Some peculiarities of burnt birch wood pyrolysis

View the article online for updates and enhancements.

Some peculiarities of burnt birch wood pyrolysis

E Khalimov[1], T Shteba[1], Y Yuryev[2]*

[1]*The Ural Institute of State Firefighting Service of Ministry of Russian Federation for Civil Defense,* 22 Mira Street, Yekaterinburg 620062,Russian Federation
[2]Department of chemical technology of wood, biotechnology and nanomaterials of the *Ural State Forest Engineering University,* 37 Sibirskiytrakt, Yekaterinburg 620100, Russian Federation

*Corresponding email:charekat@mail.ru

Abstracts. The results of thermal analysis of sound and burnt birch wood samples were compared. An attempt was made to establish a connection between the type of the TG, DTG and DSC curves and the mechanism of wood pyrolysis. The dependence of the exothermic effect of the pyrolysis process on the oxygen content in the original wood is shown.

1.Introduction
The relevance of the study is due to the annual forest fires and the related problem of efficient processing of wood damaged by fire. This is particularly true for burnt hardwood, which is most commonly sold as firewood without any significant processing [1].

One of the promising options for processing burnt wood is pyrolysis in order to produce charcoal. Pyrolysis of sound and burnt wood can have significant differences. Thermal analysis provides the information necessary to understand the pyrolysis process of wood of different quality and the subsequent choice of industrial technology.

2.Materials and methods
For the analysis we used a sample of sound birch wood and a sample of burnt birch wood, taken at the site of a ground fire in the area of the village Shabry which is situated 30 km from Yekaterinburg. Elemental analysis of wood samples was carried out on an analyzer Euro EA 3000 (EuroVector, Italy).The sample was burned in the reactor, followed by separation of the combustion products on a chromatographic column.

Thermal analysis (Figure 1) was performed on an STA 449 F5 Jupiter®. The observations were carried out at a temperature of up to 900 ºC in argon (gas flow rate 70 ml / min) with a heating rate of 10 deg / min.

3.Results and discussion
The results of determining the elemental composition of wood are shown in Table 1.

Table 1. Elemental composition of birch wood samples.

№	Element content, %		
	carbon	hydrogen	oxygen (by difference)
Sound wood	46.5	5.6	47.9
Burnt wood	70.1	3.1	26.6

From Table 1, one can draw attention to the fact that the content of oxygen in burnt wood is 44% less than in sound wood.
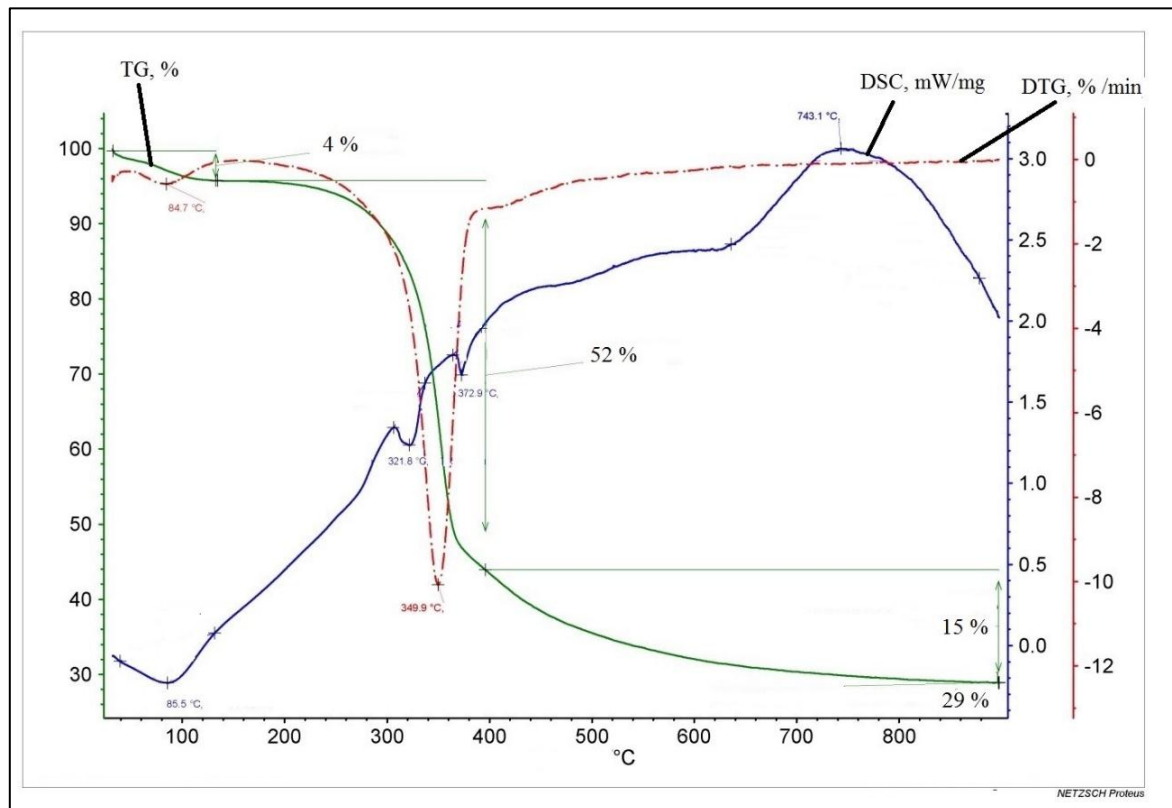
Figure 1. Thermogram of burnt birch wood.

Here: TG (TG) is the thermogravimetry curve, i.e. sample weight loss,%; DSC (DSC) - differential scanning calorimetry curve, mW / mg, DTG (DTG) - differential thermogravimetry curve, i.e. weight loss rate,% / min.

The calculation results of the thermal analysis are presented in Table 2.

Table 2. Results of thermal analysis of birch wood.

Wood sample	Weight loss at the drying stage, %	Weight loss at the pyrolysis stage, %	Weight loss at the charcoal calcination stage, %	Solid Residue, %	ΣQ_{endo}, J/g	Q_{exo}, J/g
Sound birch wood	7	64	11	18	127	1054
Burnt birch wood	4	52	15	29	36.2	614

Comparison of thermograms of sound and burnt birch wood (Table 2) showed that burnt wood is characterized by less weight loss, lower values of endothermic and exothermic effects and a slight shift of DSC and DTG peaks towards lower temperatures [2].The magnitude of theexothermic effect was reduced by approximately 42 %. Table 1 shows that the oxygen content in burnt wood is 44% lower than in sound wood, which indicates a direct correlation between the oxygen content in the original wood and the value of the exothermic effect of pyrolysis.

The pyrolysis process is carried out at a constant temperature increase. In this case lignin-carbohydrate complex of wood has to change, because energy cannot be stored in original condition due to the weak-link scission.Changes in the elemental composition of a solid residue with rising temperature lead to an increase its carbon content interrelated by strong carbon-carbon bonds. It is known that the most thermally stable forms of carbon are graphite and diamond, since the more ordered carbon structure, the better it resists the effects of temperature.

After the wood drying the process of dehydration begins, i.e. chemically bound water is removed from lignin-carbohydrate complex. Upon that, the wood becomes brown and decreases in volume.Deep dehydration leads to the formation of carboid structures (Figure 2), which are the basis for the formation of charcoal structure [3]. It has been shown that DTG curves for some species of dehydrated wood, for example, birch and pine torreficates, are almost identical [4]. Dehydration leads to a change of the chemical composition: an increase of carbon content in the solid residue due to a decrease of the oxygen content and hydrogen (removal of water). At this stage, the process of CO_2release begins.

While further temperature increase, the process of carbonization begins, accompanied by the formation of a vapor-gas mixture and the formation of the charcoal structure. Carbonization first begins in dehydrated hemicelluloses, as in the least thermostable part of wood. Shortly after that, the carbonization process of dehydrated the cellulosebegins. The last step is the carbonation of lignin. While temperature increase the carboid structures of the solid residue, consisting mainly of cyclic compounds, are increasingly enriched with carbon by reducing their content of hydrogen, and especially oxygen. An aromatization of dehydrated wood occurs, i.e. benzene rings content in charcoal increases. The degree of charcoal aromaticity by 400^0C increases to 0.95.

Over 400^0C the formation of condensed compounds, i.e. multi-nuclear aromatic structures begins in charcoal. Condensation leads to further removal of foreign oxygen and hydrogen atoms from charcoal. Charcoal condensation degree to 400^0C is 0.27, begins to increase. Polycycles grow in size and they form grids of cyclically polymerized carbon. The development of condensation processes leads to a sharp increase in the electrical conductivity of charcoal [5].

The main mass loss for most of tree species occurs up to a temperature of 400^0C [6]. It is noted that upon wood particle size reduction, the DTA and DSC curves shift to lower temperatures [7]. It is known that the main destruction of hemicelluloses occurs in the range of $225…325^0$C, the destruction of cellulose - at $325..375^0$C, and the destruction of lignin - at $250…500^0$C [8].

It is known that both the content and composition of hemicelluloses and lignin strongly depend on the wood species, which affects the position and intensity of the corresponding peaks during thermal analysis. The ranges of the main degradation of hemicellulose, cellulose and lignin mutually overlap.

Since the chemical composition of wood depends on the species, it affects the number and intensity of peaks on the curves of DTA and DTG in the temperature range 250...400^{0}C.

At temperature above 800^{0}C, the carbon content in charcoal exceeds 95% and the carbonization process goes into graphitization, that is, the process of forming a spatially ordered structure of solid carbon.
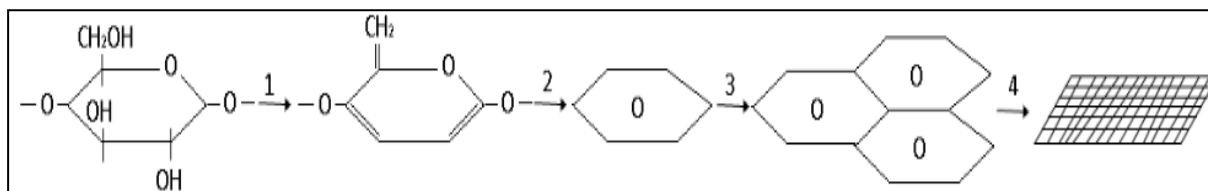
Figure 2. The main stages of wood pyrolysis.1 - dehydration, 2 - aromatization, 3 - polycondensation, 4 - formation of grids.

Charcoal refers to hard-to-graphitize materials. At temperature up to 2000^{0}C, the bulk of charcoal consists of amorphous carbon with a small content of single crystallites or crystallite blocks. The charcoal crystallites have a T-structure (turbostratic) and the crystallites are characterized by small sizes and an almost complete absence of mutual orientation of the grids, in comparison to the G-structure of graphite with large crystallite sizes and mutually oriented parallel carbon grids. With rising heat treatment temperature of charcoal the proportion of the crystalline part increases in it, but charcoal never has a completely ordered structure.The reasons for this are the original porous wood structure, the amorphous state of most of the fragments that make up the lignin-carbohydrate complex (only cellulose, and then partially consists of crystallites), and the functional groups on the charcoal surface, preventing the convergence of layers of carbon grids and their mutual orientation.

The pyrolysis mechanism, resulting in the charcoal structure is formed, is of a radical nature, that is, it proceeds with the participation of radicals - compounds that have an unpaired electron in their composition.

At the beginning of the pyrolysis process, high molecular radicals are formed, for the formation of which it is sufficient to have an energy of about 200 kJ / mol. For the formation of low molecular radicals, an energy of 320 ... .400 kJ / mol is needed, i.e. higher temperature.

During rapid pyrolysis, the formation of high molecular radicals and low molecular radicals proceeds approximately at the same time, which creates conditions for their recombination with the formation of relatively movable compounds that can leave the zone of high temperatures in the vapor-gas mixture. During slow pyrolysis, when the temperature rises slowly, the formation of high molecular radicals and low molecular radicalsis divided by time. In this case, high molecular radicals recombine with each other to form high-molecular carboid and aromatic compounds, which remain in the high-temperature zone as part of the solid residue, forming the charcoal structure.

The characteristics of this structure are important for choosing the direction of qualified use of the resulting carbon material. Charcoal and its products are carbon nanoporous materials and they contain all types of pores. Recent concerns about the global environment have led to renewed interest in such materials for energy storage and environmental protection.In particular, the number of studies on the role of textural properties of carbon in energy storage systems is growing [9].It has been shown, for example, that carbon materials of various origins that contain micropores less than 2 nm in size are used for supercapacitors; however, materials containing meso- and macropores are promising to increase capacity [10]. Charcoal and its modification productsare classified assuch materials.

4. Conclusion
The results of thermal analysis of sound and burnt birch wood samples were compared.For the analysis a sample of sound birch wood and a sample of burnt birch wood, taken at the site of a ground fire that is situated 30 km from Yekaterinburg were used.

An attempt was made to establish a connection between the type of the TG, DTG and DSC curves and the mechanism of wood pyrolysis.The dependence of the exothermic effect of the pyrolysis process on the oxygen content in the original wood is shown.

The number and intensity of peaks on the curves of DTA and DTG in the temperature range 250...400 ^{0}C depend on wood chemical composition.

References
[1]   Makarov A V 2011 Tekhnicheskie kachestva drevesiny, povrezhdennoj razlichnymi vidami pozhara. [Technical qualities of wood damaged by various types of fire]. Lesotekhnicheskij zhurnal, **4 (4)** 14-18
[2]   Khalimov E ., Bezzaponnaya O . and Zykov P I 2017 Issledovanie piroliza berezovoj drevesiny gorel'nikov metodom sinhronnogo termicheskogo analiza i mass-spektrometrii. [Study of burnt birch wood pyrolysis by the method of synchronous thermal analysis and mass spectrometry]. Tekhnosfernaya bezopasnost' **3 (16)** 26-35
[3]   Yuriev Y L 1997 Tekhnologiya lesohimicheskih proizvodstv. [Technology wood-chemical industries]. Part 1. Piroliz drevesiny, Ekaterinburg 99.
[4]   Pushkin S A, Grachev A N, Makarov A A, Kozlova L V and Gorshkova T A 2015 Termicheskij analiz torreficirovannoj drevesiny sosny i berezy. [Thermal analysis of torrefied pine and birch wood]. Vestnik tekhnologicheskogo universiteta., vol. 18. **5**. 45-47.
[5]   Levin E D 1980 Teoreticheskie osnovy proizvodstva drevesnogo uglya. [The theoretical basis for the production of charcoal]. –(Moscow: Lesnaya promyshlennost') p 152
[6]   Loskutov S R, Shapchenkova O A and Aniskina A A 2015 Termicheskij analiz drevesiny osnovnyh lesoobrazuyushchih porod Srednej Sibiri. [Thermal analysis of wood of the main forest-forming species of Central Siberia]. Sibirskij lesnoj zhurnal, **6** 17-30
[7]   Afanasyev V V, Kovalev V G, Orlov V N and Tarasov V A 2016 Issledovanie fiziko-himicheskih svojstv gazifikacii mestnyh vidov topliv. [Investigation of physical and chemical properties of gasification of local fuels]. Fundamental'nye issledovaniya, **9-2** 227-232
[8]   Serkov B B, Aseeva R M and Sivenkov A B Fiziko –himicheskie osnovy goreniya I pozharnaya opasnost' drevesiny. [Physical and chemical bases of burning and fire danger of wood]. Internet-zhurnal «Tekhnologii tekhnosfernoj bezopasnosti», 2011, 6 (40), (http://ipb.mos.ru/ttb)
[9]   Zhang J *et al*. Carbon science in 2016: Status, challenges and perspectives. Carbon, volume 98, march 2016, pp 708-732
[10]   Cheng P, Gao S, Zang P, Yang X, Bai Y, Xu H., Liu Z and Lei Z Hierarchically porous carbon by activation of shiitake mushroom for capacitive energy storage. Carbon,Volume 93, August 2015, pp 315-324