Solid-state mechanochemical technology for deep processing of brown coal: energy efficiency improvement and dust formation control

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Abstract. Energy efficiency – a compromise between reaction depth and expended energy - is an actual question for any technology implementation. Mechanochemical technology for brown coal deep processing has one more compromise - between reaction depth and dust formation. Indeed, the depth of mechanochemical reactions usually correlates with grinding efficiency, but for coal cases dust formation is an unwanted process. Here we consider a solid-state mechanochemical reaction of humic acid oxidation by sodium percarbonate in one laboratory mill at different conditions. The ratio between the grinding bodies load and the payload was varied, the reaction yield and the ground samples characteristics were controlled.

1. Introduction
The development of technologies for deep processing of brown coal is necessary to convert it from the waste of the coal mining industry or low-efficiency fuel into a valuable raw material. The potential of such developments is due to the presence of components with high added value, humic acids and rare earth elements, in the brown coal. This work will focus on the humic acids production.

It is known that humic acids are an important product for improving the soils quality by cleaning them from heavy elements [1, 2] and/or increasing the yield of agricultural crops [3]. The usual problem is low efficiency of humic acid extraction process. In previous works it was shown that mechanical treatment in the presence of sodium percarbonate allows converting an organic part of brown coal into a soluble state, and at the same time improving their sorption capacity [4, 5]. Both effects are achieved due to the oxidation of functional groups of humic acids and the destruction of their complexes with metals [6].

The efficiency of mechanical treatment can be also measured in terms of the formed particles size. On the one hand, a decrease in the particle size facilitates both the mechanochemical reaction and the further extraction of the useful product [7]. On the other hand, the formation of coal dust hampers the work of personnel and leads to the risk of detonation. Accordingly, the particle size should also be a controlled parameter. Moreover, according to literature data, the danger of spontaneous combustion of coal dust is associated with the number of paramagnetic centers [8]. Here we carry out measurements of the concentration of paramagnetic centers by the EPR (electron paramagnetic resonance) method.

In this work we search for a possibility for energy efficiency improvement by the example of laboratory planetary mill AGO-2. We will start from classical loading: 200 g of grinding bodies and 10 g of payload [9, 10] and vary it in both sides. The main measured parameter is the yield of soluble
humic acids and the amount of expended energy. Quantitative characterization of obtained product will be performed spectrophotometrically. Along with the yield of soluble humic acids the formed particles size and paramagnetic particles content is controlled.

2. Experimental section
Brown coal from the Ilatskoye deposit of the Kansk-Achinsk coal basin (Russia) was used as raw material. Mechaenochemical treatment was performed in an AGO-2 laboratory activator of planetary type. A dry mixture of brown coal and sodium percarbonate Na₂CO₃·1.5H₂O₂ (oxidizing base reagent), taken in an amount of 5 wt % relative to brown coal was treated at the calculated acceleration of milling bodies at the moment of detachment from the reactor walls of 200 m s⁻². The activation time was 2 min, the diameter of the milling bodies was 5 mm, and weight of reagents and milling bodies varied from 200 to 100 g (Table 1).

The amount of expended energy was measured by specially constructed setup [11]. The contents of water-soluble humic acids were measured according to the State Standard GOST 9517-94 (ISO 5073:2013). Chromaticity index reflecting the degree of oxidation of humic acids was measured by spectrophotometer Lomo SF-1000 in tris-hydrochloric acid buffer pH 9 as a ratio of absorption at 465 and 650 nm [12, 13].

The particle size and the width/length ratio were determined using a CAMSIZER X2 instrument (Retsch Technology GmbH, Germany) that captures the projections of the analyzed particles with digital cameras. Table 1 contains median values of particle width and width/length ratio b/l. All measurements were conducted with and without an X-Jet module, where particles were dispersed under air pressure of 75 kPa.

EPR spectra were recorded by SpinScanX (Adani, Belarus) at room temperature immediately after treatment. The particle size and the width/length ratio b/l (Table 1) were clearly seen: the amount of expended energy increased more than ten times for all samples. Then, the expended energy was almost proportional to grinding bodies mass. Indeed, a significant part of the energy was spent directly on the movement of grinding bodies and turned into heat, and only a small part was spent directly on the mechaenochemical process [14]. The obtained dependence of humic acid yield on expended energy was analyzed.

Surprisingly, this dependence had a maximum, i.e., the studied process could be really optimized in terms of energy efficiency. Here we obtained a maximum efficiency in the case of 150/20 ball/reagent loading, near 8kW*h for 1kg HA. The comparison between 200/10 and 200/20 ball/reagent cases suggests a different way to energy efficiency increase, i.e., by varying of reagent mass at constant balls mass.

3. Results and Discussion
The obtained data was summarized in Table 1. The effect of mechaenochemical treatment was clearly seen: humic acid yield increased more than ten times for all samples. Then, the expended energy was almost proportional to grinding bodies mass. Indeed, a significant part of the energy was spent directly on the movement of grinding bodies and turned into heat, and only a small part was spent directly on the mechaenochemical process [14]. The obtained dependence of humic acid yield on expended energy was analyzed. Surprisingly, this dependence had a maximum, i.e., the studied process could be really optimized in terms of energy efficiency. Here we obtained a maximum efficiency in the case of 150/20 ball/reagent loading, near 8kW*h for 1kg HA. The comparison between 200/10 and 200/20 ball/reagent cases suggests a different way to energy efficiency increase, i.e., by varying of reagent mass at constant balls mass.

Table 1. Characterization of milled samples: comparison with untreated coal (“before”)

| Sample ball/reagent | E, W*h | HA yield, g | E465/E650 | Width b/l | EPR a.u. |
|---------------------|--------|-------------|-----------|-----------|---------|
| “before”            |        | <1%         | 2.03      | -         | -       |
| 200/10              | 17     | 12.1±3.3    | 1.65      | 10.8      | 257.5   | 0.806   | 696.3   |
| 200/20              | 17     | 13.5±2.8    | 1.42      | 11.2      | 264.9   | 0.804   | 670.0   |
| 175/10              | 16     | 15.3±4.1    | 1.53      | 10.3      | 279.3   | 0.806   | 611.0   |
| 150/10              | 16     | 21.4±0.4    | 1.68      | 9.8       | 264.4   | 0.804   | 785.1   |
| 125/10              | 15     | 19.8±1.2    | 1.79      | 10.1      | 283.6   | 0.809   | 721.5   |
| 100/10              | 14     | 18.6±0.7    | 1.45      | 11.4      | 304.1   | 0.805   | 742.6   |

E, W*h – expended energy, HA yield – humic acid yield, width - particle width [nm], E465/E650 – humic acid oxidation status, b/l – width / length ratio, *xJet – measurement was performed with xJet, EPR – amount of paramagnetic centers, a. u.
Next parameter for comparison is E465/E650, the ratio of absorption at 465 and 650 nm. This parameter indicates the oxidation status of humic acid: more colored samples have flatter absorption spectra. The color, in turn, indicates the presence of long conjugated systems, which are often destroyed in the process of chemical modification. Fig.1a demonstrates clearly measurable differences between the obtained spectra. All treated samples have lower E465/E650 value than the untreated ones, that is a consistent conclusion of mechanochemical modification of humic acid. However, the maximum of E465/E650 in treated samples nearly coincides with the maximum of energy efficiency.

Consideration of size characteristics first of all shows that measuring the particle size of coal dust may be a non-trivial task. It is shown that the difference in size may be 25-30 times, depending on the measurement mode: free fall or a special air flow that breaks agglomerates of particles into separate components (*xJet). Apparently, this is due to the accumulation of surface electrostatic potential and, consequently, to the effective adhesion of particles. Let us discuss only the air flow results. A decrease in balls loading firstly leads to an increase in grinding efficiency, but after the case of 150/20 grinding efficiency reaches the limit: particle size increases and sphericity (b/l value) starts decreasing.

Finally, EPR intensity doesn't demonstrate any pronounced trend. The EPR spectrum of the sample is single line with g = 2.0035. The intensity (near 10^{20} s/g) and shape of EPR line (Gaussian, width of about 0.70-0.75mT, g ~ 2, see Fig.1b) has typical values for brown coals. The deviation from the free electron g-factor is consistent with the presence of impurity atoms such as oxygen or sulfur in brown coal (such elements have larger spin-orbit coupling) [15, 16]. So far, the dependence of the concentration of radicals is not obvious, but it should be noted that the sample with the highest yield of humic acids is characterized by the highest concentration of free radicals.

Conclusions
This work reports on the first attempt of energy efficiency optimization for mechanochemical-assisted extraction of humic acids from brown coal. Variation of ball/reagent loading ratio in parallel with the measurements of the amount of expended energy have proved to be a useful tool for such task. Rational selection of conditions for mechanochemical treatment allows increasing the yield of humic acids 1.75 times, with practically the same energy consumption.
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