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Reactivity of mechanical activated coals for special utilization

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The paper presents the coal activation effect as disintegration in the nano-submicron range and destruction carbon structure. The Slovak brown coal activated in planetary mill is characterised by destruction of organic structure of coal. The biggest activation effect connected with the destruction of C–C bonds of sp^3 carbons has been confirmed by ^{13}C NMR spectroscopy in the chemical structure of humic acids extracted from the coal sample activated for a period of 60 min. The specific surface of humic acids is much smaller then that of mechanically activated sample from which they were extracted. The black Czech coal was activated by two stage disintegration. In the first stage of mechanochemical activation using Grinding Aqueous Caustic Leaching, GACL method a fine dispersed semiproduct is formed with the size of particles from 2.5 to 9000 nm. The additional disintegration using water jet increases the effect of disintegration in the submicron area of the coal product. The volume distribution maximum achieves in this stage about 60 wt% of 750 nm grains.

1. Introduction

Coal is a strategic raw material of 21st century for power generating and non-traditional special purposes [1]. The non-traditional use of coal increases the benefit of the below mentioned applications. These are currently important from the point of view of the development of new carbonaceous technologies which serve mankind. It is mainly the case of the use of activated carbon in the environmental technologies, constructional materials for chemical industry equipment like the production of electrodes, battery charges, carbon fibres, carbides for cutting and abrasive materials, artificial diamonds, etc. [2]. The innovative use of coal also includes the production of new kinds of fuels like coal fuel water suspensions, coal-oil suspension fuels and diesel engine powder fuels [3]. In relation to the above-mentioned knowledge in coal mining, it is necessary to note that the coal material research brings new opportunities for the priority position of coal in the preparation of fullerene, pharmaceutical precursors [4, 5] and nano-carbon products. The heterogeneity of ultra-fine coal powders prefer using fractal methods [6] to characterise the volume and surface of dispersed carbonaceous substrate powders.

The advanced carbonaceous materials preparation technologies benefit from the principally new procedures of material engineering of coal science which count among the advanced coal technologies [7, 8]. It is alleged that natural coal-based nano-technologies also cover the environmental aspects connected with the use of wastes [9], greenhouse gas treatment [10] and innovation of conventional combusting methods [11].

In terms of coal treatment science, the physical [12, 13], chemical [14] and biological procedures with the

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use of thermodynamic models [15–18] play an important role and are termed the advanced coal treatment technologies [4, 19]. The preparation of activated ultra-fine powders uses mechanochemical procedures [16] which include innovative alkaline procedure called GACL (Grinding Aqueous Caustic Leaching). The presented paper describes the effect of activation grinding of coals on the preparation of powders of carbonaceous nano-product character.

2. Material and methods

The research was carried out with the samples of Slovak brown coal from Nováky locality (marked as SBC) and Czech black coal from Staříč locality (marked as SCC). The chemical analysis of studied samples is shown in Table I.

The Slovak brown coal (SBC) sample of a 0.5 mm granularity was activated by grinding using planetary mill Pulverisette 6 (Fritsch, Germany) in air atmosphere under the following conditions: mass of sample—20 g, grinding speed 300 rev/min, period of grinding 5–720 min.

The disintegration of Czech hard coal (SCC) has been tested below followed two staged mechanical activation. In the first stage the wet mechanochemical activation grinding was carried out in the attrition mill Molinex, type 075 Netzsch, Germany, under the following conditions: weight of sample—20 g, grinding volume—500 ml, grinding glass beads—685 g, 2 mm diameter, grinding temperature—20°C, grinding medium—1% NaOH, grinding period—60 min. The additional disintegration of mechanochemically treated samples using water jet hitting the solid barrier was tested in the second stage. The tests of material disintegration were carried out using high pressure pump PTV 37–60 with one pressure multiplying gear under the following conditions: maximum operating pressure—415 MPa, electrical input power—37 kW and maximum water flow rate—3.68 l/min. The pump has a two-stage filtration unit, automatic valve, slow pressure rise equipment, internal diagnostic system, closed cooling circuit and high-low pressure switching.

The specific surface of evaluated samples was measured by Micromeritics Gemini 2360 apparatus using BET method. The granulometric analysis was carried out using apparatus Sympatec Helos, Rodos, Germany, in wet conditions.

The granulometric analysis of sub-micron particles smaller than 1 μm in the area of nano-particles was carried out with dynamic laser radiation dispersion using ALV detection equipment, Germany, with ALV 5000 correlator. The experimental equipment consisted of argon laser Spectra Physics Stabilite 2017–0.4 S, USA, working within the wave length of 514.5 nm at the output of 400 mW. The data were analysed using CCNTIN method and ALV 800 transputer.

NMR spectra were measured using Varian VXR-300 apparatus with the frequency of 75 for ^{13}C nuclei. The work parameters of spectrometer were adjusted the way to guarantee the quantitative significance of integral intensities of spectral lines. The spectral areas of carbon functional groups of humic acids from NMR study are: Carbonyls in keto and aldehydic groups (280–184 ppm), carbonyls in acids and esters (184–157 ppm), aromatic carbons with C—O bond (157–143 ppm), aromatic and olefinic carbons with C—H, C—C bond (143–106 ppm), anomeric carbons (106–87 ppm), sp^3 carbons with C—O, C—N bond (87—43 ppm), sp^3 carbons with C—C bond (43–50 ppm).

TABLE I Chemical analysis of evaluated coals

Sample	Content of components (%)				
	C_t^d	H_t^d	N_t^d	S_t^d	A^d
SBC	70.25	3.85	1.35	0.54	17.00
SCC	75.83	4.02	1.49	0.54	8.20

3. Results and discussion

The activation grinding of brown coal in the intensive grinding device causes considerable surface-structural changes in the ultra-fine active powders [4]. The experimental results confirm the area of effective grinding, $t_m < 20$ min that gives the highest increase of the specific surface. The extreme prolongation of activation time, $t_m > 1$ h, incurs the aggregating secondary phenomena causing the specific surface reduction. Under these conditions of grinding time prolongation the additional spontaneous oxidation of activated powders proceeds the increase in the yield of humic acids. When characterising the distribution curves of differently activated samples it is necessary to stress that the poly-modal dependence with 4 peaks for non-activated sample changes into a mono-modal curve by the short-term 5 min activation grinding. In this case it comes to an intensive pulverisation without unwanted aggregation which is evident in each long-term activated sample. Comparing these granulometric data and specific surface values it is obvious that the aggregation of fine grains, which causes the overall specific surface reduction, is distinct after a 20 min activation. The aggregation of very fine 3 μm grains achieves the volume yield of 40%, while in case of extracted humic acids the aggregation is manifested by the increase in the density values in the granularity area of about 5 μm. The results of both distribution curves show that the aggregation maximum for the sample mechanically activated for a period of 20 min is achieved at the granularity of 8 μm and follows after the intensive pulverisation with intensive activation characterised by 1. peak at the granularity of 3 μm.

In case of extracted humic acids the course of density distribution curve is different from that of the original mechanically activated sample, as the mean granularity of this sample is much higher as proves the peak in the granularity area from 25 to 30 μm. As it has been mentioned before, in this case the pulverisation of humic acids of the granularity of less than 10 μm is accompanied with aggregation, which proceeds simultaneously with the mechanical activation. During the extraction process the granularity of humic acid increases considerably as confirmed by a very different value of specific

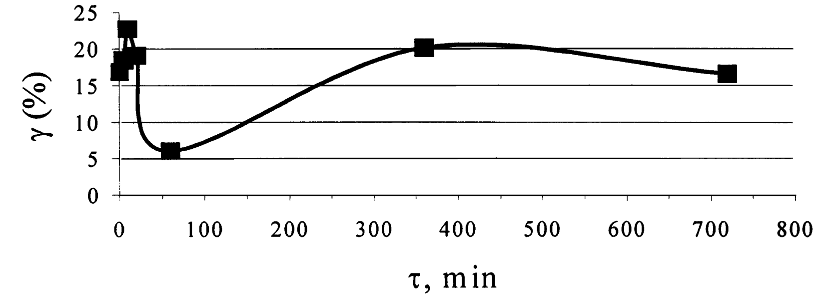

Figure 1 Dependence of the weight yield, γ of the sp^3 carbons C—C bonds of the extracted humic acids from mechanically activated brown coal on the grinding time τ.

surface $S_{A\text{-}20\ min} = 3.32\ m^2\ g^{-1}$, $S_{HA} = 1.29\ m^2\ g^{-1}$. From the above-mentioned it is possible to make a partial conclusion that humic acids of different physical properties are formed depending on different activation conditions.

Fig. 1 shows the distribution of weight yields of molar concentrations of selected sp^3 carbons with C—C bonds in the extracted humic acids based on the different mechanically activated brown coals. The first phase of activation grinding, i.e., intensive pulverisation phase, does not cause any significant change in the chemical structure of extracted humic acids. The ^{13}C NMR spectroscopy confirmed major destruction changes in sp^3carbons with C—C bond for a 60 min activation grinding. The reduction of these functional groups from 16.9% for non-activated sample to the value of 6% for 60 min activated sample is accompanied with the increase in the weight yield of aromatic carbons in humic acids with C—O bond to 11.1% compared with 7.2% for non-activated sample. The long-term 6 and 12 h grinding results in the significant reduction of carbonyls in keto and aldehydic groups and the increase in the weight concentration of sp^3 carbons with C—C, C—O and C—N bonds.

The mechanochemical disintegration Czech black coal using GACL method produces the optimal ground coal product with a specific surface of 27.18 m^2g^{-1} at the content of fractions smaller than 2.2 μm with the weight yield of 54.39% in volume. The granulometric analysis of very fine fractions of ground products smaller than 0.9 μm, which have the nano-product character, confirmed that for the coal the dependence of the volume distribution of granularity on its radius is a mono-modal function (see Fig. 2). This function achieves the maximum value of 15 vol% for the granularity less than 50 nm. In the rising part of the curve in the area of granularity finer than 10 nm the values of volume distributions are increased, thus creating an apparent additional maximum.

Fig. 3 shows the dependence of the volume yield of the 24 h settled coal product from water leachate after additional disintegration by water jet. It shows that the volume distribution maximum achieves about 60 wt% of 750 nm grains. The finest nano-particles in this water leachate appear at the granularity of 3 nm and the indistinctive maximum of the rising part of curve is at 10 nm. It was also confirmed after two stage disintegration of mechanochemically treated coal and additional disintegration using water jet gives the coal

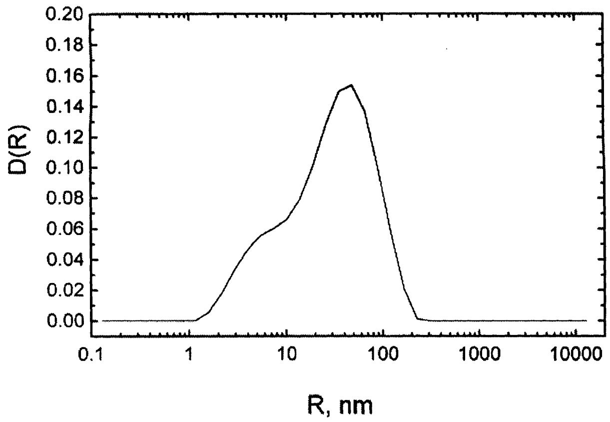

Figure 2 Dependence of volume distribution of nano-particles $D(R)$ on the grain size after mechanochemical treatment of the black coal by using GACL.

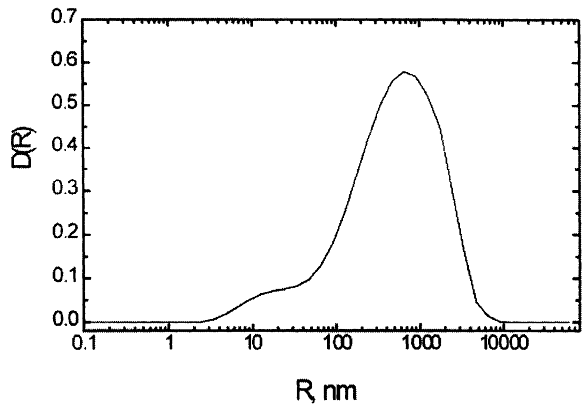

Figure 3 Dependence of volume distribution of nano-particles $D(R)$ on the grain size after water jet disintegration of mechanochemically treated black coal.

product $S_A = 19.04\ m^2\ g^{-1}$ and the coal sludge with a specific surface $S_A = 22.09\ m^2\ g^{-1}$. For the two stage treatment of coal, more favourable and more intensive disintegration of product is achieved in both nanometer and micron granularity areas.

4. Conclusion

The experimental results of Slovak brown coal grinding confirmed that humic acids of different chemical structure are formed depending on the activation conditions. During the dry mechanical activation in the planetary mill in the air atmosphere in the area of intensive pulverisation up to $t_m < 20$ min there have not been any significant changes observed in the concentration of typical functional groups. The biggest activation effect connected with the destruction of C–C bonds of sp3 carbons has been confirmed by C^{13}NMR spectroscopy in the chemical structure of humic acids extracted from the sample mechanically activated for a period of 60 min. The specific surface of humic acids is much smaller than that of mechanically activated sample from which they were extracted.

The mechano-chemical Czech black coal activation by using GACL procedure causes an intensive disintegration of coal powders characterised by the monomodal function of volume yield with the maximum at the granularity of 50 nm. The coal batch contains nanoparticles in the area from 2.5 to 9000 nm. The additional second stage disintegration of coal treated samples results in the granularity higher than 100 nm, so the maximum of distribution curve is at 750 nm with a 60% volume yield. From the treatment point of view it is very important that it comes to the concentration of ash matters in the foam product, so the coal sludge, which is a product, is additionally refined in the second stage process.

The brown coal mechanically activated powders can be used for preparation of extracted special diterpenes (kaurane derivates) with cytostatical activity for pharmaceutical effectors. Coal mechanochemistry gives invokes the development of science in the fields of clean coal technologies, nanotechnologies, material science, etc.

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