Individual and synergistic effects of modifications of the carrier medium of carbon-containing slurries on the viscosity and sedimentation stability

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ABSTRACT

The study is devoted to revealing the individual and synergistic effects of modifications of the carrier medium of the coal-water slurries (CWS) based on coking coal and carbon-containing flotation wastes of this coal on the effective viscosity and sedimentation stability. Synthetic and natural wetting agents as well as liquid solvents (alcohol, oil, conventional liquid fuel, methyl ethers) and solid organic compounds exemplified by sawdust are used for this. The relationships between the effective viscosity, water separation ratio, and zeta potential for the CWS with the separate addition of a wetting agent and a solvent is established. The categories of fuel compositions are identified according to the "stability" criterion. The synergistic effect of the additions of a wetting agent and a solvent on the sedimentation stability and effective viscosity is demonstrated. The physicochemical model of interaction between the solid particles and the additives in CWSs is proposed.

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1.   Introduction

Fuel technology of coal-water slurries (CWS) represents a class of two-phase "solid-liquid" compositions. These include compositions based on industrial crushed coal of various grades (Zhao et al., 2019), compositions with a solid phase in the form of coal preparation waste (Meng et al., 2020) as well as their various combinations, including the use of additional substances such as sewage sludge (Fu et al., 2019), spent synthetic oils (Wang et al., 2012), biosupplements in the form of alcohols (Wang et al., 2019) and oils (Jianzhong et al., 2014), biomass and biomass pyrolysis products (Feng et al., 2020). As a rule, the main research challenge in this area is associated with ensuring the viscosity and stability of the fuel compositions acceptable from the technological point of view. These characteristics are interrelated because solids tend to a more rapid sedimentation in a medium with a lower viscosity (Fan et al., 2019). Thus, this challenge consists in finding a certain compromise balance between the viscosity and stability that depend on a number of influencing parameters of the system. Among them are time (Liu et al., 2017), size of solid particles, particle size distribution and fraction of their packing (Meng et al., 2020), properties of solid particles (Yuchi et al., 2005), including coal and the additional ones, concentration of the solid phase (Meher et al., 2019), as well as the concentration and properties of other solid and liquid components of the slurry (Xu et al., 2008). With that, the CWSs are non-Newtonian fluids exhibiting both dilatant and pseudoplastic

Nomenclature

A^d	ash content of the fuel on a dry basis (%).
C^{daf}	carbon content calculated on a dry ash-free (daf) mass, (%).
D_{50}	median particle size (μm).
H^{daf}	hydrogen content calculated on a dry ash-free (daf) mass, (%).
N^{daf}	nitrogen content calculated on a dry ash-free (daf) mass, (%).
O^{daf}	oxygen content calculated on a dry ash-free (daf) mass, (%).
$Q_{s,V}^a$	specific heat of combustion (MJ/kg).
S_t^d	sulfur content in dry matter, (%).
V^{daf}	amount of volatiles (%).
W^a	fuel moisture (%).
WSR	water separation ratio (%).

Greek symbols

η	effective viscosity (mPa·s).
η_{100}	effective viscosity at a shear rate of 100 s^{-1} (mPa·s).
γ	shear rate (s^{-1}).

behavior (Jianzhong et al., 2014) and the behavior of the Bingham fluids (Meher et al., 2019). The viscosity of such fluids changes with varying shear rate (γ). In practical application, in addition to providing the acceptable fluidity for the CWS, the effective viscosity limit (η) is set that is determined at γ = 100 s^{-1} – η_{100}= 1.0–1.2 Pa·s (Loureiro et al., 2018). For this reason, this task is relevant and motivates the research in this area. In many cases, the multicomponent compositions require the addition of chemicals (often surface-active or polymeric), namely, stabilizing, wetting, and dispersing agents or plasticizers that improve the particle separation and prevent the particle aggregation and sedimentation thereby affecting the stability and viscosity. The combination of the multicomponent slurry and influencing factors generates a variety of phenomena that determine the interphase interaction as well as the associated interaction between the particles. These phenomena include attraction and repulsion between the particles expressed through electrostatic and van der Waals forces as well as the zeta potential (Fan et al., 2019).

In the study, the effects of such parameters as time, size of solid particles, particle size distribution, and fraction of their packing as well as the properties of the carrier medium of slurries caused by the additives for various purposes on the effective viscosity and stability of the CWS were studied. Therefore, further we discuss in more details the study of the influence of these parameters. Particle size polydispersity, being an important parameter in determining the rheological behavior and the amount of suspended particles in a slurry, increases the packing density of the particles in the slurry (Kyrylyuk et al., 2010; Yu and Standish, 1991) while maintaining a relatively low viscosity and yield stress (Logos and Nguyen, 1996). Not only can the effect of increasing the packing density of particles be associated with a wide distribution of particle sizes, but also with the mixing of particles of the same substance with a different median volumetric distribution (D_{50}) (Chen et al., 2011; Ghanooni et al., 2013) or particles of a larger or smaller size of another

solid (Fan et al., 2019). The influence of the parameter under consideration is well studied, but its variation is still relevant in the studies of the effective viscosity and static stability of new compositions under development with solid and liquid additives.

As a rule, changes in the properties of the carrier medium of the slurries are caused by ensuring the control of viscosity and increasing the resistance to phase separation during the transportation and storage of the CWS fuel (Egorov et al., 2018; Feng et al., 2020; Kihm and Deignan, 1995; Wang et al., 2020). Due to the use of dispersion and stabilizing agents, more stable samples with acceptable viscosity (< 1.2 Pa·s) are obtained, and due to the use of alkalis and salts the influence of the specific components characteristic of wastewater is simulated (Wang et al., 2019). The properties of the CWS can be changed by adding various solvents (Egorov et al., 2018; Feng et al., 2020), alkaline and salting solutions (Wang et al., 2019), dispersants (Das et al., 2013; Kihm and Deignan, 1995; Usui et al., 1997; Yi et al., 2014), stabilizers (Usui et al., 1997; Wang et al., 2020) as well as combinations of these substances (Dinçer et al., 2003; Yoon et al., 2009). The latter case is the most challenging in the controlled study of the effects of each individual component, and is interesting from a practical perspective. Combined additives coupled with the variation in particle size and particle size distribution *motivate this study* and moreover present *the scientific novelty* in terms of simultaneously affecting the effective viscosity and static stability. The complex interaction of these factors is rather difficult to study; the issue is initially addressed in a recently published study (Kuznetsov et al., 2021) that argues for controlling and predicting the stability and rheological characteristics of different CWS compositions. At the moment, it is known that the addition of surfactants and polymers helps to stabilize the CWS. This was shown in many studies, e.g., Tudor et al. (1996) and Yoon et al. (2009). At the same time, the use of the surfactant mixtures for stabilization remains poorly understood (Das et al., 2013). Feng et al. (2020) and Zhang et al. (2013) showed that the effective viscosity of the slurry strongly depends on the properties of oils (bio-oils) used as solvents and, accordingly, can either increase or decrease. Wang et al. (2019) established the effect of the addition of solutions of alkalis and salts on the effective viscosity. Low concentrations of the solutions facilitated an increase in the zeta potential and a decrease in the polarity of the particles. In the same work, the negative influence of the increase in the concentration of solutions on the slurryability was noted.

The aim of the present study was to experimentally determine the effect of separate and mixed addition of a wetting agent in the form of emulsifiers of direct (neonols and indirect material OP-7) and reverse (soy lecithin) emulsions as well as a liquid solvent (*n*-butanol, rapeseed oil, fatty acids methyl esters of sunflower oil, diesel fuel) and solid porous organic filler (sawdust) into the carrier medium of the CWS based on coking coal and carbon-containing wastes from the flotation of this coal on the quantitative characteristics of viscosity (effective viscosity at a shear rate of 100 s^{-1}) and sedimentation stability (water separation ratio, fluidity class). Separately, it is planned to consider the dependence of the effective viscosity of the CWS on the time, at which the stability is assessed, as well as the effect of additional mineralization of the CWS carrier medium, the size and fraction of the packing of solid particles on the effective viscosity.

Table 1 – Elemental composition and main characteristics of CC and CCS.								
	Main characteristics				Elemental composition			
Substance	W^a, %	A^d, %	V^{daf}, %	$Q_{s,V}^a$, MJ/kg	C^{daf}, %	H^{daf}, %	N^{daf}, %	S_t^d, %	O^{daf}, %
CCS	–	26.46	23.08	24.83	87.20	5.091	2.05	1.022	4.637
CC	2.05	14.65	27.03	29.76	79.79	4.486	1.84	0.868	13.016

2. Experimental

2.1. Materials

To prepare the CWSs with and without additional components, the following raw materials were used. Distilled water (DW) with a specific electrical conductivity of not more than 5 µS/cm and raw tap water as well as water-salt solutions of ammonium acetate with molar salt concentrations of 0.1 M and 1 M were used as the main liquid phase (carrier medium) of the slurries. Moreover, a group of wetting agents was used as additives to distilled water, namely, surfactants, emulsifiers of direct emulsions, including Neonols AF 9–10 and 9–12 (isononylphenols with 10 and 12 moles of ethylene oxide, respectively; CAS #127 087–87–0, manufacturer PJSC "Nizhnekamskneftekhim"), indirect material OP-7 (a mixture of mono- and dialkylphenols with ethylene oxide, GOST 8433–81) and soy lecithin (phospholipid is a natural amphoteric surfactant, E 322, Unitechem Co., Ltd., China) as well as liquid solvents, including n-butanol (chemically pure, CAS RN 71–36–3, GOST 6006–78), fatty acids methyl esters of sunflower oil (FAME, GOST 31 665–2012), rapeseed oil (GOST 31 759–2012) and commercial diesel fuel, and solid porous organic filler (pine sawdust, fine fraction). The use of various raw materials as additives to the liquid phase is due to the aim of the study. Similar approach was used in a number of studies of the suspending ability, rheology, stability and fluidity of the CWSs with additives (He et al., 2015; Jianzhong et al., 2014; Loureiro et al., 2018; Meher et al., 2019; Wang et al., 2012; Xu et al., 2014; Zhao et al., 2019). Solid particles of the slurries are the coking coal (CC, "Berezovskaya" mine, Kemerovo region, Russia) and the coking coal slime (dry, "Severnaya" concentrating plant, Kemerovo region, Russia). The substance coking coal slime (CCS) is a carbon-containing waste of coking coal flotation after extraction of the coal concentrate. Table 1 presents the results of technical analysis (W^a is the fuel moisture content, A^d is the ash content of the fuel on a dry basis, V^{daf} is the amount of volatiles, $Q_{s,V}^a$ is the specific heat of combustion) as well as the elemental composition declared by the manufacturer for the solids used. The values of W^a, A^d and V^{daf} were determined according to the international standards ("ISO, 1171:2010 - Solid mineral fuels — Determination of ash," n.d., "ISO 11722:1999 - Solid mineral fuels — Hard coal — Determination of moisture in the general analysis test sample by drying in nitrogen," n.d., "ISO 562:2010 - Hard coal and coke — Determination of volatile matter," n.d.). The heat of combustion at constant volume $Q_{s,V}^a$ for the CCS and CC was measured using the IKA C 2000 calorimeter according to the standardized procedures (ASTM, D240–19 - Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter, 2000, "ISO, 1928:2009 - Solid mineral fuels — Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value," n.d.).

2.2. Slurry preparation

Prior to mixing of the slurry components, the solid raw material was dried in a drying chamber at a temperature of 105 °C for 2.5 h. The dried material was ground in a high-speed rotor mill Pulverisette 14 (final grinding degree (depending on the inserted sieve) was 0.08–6 mm; rotor speed was 6000–20,000 rpm) for 1.5 min. Solid particles of controlled size (control methods are described in subsection 2.3.) were mixed with the carrier medium of the slurries using the AIBOTE ZNCLBS-2500 magnetic stirrer (stirring temperature was 25 ± 2 °C, rotation speed of the magnetic bar was 1500 rpm, stirring time was 30 min). The solid powder was gradually added to the volume of the dispersed system being stirred at a reduced speed to prevent the formation of clumps and, accordingly, to obtain a more uniform structure. Table S1 (see Supplementary materials) shows the component composition of the base CWSs (mono- and polydisperse powders of solid particles are used, and additional mineralization of the slurry carrier medium is introduced due to the use of raw tap water and aqueous solutions of ammonium acetate salts). The mass concentrations (wt%) of the components were used, and the weighing of solid particles was carried out using the analytical balance Vibra HT 84RCE (resolution of 10^{-4} g). Since the main task of the study is to establish the methods to control the rheological characteristics and static stability, the concentration of the solid matter as a variable parameter is taken as a constant value, 50 wt%. This concentration is typical in the studies with the CWSs of different composition. The wetting agents, solvents, and a solid organic additive were mixed with distilled water prior to adding the solid particles of higher fineness in the following concentrations: for the CWS based on CCS – 1 wt% of neonols and OP-7, 0.1 wt%, 0.5 wt%, and 1 wt% of soy lecithin, no more than 1–2 wt% of liquid solvents and sawdust; for the CWS based on CC – similar surfactant concentrations, 1–3 wt% of rapeseed oil, 1–3 wt% of FAME, 1 wt% and 2.5 wt% of diesel fuel, 1 wt% and 5 wt% of n-butanol, 1–2 wt% of sawdust. Tables S2–S4 in Supplementary materials provide a detailed component composition of all the samples prepared with the addition of the above-mentioned substances.

2.3. Particle size

The study indicated two finenesses of grinding, namely, the lower and higher ones. Fig. S1 (see Supplementary materials) shows histograms of particle size distributions with lower and higher fineness for the CCS (Fig. S1a) and CC (Fig. S1b). Different fineness of grinding was obtained by sieving the ground solids through the metal sieves with a known mesh size. To establish the particle size distributions characteristic of each fineness, the shadow method of macroimaging was used. To implement it, a system was used that included a pneumatic gun connected to an air compressor, a high-speed

video camera and a spotlight for the background illumination. The software implementation aiming to determine the mean particle size in the registration area was carried out using the "Actual Flow" software. To plot the histograms (Fig. S1), one series of experiments, including five measurements, was carried out at each fineness of grinding for the CCS and CC. The error in determining the sizes was no more than 4 µm. When analyzing the sizes of the solid particles, the median particle size (D_{50}) was generally used (Boylu et al., 2004; Shivaram et al., 2013) that determined the equivalent diameter of the sphere describing the particle, where less than 50% of the particles by volume (weight) in the sample had lower diameter. This characteristic was calculated according to the international standard ISO 9276–2:2014 "Representation of results of particle size analysis | Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions" according to formula (1).

$$D_{50} = \left[\frac{\sum_{i=1}^{\infty} n_i D_i^5}{\sum_{i=1}^{\infty} n_i} \right]^{\frac{1}{5}}, \tag{1}$$

where D_i is the diameter of the ith particle and n_i is the number of ith particles.

Fig. S1 shows that higher fineness of grinding is characterized by a greater number of larger particles for both CCS and CC. Based on this, two characteristic finenesses of particle grinding are identified in the work. In this case, for particles of CCS, a lower grinding fineness corresponds to $D_{50} \approx 41$ µm, a higher one – to $D_{50} \approx 54$ µm; for CC particles, a lower fineness corresponds to $D_{50} \approx 40$ µm, and a larger one – to $D_{50} \approx 48$ µm. Separately, the values D_{50} is determined for the case when higher and lower fineness is used in preparing a slurry (Table S1 in Supplementary materials). For CC particles with a predominance of a higher fineness, D_{50} is equal to 46 µm; in the case of lower fineness predominance, D_{50} is 42 µm. For CCS particles with a predominance of a higher fineness, D_{50} is 50 µm; in the case of lower fineness predominance, D_{50} is 45 µm.

In addition, to give a brighter representation of particle polydispersity in slurries, particle sizes D_{10} (arithmetic mean) and D_{90} were determined using Eq. (1). Particles of CCS had $D_{10} = 32$ and $D_{90} = 102$ at a lower grinding fineness; $D_{10} = 38$ and $D_{90} = 110$ at a higher one; $D_{10} = 34$ and $D_{90} = 104$ with lower fineness predominance (when higher and lower fineness is used together); $D_{10} = 36$ and $D_{90} = 107$ when a higher fineness predominates. In the case of CC particles, $D_{10} = 32$ and $D_{90} = 102$ at a lower fineness; $D_{10} = 37$ and $D_{90} = 109$ at a higher one; $D_{10} = 35$ and $D_{90} = 106$ with lower fineness predominance; $D_{10} = 36$ and $D_{90} = 107$ when a higher fineness predominates.

2.4. Rheological properties

Rheological characteristics are presented in the form of relationships "effective viscosity-shear rate" and "shear stress-shear rate". The rheological measurements were carried out with freshly made samples by the Brookfield DV3T rotational viscometer (measurement range of $1...6 \cdot 10^6$ mPa·s, accuracy of ± 1%, reproducibility of ± 0.2%), LV-2 spindle (viscosity measurement range was 50–100 000 mPa·s), and the thermostat Termex KRIO-VT-12–01 (working fluid was antifreeze, operating temperature range was −30. + 200 °C, temperature maintenance accuracy was ± 0.1 °C). The thermostat is utilized to maintain the temperature of the sample at 25 °C by

organizing of the external thermostatting circuit of a test tube with the slurry. The shear rate was varied in the range of ~10–120 s^{-1}. Lower shear rates could be achieved, but in this case the torque values fell below the values specified by the manufacturer of the viscometer. The measurements at these shear rates were not considered. For the system used, the shear rate was the calculated value:

$$\gamma = \frac{2 \cdot U_{sp} \cdot R_{sp}^2 \cdot R_c^2}{x \cdot (R_c^2 - R_{sp}^2)} \tag{2}$$

where U_{sp} is the spindle speed, R_{sp} is the spindle radius, R_c is the reservoir radius, x is the distance between the spindle and reservoir walls.

A universal method that made it possible to carry out the reliable η measurements and also facilitated the description of the rheological behavior of the basic CWSs under consideration, is the method of a short measurement duration (100 s for the entire γ range, i.e., 1 s per measurement at one γ), see the details for selecting this method in Supplementary materials. Basic CWSs exhibit very weak properties of pseudoplastic non-Newtonian fluids, since the $\tau(\gamma)$ dependences are well described by the Herschel–Bulkley model (Liu et al., 2012; Wang et al., 2012) (Eq. 3) with an approximation reliability $R^2 = 0.93$–0.99. As an example, the basic compositions #2 and #3 are given on CCS and CC, respectively. The values of rheological characteristics in Fig. S3c were obtained using method (4) of a short 100-second measurement:

$$\tau = \tau_y + K\gamma^n, \tag{3}$$

where τ is the shear stress (Pa), τ_y is the yield stress (Pa), K is the consistency coefficient (Pa·s^n) and n is the flow index. The flow structure can be determined by the flow index as follows: $n = 1$ – the Newtonian fluid, $n > 1$ – dilatant fluid, $n < 1$ – pseudoplastic fluid (the case under consideration). The yield stress values for the considered basic CWS compositions are rather low, based on this, a conclusion was made about the exhibition of a very weak pseudoplastic non-Newtonian behavior.

2.5. Static stability and fluidity measurements

Sedimentation of solid particles in slurries is the reason for their phase separation. This is a common phenomenon for CWSs. The static stability of the slurries is assessed using the water separation ratio (WSR), which is defined as the mass ratio of water separated due to the phase separation to the total amount of water in the slurry sample (Eq. 4) during its static holding for 96 h at a temperature of 25 ± 2 °C. Higher WSR values mean more pronounced phase separation and represent less stable slurries. This approach is the simplest and most effective. It is used in many experimental studies of the stability of the coal-water compositions (Wang et al., 2012).

$$WSR = \frac{M_s}{M_0} \times 100\%, \tag{4}$$

where M_s is the mass of water released due to the phase separation of the slurry sample, g, M_0 is the total mass of water in the slurry sample, g.

The fluidity of the slurry compositions was measured visually using the research technique described in Ref. (Zhan et al., 2010). When pouring a slurry from one beaker into another, the slurry may form a continuous flow or a non-

continuous flow, or no flow at all. In this case, the fluidity is assessed according to the respective classes A, B, or C.

2.6. Contact angle and zeta-potential

To measure the contact angle, the powders of solid particles of higher fineness were compressed at a load of 10 tons in the form of tablets. On the smooth surface of the obtained tablets, the static contact angle was measured by the shadow imaging method under normal conditions. The resulting images of drops on the tablet surface were processed using the Drop Shape Analysis software (Kruss). Under identical conditions, at least three measurements were taken, then the results were averaged.

The measurement of the zeta potential of the CWS was carried out on the Zetasizer Nano ZS device at a temperature of 25 °C. The Zetasizer Nano ZS featured a 4 W He-Ne laser with a wavelength of 633 nm. The DTS1070 disposable bent capillary cells were used to measure the zeta potential. The slurry was prepared first. Then 10 ml of distilled water was added to the resulting slurry with a volume of 0.2 ml, stirring occurred, and then the resulting liquid was placed in a measuring cell for analysis. Under identical conditions, at least three measurements were also taken.

2.7. Measurement uncertainty

Under identical conditions, the effective viscosity for one CWS is measured at least three times. Several effective viscosity values are recorded in each measurement at one shear rate. Given all measurements for one CWS at one shear rate, at least 8–10 viscosity values are averaged. The water separation ratio is determined based on 3–5 measurements under the same conditions. For each experimental point, the confidence interval is calculated in the work and is shown in the graphs. The expanded uncertainties in the results of measurements of the effective viscosity and the water separation ratio do not exceed ± 24 mPa·s (significant errors are typical for the increased values of the effective viscosity) and ± 2.3%, respectively. These uncertainties are based on the standard one multiplied by the coverage factor $k = 2$ providing a confidence level of ~95%.

3. Results

3.1. Measurements of effective viscosity with time

It is technologically important to establish the differences in effective viscosity for CWSs during the time periods characteristic of the life cycle of typical fuel compositions in the power industry (about 72–120 h) (Wang et al., 2012), in a wide range of shear rate variation corresponding to storage, transportation, and direct supply (in the form of jets, large sprays) (Jianzhong et al., 2014). Fig. 1 shows how the η values increase over time in the entire range of γ values under consideration taking into account the characteristic phase separation of the slurries. Thus, the separated water layer in the upper part of the test tube was removed prior to the experiment for adequate measurement of the CWS viscosity. Each day was associated with a unique sample identical in composition. At the same time, the total volume of the slurry was initially prepared, then poured into four test tubes in accordance with the four days of measurements. It became
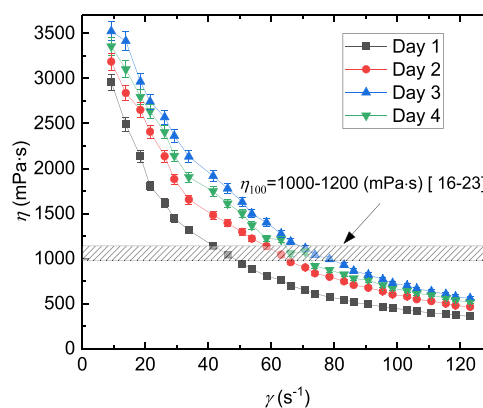

Fig. 1 – η as a function of γ with measurements during four days given the removal of the released water due to phase separation of composition #2: "50 wt% of CCS (higher fineness), 50 wt% of distilled water".

possible to trace the evolution of the "water–CWS" phase boundary.

Important conclusions based on the results obtained are as follows: (1) a pronounced increase in the η values is observed only on the first day due to the intense destruction of the internal structure of the CWS due to the sedimentation of the largest particles; (2) on the subsequent days, the evolution of the phase boundary is less pronounced; this is reflected in the η values, i.e. the mass of the separated water becomes comparatively lower day by day, and the growth of the η values is greatly slowed down; (3) at high γ values (80–120 s^{-1}) the differences in the η values are barely noticeable and do not exceed 10–15%. Similar conclusions on the increase in the effective viscosity with time and accounting for the phase separation are given in Refs. (Jianzhong et al., 2014; Wang et al., 2012).

Another practically oriented result is the acceptable values of the effective viscosity based on the results of four days of measurements at the shear rates close to 100 s^{-1}, i.e. the η values do not exceed 1000–1200 mPa·s (Fig. 1) representing the maximum set limit for effective viscosity at $\gamma = 100$ s^{-1} (Chang et al., 2015; Chen et al., 2014; Das et al., 2013; Guo et al., 2007; Li et al., 2012; Yang et al., 2007; Zhou et al., 2012; Zhu et al., 2012).

3.2. Effect of size and packing fraction of solid particles

The size distribution of the solid particles of the slurry expressed, as a rule, through the median of the volumetric distribution D_{50} determines the changes in the values of the effective viscosity (Boylu et al., 2004; Pulido et al., 1995; Shivaram et al., 2013; Yavuz and Küçükbayrak, 1998). The quick of the matter lies in several fundamental conclusions. One of them concerns the influence of the monodispersity and polydispersity of the solid particles in slurries (Yavuz and küçükbayrak, 1998). Monodisperse slurries of particles of one definite size (as a rule, small), providing acceptable characteristics in terms of stability, possess a compact structure with minimal voids between the particles. This contributes to the hindered penetration of the carrier medium into these voids and pores of the particles as well as its less free movement between the particles. The excessive internal friction is created resulting in a viscosity increase. Other conclusions (Boylu et al., 2004; Pulido et al., 1995; Shivaram et al., 2013) are related to the influence of the
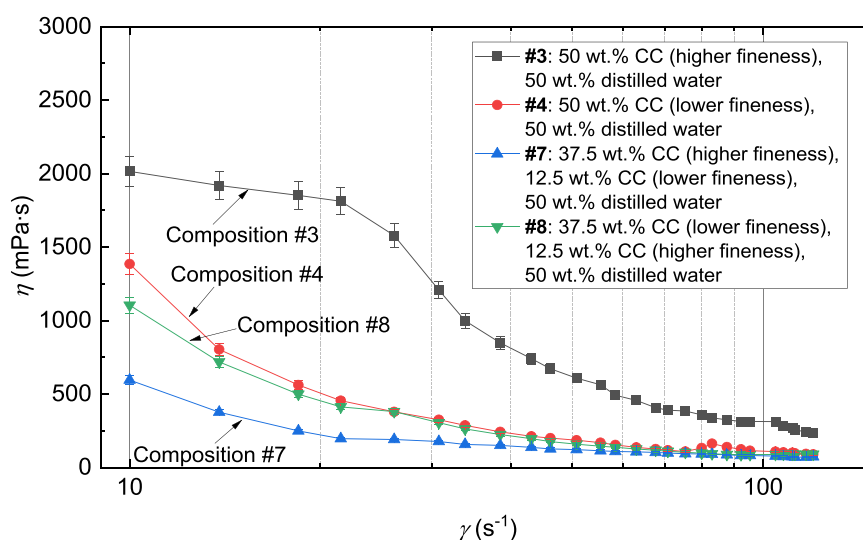
Fig. 2 – η as a function of shear rate γ for the CWS based on CC in the measurements with the increasing of γ from 10 to 120 s^{-1}.

particle size distributions, which differ in width and, accordingly, in packing fraction. The physical meaning in this case is close to the conclusions on monodispersity and polydispersity, and supplements them with the need to search for some optimal threshold values for the width of the size distributions and the average diameter of the particles. An increase in the width of the size distributions allows reducing the viscosity due to the filling of voids with small particles in the proximity of large particles, but in this case the average particle diameter should provide the required stability (Farr and Groot, 2009; Ghanooni et al., 2013). Thus, the thresholds must be accommodating, i.e. the particle size distribution should be sufficiently wide with an average diameter providing the acceptable slurry stability.

In the present study, the described approach with fuel compositions based on polydisperse coal powder is used. In particular, the coal solids with similar widths of size distributions (Fig. S1b) but with different medians of volumetric distribution D_{50}, were used individually and in the mixture. Fig. 2 demonstrates a decrease in the effective viscosity due to the selection of a certain optimal average particle diameter D_{50} in the mixture and the optimal packing fraction. When using sample #7 (Table S1 in Supplementary materials) with 75 wt% of particles of higher fineness (D_{50} =48 µm) and 25 wt % of particles of lower fineness (D_{50} =40 µm), it was possible to achieve a significant decrease in the effective viscosity in comparison with monodisperse samples #3 and #4. The effect was especially noticeable at low γ values (the η values differed by several times). Mixed composition #8 also showed a tendency to decrease in the effective viscosity compared to non-mixed compositions #3 and #4. Similarly to Refs. (Boylu et al., 2004; Pulido et al., 1995; Shivaram et al., 2013), the observed decrease in viscosity was associated with the ensuring more favorable conditions for packing and the average diameter of solid particles.

3.3. Effect of properties of slurry carrier medium: single solvents, solutions, surfactants

The concentration of the carrier medium of the basic CWS is half of the total mass of the samples. Thus, the properties of the carrier fluid largely determine the rheology and stability of the CWS. There are a number of approaches to modifying

the properties of the CWS carrier medium, among which the most common is the use of various single solvents (Egorov et al., 2018; Feng et al., 2020), solutions (Das et al., 2013; Kihm and Deignan, 1995; Usui et al., 1997; Wang et al., 2020; Yi et al., 2014), including the use of dispersion agents (surfactants) (Das et al., 2013; Kihm and Deignan, 1995; Usui et al., 1997; Yi et al., 2014) and stabilizers (Usui et al., 1997; Wang et al., 2020), salts and alkalis (Wang et al., 2019) as well as combinations of these additives (Dinçer et al., 2003; Yoon et al., 2009). Basically, these modifications have a practical focus. In particular, the use of the certain dispersion and stabilizing agents makes it possible to obtain more stable samples with the acceptable viscosity (< 1.2 Pa·s), and the use of alkalis and salts, as a rule, helps to isolate the effect of the specific components characteristic of wastewater (Wang et al., 2019).

Fig. 3 shows the $\eta(\gamma)$ dependences for compositions with different CWS carrier medium. The aqueous salt solutions of ammonium acetate (Table S1 in Supplementary materials) with various molar concentrations of the substance are used as potential components of wastewater from the chemical, perfumery, and food industries. An unambiguous conclusion from Fig. 3 lies in the fact that the presence of a small amount of dissolved salts facilitates a noticeable decrease in the effective viscosity of the CWS (# 10, # 12, and #13) or maintaining almost similar values (# 9) compared to the CWS sample based on distilled water at low γ values both for the slurries based on CCS and CC. At high γ values, similar differences are less pronounced. The results obtained are consistent with the conclusions made in Refs. (Jianzhong et al., 2014; Zhao et al., 2019). A carrier medium with a large amount of active components (salts and alkalis) improves the surface activity and the ability to suspending the coal particles and decreases the effective viscosity.

Besides, the properties of the carrier medium of the CWS are changed due to the use of the surfactants of synthetic and natural origin, namely, emulsifiers of direct (neonols and indirect material OP-7) and reverse (soy lecithin) emulsions (Table S2 in Supplementary materials). However, their use is primarily due to the need to change the wetting ability of the carrier medium in relation to the hydrophobic particles of CC and the particles of CCS with the surface characteristics formed during flotation (Chen et al., 2020). The wetting ability
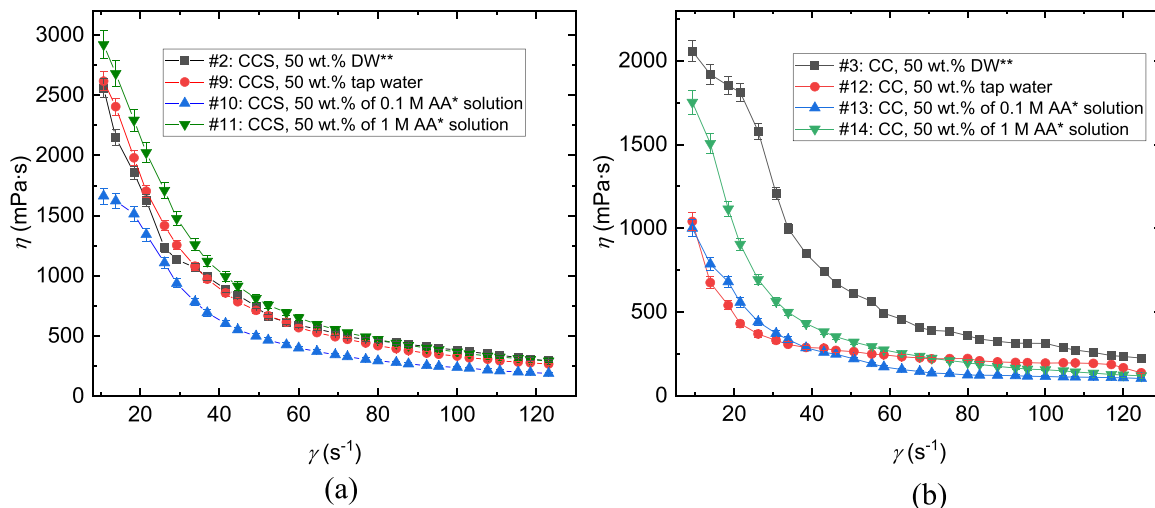
Fig. 3 – η as a function of γ during the modification of properties of the slurry carrier medium: basic CWS based on 50 wt% CCS (higher fineness) (a) and 50 wt% CC (higher fineness) (b). *AA is ammonium acetate salt. **DW is distilled water.
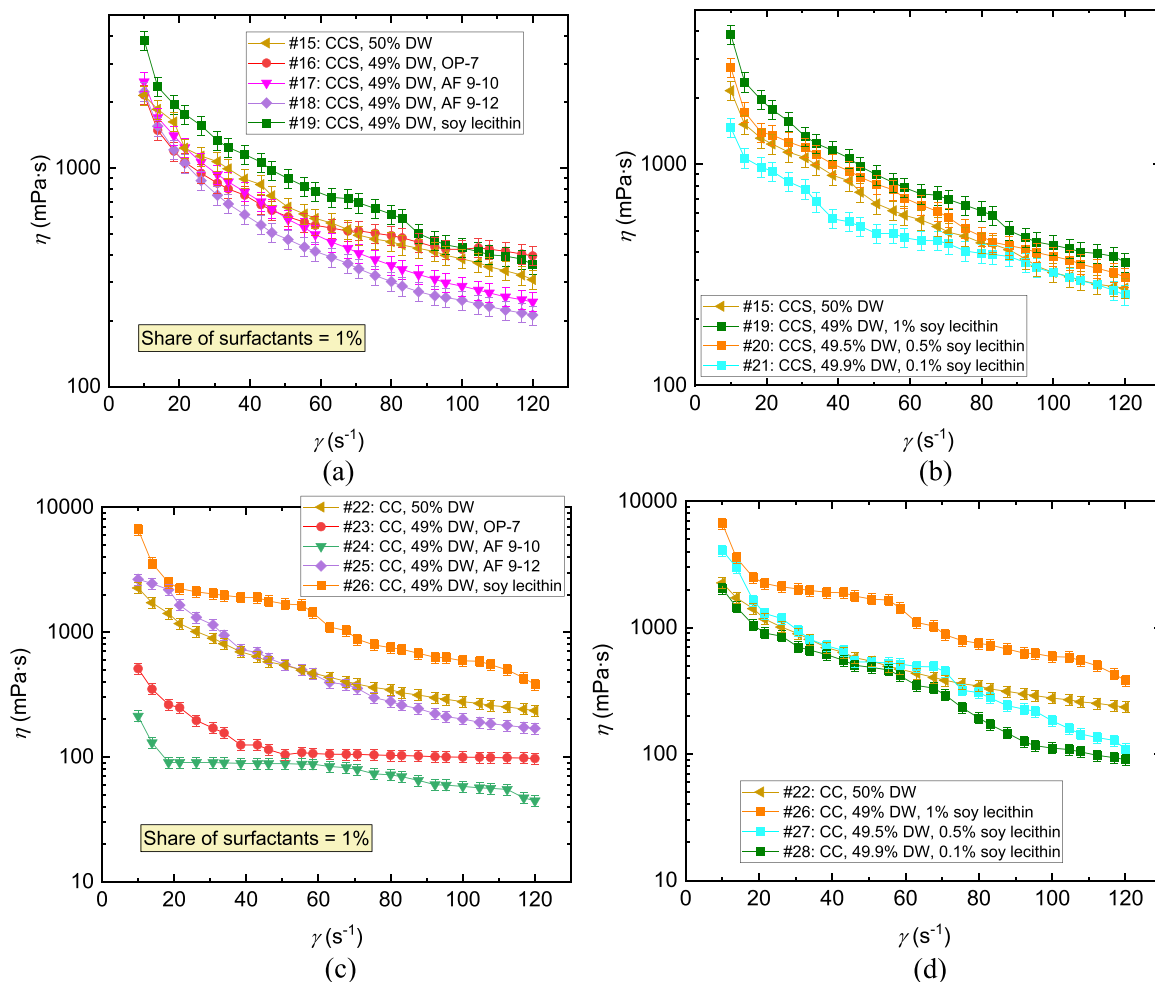

Fig. 4 – Effect of different surfactants on η of CWS based on 50 wt% CCS (a, b) and 50 wt% CC (c, d).

of the slurry particles determines the static contact angle (Wu et al., 2015), which, in turn, is the most important factor affecting the ability to form the slurries from the coal particles and coal preparation wastes (Zhan et al., 2010). The latter is undoubtedly related to the viscosity of the slurries. Fig. 4a and Fig. 4c show that the use of neonols with high hydrophilic-lipophilic balance numbers (13–14) tends to the reduction of the effective viscosity. This effect is obviously associated with a more active process of aggregation of the

particles under the influence of gravity, hydrophobic interaction, and the van der Waals attraction forces. In this case, there are no effects of electrostatic repulsion and steric hindrance caused by the adsorption of these surfactants (Zhan et al., 2010). A noticeable increase in the CWS viscosity on the CC and CCS in comparison with the basic slurry on water occurs when soy lecithin is used as a wetting and dispersing agent (Figs. 4a, 4c). The addition of soy lecithin involves the formation of micelles, which contribute to
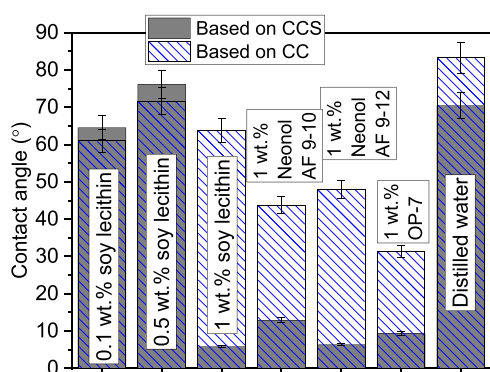
Fig. 5 – Static contact angles for the compositions based on CC and CCS prepared using different surfactants.

strengthen the internal slurry structure, thus increasing naturally the viscosity of the system as a whole. Similar conclusions on the increase of viscosity when adding lecithin are known and are, for example, made by Bentley et al. (1999) in the study of properties of poloxamer gels.

The use of soy lecithin in CWS based on CC or CCS and water is a flexible tool to influence the effective viscosity in the considered γ range, since a well-predicted effect of increasing the viscosity with an increase in lecithin concentration from 0.1 wt% to up to 1 wt% (Figs. 4b and 4d) was established. It is also noteworthy that the addition of surfactants to the coal-based compositions (Table S2 in Supplementary materials) contributes to more significant differences in viscosity values.

Fig. 5 shows that the addition of the surfactants considered in the work has a fairly predictable effect on the wetting ability of the modified CWS carrier medium. In almost all cases, the values of the static contact angle are markedly reduced relative to water and facilitate wetting. However, when a lecithin additive with a concentration below 1 wt% is used, the decrease in the contact angle values can be characterized as rather moderate. The results of these measurements are in good agreement with the results represented in Fig. 4. Practically in the entire range of the shear rates, the values of effective viscosity for the CWS prepared with the addition of lecithin differ little from those for the CWS prepared on water. For the rest of the CWSs, it is natural (Zhan et al., 2010) and justified that the viscosity significantly decreases relative to the basic composition under conditions of reduced values of the contact angle, which characterize better wetting (Fig. 5). For the CCS particles, the hydrophilic nature in the presence of synthetic surfactants is more obvious due to the presence on the particle surface of the adsorbed layer of molecules of another surfactant used in flotation, which seems to enhance the established effect. Increasing the lecithin concentration to up to 1 wt% measured on the CCS tablet results in a significant decrease in the contact angle.

The wettability of the coal particle surface with the surfactant solutions demonstrates the dependence on the type of surfactant and its hydrophilic-lipophilic properties (HLB). Among oxyethylated nonylphenols (OP-7, Neonol AF 9–10 and Neonol AF 9–12), the surfactant with seven oxyethyl groups (OP-7) provides the best wettability characterized by the smallest contact angle. As the number of moles of ethylene oxide in the surfactant molecules increases, and consequently as their hydrophilic properties enhance, the contact angle increases. These results are fully consistent

with the known concepts of the adsorption of the surfactants on non-polar surfaces, according to which less polar surfactants (with a lower HLB value) have the highest adsorption.

Another method to change the properties of the CWS carrier medium and, accordingly, the rheological and sedimentation characteristics of CWS is the use of various solvents (in the study, these include, among others, alcohols, ethers, liquid hydrocarbons, oils) (Dmitrienko et al., 2017; Glushkov et al., 2016; Yi et al., 2019) and solid organic additives (e.g., sawdust) (Nyashina and Strizhak, 2018) in the preparation. Fig. 6 shows the rheological flow curves for the CWS based on CC and CCS prepared with the addition of 1–5 wt% solvent or 1–2 wt% sawdust (Table S3 in Supplementary materials) as a dependence of the effective viscosity on the shear rate. The concentration range of the additive is determined by the maximum established limit in terms of the effective viscosity at $\gamma = 100\,\mathrm{s}^{-1}$ (Chang et al., 2015; Chen et al., 2014; Das et al., 2013; Guo et al., 2007; Li et al., 2012; Yang et al., 2007; Zhou et al., 2012; Zhu et al., 2012), i.e. 1000–1200 mPa·s.

Since more viscous slurries prepared with the addition of solvents tend to form an internal structure that ultimately helps the liquid to stay stable longer, the ensuring of the η_{100} values close to the maximum limit was the main limiting factor in the implementation of this approach. Fig. 6a demonstrates that relative to the basic CWS based on CC and water, the viscosity of the CWS with the addition of n-butanol (1–5 wt%), diesel fuel (1 wt%), and sawdust (1–2 wt%) noticeably decreases. The effect of the obvious viscosity change due to the increase in the concentrations of n-butanol and sawdust is not achieved, therefore, a further increase in their concentrations is not considered. For the CWS with the addition of diesel fuel, an increase in its concentration in the CC composition to up to 2.5 wt% significantly increases the effective viscosity in the entire range of shear rates slightly exceeding the maximum limit with respect to η_{100}. The addition of the rapeseed oil and fatty acid methyl ester (FAME) of sunflower oil increases the viscosity relative to the basic CWS on water in direct proportion to the increase in their concentration in the slurry. Such a behavior can be explained by the uniform adsorption of the water-insoluble additives on the surface of solid particles, during which the mutual concentration-proportioned isolation of the particles from each other occurs and is caused by steric hindrance. For the CWS based on CCS (Fig. 6b), when all liquid additives are used, the effect of an increase in the effective viscosity is observed in direct proportion to the increase in their concentration. The concentrations of liquid solvents are selected so as not to exceed the maximum η_{100} limit. The use of 1 wt% sawdust as additional solid particles naturally increases the viscosity of the slurry. At a shear rate of $100\,\mathrm{s}^{-1}$, the viscosity of the CWS with the addition of sawdust increases 2.5 times as compared to the basic CWS. Due to the small mass of 1 wt % sawdust it is characterized by a large amount of solid particles, which contribute to a significant filling of the space between the coal particles of the composition and thereby the formation of an even more stable and viscous internal structure. In addition, sawdust, being a highly porous material, strongly absorbs water and swells. These processes only strengthen the internal structure of the slurry. However, the described effect is not achieved in the case of the coal-based CWS. In general, it can be concluded that the addition of solvents to the slurry based on CCS makes it possible to predict a reliable increase in viscosity proportional to the
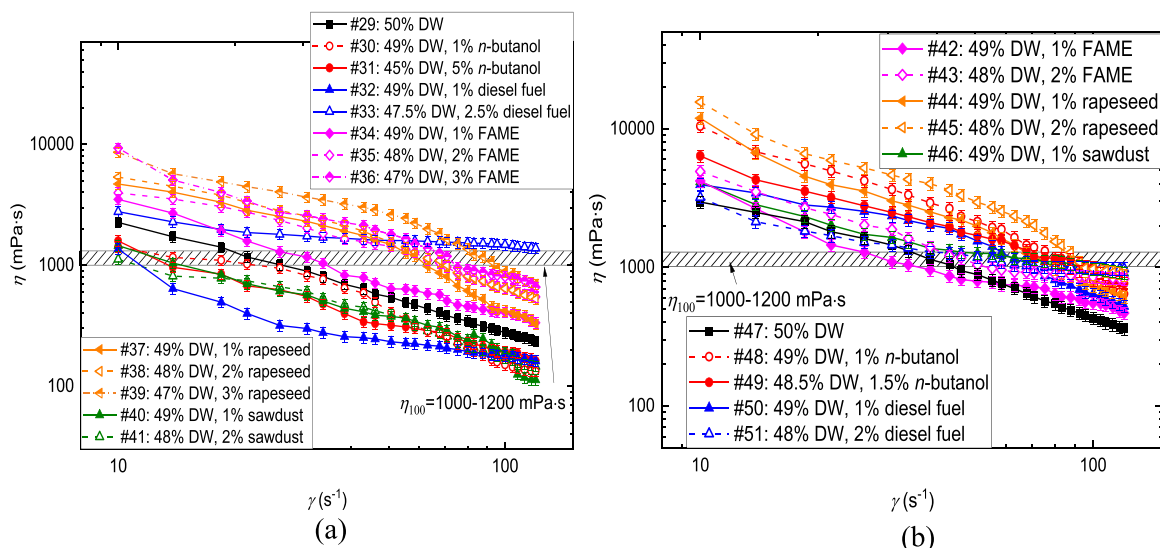
Fig. 6 – Effective viscosity of CWS based on 50 wt% CC (a) and 50 wt% CCS (b) prepared with the addition of different solvents as a function of shear rate.

concentration increase. In this case, the presence of the adsorbed layer of molecules of another surfactant (flotation agent) on the surface of CCS particles affects the dispersion of the solid particles upon addition of the solvent to reduce the effects of their flocculation and aggregation.

3.4. Effect of properties of slurry carrier medium: combination of solvents and surfactants

The results presented in subsection 3.3 became the basis for the development of a hypothesis about the effect of the wetting surfactant additive on the dispersion characteristics of the solid particles upon addition of the solvent (Table S4 in Supplementary materials). Fig. 7a shows the rheological curves of the flow of slurries based on CC prepared with the addition of the wetting agent of synthetic and natural surfactants and the dispersant in the form of various solvents. It was established that the effective viscosity of the CWS prepared with the addition of mixtures of surfactant and solvent significantly reduced relative to the basic CWS on water. Thus, the viscosity of the CWS is determined to a greater extent by the wetting additive. In this case, the result turned out to be closer to the data in Fig. 4c,d than to those in Fig. 6a. The presence of the surfactant deactivates the viscosity growth mechanism upon the addition of the solvents, which, as previously established, play the role of dispersing additives. It is obvious that the adsorbed layer of the surfactant molecules on the coal surface interacts weaker with the insoluble additives in the form of solvents than in the case of CCS. This facilitates coalescence and enlargement of the drops of insoluble liquid additives in the volume of water filled with solid particles. In general, their function on isolating the solids from each other and the effect on the effective viscosity are minimized.

Fig. 7b shows the obtained rheological curves of the flow of slurries based on the CCS also prepared with the addition of mixtures of surfactant and solvent. In general, the result obtained is close to that shown in Fig. 6b, where the solvents are added to the CWS. Relative to the basic CWS on water, the viscosity of the CWS prepared with the addition of the mixtures is still higher. However, when carefully compared with the results in Fig. 6b it can be seen that a slight decrease

in effective viscosity is present, at least in the η_{100} values (Fig. 7b). In the case of CWS prepared with the addition of mixtures of surfactant and solvent, the presence of the solvent plays a decisive role similar to the conclusions in Fig. 6b. In this case, the function of the wetting due to the addition of a surfactant appears only slightly. The initially adsorbed layer of the flocculant molecules on the surface of the CCS weakly interacts with other wetting surfactant additives considered in this study.

3.5. Stability and fluidity of slurries

Phase separation over a short period of time complicates the industrial application of the CWSs. Thus, the quality of the liquid slurry fuel strongly depends on the stability, i.e. the ensuring of proper sedimentation stability and fluidity guarantees economic transportation and combustion efficiency of such fuels (Wang et al., 2012).

Table 2 represents the water separation ratios (WSRs) and fluidity classes for all the basic CWSs based on CCS and CC (see their component composition in Table S1 in Supplementary materials).

The presence of the dissolved salts and alkalis in the carrier medium of the CWS based on CCS (compositions #9–11) generally reduces the static stability facilitating the phase separation. This means that within the framework of the electrostatic interaction of particles, the attraction between them exceeds the repulsion. Presumably, the thickness of the electric double layer near the surface of the solid particles in the presence of molecules of dissolved salts and alkalis decreases, and this facilitates the weakening of stabilization, flocculation, and aggregation of the solid particles. The changing in fineness and the use of combinations of particle sizes in the slurry moderately affect the WSR values.

Fig. 8a shows a histogram defining the relationship between WSR that quantitatively characterizes the stability of the slurry, the zeta potential, and the effective viscosity at a shear rate of $100\,s^{-1}$ for CWS based on CCS and CC prepared with the addition of the surfactants (Table S2 in Supplementary materials). Three categories of compositions are identified based on the "stability" criterion. For the first category (class), this criterion involves the lowest WSR and
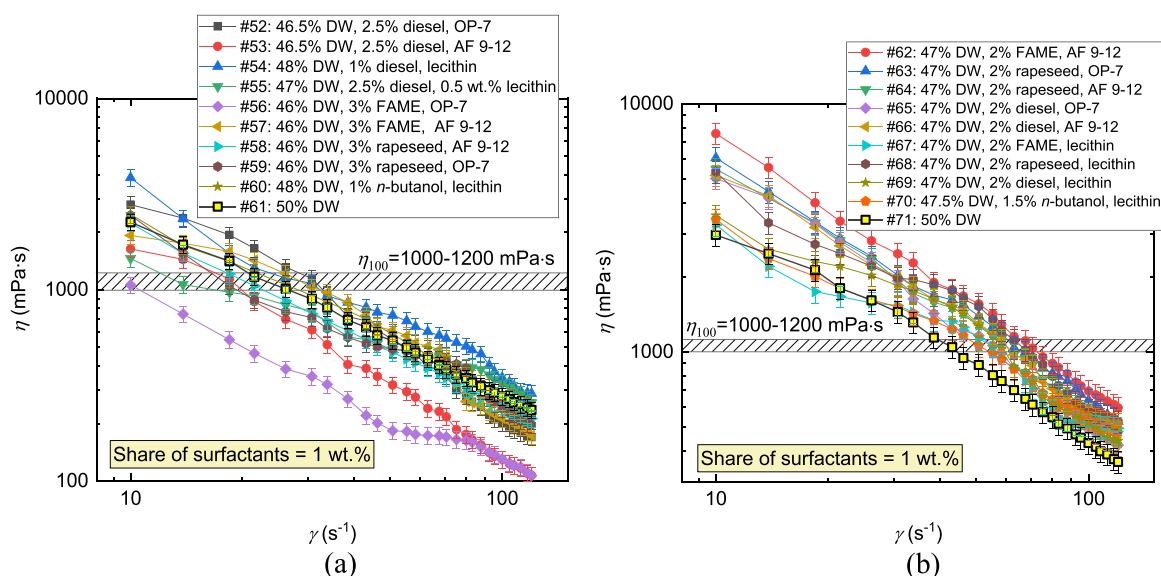
Fig. 7 – Effective viscosity of CWS based on 50 wt% CC (a) and 50 wt% CCS (b) prepared with the addition of mixtures of solvent and surfactant as a function of shear rate.

zeta potential values, as well as relatively high viscosity as compared to other classes. The first category (class) determines the most stable compositions formed on the natural surfactant, i.e. lecithin. At the same time, the compositions of the first class feature the lowest zeta potential values close to – 30 mV that indicates a higher stability of the colloidal system in comparison with the compositions of other classes as well as relatively high η_{100} values. In this case, good stability and relatively high viscosity make it possible to characterize the CWSs of the first class as compositions with a branched internal structure.

Compositions in the second class (Fig. 8a) are characterized by low WSR values and comparably higher zeta potential values. These formulations are more prone to flocculation over time and when exposed to the shear stress. This is indirectly reflected in the lower values of η_{100}. The third class includes the least stable slurries based on CC with the highest WSR values and mean zeta potential values. In addition, due to the significantly lower stability, the effective viscosity of the compositions of the third class is also significantly reduced.

A similar histogram is shown in Fig. 8b for the CWS based on the CCS and CC prepared with the addition of the liquid

solvents and sawdust. Three classes of compositions were also identified according to the "stability" criterion. The first class includes only formulations based on CCS, for which no water separation is observed in the WSR measurements for a given period of time. The compositions in this class consistently show the lowest absolute values of zeta potential (about –30 mV and below) and relatively high η_{100} values. The second class also includes compositions based on the CCS (except for the basic composition based on the CC without the addition of solvents) with the WSR values up to 15%. The compositions of the first and second classes are close in stability to the basic CWS or significantly exceed them, and the viscosity of these compositions in all cases is 2–5 times higher than that of the basic ones. Thus, the compositions of the first and second classes on CCS, while demonstrating high sedimentation stability, possess a viscosity of η_{100} close to the maximal limit (Chang et al., 2015; Chen et al., 2014; Das et al., 2013; Guo et al., 2007; Li et al., 2012; Yang et al., 2007; Zhou et al., 2012; Zhu et al., 2012). From a practical point of view, these fuel CWSs are the most attractive. In this case, the concentration of the solvent required to achieve this effect is 1–2 wt%. The addition of the considered solvents to the CWS based on CCS steadily increases the viscosity (Fig. 8c). It

Table 2 – WSR values and fluidity classes for studied basic CWSs.

| No. of fuel sample	Component composition	WSR (%)	Fluidity class
1	50 wt% CCS (lower fineness), 50 wt% distilled water	9	A
2	50 wt% CCS (higher fineness), 50 wt% distilled water	6.50	A
3	50 wt% CC (higher fineness), 50 wt% distilled water	9	A
4	50 wt% CC (lower fineness), 50 wt% distilled water	15.80	A
5	37.5 wt% CCS (higher fineness), 12.5 wt% CCS (lower fineness), 50 wt% distilled water	9.26	A
6	37.5 wt% CCS (lower fineness), 12.5 wt% CCS (higher fineness), 50 wt% distilled water	15.16	A
7	37.5 wt% CC (higher fineness), 12.5 wt% CC (lower fineness), 50 wt% distilled water	16.16	A
8	37.5 wt% CC (lower fineness), 12.5 wt% CC (higher fineness), 50 wt% distilled water	8.30	A
9	50 wt% CCS (higher fineness), 50 wt% tap water	13	A
10	50 wt% CCS (higher fineness), 50 wt% of 0.1 M ammonium acetate solution	11.20	A
11	50 wt% CCS (higher fineness), 50 wt% of 1 M ammonium acetate solution	9.50	A
12	50 wt% CC (higher fineness), 50 wt% tap water	10.2	A
13	50 wt% CC (higher fineness), 50 wt% of 0.1 M ammonium acetate solution	9.56	A
14	50 wt% CC (higher fineness), 50 wt% of 1 M ammonium acetate solution	8.36	A

(a)

(b)

(c)
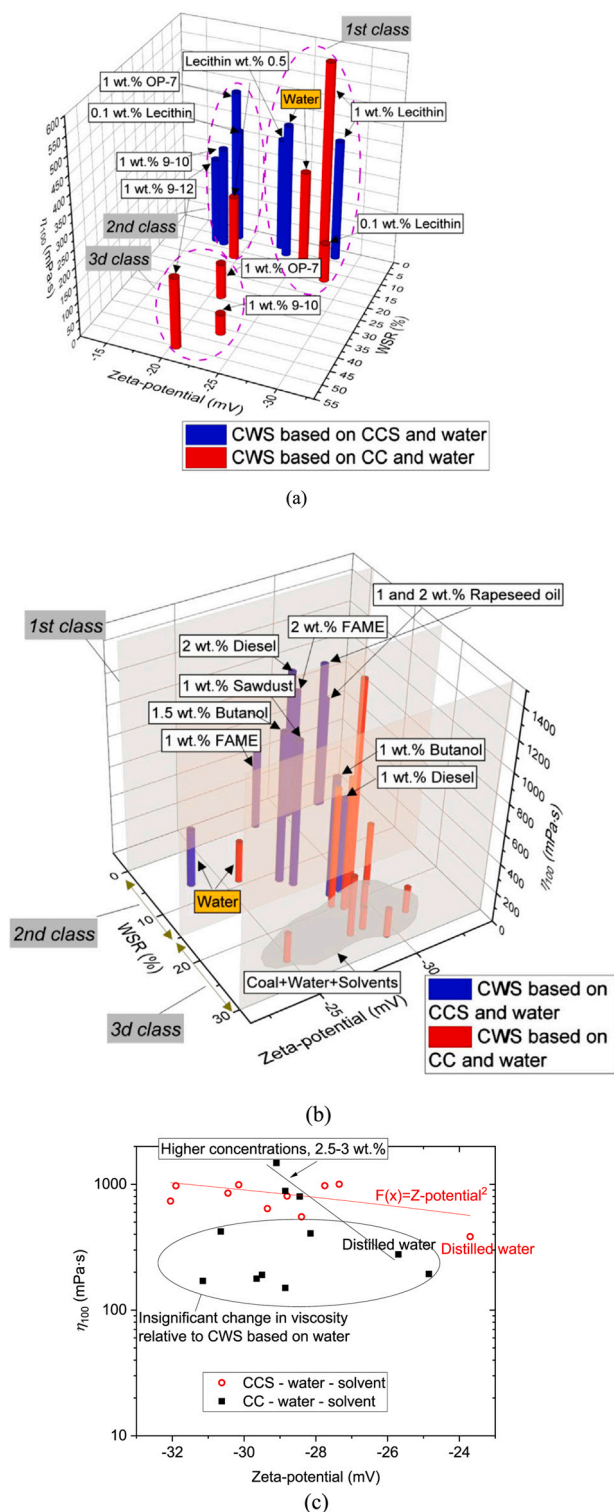
Fig. 8 – Histogram reflecting the interdependence of WSR, zeta-potential, and effective viscosity at a shear rate of $100\,s^{-1}$ for CWS based on CCS and CC prepared with the addition of surfactants (a) and solvents (b); η_{100} values as a function of zeta potential for the CWS based on CCS and CC with the addition of solvents (c).

was found that the increase in the η_{100} values is proportional to the square of the negative values of the zeta potential, η_{100} = Z-potential² (Fig. 8c, the red solid curve). An absolute decrease in the zeta potential is qualitatively reflected on the WSR in the form of the decreased values close to 0%. Under such conditions, the viscosity grows rapidly within the established law. The third class (Fig. 8b) includes mainly the

compositions based on the CC with high values of WSR ≈ 20–30%, rather lower η_{100} values (with one exception) and zeta potential in the range of – 25 mV and – 30 mV. For CWS based on CC, a decrease in zeta potential insignificantly affects η_{100} at concentrations of the solvent additives up to 2 wt% (Fig. 8c), i.e. the viscosity is practically unchanged relative to the basic CWS on water. However, even at the additive concentration of 2.5–3 wt%, the viscosity can increase several times.

4. Discussion

4.1. Separate and synergistic effects from adding the mixture of surfactant and liquid solvent

Fig. 9 shows histograms with the WSR values and fluidity classes for CWS prepared on the basis of CC and CCS that allow evaluating separately and in combination the effect of the wetting surfactant additive and the liquid solvent on the sedimentation stability. It is expressed in terms of the 100–WSR value (%) (i.e., in Fig. 9, higher values on Y-axis reflect the stabilization gain) and fluidity classes A and B.

The results in Fig. 9 facilitate the formulation of practical methods for managing the stability of CWS based on CC and CCS aimed at ensuring the required long storage duration (about 4 days of fuel supply for typical energy facilities: boiler houses and thermal power plants). These include:

(1) mixing of 2–3 wt% FAME in a slurry based on CC and CCS with the added 1 wt% wetting agent Neonol AF 9–12, OP-7, and soy lecithin significantly enhances the stability relative to the composition only with the addition of the surfactant or at least does not weaken it; in some cases, the fluidity class may change to B;

(2) the combination of 3 wt% rapeseed oil and 1 wt% Neonol AF 9–12 in slurries based on CC slightly enhances the stability relative to the presence of only solvent additive;

(3) the slurries on CCS with the addition of solvents and surfactants mainly increase their stability (phase separation is often not observed at all), the exception is the combination of rapeseed oil and OP-7 or Neonol AF 9–12 as well as diesel fuel and OP-7;

(4) "stable" combinations with soy lecithin at a concentration of 1 wt% are prone to deteriorate the CWS fluidity (class B); therefore, when using soy lecithin as a wetting agent and stabilizer, it is more likely to be limited to concentrations less than 1 wt%.

It is noteworthy that in Fig. 9 there are the cases when it is preferable to use not a combination of the solvent and the surfactant but each of the additives separately. The general conclusion is the need for individual tuning of the co-addition of the solvent and surfactant. In addition, objectively, the formulations based on the CCS with the additives are more stable, in many cases without the fixed phase separation, and mixing soy lecithin in combination or separately, as a rule, improves the stability. When comparing the results of WSR with known data (He et al., 2015; Wang et al., 2012), it is seen that the total loading of solids primarily defines the stability in terms of WSR. Our samples have a fixed lower amount of solids (50 wt%) and, therefore, are prone to phase separation stronger. At the same time, the samples contain only several percent of functional additives that make them
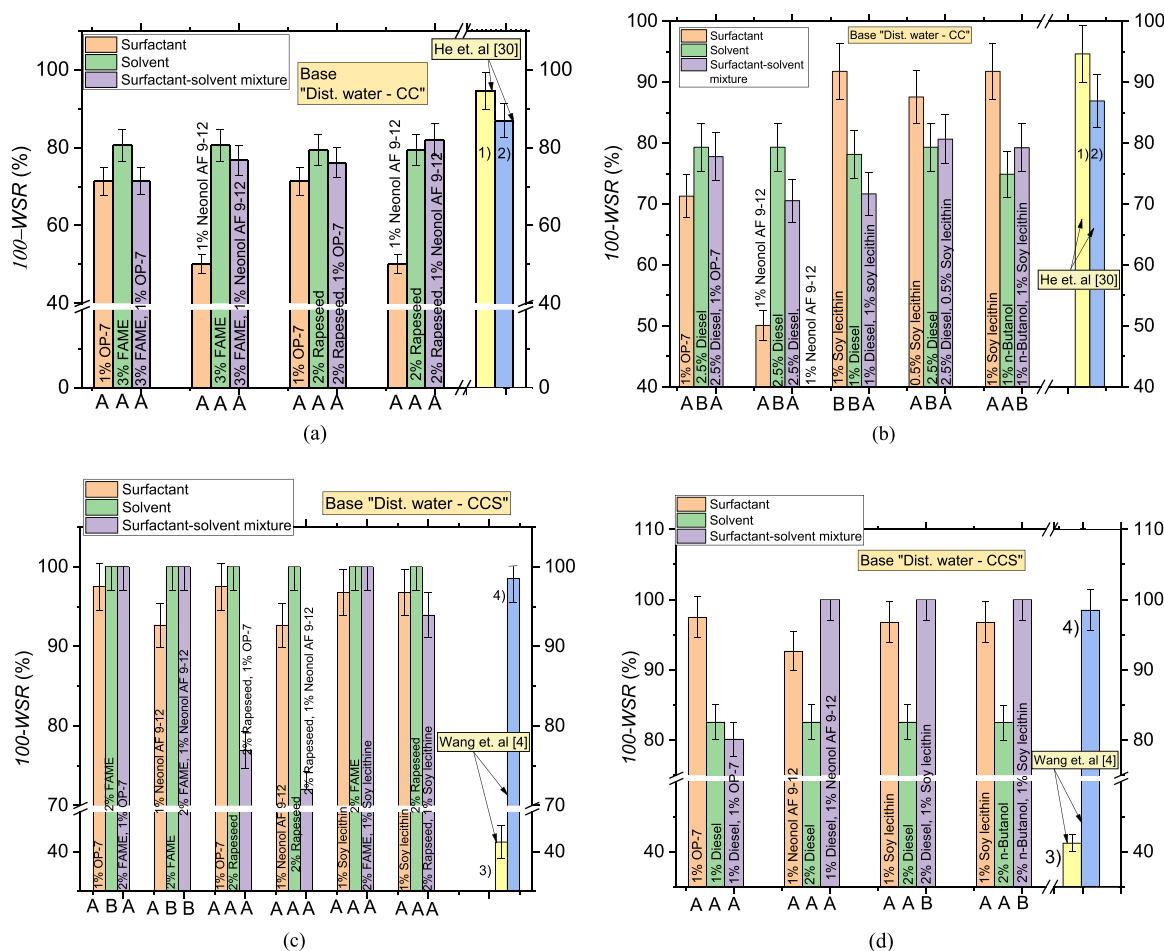
Fig. 9 – WSR values and fluidity classes for CWS prepared on the basis of CC (a, b) and CCS (c, d); know data of WSR for comparison: 1) – 57.92 wt% of coal, 27.08 wt% of water, 15 wt% of sludge (He et al., 2015); 2) – 69.78 wt% of coal, 30.22 wt% of water (He et al., 2015); 3) – 57.97 wt% of slime, 35.53 wt% of water, 6.5 wt% of wastewater sludge (Wang et al., 2012); 4) – 49 wt% of slime, 25 wt% of water, 26 wt% of wastewater sludge (Wang et al., 2012); WSR values (this study) are grouped with the condition: 1 column – CWS with the addition of surfactants, 2 column – CWS with the addition of solvents, 3 column – CWS with the addition of a mixture of surfactant and solvent.

comparably stable and attractive in terms of storage of the slurries with a low loading of solids.

To assess the separate and synergistic effects of the surfactant and the liquid solvent on η_{100} as one of the most important performance characteristics for rheology of such fuels (Chang et al., 2015; Chen et al., 2014; Das et al., 2013; Guo et al., 2007; Li et al., 2012; Yang et al., 2007; Zhou et al., 2012; Zhu et al., 2012), a corresponding histogram for CWS based on CC and CCS (Fig. 10) was plotted. According to the results in Fig. 10, the general conclusion that is valid both for the compositions based on the CCS and CC is a clear and often significant decrease in η_{100} values when the wetting agent is added to the slurry with the solvent already admixed. This trend was recorded in most cases (Fig. 10). For comparison, Fig. 10 also contains the results on η_{100} values for the slurry fuels made of petroleum coke and petrochemical sludge (Wang et al., 2012) as well as coal–sludge slurries (He et al., 2015), in which the solid loading is noticeably higher.

The established effect is the key proposed method to control and predict the viscosity values. The selection of the correct concentration of the additives will be a key challenge in ensuring the required value or range of η_{100}. It is important to emphasize the general conclusion from the results in Fig. 9 and Fig. 10 and the relationship between the obtained data

on the stability and effective viscosity. In most cases, a decrease in viscosity when a wetting agent is added to the formulations with the already admixed solvent does not significantly affect the WSR value, i.e. the latter decreases, but insignificantly or remains stably high.

4.2. Physicochemical model

For a more detailed consideration of the observed processes, we make a number of assumptions. In particular, coal particles are examined as homogeneous in composition, having a predominantly hydrophobic surface as well as pores with a wide range of size distribution, both natural and artificial (caused by grinding) origins.

When low-polar organic liquids (solvents), which are insoluble or of limited water solubility, are dispersed in CWS, the solvent droplets agglomerate with hydrophobic coal particles on the principle of affinity of polarities. The driving force of this process is the tendency of liquids to reduce their excess surface energy by decreasing the phase interface. The ultimate outcome of solvent-particle interaction is determined by properties of solvents. Low-molecular and low-viscosity liquids well-wetting coal surface, e.g., diesel or butanol, primarily seek to fill particle pores, including the smallest ones, and to displace water from them by a strongly
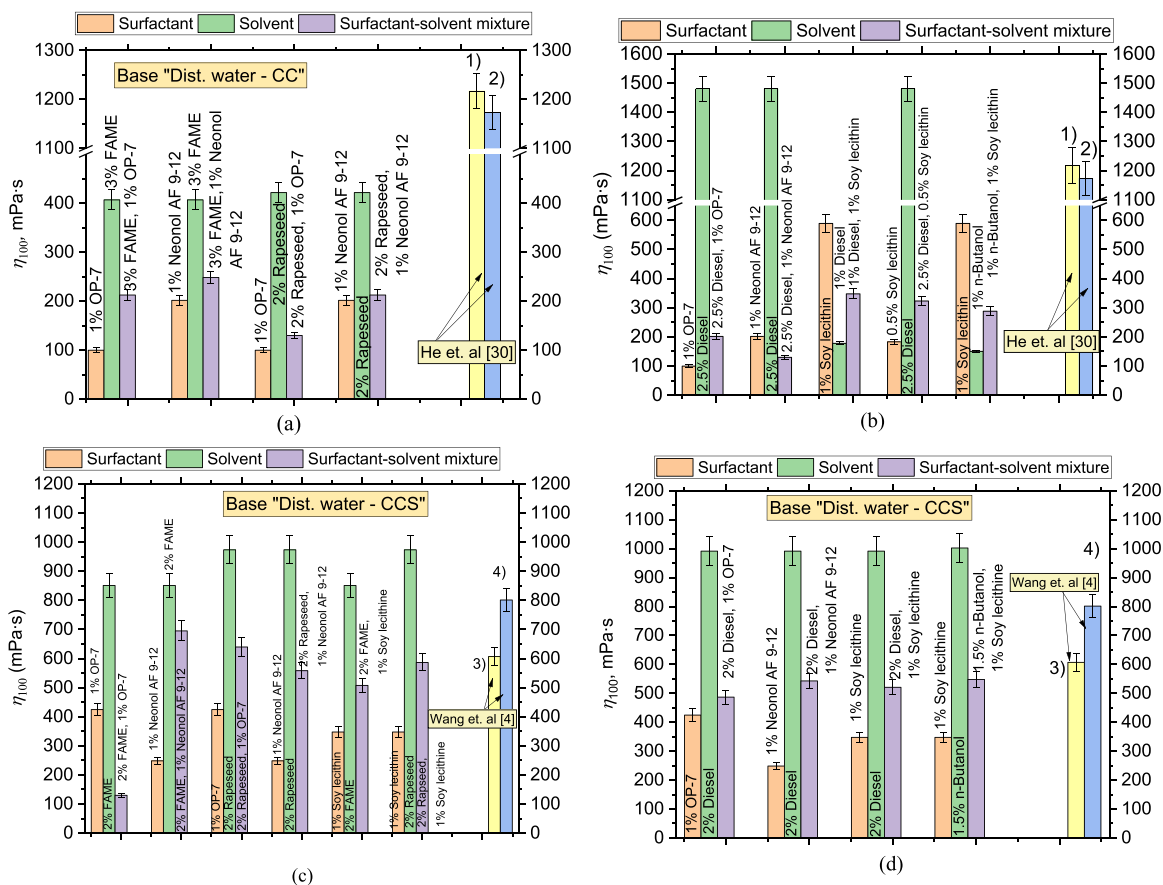
Fig. 10 – Viscosity values η_{100} for CWS prepared based on CC (a, b) and CCS (c, d); known data of η_{100} for comparison: 1) – 57.92 wt% of coal, 27.08 wt% of water, 15 wt% of sludge (He et al., 2015); 2) – 69.78 wt% of coal, 30.22 wt% (He et al., 2015); 3) – 57.97 wt% of slime, 35.53 wt% of water, 6.5 wt% of wastewater sludge (Wang et al., 2012); 4) – 49 wt% slime, 25 wt% water, 26% wastewater sludge (Wang et al., 2012); η_{100} values (this study) are grouped under the condition: 1 column – CWS with the surfactant addition, 2 column – CWS with the solvent addition, 3 column – CWS with the addition of surfactant-solvent mixture.
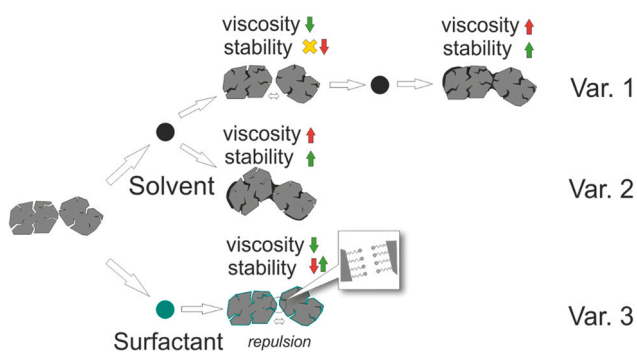

Fig. 11 – Schemes of the physicochemical mechanisms of interaction between solid particles and additives in CWSs: green arrows – positive outcome from a technological viewpoint; red arrows – negative outcome; yellow cross – no change.

pronounced capillary effect (Fig. 11, Var. 1). As a result, the amount of free water in CWS increases, and its viscosity decreases by reducing the number of interactions between the particles. The results presented in Fig. 6a clearly illustrate this effect. Meanwhile, sedimentation stability may tend to decline slightly (Fig. 9). The liquid solvent fills the pores up to a certain limit characterizing the sorption capacity of coal relative to this solvent, after which the excess quantity of solvent is distributed by film over the surface of the particles,

and causes a cross-linking (Fig. 11, Var. 1). The result of this process is a strengthening of the structure formed by the particles conglomerate and, as a consequence, a growth of rheological parameters, including the viscosity of the system. At the same time, stability is growing. Thus, by gradually increasing the share of a solvent in CWS, we first see a decrease in viscosity and stability, and after a certain limit of solvent share – their growth. The experiments with two CWS with different concentrations of diesel fuel are clear evidence of this. In the case of 1 wt% solvent concentration, the CWS viscosity is lower than in the basic composition, but in the case of 2.5 wt% – markedly higher (Fig. 6a).

The mechanism for wetting coal particles with FAME or rapeseed oil is inherently similar to that discussed above. The main difference is that these liquids have larger molecules, increased viscosity, and are unlikely to be able to effectively wet the surface of coal and penetrate into small pores. This results in lower sorption capacity of coal relative to these liquids. At the concentrations used, these liquids form the cross-linked structures (Fig. 11, Var. 2) characterized by high viscosity, as illustrated in Fig. 6a. It is not difficult to notice that the viscosity of such CWSs grows with increasing the concentration of solvents.

When adding surfactants to CWS, a typical adsorption pattern can be expected, which implies the formation of thin adsorption films of the surfactants on the particle surface (Fig. 11, Var. 3). In our case, we can talk about adsorption of

the surfactants on the hydrophobic surface, because of which the molecules of the surfactants are oriented by polar parts towards the water phase. A decrease in the static contact angle (Fig. 5) clearly indicates that the surface is lyophilized and therefore that such adsorption occurs. The result of this modification is a decrease in the inter-particle interactions and, consequently, a decrease in viscosity, as demonstrated by CWSs with the addition of OP-7, Neonol AF 9–10, and lecithin at low concentrations. The stability of such CWSs obviously depends on the nature of the surfactants. Thus, lecithin, which is an amphoteric surface-active agent and has the charged head groups, is able to increase the charge on the surface of particles by ensuring their electrostatic screening and increasing the sedimentation stability of CWS. This fully complies with the results obtained (Fig. 9b). The oxyethylated nonylphenols have no charge and therefore no such stabilization is possible.

The highly hydrophilic non-ionic surfactants, e.g., Neonol AF 9–12, have the lowest adsorption capacity with respect to hydrophobic surfaces due to their high solubility in water. For this reason, the presence of such surfactants has little impact on the viscosity of the basic CWS (Fig. 6a). However, there is a marked decrease in their sedimentation stability, probably caused by changes in the electrical double layer of particles and indirectly confirmed by a decrease in zeta potential (Fig. 8a).

The combination of different solvents and surfactants can be considered as intermediate variants within the described mechanisms of interaction in CWS (Fig. 11).

5. Conclusion

Based on the results of the experimental studies, the methods to control and predict the effective viscosity and sedimentation stability of the CWSs based on CC and CCS were proposed. The separate and combined addition of wetting agents (synthetic and natural surfactants, namely Neonol AF 9–12, Neonol AF 9–10, OP-7 and soy lecithin, respectively), liquid solvents (n-butanol, fatty acids methyl esters of sunflower oil, rapeseed oil and diesel fuel), and solid organic additives (e.g., sawdust) is considered as one of the tools for controlling the studied characteristics. Sedimentation stability was quantified in terms of the water separation ratio and fluidity classes. The main conclusions regarding the rheology of the CWS were made using the values of the effective viscosity η_{100} at a shear rate of $100\,s^{-1}$. The wetting ability of the applied surfactants was estimated by measuring the static contact angles. Electrostatic interaction between the solid particles in the presence of additives was carried out by measuring the zeta potential. The compositions based on CCS with additives were more stable, often without the phase separation, and the mixing of soy lecithin in combination or separately improved the stability. A significant decrease in η_{100} values with the addition of the wetting agent to the slurry with the already admixed solvent was recorded for both CWS based on CC and CCS. An interdependence was shown between η_{100}, the water separation ratio, and the zeta potential for the CWS with the separate addition of the wetting agent and solvent. The classes of fuel compositions were identified according to the "stability" criterion. The empirical expression was derived that described the growth of η_{100} values through the squared values of the zeta potential of the CWS based on CCS. The synergistic effect of wetting and solvent additives on the sedimentation stability and effective viscosity of the CWS was estimated, and practical methods to control the stability and viscosity were formulated to ensure the required performance indicators. The physicochemical model of interaction between the solid particles and the additives in CWSs was proposed. Moreover, the dynamics of the evolution of the effective viscosity values during the period of time to assess the water separation ratio was determined. The effect of additional mineralization (using tap and distilled water, 0.1 and 1 M ammonium acetate solutions) of the CWS carrier medium, the size and fraction of the packing of the solid particles on the effective viscosity of the fuel slurry compositions was established. A decrease in the viscosity of the polydisperse compositions was associated with the provision of more favorable conditions for packing and the average diameter of solid particles. In most of the measurements of the viscosity of the developed CWS compositions, the η_{100} values did not exceed the maximal operational limit of 1.0–1.2 Pa·s that is characteristic of typical coal-water fuels.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cherd.2022.06.005.

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