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CURRENT PROBLEMS. Alternative Feedstock

EFFECT OF FUSEL OILS ON RHEOLOGICAL PROPERTIES OF SLURRIES OF COALS AT DIFFERENT METAMORPHIC STAGES

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The salient technological properties of coal slurries are studied using fusel oil as the dispersion medium. The distinctive features of the rheological behavior and flow pattern of coal slurries as a function of the nature of coal are ascertained. It is shown that the effective viscosity of coal slurries decreases as the coal passes from the lignite to the anthracite stage. The calorific value and degree of combustion of coal slurries in fusel oil are higher than those of the original coal.

***Keywords**: coal slurry, fusel oil, rheological properties.*

Current concepts regarding the use of coal as fuel are directed mainly at reducing hazardous releases and increasing the burn-up of the solid organic fuel [1-4]. A promising direction in many countries is technology development to produce disperse fuel systems (DFS) based on natural coals. The most common DFS are highly concentrated coal—water slurries (CWS), the advantages of which are well known [5-8]. Nevertheless, research in this area suggests that the calorific value of such fuel needs to be increased. This task can be accomplished by using disperse CWS of industrial waste waters contaminated with organic compounds and liquid organic wastes.

Alcohol manufacturing plants are one example of industries that produce liquid organic waste waters and contain large amounts of organic compounds. The required purification level cannot always be attained even by the most effective biological purification systems. Fusel oil, the average heat capacity of which

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Table 1

Coal grade	Technical analysis, wt. %			Elemental composition, % per *daf*				
	W	A^d	Z^{daf}	C	H	N	O	S
B	51.0	20.0	48.5	70.1	5.0	1.2	19.7	4.0
DG	9.3	22.3	43.8	76.2	4.9	1.1	13.7	4.1
T	5.1	25.0	14.9	88.5	3.8	0.67	5.33	1.7
A	3.2	10.5	3.8	95.7	2.3	0.4	1.1	0.5

Table 2

Coal grade	Specific density, kg/m^3	S_{sp}, m^2/g	V_{pore}, cm^3/g	d_{pore}, nm
B	1120	6.31	0.049	153.8
DG	1300	1.39	0.053	7.67
T	1500	4.72	0.019	7.88
A	1780	9.34	0.022	4.67

Table 3

Indices	Value
Density, kg/m^3 at 21°C	840
Viscosity, mPa·s at 21°C	5.8
Flash point, °C	38
Spontaneous combustion temperature, °C	400
Lower heat of combustion, MJ/kg	32
Composition, %	
iso-$C_5H_{11}OH$	47.0
iso-C_4H_9OH	16.4
n- C_4H_9OH	0.8
n-C_3H_7OH	18.5
C_2H_5tOH	8.2
CH_3OH	0.015
hexyl and other higher alcohols	0.35
propionic acid	0.28
n-butyric acid	0.040
n-valeric acid	0.160
esters	0.79
aldehydes and ketones	0.42
other organic compounds	2.045
H_2O	5.0

is 32 ± 2 MJ/kg, has the highest calorific value among side products from alcohol manufacturing. A small amount of liquid organic compounds remains in waste waters after reprocessing and isolation of the principal chemical components from fusel oil. Thus, alcohol plants are potential suppliers of dispersion media for DFS based on coal because they produce waste waters contaminated by organic compounds and liquid organic wastes. On the other hand, the heterogeneous coal-particle distribution throughout the DFS volume

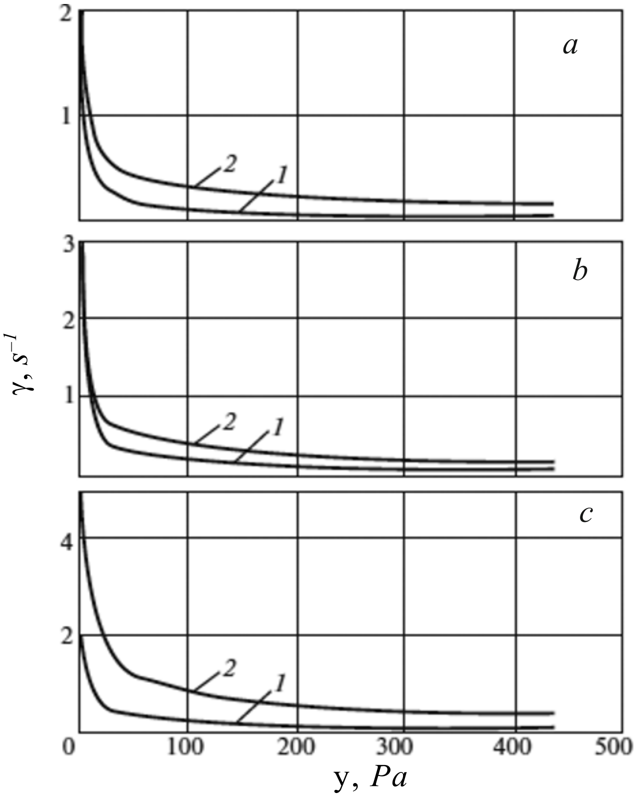

Fig. 1. Rheological flow curves of suspensions of coal grades A (1), T (2), DG (3), and B (4) prepared using fusel oil with coal particle concentration 35 % (a), 40 % (b), and 45 % (c).

complicates the production of DFS based on coals and liquid organic media and affects their rheological behavior. The rheological properties of CWS are most important and, in turn, are affected by the dispersion-medium composition and the nature of the disperse phase.

The present work studied the processing properties of coal fuel slurries prepared using fusel oil as the dispersion medium. In addition, the rheological behavior of slurries was studied as a function of the nature and concentration of coal particles.

The disperse phases were Ukrainian coal samples of grade B (Dnieper basin, MCC Aleksandriyaugol, Protopopov strip mine), grades DG and T [Donets basin (Donbass), MCC Luganskugol, Proletarskaya and Artem mines), and grade A (Donbass, MCC Sverdlovantratsit, Sverdlov mine). Table 1 presents the results from technical and elemental analyses of the coals. Original coal was ground to particle diameter 1 mm by ceramic spheres in a porcelain drum (2 dm^3) on a roller mill. The granulometric composition was determined using an SLM-200 sieve set. All powders had the same particle-size distribution (250-160 μm, 40 %; 160-100 μm, 20 %; 100-63 μm, 5%; 63-40 μm, 32 %; <40 μm, 3 %) in order to avoid effects of the granulometric composition on the rheological behavior. The structural and absorption characteristics of the coal powder, i.e., specific surface area (S, m^2/g), specific pore volume (V_{pore}, cm^3/g), and effective pore diameter (d_{pore}, nm), were determined by the Brunauer—Emmett—Teller method using low-temperature (77 K) N_2 adsorption measured with a Quantachrome Autosorb specific-surface-area analyzer (Table 2).

Table 3 presents the characteristics and composition of the coal slurry dispersion medium, i.e., fusel oil (GP Stadnitskii Alcohol Plant, Kiev Oblast). Slurries of powders of coals at different metamorphic stages were prepared by mixing them in certain proportions with fusel oil and homogenizing with

Table 4

***C*,** %	k	n	R^2	$\sigma_{\min}$, Pa	$\sigma_{\max}$, Pa	$\eta_{\min}$, Pa·s	$\eta_{\max}$, Pa·s
			Grade B coal				
35	0.108	1.968	0.994	2.99	69.0	0.16	2.99
40	0.057	2.073	0.992	4.18	74.75	0.17	4.18
45	0.017	1.953	0.997	7.16	172.5	0.39	7.16
			Grade DG coal				
35	0.054	2.647	0.993	2.69	29.25	0.07	2.69
40	0.041	2.314	0.986	4.90	57.50	0.13	4.90
45	0.030	1.922	0.998	5.97	138.0	0.32	5.97
			Grade T coal				
35	0.094	2.567	0.988	2.39	25.07	0.06	2.39
40	0.056	2.357	0.995	3.58	42.98	0.09	3.58
45	0.014	2.561	0.995	5.49	62.10	0.14	5.49
			Grade A coal				
35	0.008	3.89	0.995	2.0	17.37	0.04	2.0
40	0.085	2.358	0.991	2.5	37.64	0.09	2.5
45	0.064	2.290	0.995	2.9	46.32	0.11	2.9

an RW-11 (IKA) paddle stirrer for 15 min at rotor speed 2,000 rpm. Rheological characteristics of the slurries, i.e., shear stress (σ, Pa) and dynamic viscosity (η, *Pa·s*), were determined by rotational viscometry using a Rheotest RV2 and an S/S_2 system of coaxial smooth cylinders (ratio of cylinder radii, 1.06) at shear rates $\gamma = 0.5\text{-}437.4$ s^{-1}.

The rheological behavior of the slurries was determined mainly by the particle concentration, granulometric composition, and shape in addition to the nature of interparticle interactions. The last depended on the nature of the disperse phase and the dispersion medium [9]. The dispersion medium had a constant composition in the present work. Only the contents and types of coals changed. Accordingly, structure formation in the coal slurries depended primarily on their physicochemical properties.

Figure 1 shows that the shear stress in the flow curves increased with shear rate. The shapes of the curves indicated that the slurry structure strengthened and non-Newtonian flow was enhanced on going from coals with a high degree of metamorphism to those with a low degree of it. For example, the structure of slurries of grade A coals was destroyed at lower shear stresses than that of slurries based on grade B coals. The same trend was observed for the increase of shear stress as the coal concentration C increased and the fusel oil concentration decreased.

The flow of fusel-oil coal slurries obeyed the Ostwald—Weil equation $\sigma = k\gamma^n$, where k is a consistency factor and n, the flow index for pseudoplastic liquids. Table 4 lists the parameters approximating the curves, correlation coefficients R^2, and minimal and maximal shear stresses and dynamic viscosities $\sigma_{\min}$, $\eta_{\max}$ (at $\gamma = 1$ s^{-1}), $\sigma_{\max}$, and $\eta_{\min}$ (at $\gamma = 437.4$ s^{-1}).

Dynamic viscosities of coal slurries prepared using fusel oil decreased with increasing shear stress (Fig. 2). Curves are shown only for grade A and B coal slurries. Curves for grade DG and T slurries are not shown in order to avoid overlap because they were the same over the whole range of studied concentrations and differed only by the dynamic viscosities (Table 4). The structures of the slurries with $C = 35\%$ were destroyed most at shear rates $\gamma = 1\text{-}16.2$ s^{-1}; with $C = 40\%$, $\gamma = 1\text{-}27$; and with $C = 45\%$, $\gamma = 1\text{-}48.6$. A comparison of the viscosity curves of slurries based on

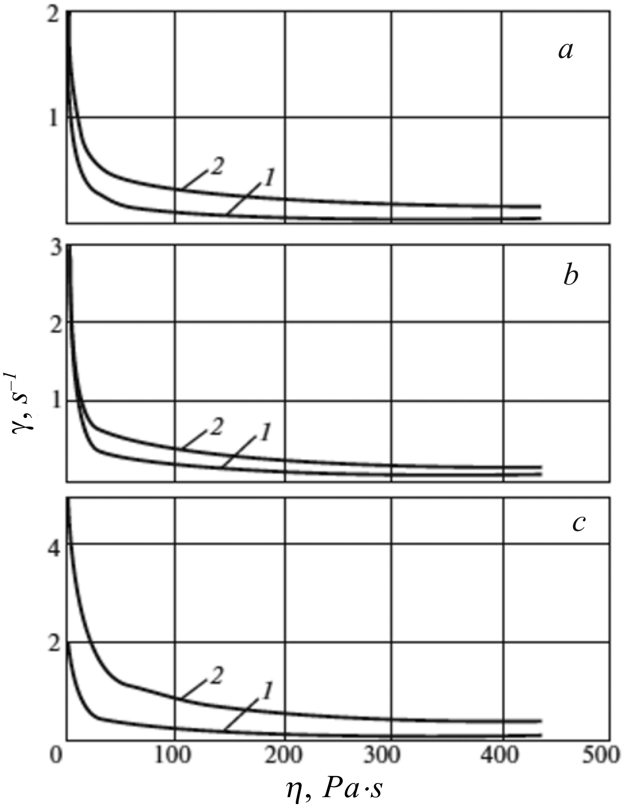

Fig. 2. Rheological viscosity curves of suspensions of coal grades A (1) and B (2) prepared using fusel oil with coal particle concentration 35% (a), 40% (b), and 45% (c).

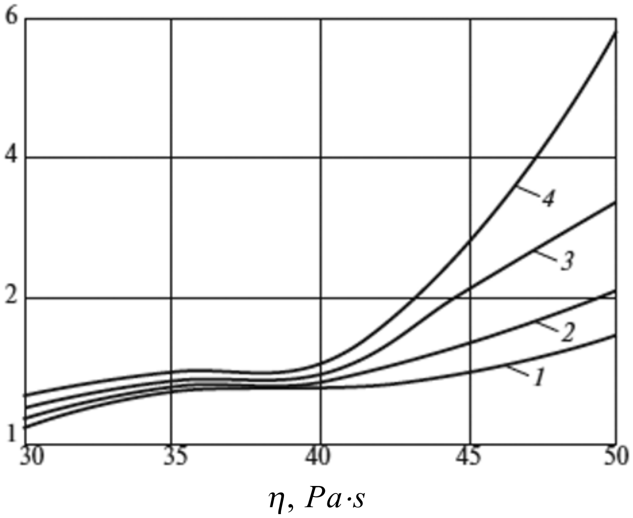

Fig. 3. Effective viscosities of suspensions of coal grades A (1), T (2), DG (3), and B (4) prepared using fusel oil.

grade A coal (Fig. 2, curve 1) and grade B coal (Fig. 2, curve 2) showed that Newtonian flow occurred at lower shear rates in the first instance. Furthermore, slurries based on grade A coal had lower dynamic viscosities than those based on grade B coal at the same concentration (Table 4).

The decrease of the rheological parameters (shear and viscosity) at the same slurry *C* could be placed in the order A < T < DG < B. In general, the density and porosity were responsible for the formation of slurry

Table 5

Coal grade	Original coal		Suspension using fusel oil	
	Q, MJ/kg	*F*, wt. %	*Q*, MJ/kg	*F*, wt. %
B	16.0	80	24.2	99.5
DG	24.8	85	28.5	99.8
T	27.5	85	30.0	99.8
A	30.3	90	31.5	99.8

structures with different strengths and viscosities from coals at different metamorphic stages. Increased metamorphism of the studied coals was associated with increased density and decreased porosity (Table 2). This facilitated reaching higher concentrations of the disperse phase at the same viscosities because more porous coals absorbed strongly the dispersion medium, which led to increased slurry viscosity. The effective viscosity ($\gamma = 9\ s^{-1}$) of the slurries as functions of coal concentration (Fig. 3) confirmed the aforementioned. For example, the effective viscosities of slurries of the studied coal grades varied little at concentrations of 30-40 %. The viscosity increased sharply if the concentration exceeded 40%. Considering the processing requirements for such DFS, the effective viscosity should not exceed 1.5 Pa•s at the maximum coal contents in the slurries [2, 6-8]. The experimental results for the maximum coal concentrations and slurry effective viscosities that were obtained using fusel oil were $C = 40$ % and $\eta = 1.13$ Pa•s for grade B; $C = 40$ % and $\eta = 0.96$ Pa•s for grade DG; $C = 45$% and $\eta = 1.39$ Pa•s for grade T; and $C = 50$% and $\eta = 1.54$ Pa•s for grade A.

It is noteworthy that highly concentrated CWS were characterized by slightly lower viscosities and strengths [7, 8] than those of the coal slurries in fusel oil that were studied by us. This difference could be related to electrical surface effects at the coal—dispersion-medium interface. Like charges on particle surfaces in spontaneous slurries are known to prevent their aggregation in the dispersion medium [10]. The electrokinetic potential of coal particles varies from –30 to –50 mV in aqueous media; from –9 to –16 mV, in organic [11, 12]. Therefore, reducing the dispersion-medium polarity weakens the mutual electrostatic repulsion of coal particles. This causes aggregation with the corresponding increased strength and slurry viscosity.

The processing properties of the coal slurries that were used as DFS were determined not only by the optimal rheological parameters but also the calorific value *Q* and the degree of combustion *F*. Therefore, we determined the energy characteristics of the coal slurries in fusel oil according to GOST 147-95. Table 5 shows that adding fusel oil to the coal slurries helped to increase the calorific value and degree of combustion. Thus, the calorific value of CWS with $C = 60$-70% at the time of combustion was 5-8 MJ/kg less than that of the original coal [13, 14]. Therefore, adding fusel oil to the coal slurry enabled even low-grade coals to be used as fuel. Incorporation into the fuel-slurry preparation cycle of not only fusel oil but also other liquid organic wastes and waste waters is just as important.

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