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Impact of Heat Treatment on the Structure and Properties of Tomsk Region Peat

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Abstract

Botanical composition of terrestrial peat and fen peat with decomposition degree (R) ranging from 25% to 45% has been studied and technical analysis has been carried out. The effect of heat treatment on peat group composition alteration was evaluated. The peculiarities defined by the preliminary heat treatment were revealed. Optical properties of peat were studied by IR spectroscopy. Conclusions about the degree of heat treatment influence on the physicochemical properties of peat were made.

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1. Introduction

Tomsk Region has significant proved reserves of such natural resources as gas, oil, wood and peat. 1444 deposits are located in Tomsk Region, only Tumen Region is characterized by greater number of peat deposits. The peculiarity of peat lies in the fact that it is quite rapidly renewable material. Under typical conditions, peat is replaced naturally at a rate of one millimetre a year. Being an effective source of heat, peat is also considered to be an effective sorbent of organic and inorganic substances. It is a well-known fact that peat is a highly organic material which is used for various agricultural and industrial purposes. Its properties mainly depend on peat vegetation composition, texture and mode of occurrence.

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2. Objects and investigation methods

Nowadays, there are a lot of treatment methods applied to achieve desirable properties of peat. One such a method is a thermal peat treatment at 250 °C in its decomposing gases^{1,2}. As shown in studies¹⁻³, this method enables to increase the yields of such important components as bitumen and humic acids. Besides, the properties of peat vary to different extents, precisely, organic and inorganic constituents of peat matrix transform to a variable degree. This brings up a rather complicated question: what determines the degree of peat transformation under heat treatment conditions? Therefore, the objective of the present study is to identify peat components which alter significantly under high temperature. To accomplish this, it is necessary to analyze different peat samples. Peat samples were taken from Tomsk peat lands. They were identified as terrestrial peat and fen peat and categorized as grass-moss and grass, with the rate of peat decomposition (R) ranging from 25% to 45%. Peat botanical composition has been studied and technical analysis has been carried out⁴⁻⁸. The characteristics of peat samples are given in Table 1.

Table 1. Peat Samples Characteristics

Peat Type, Code	Group	R, %	Peat-Forming Vegetation, (content, %)	Technical Analysis *, %		
				W ^a	A ^d	V ^{daf}
Terrestrial Peat						
Cottongrass-sphagnous (B1, B2)	grass-moss	25	cotton grass (50), sphagnum angustifolium (30), sphagnum magellanikum (10), sphagnum-fusum (5), suffrutexes, pine (5)	8.2	1.9	73.5
	grass	35	cotton grass (80), sphagnum-fusum (5), sphagnum magellanikum (5), sphagnum angustifolium (5), suffrutexes, pine (5)	6.6	2.3	71.0
Sheyhtse-rievy (B3)	grass	40	Scheuchzeria (60), sphagnum magellanikum (10), sphagnum angustifolium (10) sphagnum-fusum (5), cotton grass (5), mud sedge (5), pine (5)	40	11.1	7.8
Fen Peat						
Sedge-hypnum (H1, H2)	grass-moss	25	Hypnum moss (50), mud sedge (25), beaked sedge (15), baxtra (5), timber rests (5)	8.2	8.9	70.7
	grass-moss	45	Hypnum moss (65), bog bean (10), beaked sedge (10), mud sedge (5), sphagnum magellanikum (5), dwarf birch (5)	8.1	6.4	70.4
Sedge (H3)	grass	35	Beaked sedge (65), mud sedge (5), horsetail (5), bog bean (10), grass rests (15)	10.2	9.9	68.4

* W^a – humidity of analytical sample, A^d – ash-content per dry substance, V^{daf} – volatile content per combustible mass

Peat was divided into 0.25 mm fraction. Heat treatment was carried out on special laboratory equipment^{1,2}, with the heating rate of 5 °C per min. To evaluate the effect of heat treatment on peat group composition (GC) alteration, the components were extracted from the original and modified peat samples⁹. Compared to H1/H2/H3 samples, the results of terrestrial peat sample analysis (Table 2) revealed a high yield of such components as bitumen (B), fulvic acid (FA), cellulose (C) and low yield of water soluble and easily hydrolyzed substances (WS+HS). Humic acids (HA) and nonhydrolyzed residue (NHR) produced smaller yields. This regularity was preserved after heat treatment, which in its turn indicates conservation of the peculiarities caused by the impact of peat-forming processes on the initial substance. However, transformation intensity expressed as a relative change in the yield of individual group components (ΔGS) for terrestrial peat and fen peat was different. It was shown

that the content of bitumen ($\Delta B = 23.3 \dots 67.5\%$ rel.) fulvic acids ($\Delta FK = -21, 3 \dots -23.1\%$ rel.) changed considerably in comparison with B1/B2/B3. The values of ΔGC were low in fen peat.

Table 2. Peat Group Composition

Peat	T, °C	Group composition, % daf					
		B	WS+HS	FA	HA	C	NHR
Terrestrial Peat							
B1/B2 /B3	-	6.3/8.2/8.0	32.6/31.3 /30.3	18.3/18.6 /19.7	25.0/28.0 /28.9	5.4/5.7 /2.8	12.4/8.2 /10.3
	250	6.8/9.0/8.6	27.2/25.1 /26.9	15.1/14.9 /16.2	31.0/35.0 /34.0	4.8/5.1 /2.6	15.1/10.9 /12.0
ΔGS after heat treatment, % rel.							
ΔB		ΔWS+HS		ΔFA	ΔHA	ΔC	ΔNHR
+7.5...+9.6		-11.2...-19.8		-17.5...-19.9	+17.6...+25.0	-7.1...-11.1	+16.5...+32.9
Peat	T, °C	Group composition, % daf					
		B	WS+HS	FA	HA	C	NHR
Fen Peat							
H1/H2 /H3	-	3.0/3.1 /2.9	33.5/28.3 /26.2	13.0/13.0 /12.7	30.0/38.0 /40.0	2.3/1.7 /1.9	18.2/15.9 /16.5
	250	3.7/3.3 /3.4	27.6/25.0 /22.8	10.2/10.0 /10.0	36.0/42.0 /44.0	2.2/1.6 /1.8	20.3/18.1 /18.0
ΔGS after heat treatment, % rel.							
ΔB		ΔWS+HS		ΔFA	ΔHA	ΔC	ΔNHR
+23.3...+67.5		-11.7...-17.6		-21.3...-23.1	+10.0...+20.0	-4.3...-5.9	+7.5...+11.5

The results of the elemental analysis of peat¹⁰ also allowed revealing the peculiarities caused by the preliminary heat treatment. Thus, the amount of carbon and nitrogen (C+N) increases while the amount of hydrogen and sulfur decreases (Table 3) after peat heating. This clearly demonstrates the character of organic peat matter alteration during heat treatment up to 250 °C in decomposing gases. This process is accompanied by peat decomposition and formation of carbon dioxide and pyrogenetic moisture. At the same time, the aromatic fragment condensation reaction can be observed^{3,11,12}.

Table 3. Peat Elemental Content

Peat	T, °C	Elemental content (EC), % daf			
		C	H	N	O+S*
Terrestrial Peat					
B1/B2/B3	-	55.8/57.1/57.9	6.0/6.0/5.9	1.5/1.3/2.5	36.7/35.6/33.7
	250	58.7/62.2/59.8	5.8/6.0/5.7	2.3/1.9/3.1	33.2/29.9/31.4
ΔEC after heat treatment, % rel.					
ΔC		ΔH	ΔN	ΔO+S	
+3.4...+8.8		-2.0...-3.4	+27.1...+51.9	-6.8...16.0	
Fen Peat					
H1/H2/H3	-	4.4/53.7/52.8	5.6/6.1/6.3	5.9/2.9/4.5	45.1/37.3/36.4
	250	54.6/59.6/58.1	5.3/5.7/5.8	6.3/3.5/4.6	33.8/31.2/31.5
ΔEC after heat treatment, % rel.					
ΔC		ΔH	ΔN	ΔO+S	
+9.9...+25.9		-4.7...-8.0	+4.3...+19.2	-7.1...-15.3	

Optical properties of peat were studied by IR spectroscopy. IR spectra were obtained at National Research Tomsk Polytechnic University laboratory through the application of FTIR spectrometer, Nicolet iS10 Corporation Thermo Fisher Scientific (USA), equipped with the special attachment of frustrated total internal reflection (FTIR) with a ZnSe crystal. Experiment parameters were as follows: resolution - 4 cm⁻¹, number of sample scans and

comparison spectrum - 128 scan range from 4000 to 650 cm^{-1} . In order to obtain spectra of peat samples, they were crushed and sieve-grinded upto 0.25 mm.

All peat spectra were registered and processed using Omnic 8.3. Automatic baseline correction was carried out to eliminate the tilting effects caused by the FTIR method. This method was used to register absorption band shifts and the wavelength influence on the depth of penetration into the sample.

The absorption bands in IR spectra of B1/B2/B3 H1/H2/H3 samples are common to peat and located in the stretching zone of OH-groups (3400 cm^{-1}) joined by intramolecular hydrogen bonds, methylene CH_2 -groups and methyl CH_3 -groups (2920 cm^{-1} and 2850 cm^{-1}), carboxyl $\text{C}=\text{O}$ -groups ($1725 - 1700 \text{ cm}^{-1}$), $\text{C}=\text{C}$ poly-coupling aromatic system ($1620 - 1600 \text{ cm}^{-1}$) and monoaromatic structures ($1520 - 1500 \text{ cm}^{-1}$). Faint absorption bands are seen in deformation vibration zone of $\text{C}-\text{CH}_3$ -groups ($1390-1370 \text{ cm}^{-1}$) and the stretching zone of acid $\text{C}-\text{O}$ -groups, phenols ($1250-1200 \text{ cm}^{-1}$). In accordance with¹³, the band $1100-1000 \text{ cm}^{-1}$ corresponds to the stretching zone of alcohol $\text{C}-\text{O}$ -groups. Identification of absorption bands within the area below 1000 cm^{-1} was not carried out.

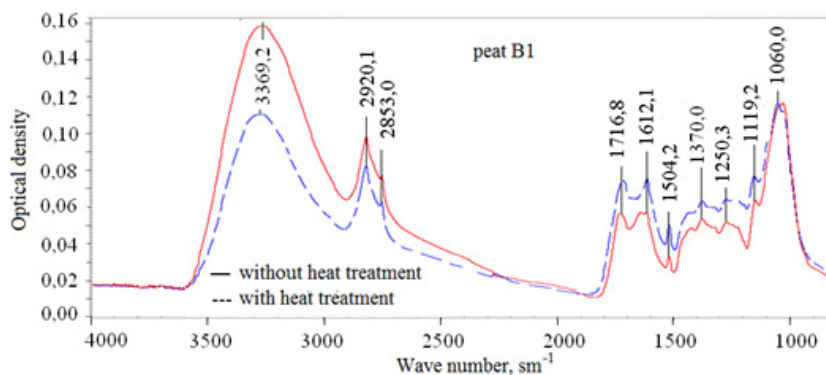


Fig. 1. The IR Spectra of Cotton Grass-Sphagnum Peat, R=25%

All samples have the same type of functional composition, the similarity of which is detected by comparing IR spectra of the studied samples with peat samples from other regions¹³⁻¹⁴. Peculiar features of functional composition related to the type of peat preserve after heat treatment under given conditions (Fig. 1).

As a result of the peat heat treatment in the IR spectra, it is possible to trace intensity decrease in the stretching of OH groups and C-H groups at 3400 cm^{-1} and 2920 cm^{-1} . This fact confirms the presence of dehydration reaction at low temperature thermal decomposition. The intensity of absorption bands for the $\text{C}=\text{O}$ groups at $1725-1700 \text{ cm}^{-1}$ and $\text{C}-\text{O}$ -groups of acids, phenols at $1250-1200 \text{ cm}^{-1}$ increases. It indicates the changes in peat functional composition due to the interaction of thermal decomposition products (esters, aldehydes, ketones) with pyrogenetic water. This results in the formation of new carboxyl groups^{1-3,15}. More noticeable changes are typical for B1/B2/B3.

Paramagnetic properties were studied using the EPR radio spectrometer Bruker ELEXSYS E-540: X-band at a frequency of 10 GHz microwave radiation in a high cylindrical resonator. G-factor was determined from the spectra using the internal frequency meter calibrated to g-factor DPPH. Measurements were carried out at 10dB power in EPR ampoules, with inner diameter being 5 mm.

Based on the measurement of resonator quality at microwave field being 33 dB and without using external reference, determination of the spin content was carried out according to the procedure developed by «Bruker» - Absolute spins. The calculation was made assuming that electron shell had doublet state ($S = 1/2$). The accuracy of the spin content: $\pm 15\%$.

The findings show that the heat treatment leads to a significant increase of EPR signal. The concentration of paramagnetic centers becomes higher (Table 4). This fact can be explained by an increasing degree of inner peat aromatic poly-couplings.

Table 4. Electronic Paramagnetic Resonance of Peat

Peat	T, °C	Spin number with $s=1/2$, $I \cdot 10^{17} \text{ spin/g}$	Narrow singlet g-factor
Terrestrial Peat			
B1/B2/B3	-	0.239/0.362/0.367	2.0020/2.0018/2.0019
	250	2.042/2.700/3.322	2.0061/2.0060/2.0061
Fen Peat			
H1/H2/H3	-	0.065/0.093/0.099	2.0018/2.0022/2.0024
	250	2.521/0.916/1.641	2.0064/2.0064/2.0063

3. Conclusion.

- Heat treatment of different peat types contributes to increasing bitumen, humic acids and nonhydrolysable residue in their group composition, while the content of other components decreases.
- The differences related to the influence of peat type on the content of group components preserve after peat preliminary heat treatment in the given conditions.
- The influence of heat treatment on the peat group content is defined by peat type: the greatest relative changes in the content of bitumen and fulvic acids are typical of fen peat, while the greatest relative changes in the content of humic acids, cellulose and nonhydrolysable residue are common to terrestrial peat.
- Heat treatment increases the carbon and nitrogen content in the elemental composition.
- The dependence of elemental composition upon the peat type preserves after heat treatment.
- The greatest relative changes of carbon and hydrogen content are obtained in fen peat, the greatest relative changes of nitrogen content - for terrestrial peat.
- Typical absorption bands preserve in IR spectra of heat treated samples.
- The reduction of stretching intensity of OH groups and C-H groups at 3400 cm^{-1} and 2920 cm^{-1} and the increase of absorption band intensity of C = O groups at $1725\text{-}1700 \text{ cm}^{-1}$ and phenols at $1250\text{-}1200 \text{ cm}^{-1}$ are observed after heat treatment, which in its turn indicates that dehydration reaction and further interaction of pyrogenetic water with peat thermal decomposition products take place to form new carboxyl groups.
- Heat treatment of peat contributes to increasing the paramagnetic properties (ESR signal and concentration of paramagnetic centers).

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