SURFACE MODIFICATION OF THE BROWN COAL AND ITS INFLUENCE ON PHYSICOCHEMICAL PROPERTIES OF THE BROWN COAL SUSPENSIONS

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Abstract: *An influence of various modifying agents (isopropanol and butanol) on properties of the highly concentrated water-coal suspensions based on the brown coal has been determined. The systems with ratio of the modifying agent concentration in the dispersed phase and dispersion medium of 3 : 1 (for isopropanol) and 1 : 1 (for butanol) ensure the most optimal physicochemical parameters. Such systems reveal low viscosity and comparatively high sedimentation stability. Inner structure of such systems can quickly restore after the external impact. An influence of the modifier adding regime on properties of the highly concentrated water-coal systems has also been investigated.*

Introduction

Wider use of various energy carriers is vital to resolve numerous energy supply problems in Ukraine and Romania. Coal is the only abundant energy carrier in both countries. New coal processing technologies still do not receive proper attention nevertheless own oil resources are rather limited especially in Ukraine. On other hand, such coal processing methods are quite popular in other less energy-dependant countries. Burning of products of the modern coal processing and transformation technologies is highly effective and ecologically safe [1–5]. Such products are easy to transport through the pipelines and can be directly burnt in the boilers ensuring better utilization of the coal energy potential and lower emission of the air pollutants. This emission can be lowered down to 30-50 % comparing to the direct coal burning [6–10].

Highly concentrated water-coal fuel consist of well-ground coal particles (coal content should be about 60-70 wt %), water and plastizers ensuring needful fluidity and stability of the system. A content of the combustible components should be kept high at low viscosity and good sedimentation stability in order to use the suspensions for the direct burning. Both low (brown coal, "T" brand coal) and high grade coals and the coal refining waste materials can be used for production of the water-coal fuel [11].

Brown coal is used mostly near its deposits and considered as a second-rate fuel because its long-ranged transportation is rather unprofitable. On other hand, long storage of the brown coal is unsafe because the coal particles surface can be intensively oxidized, which sometimes results in spontaneous ignition of the coal heaps. There were some investigations [5-9] related to transformation of the brown coal into the highly concentrated fuel compositions, which can be transported through the pipelines. However, a concentration of the volatile combustible components in the suspensions was too low and they were not intended for the direct burning. This content should be significantly increased in order to burn the suspensions directly from the pipeline.

As shown in [12, 13], there are two possible ways of adding combustible substances to the suspensions:

- some combustible compound can be used as a dispersion medium or part of the medium (together with water);
- combustible compounds can be added to the brown coal particles through their modification, which results in filling the particles' surface pores with a combustible modifier.

Influence of order of adding the modifiers on properties of the water-coal fuel has been investigated in this work. We also determined the most optimal conditions for modification of the brown coal suspensions. It is known that such modification can influence properties of the coal surface layer, which changes character of the interparticle processes and governs the structurization processes in the suspensions.

Experimental

The "**B**" brand brown coal from the Alexandria coal field (Ukraine) has been used as a source material in this work. This is brown substance with ash content of 22.5 % and specific humidity of 32.3 %. Particles size is ranged from 0.1 to 5 mm. Specific humidity has been determined as difference in a sample weight before and after its drying at 105 ^{0}C. The drying was kept until a sample reaches the stable weight. Ash content was determined similarly as a difference in a preliminary dried sample weight before and after its annealing at 850 ^{0}C.

The coal modification with isopropanol and butanol has been carried out according to the method [14]. Special sieves have been used in order to separate the coal particles of 1-3 mm, which have been used as a source material for modification.

Coal intake capacity (adsorptance) has been determined as amount of a liquid modifier, which can be added to 5 g of the preliminary dried coal until liquid phase appears. The drying was kept at 85-90 ^{0}C for about 4 hours, which lowered the coal specific humidity from ~ 32 % to 12 %.

Sodium lignosulfonate (SLS) has been used as the plastizer at the coal grinding. This compound ensured good and well-predictable results at production of various water-coal suspensions, which promises similar results for the non-water and mixed liquid coal fuels.

A ball grinder of 1.3 liters with the steel balls of 28 and 10 mm has been used to grind the brown coal particles sized up to 2.5 mm. The grinding time was determined experimentally as a period required to grind the coal particles down to 300 μm. A content of the particles of >250 μm should be lesser than 0.1 wt %. This requirement was achieved during 20 min grinding at 75 RPM.

Then the viscosity of the freshly-ground disperse systems has been determined using "Reotest-2" at the shifting rate 9 s^{-1}.

Sedimentation stability of the suspensions has been measured as a time passed until disintegration of the system.

The particles of 100 μm or more have been separated from the system using a standard sieve in order to determine its granulometric composition. Then the separated fraction was washed out with ethanol followed by the standard sedimentation analysis of the ethanolic suspension.

Electrokinetic potential of the suspensions has been measured through microelectrophoresis in the aqueous medium according to [15].

A heat of the brown coal samples wetting before and after modification has been measured calorimetrically in order to determine influence of the modification process on properties (the surface hydrophobicity and some other) of the coal particles. A heat balance of the calorimetric investigation can be written as:

$$\Delta H = K\Delta t ,$$

where ΔH is a heat generation of the process;
К – the calorimeter constant.

The latter parameter has been determined through investigation of the heat generation at adding some fixed amounts of the sulfuric acid to water. Measuring the temperature changes every 10 minutes we can calculate the K constant.

Results and discussion

The brown coal has very well developed surface and also numerous pores in the particle's body. Therefore, the modifier can be fixed both on the surface and in the inner pores. The modifier's nature does not significantly influence intensity of this process and 1 g of the coal can fix about 0.8 ml of the modifier. A wetting heat has been determined in order to find the modification ratio of the coal particles.

As seen from Fig. 1, the coal modification results in the decrease of the wetting heat caused by hydrophobisation of the coal surface. The latter process can be caused by selective adsorption of the modifying agent molecules when the hydrophilic end of the molecules fixes on the hydrophilic part of the coal surface. Then the hydrophobic part of the molecules orients towards the solution resulting in decrease of the hydrophilic area of the mosaic surface of the brown coal particle. Increased hydrophobisity causes lower possibility of structurization in the disperse system.

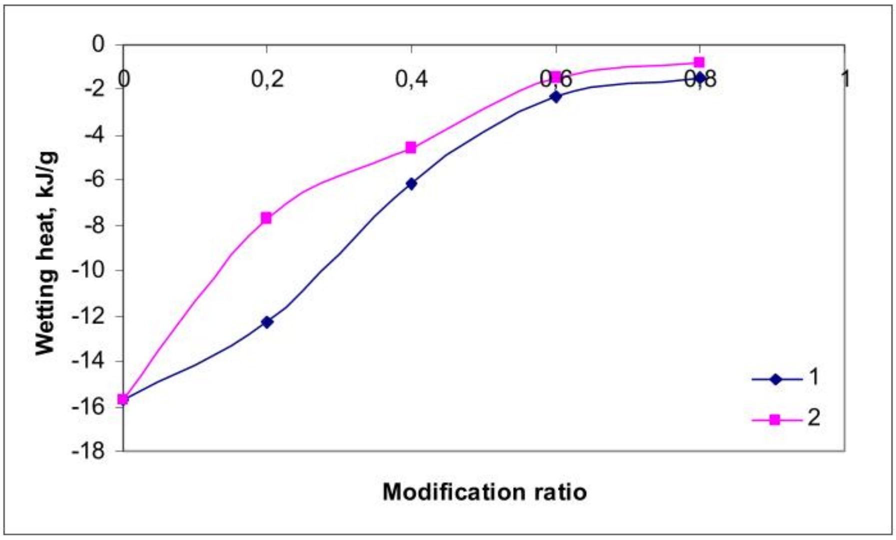

Figure 1. Influence of the brown coal modification on hydrophilicity of its surface. 1 – modified with isopropanol; 2 – modified with butanol.

Disperse systems containing 30 % of modified or non-modified dispersed coal have been investigated in order to check if the process of modification influences their properties. Some characteristics of the both types of systems are shown in Table 1. It is seen that modification provides insignificant influence on the system's viscosity but lowers (especially in case of the insoluble butanol) its sedimentation stability. Changes in the rheological properties and sedimentation stability of the coal-water systems depend on adsorption/desorption of the modifier on the coal surface and in the pores. As seen from the granulometric composition data (Table 2), the modification process facilitates better grinding. This effect can be caused by increased contribution of the adsorptive part of disjoining pressure, which also revealed itself through the grinding time shortening to 25 min. Lower sedimentation stability can be ăcaused by the decrease of the dispersed phase particles charge because of formation an adsorption layer on their surface (Table 3).

Table 1: Some characteristics of the modified and non-modified brown coal suspensions

Composition	Wt. percentage of the solid phase, %	Wt. percentage of the combustible components,%	Viscosity, Pa s	Sedimentation stability, days
Brown coal – 120 g ; Water – 280 g; SLS – 1,2 g	30	23.25	1.22	4.5
Brown coal – 120 g ; Isopropanol – 96 g; Water – 184 g; SLS – 1,2 g	30	47.25	1.3	4.0
Brown coal – 120 g ; Butanol – 96 g; Water – 184 g; SLS – 1,2 g	30	47.25	1.42	2.5

Table 2: Size distribution of the brown coal particles in the coal/water suspension

Fraction size (d, μm)	Non-modified coal	Modified with isopropanol	Modified with butanol
250–100	45,5	33,4	29,6
100–80	13,3	17,6	16,8
80–40	14,7	14,2	17,0
40–20	10,4	14,3	12,2
20–10	6,3	6,8	7,5
10–5	7,3	8,8	11,1
5,0–0	2,5	4,9	5,2

Table 3: Electrokinetic potential for the dispersed phase particles in the brown coal/water suspension

Modifier	Electrokinetic potential, mV
–	– 44
Isopropanol	– 39
Butanol	– 27

Previous investigations [12, 13] proved that an order of adding the modifiers have significant effect on properties of the coal/water suspensions. Previously modified coal and freshly-modified coal (just before the grinding stage) form systems with different physicochemical properties. Some properties of previously and freshly modified systems are shown in Tables 4 and 5.

Table 4: Relative amounts (parts) of previously and freshly used modifiers for some coal samples (Previously used : freshly used)

Sample	Part of previously used modifier	Part of freshly used modifier
1	1	0
2	3	1
3	1	1
4	1	3
5	0	1

Data from the above tables prove that the more modifier is applied previously, the lower viscosity and sedimentation stability exhibits the system.

Preliminary modification of the coal surface results in the increase of its hydrophobity, which leads to lowering of the inter-particle attraction in the dispersion medium. Such changes manifest themselves through decreased viscosity and sedimentation stability of the system.

Freshly-added modification agent acts differently. It is known that the coal surface has some hydrophobic and hydrophilic parts and can be characterized as a mosaic structure. Therefore, water molecules from the dispersion medium would adsorb on the hydrophilic parts while modifier agent would be fixed on the hydrophobic ones. This processes results in formation of the double structure and more active attraction between the opposite mosaic areas of different particles. Such structure exhibits higher stability and can recover quickly after the external impact. All these factors result in comparatively higher sedimentation stability of the systems with freshly-added modifier.

Table 5: Some properties of the coal/water suspensions containing some coal samples

Sample	Viscosity, Pa*s	Sedimentation stability, days
Isopropanol		
1	1.3	4.0
2	1.35	4.5
3	1.4	5
4	1.48	6
5	1.63	6
Butanol		
1	1.42	2.5
2	1.45	4
3	1.48	7
4	1.52	7
5	1.56	7.5

It was found that the most optimal characteristics can be achieved for the ratio between previously and freshly added modifier of 3 : 1 (for isopropanol) and 1 : 1 (for butanol) (see Table 4). Such ratios ensure comparatively low viscosity at sufficient sedimentation stability and good recovering rate after the structure destruction.

It is needful to emphasize that the above-mentioned systems also have double structure, which consists of the modifier's molecules adsorbed in the pores and the molecules remaining in the dispersion medium. Such composition ensures high stability of the system.

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