

Impact of Hydrodynamic Cavitation on the Properties of Coal-Water Fuel: An Experimental Study

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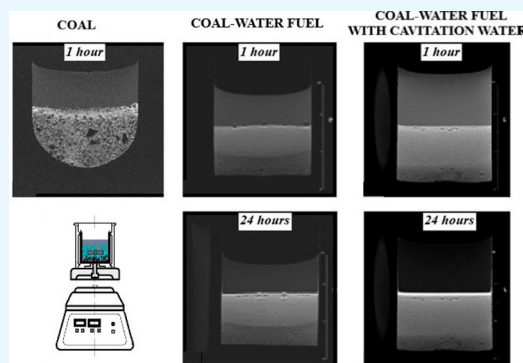
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ABSTRACT: It is common to use coal as raw material in heat power engineering. A number of shortcomings of coal such as ignitability cannot be easily eliminated. The use of water-slurry-based coal-water fuel instead of coal eliminates this problem. The coal-water fuel (CWF) is liquid fuel, which means that the main line of investigation is to study its sedimentation and rheological properties responsible for the transport and atomization in the boiler and thermal-physical properties which determine the expedience and efficiency of its application. The paper shows that the final performance properties of suspended coal fuel can be determined at the stage of CWF preparation by hydrodynamic treatment of aqueous coal slurry. The rheological and sedimentation properties and combustion parameters of water-coal fuel, ignition time of the drop, its completeness of combustion, and amount of man-made emissions, have been studied. Studies have been carried out on coals from the Kansk-Achinsk coal basin (Russia). The studies were performed under laboratory conditions with a hydrodynamic rotary mixer, making it possible to attain cavitation effects in the processed medium. Two CWF types have been considered: the first was produced by cavitation dispersion of the solid coal fraction in distilled water, and the second was produced in analogy, but the dispersion medium was water pretreated by cavitation. The paper shows that the cavitation method of producing CWF improves the rheological and sedimentation properties of the end-use fuel, reduces hazardous emissions in combustion, and affects the combustion parameters.



1. INTRODUCTION

Coal as an energy resource is used over considerable parts of Russia and China. The Asian part of Russia is rich with coal deposits. Krasnoyarsk krai where the Kansk-Achinsk coal deposit is located is the Russian leader in the balance reserve of standard quality coal (more than 4 trillion tons), including bituminous, brown coal, and anthracite. Notwithstanding the years of the COVID-19 crisis, coal production and coal use have exhibited positive dynamics. Resource-saving consumption of coal is a challenge for efficient use of natural resources. For example, after extraction, conventional coal beneficiation technology leaves considerable amounts of fine moist fraction which need to be additionally dried. Frequently, such flooded remains are specified by high ash content, unsatisfactory calorific efficiency, and a high impurity level. It is expedient to use this raw material to prepare water-slurry-based liquid fuel. This solves the issues of ecological safety of storage, transport, combustion, and energy supply to the areas running low on coal.

According to global trends, coal energy is being developed through the path of upgrading and implementing new environmentally clean coal-using technologies to reduce the adverse environmental impact of the fuel and energy complex.^{1,2} Application of the water-coal fuel is among these

technologies. This is an alternative fuel type which is a suspension of the dispersed phase of coal, including fine low-grade coal with a mass fraction from 35 to 70 mass %, and the dispersion medium is water of various qualities, including service water. The coal-water fuel can be produced from anthracites, bituminous and brown coals of different grades and ash content, and water of any quality, including mining and industrial waters. One of the most important characteristics of the fuel from the viewpoint of storage, transportation, and combustion is its dynamic stability.

Successful practical application of highly loaded liquid systems comprising a solid phase necessitates in-depth investigation of their properties, which include kinetic and aggregative stability; i.e., the stable concentration homogeneity of the distribution of the dispersed phase particles in the dispersion medium volume is held in place. In ref 3, it was

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shown that preliminary modification of the surface of fine coal particles by kerosene suspension and ultrafine petroleum coke substantially improved the rheological properties of ready coal water fuel (CWF) in the presence of a dispersing agent. However, the distribution of the solid coal fraction was strictly controlled and was bimodal. The CWF rheological and stable properties have been found to depend on the initial water cut and the extent of degree of association of water and coal particles. The rheology of CWF produced from low-grade coals is most frequently affected by additions^{4,5} which may be NaOH alkali.⁶ This increases the cost of using CWF as a liquid fuel.

Meanwhile, it would be necessary to consider the expedience of using CWF as fuel, taking into consideration its characteristics during combustion. The authors of ref 7 showed that the thermophysical properties of CWF combustion depend on the percentage of water in the suspension: the optimal content of the water phase is 36% and does not depend on the degree of the metamorphization of initial coal used to produce the fuel and the temperature of the furnace medium. Increased content of the water phase in CWF up to 42 mass % and higher makes the preparation stages of fuel combustion processes longer and affects its parameters. The authors do not report precisely at which parameters the water-coal slurry was prepared in a planetary mill and if the modifying additives were used. In ref 8, the authors showed that the combustion parameters were weakly connected with the quality of the water phase (natural, process water, and liquid waste) when its rational content in the fuel is within the limits of 59–65%. Many authors show that the addition of combustibles positively affects the CWF combustion and burning-out processes. Most commonly, such substances are coal and oil processing wastes,^{9,10} industrial waste,¹¹ and the biomass.¹² The optimum ratio of all components of the fuel mixture can be found empirically. Even though the number of publications on combustion characteristics of water-coal fuel is significant, the issue of the method of preparing the fuel composition remains open.

The in-depth and comprehensive knowledge of the specifics of the rheological behavior of the suspension and processes during combustion notwithstanding, the preparation processes of the water-coal fuel are given little attention. The measures that make it possible to attain optimum grain-size distribution required sedimentation and rheological key figures, and environmental safety in combustion should be well studied and be predictable at every stage. The regularities of ignition and burning of the water-coal fuel can also depend on the method of mixing its components. Simple manual mixing of hydrophobic coal and water is obviously insufficient to produce a stable suspension. Hydrodynamic cavitation can affect the physical parameters of the suspension and chemical transformation of the multicomponent mixture of the liquid coal fuel.

Cavitation is the formation, growth, and collapse of bubbles filled with gas, vapor, or their mixture when pressure in the liquid drops to the saturated vapor pressure of this liquid. Irrespective of its nature, cavitation is a multicomponent process accompanied by a local increase of temperature and pressure inside the collapsing bubble, turbulent mixing and micromixing due to the formation of microjets during explosion of the bubble, and thermal dissociation of the water molecules forming hydroxyl radicals.^{13,14} Contrary to ultrasonic cavitation in the case of hydrodynamic cavitation, the mixing of the processed liquid volume is more intensive

and turbulent, resulting in impetuous mass transfer. The bubble quickly collapses in adiabatic conditions because the extremely short collapsing time inhibits heat exchange inside and outside the bubble. The totality of physical and chemical processes during cavitation necessarily changes the properties of the processed liquids.¹⁵ Results of cavitation treatment can be conditionally divided into an increase of the oxidation reaction, increasing dispersivity of components of heterogeneous liquids (emulsions or suspensions), and changes in colloidal stability (Figure 1).

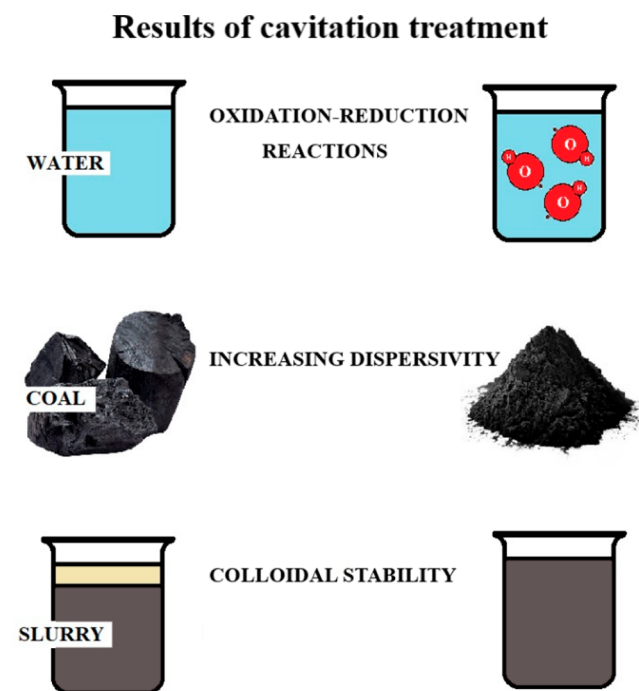


Figure 1. Effects observed in cavitation treatment of a suspension.

Hydrodynamic cavitation arises in rotor-stator machines when local pressure in a liquid decreases to the threshold pressure—the pressure of the liquid vapor at operating temperature due to high liquid velocity. Cavitation is considered a green technology because it makes it possible to avoid excessive use of toxic compounds, replacing them for more environmentally safe solvents, and in a number of cases to completely avoid application of chemical additives.¹⁶ The processes involving cavitation are specified by improved reaction conditions and selectivity, no formation of toxic sediment, and reduced energy for chemical transformations.¹⁷

In ref 18, the authors note that hydrodynamic cavitation used at the stage of preparing the water-coal fuel from brown coal with a solid fraction content of 50% makes it possible to produce slurry that is stable for 1 week. The authors note the overmilling of the dispersed phase (of coal) after cavitation—this seems to be due to a too intensive cavitation treatment. The authors of ref 19 have found that hydrodynamic cavitation treatment at the stage of CWF preparation not only mechanically destroys the coal but also changes the chemical composition of the surface layers of the coal particles by oxidation–hydrolysis reaction in the cavitation water of the slurry. This entails a decrease of viscosity and increase of stability of the ready fuel slurry. In ref 20, a method of preparing a water-coal slurry by initiation of high-voltage pulse

discharges in the mixture of coal is reported. Water and organic solvent accompanied by a hydrodynamic cavitation effect is described. High-molecular and low-molecular organic coal substances bound by molecular interaction depolymerize, and as a consequence, the conversion of coal in combustion increases, and the amount of ash decreases. In our opinion, the literature data on the association between the methods of preparing the water-coal slurries and their basic operating properties (rheological, thermal-physical, and environmental) are insufficient.

So, the optimum ratio of solid and water phases and a selected preparation method allow us to improve the operational characteristics of CWF.^{21,22} The main purpose of this study was to define the effect of hydrodynamic impact at the stage of CWF preparation on its rheological and sedimentation properties and combustion parameters.

In the furtherance of this goal, we have performed the following tasks:

1. Studied the effect of hydrodynamic cavitation on the size of particles, sedimentation, and viscosity of CWF.
2. Studied the effect of cavitation on structural changes of the coal-making part of CWF.
3. Experimentally studied CWF combustion parameters, including the amount of hazardous emissions.

2. MATERIALS AND METHODS. EXPERIMENTAL BASE

2.1. Characteristics of Coal and CWF. Experimental studies were carried out with CWF based on Kansk-Achinsky basin coals (Borodinsky deposit, Russia). Characteristics of the bituminous coal are given in Table 1. The coal was crushed in ball mill MBL-100.

Table 1. Characteristics of the Coal-Forming Part of CWF^{23,24}

coal	W^a , not more than %	A^d , not more than %	V^{daf} , not more than %	$Q_{s,v}^a$, MJ/kg
coal	20	8	48	22.91

^a W^a , % is the moisture content; A^d , % is the ash content; V^{daf} , % is the volatile content; and $Q_{s,v}^a$, % is the higher calorific value (MJ/kg).

The water-coal fuel was prepared in the form of a suspension of water and coal. For this purpose, 75 g of coal powder and 75 mL of water were at the same time placed in the beaker of a hydrodynamic rotary-type mixer Waring blender 80100 with a two-blade impeller of wedge profile, and the wedge angle of the cavitator was $\alpha = 60^\circ$ (rotor) in supercavitation mode. The motor power was 1 kW, and the working chamber volume was 10^{-4} m^3 (Figure 2).

The mixture was processed for 3 min in the mixer at a rotor rotation speed of 10 000 rpm. After that the ready suspension was investigated, for CWF1 the water was distilled at pH = 4.91 at room temperature of $T = 20^\circ \text{C}$. It is common knowledge that the cavitation treatment increases the pH of water and decreases the oxidation–reduction potential by mechanolysis of the water molecule.²⁴ To find out the effect of more alkaline water on CWF properties, a CWF2 sample was prepared in analogy, in which the dispersion medium was distilled water (pH = 5.70 at the temperature immediately after preparation of $T \approx 37^\circ \text{C}$) pretreated in the cavitation mixer for 5 min. The formulation of the liquid composition and some

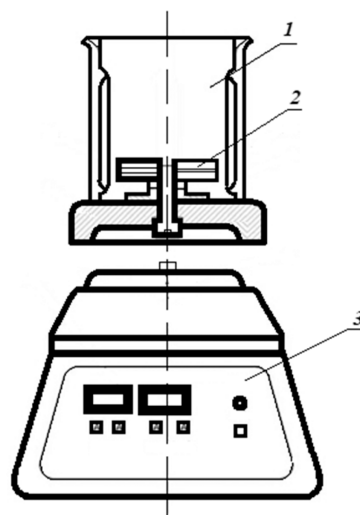


Figure 2. Rotary-type supercavitation mixer Waring blender 80100. 1—Operating reactor. 2—Rotor (cavitating impeller). 3—Control board.

properties of the suspension and its components are given in Table 2.

The size distribution of initial coal, CWF1, and CWF2 made by particle size analysis on the vibration stand with a traditional set of sieves by dry fractionation on sieves is given in Figure 3.

2.2. Methods of Examination. The size distribution of the coal particles of a class size lower than $40 \mu\text{m}$ was found by the instrument CPS Disc Centrifuge DC 2400. The dynamic viscosity of CWF was measured with the rotary viscosimeter Rheotest-2. pH was measured with a WaterTest instrument (Hanna Instruments). The optical images were done by an OLUMPUS BX43 microscope (Japan, $\times 100$).

Sedimentation properties were measured by two methods. First, the relative sedimentation volume $V = V_{\text{sediment}}/V_0$, was measured, where V_{sediment} is the volume of sediment formed at time moment t and V_0 the volume of suspension. The second method was magnetic resonance tomography (MRT) on a nuclear magnetic resonance microtomograph based on Bruker AVANCE DPX 200 (radio frequency coil diameter 25 mm) software (PARAVISION 4.0). The nuclear magnetic resonance (NMR) microtomograph visualized a proton solvent dispersion medium of CWF. The spin system (water proton system) is in the external magnetic field (4.7 T), excited by a nonhomogeneous field in the form of pulses. The image is formed by the response of a spin system to this excitation. The rheological properties were measured with rotary viscosimeter Rheotest-2 by the coaxial cylinder method.

The electronic structure of coal was studied by electron paramagnetic resonance at temperatures 80 and 300 K (EPR spectrometer of X-range SE/X-2544, Bruker). Thermophysical characteristics of the dried powder dispersed phase of CWF were obtained on the simultaneous thermal analysis instrument STA Yupiter Netzsch (STA 449C).

The ignition delay time, burning-down period, and burning behavior of the fuel (temperature profile) were studied by a rapid video recording of the burning process of a CWF drop at fixed temperatures of the oxidizer; the recorder was fixed on a ceramic rod in a muffle furnace. When the temperature was measured in the center of the drop in combustion, the size of the drop was 1 mm. The thermocouple with a suspended water-coal fuel droplet was placed in a motorized traversing

Table 2. Composition Formulation and Several Parameters of CWF

	dispersed phase, g	dispersion medium, mL	dispersion medium type	immediately after preparation of CWF		30 min after preparation of CWF	
				pH	T , °C	pH	T , °C
CWF1	75	75	distillate	5.71	34.2	5.75	24.2
CWF2	75	75	distillate after cavitation	5.69	36.7	5.76	26.4

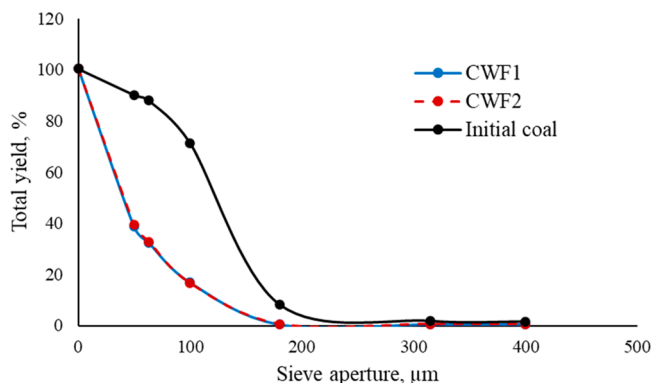


Figure 3. Curves of combined characteristics of the size of coal and solid fraction of CWF1 and CWF2.

indexing mechanism which moved the droplet into the muffle furnace which was heated to 973 K. The temperature value in the center of a single droplet was defined with a temperature recorder with 1 s intervals. The domineering heat transfer mechanism was radiant heating, and the measurement errors were $\approx 2\%$. Concentrations of anthropogenic emissions were measured with a «Test» multicomponent gas analyzer. For this purpose, the temperature in the muffle furnace was set at 800 °C. A 2.0 g sample of fuel was placed on a cylindrical metal mesh (height 10 cm, radius 2 cm, mesh size 0.05 mm). The mesh was in the center of the heated muffle furnace, and after that the gas analyzer probe was brought close to the mesh. The aperture to insert the mesh into the muffle furnace was closed with a high-temperature insulation layer, thus monitoring the excess air factor (~ 1.1). The time of each experiment varied from 2 to 5 min, and the measurement errors were $\approx 4\%$.²⁵ The experimental installation and methods of measurement are described in more detail in ref 9.

3. RESULTS AND DISCUSSION

3.1. Size of Particles and Rheological Properties of CWF. The surface of coal is inhomogeneous and consists of hydrophilic and hydrophobic areas (Figure 4). To make liquid coal-water fuel achieve a high performance of operating rheological and sedimentation properties, it is necessary to affect the wettability and dispersibility of the CWF solid phase

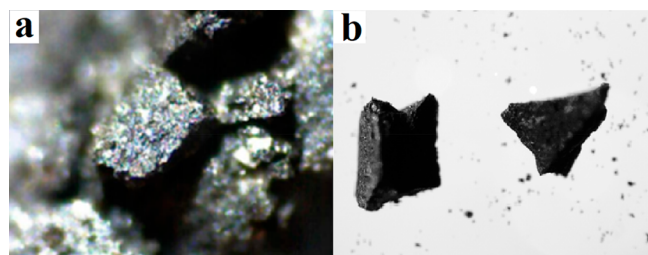


Figure 4. Coal particles in CWF: (a) surface the coal particles and (b) shape of coal particles ($\times 100$).

and stabilize the system on the whole. The aggregate and sedimentation stability and efficient rheological properties depend to a great extent on the conditions of activating the fuel mixture components and most frequently are found by empirical studies.

The maximum size of particles permissible for the production of coal-water fuel for hydrotransport is $\sim 300 \mu\text{m}$. Larger particles can plug the pipe. If for combustion applications the size of the particles is decreased from 300 μm , the dynamic viscosity of the slurry is observed to decrease. The size of particles less than 50 μm also considerably increases the dynamic viscosity of the slurry due to high agglomeration of the particles. Therefore, the distribution of particles by size plays its role when, depending on the coal type, the distribution of particles by size is optimized to produce the minimum possible dynamic viscosity of the liquid fuel.²⁶

Hydrodynamic cavitation treatment affects the size of the particles in treated suspensions (Figure 3), and the size of the loose material can be inferred from the nature of the curve. It can be seen that for the initial coal sample it is convex, indicating the prevalence of coarse fraction, and for CWF1 and CWF2 samples the curves are concave and almost coinciding. A very slight difference in the size yield for CWF1 and CWF2 samples suggests that cavitation pretreatment of water does not contribute to an increase or decrease of the dispersibility of coal particles larger than 40 μm . In CWF1 and CWF2 samples in the 50 μm size class, it is possible to point out the average size of the particles (Figure 5).

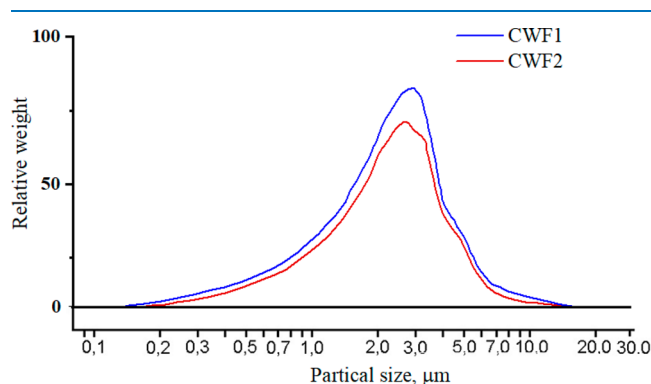


Figure 5. Curves of the particles' size distribution (less than 40 μm) of the solid fraction of CWF1 and CWF2.

The sedimentation stability of the slurry is its capability to maintain a constant distribution of particles of the system volume in time, i.e., the capability of the system to withstand gravity. Dependences of the sedimentation volume on sedimentation time are given in Figure 6. The sedimentation curve for CWF2 with activated water can be seen to be below the curve for CWF1 with ordinary distilled water. This means that the coagulation capacity of the dispersed phase in the

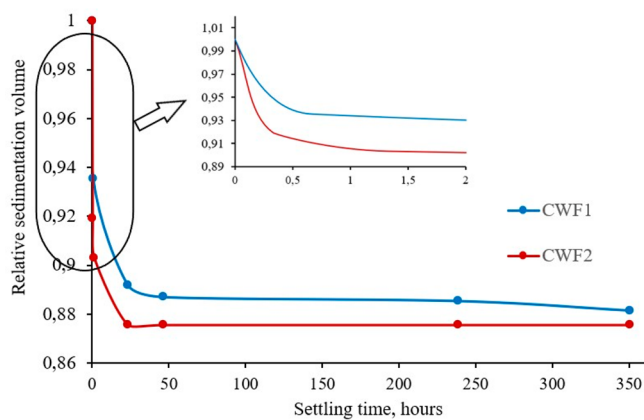


Figure 6. Dependence of the relative sedimentation volume on the settling time for CWF1 and CWF2 samples.

slurry with a preactivated dispersion medium is lower (sediment volume is less).

During the sedimentation process in the coal-water slurry, the magnetic resonance tomography makes it possible to study the motion of water in the coal-water slurry after its preparation. The NMR microtomograph visualized a protic solvent dispersion medium of CWF. Because of the presence of solid coal particles, the image is inhomogeneous and contains information about the condition of the water-coal system (Figure 7).

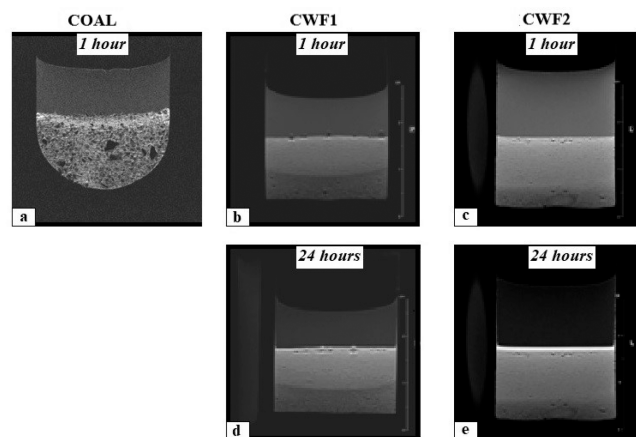


Figure 7. MRT visualization of the sedimentation process of a simple mixture of water and coal immediately after preparation (a), CWF1 immediately after preparation (b) and the next day (d), and CWF2 immediately after preparation (c) and the next day (e).

The NMR image (Figure 7a) clearly shows particles of coal in an ordinary coal-water mixture; CWF1 (Figure 7 b, d) and CWF2 (Figure 7 c, e) are more homogeneous, and the particles in them are smaller. Besides, in the images we observe a layer structure which can be caused by the broad curve of the size distribution of the dispersed phase of CWF1 and CWF2. Stratification in the CWF1 sample is observed more distinctly than in CWF2 prepared with pretreated water.

The preparation of CWF is based on mechanochemical activation, which breaks down the structure of coal. In CWF, a chemically active dispersion medium forms, including that saturated with components of mineral constituents of the coal with pH different from that of distilled and cavitation water.

Cavitation treatment of the slurry forms the surface of the coal particles, with elevated reactive capacity and primary adsorption (hydrophilic) centers (PACs) actively interacting with the water molecule form.²⁷

Present in the water after cavitation treatment are H^+ and OH^- ions, H^* and OH^* radicals, decomposition products of hydrogen peroxide H_2O_2 , and active molecules of water. All of them can be additional sources of PACs. Due to H bonds, the water molecules and continuous or not continuous monomolecular films of H_2O which form around PAC can grow into space domains. As a result, the amount of bound water in CWF2 grows. When the dispersed phase reaches a certain concentration and dispersivity of the solid phase decreases, space bulk structure forms. Such a structure emerges as a result of coagulation contacts forming between the particles through the liquid medium interlayer. The necessary condition for the coagulation structure to form is the presence in the solid phase of particles of colloid size. Distributing in the volume of the slurry, they in totality with larger particles form a space 3D frame consisting of chains or aggregates.²⁸ The coagulation structures increase with the amount of bound water in CWF2 and, consequently, improve the rheological properties of CWF, imparting it with plasticity and elasticity.

Coal-water fuel is known to tend to improve rheological properties in the alkaline medium. Studies of the dynamic viscosity of CWF prepared on distilled water with preliminary cavitation treatment of water showed that in both cases CWF can be considered pseudoplastic fluid, in which the dependence of the shearing force on the shearing rate follows the power law. The dynamic viscosity of CWF2 (Figure 8) prepared with activated water is, on the average, 30% lower than the viscosity of CWF1 in the shearing rate range.

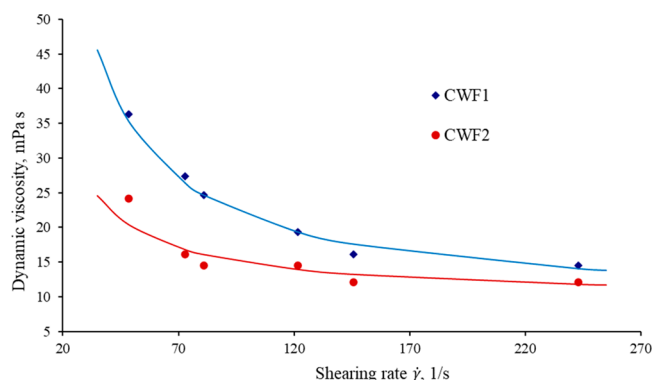


Figure 8. Dynamic viscosity depending on shearing rate at 25 °C.

To determine the rheological behavior of these suspensions produced by a rotational viscosimeter, the data on the dependence of viscosity of suspensions on the shear rate were used to define the parameters of rheological models by least-squares approximation. The coal-water fuel can be a non-Newtonian viscoplastic fluid, and its behavior can be described by one of the most frequently used rheological models: power law and Bingham.²⁹

To approximate the rheological parameters of water-coal suspension, we used the power law model

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

where K is the consistency factor, $\text{Pa}\cdot\text{s}^n$; $\dot{\gamma}$ is the shear rate, s^{-1} ; and n is the flow behavior index. The Bingham model is also used:

$$\eta = (\tau_0 + k_v \dot{\gamma}) \dot{\gamma}^{-1} \quad (2)$$

Here τ_0 is the yield point of viscoplastic liquid, Pa, and k_v is the plastic viscosity, Pa s.

Analysis of the certainty factor of approximation of the produced data showed that on average the Bingham model describes the rheology of considered suspensions better. For this Bingham model, the certainty factor (R^2) on average was higher than 0.96, while for the power law model it was 0.91. The data on coefficients of rheological models are presented in Table 3. As we can see, the yield point of the CWF1 suspension is 2.5 times higher than that of the CWF2 suspension.

Table 3. Coefficients of Rheological Models for CWF

model	CWF1		CWF2	
	power-law	Bingham	power-law	Bingham
τ_0 , Pa	0	1.28618	0	0.52481
k_v , Pa s ⁿ	0.27137	0.008807	0.0579	0.009606
n	0.45706	1	0.70809	1
R^2	0.91901	0.96683	0.93842	0.96179

3.2. Structural Changes of Coal. The breakdown of the coal structure triggers changes in the electron structure of the surface of coal particles. The emergence of coagulation structures comprising enlarged particles of iron oxides and other elements is evident by the emergence of additional hyperfine lines in the EPR³⁰ spectra.

The width of the coal EPR signal depends on the paramagnetic impurities of its mineral part and organic part as is. The unpaired electrons in the carbon matrix make a considerable contribution to the width of the EPR signal in the highest-grade metamorphic mineral coals. In the medium-grade metamorphic mineral, the coals determined are both types of paramagnetic centers—the minerals of the mineral part of coal and unpaired carbon. The cavitation treatment of the slurry at the stage of CWF preparation and separate hydrodynamic impact on the water can affect the condition of oxidizing native impurity ions as part of the coal. The EPR spectrum of the dispersed phase of CWF1 and CWF2 at nitrogen temperature (Figure 9) consists of the central intensive line and side narrow peaks (hyperfine structure). The central peak is formed by the radical center specific for the carbon systems, and parameters of the peak including the g factor and width of line ΔH (2.0034 and 6.74 Oe, respectively) for CWF1 and CWF2 are practically identical. The hyperfine structure determined by the interaction of carboxy groups with the nearest hydrogen ions reflects the condition of the coal surface. The hyperfine structure of CWF1 and CWF2 differs: the number and intensity of lines in the EPR spectrum for CWF2 differ as compared to CWF1. This is connected with oxidation of the coal surface increasing due to the presence of H_2O_2 molecules in the activated water and additional absorption of OH^- ions due to higher pH in CWF2. The increasing potential of the surface due to OH^- adsorption decreases coagulation of the particles and stabilizes the slurry, changing the rheological properties.

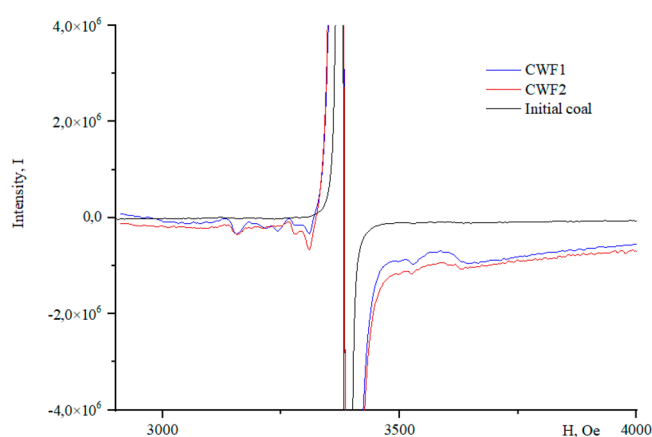


Figure 9. EPR spectra of the initial coal and dispersed phase of CWF.

The produced improved characteristics of the coal-water fuel made with water preliminarily treated by cavitation (CWF2) suggest expedience of further research in the application field as a dispersion medium of the cavitation water. The hydrodynamic cavitation helps improve the stability of coal-based fuel heterogenic compositions, decreases the viscosity, and holds promise to integrate the coal-water fuel into the preparation process flow and its use.

3.3. Simultaneous Thermal Analysis of CWF. Thermogravimetric characteristics of coal and the dried dispersed phase of CWF powders (Figure 10) studied in this work did not reveal fundamental differences between DSC spectra of CWF1 and CWF2 samples. The nature of process behavior is identical. When the temperature of the sample changed from 45 to 120 °C, the TG curve exhibited a slight loss of the mass of ~3% due to evaporation of weakly bound water from the surface of the particles, and the process is not accompanied by anomalous absorption or release of energy. In the range from 120 to 660 °C, the DSC curve is observed to have an exothermic effect. This effect is extended, is of irregular shape with numerous overlapping peaks, and is accompanied by considerable loss of the sample mass at different rates. The coal mass burns in this range. In the temperature range from 120 to 255 °C, the TG curve shows slight loss of the weight of ~2% associated with evaporation of bound water inside the pores and channels of the solid part of CWF. The weight loss rate increased in the temperature range 255–500 °C, and the weight loss in this range was ~86%. In addition, from 500 to 570 °C, the rate decreased, and the loss was ~3%. In the temperature range 570–660 °C, the loss was only 1% of the sample mass. A considerable part of coal burnt out before 500 °C. The difference between the burning processes of coal and CWF in the temperature range 500–570 °C for the CWF DSC curve is observed to have a sharp peak, and the angle is smeared and is wing-shaped.

Taking into account the fact that the dispersed CWF phase for STA analysis has been predried, it can be said that the burning behavior was analogous: there was no fundamental difference in the residual mass after combustion, and the temperature intervals of exothermic reactions coincide. Therefore, the presence of water is fundamental for the use of suspension fuel—this will be demonstrated by analysis of gases released in the burning of coal and CWF.

3.4. CWF Combustion Characteristics. Even though the water in the suspension fuel combustion reactor reduces its specific heat due to replacing a part of the suspension volume,

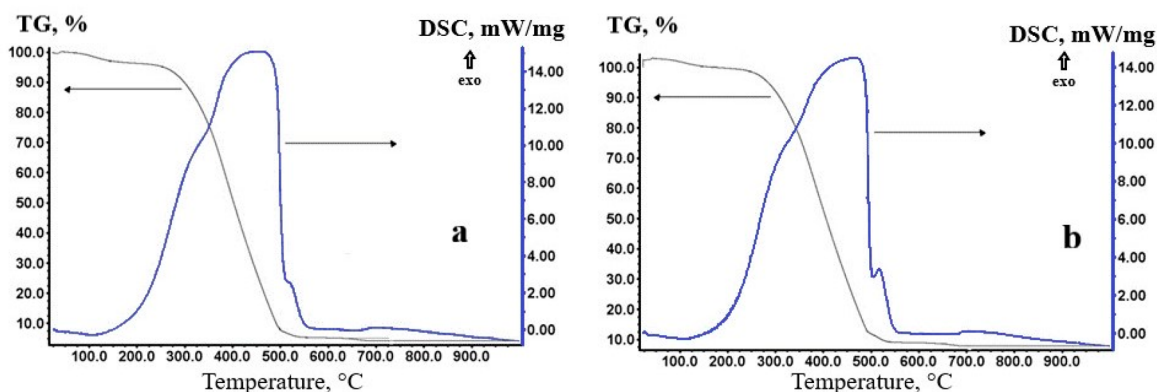


Figure 10. STA curves for coal (a) and for CWF (b) (TG—mass loss curve and DSC differential scanning calorimetry curve).

it does not facilitate stability of the jet fire, and it affects the energy characteristics of burning on the whole. To select such conditions is to find optimum methods of preparing the suspension, the ratio of solid and liquid phases, and size distribution of the coal, minimizing environmentally hazardous emissions and acceptable thermal-physical indicators during ignition and burning of CWF.³¹

Combustion of the coal-water fuel is a heterogenic process in which combustion of coal in the oxidizing medium is attended by parallel generation of steam from the dispersion medium of the slurry. In this droplet combustion, the reaction characteristics of the fuel and conditions of heat and mass exchange on the surface and inside a CWF droplet depend on the properties of not only coal but also the carrying medium. The radical chain nature of oxidation and combustion of coal determine the decisive role of water and water vapor. The main reactions of coal-water slurries in the oxidizing medium are reactions of coal oxidation and combustion with oxygen and water vapor and reactions of the reduction of carbon dioxide, conversion of carbon oxide, etc. Specific to these reactions is their behavior at high water vapor concentration, and the formation kinetics of this vapor is determined by the properties of water. Thus, the presence of water in the coal-water fuel intensifies the total rate of burning-out of the fuel droplet. The cavitation treatment of water reduces the surface tension of water to help it penetrate deep into the pore space of coal and allow better admission of moisture into mesopores and macropores in CWF2. As discussed above, the molecular layer of water is connected by hydrogen bonds to the hydrophilic centers of coal. Accumulation of water around areas densifies the capillary structure. A part of the hydrophilic area forms functional groups comprising oxygen, and in the case of CWF2 they are more numerous. In spite of evaporation of water, the coal aggregates remain intact.²⁸

Cavitation pretreatment of the dispersion medium in the coal-water suspension does not change the combustion dynamics of a CWF drop: the ignition delay time and total burning-out time of a CWF drop decrease with the size of the drop and increase of the temperature in the furnace. However, when the temperature in the furnace is 900 °C, the CWF2 drop starts burning earlier (Figure 11, black curves), but its total burning-out time does not practically differ from the total burning-out time of the CWF1 drop (Figure 11, blue curves).

With the minimal investigated size of the drop at 0.6 mm, the time of total burning-out for CWF2 is smaller (Figure 12). The ignition delay time of CWF droplets 0.6 mm in size is

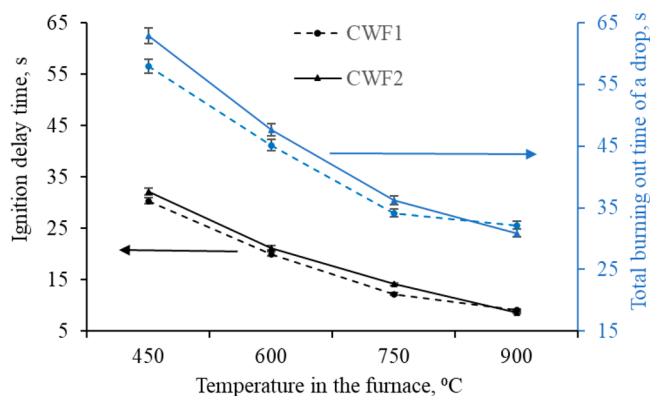


Figure 11. Dependence of ignition delay time (black curves) and total burning-out time of the (blue curves) CWF drop on temperature in the furnace.

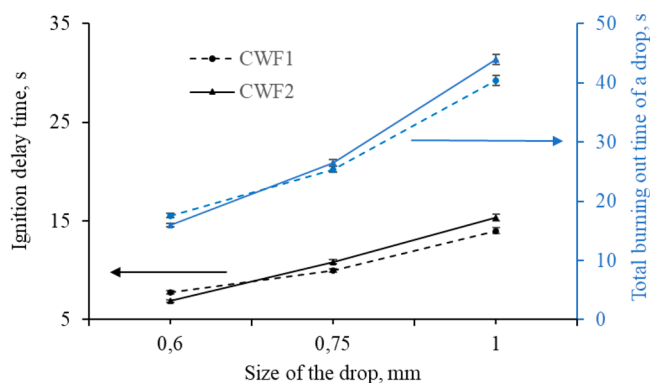


Figure 12. Dependence of ignition delay time (black curves) and total burning-out time of the (blue curves) CWF drop on the size of the drop at the furnace temperature of 700 °C.

twice as small as the ignition delay time of the droplets 1 mm in size, and the complete burning time of a 1 mm droplet more than doubles compared to that of the 0.6 mm droplet. The porosity of dried layers increases with the size of the droplet; this decreases the heat transfer into the central part of the droplet and decreases moisture evaporation time and thermal decomposition of the coal particles. For industrial use of the coal-water fuel, it is important to achieve stability and completeness of combustion of the fuel in the combustion chamber; therefore, the dispersivity of the droplet spray fed into the fuel chamber should be high. These properties should provide for reliable ignition conditions and flame stabilization,

reliable mixing of the fuel with the oxidizer and temperature distribution, and optimal conditions of fuel burnout over the entire volume of the chamber.

The change of temperature in the center of CWF1 and CWF2 droplets heated by the oxidizer is shown as droplet temperature trends (Figure 13) on which characteristic

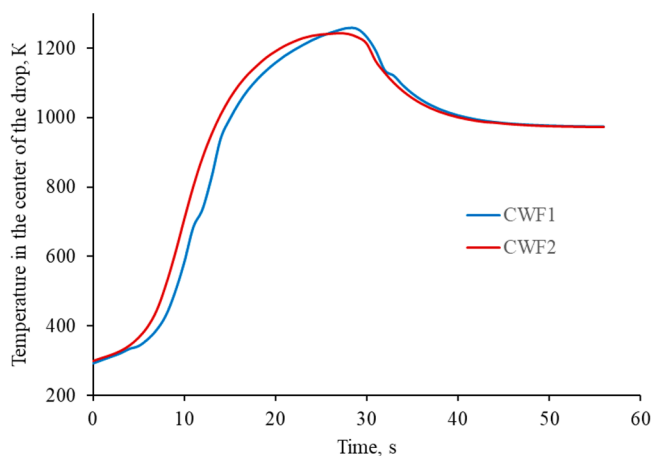


Figure 13. Variation of temperature in the center of a CWF drop at the temperature in the furnace of 973 K.

combustion stages of the droplet are observed. The first stage is the heating of a near-surface layer with moisture evaporation and emission of volatiles. The processes in the CWF droplet run nonuniformly over the volume and occur layer-by-layer: they start in the top layers and are suspended due to the passing of heat inside the droplet where undecomposed coal mass and water remain. Then, when the combustible products of thermal decomposition of coal reach required concentrations, the gas-phase ignition and heating of the carbon residue occur. Burn-out of the fuel mixture around the droplet intensifies heating of the entire volume of the fuel droplet, and when the heating is sufficient, the solid component of the fuel slurry ignites and carbon burns out. The final stage is inert heating of the ash residue in the oxidizer flow. A sequence of the described combustion stages is specific for both samples, CWF1 and CWF2.

The temperature in the center of a CWF drop was measured at a constant temperature in the furnace of 973 K (Figure 13). A significant difference in the temperatures exceeding the experimental error is observed in the interval from 5 to 16 s from the moment the drop is placed in the furnace. During this time, the temperature in the center of the drop varies from ~350 to 1050 K. The maximum difference between the temperatures in the center of the drop is observed within the interval 450–800 K, where the main exothermic effects occur. The rate of temperature variation in the drop during the time period from 8 to 13 s is 20% higher for CWF2. Then, the temperatures level out and starting from the 17th second after the beginning of the burning do not differ significantly.

The arrangement of coal particles in CWF is nonuniform. Water as a dispersion medium in the slurry allows the formation of large agglomerates from individual coal particles. In the case of CWF2 made with water preliminarily treated by cavitation consisting of coal particles of different size, a tendency to form stable groups of larger particles inside the slurry was observed. All this affects the radical-chain nature of the CWF2 combustion process. The cavitation treatment of

the water makes it possible to intensify the combustion process, decreasing the ignition delay time of the droplet center.

3.5. Gas Emissions During CWF Combustion. Similar to combustion of coal, the combustion of coal-water fuel released highly toxic gases collectively known as manmade. Among them are nitrogen oxides NO_x (sum of NO and NO_2), carbon monoxide CO and carbon dioxide CO_2 , and sulfur oxides SO_x (sum of SO_2 and SO_3). Oxide SO_3 is not stable, and its concentration as compared to SO_2 content is insignificant. NO_x , SO_x , and CO form in high-temperature combustion of fuel. The presence of water, or to be more precise of water vapor, in the zone of combustion of hydrocarbon suspension or emulsion fuel was shown by many authors^{25,32} to reduce the amount of these compounds. The water vapor reduces the temperature in the combustion zone; this affects the oxidation and decomposition rate of sulfur and nitrogen oxides in the fuel. The oxygen, produced in dissociation of water molecules at the initial stage of CWF combustion, intensifies the process of coal burning. Hydrogen and CO reduce nitrogen oxide³³ at a temperature in the reactor higher than 200 °C:

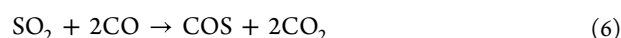
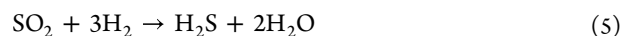


With a further increase of temperature and the formation of carbon dioxide during coal burning, the following reaction is observed:

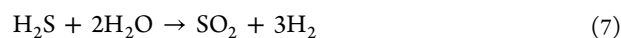


In the coals, sulfur is present in two basic forms: inorganic and organic. The inorganic sulfur is represented mainly by inorganic ferrous disulfides and calcium and iron sulfates. The organic form of sulfur immediately connected with the organic part of coal is usually in the form of organic sulfides, disulfides, etc. During combustion, sulfur starts reacting to divide into solid and gaseous phases. The mineralized sulfur as part of the compounds is deposited in the form of ash, and gaseous forms of sulfur are defined as gas emissions. Oxidation of inorganic sulfur compounds (pyrite, iron sulfates) produces SO_2 and SO_3 , and decomposition of organic sulfur compounds produces radicals $\bullet\text{SH}$, which, then, secondarily react with the organic part of coal to form various sulfur compounds, such as SO_2 , H_2S , CS_2 , and COS and elemental sulfur.³⁴

An increase of water share in the fuel slurry affects the concentration of sulfur oxides in the gas emissions. A part of the sulfur-containing component is replaced by water to result in reduced SO_2 concentration. During combustion of the water-coal droplets and additional hydrogen and carbon monoxide as reducing agents:



In the presence of water vapor, concurrent reactions form additional amounts of SO_x and other sulfur-containing compounds interacting with metal structure elements of the combustion equipment (furnaces, boilers) and metal compounds of sulfur:³⁵



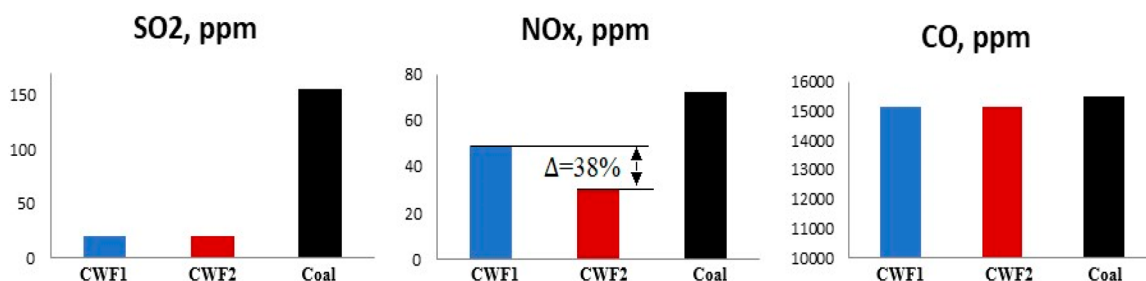


Figure 14. Average values of emissions of nitrogen, sulfur, and carbon oxides in the process of burning CWF and coal.

The results of investigating the content of carbon, nitrogen, and sulfur oxides in the combustion of CWF samples and coal are presented in Figure 14. Emissions of sulfur SO₂ in CWF samples decrease compared to emissions during coal combustion 7.75 times, NO_x emissions for CWF 1–1.4 times, and for the CWF2 sample –2.37 times. The CO emissions practically did not change, at this. We should note that the use of cavitation pretreated water as the dispersion medium additionally decreases emissions of nitrogen oxide by 38%.

Nitrogen oxides in high-temperature combustion of the fuel most frequently form as a result of oxidation of molecular nitrogen by air immediately in the combustion zone. Emission of nitrogen oxides is observed to be maximum in the active combustion zone. The temperature in the furnace during analysis of the emissions is 800 °C, and at this temperature the difference in temperature trends of CWF1 and CWF2 droplets is observed to be the maximum (Figure 13). Water as a component of the coal-water fuel decreases the temperature and rate of combustion as compared to the pulverized coal combustion, and this decreases the formation of NO_x, which is the main reason for the decrease of underburning. The presence of a suspension in the form of overheated vapor in the combustion zone promotes finer grinding of the carbon base due to microexplosions of the slurry droplets. Radicals, active molecules of H₂O, and products of decomposition of H₂O₂ contained in the activated water seem to be additionally able to initiate reaction 3 at the stage of water evaporation during burning of CWF2.

4. CONCLUSION

Studies in the field of development and the use of liquid coal-water fuel consisting of water and coal are topical for the territories with a well-developed coal-mining industry. Reagentless cavitation technologies to prepare CWF make it possible to attain rheological, environmental, and thermal-physical properties of the fuel with environmentally less hazardous properties during combustion due to reduced hazardous emissions as compared to combustion of pure coal. We have produced experimental results on the dependence of parameters of hydrodynamic impact on basic operating characteristics of coal slurries.

1. The cavitation treatment has been shown to increase the dispersivity of the solid coal fraction in CWF, changing the prevalent size category from 180–0.100 μm to 50–0.0 μm. Preliminary cavitation treatment of water does not affect additional grinding of coal particles.
2. Dynamic viscosity of CWF2, prepared on cavitation-activated water, is less than that of CWF1, made on

distilled water, and the yield point τ_0 of CWF2 is 2.5 times less than that of CWF1.

3. Coagulation capability of the dispersed phase CWF2 sample to the preactivated dispersion medium is lower (the sediment volume is smaller), and an increasing amount of bound water around primary adsorption (hydrophilic) centers on the surface of the coal particle in CWF2 facilitates an increase of coagulation structures.
4. Cavitation treatment of the entire suspension or separately of the dispersion medium of the coal-water fuel makes it possible to decrease nitrogen oxide by 38% in combustion.
5. Cavitation treatment changes the electron structure of the dispersion phase of CWF, and the surface of coal is additionally oxidized to help increase the stability of CWF.

So, hydrodynamic treatment is an efficient method of controlling operating properties of CWF.

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Notes

The authors declare no competing financial interest.

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