Investigation of Thermal Properties of Fuel Briquettes by DSC Method

L A Nikolaeva¹, T M Solovev²,³

¹IPOG SB RAS, 1 Oktyabrskaia st., Yakutsk 677980, Republic of Sakha (Yakutia), Russia
²IPOG SB RAS, 1 Oktyabrskaia st., Yakutsk 677980, Republic of Sakha (Yakutia), Russia
³Department, Organization, Address, City and Postcode, Country
12IPOG SB RAS, 1 Oktyabrskaia st., Yakutsk 677980, Republic of Sakha (Yakutia), Russia

E-mail: ¹lanikolaeva_ipng@mail.ru, ²TuskulSolovev@yandex.ru

Abstract. The article presents the investigation of thermal destruction of wood (pine), brown coal, oil sludge, and bitumen of BND 90/130 grade by the method of differential scanning calorimetry. A thermal analysis of the samples was accomplished in an oxidizing environment (air). The stages of the thermal decomposition under the conditions of programmed heating from 40°C to 600°C at a rate of 20°C /min, their temperature ranges, and maximum temperatures on the DSC curves have been established. The thermal effects of the evaporation of bound moisture and the process of thermal decomposition of the fuel have been determined.

1. Introduction

Previous studies have shown regularities of changes in the physical-mechanical properties of fuel briquettes containing organo-mineral fillers from local raw materials of Yakutia – natural zeolite and brown coal. Production of briquettes includes the following main stages: heat treatment of low-grade fuel, the formation of raw briquettes, and drying, which allows obtaining the required physical-mechanical characteristics [1-11].

The DSC method was used to determine the temperature ranges at which physical-chemical transformations occur in fuels, as well as to measure the thermal effect of the processes. Physical and chemical properties of wood, such as density, heat capacity, thermal conductivity, moisture content, and chemical composition (ratio of the main polymer components, physical-chemical characteristics of hemicelluloses, cellulose, and lignin, the content of extractive substances), determine the parameters of thermal destruction. The products of thermal decomposition of wood in an inert atmosphere are non-condensable gases, heavy volatile substances (including wood tar), and charcoal. In an oxidizing environment, thermal destruction of wood is performed in two stages: the first stage is where the main components are volatilized, and coal is formed at low temperature; the second stage is where the decomposition of lignin is completed, and the coal formed at an early stage is oxidized (burns).

In general, the thermal destruction of wood, both in an inert and in an oxidizing environment, can be represented by the sum of the reactions of thermal decomposition of individual components: hemicelluloses, cellulose, and lignin. It is known that the temperature ranges of the thermal destruction
of these components partially overlap. The thermal decomposition of hemicelluloses, cellulose, and lignin occurs at 225-325, 305-375, and 250-500 °C, respectively. Extractive substances, despite a small proportion (2-5%) in the wood composition, significantly affect mechanical strength, color, and thermal stability [12-18].

2. Research objects and objectives
Samples of pinewood were a shredded mass, which was previously sieved (fraction 0.5 mm <) and dried in a drying cabinet at a temperature of 105°C to remove external moisture. Brown coal from the Kangalasskoye deposit was previously crushed and dried at a temperature of 105 °C.

In the study, mixtures of coal and wood were analyzed in the form of powder and briquette. Oil sludge and oil bitumen of BND 90/130 grade were also investigated as a binding agent. Oil sludge was taken from oil product storage tanks of the OA Tuymaada-Neft oil company. These oil slimes are formed during the storage of oil products at the bottom of the special sedimentation tanks. Before the analysis, the sludge was kept in a drying oven at 105°C. The chemical group composition of oil sludge and bitumen is presented in Table 1.

Table 1. Chemical group composition of BND 90/130 bitumen and oil sludge.

| Component       | Oils  | Benzene | Alcohol-benzene | Asphaltenes |
|-----------------|-------|---------|-----------------|-------------|
| Oil sludge      | 57,17 | 14,98   | 25,32           | 2,53        |
| BND 90/130 bitumen | 36,53 | 25,62   | 20,75           | 17,1        |

Differential scanning calorimetry was performed with DSC 204 F1 (NETZSCH, Germany). The samples were analyzed in the air under the following conditions: the heating rate was 20°C/min from 40 to 600°C, protection gas (helium) flow rate was 50 ml/min, purge gas flow rate was 30 ml/min, sample weight was 1.41 -3.00 mg, the crucible was aluminum with a perforated lid, the standard is an empty aluminum crucible.

3. Assessment of thermal destruction of briquettes
The main reasons that determine the difference in the thermal destruction indices of the samples are its chemical composition and the nature of their interaction. Common to all the samples in the oxidative thermal destruction is the presence of two temperature ranges: in the first one, there is an endothermic effect associated with moisture evaporation; in the second, there is the actual thermal decomposition of the fuel accompanied by the release of heat with two maxima on the curves.

Table 2 shows the most crucial quantitative DSC indicators of all samples. At relatively low temperatures from 80-120°C, phase transformations or chemical reactions take place in the samples, accompanied by heat absorption. An endothermic maximum is fixed on the wood DSC curves, which refers to the evaporation of a noticeable amount of strongly adsorbed water. In the temperature range of 110-120°C, the transformations are completed, and the temperature starts to rise again. Exothermic peaks at 369 and 497°C are caused by the destruction of wood components, primarily cellulose. Similar results were obtained in work. In the present work, it has been shown that in an oxidizing environment, thermal destruction of wood is performed in two stages: the first stage is the removal of the main components and the formation of coal at low temperature; the second stage is lignin
decomposition and oxidation (burning-out) of the coal formed at an early stage. In general, the thermal destruction of wood can be represented by the sum of the reactions of thermal decomposition of individual components: hemicelluloses, cellulose, and lignin. It is also known that the temperature ranges of thermal destruction of these components partially overlap. Thermal decomposition of hemicelluloses, cellulose, and lignin occurs in the ranges 225–325, 305–375, and 250–500 °C, respectively. Cellulose is characterized by higher thermal stability than hemicelluloses and lignin, which is due to its high crystallinity (degree of structure ordering). Hemicelluloses are less thermally stable than cellulose and lignin, which is due to the presence of acetyl groups [12-13, 19-20]. Exoteric peaks above 500°C are caused by the final destruction of all components of the lignocellulose mass.

The temperature transitions detected on the DSC curves are complex, and the processes accompanied by the absorption or release of heat include many reactions proceeding at a high rate and ending either with the formation of new components or destruction of the wood pulp constituents.

It follows from the obtained data that the optimal temperature for pressing the briquette composite material should not exceed the temperature of the beginning of the intensive thermal destruction of the fibrous mass.

**Table 2.** Basic parameters of samples obtained in the DSC experiment at a heating rate of 20°C/min in an oxidizing environment.

| Fuel type          | Endothermic | Endoeffect, Minimum | Temperature range, °C | Exothermal Maximum |
|--------------------|-------------|---------------------|-----------------------|-------------------|
|                    | Endo-effect, Temperature, °C | J/g                |                      | kJ/g              |
| Pine               | 68,7        | 40,3                | 330-526               | 369, 497          | 8,8               |
| Lignite            | 77,3        | 40,3                | 350-557               | 427, 532          | 21,2              |
| Coal/wood (Powder)| 79,6        | 98,7                | 361-557               | 431, 531          |                   |
| 21,2               |             |                     |                       |                   |                   |
| Coal/wood (Briquette) | 91,4        | 52,3                | 352-557               | 437, 513          | 18,5              |
| Oil sludge        | 54,6        | 61,8                | 297-539               | 340, 511          | 11,1              |
| Bitumen           | 44,3        | 76,4                | 312-566               | 532               | 6,6               |

**4. Conclusion**

The results of the investigation of fuel briquettes by the DSC method have revealed that thermal processing can be organized at the expense of the internal calorific value of the fuel without attracting additional heat sources. The use of its thermal resources will significantly reduce the energy consumption of the process of obtaining refined fuel briquettes, predict the conditions for their storage and processing. In this case, the optimal pressing temperature of the briquette composite material
should not exceed the temperature of the beginning of the intensive thermal destruction of the fiber mass.

Maintaining the production of coal briquettes will allow obtaining high-grade and transportable fuel of improved quality, will lead to reduction of coal losses during storage, utilization of oil waste and waste from timber industry and woodworking enterprises. Moreover, it will increase the extraction of brown coals for their use for energy and technological processing, and consequently, intensify the industrial development of the adjacent territories.

5. References

[1] Nikolaeva L A, Burenina O N, Solovev T M Development of Technologies for Processing Large-Tonnage Accumulations of Oil Sludge and Wood Waste with Obtaining Binders to Improve the Quality of Household Briquetted Fuel Based on Brown Coal IOP Conference Series: Earth and Environmental Science 2019 Vol 272 P 022146 https://doi.org/10.1088/1755-1315/272/2/022146

[2] Solov'ev T M, Nikolaeva L A, Burenina O N 2019 Povyshenie kachestva buryh ugley putem briketirovaniya s drevesnymi othodami [Improving the quality of brown coal by briquetting with wood waste] Uglehimija i iekologija Kuzbassa [Coal chemistry and ecology of Kuzbass]: Book of abstracts of the VIII International Russian-Kazakh Symposium (KemeroVo) Kemerovo: The Federal Research Centre of coal and Coal Chemistry of SB RAS pp 56

[3] S N Popov, O N Burenina, L A Nikolaeva, T M Solov'ev TU 19.30.12-001-03534081980004-2019 Brikety iz ugley buruh Kangalasskih Tehnicheskie usloviya [Briquettes from Kangalassky brown coals. Specifications] Registered 15.07.2019 No 037/000218 (Yakutsk: FBU «Yakutsk center for standardization, metrology and testing») pp 14

[4] Nikolaeva L, Burenina O, Latyshev V 2009 Toplivnye brikety iz buryh ugley Yakutii Himiya tverdogo topliva 2 pp 55–59

[5] Nikolaeva L and Burenina O 2017 Justification of Rational Parameters of Briquetting Using Mechanic Activation AIP Conference Proceedings 1915 040042 http://aip.scitation.org/doi/abs/10.1063/1.5017390

[6] Nikolaeva L and Popov S 2013 Svyazuyushchie kompozicii dlya briketirovaniya burugol'nyh othodov Izvestiya vuzov Gornyj zhurnal 3 pp 127-132

[7] Burenina O, Popov S, Nikolaeva L, Davydova N, Solovev T 2017 Sposob polucheniya ugol'nyh briketov RU 2017116319

[8] Nikolaeva L, Popov S, Burenina O and Solov'ev T 2017 Utilizaciya othodov derevopererabatvayushchih predpriyatij Respubliki Saha (Yakutiya) v toplivnye brikety Naukovedenie Vol 9 6 https://naukovedenie.ru/PDF/64TVN617.pdf

[9] Nikolaeva L 2017 Razrabotka i strukturnye issledovaniya okuskovannogo topliva iz ugol'nyh othodov Othody i resursy Tom 4 4 https://resources.today/PDF/06RRO417.pdf DOI: 10.15862/06RRO417

[10] Popov S, Zarovnyaev B, Burenina O., Nikolaeva L 2014 Osobennosti briketirovaniya buryh ugley Yakutii Gornyi informacionno-analiticheskij byulleten' 9 pp 405–412

[11] Nikolaeva L and Burenina O 2012 Osobennosti briketirovaniya buryh ugley Lenskogo bassejna Fiziko-tekhнические проблемы razrabotki poleznых iskopаемых T 48 3 p 168

[12] Shen D K, Gu S, Luo K H, Bridgewater A V, Fang M X 2009 Kinetic study on thermal decomposition of woods in oxidative environment Fuel V 88 pp 1024-1030

[13] Vichnevsky S, Fuhr B, Melnichuk J 2003 Characterization of wood and non-wood mechanical pulps by differential thermal analysis J. Pulp & Paper Sci Vol 29 No 1 pp 17-20

[14] Loskutov S R 2015 Termicheskij analiz drevesnyh osnovnyh lesobrazujuvshhих porod Srednej Sibiri Thermal analysis of wood of the main forest-forming species of Central Siberia Siberian Journal of Forest Science pp 17-30

[15] Nasonov A D, Skurydin Ju G, Skurydina E M, Nasonov A D 2006 Vlijanie komponentov drevesnogho kompozicionnogo materiala na ego vjazkoaprugie karakteristiki [Influence of
components of wood composite material on its viscoelastic characteristics] Vestnik BSPU: Estestvennye i tochnye nauki [Natural and exact sciences] 6-2 pp 100-105

[16] Smirnov V G, Manakov A Ju, Dyrdin V V, Hicova L M, Mihajlova E S Smirnov V G 2017 Termogravimetricheskij analiz desorbcii vlagi iz prirodnyh uglej [Thermogravimetric analysis of moisture desorption from natural coals] Coke and Chemistry 10 pp 2-7

[17] Plahova T M, Dolzhina A D, Tabakaev R B 2011 Issledovanie teplovogo jeffeka piroliza torfa [Investigation of thermal effect of peat pyrolysis] Proceedings of the XVII International Research-to-Practice Conference «Sovremennaja tehnika i tehnologii [Modern machinery and technology]» pp 249-250

[18] Khare P, Khare B, Sarmah M, Baruah B P 2014 Chemometric Application for Thermal Behavior of Blends of Bamboo with Solid Fossil Fuel Environmental Progress & Sustainable Energy Vol 33 1 pp 315-321

[19] Skurydin Ju G, Nasonov A D 2016 Issledovanie vjazkouprugih svojstv listvennyh porod drevesiny [Investigation of viscoelastic properties of hardwoods] Vestnik Buryat State Uni. 4 pp 42-47

[20] Skurydin Ju G, Skurydina E M 2016 Vlijanie komponentov drevesnogo kompozicionnogo materiala na temperaturu fazovyh perehodov [Influence of components of wood composite material on the temperature of phase transitions] Physics and Chemistry of Materials Treatment 4 pp 57-62

Acknowledgments
The work was accomplished within the framework of the State Order of the FASO Russia (project No. AAAA-A17-117040710038-8 dated 04.07.2017).