



THE EFFECT OF MECHANICAL IMPACT OF HIGH ENERGY ON THE STRUCTURAL PROPERTIES OF BROWN COAL AND THE REACTIVITY FOR LIQUEFACTION

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ABSTRACT

The effect of preliminary mechanical activation in the energy-intensive mill-activator on the structural and chemical transformations of brown coals and their reactivity in contact with solvents has been established. Mechanical treatment of the brown coals from Kansk-Achinsk Basin was performed in a high-energy AGO-2 centrifugal planetary ball mill. Mechanical activation led to a partial destruction of the supramolecular structure of coal, reduction of the cross-linking degree of nano-sized polyaromatic clusters in the organic matter coal. This results in the increased reactivity of coal in the liquefaction processes (extraction and hydrogenation) to form liquid products.

Keywords: brown coal, mechanical activation, swelling, extraction, supramolecular structure, the hydrogenation liquefaction.

INTRODUCTION

Coal is a complex mixture of mineral matter and organic oligomeric and multimeric molecules of predominantly aromatic nature. In terms of structural properties, it can be classified as a cross-linked amorphous-crystalline polymer-like solid of inhomogeneous composition and irregular spatial structure having some porosity with the narrow open and as well as closed pores (Krichko and Gagarin, 1990). The organic coal matter consists of both rather ordered and non-ordered spatial carbon structures. Rather ordered nano-sized graphite-like fraction consisting of polycondensed aromatic molecules stacked in parallel are the principal structural units. The other aromatic and aliphatic molecules located at the periphery of the polyaromatic clusters and not included in the stacking structure are referred to the less ordered fractions. Because of highly cross-linked structure, access of reagents (solvents, catalysts) to the fragments of the organic matter may be restricted or diffusion limited. Another consequence is that the intrinsic reactivity of coal organic fragments can be also suppressed due to low mobility because of high cross-link density.

Different kinds of chemical bonds, such as short C-C aliphatic chains, different C-O bonds, etc. can serve a role of the cross-links. In brown coals, calcium carboxylate complexes were shown (Kuznetsov *et al.*, 2008) to be one of the most important fragments contributing to the organic matter cross-linking. Directed destruction of crosslinks in the organic matter of coal is one of the effective ways towards the creation of a new selective thermochemical processes to produce liquid fuels, chemicals, carbon-based materials for various

applications purposes, including binders for electrodes. For this purpose, the coal is subjected to a preliminary activation treatment by solvents (Joseph *et al.*, 1992; Shui *et al.*, 2008; Yan *et al.*, 2015), chemicals (Sakanoshi *et al.*, 2001; Marsh and Rodriguez-Reinoso, 2006; Lillo-Rodenas *et al.*, 2003; Tamarkina *et al.*, 2009; Manina *et al.*, 2012), physical ionizing irradiation (Likhterova and Lunin, 1998; Guo *et al.*, 2015), and mechanical processing in various mills (Saranchuk *et al.*, 1982; Polubentsev *et al.*, 1999; Hrenkova, 1993; Boldyrev, 2006). The last way of impact on coal is among rather simple and technological (Baláz *et al.*, 2013; Boldyrev and Boldyreva, 2010).

Earlier, successful application of mechanical treatment of oxides and sulfides in various ball mills for the preparation of nanocrystalline particles has been reported by Boldyrev, 2006; Boldyrev and Boldyreva, 2010. Mechanical treatment in a high-energy centrifugal planetary ball mill has been shown (Kuznetsov *et al.*, 2006) to stimulate several processes, such as dehydration, crystallization, and accumulation of structural defects, brittle fracture and agglomeration. Solid phase transformation into metastable phases can also occur as a result of high energy impact. Mechanical treatment in a vibrating ball mill with much less energy impact resulted in particle disintegration, accumulation of strains, and gradual amorphization of the crystalline structure; however, the phase transformation did not occur.

A number of works (Hrenkova, 1993; Hrenkova and Kirida, 1994; Fedorova *et al.*, 2014) on studying the properties of coals after mechanical treatment is published. It was shown, that not only disintegration of coal particles and increase in the specific surface area occur, but also the disruption of both non-covalent interactions and covalent



bonds (first of all C-C, and C-O cross-links) is stimulated, resulting in the changing of the functional group composition. As a result coal heat stability (Saranchuk *et al.*, 1982; Polubentsev *et al.*, 1991) decreases, and increase is observed in solubility in organic solvents, liquefaction level at the hydrogenation (Kuznetsov, 1991; Krychko *et al.*, 1971; Polubentsev *et al.*, 1999), humic acid yield at decomposition in alkaline environments (Girina *et al.*, 1991). Coal crystalline transformation at mechanochemical impact is relatively understudied.

The purpose of this work is to study the preliminary mechanical activation impact in high-energy mill-activator on the structural and chemical transformation of brown coals and their reactivity when interacting with solvents.

MATERIALS AND METHODS

The brown coals from the Borodino (samples B1 и B2) and Latyntsevo (sample B3) deposits of the Kansk-Achinsk Basin were used in this study. The coal samples were crushed, and the fraction of 0.5–1.0 mm dried in a vacuum oven at 85°C was used.

Mechanical treatment was performed in a high-energy AGO-2 centrifugal planetary ball mill (Novis Co, Russia). The mill was equipped with two 150 ml air-tight stainless-steel drums cooled with water while operating. The drums were loaded with 100 g of stainless steel balls of 3 mm in diameter and 10 g of coal sample. The speed of drum rotation was 1,820 r.p.m. Milling time was varied from 1 min to 30 min.

The composition of coals was characterized by proximate and ultimate analysis. The analyses of C, H, N, S and O elements were performed on an elemental analyzer FlashEA 1112 (ThermoQuest). The metal contents were measured by X-ray fluorescence analysis using the Axios Advanced (PANalytical) spectrometer. The FT-IR spectra were recorded on a Bruker IR-FT spectrometer by using the samples prepared as KBr pellets dried at 105°C for 24 h in vacuum. The particle sizes were determined by TEM (JEOL, Japan).

Coal extraction and solvent swelling were used to characterize the chemical properties and supramolecular structure of coal. The extraction was performed in the Soxhlet apparatus by using ethanol-benzene mixture (with 1:1 ratio) as a solvent. An attractive method for the investigation of macromolecular structure of coal is to observe its response to a swelling agent. The degree to which coal swells in the presence of specific solvent is a measure of the cross-linking density and the flexibility of coal segments. The swelling measurements were performed according to the conventional volumetric procedure with the glass tubes. Tetrahydrofuran was used as a swelling agent. The swelling ratios (Q) were calculated as $Q = h_t/h_0$, where h_0 is the height of the initial coal bed and h_t is the height of the swollen coal bed at the current time t .

The structural characterization of the spatial structure of organic matter was monitored by X-ray

diffraction. The XRD patterns of powdered coal samples packed into aluminum holder were recorded by using a PANalytical X'Pert PRO materials research diffractometer with PIXcel detector and Cu K α -radiation at a step size of 0.02°. The parameters of the stacking structure of coal carbon matter were determined based on the (002) band which reflected an intermolecular ordering, the band being corrected according to the recommendations described in (Lu L., *et al.*, 2001; Everson R.C., *et al.*, 2013). A broad band was deconvoluted by using the Origin 8.0 software and the HighScorePlus™ curve fitting functions.

An example of reflex (002) computer-aided decomposition is shown in Figure-1.

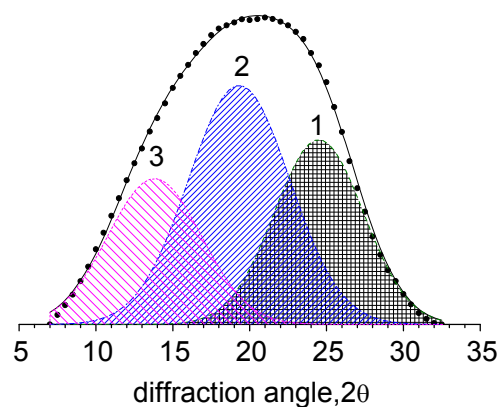


Figure-1. Fragment of the coal B1 diffraction pattern: 1 - γ_2 -fraction, 2 - γ_1 -fraction; 3 - graphite-like fraction.

The spacing between the graphene layers, d_{002} , in the stacking structure was calculated from the peak position by means of Bragg's equation. The average thickness of the stacks, L_c , was evaluated from the width at the half maximum of the (002) band using Scherrer equation. The average number of graphene layers, n , in the stacks was calculated by means of the equation $n = (L_c/d_{002}) + 1$. The diffraction peak (10) due to intramolecular ordering was poorly developed and not analyzed.

Coal hydrogenation tests were carried out using the experimental unit equipped with five 90 cm³ stainless steel autoclaves inserted into a rotated heated sand-bath. Each autoclave was charged with 3 g of char and 4 g of solvent. Tetralin and toluene were used as liquefaction solvents. The autoclaves were purged with nitrogen from the air and hermetically sealed. The heating rate was 7–8°C/min. After the reaction was over, the autoclaves were allowed to cool and the gaseous products were analyzed by a gas chromatograph. The solid-liquid product was extracted successively firstly with hexane and then with benzene. The total coal conversion was evaluated based on the amount of organic matter in the coal sample and in the coal residue after extraction.



RESULTS AND DISCUSSIONS

Mechanical activation impact on the coal composition and structure

Shown in Table-1 is the list of the coal samples with the data on the composition. The samples had rather close contents of C, H, N, S, and O elements (based on

daf), mechanical activation (MA) hardly affected the composition. The ash contents ranged from 4.4 to 7.8 wt. %. Besides silicon and aluminum, Ca was predominant metal with the concentrations of 0.8 to 2.0 wt. %, B3 coal differing with the largest calcium content (2 wt.%). Mg concentrations were less than those of Ca by factor of 6 to 10.

Table-1. Characteristics of structure of initial samples of coals.

Sample code	Content, wt. % on organic matter of coal					Ash content A ^d , wt. %	Content, wt. %	
	C ^{daf}	H ^{daf}	N ^{daf}	S ^{daf}	O ^{daf}		Ca	Mg
B1	69.7	4.9	0.8	0.3	24.3	4.4	0.8	0.1
B2	71.3	4.8	0.9	0.2	22.8	7.8	1.3	0.2
B3	73.4	5.1	1.1	0.7	19.7	7.7	2.0	0.2
B2(MA)	70.9	4.7	0.8	0.2	23.4	–	–	–
B3(MA)	73.7	5.0	1.0	0.7	19.6	–	–	–

Mechanical processing in the AGO-2 apparatus resulted in a fine dispersion of the coal particles. Figure-2 presents the particle size distribution in raw coal and B2 after mechanical impact in the apparatus. It is seen that

with increasing time of mechanical action from 5 to 30 min. the proportion of fine particles increases gradually. After 30 min. the proportion of particles with a size up to 10 microns is about 50%.

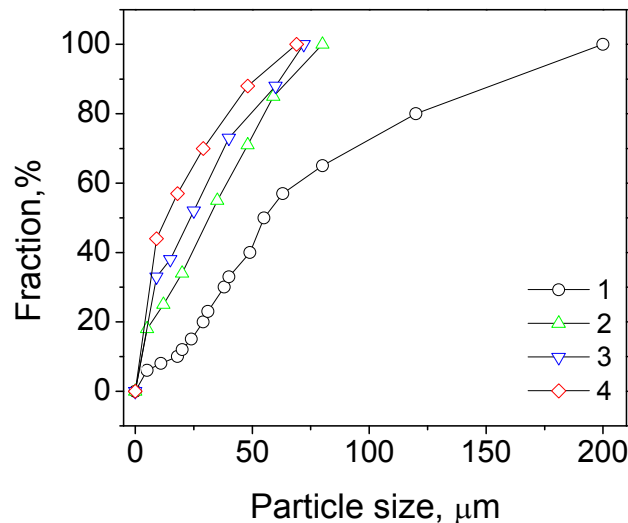


Figure-2. Particle size distribution for initial and mechanically activated coal B2: 1 - raw coal; 2, 3 and 4 coal mechanically activated for 5, 15 and 30 min., respectively.

In the course of mechanical treatment of coal in drums gases were accumulated that have been analyzed by chromatographic analysis. The results are given in Table-2. It is seen that during the mechanical impact the organic matter destruction occurred with the gaseous products

formed. The gas composition was dominated by carbon monoxide, which probably points at the destruction of oxygen-containing groups. Hydrogen and methane evolution may be associated with degradation of the hydrocarbon fragments.



Table-2. The composition of the gas samples after mechanical activation of brown coal in argon for 15 min.

Sample	Content, vol. %					
	H ₂	O ₂	N ₂	CH ₄	CO	CO ₂
coal B1 coal B3	0.38	0.01	0.19	0.35	1.83	–
	0.41	0.02	0.21	0.31	1.67	0.01

The changes in the spatial structure of brown coals as a result of mechanical impact were monitored by X-ray diffraction. It was found that the XRD patterns showed typical broad asymmetrical (002) peak centered at 2θ 24.5° which was well deconvoluted into a superposition of three Gaussians. According to (Lu *et al.*, 2001; Everson *et al.*, 2013), they represented three different portions of carbon structure which were referred to graphite-like carbon and to two less ordered γ -fractions. The obtained data that are presented in Tables 3 and 4 demonstrate that the increased time of mechanical treatment of coal B2 results in the decreased share in graphite-like components from 30% to 26% and the increased share of the least ordered γ_2 -fractions from 16% to 19%. In graphite-like phase of coal B2 the package thickness slightly increases (from 12.6 to 13.9 Å) due to the increase in the average number of layers therein (from 4.6 to 5.0), while the distance between the layers is 3.47-3.49 Å. For coal B1 containing less calcium (0.75%) the changes in the x-ray diffraction component composition are small (Table-4).

Table-3. Mechanical activation impact on the x-ray component content.

Sample	Time of mechanical activation, min	Share of x-ray component, %		
		graphite-like component	γ_1 -fraction	γ_2 -fraction
B1	0	33	49	18
B1	5	34	51	15
B1	60	33	51	16
B2	0	30	54	16
B2	5	32	51	17
B2	60	26	55	19

Table-4. Mechanical activation impact on the x-ray characteristics of the samples.

Sample	Mechanical activation duration, min	d_m , Å	L_c , Å	N
B1	0	3.52	11.7	4.3
B1	5	3.53	10.5	3.9
B1	60	3.49	10.9	4.1
B2	0	3.47	12.6	4.6
B2	5	3.49	12.0	4.4
B2	60	3.47	13.9	5.0

The change of coal molecular composition after mechanical activation was studied by IR spectra. Figure-3 demonstrates that the processing leads to significant increase in intensity of absorption bands, their resolution improves a little. The noted spectral singularities are apparently caused by increase in coal dispersion. At the same time essential reduction of absorption band intensity in the range of 3400-3500 cm^{-1} and 1700-1800 cm^{-1} in relation to band intensity at 1600 cm^{-1} , which is responsible for fluctuations of aromatic rings (Czuchjowski and Lawson, 1961; Guiliano *et al.*, 1990), is noticeable by the differential range in Figure-5. Also relative band intensity determined by the valence vibrations of C-O groups of phenols and ethers with maxima at 1170 cm^{-1} , 1093 cm^{-1} and 1036 cm^{-1} decrease. This indicates that mechanical treatment was accompanied not only by the particle dispersion, but also by the partial destruction of fragments of carboxylic acids, simple and complex esters and lactones. It is also important to note that in the original coal spectrum the 1613 cm^{-1} absorption band contains low-frequency asymmetry, which apparently appears due to the presence of metal-carboxylate fragments. In the spectrum of the mechanically activated sample this asymmetry disappears, the profile band is narrowed, and the maximum moves appreciably (by 14 cm^{-1}) towards low frequencies. These spectral manifestations apparently suggest that mechanical treatment stimulated the degradation of oxygen-containing fragments associated with aromatic rings, including metal-carboxylate structures.

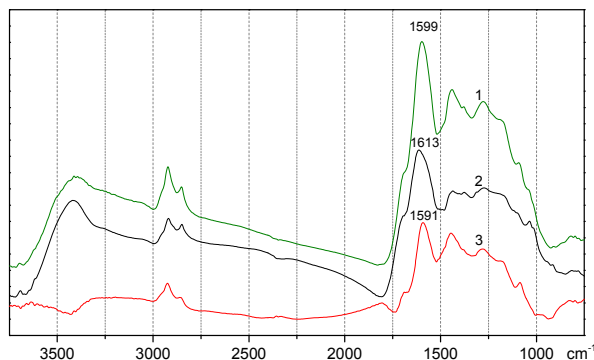


Figure-3. The IR spectra of the initial coal B2 (2) and after B2 mechanical activation (MA) for 15 min (1); 3-differential range (the difference between 1 and 2).

Thus, on the strength of all the evidence obtained from the analysis of gases released in the process of mechanical activation, X-ray diffraction data and IR spectra it can be assumed that the mechanical activation reduced the degree of ordering of the spatial structure, disturbed intermolecular association, partially destructed various oxygen-containing groups - carboxylic acids, esters, metal-carboxylate complexes, and aromatic ring substituents. As a rule, these groups contribute significantly to the cross-linking of polycondensed aromatic structures of the organic matter of brown coal.

Behavior of the mechanically stimulated degradation reactions resulted in the increase in the ability of coal to interact with solvents. The data provided in Figure-4 show a significant increase in the coal swellability that reflects the decrease in the number of crosslinks in the structure of the organic matter, and, accordingly, the increase the mobility of its fragments.

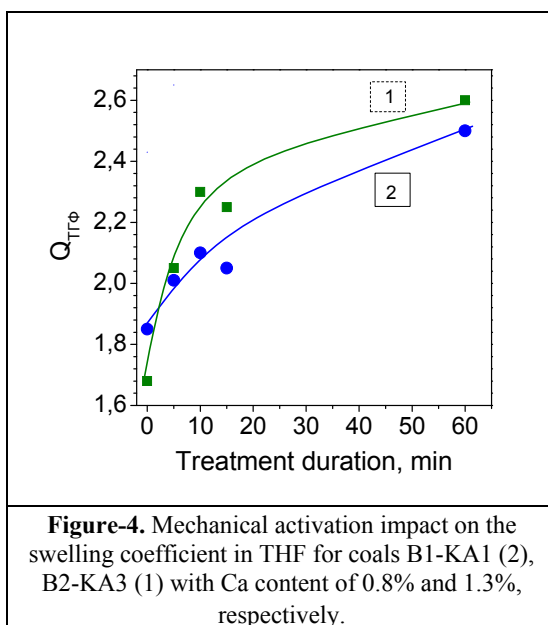


Figure-4. Mechanical activation impact on the swelling coefficient in THF for coals B1-KA1 (2), B2-KA3 (1) with Ca content of 0.8% and 1.3%, respectively.

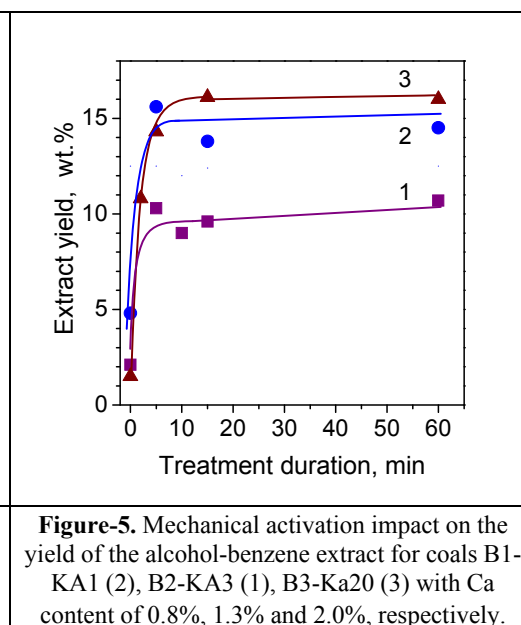


Figure-5. Mechanical activation impact on the yield of the alcohol-benzene extract for coals B1-KA1 (2), B2-KA3 (1), B3-Ka20 (3) with Ca content of 0.8%, 1.3% and 2.0%, respectively.

Outputs of the alcohol-benzene extract coals of Borodinskoe deposit with low (0.8%) and high (1.3%) Ca content after machining increased from 4.8 and 2.1 by 14.5% and 10.0%, i.e. approximately threefold and fivefold, respectively (Figure-5). During mechanically activated coal extraction of B3 sample with the highest content of calcium the extraction yield was 10 times as large.

The data obtained show that the mechanical activation is an effective way to influence the brown coal structure. It leads to partial degradation of the crosslinks, the decrease in the degree of ordering in the organic matter, which results in a greatly increased yield of extractable substances. The most significant changes occur during the mechanical activation of coal with a high

content of Ca, which, as previously established (Kuznetsov *et al.*, 2008), is present in the organic matter composition in the form of carboxylates, acting as strong ionic crosslinks.

Reactivity of mechanically activated coal in the supercritical extraction and hydrogenation liquefaction processes

Reactivity of mechanically activated samples was investigated in the processes of thermochemical conversion in solvents that were undergoing reaction under supercritical conditions and hydrogenation liquefaction in tetralin environment. Supercritical solvent extraction has several advantages compared to the traditional liquefaction processes (Shishido *et al.*, 1991; Kashimura *et al.*, 2004).



Firstly, the method makes it relatively easy to extract and separate the coal residue (minerals, dissolved organic matter). Secondly, higher solubility of the hydrocarbons in the solvent at supercritical parameters gives the possibility to increase the coal conversion of into liquid and gaseous products (Shishido *et al.*, 1991; Kashimura *et al.*, 2004). Of special interest as the solvent is toluene, being a typical component of the low-boiling fractions of the products resulting from coal processing and having a relatively low critical temperature (318.6 °C), pressure (4.06 MPa) and density (0.292 g/cm³). A hydrogen donor additive (tetralin) was used in small quantities (15 wt. %).

According to the obtained experimental data it has been established that the mechanochemical activation leads to increase in the extent of coal conversion to liquid and gaseous products. As Table-5 shows at 380°C and initial pressure of hydrogen of 5 MPa coal conversion in tetralin medium increases by 13-15%.

Table-5. Mechanical activation impact of coal B2 and B3 on conversion when dissolved in tetralin at 380°C.

Coal	Conversion of organic matter of coal, %
B2	52.8
B2 (MA)	67.2
B3	50.4
B3 (MA)	63.3

Table-6 gives the data on the conversion of brown coal in toluene-containing media under different conditions. During coal extraction with boiling toluene in the Soxlet apparatus the yield of soluble substances accounted for only 1.7%. Mechanical activation by partial depolymerization of organic matter of coal increased the yield of soluble substances to 11.6 %, i.e. sevenfold.

During the brown coal conversion in toluene at 400 °C under subcritical and supercritical conditions, the conversion degree of organic matter of coal was 26-28%. Preliminary mechanical activation of brown coal enabled significantly (6-17%) to increase the conversion degree both in the individual toluene and mixed with tetralin.

Table-6. B1 coal conversion during extraction in the toluene-containing solvents at 400°C and the initial pressure of hydrogen of 1 MPa.

Solvent	Vapor density Solvent, g/cm ³	Working pressure, MPa	Conversion of organic matter of coal, wt. %	
			source coal	After mechanical activation
Toluene (Soxhlet apparatus)	-	-	1.7	11.6
Toluene	0.40	16	28	45
Toluene+tetralin (15 wt. %)	0.34+0.06	12	55	61

The data obtained show that mechanochemical activation of brown coal results in the increase in their reactivity both during liquefaction in the hydrogen donor solvent tetralin medium and in the course of supercritical extraction in toluene-containing media. Addition of small amounts of the hydrogen donor - tetralin to the toluene contributes to further increase in the conversion rates.

4. CONCLUSIONS

Thus, the mechanical impact leads not only to the increased dispersion of coal, but also to the effective way of regulating the structure of organic matter of coal. Under the influence of mechanical activation the supramolecular organization of coals is partially destructed, the cross-linking degree of nano-sized polyaromatic clusters forming a graphite-like component of the organic matter of coal is reduced.

As a result, in the coals with a partially depolymerized structure the availability of its fragments significantly increases for efficient interaction with large molecules of solvents, the increase in the reactivity of coals in the liquefaction (hydrogenation and extraction) processes with liquid products formed. The latter can be used as raw material for the production of valuable liquid products for various purposes; high-boiling hydrocarbon fractions can find effective application to produce pitch products.

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