Eurasian Chem.-Technol. J. 24 (2022) 131–136

https://doi.org/10.18321/ectj1325

Mechanical Activation as a Method to Regulate Morphology, Texture and Surface Functional Composition of Carbon-Mineral Materials Derived from Sapropel

O.I. Krivonos[1]*, O.B. Belskaya[1], V.A. Likholobov[2]

[1]Center of New Chemical Technologies BIC, 54, Neftezavodskaya str., Omsk, Russia
[2]Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 5, Lavrentyev ave., Novosibirsk, Russia

Article info

Received:
10 March 2022

Received in revised form:
24 April 2022

Accepted:
5 June 2022

Keywords:
Sapropel
Mechanical activation
Pore distribution
Carbon-mineral material

Abstract

Data on the synthesis of carbon-mineral materials (CMM) through carbonization of native sapropel after preliminary mechanical activation (MA) in the air environment are presented. The effect of MA parameters (time, the size and acceleration of milling bodies) on the fractional composition and morphology of sapropel is investigated. MA for 5–10 min promotes the dispersion of sapropel particles, while a further increase in treatment time causes their partial agglomeration. It is demonstrated that preliminary MA of native sapropel leads to changes in the texture parameters and acidity of the surface of CMM obtained after the carbonization stage. An increase in specific surface area from 90 to 560 m^2g^{-1} is observed, with an increase in the adsorption pore volume from 0.16 to 0.52 cm^3g^{-1} as a result of an increase in the fraction of micropores in the formed CMM. Despite this fact, CMM samples still contain large pores, and the fraction of meso- and macropores is 70%. In addition, a decrease in pH of the point of zero charge occurs as a consequence of an increase in the content of acidic oxygen-containing groups. The discovered effect is essential for the formation of sapropel-based materials with required properties and for broadening their application area.

1. Introduction

Expansion of the raw material basis by involving low-grade kinds of renewable raw materials (brown coal, bitumen, oil shale, peat, sapropel, biomass) into power engineering, petrochemical synthesis and other directions of the industry to obtain valuable chemical products, in particular carbon-containing porous materials, is a relevant direction [1–3]. A special position among caustobioliths is occupied by sapropel, but the problem of its rational application has not been solved yet. Sapropel is renewable natural organic-mineral raw material, a complicated structured complex of chemical substances, which contains the products of anaerobic decomposition of zoo- and phytoplankton (humic, readily hydrolysable, hardly hydrolysable and water-soluble substances, enzymes, vitamins, hormone-like substances), as well as the mineral component, incorporating macro- (Si, Al, Ca, Na) and microelements (Ni, Co, Mo, Se) (Table 1). Depending on the sapropel type, the content of the organic matter varies within the range of 10–90%, and carbon content may reach 70% [4–7].

Previously we demonstrated the possibility to obtain CMM based on sapropel, and regulating their physicochemical properties by means of preliminary chemical action on initial raw material. It has been shown that chemical treatment of sapropel with diluted acidic or alkaline solutions can increase pore volume and develop specific surface in CMM obtained by sapropel carbonization. The major fraction of pores was represented by mesopores 3.4–5.4 nm in diameter and macropores, more than 600 nm in diameter [8–10].

Along with traditional approaches involving chemical activation to modify the structure and properties of the surface of materials, technologies

*Corresponding author.
E-mail addresses: oksana@ihcp.ru

based on extreme kinds of activities such as radiolysis, plasma chemistry, supercritical extraction are currently under development [11–14]. One of these technologies is mechanical activation (MA), which involves the deformation of the multimeric structure of organic matter, with the rupture of interatomic and intermolecular bonds and the formation of a large number of defects. As a result, the thermal stability of the organic raw material decreases and its reactivity increases, which may have a positive effect on subsequent processing [15–21]. For instance, as far as brown coal processing is concerned, it has been established that its preliminary mechanical activation provides a decrease in the time of oxidative treatment by a factor of 1.5–2 in comparison with the traditional technology, with simultaneous improvement of the parameters characterizing pores size and adsorption properties [21, 22]. Despite additional energy consumption, mechanochemical processes have good potential due to their ecological safety [23].

The goal of the present work was to apply mechanical action to native sapropel to regulate the properties of CMM obtained on its basis.

Table 1
Composition and physicochemical characteristics of initial sapropel

Parameter	Value of the parameter
Ash content, %	29.0
pH	5.64
Bulk density, g cm^{-3}	0.32
Elemental composition, % per daf:	
C	52.1
H	7.4
N+O	39.7
S	0.8
H/C	1.70
Composition of the mineral part, wt.%:	
SiO_2	67.3
K_2O	0.1
CaO	1.4
Fe_2O_3	1.3
Al_2O_3	12.8
PO_4^{3-}	0.5
SO_4^{2-}	3.0

2. Materials and methods

Sapropel from the Siberian region (S) was used as the raw material. Its characteristics are presented in Table 1. This sample relates to the typical representatives of sapropelites at the peat stage of maturity (atomic ratio H/C >1, the fraction of heteroatoms 40.5 wt.%) with the ratio of organic to mineral part equal to 2.45 [5, 24].

Mechanical activation of native sapropel was carried out in the air in water-cooled high-energy centrifugal-planetary mill AGO-2 (NOVITS, Novosibirsk, Russia) with the milling bodies acceleration of 500 and 1000 ms^{-2}. Milling bodies were balls made of ShKh-15 steel, 5 and 10 mm in diameter. The ratio of sapropel mass to ball mass was 1:50. The time of MA was varied within the range from 5 to 60 min. Sapropel sample after mechanical activation is designated as S-MA.

Carbonization was carried out in a SNOL 7.2/1100 tubular furnace in Ar flow at a temperature of 600 °C for 30 min, with the heating rate 5 °C min^{-1}. The sample of native sapropel after thermal treatment is designated as CMM, and S-MA sample after thermal treatment is designated as MA-CMM.

The size of sapropel particles was determined by means of laser diffraction using a SALD-2101 laser analyzer (Shimadzu) with a measurement range of 0.03–1000 μm. Anionic surfactant sodium dodecyl sulfate was chosen as a surfactant for the tests on particle size determination.

Texture characteristics of the samples were studied using nitrogen adsorption at 77.4 K with the help of Sorptomatic 1900 instrument with preliminary high-temperature vacuum pumping to remove contamination or adsorbed substances from the surface. The specific surface of the samples was determined using Brunauer-Emmett-Teller procedure at the equilibrium relative pressure of nitrogen P/P_0 = 0.05–0.25. The fractions of the pores of different sizes were calculated by means of normalization.

Electron microscopic studies (SEM) of the samples were carried out with a JSM-6610LV scanning electron microscope (JEOL) with the attachment of X-ray energy dispersive spectrometer INC Ax-act (Oxford Instruments) for local chemical analysis. The morphology of the sample surface was investigated in secondary electrons at the accelerating voltage of 20 kV.

To evaluate the acid-base characteristics of the surface of resulting carbon-mineral materials, the points of zero charge (pHPZC) were determined according to the procedure described by Park and Regalbuto [25]. To determine PZC, the samples were placed in aqueous solutions with different initial pH. After establishing a constant pH value, measurements were carried out using Seven Multi ionomer (Mettler Toledo). A plateau in the dependence of the final equilibrium pH on initial pH corresponded to the PZC value.

The amount of surface carboxyl and hydroxyl (phenol-type) groups was determined by means of selective neutralization according to the procedure proposed in [26]. The total amount of acid groups (TAG) was determined by treating the weighted portion of a sample with a 0.01N solution of sodium hydroxide, followed by titration with 0.01N solution of hydrochloric acid to the neutral reaction determined with phenolphthalein.

3. Results and discussion

3.1. Investigation of the effect of MA parameters (acceleration of milling bodies, activation time, ball diameter) on the size and size distribution of sapropel particles

Particle size is an essential parameter affecting the conditions of further transformation of native sapropel. For this reason, the investigation into the effect of the time of mechanical activation on particle size was carried out. Analysis of the histograms of the particle size distribution for the native sapropel sample and after its MA with the balls 5 mm in diameter for 5, 10, 20 and 30 min (Fig. 1) showed that MA caused the dispersion of the material and the formation of particles 0.5–100 µm in size, but longer treatment time (20 and 30 min) caused redistribution, with the prevailing contribution from the particles 30 µm in size.

Results of the studies of the effect of milling body diameter and acceleration on the size and size distribution of the particles are presented in Fig. 2. It is demonstrated that after mechanical activation of sapropel for 10 min with milling bodies 10 mm in diameter at the acceleration of 500 ms^{-2} a narrower particle size distribution is observed, with the major fraction of particles 3–30 µm in size (Fig. 2a(1)). An increase in acceleration to 1000 ms^{-2}, with the same parameters, leads to the additional formation of particles larger than 50 µm, which is evidence of partial agglomeration of the particles under the shock regime (Fig. 2a(2)).

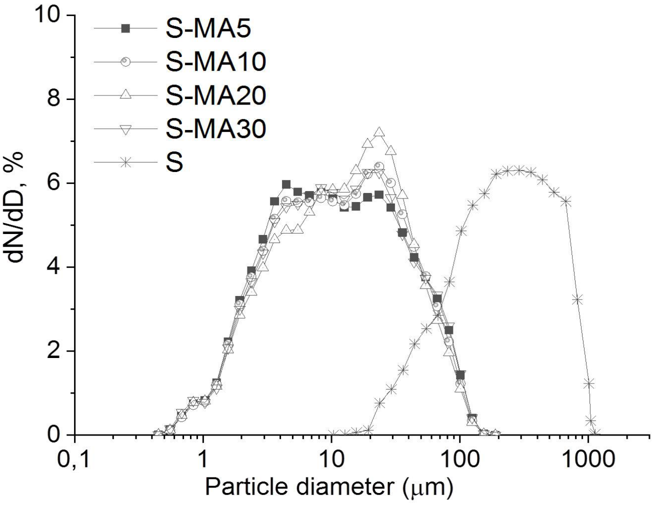

Fig. 1. Distribution of particles over size D (µm) for S and S-MA samples for different activation times. MA conditions: 5, 10, 20 and 30 min; diameter of milling bodies 5 mm; centrifugal acceleration of milling bodies 1000 ms^{-2}.

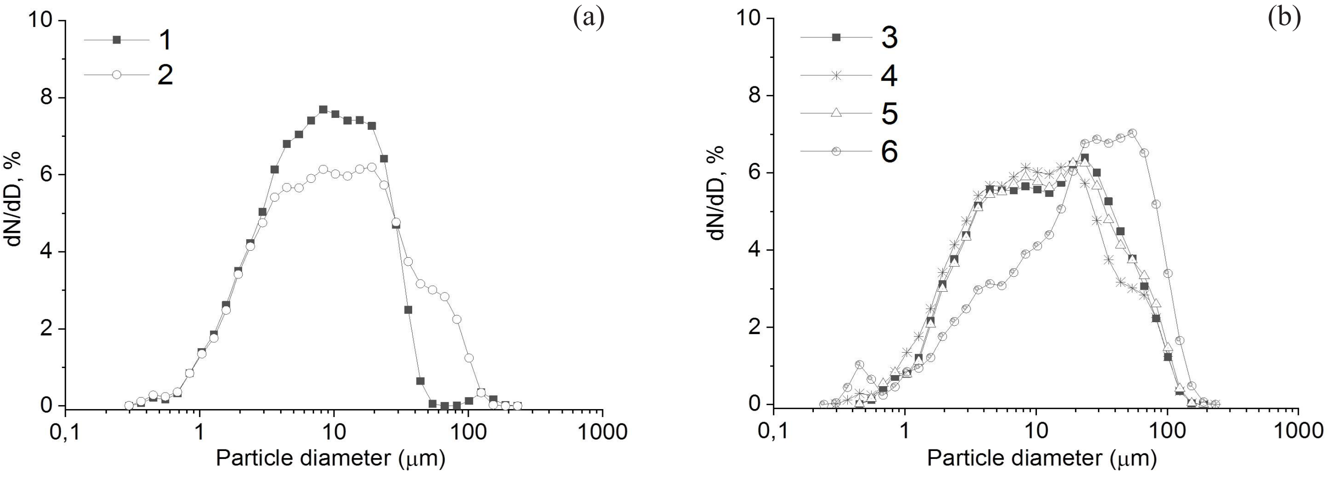

Fig. 2. Distribution of particles over size D (µm) for S-MA samples obtained under different conditions of MA: (a) – diameter of milling bodies 10 mm, 10 min with the centrifugal acceleration of milling bodies 500 (1) and 1000 (2) ms^{-2}; (b) – centrifugal acceleration 1000 ms^{-2}, activation time 10 (3, 4) and 30 (5, 6) min, diameter of milling bodies 5 (3) and 10 (4) mm.

It is determined that mechanical activation with milling bodies 5 mm in diameter (Fig. 2b) even for a longer time (30 min) and at the maximal acceleration does not lead to any changes (Fig. 2b(3,5)). A similar picture is also observed for the process carried out with milling bodies 10 mm in diameter for 10 min at the acceleration of 1000 ms^{-2} (Fig. 2b(4)) – the distribution curve is broad, with the major contribution from the particles not more than 30 µm in size. However, MA with milling bodies 10 mm in diameter for a longer time (30 min) causes a redistribution of particle size, with the maximum shifting to larger particles, 60 µm (Fig. 2b(6)). Particles 0.4–0.5 µm in size appear, maybe as a result of dispersing of the components with low strength belonging to the mineral part of sapropel.

Investigation using electron microscopy showed that the morphology of sapropel surface changes substantially after mechanical activation (Fig. 3). The electron microscopic image for S sample (Fig. 3a) reveals a non-uniform surface, which is a united conglomerate of the mineral and organic parts, with irregular granule shapes and granule size of 500–1000 µm. After MA, the particles of irregular fragmental shapes are visualized on the surface of S-MA sample. They are distributed either as sole particles or in agglomerations not more than 50 µm in size (Fig. 3b). So, mechanical activation of sapropel allows decreasing particle size by an order of magnitude.

3.2. Synthesis of carbon-mineral materials and investigation of the effect of MA of sapropel on their physicochemical properties

Thermal treatment of sapropel in Ar flow shows that the yields of MA-CMM and CMM are 52–54 wt.% and 49 wt.%, respectively, with the mass of native dried sapropel. Variation of sapropel MA time within the range of 5–30 min has no substantial effect on this parameter.

One can see in the electron microscopic image (Fig. 4) that, unlike for CMM, the MA-CMM sample is composed of particles not larger than 20 µm in size, with rounded and plate-like shapes (Fig. 4b); no film of amorphous carbon is visualized in this case, while it is seen coating uniformly the surface of CMM (Fig. 4a).

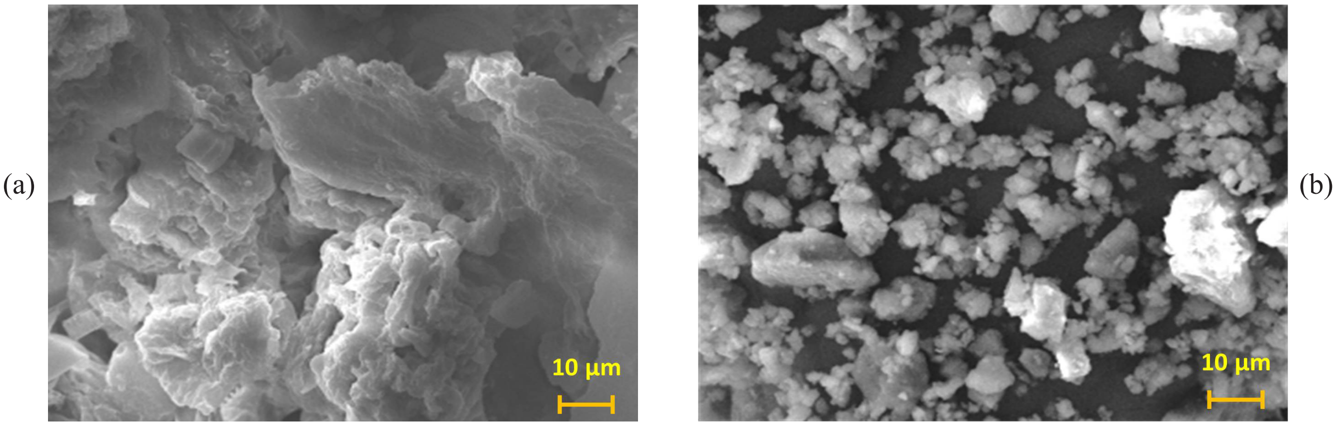

Fig. 3. SEM images of the samples S (a) and S-MA (b). MA conditions: diameter of milling bodies 10 mm, centrifugal acceleration 1000 ms^{-2}, time 10 min. Magnification × 1000.

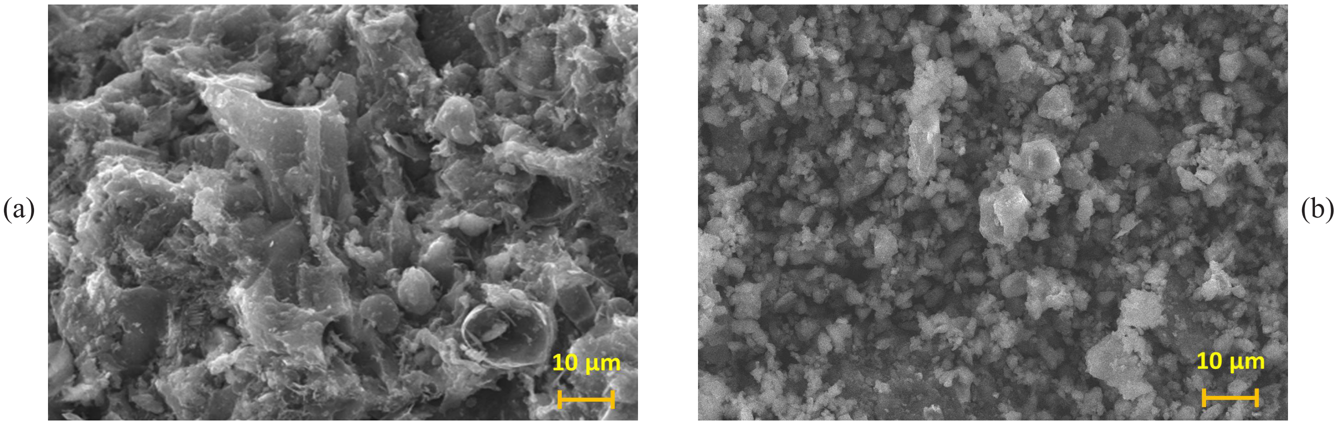

Fig. 4. SEM images of samples CMM (a) and MA-CMM (b).

Table 2
Elemental composition of carbon-mineral materials

Sample	Content, wt.%									
	C	O	Na	Mg	Al	Si	S	K	Ca	Fe
CMM	49.91	41.83	0.18	0.32	1.09	4.97	0.75	0.23	0.36	0.30
MA-CMM	52.14	30.80	0.26	0.47	2.45	9.76	0.86	1.03	0.69	1.54

Table 3
Characterization of carbon-mineral materials

Sample	V_{ads} cm^3g^{-1}	Fraction of pores, %			S_{BET}, m^2g^{-1}	pH_{PZC}	TAG, $mmolg^{-1}$
		Macro*	Meso**	Micro***			
CMM	0.158	20	76	4	87±4	8.05	0.29
MA-CMM	0.517	17	57	25	557±16	6.01	0.43

*(600>D>50 nm); **(50>D>2 nm); ***(D<2 nm)

The study of the elemental composition of separate regions on MA-CMM surface, studied by the EDS method, showed that the major elements (carbon, oxygen, silicon, aluminium, magnesium) are uniformly distributed over the surface as regions with a size smaller than 1 μm.

In comparison with CMM sample, for MA-CMM we observe the relative increase in carbon content from 49.91 to 52.14 wt.% and in the content of the main macro- and microelements by a factor of 1.5–2 (Table 2) with simultaneous decrease in total oxygen content.

The effect of preliminary MA (10 min, balls 5 mm in diameter, acceleration 1000 ms^{-2}) of native sapropel on the texture characteristics of the resulting CMM and the functional composition of the surface was investigated. Analysis of the data on the texture, calculated from the isotherm of nitrogen adsorption, showed that more than a 6-fold increase in specific surface area (from 87 to 557 m^2g^{-1}) is observed for MA-CMM sample, with simultaneous increase in the average pore size from 0.158 to 0.517 cm^3g^{-1} as a consequence of the formation of additional amount of micropores. However, despite this fact, CMM samples remain large porous: the total fraction of meso- and macropores exceeds 70% (Table 3).

One can see in the curves of the pore size distribution for CMM and MA-CMM (Fig. 5) that preliminary mechanical activation of native sapropel leads to the formation of carbon-mineral material MA-CMM with somewhat different porous structure (Fig. 5(b)). The peak of the distribution curve has substantially shifted to smaller pores, and the curve is polymodal in the region up to 200 nm, with a pronounced maximum at 110 nm. The CMM sample obtained without MA stage contains pores with prevailing sizes 350 and 1000 nm.

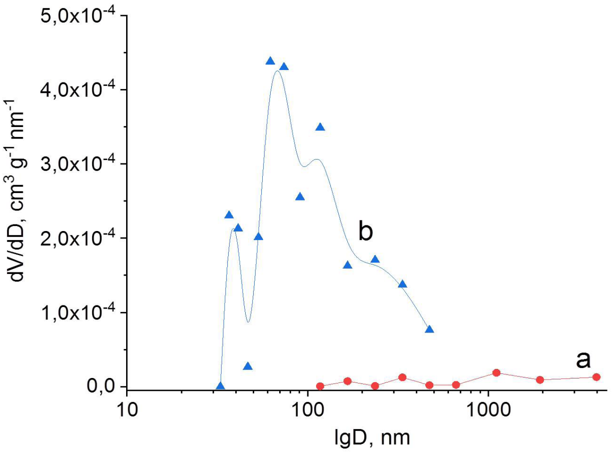

Fig. 5. Pore size distribution curves for CMM (a) and MA-CMM (b).

The surface of CMM is weakly basic (pH_{PZC} is 8.05), which is confirmed by the low content of acidic oxygen-containing groups: 0.29 $mmolg^{-1}$ (Table 2), while the pH_{PZC} value of MA-CMM surface is 6.01, and the content of acidic oxygen-containing groups increases to 0.43 $mmolg^{-1}$. So, the chosen modification method leads to the formation of more developed CMM surface with a larger amount of acid centers.

4. Conclusion

In the present work, an approach is proposed to regulating the morphology, texture and surface functional composition of carbon-mineral materials derived from the available natural organic raw material (sapropel) using mechanochemical action on native sapropel. The effect of the parameters of mechanical activation (time, acceleration, diameter of milling bodies) of sapropel on its fractional composition and morphology are investigated. It is established that preliminary mechanochemical treatment of native sapropel causes changes in the structure of the solid organic mass, thus providing a higher yield of the carbon-mineral materials after subsequent thermal treatment.

It is determined that the introduction of the stage of MA of native sapropel allows regulating the morphology and texture parameters of CMM formed in subsequent thermal treatment. Thus, mechanical action for 10 min at 1000 ms^{-2} on the initial raw material is sufficient for a noticeable increase in the fraction of pores ≤ 2 nm in diameter in the corresponding CMM and an increase in its specific surface to 557 m^{2}g^{-1} (which is more than 6 times higher in comparison with CMM obtained from native sapropel without preliminary MA). Preliminary MA of sapropel also promotes the formation of acid centers on CMM surface; the presence of these centers is an essential factor for broadening the area of CMM application as adsorbents and catalyst supports.

Acknowledgment

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the State Assignment for Boreskov Institute of Catalysis (AAAA-A21-121011490008-3).

The research was performed using equipment of the Shared-Use Center “National Center for the Study of Catalysts” at the Boreskov Institute of Catalysis and the Omsk Regional Center of Collective Usage, SB RAS. The authors are very grateful to K.E. Ivlev, G.G. Savelyeva and I.V Muromtzev for their participation in the studies of the samples.

References

[1]. V.S. Arutyunov, G.V. Lisichkin, *Russ. Chem. Rev.* 8 (2017) 777–804. DOI: 10.1070/RCR4723

[2]. D. Pudasainee, V. Kurian, R. Gupta. Coal: Past, Present, and Future Sustainable Use. In: Future Energy (3rd ed.) (2020) 21–48. DOI: 10.1016/B978-0-08-102886-5.00002-5

[3]. H. Katalambula, R. Gupta, *Energy Fuels* 23 (2009) 3392–3405. DOI: 10.1021/ef801140t

[4]. V. Obuka, Sapropel for the development of biocomposite materials: properties and application possibilities, 2021.

[5]. V. Obuka, M. Boroduskis, A. Ramata-Stunda, L. Klavins, M. Klavins, *Agronomy Research* 16 (2018) 1142–1149. DOI: 10.15159/AR.18.119

[6]. O.I. Krivonos, O.B. Belskaya, *J. Supercrit. Fluids* 166 (2020) 104991. DOI: 10.1016/j.supflu.2020.104991

[7]. A. Klavina, A. Auce, I. Vanadzins, A. Silova, L. Dobkevica, Environment Technology Resources Proceedings of the International Scientific and Practical Conference, June 2019, 3:114. DOI: 10.17770/etr2019vol3.4135

[8]. O.I. Krivonos, G.V. Plaksin, *Solid Fuel Chem.* 49 (2015) 36–40. DOI: 10.3103/S0361521915010061

[9]. E.N. Terekhova, A.V. Lavrenov, A.V. Shilova, T.V. Kireeva, G.G. Saveleva, M.V. Trenikhin, O.B. Belskaya, *Russ. J. Appl. Chem.* 90 (2017) 1990–1997. DOI: 10.1134/s107042721712014x

[10]. E.N. Terekhova, O.I. Krivonos, O.B. Belskaya, *Solid Fuel Chem.* 54 (2020) 373–384. DOI: 10.3103/S0361521920060129

[11]. A. Ahmadpour, D.D. Do, *Carbon* 34 (1996) 471–479. DOI: 10.1016/0008-6223(95)00204-9

[12]. B.G. Ershov, *Her. Russ. Acad. Sci.* 83 (2013) 437–447. DOI: 10.1134/S1019331613090050

[13]. S.A. Semenova, N.I. Fedorova, A.N. Zaostrovskii, Z.R. Ismagilov, *Solid Fuel Chem.* 47 (2013) 83–87. DOI: 10.3103/S0361521913020109

[14]. O.I. Krivonos, G.V. Plaksin, *Russ. J. Phys. Chem. B* 4 (2010) 1171–1177. DOI: 10.1134/S1990793110080014

[15]. E. Boldyreva, *Chem. Soc. Rev.* 42 (2013) 7719–7738. DOI: 10.1039/C3CS60052A

[16]. H. Ji, X. Mi, Q. Tian, C. Liu, J. Yao, S. Ma, G. Zeng, *Sci. Total Environ.* 784 (2021) 147100. DOI: 10.1016/j.scitotenv.2021.147100

[17]. J. Li, Z. Li, Y. Yang, C. Wang, L. Sun, *Powder Technol.* 339 (2018) 102–110. DOI: 10.1016/j.powtec.2018.08.006

[18]. A.P. Burdukov, E.B. Butakov, A.V. Kuznetsov, G.V. Chernova, P.E. Plyusnin, *Combust. Explos. Shock Waves* 55 (2019) 562–565. DOI: 10.1134/S001050821905006X

[19]. S.M. Kolesnikova, P.N. Kuznetsov, *Soil Fuel Chem.* 42 (2008) 80–81. DOI: 10.3103/S0361521908020043

[20]. G.E. Christidis, F. Dellisanti, G. Valdre, P. Makri, *Clay Miner.* 40 (2005) 511–522. DOI: 10.1180/0009855054040188

[21]. Q. Hou, Y. Han, J. Wang, Y. Dong, J. Pan, *Sci. Bull.* 62 (2017) 965–970. DOI: 10.1016/j.scib.2017.06.004

[22]. Z. Hu, H. Zhou, W. Zhang, S. Wu, *Processes* 8 (2020) 900. DOI: 10.3390/pr8080900

[23]. E.G. Avvakumov, M. Senna, N.V. Kosova, Soft mechanochemical synthesis: a basis for new chemical technologies. Springer Science & Business Media, 2001, 208 p.

[24]. D. Dimitrov, Geology and Non-traditional resources of the Black Sea. Lambert Academic Publishing, 2010. Saarbrucken, Germany, 244 p.

[25]. J. Park, J.R. Regalbuto, *J. Colloid Interf. Sci.* 175 (1995) 239–252. DOI: 10.1006/jcis.1995.1452

[26]. H.P. Boehm, *Adv. Catal.* 16 (1966) 197–274. DOI: 10.1016/S0360-0564(08)60354-5