


## Article

# Some Results of Poultry Litter Processing into a Fertilizer by the Wet Torrefaction Method in a Fluidized Bed

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**Abstract:** Poultry litter mass is formed in large quantities at poultry farms producing poultry meat (1–3 kg of litter mass per 1 kg of produced meat). These wastes represent a threat to the environment because of the presence of pathogenic microflora in them and the greenhouse gas emitted during the storage of these wastes. The procedure of poultry litter mass processing by wet torrefaction in a superheated water vapor environment at a temperature of 150–260 °C is studied. It is shown that after torrefaction at a temperature of 150 °C, the poultry litter mass retains high humidity, i.e., it represents an environment suitable for the re-development of pathogenic microflora. Only after wet torrefaction at a temperature of 260 °C does the humidity of the poultry litter mass decrease to 4%, and the risk of re-infection with pathogenic microflora decreases sharply. The absence of nitrates in the samples after torrefaction at a temperature of 260 °C indicates the termination of the activity of nitrifying bacteria. After torrefaction at a temperature of 260 °C, the poultry litter mass has a pH close to 7. This increases the mobility and availability of microelements for plants. Torrefaction at a temperature of 260 °C increases the content of ash, phosphorus and potassium by 30–40% and nitrogen by 15–20%, which makes the fertilizer more concentrated and optimizes the ratio of nitrogen, phosphorus and potassium. After wet torrefaction, due to the burning of the most easily degradable nitrogen-containing organic compounds and the destruction of some organophosphorus compounds, the mobility of nitrogen decreases, and the mobility of phosphorus increases. As a result of the research, it was found that the treatment of poultry manure by wet torrefaction in an environment of superheated water vapor at a temperature not lower than 260 °C makes it possible to obtain organic fertilizer with the most optimal nutrient content.

**Keywords:** poultry litter; wet torrefaction; fluidized bed; biochar; soil improver



**Citation:** Isemin, R.; Mikhalev, A.; Milovanov, O.; Nebyvaev, A. Some Results of Poultry Litter Processing into a Fertilizer by the Wet Torrefaction Method in a Fluidized Bed. *Energies* **2022**, *15*, 2414. <https://doi.org/10.3390/en15072414>

Academic Editor: Javier Feroso

Received: 26 January 2022

Accepted: 23 March 2022

Published: 25 March 2022

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## 1. Introduction

A lot of research papers have been devoted to the production of bio-coal from bio-waste [1–9]. The obtained bio-coal can be applied as a raw material for the production of sorbents, as fuel, or can be used as a fertilizer to improve the soil [10–15]. This direction of using bio-coal seems very promising because it allows one to return the nutrients contained in the biomass to the soil.

Bio-coal is produced from biomass in a process called torrefaction. Torrefaction or mild pyrolysis is a thermochemical process occurring in the range of 200–300 °C, often at atmospheric pressure in the absence of oxygen or in the presence of a small amount of oxygen. As a result of torrefaction, biomass dries up, and the gases are partially removed from it [16]. Torrefied biomass is known for its properties such as improved hydrophobicity and grindability, high energy density, as well as resistance to biodegradation, which makes it suitable for a number of applications [17].

Most research so far has mainly focused on the production of torrefied biomass as a fuel or energy source. Very few studies are devoted to its application as a biochar for soil improvement. In [18], torrefied biomass was considered as an effective additive to

the soil to improve moisture retention, increase the structural stability of the soil and the development of soil microflora. In [19], the efficiency of using bio-coal obtained from different types of biomasses for soil improvement was analyzed.

In the above-mentioned works, the obtained bio-coal during the torrefaction of lignin-cellulose biomass (pine chips, rice husk, wheat cleaning waste, sugar beetroot processing waste, grape juice production waste, wheat straw, spruce bark, spruce chips, spruce sawdust, hay, rapeseed straw, beer production waste and other waste) was studied. Biochar manufactured from plant residues is generally applied as a soil conditioner rather than as a fertilizer, given that it tends to have low contents of leachable nutrients [20]. Conversely, biochar derived from manures are more suitable as fertilizers, owing to their release of plant essential nutrients such as N, P and K [21].

However, a type of waste such as poultry litter mass, which (1–3 kg of poultry litter mass per 1 kg of produced poultry meat) is formed in large quantities at poultry farms, has so far been out of sight of researchers occupied with obtaining bio-coal from bio-waste to improve the soil and fertilizer [22]. Poultry litter mass usually has a fairly high moisture content. For the processing of wet biowaste, the process of hydrothermal carbonization is used. Although hydrothermal carbonization produces a final carbonaceous material from wet feedstock, in the absence of the energy-intensive pre-drying step [23], additional thermal energy is typically required for the post-treatment of hydrothermal carbonization material, such as separating the solid and liquid products [24].

The hydrothermal carbonization or wet torrefaction of dry poultry litter mass to be carried out in a fluidized bed in a superheated water vapor environment was proposed [19,25]. The use of superheated vapor ensures the fire safety of the process and the possibility of the torrefaction process being conducted in a wide temperature range. The obtained condensate after cooling the superheated vapor can be used for the production of biogas or for the production of valuable chemical products [26]. Waste superheated steam can be used to dry off wet poultry litters.

After wet torrefaction in a fluidized bed, the ash content in biochar increases 1.9 times compared to the ash content in the original poultry litter [25]. However, the ash from these wastes is also a rich source of potassium, and its use replaces the commonly used potassium salts  $K_2SO_4$  and  $KNO_3$  [27].

The purpose of this paper is to study the changes in the chemical content of the poultry litter mass during its torrefaction in a superheated water vapor environment in relation to the use of the obtained biochar as a soil improver.

## 2. Materials and Methods

In order to study the process of wet torrefaction in a fluidized bed in an environment of superheated water vapor, an installation was created [19].

The installation consisted of a reactor for wet torrefaction in the fluidized bed, a hopper for the initial biomass, a hopper for bio-coal, a cyclone for separating the vapor-gas flow from the bio-coal particles removed from the reactor and a condenser of the vapor-gas mixture.

A mixture of chicken manure with sawdust was subjected to torrefaction. With the start of the feed of the initial material, the gas analyzer “Vario Plus Industrial Syngas” continuously selected non-condensable gases behind the condenser and determined the content of CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. From the beginning of the biomass supply to the reactor, the concentration of CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> in non-condensable gases began to increase and reached a maximum after loading the entire portion of the initial biomass into the reactor. Then the concentration of these components began to decrease and eventually reached the values that were before the initial biomass was fed into the reactor for torrefaction. It is believed that at this moment, the torrefaction of the biomass portion was completed, and the biochar was discharged from the reactor.

The initial biomass was fed into the reactor in the form of powder or pellets. During the heat treatment of biomass in the form of pellets, the fluidized bed was formed by quartz sand particles.

The obtained biochar was subjected to chemical analysis to determine the effect of biomass heat treatment temperature on moisture content, ash content, total content of organic carbon, total content of nitrogen, nitrogen compounds, total content of potassium, phosphorus and their water-soluble compounds.

Humidity was determined by the thermostatic-weight method. The method consisted of placing 2–3 g of ground and sifted fertilizers through a 0.25 mm sieve in a glass weighting bottle previously dried to a constant mass and dried in a drying cabinet Type 2B-151 at a temperature of 106 °C to a constant mass, then weighed with an error of 0.002 g.

The ash content was determined after burning the sample in a muffle furnace MP2UM at a temperature of 800 °C. The method consisted of taking a weight of 3 g from the dry residue after thorough mixing and placing it in porcelain crucibles, which must be pre-annealed in a muffle furnace at a temperature of 800 °C and annealed in a muffle furnace first for 2 h, then for an hour to a constant mass.

The acidity (pH of 1% of the water extract) was determined potentiometrically by pH meter pH 512.

The total content of organic carbon was determined by a method based on the oxidation of organic matter of fertilizers with a solution of potassium bicarbonate in sulfuric acid, followed by the determination of trivalent chromium equivalent to the content of organic matter by titration with Mohr salt. Phenylanthranilic acid was used as an indicator during the titration of potassium bichromate. No-load titration was carried out in parallel.

Calculation of the results of carbon determination is carried out according to the equation:

$$\%C = \frac{(a - b) * n * 0.003}{m} * 100 \quad (1)$$

where  $a$  is the amount of Mohr's salt used for titration when determining the normality of the bichromate solution, mL;  $b$  is the amount of Mohr's salt used for the titration of the chromium mixture after burning the sample, mL;  $n$  is the normality of the Mohr's salt; and  $m$  is the fertilizer sample.

The water-soluble organic matter was determined by a method which consisted of extracting labile easily decomposable organic matter with hot distilled water (boiling with a reverse refrigerator for 5 min) and filtering the solution through a folded filter. Aliquot filtrate was evaporated in a water bath to wet salts. Then, the water-soluble organic matter of fertilizers was oxidized with a solution of potassium bicarbonate in sulfuric acid, followed by the determination of trivalent chromium equivalent to the content of organic matter by titration with Mohr's salt. Phenylanthranilic acid is used as an indicator during the titration of potassium bichromate. No-load titration is carried out in parallel.

Calculation of the results of carbon determination is carried out according to the equation:

$$\%C = \frac{(a - b) * n * 0.003 * V_1}{m * V_2} * 100 \quad (2)$$

where  $a$  is the amount of Mohr's salt used for titration when determining the normality of the bichromate solution, mL;  $b$  is the amount of Mohr's salt used for titration of the chromium mixture after burning the sample, mL;  $n$  is the normality of the Mohr's salt,  $m$  is the fertilizer weight,  $V_1$  is the volume of distilled water and  $V_2$  is the aliquot of the solution taken for evaporation.

The total N was determined by the following method. The mineralization of the samples was carried out by wet ashing in Kjeldahl flasks with hydrochloric acid with hydrogen peroxide. Boiling was continued until the solution was completely discolored. The obtained mineralized solution served as a starting point for determining the mass fraction of the total forms of nitrogen, phosphorus and potassium. In order to determine the total nitrogen, an aliquot of mineralizate was placed in the reaction flask. Then, 30–40 mL of 4% boric acid solution and 3–5 drops of mixed indicator were placed in the receiver; 25 mL of 40% sodium hydroxide was poured into the reaction flask and boiled until there was no reaction to ammonia according to the indicator paper. The contents of the receiver

were titrated with a solution of 0.05n sulfuric acid until the green color changed to crimson. In parallel, we conducted a no-load experiment.

The mass fraction of total nitrogen ( $X$ ) is calculated by the formula:

$$X = \frac{0.0014 * (V_2 - V_3) * V_1}{V_4 * m} * 100 \quad (3)$$

where  $m$  is the fertilizer weight;  $V_1$  is the volume of the initial solution;  $V_2$  is the volume of the 0.05n sulfuric acid solution consumed for titration of the analyzed solution, mL;  $V_3$  is the volume of the 0.05n sulfuric acid solution in the no-load experiment; and  $V_4$  is the volume of the analyzed solution taken for distillation.

$\text{NO}_3$  content was determined photometrically with hydrazine by spectrophotometer—KFK-3KM. The method consists of placing a weight of 20 g of fertilizers ground and sifting through a 0.25 mm sieve into a 250 mm conical flask, pouring 100 mL of 1n  $\text{KS}_1$ , shaking on a rotator for 1 h and filtering through a folded filter. To 5 mL of the filtrate, 10 mL of an alkaline solution of sodium pyrophosphate and 10 mL of a working reducing solution were poured and mixed. After 10 min, 25 mL of a coloring solution was added, and after 15 min, it was photometered at a wavelength of 545 nm.

The calculation is carried out according to the formula:

$$\text{NO}_3 = \frac{a * P * 1000 * K}{m} \quad (4)$$

where  $a$  is the nitrate content according to the graph, mg/mL;  $P$  is the dilution;  $K$  is the conversion factor for a dry weight; and  $m$  is the weight of the weighted portion.

The  $\text{NH}_4$  content was determined by extracting ammonium nitrogen from a sample of organic fertilizer with a solution of 0.05n hydrochloric acid, followed by the distillation of ammonia in a solution of boric acid and titration with sulfuric acid.

The mass fraction of total ammonium nitrogen ( $X$ ) is calculated by the formula:

$$X = \frac{0.00028 * (V_2 - V_3) * V_1}{V_4 * m} * 100 \quad (5)$$

where  $m$  is the fertilizer weight;  $V_1$  is the volume of the initial solution;  $V_2$  is the volume of the 0.05n sulfuric acid solution consumed for titration of the analyzed solution, mL;  $V_3$  is the volume of the 0.05n sulfuric acid solution in the no-load experiment;  $V_4$  is the volume of the analyzed solution taken for distillation.

$\text{SiO}_2$  (silicate residue) was determined by the weight method. A silicate residue remained in the mineralization after wet ashing with concentrated acid. The mineralizate was filtered through a folded decontaminated filter. The residue on the filter was repeatedly washed with distilled water, placed in porcelain crucibles, which must be pre-calcined in a muffle furnace at a temperature of 800 °C and annealed in a muffle furnace first for 2 h, then for an hour to a constant mass.

The total content of  $\text{P}_2\text{O}_5$  was determined photometrically by spectrophotometer—KFK-3KM. After wet ashing, the mineralizate was poured into a 100 mL volumetric flask. An aliquot (0.2–2 mL) was taken from it into a 50 mL measuring flask, 20 mL of distilled water was poured and neutralized with ammonia. Next, 2 mL of ammonium molybdenum solution and 3 drops of tin chloride solution were added and brought to the mark with water. After 10–15 min, colorimetry was performed on a spectrophotometer at a wavelength of 725 mL. The calculation is carried out according to the formula:

$$\text{P}_2\text{O}_5\% = \frac{a * V_1 * 100 * K}{m * V_2 * 1000} \quad (6)$$

where  $a$  is the content of  $\text{P}_2\text{O}_5$  according to the graph, mg/mL;  $V_1$  is the volume of the solution;  $V_2$  is the volume of the aliquot taken for analysis;  $K$  is the conversion factor for a dry sample; and  $m$  is the weight of the sample.

The total K<sub>2</sub>O content was determined by flame photometric method by spectrophotometer—KFK-3KM. After wet ashing, the mineralizate was poured into a 100 mL volumetric flask. An aliquot (0.2–2 mL) was taken from it into a 50 mL measuring flask, brought to the mark with water and injected into the suction device of a flame photometer. The calculation was carried out according to the formula, similar to formula (6).

The total Ca content was determined titrimetrically. The mineralization of the samples was carried out by dry salting in porcelain crucibles in a muffle furnace at a temperature of 800 °C. The mineral residue was dissolved with 5 mL of concentrated hydrochloric acid and transferred to 100 mL volumetric flasks, brought to the mark with water. The 1–20 mL aliquot into 250 mL conical flasks was taken and diluted to 50 mL with distilled water; 10 mL of 20% NaOH solution and the murexide indicator on the tip of the knife were added. A solution of 0.02n with a solution of trilon B was titrated until the color changed from pink to purple. In parallel, a no-load experiment was carried out.

The mass fraction of calcium (*X*) is calculated by the formula:

$$X = \frac{20 * (V_2 - V_3) * n * V_1}{V_4 * m} * 100 \quad (7)$$

where *m* is the fertilizer weight; *V*<sub>1</sub> is the volume of the initial solution; *V*<sub>2</sub> is the volume of the trilon B solution consumed for titration of the analyzed solution, mL; *V*<sub>3</sub> is the volume of the trilon B solution in the no-load experiment; and *V*<sub>4</sub> is the volume of the aliquot taken for analysis.

The total Mg content was determined titrimetrically. The mineralization of the samples was carried out by dry salting in porcelain crucibles in a muffle furnace at a temperature of 800 °C. The mineral residue was dissolved with 5 mL of concentrated hydrochloric acid and transferred to 100 mL volumetric flasks, brought to the mark with water. A 1–20 mL aliquot into 250 mL conical flasks was taken. After, it was diluted to 50 mL with distilled water, neutralized with ammonia, and 10 mL of ammonium chloride buffer and a chromogen indicator at the tip of the knife were added. A solution of 0.02n with a solution of trilon B was titrated until the color changed from wine-red to blue. In parallel, a no-load experiment was carried out.

The mass proportion of calcium (*X*) is calculated by the formula, similar to formula (7).

The total content of Na<sub>2</sub>O was determined by flame photometric method by flame photometer FPA-2-01 automatic. After wet salting, the mineralizate was poured into a 100 mL volumetric flask. An aliquot (0.2–2 mL) was taken from it into a 50 mL measuring flask, brought to the mark with water and injected into the suction device of a flame photometer. The calculation is carried out according to the formula:

$$\text{Na}_2\text{O} \% = \frac{a * V_1 * 100 * K}{m * V_2 * 1000} \quad (8)$$

where *a* is the Na<sub>2</sub>O content according to the graph, mg/mL; *V*<sub>1</sub> is the volume of the solution; *V*<sub>2</sub> is the volume of the aliquot taken for analysis; *K* is the conversion factor for a dry sample; and *m* is the weight of the sample.

The total content of water-soluble salts was determined by conductometric method. The essence of the method was to extract water-soluble salts from the soil with distilled water at a ratio of organic fertilizer to water of 1:5, and the total salt content was determined using a conductometer by specific electrical conductivity.

Water-soluble K<sub>2</sub>O was determined by flame photometric approach by flame photometer FPA-2-01 automatic. An aliquot (0.2–2 mL) was taken from a water extract into a 50 mL volumetric flask, brought to the mark with water and injected into the suction device of a flame photometer. The calculation is carried out according to the formula, similar to formula (8).

Water-soluble P<sub>2</sub>O<sub>5</sub> was determined photometrically flame photometer FPA-2-01 automatic. An aliquot (0.2–2 mL) was taken from an aqueous extract into a 50 mL measuring

flask, 20 mL of distilled water was poured and 2 mL of ammonium molybdenum solution and 3 drops of tin chloride solution were added, brought to the mark with water. After 10–15 min, colorimetry was performed on a spectrophotometer at a wavelength of 725 mL. The calculation is carried out according to the formula, similar to formula (8).

$\text{NCO}_3$  was determined titrimetrically. An aliquot was taken from an aqueous extract, 2–3 drops of methylorange solution were added and titrated with 0.01n sulfuric acid solution until the transition from yellow to orange occurred. The calculation is carried out according to the formula:

$$X = \frac{61 * V_2 * n * V_1}{V_3 * m} * 100 \quad (9)$$

where  $m$  is the fertilizer weight;  $V_1$  is the volume of the initial solution;  $V_2$  is the volume of the sulfuric acid solution consumed for titration of the analyzed solution, mL;  $V_3$  is the volume of the aliquot taken for analysis; and  $n$  is the normality of the sulfuric acid solution.

Cl content was determined argentometrically. The essence of the method was the titration of the chloride ion into the aliquot of the aqueous extract with a solution of silver nitrate, which forms a difficult-to-dissolve compound with the chloride ion. In order to establish the end point of titration, potassium chromate was added to the solution, forming a residue with an excess of silver, causing the color of the solution to change from yellow to red-brown. The calculation is carried out according to the formula:

$$X = \frac{35 * V_2 * n * V_1}{V_3 * m} * 100 \quad (10)$$

where  $m$  is the fertilizer weight;  $V_1$  is the volume of the initial solution;  $V_2$  is the volume of the silver nitrate solution consumed for titration of the analyzed solution, mL;  $V_3$  is the volume of the aliquot taken for analysis; and  $n$  is the normality of the silver nitrate solution.

The  $\text{Ca}^{2+}$  content was produced by titrimetric method. An aliquot of water extract was taken into a 250 mL conical flask, diluted to 50 mL with distilled water and 10 mL of 20% NaOH solution and a murexide indicator on the tip of the knife were added. A solution of 0.02n was titrated with a solution of trilon B until the color changed from pink to purple. In parallel, a no-load experiment was carried out.

The mass proportion of calcium ( $X$ ) is calculated by the formula:

$$X = \frac{20 * (V_2 - V_3) * n * V_1}{V_4 * m} * 100 \quad (11)$$

where  $m$  is the fertilizer weight;  $V_1$  is the volume of the initial solution;  $V_2$  is the volume of the trilon B solution consumed for titration of the analyzed solution, mL;  $V_3$  is the volume of the trilon B solution in the no-load experiment;  $V_4$  is the volume of the aliquot taken for analysis.

The  $\text{Mg}^{2+}$  content was determined titrimetrically. An aliquot of water extract was taken into a 250 mL conical flask, diluted to 50 mL with distilled water and 10 mL of ammonium chloride buffer and a chromogen indicator at the tip of the knife were added. A solution of 0.02n was titrated with a solution of trilon B until the color changed from wine-red to blue. Simultaneously, a no-load experiment was carried out.

The mass proportion of calcium ( $X$ ) is calculated by the formula:

$$X = \frac{12 * (V_2 - V_3) * n * V_1}{V_4 * m} * 100 \quad (12)$$

where  $m$  is the fertilizer weight;  $V_1$  is the volume of the initial solution;  $V_2$  is the volume of the trilon b solution spent on titration of the analyzed solution, mL;  $V_3$  is the volume of the trilon bz solution spent on calcium titration; and  $V_4$  is the volume of the aliquot taken for analysis.

The  $\text{SO}_4^{2-}$  content was determined by turbidimetric method. The essence of the method consisted of precipitation of the sulfate ion with barium chloride and the tur-

bidimetric determination of it in the form of barium sulfate. Glycerin was used as a suspension stabilizer.

To perform this, an aliquot of water extract was placed in a 25 mL volumetric flask, and 5 mL of the precipitation mixture was added, brought to the mark with water. After 15 min, it was proceeded to photometry at a wavelength of 520 nm.

The calculation is carried out according to the formula:

$$\text{SO}_4 \% = \frac{a * V_1 * 100 * K}{m * V_2 * 1000} \quad (13)$$

where  $a$  is the  $\text{SO}_4$  content according to the graph, mg/mL;  $V_1$  is the volume of the solution;  $V_2$  is the volume of the aliquot taken for analysis;  $K$  is the conversion factor for a dry sample; and  $m$  is the weight of the sample.

The content of  $\text{Na}^+$  was determined by the flame photometric method. From the water extract, an aliquot was taken into a 50 mL volumetric flask, brought to the mark with water and injected into the suction device of a flame photometer. The calculation is carried out according to formula (13).

### 3. Results and Discussion

Table 1 shows the results of the chemical analysis of bio-coal obtained from the poultry litter mass by wet torrefaction in a fluidized bed in an environment of superheated water vapor at different processing temperatures.

**Table 1.** Results of chemical analysis of initial material and bio-coal obtained from poultry litter.

Experimental conditions	Duration, min.	Raw Poultry Litter	Biochar (Powder)	Biochar (Pellets)	Biochar (Pellets)	Biochar (Pellets)	Biochar (Pellets)
	Temperature, °C	-	60	80	110	140	40
			250	145–155	145–155	145–155	260
Humidity	% from weight	10.92 ±0.04	4.14 ±0.03	4.80 ±0.04	5.37 ±0.03	5.79 ±0.07	4.62 ±0.04
pH 1% of water solution	unit. pH	7.12 ±0.06	7.23 ±0.04	6.39 ±0.09	6.28 ±0.06	6.28 ±0.07	6.76 ±0.07
C org (general)	% from weight	33.9 ±2.6	40.8 ±2.7	35.5 ±0.8	37.5 ±0.7	38.7 ±1.6	39.2 ±0.8
C org (water-soluble)	% from weight	6.6 ±0.1	2.8 ±0.3	5.5 ±0.2	4.7 ±0.1	5.0 ±0.3	1.5 ±0.2
N general	% from weight	8.43 ±0.56	7.08 ±0.19	8.41 ±0.19	8.01 ±0.21	7.63 ±0.27	8.78 ±0.34
N water-soluble	% from weight	0.88 ±0.06	0.58 ±0.03	0.93 ±0.03	0.93 ±0.03	0.86 ±0.12	0.67 ±0.15
$\text{NO}_3^-$	mg/kg	958 ±115	0	0	0	0	0
Ash	% from weight	12.42 ±0.23	18.14 ±0.63	12.42 ±0.12	12.62 ±0.27	12.82 ±0.30	17.31 ±0.09
$\text{SiO}_2$	% from weight	1.59 ±0.07	1.70 ±0.17	1.51 ±0.18	1.30 ±0.10	1.53 ±0.15	2.19 ±0.07
$\text{P}_2\text{O}_5$	% from weight	2.98 ±0.23	4.11 ±0.15	2.74 ±0.06	2.75 ±0.04	2.88 ±0.07	3.71 ±0.24

Table 1. Cont.

		Raw Poultry Litter	Biochar (Powder)	Biochar (Pellets)	Biochar (Pellets)	Biochar (Pellets)	Biochar (Pellets)
K <sub>2</sub> O	% from weight	3.01 ±0.06	3.33 ±0.01	2.14 ±0.07	2.18 ±0.31	2.08 ±0.03	2.73 ±0.08
Na <sub>2</sub> O	% from weight	0.27 ±0.01	0.45 ±0.01	0.56 ±0.01	0.49 ±0.02	0.48 ±0.02	0.52 ±0.01
CaO	% from weight	0.71 ±0.02	0.72 ±0.03	0.59 ±0.03	0.58 ±0.01	0.54 ±0.03	0.32 ±0.03
The content of water solutions. Salts	% from weight	4.59 ±0.10	5.02 ±0.09	5.44 ±0.12	5.18 ±0.15	5.17 ±0.10	4.80 ±0.08
Na <sub>2</sub> O water-soluble	% from weight	0.27 ±0.01	0.44 ±0.01	0.56 ±0.01	0.49 ±0.02	0.48 ±0.02	0.50 ±0.04
CaO water-soluble	% from weight	0	0	0	0	0	0
MgO water-soluble	% from weight	1.41 ±0.15	1.60 ±0.05	1.87 ±0.05	1.94 ±0.08	1.94 ±0.03	1.98 ±0.16
K <sub>2</sub> O water-soluble	% from weight	2.91 ±0.10	3.19 ±0.08	2.07 ±0.03	2.00 ±0.01	1.93 ±0.10	1.92 ±0.10
P <sub>2</sub> O <sub>5</sub> water-soluble	% from weight	0.337 ±0.014	0.529 ±0.021	0.509 ±0.016	0.518 ±0.008	0.533 ±0.042	0.553 ±0.029
Cl water-soluble	% from weight	1.20 ±0.04	0.95 ±0.09	1.03 ±0.06	0.89 ±0.07	1.20 ±0.04	2.00 ±0.04
NCO <sub>3</sub>	% from weight	4.34 ±0.23	3.24 ±0.02	3.12 ±0.31	2.82 ±0.05	2.87 ±0.15	2.33 ±0.20
SO <sub>4</sub> water-soluble	% from weight	0	0	0	0	0	0

As expected, the torrefaction temperature has a significant effect on the moisture and ash content of the resulting biochar.

The initial material (poultry litter mass), even in the dried state, has a humidity of 10–11%, after heat treatment at a temperature of 150 °C it decreases to 5–8% and to 4–5% after treatment at 260 °C.

The initial ash content of the material was 12.42%. After heat treatment at a temperature of 145–155 °C, the ash content of the biomass was practically unchanged. Only as a result of heat treatment at a temperature of 260 °C was there a noticeable increase in the ash content of biochar: up to 17.31% when processing poultry litter in the form of pellets and up to 18.14% when processing poultry litter in the form of powder. The yield of biochar after heat treatment at a temperature of 260 °C was 95.11% (when processing poultry litter in the form of pellets) and 94.28% (when processing poultry litter in the form of powder).

Previously [28], it was proven that poultry litter can be completely decontaminated at a temperature of 260 °C. Therefore, during the heat treatment of this type of biowaste by the method of wet torrefaction, it is obviously possible to limit the temperature to 260 °C.

It should be noted that during the processing of poultry litter by the method of wet torrefaction with an increase in the processing temperature, the yield of biochar decreases [29]. As a result of wet torrefaction at a temperature of 300 °C, the yield of biochar is 89.2%, and as a result of wet torrefaction at a temperature of 350 °C, it is 86.4%.

Torrefaction ensures sufficient low humidity. Torrefaction ensures the hydrophobicity of pellets, which reduces the risk of secondary contamination, even in contact with the environment during transportation.



Torrefaction changes the reaction of heat-treated poultry litter. The poultry litter mass has an initial alkaline reaction. Partial decarbonization occurs during heat treatment. As a result, the reaction of the poultry litter mass decreases to values close to neutral (pH—6.2–6.8), the most favorable for plant development. Confirmation of this fact is the decrease in the content of  $\text{HCO}_3^-$  in the aqueous extract from the samples after heat treatment.

Torrefaction changes not only the content of various components in biochar but also the mobility of these components. This is important from the point of view of the efficiency of using the obtained biochar as a fertilizer [22].

The content of organic matter in the initial poultry litter mass is 33–34% in terms of carbon. Organic matter is easily decomposable and very mobile (up to 15% of the total carbon goes into an aqueous extract).

Heat treatment leads to the charring of organic matter and a sharp decrease in its mobility (only 3–4% of the total carbon goes into water extraction). However, the total content of organic matter in the final product increases with raised intensity of heat treatment. During heat treatment with a temperature of 260 °C, the carbon content reaches 40%, and the color of the pellets turns black.

The total nitrogen content in the feedstock is 8–9%, 10–12% of which is in an easily degradable water-soluble form. The presence of nitrates in raw materials indicates the development of microbiological processes caused by the action of nitrifying bacteria.

Heat treatment at a temperature of 155 °C does not reduce the total nitrogen content, but at the same time, the proportion of water-soluble, easily decomposable forms does not decrease. The activity of nitrifying bacteria is significantly suppressed. This is shown by the absence of nitrates in all samples after heat treatment. Heat treatment at a temperature of 260 °C leads to a sharp decrease in the content of water-soluble, easily decomposable forms of nitrogen and the absence of an unpleasant smell in the samples.

The amount of water-soluble salts in bio-coal is about 5%, i.e., more than a third of the ash weight is easily dissolved in water. Almost the entire amount of sodium, potassium, magnesium, chlorides and bicarbonates passes into the water extract. This is indicated by the equal content of their gross and water-soluble forms. There are significantly fewer water-soluble forms of phosphorus. Only 0.3% of the 3% phosphorous content is in a mobile water-soluble form. Silicon and calcium practically do not pass into the water extract.

After heat treatment at a temperature of 155 °C, the ash composition is practically unchanged. Only the mobility of the phosphorus changes slightly. Due to the partial decomposition of organophosphorus compounds, the content of water-soluble forms of phosphorus increases from 0.3 to 0.5%.

After heat treatment at a temperature of 260 °C, due to the partial combustion of organic components, the proportion of ash in the final product increases to 18 to 20%. Accordingly, the proportion of all mineral components increases. At the same time, the mobility of potassium decreases slightly (70–80% goes into an aqueous solution against 100% in the initial material), and the mobility of phosphorus increases (the content of water-soluble forms increases to 0.6%). It should be noted that the ratio of nitrogen–phosphorus–potassium due to the loss of a certain proportion of nitrogen becomes more balanced (namely, 8–4–3). At the same time, the rate of decomposition of nitrogen-containing compounds slows down, and the mobility of phosphorus increases.

#### 4. Conclusions

To obtain fertilizer from poultry litter, the technology of the wet torrefaction of biowaste in a fluidized bed in an environment of superheated steam was applied for the first time.

In this work, the effect of increasing the torrefaction temperature on the characteristics of the resulting biochar was assessed. The maximum change in the characteristics of poultry litter is observed with an increase in temperature up to 260 °C.

When carrying out the process of wet torrefaction, the process can be limited with a temperature of 260 °C because, according to our previous studies at this temperature, the poultry litter is completely disinfected.

The combination of pelletizing and heat treatment at a temperature of 260 °C due to the cementation of pores with resins released at this temperature reduces the influence of the environment, as the material acquires hydrophobic properties as a result. This practically eliminates the risk of secondary infection.

The heat treatment at a temperature of 260 °C increases the content of ash, phosphorus and potassium by 30–40% and nitrogen by 15–20%, which makes the fertilizer more concentrated and optimizes the ratio of nitrogen, phosphorus and potassium.

For the first time, the influence of the temperature of the wet torrefaction process on the mobility of nitrogen and phosphorus compounds in the obtained fertilizer was established.

After the heat treatment at a temperature of 260 °C, the mobility of nitrogen decreases and the mobility of phosphorus increases due to the combustion of the most easily degradable nitrogen-containing organic compounds and the destruction of part of the organo-phosphorus compounds.

**Author Contributions:** Conceptualization, R.I.; methodology, A.M.; validation, O.M. and A.N.; investigation, O.M.; resources, R.I.; data curation, R.I.; writing—original draft preparation, R.I.; writing—review and editing, A.N.; visualization, A.N.; supervision, R.I.; project administration, R.I.; funding acquisition, A.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Ministry of Science and Higher Education of the Russian Federation (Agreement № 075-11-2020-035 of 15.12.2020 IGK 000000S207520RNV0002. Project name: “Development of technology and equipment for accelerated hydro thermal carbonization of poultry waste in order to obtain an intermediate product (biochar) suitable for the production of a highly effective sorbent or soil improver”. Lead contractor—Tambov State Technical University).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The work was carried out with financial support of the Ministry of Science and Higher Education of the Russian Federation (Agreement № 075-11-2020-035 of 15 December 2020 IGK 000000S207520RNV0002. Project name: “Development of technology and equipment for accelerated hydro thermal carbonization of poultry waste in order to obtain an intermediate product (biochar) suitable for the production of a highly effective sorbent or soil improver”. Lead contractor—Tambov State Technical University).

**Conflicts of Interest:** The authors declare no conflict of interest.

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