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Dispersed-colloidal fuel systems

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Abstract. A substantiation of the action mechanism of alkaline additives on the rheological characteristics of binary fuel systems is proposed, which will allow us to proceed to numerical methods for studying the technological processes of production. The possibility of increasing the stability of the suspension by using a nanomodifier obtained by ultradispersing to a submicron size of a portion of the same suspension is shown.
Key words: rheology, fuel system, numerical methods, nanodispersions

Getting fuel water-coal suspensions from coals of different degrees of metamorphism and from waste of coal-enrichment and coal processing is still relevant, especially for coal regions, because solid-fuel energy generation leads to global pollution of the environment [1]. The transfer of coal and coal sludges to water-coal suspension fuel makes it possible to improve the situation when burning coal in this form [2]. Essentially fuel water-coal suspensions are binary systems in which the solid phase should have the smallest possible size and maximum fluidity with a minimum content of the carrier medium. For this, plasticizer reagents are added to the system, also in a minimal amount, up to 1% for a dry weight of coal [3].

In the course of active mechanical and chemical destruction of coal particles in the aqueous phase, a binary system is formed. This system is called a suspension, but the carrier medium is colloidal solutions of nanoparticles in a liquid solvent. Due to the small size of the inclusions, such systems have special physical and chemical properties. Systems have an increased surface energy due to a large number of atoms in an excited state and having at least one free electron at an external energy level. Such systems may well be attributed to nanodispersions. Because of its structure and instability in the size of aggregates of nanoparticles, nanodispersions, as a rule, are rather unstable. Their properties are easily changed and depend on external influences. The main task that must be solved on the way to their industrial use is to obtain stable nanodispersions with reproducible properties. Thus, the technological and thermal characteristics of fuel water-coal suspensions intended for direct combustion are largely determined by the degree of grinding and the physical and chemical composition of the used coals [4].

The purpose of this work was to develop theoretical foundations for technological solutions for the production, transport and combustion of water-coal suspensions from brown coal.

To ensure that the fuel can be stored, transported through pipes, fed for combustion and burned in furnaces, it is necessary to comply with the requirements for rheological characteristics [5] and stability. It is known that mineral impurities contained in the solid phase contribute to the formation of coagulation structures in the WUS, thereby affecting on rheological properties and sedimentation resistance. During the work a number of experiments were carried out to study the effect of the amount of mineral impurities on the viscosity and stability of suspensions. For this purpose, brown coals of grade B2 were used with an ash content of 10.6 to 34.7%. From each coal sample with a certain ash content, a series of suspensions with different mass fraction of the solid phase were obtained. The content of the solid phase of the obtained suspensions without the use of plasticizing additives was, on the average, 43-46%, depending on the ash content. The lowest heat of WCS combustion in this case is 5.61-7.66 MJ / kg.

To increase the solid content in the WCS, a number of plasticizing additives having an alkaline medium, such as technical lignosulfonates of KBP, Lifrin-P, Ligrin, Lipor, were studied. It was found that as the ash content of the initial coal increased, the diluting effect of the additive decreased, which led to the need to increase the amount of plasticizer or to use the complex composition of the additive.

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But the positive point, in this case, was that, unlike sodium hydroxide, when using lignosulfonate there is no reversion of the change in structural viscosity. This circumstance is extremely important, since the introduction of KBP in industrial conditions exceeding the optimal dosages (1%) will not cause a deterioration in the fluidity of the suspensions. In the case of using *NaOH*, strict regulation of its concentration (0.2-0.5%) is required. This concentration for alkali is critical, since exceeding the indicated concentration, the structural viscosity of the WCS increases, also there is the formation and precipitation of a dense precipitate. The noted properties indicate the possibility of optimizing the parameters of suspensions under industrial conditions by a joint change in the amount of the additive and by regulating the ash content of the coal [6-8]. It was found that the effective dilution of the water-coal system depends on the content of native humic acids in brown or oxidized coal.

The nature of the alkalis effect on the stability of coal-water suspensions based on brown coal is practically not investigated and is not discussed in the literature. Understanding the mechanism of action of alkaline additives on the rheological characteristics of binary fuel systems will ultimately allow us to avoid the costly experiments and switch to numerical methods for studying the technological processes of production. The dependence of the structural viscosity of the WCS on the concentration of the introduced alkali has an extreme character with a minimum in the range of alkali concentrations from 0.2 to 0.5%. With the increase in coal ash content from 5 to 8%, the amount of sodium hydroxide needed to be increased at least twice. But an increase in the content of alkali to 1% led to the stratification of the suspension to form a solid precipitate. The following mechanism is suggested for the impact of alkali and its concentration on the viscosity of the WCS.

Water alkali, reacting with brown coal, in the first stage, transfers to the aqueous phase the humic acids in the form of sodium salts:

$$\text{NaOH} + (\text{HO-Humin})_{\text{coal}} \rightarrow (\text{NaO-Humin})_{\text{aque.}} + \text{H}_2\text{O} \quad (1)$$

where $(\text{HO-Humin})_{\text{coal}}$ – humic acids in coal, $(\text{NaO-Humin})_{\text{aque.}}$ – dissolved sodium salts of humic acids. The sodium salts of humic acids in the aqueous solution are in the form of a true solution, and this composition has an aqueous phase of the WCS at high concentrations of alkali (more than 0.5%), providing a complete transition of humic acids to the corresponding salts.

At low concentrations of alkali, the first stage of its interaction with coal is described by equation (1), followed by the stage of hydrolysis of salts of humic acids and migration of sodium ions from solution to the solid phase of coal:

$$(\text{NaO-Humin})_{\text{aque.}} + (\text{HO-Humin})_{\text{coal}} \rightarrow (\text{HO-Humin})_{\text{gel}} + (\text{NaO-Humin})_{\text{coal}} \quad (2)$$

Process (2) can proceed precisely at low concentrations of alkali, and this will lead to coagulation of humic acids, the transition of a true solution of sodium salts of humic acids to a colloidal solution, a gel of humic acids. The thus formed gel stabilizes the water-coal suspension and reduces its viscosity. At high concentrations of alkali, process (2) is impossible, because all acid groups of humins are deprotonated, and this leads to precipitation of hard sediments with an alkali concentration of about 1% [9].

The observed regularities demonstrate the possibility of optimizing the properties of suspensions under industrial conditions by a joint change in the amount of the additive and by regulating the physical and chemical composition of the coal.

Water-coal fuel is classified as ballasted and its burning requires a special approach. Nanoactivators and nanomodifiers are used to improve physical-chemical and physico-mechanical characteristics of dispersed-colloidal systems to control their structural-rheological and thermophysical characteristics, as well as the process of ignition and stability of the combustion process. Nanoactivators are organic compounds of cluster type - nanoparticles (20 nm), consisting of several identical molecules. They have a secondary structure due to internal hydrogen bonds, which provide the activation effect at relatively low temperatures (40^{o}C), since hydrogen bond protons have very low rotational-vibrational excitation levels. The nanomodifier was obtained from a sample of the basic composition of the suspension, ground to submicron sizes. The addition of 1% modifier increases the stability of the suspension by approximately 100% (with the same amount of stabilizing chemical additives).

The developed nanoactivators have a very strong overall structure, due to which they are able to activate flue gases at high temperatures. It should be noted that there are problems with determining the percentage of injected nanoactivators. If the concentration of the nanoactivator in the activated liquid medium is higher than a certain limiting level, then the activation process does not arise, because the internal energy of the medium is not sufficient to transfer more particles of the nanoactivator into a pseudostable excited state. With insufficient concentration of the nanoactivator, the intensity of the coherent radiation is not sufficient to activate the medium at multiple frequencies. Therefore, for different media and conditions, there are two concentration levels - the lower and upper, within which the process is stable. The activation process takes place in the combustion chamber and spreads to the combustion gases. For coal-fired boilers, an aqueous solution of the nanoactivator is used, which is injected into the combustion chamber. Specific fuel consumption is reduced by 5-7% with a nanoactivator consumption of about 0.5 g / t coal.

Conclusion

The influence of the amount of ash component of brown coal and native humic acids on the rheological characteristics and static stability of water-coal fuel suspensions is established.

A substantiation of the action mechanism of alkaline additives on the rheological characteristics of binary fuel systems is proposed, which will allow us to proceed to numerical methods for studying the technological processes of production.

The possibility of increasing the stability of the suspension by using a nanomodifier obtained by ultradispersing to a submicron size of a portion of the same suspension is shown. The addition of up to 1% of the modifier increases the suspension stability on 50-100%. Specific fuel consumption is reduced by 5-7% with a nanoactivator consumption of about 0.5 g / t coal.

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