Drying and heat decomposition of biomass during the production of biochar

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Abstract. The process of wood torrefaction provides an opportunity to combine properties of biofuel and steam coal. Different degrees of biofuel heat treating leads to varied outcomes and varied biochar heating value. Therefore, the torrefaction process requires optimal operation that ensures the highest heating value of biochar with the lowest energy loss. In this paper we present the experimental results of drying cycle and thermal decomposition of particles of spruce stem wood and hydrolytic lignin in argon under various temperature conditions and basic material humidity as well as changes in the morphological structure of the biomass and its grain size composition during the torrefaction.

1. Introduction
The Russian Federation possesses a heavy stock of conventional energy sources (gas, oil and coal). This fact has a restraining influence on development of renewable power generation in the RF. The pressing challenges include enhancing of renewable energy use, primarily biomass energy, and improving of energy security in forest-rich regions. Replacement of fossil fuels with biofuel is encouraged in industrially developed countries for mitigation of greenhouse gases impact on the Earth’s climate. However, by-products of wood harvesting, woodworking and processing of wood belong to slow-burning fuels due to their high humidity, low energy density and diverse grain-size composition.

Granulation is a prospective direction for refining biomass conversion wastes that allows to multiply specific calorific value by 2.5-3.5 times and transportability by 3-4 times [1]. Biomass torrefaction, which is based on thermal processing at temperatures from 250 to 330 °C in absence of air, is a further step in increasing energy density and fuel efficiency. Biochar is obtained as the result of this process, which might be used in its powder form or for manufacturing of pellets and briquettes. Torrefaction allows us to approximate biofuel properties to the properties of power generating coals. Varying degrees of heat treatment lead to different outputs and different heat values (from 18.0 to 31.9 MJ/kg - charcoal heat values) of final product. Therefore, torrefaction requires optimal operation that ensures the highest heat value with the lowest energy loss.
Black pellets are free-flowing, solid, hydrophobic and are subjected to the same grinding principles as charcoal. High energy density defines economic feasibility of its long-distance transportation. Black pellets surpass wood pellets in all parameters. This replacement does not reduce boiler output and does not require modernization of fuel preparation system [2].

Heat treatment and granulation studies of biomass torrefaction are carried out in many countries around the world. There are several industrial plants producing black pellets. Work experience of the first Russian enterprise (“Bionet”) that produces black pellets from hydrolyzed lignin shows that the lower heating value per working mass is at least 21.34 MJ/kg (at humidity \( W_r = 6.27 \% \) and ash in the working mass \( A_r = 2.45 \% \)).

2. Experimental

The main factors influencing nature of technological process of torrefaction are its temperature and length. Overall duration of torrefaction is composed of warm up time of raw material to evaporation point, evaporation time, further heating of biomass up to thermal decomposition temperature and decomposition of organic compounds. Spruce stem wood and hydrolysed lignin are chosen for the study on drying kinetics and thermal decomposition of organic biomass compounds. Selection of wood species is justified by the fact that Arkhangelsk woodworking plants process up to 65% of spruce wood. Hydrolysed lignin is large-tonnage waste of hydrolytic production and currently its stocks in disposal areas of former microbiological industry enterprises exceed 30 million tons.

The samples of spruce stem are pulverized in the hammer mill “Borey” and sifted in the analytical sieve shaker Retzsch AS 200 Control. In course of investigation, fractions with particle size from 250 to 500 microns are used in the simultaneous thermal analyser STA 449 F3 Jupiter, “Netzsch Geratebau GmbH Selb”. Heat value of investigated samples are measured in the calorimeter IKA C 2000 Basic Version 2. Spruce elemental composition on dry weight basis is the following: \( A_d = 0.49 \% \); \( C_d = 51.72 \% \); \( H_d = 7.52 \% \); \( N_d = 0.38 \% \); \( O_d = 39.89 \% \); lower heating value on dry weight basis \( Q_{daf}^t = 18.834 \) MJ/kg and volatile yield on dry weight basis \( V_{daf} = 85.39 \% \). Hydrolysed lignin has following features \( A_d = 4.70 \% \); \( C_d = 56.67 \% \); \( H_d = 6.22 \% \); \( N_d = 0.30 \% \); \( O_d = 32.08 \% \); \( Q_{daf}^t = 21.826 \) MJ/kg and \( V_{daf} = 64.40 \% \).

3. Results and discussion

Thermal analysis of biofuels is conducted in three temperature condition: 250, 275, 300 \( ^\circ \)C in argon with gas flow of 20 cm\(^3\) /min. The tasted samples are heated at rate of 10 and 50 \( ^\circ \)C/min to corresponding temperatures, then they are held 60 minutes under isothermal conditions. Initial relative humidity of the tested material is \( W_r = 10.0; 30.0 \) and \( 50.0 \) %.

The thermograms are obtained as a result of recent research, one of which is given in figure 1. For the analysis of drying kinetics and thermal decomposition of organic biomass compounds the curves are used that characterize mass change (TGA), velocity change per unit mass (DTG) and heat effects occurring in the samples (DTA).

**Figure 1.** The spruce thermogram with relative humidity of 10%, at heating rate of 10 \( ^\circ \)C/min up to 250 \( ^\circ \)C, with subsequent isothermal exposure: 1 – TGA; 2 – DTG; 3 – DTA.
As a basic classification for moisture-material connection forms the scheme is used where connection forms are divided into chemical, physicochemical and physico-mechanical forms. Chemically bound moisture has the largest binding energy and specific quantitative correlation with dry matter. This moisture could be removed from wood biomass at temperatures above 180 °C, but molecular structure will be changed.

The relations characterizing drying kinetics of biomass are formed on the results of thermogravimetric analysis (fig. 2). In the warm-up period (AB section), heat is spent on material warming and moisture evaporating, which progresses relatively slow. With increase of relative humidity rate from 10 to 50 %, the duration of warm-up period is growing from 1.8 to 3 minutes while heating rate is permanent (10 °C/min).

![Figure 2. The change in relative humidity (a) and drying rate (b) of spruce wood with initial humidity of 50% and heating rate of 10 °C/min in argon.](image)

The period of constant drying rate (BC, fig. 2a) conforms to physico-mechanical moisture removal, being limited by its external diffusion rate. Raise of biomass humidity leads to increased duration of this period. The overall length of these drying periods in the studied range of wood moisture content amounts to 5.10-7.75 minutes at heating rates of 10 °C/min. The removal of the bound moisture (physicochemical moisture, CE, fig. 2a) begins in the following period – period of decreasing drying rate. The point B, which separates the two periods of drying, is called a critical point; material moisture content at this point is called the first critical moisture content. The final moisture content of the material (E, fig. 2a) marks its equilibrium moisture content under drying conditions.

In order to plot the correlation between drying rate of wood and time, moisture content (\(\omega\)) curves over time are build, by applying the following formula:

\[
\omega = \frac{100W_r}{(100-W_r)}, \%.
\]

It is proceeded with graphical differentiation, from results of which the following function is gained: \(U = d\omega / dt, \%/\text{min}\) (fig. 2b). This function depicts drying rate of biomass and has the same periods as the drying curve (fig. 2a). The dependence \(U = d\omega / dt\) (fig. 2b) has a rather complex form at the period of decreasing rate. At this period occurs the change of curve direction, which means that there is a bending point, which corresponds to the point of the second critical moisture content (D). The moisture values of the second critical point decrease as biomass moisture content is reduced.

The final temperature of the drying process is changing from 105 to 140 °C, growing with the increase of moisture content and heating rate of the studied material. Pyrolysis reactions begin to occur approximately at 190°C in surface levels of wood; pyrolysis reaction fronts, in the course of heating, shifts towards inner layers of the material. At the same time, less heat-resistant components of biomass are decomposing, accompanied by emission of carbon and nitrogen monoxide, chemically bound moisture and other decomposition products \[3\]. Blend composition of biomass begins to change.

Consequently, densification of potential biomass energy occurs in torrefaction through removal of moisture and volatile products, emerging during hemicellulose decomposition and partial decomposition of cellulose and lignin. Given that, spruce wood contains lot more lignin and cellulose
rather than hemicellulose (by 8.0 and 5.2 times respectively), the torrefaction is determined by thermal decomposition of two main components (lignin and cellulose). This conclusion is valid for hydrolysed lignin since its content of lignin and cellulose is bigger than its content of hemicellulose by 20.8 and 4.3 times respectively [5].

Several results of the research of biomass torrefaction in nitrogen at heating rate of 10 °C/min [3], with measurements of volume concentration of hydrocarbons (HC), nitrogen and carbon monoxides (NO and CO) in the thermal decomposition products are given in table 1. The ratio calculation of HC/NO/CO is conducted without regard for moisture vapour; volume concentration of 10 ppm is taken as a unit. Obtained results show that the process of spruce torrefaction should be operated at a temperature not exceeding 275 °C in order to minimise the loss of combustion agents. The maximum temperature for the torrefaction of hydrolysed lignin can be increased to 300 °C. Such temperature limitations allow for significant decrease in formation and entrainment of soot particulates, with an “aerodynamic” diameter smaller than 0.1 microns, from a reactor. Apart from that, it reduces the risk of biochar spontaneous ignition while cooling after a reactor.

### Table 1. Composition of volatile products, which release from biofuels in torrefaction.

| Title            | The correlation of concentration ratios of HC/NO/CO when heated to the temperature, °C |
|------------------|---------------------------------------------------------------------------------------|
| Spruce           | 2.25/0.4/5.0                                                                           |
| Hydrolysed lignin| 0.25/0.2/5.0                                                                           |
|                  | 3.1/0.7/12.7                                                                           |
|                  | 3.1/1.0/19.1                                                                           |
|                  | 0.25/0.42/8.7                                                                          |
|                  | 1.9/0.61/16.5                                                                          |

Porous and fibrous structures of spruce and hydrolysed lignin undergo restructuring in course of torrefaction. The studying of biomass structural changes is conducted with the field emission scanning electron microscope Zeiss SIGMA VP. An indicator of occurring changes is primarily a shape of tracheids that are core elements of coniferous wood. In their initial state, tracheids are elongated spindle structures 30 microns in width with a line of coated pores approximately 15 microns in diameter, pit aperture is around 4-5 microns [4]. At temperature of 250 °C, fine cracks in the periphery of coated pores are emerging on spruce samples. When temperature is risen to 275 °C, large arched cracks are emerging on the surface of coated pores. At 300 °C the crack formation process is amplifying, areas close to pit aperture and beyond its borders become involved, radial crack-pores are appearing. Delamination and destruction of cellulose microfibrils occur [4].

A process of hydrolysed production influences structure of wood biomass, yet morphological structure of cell walls remains unchanged to a large extent, but the structure becomes more loose (fig. 3). In the studied range of temperatures from 250 to 300 °C, the emergence of cracks on the surface of coated pores of hydrolysed lignin is not observed, as opposed to the spruce torrefaction under similar conditions [4]. However, thermopores not exceeding 1 microns occur beyond this area in the torrefaction at 250 °C (fig. 4). As temperature of isothermal exposure is raised to 275 °C, the maximum crack width increases to 1.7 microns. The heat and exposure of hydrolysed lignin samples at 300 °C results in twisting of coated pores borders and amplification of bore diameter to 8.5 microns. Furthermore, the tracheid surface is covered with the thermal cracks up to 3 microns in width.

On the bases of cracking dynamics of tracheid walls, we may assume that cracks occur due to intensive volatile and moisture yield from the interior cell volume, emerging from the heating of wood biomass in the torrefaction that is accompanied with fracturing of cell surfaces in the pattern of heat-determined cracks.

Grain-size composition of raw wood is transformed in the course of torrefaction. The pyrolytic decomposition of spruce stem particles ranging from 250 to 500 microns at heating rate of 50 °C/min up to 300 °C with their subsequent 130-minutes isothermal exposure leads to formation of the smaller fractions in biochar. The values of screening sections (F) with the size of a cell 250, 125, 63 and 45
microns amount to: \(F_{250} = 87.45\%\); \(F_{125} = 9.76\%\); \(F_{63} = 0.8\%\); \(F_{45} = 0.54\%\). The fraction proportion in biochar, size of which is lower than bottom boundary of raw material, is increasing with the enlargement of grain-size composition of raw material. So heat treatment of spruce particles with a size from 500 to 1000 microns under similar operating conditions shows that more than 34% of biochar particles (by mass) are 500 microns or smaller \(F_{500} = 65.11\%\). The similar process of grain-size composition change occurs during the heat treatment of hydrolysed lignin.

![Figure 3](image1.png)  
**Figure 3.** Electronic microphotographs of hydrolysed lignin samples: (a) – approximation scale 380:1; (b) – approximation scale 2200:1.

![Figure 4](image2.png)  
**Figure 4.** Electronic microphotographs of biochar samples, resulting from isothermal exposure of hydrolysed lignin at temperatures: (a) – 250 °C; (b) – 275 °C; (c) – 300 °C.

The conducted research shows that the constitutive parameters of biochar manufacturing are temperature and length of torrefaction. Heat value of torrefaction product is growing when temperature and duration of heat treatment is increasing [5]. It is expected that heat value is asymptotically tending to calorific value of charcoal. The humidity level of wood raw material has no determining influence on torrefaction [5], therefore in order to simplify technological scheme and to minimize material and financial costs, drying and heat treatment processes should be carried out within one device (reactor).

The experimental research shows that spruce wood at heating rate of 10 °C/min in argon with subsequent 90-minutes isothermal exposure at temperatures of: 250, 275, 300 °C produces the output from the mass of dry material that equals respectively: 73.76; 49.74; 41.08 %. The biochar output for hydrolysed lignin has bigger values under similar conditions: 91.9; 85.6; 76.9 %, due to lower content of volatile products and high ash content of the material.

The raise of wood biomass heating rate to the values that are typical for industrial plants (50 °C/min) reduces the torrefaction time by 19-24 minutes with relatively equal output and quality of biochar. At this heating rate, the drying and volatile yield processes are carried in large part simultaneously, that is, the inward biomass particles motion of two fronts is encountered: moisture evaporation and volatile yield. These circumstances significantly complicate the thermograms processing.

The finished product, after the reactor, passes through a cooling zone under exclusion of air in order to prevent spontaneous ignition. The cooled material is supplied to a hammer mill for
pulverizing. The heat treatment of biomass considerably reduces energy costs for pulverizing [6]. Torrefaction powder is screen through a system of separating sieves; coarse particles are withheld for regrinding. The powder, which dominantly contains particles of $0.25 < \delta < 2.0$ mm in size, shall be regarded as the powder of optimal technological dispersion. Afterwards, the torrefaction powder is transported to a pellet-press; the powder undergoes air-conditioning be means of saturated or slightly superheated steam before it enters the pellet-press. In order to improve effectiveness of the process, the combustion components, which escape in the wood modification, should be used for heating of an active agent in a reactor. The granulation of biochar is a significant improvement for the transportability and utilization efficiency in fire grate energy plants.

4. Conclusions

The experimental research of drying and thermal decomposition of spruce stem wood particles and hydrolysed lignin shows that densification of potential biomass energy occurs in the torrefaction through the removal of moisture and volatile products, which emerge during the hemicellulose decomposition and partial decomposition of cellulose and lignin. Given that, hydrolysed lignin and spruce wood contain lot more lignin and cellulose rather than hemicellulose, the torrefaction is determined by thermal decomposition of two main components (lignin and cellulose).

The constitutive parameters of biochar manufacturing are temperature and length of the torrefaction. Heat value of a torrefaction product is growing when temperature and duration of heat treatment is increasing, and is asymptotically tending to calorific value of charcoal. However, in order to minimise the loss of combustion agents the process of spruce torrefaction should be operated at a temperature not exceeding $275 \, ^\circ \mathrm{C}$, and not exceeding $300 \, ^\circ \mathrm{C}$ for hydrolysed lignin. The humidity level of wood raw material has no determining influence on torrefaction, therefore in order to simplify technological scheme and to minimize material and financial costs, drying and heat treatment processes should be carried out within one device (reactor).

The raise of wood biomass heating rate from $10 \, ^\circ \mathrm{C}/\mathrm{min}$ to the values that are typical for industrial plants ($50 \, ^\circ \mathrm{C}/\mathrm{min}$) reduces the torrefaction time by 19-24 minutes with relatively equal output and quality of biochar. At this heating rate, the drying and volatile yield processes are carried in large part simultaneously, that is, the inward biomass particles motion of two fronts is encountered: moisture evaporation and volatile yield. Porous and fibrous structures of spruce and hydrolysed lignin undergo restructuring in course of torrefaction; grain-size composition of raw wood is also transformed, biochar become loose, which allows to considerably reduce energy costs for pulverizing.

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