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# Efficiency of high energy impact in synthesis of coal-water suspensions

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## Abstract

A study of thermophysical and ecological properties of highly loaded (50% mass.) coal-water slurry based on Kansk-Achinsk brown coal and distilled water (coal-water slurry fuel – CWSF) with exposure of used water to cavitation-treatment, microwave processing of coal powder, T-900 nanocarbon additions is presented. The study shows that under the conditions of this experiment the thermal physical properties of CWSF are most affected by the use of cavitation-activated water.

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## 1. Introduction

### Nomenclature

DW	distilled water
CW	cavitation-treated water
V	the volume of dispersed phase
M	the mass of dispersed phase (coal powder)
$\Delta m$	the mass of T-900 nanocarbon addition

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$\omega$	the angular rotor speed
$\tau_k$	the time of rotor spinning
$\tau_{mw}$	the time of microwave drying of the coal powder

Fossil coals feature fuel and material science potential. Coal in Russia is used predominantly for fuel to produce electrical and thermal power. As compared to other types of organic power resources coal is specified by highest ecologically harmful gaseous emissions forming in its combustion, such as CO, carbonic acid gas CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>, polycyclic aromatic hydrocarbons, soot, and great quantity of wastes in the form of ash and slag [1]. Under conditions of natural depletion of power-generating coal reserves by intensive coal mining, the used low-quality raw material denies meeting requirements of energy efficiency and ecological safety with respect to the geosphere shell of the Earth and, consequently humans. Human impact on his natural habitat is known to be the cause of global environmental problems. Specifically, increase of CO<sub>2</sub> concentration as the main greenhouse gas in the atmosphere is connected with the Earth’s climate change. To stabilize global warming the International Energy Agency suggests to decrease global CO<sub>2</sub> emissions by 2050 to half of the level of 2007 (29 Gt CO<sub>2</sub> per year).

Coal-water slurry fuel (CWSF) – structured coal-water suspension with high concentration of dispersed phase (more than 50% mass) belongs to the «green», biosphere-compatible technology of coal use. This is fine powder ground to micron size produced not from power-generating coal only, but also from low-grade coal, peat, by-product coal, etc. The dispersion medium is water of various quality, including non-treated mine and technogenic water and various surfactants used to regulate rheological, sedimentation, aggregative properties of the slurry. Positive aspects of CWSF combustion are: practically complete combustion of coal (96-99%), reduced gaseous atmospheric discharge, feasibility of utilizing by-product coal when added to CWSF, conversion of contaminated water into clean water. Establishment of CWSF-employing hydrotransport fuel and energy complexes makes possible to solve the problems associated with coal handling [2–4].

**2. Experimental techniques**

The aim of the work is to study thermal physical and ecological properties of CWSF based on Kansk-Achinsk brown coal and distilled water exposed to cavitation [5] and microwave [6, 7] treatment with addition of small T-900 nanocarbon concentrations into the slurry [8]. To prepare CWSF the initial coal was ground in laboratory pulverizing plant MBL-100 (МБЛ-100) and wet ground in Waring 8010D instrument-based laboratory blender. The produced CWSF dispersed phase is a fine polydisperse coal powder with bimodal particle size distribution. For CWSF1 – 50...3.5 μm, for CWSF2 – 50...3.8 μm (dry sieve fractionation, CPS Disc Centrifuge DC 2400). Water (cavitation-activated water) was activated in hydrodynamic rotary type oscillator with governed rotor speed. The distilled water was treated (GOST 6709-72) at 20°C for 5 min at rotor speed 10000 rpm (Description of the samples under study is given in the Table).

Table 1. CWSF composition and production conditions

Sample	Dispersed phase	V, ml	M, g	Δm, g	ω, rpm	Cavitation	τ <sub>k</sub> , s	τ <sub>mw</sub> , s
CWSF1	DW	75	75	–	10000	+	3	–
CWSF2	CW	75	75	–	10000	+	3	–
CWSF3	DW	75	73.5	1.5	10000	+	3	–
CWSF4	DW	75	73.5	1.5	5000	–	3	–
CWSF5	DW	75	75	–	5000	–	3	1
CWSF6	DW	75	75	–	10000	+	3	1
CWSF7	DW	75	75	–	5000	–	3	2
CWSF8	DW	75	75	–	10000	+	3	2

Ignition delay time ( $\tau_d$ ), complete combustion of the droplet ( $\tau_c$ ) and burning behavior (temperature profile) of the fuel were investigated by high-speed videorecording of combustion process of a CWSF droplet fixed on a ceramic rod in a muffler at fixed temperatures of the oxidizer  $T_g$ , °C. Systematic measurement errors  $\approx 2\%$  [9].

Concentrations of anthropogenic emissions during CWSF combustion ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{NO}_x$ ) were measured with «TEST» multiple gas analyzer. The gas analyzing probe was brought close to CWSF weighed sample (1.5 – 2.0 g), put on a metal screen in the center of the muffler heated to 800°C.

### 3. Results and discussion

Major organic mass of coal (OMC) is a complex mixture of organic compounds comprising aliphatic and aromatic structures arranged as a three-dimensional polymer of irregular structure [10, 11]. Superfine grinding in the blender comes with changes in the physical structure of the coal (pore size, surface area) and structural-chemical changes (reduced length of OMC molecular chains, increased part of low-molecular fractions, destruction of oxygen-containing and carboxyl polar functional groups  $\text{COOH}$ ,  $\text{OH}$ ,  $\text{C}=\text{H}$ ). X-ray phase analysis spectra of coal particles are observed to reduce the width of amorphous ring assigned to OMC (Fig. 1a).

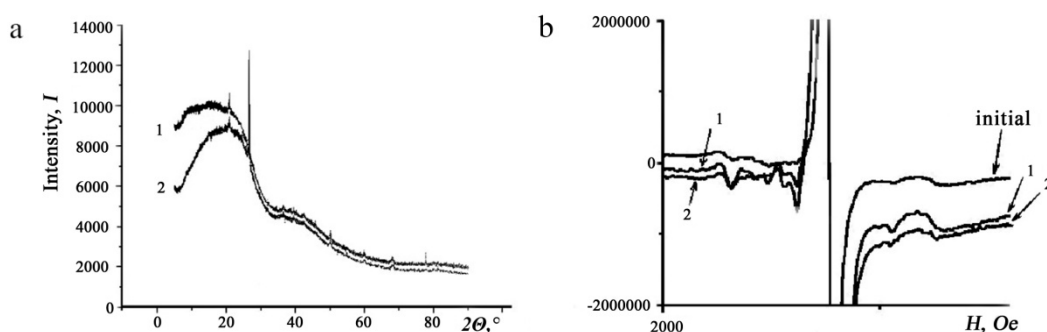


Fig. 1. (a) XRF spectrum of dispersed phase of CWSF7 (1), CWSF8 (2); (b) ESR spectrum of dispersed phase of initial water-coal mixture (1), CWSF1 (2), CWSF2 (3)

In the coal moisture is separated into free and bound. The free water is localized on the surface, in capillaries, pores, cracks of coal particles (physical-mechanical bond). Its properties are defined by the surface tension forces and adhesion, it can be easily removed. The bound water is the water molecules adsorbed and chemisorbed on the coal surface, crystalhydrate water in the mineral part of the coal. OMC breaks down to form surface with elevated reactivity, primary adsorption (hydrophilic) centers (PAC) form to actively interact with water molecules. According to the electron microscopy data (scanning-electron microscope Hitachi TM-30000, microprobe analyzer Bruker Quantax 70) the surface of particles of CWSF dispersed phase is chemically non-uniform, it was found to have chemisorbed oxygen atoms. H-bonds form around PAC clusters of water molecules and solid monomolecular  $\text{H}_2\text{O}$  films. Additional sources of PAC may be oxygen atoms entering the composition of  $\text{H}^+$  and  $\text{OH}^-$  ions,  $\text{H}^*$  and  $\text{OH}^*$  radicals, hydrogen peroxide  $\text{H}_2\text{O}_2$  decomposition products, active water molecules present in the cavitation-treated water [5, 12]. Consequently the amount of bound water in CWSF2 grows. Electronic state of coal surface was studied by electron paramagnetic resonance (spectrometer SE/X-2544, Bruker) at temperature 85 K. The EPR spectrum (Fig. 1b) consists of the central intensive line and side narrow peaks (superfine structure). The central peak is formed by radical center specific for carbon systems and the superfine structure of the spectrum yields information about the surface. Superfine structure of CWSF1 and CWSF2 is different. In the EPR spectrum of CWSF2 as compared to CWSF1 the quantity and intensity of lines varies, this is due to increased oxidation of the coal surface.

Cavitation treatment reduces water tension by 30% [13, 14] to promote its deep penetration into the pore volume of the coal and more complete filling of meso- and macropores with moisture. Due to hydrophobicity considerable part of coal meso- and macropores is not filled with water. At temperature 160°C the process of removal of free and

bound water (first endothermic peak on the DTA curve, STA 449 C Netzsch instrument) is completed. According to the thermogravimetry data in the temperature range up to 160°C the weight of CWSF2 samples varies by 10% less than in CWSF1. Maximum escape of water from the filled pore volume in CWSF2 can be denied by the pore shrinkage, disturbed connectivity of the structure. I.e. the residual moisture content in CWSF2 is higher than in CWSF1. This seems to explain the fact that during combustion of the samples under study the ignition delay time  $\tau_d$  of a droplet and complete combustion time  $\tau_c$  of a droplet for CWSF2 is more than for CWSF1 (Fig. 2a, b).

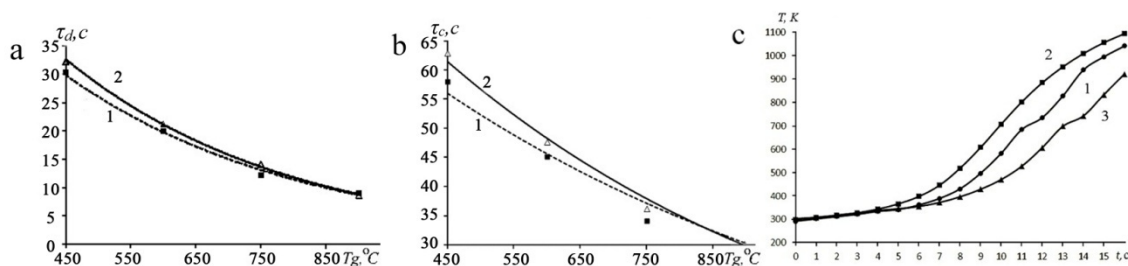


Fig. 2. (a) ignition delay time  $\tau_d$  of a droplet; (b) complete combustion time  $\tau_c$  of a droplet; (c) temperature dependence in the droplet center vs. time at the initial combustion segment for CWSF1 (1), CWSF2 (2) and CWSF8 (3)

Radicals  $H^*$ ,  $OH^*$ , active water molecules  $H_2O$ ,  $H_2O_2$  decomposition products present in the cavitation-treated water can be initiators of chains in oxidizing reactions and take part in their development, i.e. affect the radical-chain nature of the CWSF combustion process [15]. As a result the temperature trend of CWSF2 combustion differs from other samples (Fig. 2c).

All technologies used in the work to synthesize CWSF help reduce content of carbon oxides (Fig. 3a, b), nitrogen (Fig. 3c) and sulfur (Fig. 3d) in combustion. Cavitation treatment of CWSF dispersed phase makes possible to reduce  $N_{ox}$  emissions by more than 50% relative to coal, microwave treatment of the dispersed phase reduces  $SO_2$  emissions by more than 70%, addition of T-900 reduces  $CO_2$  by 25%.  $NO_x$  emissions for CWSF2 as compared to CWSF1 decreased 1.8 times. In combustion of CWSF8  $SO_2$  emissions are 3 times less than for CWSF3.

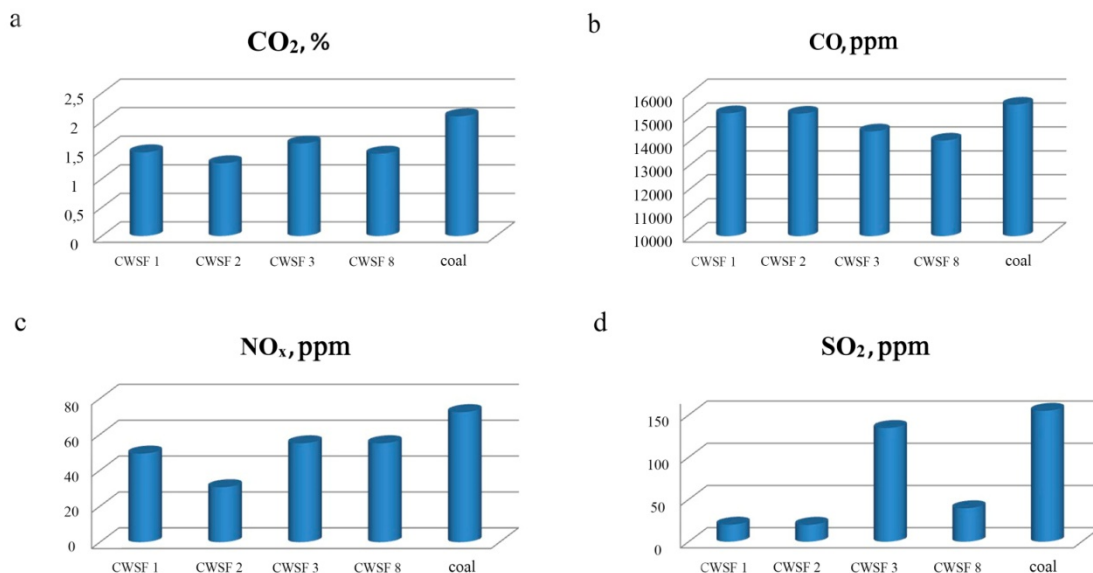


Fig. 3. Average emissions of (a) carbon oxides  $CO_2$ ; (b) carbon oxides CO; (c) nitrogen; (d) sulfur in the process of CWSF combustion and in CWSF combustion

## 4. Conclusions

1. Complexity of the structure of natural coal matter, drastic difference of physical and physical-chemical properties of coals of different grade even within the limits of one deposit considered, the produced experimental data make possible basically identify specific features of CWSF behavior in different processes.

2. Under conditions of this experiment the thermal-physical properties of CWSF (ignition delay time  $\tau_d$ , complete combustion time  $\tau_c$  of a droplet,  $\tau_d$ ,  $\tau_c$  dependence on the droplet size, nature of temperature trends of droplet combustion) is most substantially affected by the use of the cavitation-activated water. For other samples the variation of thermal-physical properties is within the experiment error.

3. The cavitation treatment reduces surface tension of water to promote more complete filling of meso- and macropores in the coal particles with moisture. In combustion the ignition delay time  $\tau_d$  of a droplet and complete combustion time  $\tau_c$  of a droplet for CWSF2 is more than for CWSF1.

4. According to EPR data oxidation of coal surface increases due to presence in the cavitation-treated water of oxygen which is part of  $H^+$  and  $OH$  ions,  $H^*$  and  $OH^*$  radicals, hydrogen peroxide  $H_2O_2$  decomposition products, active water molecules.

5.  $H^*$  and  $OH^*$  radicals, active water molecules  $H_2O$ ,  $H_2O_2$  decomposition products present in the cavitation-treated water can be initiators of chains in oxidizing reactions and take part in their development, i.e. affect the radical-chain nature of CWSF combustion. As a result the temperature trend of CWSF2 combustion differs from other samples.

6. All used in the work processes (cavitation treatment of water, microwave heating of coal powder, addition of nanoglobular T-900 carbon into the slurry) help reduce anthropogenic gas content (nitrogen, sulfur, carbon oxides) in CWSF combustion as related to coal. The degree of their impact on reduction of harmful emissions is different.

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