

Influence of the parameters of the hydrothermal carbonization of the biomass on the biocoal obtained from peat

Kristina Krysanova^{1*}, Alla Krylova¹, Victor Zaichenko¹, Vladimir Lavrenov¹, Vladimir Khaskhachikh¹

¹Joint Institute for High Temperatures of Russian Academy of Sciences, Izhorskaya 13, str. 2, Moscow, Russia

Abstract. Hydrothermal carbonization is modern low-temperature method to improve characteristics of peat and other types of biomass as a fuel. The influence of methods at different temperatures and different reaction time the physical-chemical and energy properties of the resulting biochar is studied. Characteristics of the initial peat and hydrochar were determined such as elemental composition, ash content, moisture content, heating values. It has been established that with an increase in temperature and reaction time, yield of hydrochar oxygen in it decreases (from 33.1% - initial peat to 19.47% - hydrochar obtained at 230 °C), but carbon (from 52.09% - initial peat to 68.17% - hydrochar obtained at 230 °C) and heating value increases. Also was observed leaching the inorganic component from hydrochar into the water.

1 Introduction

Peat is a combustible mineral of plant origin and the precursor of the genetic series of coals. Peat is also a renewable source of energy and its accumulation occurs constantly. Therefore, its rational use will allow achieving a large economic effect while minimizing damage to natural ecosystems.

According to expert estimates a huge reserves of peat are deposited in Russia (about 150 mlr. tonn). Annual natural growth of peat reserves in Russia will be more than 1 billion m³. Unfortunately, the extensive deposits of minerals are practically not used at present. In the mid-1970s, the extraction of peat used for energy purposes amounted to about 50 million tons per year, however, it has now decreased to 1.5–3 million tons per year.

However, peat as a fuel has a number of disadvantages such as high moisture content and low thermal characteristics, so it could not be co-burnt with coal. So it would be useful to pretreat peat with the aim of its fuel properties enhancement.

The modern method to improve characteristics of a renewable biomass including peat is hydrothermal carbonization (HTC). HTC sometimes called wet torrefaction or wet mild pyrolysis. The main product of HTC is hydrochar, that has a higher energy density, lower moisture and mineral content compared to raw biomass. Hence, obtained hydrochar is easier to transport and store.

HTC carried out at temperatures from 180 to 280 °C, in aerobic conditions and in presence of subcritical liquid water [2]. One of the main advantages of this process is the possibility to pretreat biomass with high moisture [3].

The main aim of this paper is the investigation of the temperature and reaction time influence on physico-chemical properties of the resulting biochar obtained via HTC

2 Material and methods

2.1 Initial raw material

The initial peat was characterized by a 34% moisture content and a relatively low ash content (9.3%). The elemental composition of peat (wt. %) was the following: nitrogen, 1.42; carbon, 52.09; hydrogen, 5.72; sulfur, 0.15; and oxygen, 31. The yield of volatile substances was 80%. The net and gross calorific values were 20.2 and 21.5 MJ/kg, respectively.

2.2 Hydrothermal carbonization: experimental procedures

Hydrothermal carbonization was conducted at four temperatures such as 160, 190, 210, and 230 °C (these experiments were carried out in a previous study [4]) and for reaction durations 1 h. Stainless steel batch reactor was used. Raw material with weight of $m_{\text{feed}}=50$ g was mixed with water in ratio 1:3 and then placed into reactor. If necessary catalyst was added into the mixture. The reactor was heated to the required temperature and held for 8 hours. Then the reactor was cooled down to room temperature. The resulting suspension was separated on filter paper into a solid residue and liquid. Filtration paper with a pore size of 3-5 μm was folded and placed in a glass funnel. The suspension was poured onto the filter paper and filtration occurred naturally

vermont.content@gmail.com

without additional influences. Solid residue dried at 20 °C for 48.

2.3 Analytical methods

A SDTQ 600 thermal analyzer, which allows simultaneous thermal analysis including thermogravimetric and differential thermogravimetric analysis and differential scanning calorimetry, was used to determine the moisture and ash contents of compounds.

The calorific values of materials were determined based on elemental analysis, which was carried out on a Vario MICRO Cube elemental analyzer intended for the simultaneous determination of the elements C, H, N, and S in the samples. Oxygen (O, wt.%) for dry state was calculated from material balance:

$$O = 100 - (C + H + N + S + A) \quad (1)$$

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

$$HHV = 0.339[C] + 1.256[H] + 0.109[S] - 0.109[O] \quad (2)$$

$$LHV = 0.339[C] + 1.256[H] + 0.109[S] - 0.109[O] - 0.0252[9H+W] \quad (3)$$

where HHV, 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 and it is calculated as the ratio of carbonized product in weight (m_c) to raw biomass weight (m_b),%:

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

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

$$y_e = y_m \frac{HHV_c}{HHV_b} \quad (5)$$

where HHV_c and HHV_b are the highest heating values of product and feedstock respectively.

3 Results and discussion

3.1 Yields

Fig.1 shows the effect of two different operating parameters on mass and energy yields of initial peat: reaction time, reaction temperature, catalyst presence.

As expected, the mass yield of hydrochar samples was reduced with an increase in the reaction time and temperature. The greatest influence in a series of experiments is observed in the case of reaction time. The

maximum difference was 27% between samples obtained at 1 h and 8 h. The graph shows that the mass yield varies with time inversely.

It is not surprising that the sample had the smallest mass yield with the longest reaction time and highest temperature (230 °C, 8 h) and was only 52.8%.

The addition of citric acid catalyst has virtually no effect on the mass yield of the hydrochar. The decrease in mass yield with an increase in the severity of HTC is explained by the chemical reactions that take place in the process. The main reactions that take place during HTC: hydrolysis, dehydration, decarboxylation, aromatization and polymerization. Hydrolysis is one of the most significant reactions in the process and goes at the first step of HTC [6]. Degree of hydrolysis of polysaccharides increases with temperature and reaction time in direct ratio. Hence, degree of depolymerization increases and the mass yield decreases accordingly.

The yield of the sample with the addition of citric acid and pH 4.5 was lower than that of the sample without, since the acid intensifies hydrolysis, and therefore depolymerization.

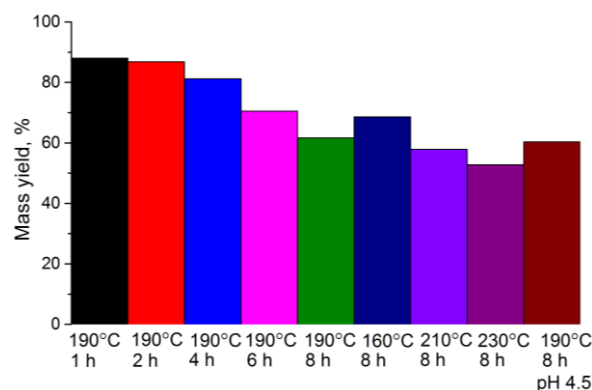


Fig. 1. Mass yield of hydrochar.

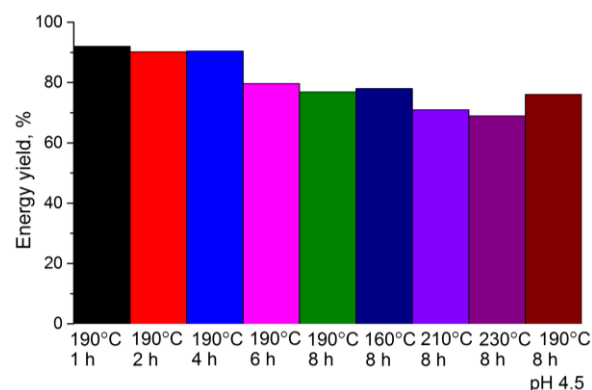


Fig. 2. Energy yield of hydrochar.

3.2 Element analysis and heating values

Elemental composition of initial peat and biochar produced via hydrothermal carbonization at different operation conditions are presented at Table 1.

Table 1. Elemental composition of initial peat and hydrochars.

Material	Elemental analysis, wt. %					
	N	C	H	O	S	A
Initial peat	1.42	52.09	5.72	31.00	0.15	9.63
Hydrochars:						
190 °C, 1h	1.54	55.91	5.71	38.55	0.11	2.87
190 °C, 2h	1.74	56.38	5.36	32.65	0.14	3.72
190 °C, 4h	1.64	58.60	5.73	29.19	0.19	4.64
190 °C, 6h	1.97	60.24	5.38	26.93	0.16	5.33
190 °C, 8h	2.12	64.84	5.71	22.13	0.15	5.05
160 °C, 8h	1.8	60.5	5.76	30.51	0.13	1.30
210 °C, 8h	1.92	64.89	5.36	22.16	0.09	5.58
230 °C, 8h	1.97	68.17	5.6	19.47	0.11	4.68
190 °C, 8h, pH 4.5	2.06	65.49	5.82	22.45	0.14	4.04

Due to the data showed in table 1 it could be said that all the samples made by HTC were carbonized and deoxygenated compared to the initial peat. Again, this is due to chemical reactions that provoke a decrease in oxygen and ash in samples, specially dehydration and decarboxylation of hydrolyzed products [7]

Hydrothermal treatment of peat at a relatively low temperature (160 °C) increased the carbon concentration to 60.5% compared to initial peat, and an increase in the treatment temperature (230 °C) made it possible to increase it to 68.17%. At the same time, a decrease in the oxygen content of the sample by almost 10% was observed.

With an enhance in the reaction time, carbon increases (from 55.91% at 1 h to 64.84% at 8 h)and oxygen decreases (from 33.51% at 1 h to 22.13% at 8 h). The addition of citric acid catalyst increases carbon (from 64.84% pure sample to 65.49% sample with catalyst).

An interesting trend is observed in the case of ash content in samples.

In the case of hydrothermal carbonization, unlike other thermal methods, mineral components are washed into the water and there is a noticeable decrease. The similar trend for inorganics removing from biomass in water during HTC is described in [8]. This is due to the destruction of lignocellulose, in which there is a large amount of mineral components. Under hydrothermal conditions, the depolymerisation of hemicellulose and cellulose takes place, which results in the formation of slightly porous structures of hydrochars [9]. It has been reported that these porous structures may allow the leaching metals that were previously held/bonded in the cross-linked matrix structure of biomass into the liquid form [10].

During HTC, in addition to ash leaching,

concentration process due to the destruction of the structures is observed too. Therefore, it is difficult to assume the exact amount of ash in the obtained sample.

The smallest amount of ash is observed in the sample obtained at 160 ° C (ash - 1.3 %, which is 7 times less than that of the initial peat (9.63%). With an increase in the duration of the reaction (from 2.87% at 1 h to 5.05% at 8 h), ash increases in percentage, which is associated with an increase in the depolymerization of feedstock.

Heating values (Fig. 3) reliably dependent on carbon and oxygen in the material. With increasing amounts of oxygen and decreasing oxygen, the calorific value will increase. Therefore, the highest heating values will be obtained by a sample obtained at 230 ° C (26.77- LHV, 28.03-HHV, MJ/kg) as having less carbon and oxygen.

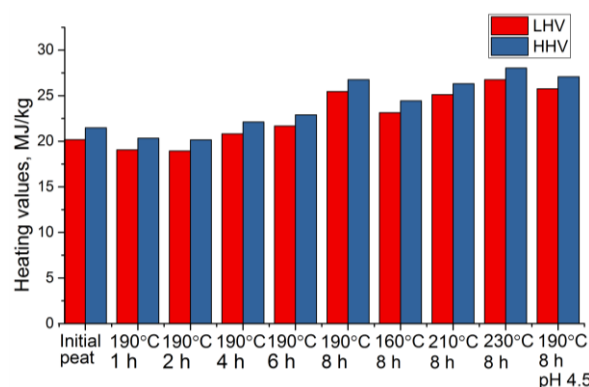


Fig. 3. Heating values of initial peat and hydrochars.

During the process, cellulose and hemicellulose have the least stability, unlike lignin, which has the highest heating value among those mentioned above. After the destruction of cellulose and hemicellulose, lignin remains, thereby increasing the calorific value of obtained hydrochar. Furthermore under subcritical water conditions the degradation of hemicellulose and cellulose a huge amount monomers are formed like furfurals, and 5-Hydroxyl Methyl Furfural (HMF) which have a higher heating values then cellulose and hemicellulose [11].

These intermediates increase energy yield and HHV by precipitating into the porous structure of hydrochar [12]. The increase in the duration and reaction time is accompanied by an increase in heating values, such dependencies are described in the literature [13].

3.3 Van Krevelen diagram

The variation of the O/C and H/C atomic ratios indicates the degree of deoxygenation of biomass by decarboxylation, dehydration or demethanation. The reduction of O/C atomic ratio mainly attributed to dehydration and decarboxylation, while that of H/C atomic ratio is related to the dehydration and increased degree of aromatization [14]. Materials with low O/C and H/C could avoid energy losses in combustion., so the closer sample to the 0 in Van Krevelen diagram the better fuel properties it has.

As shown in Fig. 4, the reduction of O/C and H/C atomic ratios illustrated the important improvements of

hydrochar obtained by HTC through dehydration and decarboxylation.

With an increase in the severity of the reaction, the samples move closer to exactly 0 on the van Krevelen diagram, and therefore have better thermal characteristics. Both temperature and reaction time influence the performance improvement and the samples are shifted.

Thus the main reactions affect the properties of hydrochar are decarboxylation and dehydration, but not demethanation. Similar trends are observed in the literature [15].

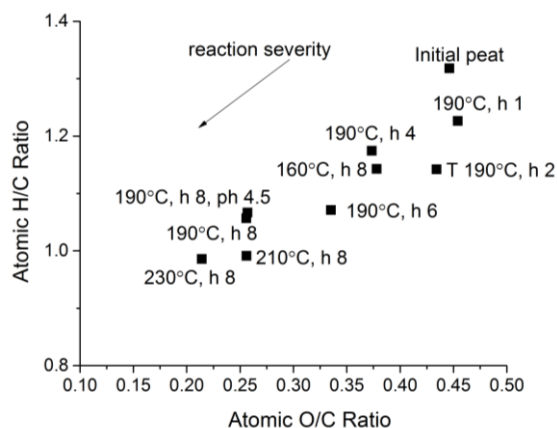


Fig. 4. Diagram van Krevelen.

6 Conclusions

Hydrothermal reaction is a modern method of processing various types of biomass for producing biocoal with high thermal physical properties close to that of fossil fuel such as coal.

Hydrothermal carbonization of peat has demonstrated the ability to process biomass without pretreatment particularly drying.

The reaction times, temperature, the presence of a catalyst significantly affect the resulting hydrochar. The most important parameter influencing the process is the temperature.

As a result, the work revealed the following dependencies: with an increase in temperature and reaction time, yield of hydrochar and oxygen decreases, but carbon and heating value increases. Catalyst addition had little effect on properties of hydrochar, however, most likely influenced the reaction rate. Also was observed leaching the inorganic component from hydrochar into the water.

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