

Production of Activated Carbon from Biochar Obtained by Wet Torrefaction of Chicken Manure as Sole Feedstock, and in Mixture with Sawdust in a Fluidized Bed Powered with Superheated Steam

Rafail L. Isemin^{a,*}, Alexander V. Melezhyk^a, Sergey N. Kuzmin^a, Artemiy V. Nebyvayev^a, Natalia S. Muratova^a, Alexander V. Mikhalev^a, Oleg Yu. Milovanov^a, Yuri S. Teplitskii^b, Eduard K. Buchilko^b, Eugeni A. Pitsukha^b, Anatoly J. Grebenkov^b, Mathieu Brule^c, Fouzi Tabet^d

^aTambov State Technical University, 112 I, Michurinskaya str, Tambov, Russia, 392032

^bA.V. Luikov Heat and Mass Transfer Institute, 15, P. Brovka str, Minsk, Belarus, 220072

^c Department of Natural Resources Management and Agricultural Engineering, Agricultural University of Athens (AUA), Iera Odos 75, 11855 Athens, Greece

^d InterCenter GmbH, Allee der Kosmonauten 32 B, D-12681 Berlin, Germany
penery@list.ru

The process of wet torrefaction (WT) in a fluidized bed powered by superheated steam is applied to produce biochar, which can be subsequently processed into activated carbon, as an interesting bioproduct with high specific surface area. In this study, WT process was carried out at a temperature of 300-350 °C using mixtures of chicken manure and pine sawdust. Both the composition of the initial biomass, and the temperature of WT process had a considerable effect on the contents of non-condensable gaseous torrefaction products. Increasing the proportion of chicken manure in the mixture increased processing time from 30 to 46 minutes. Hence, in this work, it is hypothesized that two processes may have taken place concomitantly in the reactor: wet torrefaction of chicken manure and wet gasification of sawdust. Biochar obtained after WT of chicken manure as sole feedstock, and in mixture with sawdust was further activated using potassium hydroxide at a temperature of 750 °C. The activated carbon had following characteristics: specific pore surface area according to BET: 2031-3392 m²/g, and specific volume of pores with a size of less than 2 nm (micropores): 0.592-0.841 cm³/g. Furthermore, the quality of activated carbon in terms of porosity decreased with higher shares of sawdust in the mixture.

1. Introduction

Previously, the raw material for the synthesis of activated carbon was coal and charcoal. Currently, active carbon is obtained from various carbon-containing raw materials: wood and cellulose, peat, brown and hard coal, liquid and gaseous hydrocarbons, synthetic polymers, as well as various types of waste (car tires, waste from the production of polyvinyl chloride and other synthetic polymers, sewage sludge). These recent years, hydrothermal carbonation (Fiori et al., 2014) or wet torrefaction (Bach et al., 2013) attracted much attention of researchers, due to its ability to produce biochar, which can be applied for the synthesis of activated carbons. Biochar from hydrothermal carbonation has a high concentration of oxygen functional groups and a low degree of aromatization, which makes it more suitable for further chemical activation (Sevilla, Fuertes, 2013) (Falco et al., 2013). According to (Sevilla, Fuertes, 2013), an activated carbon with a pore surface of up to 2700 m²/g and a hydrogen absorption rate of up to 16.4 μmol/m² could be obtained from biochar derived from furfural, glucose, starch, and eucalyptus sawdust using chemical activation with KOH, Activated carbon from

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rye straw biochar, had a pore area of up to 2200 m²/g and could absorb 20 μmol of CO₂/g at a temperature of 25 °C and a pressure of 4.0 MPa (Falco et al., 2013).

It should be noted that nitrogen-containing biochar, obtained by wet torrefaction of manure or bird droppings, acts as a pH adsorbent. This means that it is a promising candidate for the use as sorption materials for water purification from heavy metals (e.g., Pb²⁺, Cd²⁺, Cu²⁺, U⁶⁺) or from organic pollutants (e.g., dyes) due to the abundance of surface functional groups (Straten et al., 2018).

WT can be achieved in a vapor medium under high pressure up to 4 MPa (Brachi et al., 2017) or near atmospheric pressure in a superheated water vapor medium at a temperature of up to 350 °C (Zhang et al., 2013). A WT installation operating with superheated steam at atmospheric pressure was built. This system can provide a heating rate of more than 120 °C/min. Biochar produced by this technology showed similar characteristics to biochar obtained from slow pyrolysis, in the case of sawdust. In addition, the carbonization reaction was achieved within 15 minutes, and the calorific value of biochar reached 27.84 MJ/kg.

Also, these findings grant this technology a clear advantage over hydrothermal carbonization (HTC), which requires a temperature of 180-260 °C and a pressure of 2.0-2.5 MPa. Moreover, the use of superheated steam at low pressure simplifies the design and reduces the metal consumption of the reactor. In addition, no process water disposal is needed (Zhang et al., 2013).

The WT process in a superheated water vapor medium was previously studied in (Zhang et al., 2013), in which a laboratory batch reactor with a complex scheme for loading and unloading biomass was used, whose reactor design might be difficult to transfer into industrial-scale.

Taking into account the fact that dry biomass is processed, the particles of which are smaller than 5 mm in size, we proposed the WT process, by analogy with the process of oxidative torrefaction (Isemin et al., 2020), to be carried out in a fluidized bed, using superheated water vapor as a fluidizing medium. At the same time, this reactor can be considered as a prototype for future up-scaling of the WT process in a fluidized bed.

The purpose of this paper is to study the possibility of obtaining activated carbon from biochar obtained from chicken manure and its mixture with sawdust by WT method in a fluidized bed in a superheated water vapor medium.

2. Material and methods

In order to study WT process in the fluidized bed, an installation was created, the scheme of which is shown in Figure 1.

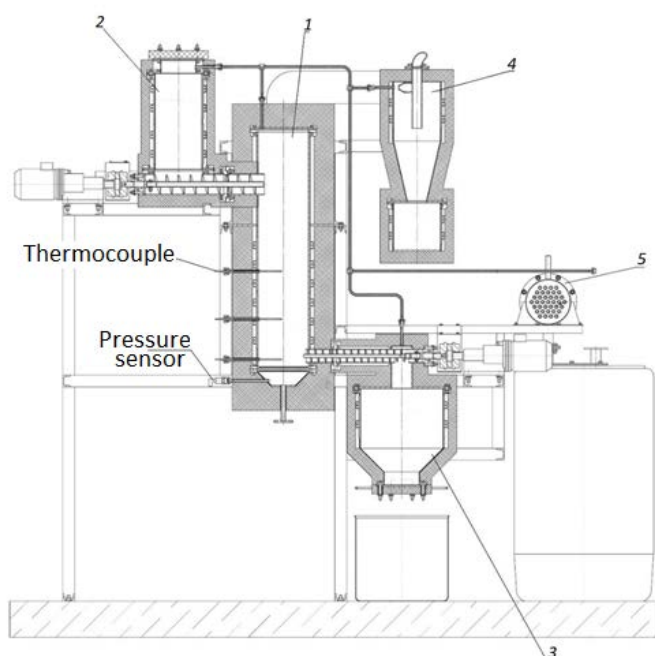


Figure 1. Diagram of the installation for the study of biomass WT process

1 - wet torrefaction reactor, 2 - initial biomass bunker, 3 - biochar bunker, 4 - cyclone, 5 - heat exchanger for cooling used superheated water vapor.

The installation consists of a reactor for WT in the fluidized bed 1, a bunker for the initial biomass 2, a bunker for biochar 3, a cyclone 4 for separating the steam-gas flow from biochar particles leaving the reactor, a condenser for the steam-gas mixture 5. Figure 1 does not show the boiler for steam generation and the superheater. The reactor for WT is equipped with a gas distribution grid for introducing superheated water vapor under the fluidized bed. Electric heaters are installed on the side wall of the reactor, with the help of which the required temperature is maintained in the reactor. The internal diameter of the reactor is 210 mm, the total height of the reactor is 1351 mm, the height of the heated part of the reactor is 540 mm. At the height of the reactor, 3 thermocouples are arranged one above the other in order to measure the temperature inside the reactor. The lower thermocouple is located at a height of 40 mm above the gas distribution grid, the middle thermocouple is located at a height of 210 mm, the upper thermocouple is located at a height of 410 mm. The zone of the side-heated surface of the reactor is 0.42 m². The bunker for the initial biomass has a volume of 0.13 m³. The bunker is designed to be heated in order to avoid condensation of steam when it comes into contact with cold biomass particles. The bunker for biochar collection is also heated, and has a volume of 0.07 m³. The cyclone for separating biochar particles removed from the reactor from the steam-gas flow is also heated to prevent premature condensation of steam, which may result in clogging of the cyclone with biochar particles.

The heat exchanger 5 for cooling used water vapor is made of shell-and-tube: superheated steam enters the pipe space, and water with a temperature of 10 °C enters the inter-pipe space. In order to collect the resulted condensate, a special container is used, which is not shown in Figure 1.

Chicken manure and its mixtures with sawdust were processed by WT (in the ratio 1:1, 1:2, 2:1 w/w), since the activated carbon obtained from such biomass is a good adsorbent for water purification from heavy metal ions or from organic pollutants due to the abundance of surface functional groups.

The fractional composition of manure and manure with sawdust is given in Table 1. Data on the ash content and bulk density of the initial biomass and the resulted biochar are given in Table 2.

Table 1: Fractional content of the studied biomass

	Manure-sawdust 1:1 w/w	Manure-sawdust 2:1 w/w	Manure-sawdust 1:2 w/w	Manure (as sole feedstock)
Size of sieve, mm	%	%	%	%
10	0	0	0	0
5	0	0	0	0
2	0.12362	0.26580	0.19659	0.12181
1	9.96181	10.4832	14.5530	22.4597
0.4	35.6509	30.5458	37.9259	52.9983
0.2	35.9602	34.6665	32.951	20.6642
0.09	17.4009	20.3815	13.0135	3.75598
0.045	0.90255	3.1563	1.36	0
< 0.045	0	0.50093	0	0
TOTAL	100	100	100	100

The humidity of the initial biomass and the biochar was determined using Ohaus MB45 humidity analyzer (relative measurement error ± 0.1 %). The ash content (A) in the initial biomass and in the biochar was determined according to the method provided for ASTM E1755-01.

The content of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) in the initial biomass and in the obtained biochar was determined using Elementar Vario Macro Cube element analyzer (relative error less than 0.2%).

The oxygen content (O, wt. %) in the initial biomass and in the biochar was determined by the formula: $100 - (C + H + N + S + A)$

Table 2: Ash content and bulk density of the initial biomass and obtained biochar

Parameter	The ratio of the components in the mixture of CD and sawdust (w/w)					
	1:2		1:1		2:1	
	300°C	350°C	300°C	350°C	300°C	350°C
Initial ash content, %	6.9		10.8		13.2	
Ash content of biochar, %	24.6	34.3	24.3	36.4	25.2	37.2
Initial bulk density, kg/m ³	171		207		229	
Bulk density of biochar, kg/m ³	191.7	219.3	217.8	232.7	239.2	259.3

The Higher Heating Value (HHV) of the initial biofuel and the obtained biochar was determined by the formula:

$$\text{HHV} = 4.18 \cdot 10^{-3} \cdot [81\text{C} + 300\text{H} + 26(\text{S} - \text{O})], \text{ MJ/kg}$$

The minimum fluidization rate of the manure and its mixture with sawdust was 0.35 – 0.4 m/s. The vapor velocity related to the empty reactor cross-section for WT was maintained in the range of 0.5 – 0.55 m/s.

Preliminary experiments on WT in the fluidized bed using quartz sand as an inert material to improve heat and mass transfer were unsuccessful. It was difficult to separate the resulted biochar from the quartz sand, resulting in a sharp increase in the ash content of the resulted biochar. Hence, it was decided to apply the biochar obtained in previous batches as an inert material. This biochar was obtained from the same biomass and under same experimental conditions.

Before the start of the experiment, approximately 6 liters of biochar were filled up into the reactor for WT. Then, 2 kg of the original biomass (manure or a mixture of manure with sawdust) was poured into the bunker for the initial biomass.

During the heating process, the system was purged with nitrogen. After initiating the operating mode, the nitrogen supply was stopped, the supply of saturated water vapor was turned on, which, passing through the superheater, was fed under the grid. The temperature under the grid was fixed in range 300-350 °C. The initial biomass was then loaded into the wet torrefaction reactor. Loading of the material was completed after 15 minutes, when 2 kg of the initial biomass was fed into the reactor. Since the beginning of the feed of the initial material, the gas analyzer “Vario Plus Industrial Syngas” was continuously used to select non-condensable gases behind the condenser and determine the content of carbon dioxide, carbon monoxide, hydrogen and methane in gases. After initiating biomass feeding into the WT reactor, the concentration of carbon dioxide, carbon monoxide, methane, and hydrogen in the non-condensable gases began to increase and reached a maximum a little time 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 initial values preceding the biomass feeding operation. Hence, we considered that at this point, the torrefaction of the fed biomass had been completed, and the biochar was subsequently unloaded from the reactor. Thus, the experimental duration required to complete the WT process could be estimated.

The reactor for WT operated in a sequential mode: (1) loading of the initial biomass, (2) holding of the loaded biomass in the reactor, (3) unloading from the reactor.

Chemical activation was carried out using potassium hydroxide (KOH). Biochar was loaded into a steel glass in the amount of 5 g. Potassium hydroxide (KOH 85%) was added to biochar in the form of granules in the amount of 15 g (corresponding to a ratio of 3:1 w/w to biochar). The glass was then covered with a steel cover with a sluice for purging inert gas (argon), which was supplied throughout the activation process. The activation process was performed in a muffle laboratory furnace. Heating was carried out at a rate of 10 °C/min. At a temperature of 400 °C, the technological exposure was carried out for 1 hour, then heating was continued to 750 °C (operating temperature). Activation at 750 °C lasted 3 hours.

Then, the steel glass was cooled in air to room temperature. Flushing with argon gas through the sluice was continued throughout the entire cooling period. Finally, activated carbon was removed from the glass, suspended with distilled water and left for 12 hours (minimum).

The received suspension of activated carbon in an aqueous alkaline solution was filtered, washed with water until reaching a neutral pH. The washed material was filled with hydrochloric acid (to remove impurities of metal compounds) and left for 12 hours (at least), then washed again with water until reaching a neutral pH.

The washed product was dried to a constant mass in air in a laboratory drying cabinet at 110 °C. The finished material was packed in plastic Zip-bags.

The surface and porosity parameters were measured using Autosorb iQ (Quantachrom instruments) instrument for nitrogen adsorption at 77 K. Preliminary preparation of the samples was carried out at 350 °C in a vacuum. In order to determine the pore size distribution, DFT method (built into the device software) was used. The mathematical model of DFT was chosen based on the best match of the theoretical curve with the experimental points. For these materials, the best agreement was given by the calculation model “N₂ at 77K on carbon, slit/cylinder. pores, NLDFE equilibrium model”.

3. Results and discussion

According to the method described above, as a result of the analysis of changes in the composition of non-condensable gases at WT of chicken manure, it can be stated that the duration of the WT process at a temperature of 350 °C is 42 minutes (Figure 2a). Replacement of a fraction of the chicken manure with pine sawdust reduces the duration of WT process: for a mixture of manure and sawdust with a 1:2, 1:1 and 2:1 (w/w), the duration of the process amounts to 30 minutes (Figure 2b), 40 minutes (Figure 2c), and 40 minutes (Figure 2d), respectively. At a temperature of 300 °C, the respective durations are 30 minutes, 40 minutes and 46 minutes. Hence, the duration of WT process of the mixture of manure and sawdust is determined by the

duration of the torrefaction of the manure as sole feedstock, and the duration of WT process of the mixture of manure and sawdust is slightly affected by the increase in the process temperature from 300 °C to 350 °C.

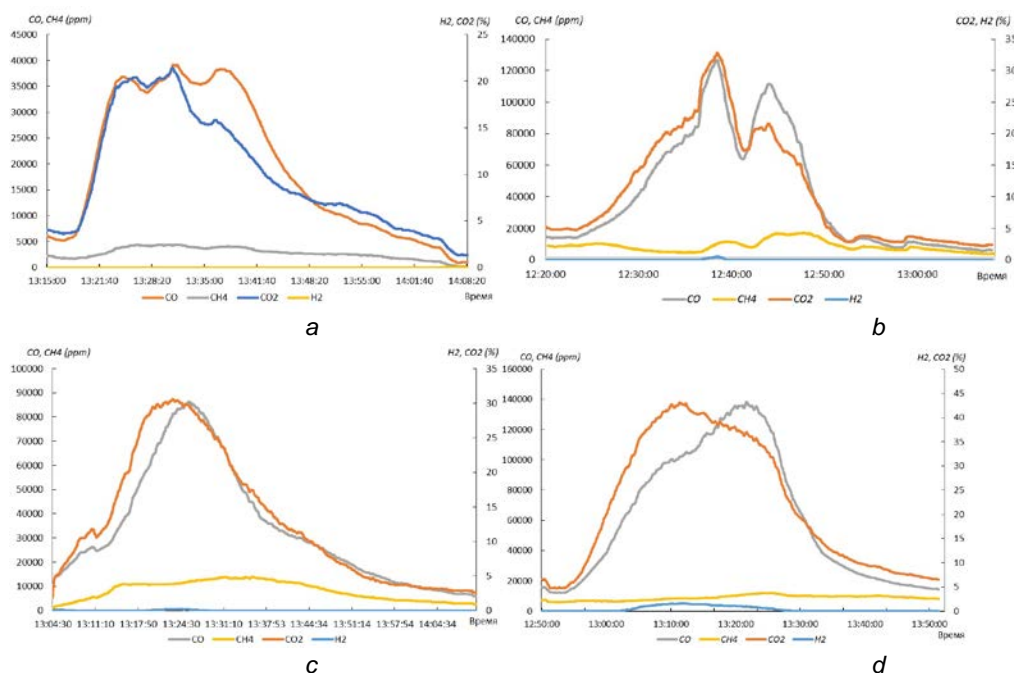


Figure 2. Changes in the composition of non-condensable gaseous products of the WT process at 350 °C. (a) manure, (b) mixture of manure with sawdust 1:2, (c) mixture of manure with sawdust 1:1, (d) mixture of manure with sawdust 2:1)

The analysis of the data on the ash content of biochar (Table 2) shows that these indicators are poorly affected by the content of the mixture. Since the ash content of the manure is 12.8 %, and the ash content of sawdust is 0.5 %, it can be stated that the ash content of biochar is determined only by the ash content of the manure, while biochar obtained from sawdust is present in a minor share.

On the other hand, the content of non-condensable gases is largely influenced by the temperature and the content of sawdust in the mixture (Table 3). Even for a mixture containing 33 % of sawdust, in comparison with the content of non-condensable gases for pure manure, the content of CO₂ increases 1.5-1.96 fold, CO 3.6 fold, CH₄ 3.19 fold.

Table 3. Maximum content of gas components in the received gas mixture

Gas component	The ratio of the components in the mixture of CD and sawdust							
	Manure		1:2		1:1		2:1	
	300°C	350°C	300°C	350°C	300°C	350°C	300°C	350°C
CO ₂ , %	10.5	22	13.9	32.8	15.9	30.6	15.3	43.1
H ₂ , %	0	0.02	0.01	0.43	0	0.21	0.04	1.6
CO, ppm	9500	38000	59500	126350	32900	86837	35180	138370
CH ₄ , ppm	690	3700	3900	17100	2100	13900	2200	11800

In total, these facts suggest that in the process of WT at a temperature of 300-350 °C, two parallel processes may occur concomitantly: the process of WT of manure, and the process of wet gasification of sawdust.

As a result, WT reduces the carbon content of the received biochar by 1.15-1.2 fold compared with the original biomass, and reduces the oxygen content by 2.7-3.2 fold.

Table 4 shows the characteristics of the obtained activated carbon.

Table 4. Characteristics of the obtained activated carbons

Type of initial biomass	Activated carbon output, %	S BET, m ² /g	S DFT, m ² /g	Total pore volume, V, sm ³ /g	Micropore volume, V, DFT, sm ³ /g	Pore volume, size <2 nm, V, DFT cm ³ /g	Micropore volume, DR*, sm ³ /g
Manure	10.6	3392	3220	1.997	1.914	0.841	1.366
Manure with sawdust (1:1 w/w)	12.0	2505	2468	1.609	1.546	0.604	1.001
Manure with sawdust (1:2 w/w)	15.0	2031	2178	1.182	1.134	0.594	0.837
Manure with sawdust (2:1 w/w)	13.0	2591	2555	1.508	1.517	0.653	1.036

*DR = according to Dubinin-Radushkevich

As can be seen from Table 4, activated carbon with a specific pore surface of up to 3392 m²/g can be obtained from biochar produced by WT of manure, and a mixture of manure with sawdust after chemical activation. The maximal specific pore surface and maximum pore volume of up to 1,914 cm³/g, including the maximum volume of mesopores and micropores, was obtained from chicken manure as sole feedstock, without incorporation of sawdust. On the other hand, the yield of activated carbon from biochar produced from manure applied as sole feedstock was minimal (10.6 %). The maximum yield of activated carbon (15 %) was obtained from biochar produced from a mixture of manure and sawdust at a ratio of 1:2 w/w, but this activated carbon had a lower porosity, with a specific pore surface of 2031 m²/g according to BET, and 2178 m²/g according to DFT.).

4. Conclusions

The WT process is a rather complex process. It is hypothesized that two parallel processes may have taken place concomitantly: WT of manure, and the wet gasification of sawdust. Biochar produced by wet torrefaction of this feedstock was used as a raw material for the production of activated carbon by chemical activation with KOH at a temperature of 750 °C. The specific surface area of activated carbon pores according to BET reached 2031–3392 m²/g, and the specific volume of pores with a size of less than 2 nm (micropores) reached 0.592–0.841 cm³/g. It should be noted that the quality of activated carbon produced from biochar obtained by processing a mixture of chicken manure with pine sawdust was of lower quality, compared with activated carbon obtained by processing chicken manure as sole feedstock, and the quality of activated carbon decreased with higher shares of sawdust in the mixture.

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