sub-bituminous coal, was produced at the highest temperature and longest residence time (260 °C, 120 min). The best mass and energy yield (75 % and 79 %, respectively) were obtained in the hydrochar generated at 180 °C for 30 minutes. The hydrochar with the best calorific value (19.37 MJ/kg) and EDr (1.27) was produced at 180 °C for 120 min. The hydrochar produced under these conditions was selected as the best due to its fuel properties in addition to its reasonable mass yield (around 50 %). This study found that HTC could produce CM-hydrochar with superior properties as solid fuels compared to raw material. Before scaling up the process, optimization should be carried out to achieve a sustainable process.

Acknowledgements

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