Treatment of granulated organic manure based on bird droppings by hydrothermal carbonization and torrefaction methods

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Abstract. Hydrothermal carbonization (HTC) and torrefaction are modern low-temperature methods of converting different types of biomass into biochar. In both processes temperature significantly affects the product distribution and character of solid product. The heating values of HTC biochar was much higher than torrefacted biochar and 40% higher compared to the initial raw materials (15.68 MJ/kg for raw materials, 22.3 MJ/kg for HTC 210 °C). Biomass has increased carbon content. The maximun one has biochar obtained at 210 °C (55% higher compared to the initial raw materials). The energy densification ratio and energy yield was also higher in HTC process compared to torrefaction process. Hydrochar has less ash that biochar obtained by torrefaction due to washing part of inorganic into the liquid phase.

1. Introduction
The constantly worsening environmental situation in Russia is a real problem. Particularly the problem of recycling livestock has recently become quite acute. Meat consumption is growing. According to official statistics, about 700 million tons of liquid waste from poultry and livestock production are generated annually in Russia. Unfortunately, there is no universal technology that could process animals to produce value-added products.

Dry chicken litter can be used as fertilizer. However, at present there is a tendency to prohibit fertilizers of this type due to the fact that they may contain pathogenic microbes. But chicken litter could be used as an organic material for biocoil obtaining in spite of to its high humidity. In this paper the possibility of chicken litter processing by hydrothermal carbonization (HTC) and torrefaction was studied. HTC and torrefaction are modern low-temperature methods of improving characteristics of biomass of different origin. The main difference in methods is the ability to process biomass of high humidity via hydrothermal carbonization.

Hydrothermal carbonization is carried out in anaerobic conditions in presence of subcritical, liquid water. It proceeds usually at temperatures ranging from 180 to 280 °C. The main products, that obtained in this process are gases, aqueous chemicals, and a solid hydrochar. Hydrochar is a homogenized, carbon-rich, and energy-dense solid fuel, which is biologically sterilized due to thermal treatment [1]. Hydrothermal carbonization also could be used as a sterilization step within fermentation processes to destroy bacterial cultures dangerous for the environment.

Torrefaction is a low-temperature biomass processing method that is carried out in anaerobic conditions and where the hydroxyl groups are removed. Thus producing hydrophobic material-
biocoil [2]. The biomass moisture should be reduced down to 15% before torrefaction treatment. The process temperature is 200–300 °C and pressure is atmospheric [3, 4]. Sterilization during torrefaction also occurs (bacteria do not survive at temperatures above 122 °C).

The influence of methods at different temperatures on the physicochemical and energy properties of the resulting biochar (biocoil made by torrefaction) and hydrochar (biocoil made by HTC) is studied.

2. Material and methods

2.1. Raw material

The material in this work is granulated organic manure based on bird droppings. The samples for torrefaction was dried at 105 °C until moisture content was reduced to a level of less than 2% by weight. Samples for HTC do not processed previously.

2.2. Hydrothermal carbonization

Hydrothermal carbonization has been carried out in a steel autoclave reactor that was heated by electric tube furnace. Raw material was mixed with water in a ratio of 1 : 3. The suspension was placed into a reactor and was kept there 4 h at the chosen temperature from 180 to 210 °C. After the process was completed, the reactor was removed from the furnace and forcibly cooled with water to a room temperature. The resulting suspension was divided into liquid and solid residue on filter paper. The solid particles were dried at open space at laboratory without extra heating at temperature for 72 h.

2.3. Torrefaction

Torrefaction process has been carried out in reactor and was heated by an electric tube furnace. Raw material was put into the reactor. Before the heating begin the reactor was blown by argon to provide oxygen-free environment. The target torrefaction temperatures were selected from 230 to 300 °C. The reactor was heated to the target temperature under heating rate at 7 °C/min and then holds there for 1 h. After torrefaction was completed, solid products were collected and placed to desiccator for further analysis.

2.4. Analytical method

Raw materials and processed materials were analyzed with the use of elemental analysis. The weight percentages of N, C, H, and S in the starting materials were measured using a Vario Macro Cube analyzer. For the determination of ash content, a muffle furnace was used. The oxygen content was determined by difference. Calorific value was calculated based on the elemental analyses by Mendeleev equation. Oxygen (O, wt %) for dry state was calculated from material balance:

\[ O = 100 - (C + H + N + S + \text{Ash}), \]

where C, H, N, S, Ash are the content of carbon, hydrogen, nitrogen, sulfur and ash content calculated on dry basis, wt %. The heating values were calculated from the Mendeleev’s equation on the basis of elemental composition [5]:

\[ HHV = 0.339C + 1.256H + 0.109S - 0.109O, \]

\[ LHV = 0.339C + 1.256H + 0.109S - 0.109O - 0.0252(9H + W), \]

where HHV and LHV are the highest and lowest calorific values respectively, kJ/kg; C, H, O, S, W are carbon, hydrogen, oxygen, combustible sulfur and moisture calculated on dry basis, wt %.
The mass yield $y_m$ describes a percentage of raw material remaining in biochar; it is calculated as the ratio of carbonized product in weight ($m_c$) to raw biomass weight ($m_b$) in %:

$$y_m = \frac{m_c}{m_b}.$$ \hfill (4)

The energy yield $y_e$ indicates a percentage of feedstock caloricity remains in the solid residue in %. The index is calculated as

$$y_e = \frac{y_m \text{HHV}_c}{\text{HHV}_b},$$ \hfill (5)

where $\text{HHV}_c$ and $\text{HHV}_b$ are the highest heating values of product and feedstock respectively.

3. Results and discussion

3.1. Elemental composition

In table 1, some results of the analysis of initial biomass, biocoil made by HTC and torrefaction at different temperatures are shown. One can see that the ash content of hydrochar rise due to a decrease in the organic part of the raw material, which is associated with an increase in the temperature of the hydrothermal carbonization process (from 16.7% at 180 °C to 22.2% at 210 °C). In the case of torrefaction there is the same temperature dependence and a higher amount of ash components is observed. It may be due to leaching of the mineral component part into the water during HTC [6]. According to the [7] it was mentioned, that a large proportion of the potassium and sodium is extracted during HTC, while magnesium and calcium along via HTC process are more desirable than their counterparts produced via torrefaction process in terms of ash content, regarding further thermochemical conversion (combustion, gasification, pyrolysis) of the chars require low inorganics content to prevent fouling, slagging in these processes [8].

In the elemental composition of the resulting biocoil changes were observed too. The share of carbon in the feedstock was 39.27%. The maximum value of carbon was received in the sample obtained by hydrothermal carbonization at 210 °C (53.33%), which is 25% more than the carbon concentration of the raw material. The biocoil made by torrefaction at 300 °C has a little less value in contrast with maximum one (47.10%). Also, degradation of oxygen more than 50% is noted. In the both cases carbon increases and oxygen reduced with the temperature rise. This pattern corresponds with the data from the literature [9].

3.2. Heating values

A change in the elemental composition of a substance, of course, occurs in the order of change in its calorific value. Heating values of the raw material and biocoils are presented in figure 1. The maximum data of the calorific value corresponds to the sample obtained by hydrothermal carbonization at 210 °C (22.3 MJ/kg), which is 40% more compared to the raw materials. In the general trend, calorific abilities of hydrochars are higher than samples made by torrefaction at a lower temperature. A similar trend is observed with other types of biomass [10].

3.3. Mass and energy yield

One of the most important parameter influencing on the mass and energy yield is temperature [11, 12]. The energy yield of biocoil made by the torrefaction (65–80%) is slightly higher than obtained by the carbonization (65–75%) (figure 2), although the calorific values of the samples obtained by HTC are higher. This is due to the mass yield of biochar is from 50 to 75% for torrefaction and from 50 to 60% for hydrothermal carbonization (figure 3). In the article, the data [8] on the energy outputs of the hydrochars coincide, however, in the case of torrefaction, the energy output is slightly higher compered to obtained data. Most likely this is due to the biomass structure (in the article [8] presents the results of processing of grape pomace). Energy
Table 1. The effect of temperature ($t$) of hydrothermal carbonization and torrefaction on the composition of biocoil.

| Processing temperature $t$, °C | HTC (hydrochar) | Torrefaction (biochar) |
|-------------------------------|-----------------|-------------------------|
| Raw 180 190 200 210 230 250 270 300 |                 |                         |
| Ultimate analysis, wt %:       |                 |                         |
| C 39.27 49.1 50.27 49.65 53.33 44.56 46.97 47.05 47.10 |                 |                         |
| H 5.46 5.47 5.45 5.35 5.56 4.96 4.60 4.58 4.58 |                 |                         |
| N 3.59 3.31 3.51 3.63 3.97 3.86 4.23 4.24 4.24 |                 |                         |
| S 0.76 0.49 0.44 0.45 0.48 0.64 0.81 0.81 0.81 |                 |                         |
| O 31.54 24.28 22.47 17.50 13.79 26.82 21.82 19.39 15.68 |                 |                         |
| Ash 14.84 16.7 17.15 22.78 22.2 19.16 21.57 23.93 27.59 |                 |                         |

Figure 1. Heating values of biocoil.

densification ratio is a measure which indicates the ratio of HHV of product to HHV of raw biomass. As it was already said HHV of hydrochar slightly higher than biocoil obtained by torrefaction, therefore, in case with energy densification ratio it will have the same dependency (figure 4).
Figure 2. The energy yield of biocoil for HTC \((a)\), torrefaction \((b)\).

Figure 3. The mass yield of biocoil for HTC \((a)\), torrefaction \((b)\).

Figure 4. Energy densification ratio of biocoil for HTC \((a)\), torrefaction \((b)\).
3.4. Diagram of van Krevelen

Atomic $[\text{H}]/[\text{C}]$ and $[\text{O}]/[\text{C}]$ ratios of biochar and hydrochar were shown on van Krevelen diagram to observe the changes in atomic content (figure 5). There $[\text{H}]/[\text{C}]$ and $[\text{O}]/[\text{C}]$ ratio shows the steadily decrease due to the increment of temperature. Figure 5 shows that dehydration had the greatest effect on the atomic ratios of biochar made by both methods. The data indicate that the treated raw materials were update in both methods. In literature there is the same trend is observed [13, 14]. However, samples obtained by the method of hydrothermal carbonization fall into the areas of lignin (HTC 210 °C and HTC 200 °C) and peat (190 °C) on van Krevelen daigram. Biochar obtained by torrefaction at 300 °C falls on the cross line of peat and lignin area.

4. Conclusion

HTC and torrefaction are promising methods to convert different types of biomass to a high dense solid fuel for subsequent thermochemical conversion. In both processes temperature significantly affects the product distribution and character of solid product. In torrefaction process mass and energy yield was greater than HTC process. However the heating values of HTC biocoal was much higher than biochar. Biomass has increased carbon content indicating that the biomass has been transformed into a fuel with resembling to coal. The energy densification ratio and energy yield was also higher in HTC process than torrefaction process. The samples obtained by the method of hydrothermal carbonization fall into the areas of lignin and peat on van Krevelen diagram. Also worth noting that hydrochar has less ash, which gives it an advantage when it is burned to produce energy.
References
[1] Wilk M and Magdziarz A 2017 Energy 140 1292–304
[2] Shen Y, Yu S, Ge S, Chen X and Ge Xinlei Chen M 2017 Energy 118 312–23
[3] Guizani C, Haddad, Khouloud Jeguirim M, Colin B and Limousy L 2016 Energy 107 453–63
[4] Cellatoglu N and Ilkan M 2016 BioResources 11 6286–98
[5] Beskov S D 1962 Tekhno-khimicheskie Raschety (Moskva: Vysshaya Shkola)
[6] Smith A M, Singh S and Ross A B 2016 Fuel 169 135–45
[7] Toufiq Reza M, Lynam J G and Helal Uddin M Coronella C J 2013 Biomass Bioenergy 49 86–94
[8] Palaalsmail M, Hasan C K, Buyukisikc B and Yanikabc J 2014 Bioresour. Technol. 161 255–62
[9] Kambo H and Dutta A 2015 Energy Convers. Manage. 105 746–55
[10] Gultekin S Y, Olgun H and Celiktas M S 2018 Int. J. Eng. Technol. 7 143–7
[11] Roy P and Dutta A 2018 Energies 11 1–14
[12] Ahiduzzaman M and Islam A K M S 2015 Procedia Eng. 105 719–24
[13] Cardona S, Gallego Morales L, Valencia V, Martinez E and Alberto Rios L 2019 Sustainable Energy Technol. Assess. 31 17–24
[14] Wei Y, Hui W, Meng Z, Jiayu Z, Jie Z and Shengji W 2016 Bioresour. Technol. 205 199–204