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ENVIRONMENTAL SAFETY IMPROVEMENT AND COMPOSITION (WATER-COAL) FUEL EFFICIENCY INCREASE WITH VARIOUS ADDITIVES AT FUEL AND ENERGY COMPLEX ENTERPRISES

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Abstract:

The performed studies create the preconditions for the development of production technology and composite fuel study with regulated the rheological properties within the conditions of their transportation and use at the enterprises of fuel and energy complex with various additives, including nanoparticle additives of various nature

Keywords: hydrocarbon fuel, nanoparticles, fuel and energy complex, rheology

1. Introduction

During recent years, Russia and other countries have an increased interest in the use of small and medium-carbon energy and coal-water fuel prepared on its basis [1-3]. The industrial reserves of coal are much larger and more evenly distributed around the globe than the combined oil and gas reserves, and they are many times superior in energy terms. Therefore, the prospect of coal use burned as a fuel oil instead of oil products in order to reduce the dependence of the industrial countries on oil supply is very tempting [1]. Besides, the use of local fuels, which include low-grade coal, peat, shale, bitumen and heavy oil residues is the priority one for the needs of small-scale power engineering. The direct burning of these fuels is inefficient and is accompanied by the environmental pollution due to their incomplete combustion. The preparation of liquid composite mixtures on their basis by adding water is more promising one. These mixtures are much more efficient and environmentally friendly during the production of heat and electricity [3]. Coal occupies one of the leading places in fuel-energy balance. Moreover, the development of major oil and gas deposits the reserves of which are ten times less than the reserves of coal, will lead to the change of energy consumption pattern in the direction of coal fuel consumption increase. Despite the fact that coal is much cheaper than gas and fuel oil with its use in a pure form a number of difficulties appears associated with transportation, the provision of safe working conditions and the presence of coal self-combustion threat. It is necessary to improve the operational properties of coal as energy fuel for a broad and efficient use of coal during heat and power production. The increased requirements for environmental safety also dictate the development and the introduction of new coal technologies that provide high economic and environmental efficiency of fuel use. In this regard, the problems of new types of fuels, the creation new resource-saving for energy conversion, as well as scientific approaches, methods and technologies providing the reduction of energy system harmful effects on the environment become important ones. Water-coal fuel (WCF) is a composite liquid fuel based on crushed coal and water. It is a promising fuel for power plants and industrial boilers [1-5]. The advantages of coal-water fuel include: environmental safety as well as fire and explosion safety at all stages of its production, transportation and use; the reduction of harmful emissions into the atmosphere. The advantages of coals include their relative cheapness, large reserves, which enable a reliable supply for a longer period for the needs of the fuel and energy complex enterprises. WCF attractiveness is also associated with the ability to improve their thermal characteristics by varying the composition and the use of various additives. The development of research in the field of coal-water slurry is held both in Russia and abroad (in Germany, Austria, Italy, China, Japan, the USA and other countries). However, there are still no scientifically-based guidelines for the calculation of physical and chemical influence processes on the original coal in order to prepare the suspensions with the given technological properties, ensuring minimal maintenance costs during its preparation, storage, transportation, combustion or gasification. The mechanism of coal-water fuel and crushed dry coal combustion are significantly different [3]. The use of coal-water slurry increases the effectiveness and the efficiency of power plants by reducing underburning, the pollution of boiler aggregate heating surfaces and environmental fees and fines. The reduction of unburning is conditioned by the fact that the suspension components within the combustion zone in the form of superheated steam contribute to finer atomization of hydrocarbon base due to the microexplosions of slurry droplets. The fuel moisture is actively involved in the reaction with carbon passing through a combustion zone and contributing to the development of hydrogen and oxygen. Oxygen stimulates combustion processes and hydrogen and carbon monoxide, which are strong restoring agents, promote the reduction of nitrogen and sulfur oxide content in flue gases. The developing reaction products burn down completely around the surface of the developed drop sinter. Besides, it was found out experimentally that the presence of water vapor accelerates the combustion process. These important features of the laws of coal-water slurry burning process result in a high completeness of fuel combustion (99-99,5%); the possibility of air excess reduction from 25% (for coal) to 5.7% (for suspension); to a sharp decrease of fly ash development and to the elimination of the need for periodic cleaning of boiler heating surfaces from contamination; the substantial reduction of soot in exhaust gases, benz(a)pyrene and other harmful emissions. The main problem during the use of coal-water fuel is a high suspension viscosity at the desired concentration of crushed coal. The development of management methods by viscosity characteristics due to the change of WCF composition is a very urgent task. The aim of this work is to identify the mechanism of various additive influence on WCF viscosity characteristics, which is an important performance factor influencing the efficiency of its transportation through pipelines, WCF spray quality and the completeness of its combustion.

2. Materials and Methods

The samples of coal-water fuel, prepared on the basis of lean coal from Kuznetsky deposit containing 40% coal and 60% water were taken for the study. The preparation of coal-water slurry samples was carried out as follows. Crushed coal was sent for grinding in a vibratory mill. The resulting coal dust was sifted into different fractions with the following dimensions: 0.2; 0.125; 0.09; 0.063; 0.05 mm. The particles with the sizes up to 90 microns were separated on sieves, weighed and fed into a mixer, in which water was dosed water from a measuring container.

The following additives were used: 1) Diproksamin-157 produced by KAZANORGSINTEZ (http://www.kazanorgsintez.ru) - neogenic surfactant used as paraffin sediment demulsifier and inhibitor at the concentration of 0.5 wt. %; 2) suspension in the diproxamine of the carbon nanomaterial "Taunit" produced by LLC "NanoTehTsentr" (Tambov, http://www.nanotc.ru), including multi-walled carbon nanotubes (CNT), the concentration of additives made 0.0125 wt. % CNT + 0.5 wt. % of diproxamine; 3) the suspension of carbon nanotubes in diproxamine, used in conjunction with dehydrated carbonate sludge, which is the waste of thermal power stations chemical water treatment. The carbonate slurry obtained in the process of chemical deposition has a variety of chemical compositions, a high dispersibility and surface activity. Two concentrations of additives were chosen comprising carbonate slurry: 3a) 0.0062 wt. % CNT + 0.25 wt. % of diproxamine + 0.5 wt. % of carbonate waste; 3b) 0.0125 wt. % CNT + 0.5 wt. % of diproxamine + 0.5 wt. % of the carbonate waste. The selection diproxamine, carbonate waste and carbon nanotubes was dictated by previously obtained good results for fuel oil rheological properties improvement using these substances as additives [6-9] and the experience of operation with carbon nanotubes dispersed in surfactant solutions [10-12]. The samples of coal-water fuel, the mixtures of coal-water fuel with Diproxamine-157 and nanoadditives were tested using the rotational viscometer Rheomat RM 100 to determine the dynamic viscosity values at different shear rates. The determination of dynamic viscosity was performed by the measurement of shear stress occurring in a studied black oil sample. The angular velocity ranged from 50 to 300 s-1. The measurements of black oil viscosity were performed at several temperatures in the range of 60 - 75 °C and at different shear rates. The viscometer operation is controlled from a PC via the software «VISCO-RM SOFT».

3. Results And Their Discussion

Hydrocarbon fuel has a high viscosity, depending on the solid content, the suspension temperature, the composition of the coal, the degree of grinding, the surface state of coal particles, used additives, etc. [13-16]. The determination of WCF viscosity control mechanisms will not only increase the fuel flow that will allow to transport oil via pipelines at the lowest energy consumption, but will also provide the opportunity to produce the fuel compositions with predetermined properties. To this end, we conducted a pilot study of coal-water fuel sample viscosity with the addition of diproxamine, diproxamine with carbon nanotubes, as well as diproxamine with carbon nanotubes in the presence of carbonate waste. The dependences of pure coal-water fuel viscosity, also prepared on the basis of Kuznetsky deposit lean coal were presented for comparison. The results of experimental research taking into account the experimental error in graphical form are shown on fig. 1-2.

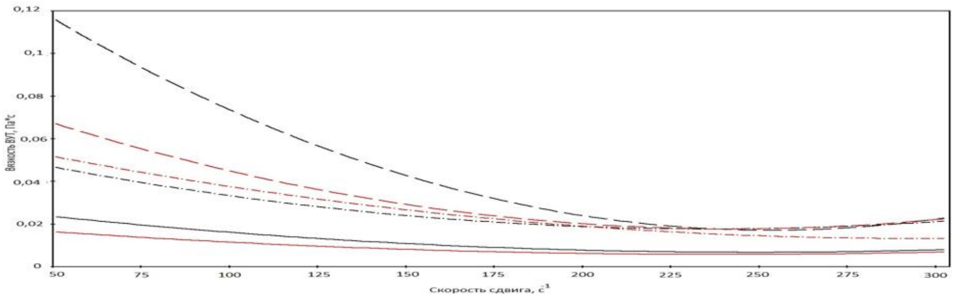

Fig. (1) – The dependence of dynamic viscosity of coal-water fuel samples and the compositions on its basis on shear rate at various temperatures

pure hydrocarbon fuel at 60°C;
pure hydrocarbon fuel at 75°C;
0,5 ml of Diproxamine +99,5 ml of WCF at 60°C (0.5 wt.% of Diproxamine);
0,5 ml of Diproxamine +99,5 ml of WCF at 75°C (0.5 wt.% of Diproxamine).
0,5 ml of suspension +99,5 ml of WCF at 60°C (0.0125 wt. % of WCF + 0.5 wt.% of Diproxamine);
0,5 5 ml of suspension +99,5 ml of WCF at 75°C (0.0125 wt. % WCF + 0.5 wt.% of Diproxamine)

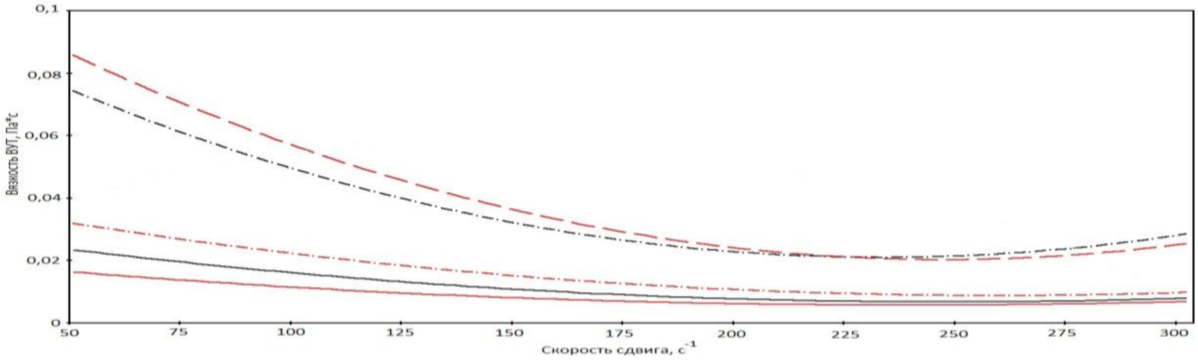

Fig. (2) – The dependence of the dynamic viscosity of coal-water fuel (CWF) samples and the corresponding compositions on the shear rate at different temperatures.

pure hydrocarbon fuel (CWF) at 60 °C;
pure hydrocarbon fuel (CWF) at 75°C;
0.25 ml of suspension + 0.5 g of carbonate waste + 99.25 ml of CWF at 68.5 °C (0.0062 wt% CNT + 0.25 wt % of Diproxamine + 0.5% wt. of carbonate waste);
0.5 ml of suspension + 0.5 g of carbonate waste + 99 ml of CWF at 60 °C (0.0125 wt. % of CNT + 0.5 wt. % of Diproxamine + 0.5 wt. % of carbonate waste);
0.5 ml of suspension + 0.5 g of carbonate waste + 99 ml of CWF at 67.1 °C (0.0125 wt. % of CNT + 0.5 wt. % of Diproxamine + 0.5 wt. % of the carbonate waste).

Highly concentrated types of coal-water fuel containing more than 40-45% wt. of coal dust are non-Newtonian fluids. In the abovementioned cases, the curves of viscosity demonstrate this depending on shear rate. In order to describe the dependences of suspension viscosity from the proportion of solids numerous models are used shown, for example, in [17,18]. The most commonly used models in non-Newtonian fluids rheology are the models of pseudoplastic fluid (Ostwald degree model) or plastic fluid (Bingham-Shvedov model). The constants of these models are determined from the experimental data obtained on tubular or rotational viscometers. Fig. 1-2 show that the change in dynamic viscosity in all studied samples are of the same character. With the increase of fuel layer movement velocity viscosity is reduced to a certain limit. This phenomenon is conditioned by the presence of high molecular weight alkanes in CWF. As soon as the shear rate increases, the dynamic viscosity of CWF at the temperatures of 60˚C and 75˚C decreases. When the whole structure is completely destroyed a minimum viscosity is observed. After some time, the spatial structure of hydrocarbons recovers and viscosity is increased slightly, which suggests that CWF behaves as a non-Newtonian fluid with thixotropic properties. When temperature is decreased from 75 °C to 60 °C, the viscosity increases for clean coal-water suspension from 0.018 to 0.025 Pa x s, due to the development of the rigid spatial structure because of paraffin high content, which is strengthened increasingly at temperature decrease.

Lean coal of Kuznetsk deposits are characterized by high hydrophilic surface due to a significant amount of oxygen containing fragments. Consequently, they have a pronounced ability to develop hydrated layers around the particles and the structural developments in suspension fuels [15]. Coal binds the dispersion medium and "swells" - the physical volume and the density change due to the interaction with liquids. It was noted [17] that all formulae used for technological calculations have the effective viscosity of suspensions proportional to the viscosity of dispersion medium. Therefore, the main parameter determining the viscosity of suspensions is the volume content of solid φ particles. The particle shape and characteristics of their interaction are taken into account by introducing the empirically determined numerical coefficients. For the suspensions prepared from dry powder the weight content of which in the suspension is equal to $\varphi_{\text{м}}$, the volume content of a solid phase is set by the following expression:

$$\varphi = \varphi_{\text{м}}\rho_{\text{м}}^{-1} \cdot [\, \varphi_{\text{м}}\rho_{\text{м}}^{-1} + (1 - \varphi_{\text{м}})\rho_c^{-1}]^{-1}, \qquad (1)$$

where $\rho_м$ – solid phase density and ρ_c – dispersion medium density, kg/m^3.

It was considered in [17,18] that the solid phase particles may bind the dispersion medium in the volume of particles and on the surface, and hence the dispersion medium content is reduced, and the volume of the dispersed phase is increased on the contrary. This leads to the thinning of dispersion medium layers responsible for the suspension viscosity of free interlayers. Since the viscosity of two-phase media, which include coal-water suspensions is determined by the total thickness and viscosity of layers in the dispersion medium, it is necessary to take into account the changes in the mass content of solid particles in a liquid $\varphi_м$ and their density $\rho_м$. The degree of these changes is determined by the physical and chemical properties of the liquid and the solid phase and the specific conditions of suspension preparation. The actual volumetric content in the solid phase suspension φ_0, which determines the viscosity of suspensions taking into account the binding dispersion medium is set by the following formula

$$\varphi_0 = [\varphi_м\rho_м^{-1} + (\Gamma_м + S_м\delta)\,\varphi_м\rho_c^{-1}]\cdot[\,\varphi_м\rho_м^{-1} + (1 - \varphi_м)\rho_c^{-1} - (\Gamma_м + S_м\delta)\,\varphi_м\rho_c^{-1}]^{-1}. \quad (2)$$

Here $S_м$ – dry powder specific surface area, cm^2/g; δ – the thickness of dispersion medium layer adsorbed by particle surface, cm; $\Gamma_м$ – the absorption of particle mass by a unit.

Due to the hydrophilic surface and the propensity to structure formation the studied samples of coal-water suspension, prepared on the basis of Kuznetsk deposit coal are related to highly filled suspensions (φ_0>0.5), where one should take into account not only the specified above factors binding the dispersion medium, but also the appearance of particle aggregates and the volume of the dispersion medium enclosed in these units ($\Delta\varphi_0$). As we showed in [17], the viscosity of such suspensions is determined by the following equation

$$\mu/\,\mu_0 = 5\{1 - [1.5(1-\varphi_0)^{1.5}+1+\Delta)]\,\varphi_0\}^{-1}, \qquad \varphi_0 \geq 0.5 \qquad (3)$$

where μ – the kinematic viscosity of the suspension, and μ_0 – the kinematic viscosity of the dispersion medium.

Thus, in equation (3) they took into account the binding of the dispersion medium dolid phase - its lyophilic and sorptive capacity, proportional to its specific surface area, as well as the additional binding due to the structure formation in the suspension. The equations (2) and (3) reflect the positions of the phase rheology for coal-water suspensions and other dispersion media.

Surfactants may induce aggregation increase and an increased sorption capacity of a solid phase. The action of the surfactant Diproxamine-157 on the suspension viscosity in the equation (3) is reflected by the change of parameters Δ (the relative volume of the dispersion medium, occluded in particle aggregates) and φ_0 (solid phase volumetric content). The change of coal-water fuel viscosity with nanoadditives can be explained by the concept of a universal reinforcing mechanism of various materials nanomodification by nanoparticles extended in [19] and generalized by us in [20], which is in the formation of material ordered regions (heterosphere) around particles. Such regions are represented by structured layers, the nanoparticles formed around under the action of their excess surface energy. The nanoparticle concentration increase leads to almost complete structuring in a sample volume where heterosphere are separated by thin layers of less dense part of a dispersion medium. In this case, the slip plane of the applied deformation will occur, mainly, on this layer, resulting in the emergence of stratified shear flow at which heterospheres may rotate freely, and, accordingly, in a sharp decrease of viscosity for a small range of concentrations. This situation is somewhat similar to the effect of composition viscosity reduction in the case of bifractional composition of a dispersed phase [16]. The subsequent increase of nanoparticle concentration leads to the adhesion of heterospheres and kinematic viscosity increase up to the original, and in some cases up to higher values. This effect is associated with a spatial aggregation of particles and leads to the coal-water fuel viscosity increase and it was observed in our experiments. Heterosphere formed around the nanoparticles at rotation speed increase break down either completely or to the level at which the viscosity of coal-water fuel with nanoparticles is determined by the viscosity of pure coal-water fuel. When shear stresses are large enough the destruction of the original structural frame elements takes place. At a certain exceeding of some shear stress threshold free liquid layers increase in proportion to the shear stress increase; the dispersion medium encased in aggregates becomes idle and thus the suspension viscosity is reduced. The application of diproxamine, carbonate waste and carbon nanotubes resulted in our previous good results improving the rheological properties of black oil fuels with the specified substances as additives [6-9]. This meant that the used concentrations of nanoparticles led to such a structure formation, at which a stratified shear flow was observed. We did not fall into the viscosity reduction area of coal-water suspension we are interested in during the experiments discussed in this paper. Nevertheless, the obtained results may be of interest for the development of other types of composite fuels, such as water oil coke fuel [21], which requires the use of thickening agents.

4. Conclusions

As the result of the pilot study concerning the viscosity of coal-water fuel samples with the addition of diproxamine, diproxamine with carbon nanotubes, as well as diproxamine with carbon nanotubes in the presence of carbonate waste, we revealed that the changes of the dynamic viscosity have the same character in the samples studied by us. With the increase of fuel layer velocity the viscosity is reduced to a certain limit. While the shear rate increases, the dynamic viscosity of WCF at the temperatures of 60˚C and 75˚C decreases. After some time, the spatial structure of hydrocarbons is recovered, which leads to viscosity increase. In order to explain the obtained results, the concept of heterospheres is introduced along with the standard model - the ordered regions around the nanoparticles, the appearance of which leads to an almost complete structuring in a sample volume. When the temperature decreases from 75 °C to 60 °C, the viscosity increases for clean coal-water suspension by 0,007 Pa x s that is caused by the formation of a spatial rigid structure that is strengthened increasingly with temperature decrease.

5. Summary

Thus, the performed studies revealed the mechanism of composite fuel viscosity management, which will contribute to the increase of fuel flow, resulting in cost reduction during the transportation and the use of fuel; and they provide the possibility to produce fuel compositions with predetermined properties using various additives including the nano-additives of diverse nature.

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