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*V.V. Zinin*<sup>a, b</sup>, *Yu.V. Polishchuk*<sup>a</sup>, *O.V. Shkutkova*<sup>c</sup>**THERMORHEOPEXY AND STRUCTURAL STABILITY OF CARBONACEOUS SUSPENSIONS BASED ON PYROCARBON**<sup>a</sup> Ukrainian State University of Science and Technologies, Dnipro, Ukraine<sup>b</sup> LLC «Liquid Carbo», Kyiv, Ukraine<sup>c</sup> A.V. Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine

The thermo-rheological behavior of composite suspension fuels based on pyrocarbon obtained by low-temperature pyrolysis of waste automobile tires was investigated. Pyrocarbon is characterized by a specific nanoglobular structure and high hydrophobicity, which distinguishes it from traditional fossil coal. Using scanning electron microscopy and energy-dispersive X-ray spectroscopy, the multiphase structure of the material was established, including a carbon matrix and nanodispersed inclusions of zinc sulfide (ZnS). The rheological parameters of the system (58 wt.% solid phase) were calculated using the three-parameter Herschel–Bulkley model in the temperature range of 10–50°C. An anomalous thermorheopexy (anti-thixotropy) effect was revealed upon heating above 42°C, accompanied by a sharp increase in yield stress and consistency coefficient. Calculation of the viscous flow activation energy according to the Arrhenius equation confirmed a change in the thermodynamic regime for almost all measured shear rates: from thermal thinning (10–42°C,  $E_a = +9.87$  kJ mol<sup>-1</sup>) to thermo-induced flocculation (42–50°C,  $E_a = -18.18$  kJ mol<sup>-1</sup>). It was established that the mechanism of anomalous thickening is caused by destabilization of the adsorption layers of the non-ionic surfactant near its cloud point, intensified by the high ionic strength of the solution and the presence of hydrophobic aggregation centers in the form of micro- and nanoparticles of ZnS. The obtained results make it possible to optimize the temperature regimes for transportation and combustion of pyrocarbon-based suspensions.

**Keywords:** thermorheology, thermorheopexy, Herschel–Bulkley model, activation energy, effective viscosity, composite suspension fuels, pyrocarbon.

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**Introduction**

The global strategy of the circular economy stimulates the search for rational ways to recycle end-of-life automobile tires, whose accumulation volumes increase annually. Low-temperature pyrolysis of elastomers yields a solid carbon residue (pyrocarbon) which is considered a promising alternative to fossil coal in the production of composite suspension fuels

(CSF). Pyrolysis is the most environmentally balanced method for converting polymer waste [1]. However, the widespread implementation of pyrocarbon dispersions is hindered by their specific physicochemical nature, which differs significantly from traditional coal-water slurries described in classical works [2].

Unlike anthracite, pyrocarbon is characterized

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by nanoglobular morphology and the presence of incomplete rubber degradation products on the particle surface. In our previous study [3], it was established that this leads to extremely high hydrophobicity of the material and specific interparticle interaction energy. The rheological behavior of such systems is usually described by thermal thinning models, where viscosity monotonically decreases with heating. However, the presence of specific mineral inclusions in pyrocarbon, in particular zinc sulfide (ZnS) formed by the transformation of vulcanization components [4], creates preconditions for anomalous structural transitions.

Of particular scientific interest is the stability of surfactant adsorption layers in such multiphase systems under temperature changes. Despite extensive studies on the thixotropic properties of carbon black presented in works [5,6], the issue of temperature-induced inversion of the flow regime in pyrocarbon suspensions in the presence of ionic impurities remains insufficiently explored. There is a scientific contradiction between the expected thermal viscosity reduction and the observed destabilization of the system due to specific hydrophobic aggregation centers in the form of micro- and nanoparticles (ZnS).

The aim of this work is to establish the regularities of changes in the structural-mechanical parameters of pyrocarbon-based suspensions in the temperature range of 10–50°C and to provide a theoretical substantiation of the mechanism of anomalous thickening (thermorheopexy) involving zinc transformation products and non-ionic surfactants.

### **Experimental**

The object of the study is pyrocarbon: the solid residue of low-temperature pyrolysis (400–430°C) of waste automobile tires (WAT). The pyrolysis duration was 8 hours, which ensured a stable yield of the solid phase with the following characteristics: total moisture content ( $W^{\text{rt}}$ ) 3.0%, ash content ( $A^{\text{d}}$ ) 16.4%, and volatile matter yield ( $V^{\text{daf}}$ ) 19.65%. The higher heating value of the dry ash-free fuel ( $Q_{\text{gr,daf}}$ ) was 37.2 MJ/kg, and the lower heating value of the as-received fuel ( $Q_{\text{v,net,m}}$ ) was 29.5 MJ/kg.

Surface morphology and local elemental analysis were performed using a high-resolution field-emission scanning electron microscope TESCAN MIRA3 LMU (Czech Republic). Surface texture visualization was carried out in secondary electron mode (in-beam SE), and mineral phases were detected by Z-contrast in backscattered electron mode (BSE). Elemental composition was determined by energy-dispersive X-ray spectroscopy (EDS) using an Oxford Instruments X-Max detector at an accelerating voltage of 20 kV.

Rheological studies were conducted on a

rotational viscometer Rheotest 2 (Germany) with a coaxial cylinder measuring system S1/S2. The shear rate ( $\dot{\gamma}$ ) was varied in the range of 1.0–437.4  $\text{s}^{-1}$  (12 fixed shear rates). Temperature control in the range of 10–50°C was maintained by a circulating thermostat U15C MLW with an accuracy of  $\pm 0.1^\circ\text{C}$ . Each sample was pre-thermostated for 15 min.

The composite suspension fuel (CSF) with a solid phase concentration of 58 wt.% was prepared by mixing pyrocarbon (fraction  $< 200 \mu\text{m}$ ) with a dispersion medium containing 2% plasticizer C3 (product of polycondensation of  $\beta$ -naphthalene sulfonic acid and formaldehyde, according to the technical specifications TU 5870-005-58042865-05) and 0.5% stabilizer OP-10 (product of ethoxylation of a mixture of mono- and dialkylphenols with 10 degrees of ethoxylation, UCGFE code 3402 90 10 00). Homogenization was carried out in two stages: mechanical stirring for 40 min followed by cavitation treatment in a rotor-pulsation disperser to achieve colloidal stability.

### **Results and discussion**

Unlike fossil coal, pyrocarbon has a complex heterogeneous structure. According to the obtained SEM micrographs (Fig. 1), the material consists of aggregated carbon nanoglobules with a pronounced fragmented relief.

Scanning electron microscopy in backscattered electron (BSE) mode revealed the heterogeneous structure of pyrocarbon, which consists of a carbon matrix with a high degree of particle aggregation. The material exhibits a characteristic fragmented structure with sharp-angled fractures of particles. The aggregate size varies widely from 10 to 300  $\mu\text{m}$ , indicating intensive mechanical grinding of the initial pyrolysate.

White inclusions ranging in size from 0.2 to 2.0  $\mu\text{m}$  were identified as the mineral phase, predominantly zinc sulfide (2.71 wt.%), confirming their exogenous origin as residues of vulcanization activators.

It was also established that the surface of the carbon particles is characterized by low visible porosity and the presence of adsorbed films. This «smoothed» relief morphology and the absence of a developed system of open micropores in contrast to carbon black micrographs at the same scale correlate well with the high content of volatile matter (19.65 wt.%). In particular, the presence of heavy petroleum oils and resinous products of elastomer degradation (styrene and isoprenoid compounds) leads to shielding of the carbon framework and filling of internal voids with a condensed liquid phase.

Local energy-dispersive X-ray spectroscopy (EDS) allowed identification of the chemical nature of the high-contrast inclusions in the pyrocarbon matrix

(Fig. 2, Table 1). The most representative data were obtained for Spectrum 3 (Zn 18.48%, S 8.63%) and Spectrum 2 (Zn 12.40%, S 5.98%). Calculation of the atomic ratios for both points ( $n(\text{Zn}):n(\text{S})=1.05:1$  and  $1.02:1$ , respectively) confirms the presence of the stable zinc sulfide phase (ZnS) with a 1:1 stoichiometry. Spectrum 1 shows dominance of calcium (Ca 21.75%) and silicon (Si 16.20%), corresponding to hydrophilic silicates and calcium oxides. Spectrum 4 was identified as the carbon matrix of pyrocarbon. Spectrum 1 corresponds to an oxide-calcium mineral inclusion.

It should be noted that after the pyrolysis process zinc is present in the form of hydrophobic ZnS [4] and is localized as separate bright nano- and micro-inclusions, which result from the transformation of vulcanization components of the original rubber feedstock.

Pyrocarbon obtained after low-temperature pyrolysis of tires (400–430°C for 8 hours) is a multiphase material consisting of a carbon matrix, mineral (ash) fraction, volatile substances, and surface products of incomplete destruction (Table 2). The carbon matrix constitutes approximately 61 wt.% and is the main carrier of mechanical stability. It consists of amorphous–turbostratic carbon, and this phase determines the rheological properties of the suspension by forming a rigid network of interparticle contacts.

The mineral ash additives (16.5%) are distributed almost uniformly throughout the volume of the pyrocarbon particles, as confirmed by recent studies [7,8]. Fine-dispersed  $\text{SiO}_2$  increases viscosity due to the formation of contacts with the carbon matrix, while ZnS and MgO can act as aggregation centers.

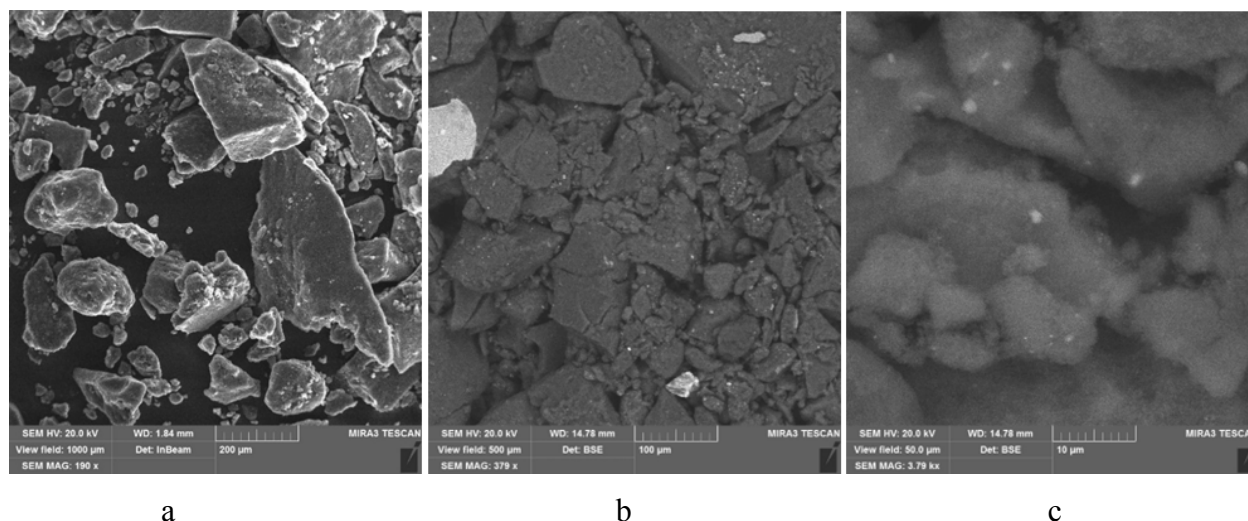
Light gaseous inclusions (methane, ethane,

propane, butane,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ) remain predominantly trapped in the internal pores of pyrocarbon. This explains the presence of a microporous structure and its effect on rheology upon heating: at low temperatures they remain encapsulated, while at elevated temperatures they partially desorb, reducing internal friction [9]. This component of pyrocarbon is responsible for the pronounced non-determinacy of suspension rheology during preparation and colloidal system homogenization.

The surface of pyrocarbon particles is coated with rubber degradation products that did not complete their pyrolytic transformation, as well as condensation products formed during cooling of the pyrolysis furnace after incomplete extraction of liquefied and gasified hydrocarbons [10]. As a result of this condensation, the pyrocarbon surface becomes extremely hydrophobic. This property determines the specific rheological and thermorheological behavior of the water-pyrocarbon suspension: hydrophobic particle surfaces hinder wetting by water, promote aggregation and cluster formation, increase the yield stress, and induce thixotropic effects [5,10,11].

Thus, pyrocarbon obtained from tire pyrolysis is a multiphase system in which the carbon matrix provides stability, mineral ash components are uniformly distributed within the particles, gaseous inclusions remain encapsulated in pores, and the surface acquires hydrophobicity due to products of incomplete destruction and condensation. The combination of these factors governs the rheological properties of the suspension and their temperature dependence.

The system under study is an aqueous carbon-



**Fig. 1.** SEM micrographs of pyrocarbon: in-beam detector image showing detailed surface texture (a); BSE detector images (b, c)

containing suspension with a high solids content (58 wt.%), modified with plasticizer C3 (2.0 wt.%) and stabilizer OP-10 (0.5 wt.%). Such a composition is typical for suspension fuels, where the balance between high concentration of the energy carrier and rheological stability is critical.

During the experiments, a clear dependence of the rheological characteristics on temperature was revealed. Analysis of the shear stress versus shear rate curves showed pronounced nonlinearity, indicating non-Newtonian behavior of the system.

In a previous study [12], the nonlinearity of the rheological behavior of such carbon-containing suspensions at different temperatures and solids concentrations was demonstrated, and their thixotropic properties were established. At low temperatures (10–20°C), the suspension is characterized by high shear stress values and pronounced pseudoplasticity: the effective viscosity decreases sharply with increasing deformation rate. Further heating of the system to

approximately 40°C is accompanied by significant thinning, caused by a decrease in the viscosity of the aqueous phase and softening of the resinous components coating the pyrocarbon particles. At 50°C, a certain rheological anomaly was detected, manifested by a significant increase in flow resistance, which contradicts the classical concept of suspension behavior under thermal thinning of water.

This complex dynamics from the initial viscoplastic state to the zone of maximum fluidity followed by anomalous thickening via the thermorhepepy mechanism makes the use of simple linear models impossible.

To adequately describe these dependences, several rheological models were considered. The Newtonian model proved unsuitable because it does not account for either the yield stress or nonlinearity. The Bingham model ( $\tau = \tau_0 + \eta \cdot \dot{\gamma}$ ) takes the yield stress into account but assumes a linear dependence after it is exceeded, which does not correspond to our data. The power-

Table 1  
Elemental composition of pyrocarbon determined by local energy-dispersive X-ray spectroscopy (EDS)

Area in Fig. 2	Content, %									
	C	O	Mg	Al	Si	S	Ca	Cu	Zn	Total
Spectrum 1	33.35	40.06	–	–	0.21	0.31	24.70	0.88	0.50	100.00
Spectrum 2	75.10	3.76	–	0.07	0.93	5.98	0.88	0.88	12.40	100.00
Spectrum 3	62.05	7.88	0.28	0.09	0.76	8.63	0.32	1.50	18.48	100.00
Spectrum 4	91.30	2.36	–	0.06	0.16	1.92	0.08	0.50	3.60	100.00

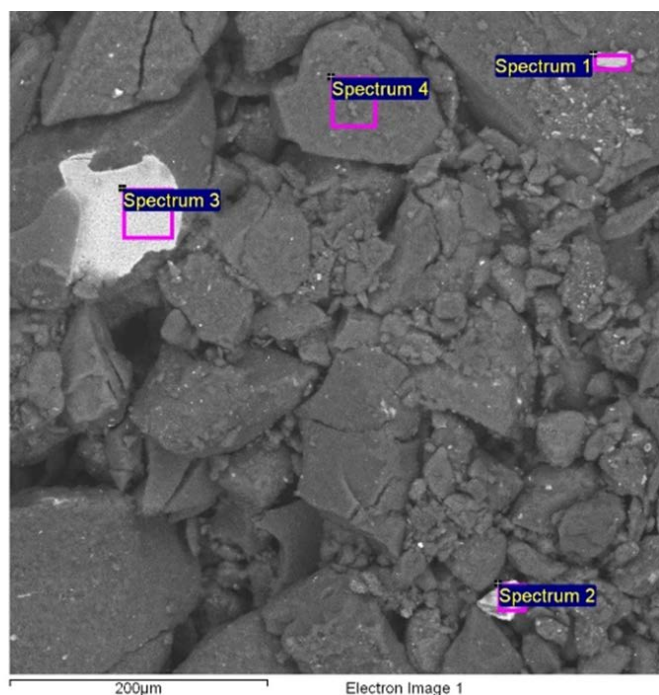


Fig. 2. SEM micrograph of the pyrocarbon surface with marked areas where the chemical composition was determined by EDS

law Ostwald–de Waele model ( $\tau = \kappa \cdot \gamma^n$ ) describes pseudoplastic fluids but does not include the yield stress, which is crucial for carbon suspensions.

The three-parameter Herschel–Bulkley model was chosen to describe the rheological behavior of the investigated system:

$$\tau = \tau_0 + \kappa \cdot \gamma^n, \quad (1)$$

where  $\tau$  is the shear stress (Pa),  $\tau_0$  is the yield stress (Pa),  $\kappa$  is the consistency coefficient,  $\gamma$  is the shear rate ( $s^{-1}$ ), and  $n$  is the flow behavior index (structure breakdown index).

The selection of this model made it possible to

quantitatively differentiate the contribution of the strength of the coagulation framework ( $\tau_0$ ) and the viscous resistance of the broken-down structure ( $\kappa$ ).

Quantitative evaluation of the rheological parameters of the investigated system ( $\tau_0$ ,  $\kappa$ ,  $n$ ) was performed by non-linear regression analysis of the experimental data presented in Table 3.

The adequacy of the selected model was assessed by the coefficient of determination ( $R^2$ ), calculated according to the following formula:

$$R^2 = 1 - \frac{\sum (\tau_{\text{exp}} - \tau_{\text{theor}})^2}{\sum (\tau_{\text{exp}} - \tau'_{\text{exp}})^2}, \quad (2)$$

Table 2

Complete structural model of pyrocarbon after low-temperature pyrolysis of waste automobile tires

Group	Component	Content in total pyrocarbon, wt. %	Content within group, %
Carbon matrix	Carbon	60.95	100.0
Mineral (ash) fraction	SiO <sub>2</sub>	8.45	51.51
	ZnO	2.71	16.50
	MgO	2.13	13.01
	CaO	0.98	6.01
	SO <sub>3</sub>	0.96	5.85
	Others (Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , etc.)	1.17	7.12
	Subtotal	16.40	100.0
Volatile substances			
Gas phase (light)	Methane, ethane, propane, butane	0.26	1.33
	Hydrogen sulfide	0.03	0.15
	Pentane, hexane	0.05	0.25
	Carbon dioxide	0.05	0.25
	Subtotal	0.39	1.98
Oils and resins (liquid)	Paraffins and naphthenes	3.34	16.99
	Heavy petroleum oils	3.34	17.00
	Subtotal	6.68	33.99
Products of natural (NR) and synthetic (SR) rubber degradation	Styrene compounds	5.70	29.01
	Isoprenoids (NR/limonene)	4.92	25.04
	Subtotal	10.62	54.05
Aromatic compounds and heteroatoms	Polycyclic aromatic hydrocarbons (anthracene, pyrene, etc.)	1.33	6.77
	Organic sulfur (thiophenes)	0.63	3.21
	Subtotal	1.96	9.98
Volatile substances total	Subtotal	19.65	100.0
Residual moisture		3.00	100.0
Pyrocarbon	TOTAL	100.00	–

where  $\tau_{\text{exp}}$  are the experimental shear stress values,  $\tau_{\text{theor}}$  are the theoretical values calculated by the model, and  $\tau'_{\text{exp}}$  is the arithmetic mean of the experimental shear stress values.

The high adequacy of the chosen model is confirmed by the coefficient of determination values ( $R^2=0.9910-0.9989$ ) over the entire investigated temperature range.

The dynamics of the calculated parameters revealed a unique evolution of the system microstructure under the influence of temperature. Figure 3 shows the complex interrelationship of the model parameters as the suspension temperature changes.

At 10°C, the yield stress is zero ( $\tau_0=0$ ), indicating the absence of a rigid spatial framework. The system behaves as a classical pseudoplastic fluid, where flow resistance is determined solely by the viscosity of the water-resin medium and the orientation of nanoglobules in the flow. This allows identification of the system as a power-law pseudoplastic fluid (Ostwald–de Waele model) and indicates the absence of strong coagulation bonds between particles at rest. The high consistency coefficient ( $\kappa=3.267$ ) and low flow behavior index ( $n=0.592$ ) indicate significant internal resistance of the system, which, however, decreases sharply with increasing deformation rate due to the orientation of nanoglobules in the flow.

An increase in temperature to 20°C initiates the appearance of the first non-zero yield stress ( $\tau_0=0.312$  Pa), which at 30°C increases almost five-fold to 1.448 Pa, while the consistency coefficient  $\kappa$  continues to decrease quite sharply. Physically, this means «softening» of the surface resins and the beginning of partial dehydration of the surfactant, allowing pyrocarbon particles to overcome the energy barrier and form the first unstable bridges. The

framework strengthens, but the flow resistance decreases, and the overall fluidity remains almost unchanged. The system transitions from a power-law fluid to a viscoplastic body, i.e., the framework begins to form.

With a further temperature rise to 42°C, a progressive increase in  $\tau_0$  to 3.254 Pa is observed, indicating intensification of interparticle contacts. Simultaneously, the consistency coefficient  $\kappa$  decreases regularly from 3.267 to 1.223 Pa·s<sup>n</sup>, which correlates with thermal thinning of the dispersion medium and softening of the adsorbed hydrocarbon resins. In this zone, the rheological optimum is reached (at 42°C), where the viscous resistance of the broken-down structure is minimal.

However, upon reaching 50°C, a sharp inversion of the rheological trend is recorded. The coefficient  $\kappa$  anomalously increases more than twofold (to 2.898 Pa·s<sup>n</sup>), and the flow behavior index  $n$  drops to its minimum value ( $n=0.527$ ), indicating the transition of the system to a highly structured viscoplastic gel state. This thermorheopexy effect is explained by destabilization of the adsorption barrier of the non-ionic surfactant OP-10 (near its cloud point).

The loss of steric protection triggers spontaneous flocculation of ZnS nanoparticles and pyrocarbon nanoglobules, forming a rigid spatial network. The high value of  $\tau_0=3.756$  Pa and the low  $n$  confirm that at 50°C the deformation resistance is determined no longer by the viscosity of the phases but by the mechanical strength of the formed coagulation framework.

It has been established that the observed thermorheopexy effect is a direct consequence of the destabilization of the adsorption layers of the surfactant OP-10 (technical analogue of Triton X-100) near its cloud point. This process is accompanied by intensive

Table 3

Experimental values of shear stress at different temperatures

Shear rate, $\gamma, \text{s}^{-1}$	Shear stress, $\tau, \text{Pa}$				
	10°C	20°C	30°C	42°C	50°C
1.0	4.776	4.78	4.776	4.179	6.57
1.8	5.97	5.37	4.776	5.373	7.76
3.0	6.567	5.97	5.97	5.97	8.66
5.4	8.358	7.76	7.761	7.164	11.34
9.0	11.343	10.75	9.552	8.955	12.54
16.2	15.522	14.93	10.746	10.746	17.31
27.0	20.895	20.90	13.731	14.925	20.30
48.6	31.044	25.67	20.895	19.104	24.48
81.0	41.79	40.60	30.447	28.656	34.03
145.8	63.25	60.38	44.775	37.611	42.98
243.0	92.0	92.0	63.25	54.625	57.50
437.4	115.0	115.0	80.5	78.0	74.75

dehydration of the polyoxyethylene chains of the surfactant and loss of the steric barrier [13]. This leads to exposure of the hydrophobic regions of pyrocarbon nanoglobules and ZnS nanoparticles, causing the dominance of interparticle attraction forces over the thermal viscosity reduction of the dispersion medium [2]. Thus, at 50°C a thermodynamically driven flocculation occurs in the system, which provides anomalous strengthening of the structural network and ensures high sedimentation stability of the suspension at rest.

The presence of zinc specifically in the form of hydrophobic ZnS, which is the second most abundant mineral component in pyrocarbon (2.71 wt.% recalculated as oxide), is an additional factor explaining the rheological anomaly at 50°C. Due to its low wettability and high affinity for adsorbed resins, micro- and nanoparticles of ZnS act as active centers of hydrophobic flocculation during thermal destabilization of OP-10 (cloud point). This leads to the formation of a strong spatial framework through the formation of coagulation contacts between zinc sulfide and pyrocarbon nanoglobules. This mechanism accounts for the experimentally observed sharp increase in yield stress ( $\tau_0$ ) and consistency coefficient ( $\kappa$ ), which dominates over the thermal viscosity reduction of the aqueous phase.

To gain deeper insight into the structural changes in the suspension, the activation energy ( $E_a$ ) was calculated. In accordance with recommendations for the analysis of non-linear systems, the calculation

was based on the temperature dependence of the effective viscosity ( $\eta_{app}$ ) at a fixed shear rate  $\dot{\gamma}=81 \text{ s}^{-1}$ . The use of the integral parameter  $\eta_{app}$  made it possible to eliminate the mutual influence of the Herschel–Bulkley model parameters and to ensure high reliability of the approximation by the Arrhenius equation:

$$\ln \eta_{app} = \ln \kappa_0 - \frac{E_a}{RT}, \quad (3)$$

where  $\eta_{app}$  is the effective viscosity (Pa·s),  $\kappa_0$  is the pre-exponential factor (structural factor, Pa·s<sup>n</sup>),  $E_a$  is the viscous flow activation energy (J·mol<sup>-1</sup>), R is the universal gas constant (8.314 J·(mol·K)<sup>-1</sup>), and T is the absolute temperature (K).

The results of regression analysis in the coordinates  $\ln \eta_{app}$  vs. (1000/T) (Table 4) allowed identification of two fundamentally different thermorheological regimes.

Thermodynamic confirmation of the revealed rheological anomaly was obtained by calculating the activation energy ( $E_a$ ) based on the temperature dependence of the effective viscosity ( $\eta_{app}$ ) at a fixed shear rate  $\dot{\gamma}=81 \text{ s}^{-1}$ . Construction of the Arrhenius plot ( $\ln \eta_{app}$  vs. 1000/T) allowed identification of the rheological inversion point at 42°C (3.17·10<sup>-3</sup> K<sup>-1</sup>), which corresponds to the state of minimum structuring of the system (Fig. 4, Table 5).

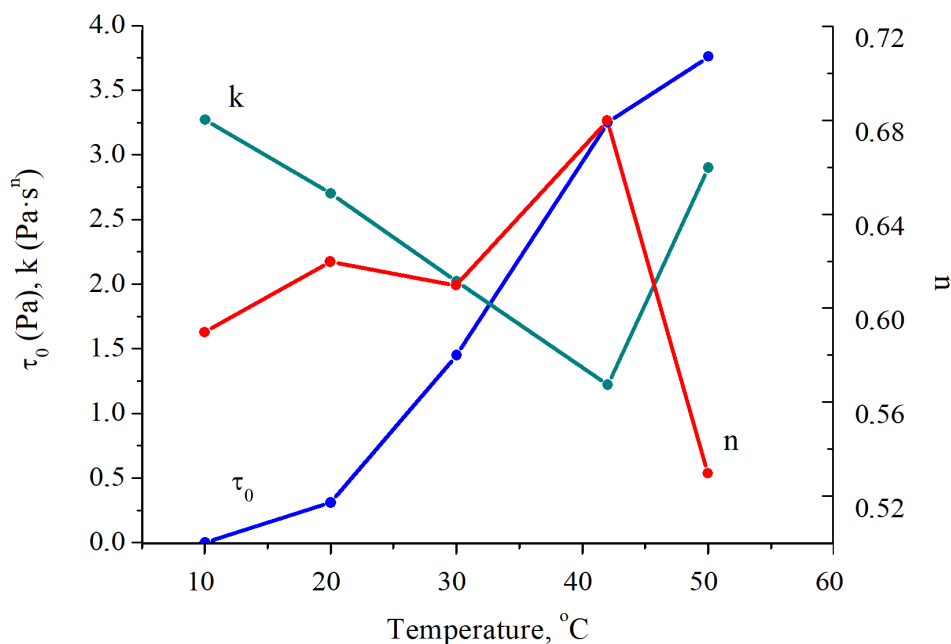


Fig. 3. Rheological parameters of the Herschel–Bulkley model for pyrocarbon suspension

In the range of 10–42°C, the flow process is characterized by a positive activation energy  $E_a=+9.87 \text{ kJ}\cdot\text{mol}^{-1}$ . The coefficient of determination  $R^2=0.8829$  indicates a complex nature of structural rearrangements in this zone: thermal thinning of the aqueous phase is accompanied by significant resistance from viscous resinous components and gases encapsulated in the micropores of pyrocarbon, which causes some nonlinearity of the trend in the 10–20°C range.

In contrast, in the narrow range 42–50°C, a sharp change in the slope of the approximating straight line ( $R^2=1.000$ ) and a transition to negative values of the apparent activation energy ( $E_a=-18.18 \text{ kJ}\cdot\text{mol}^{-1}$ ) were observed. This anomalous thermodynamic response is indisputable proof of thermo-induced flocculation. The increase in viscosity upon heating above 42°C confirms the formation of a rigid spatial framework due to destabilization of the adsorption layers of OP-10 (dehydration of polyoxyethylene chains) and aggregation of micro- and nanoparticles of ZnS with pyrocarbon nanoglobules. This mechanism completely nullifies the contribution of thermal thinning of the dispersion medium, transforming the

suspension into a structured viscoplastic gel.

Although the cloud point of aqueous solutions of the non-ionic surfactant OP-10 is usually 65–75°C, a significant decrease in this temperature threshold is observed in the studied dispersion system. This phenomenon is caused by an increase in the ionic strength of the dispersion medium due to partial dissolution of the mineral components of pyrocarbon. Upon heating the system to 50°C, the mineral inclusions containing elements identified by EDS (Zn, Ca, Mg) act as a source of inorganic electrolytes (mainly metal sulfates and oxysulfates). The presence of multiply charged cations ( $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in the solution leads to intensive dehydration of the polyoxyethylene chains of the surfactant due to the «salting-out» effect. This causes thermodynamic instability of the OP-10 adsorption layers already at 50°C (15–20°C below standard values), resulting in the transition of the system to the thermorhepepy state [14]. The process is confirmed by the sharp increase in activation energy and the formation of a rigid flocculation framework, where micro- and nanoparticles of sulfides (ZnS) and oxide phases act as active aggregation centers under the conditions of a

Table 4

Calculated thermodynamic flow parameters of the suspension at  $\gamma=81 \text{ s}^{-1}$ 

Temperature interval, °C	Activation energy $E_a$ , $\text{kJ}\cdot\text{mol}^{-1}$	Coefficient of determination $R^2$	Character of the process
10–42	+9.87	0.8829 (4 points)	Thermal thinning of phases
42–50	-18.18	1.000 (2 points)	Thermo-induced flocculation

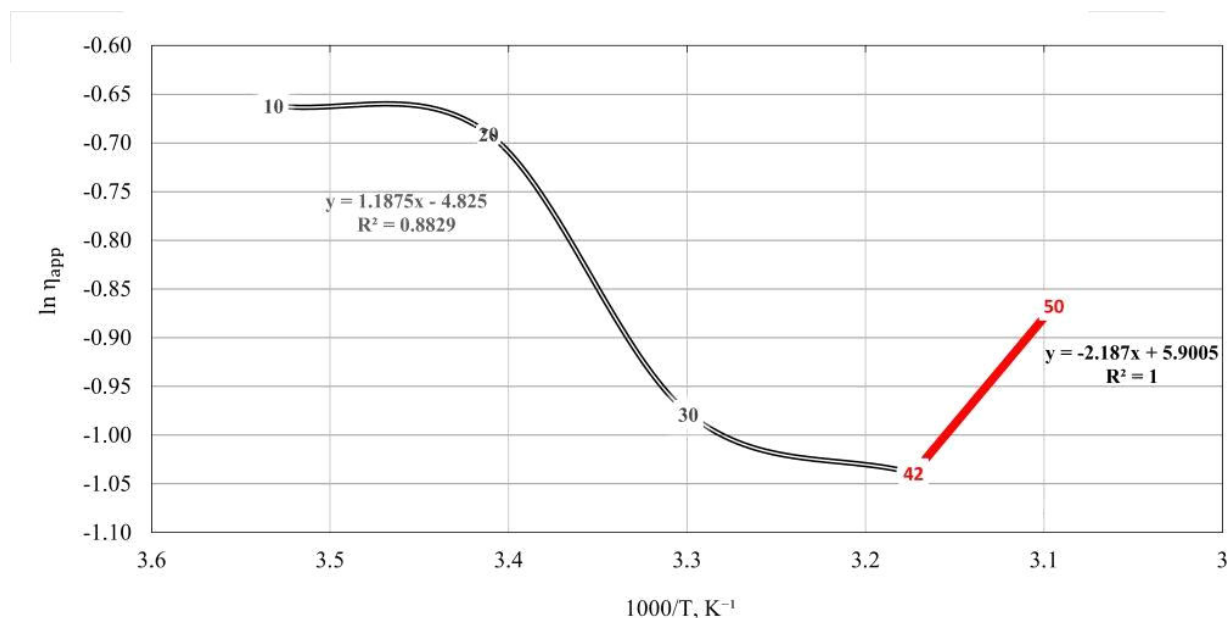


Fig. 4. Temperature dependence of the effective viscosity in Arrhenius coordinates for the suspension at  $\gamma=81 \text{ s}^{-1}$ . The numbers on the curve are temperature (in °C)

destabilized protective surfactant layer.

Comparative analysis of the rheological behavior of the obtained suspension with classical coal-water fuel (CWF) based on anthracite (grade A) and long-flame coal (grade DG) reveals fundamental differences in temperature trends. Traditional CWFs stabilized with non-ionic surfactants of the OP-10 type exhibit a monotonic decrease in viscosity and yield stress upon heating from 20 to 60°C [2]. This is explained by the dominance of thermal thinning of the aqueous phase and the relatively low specific surface area of fossil coal particles, which neutralizes the surfactant dehydration effect. In the case of pyrocarbon, the presence of 19.65% adsorbed oils and resins together with the nanoglobular morphology makes the system critically sensitive to the state of the adsorption layer, leading to viscosity inversion at 50°C.

Unlike grade DG coal, where volatile substances are located mainly inside macropores, in the studied pyrocarbon the hydrocarbon fraction is localized on the surface of the nanoglobules, forming a «sticky» adhesive layer. This structure brings the material closer to technical carbon black. However, according to studies of nanodispersions of carbon black [15], their stability is usually limited only by Brownian motion and electrostatic repulsion. In our system, the presence of 2.71% nanodispersed ZnS (identified by EDS) acts as an additional factor of thermorheopexy. Upon destabilization of OP-10, the hydrophobic zinc sulfide particles become centres of flocculation, forming rigid «bridges» between pyrocarbon aggregates – a phenomenon not characteristic of pure carbon black suspensions.

To confirm the systematic nature of the obtained result, the experimental data presented in Table 3 were analyzed for all 12 measured shear rates. All calculation results are summarized in Table 6.

The thermodynamic analysis (Table 6) confirmed that the thermorheopexy effect is systematic: in the 10–42°C interval,  $E_a$  is positive (from +2.0 to +13.5 kJ·mol<sup>-1</sup>), corresponding to normal thermal thinning. Upon transition through 42°C,  $E_a$  becomes sharply negative for 11 out of 12 shear rates (from –50.5 to –5.4 kJ·mol<sup>-1</sup>). With increasing shear rate,

the thermorheopexy effect gradually weakens and disappears at  $\dot{\gamma}=437$  s<sup>-1</sup>. The negative value of  $E_a$  is direct thermodynamic evidence of the dominance of the flocculation process over thermal thinning, confirming the mechanism of destabilization of the adsorption layers of OP-10 and the participation of hydrophobic micro- and nanoparticles of ZnS.

### Conclusions

For the first time, it has been established that carbon-containing suspensions based on pyrocarbon exhibit inversion of the rheological trend at 42°C. Up to this point, classical thermal thinning is observed, while above this temperature anomalous thickening occurs via the thermorheopexy mechanism.

Mathematical modelling confirmed the adequacy of the Herschel–Bulkley model ( $R^2>0.99$ ) for describing the system. At 50°C, the yield stress ( $\tau_0$ ) increases to 3.76 Pa, indicating the formation of a rigid coagulation framework.

It has been proven that the cause of thermorheopexy is dehydration of the OP-10 surfactant, accelerated by the «salting-out» effect of metal cations (Zn<sup>2+</sup>, Ca<sup>2+</sup>) released into solution from the mineral phase of pyrocarbon.

The role of micro- and nanoparticles of ZnS, identified by EDS, has been determined as active centers of hydrophobic flocculation that provide high sedimentation stability of the fuel upon heating.

The obtained results allow optimization of the temperature regimes for the use of composite suspension fuels, avoiding zones of excessive thickening during transportation and combustion.

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Table 5

Summary table for calculation of activation energy  $E_a$  (at  $\dot{\gamma}=81$  s<sup>-1</sup>)

$t, ^\circ\text{C}$	$\tau, \text{Pa}$	$\eta_{\text{app}}, \text{Pa}\cdot\text{s}$	$\ln \eta_{\text{app}}$	$1000/T, \text{K}^{-1}$
10	41.790	0.520	-0.662	3.532
20	40.596	0.501	-0.691	3.411
30	30.447	0.376	-0.979	3.298
40	28.656	0.354	-1.039	3.173
50	34.029	0.420	-0.867	3.095

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Table 6

Calculated activation energy ( $E_a$ ) values at various shear rates for a pyrocarbon suspension

$\dot{\gamma}$ , $\text{c}^{-1}$	$E_a$ , $\text{kJ}\cdot\text{mol}^{-1}$	$R^2$	$E_a$ , $\text{kJ}\cdot\text{mol}^{-1}$	$R^2$	Character of the process
	range of temperatures				
	10–42 <sup>0</sup> C		42–50 <sup>0</sup> C		
1.00	+2.84	0.615	–47.89	1.000	strong flocculation
1.80	+2.97	0.361	–38.91	1.000	strong flocculation
3.00	+2.00	0.598	–39.37	1.000	strong flocculation
5.40	+3.25	0.910	–48.61	1.000	strong flocculation
9.00	+5.77	0.974	–35.64	1.000	strong flocculation
16.20	+9.93	0.826	–50.46	1.000	strong flocculation
27.00	+9.87	0,679	–32.55	1.000	strong flocculation
48.60	+11.59	0.970	–26.24	1.000	strong flocculation
81.00	+9.87	0.883	–18.19	1.000	thermo-induced flocculation
145.80	+12.97	0.935	–14.12	1.000	flocculation
243.00	+13.50	0.881	–5.43	1.000	weak flocculation
437.40	+10.56	0.819	+4.50	1.000	inversion not manifested

## ТЕРМОРЕОПЕКСІЯ ТА СТРУКТУРНА СТАБІЛЬНІСТЬ ВУГЛЕЦЬВМІСНИХ СУСПЕНЗІЙ НА ОСНОВІ ПІРОКАРБОНУ

V.V. Zinin, Yu.V. Polishchuk, O.V. Shkutkova

Досліджено терморологічну поведінку композиційних суспензійних палив на основі пірокарбону, отриманого шляхом низькотемпературного піролізу відпрацьованих автомобільних шин. Пірокарбон характеризується специфічною наноглобулярною структурою та високою гідрофобністю, що відрізняє його від традиційного виваленого вугілля. Методами сканувальної електронної мікроскопії та енергодисперсійної спектроскопії встановлено багатофазну структуру матеріалу, яка включає вуглецеву матрицю та нанодисперсні включення сульфиду цинку ZnS. Реологічні параметри системи (58% твердої фази) розраховано за трипараметричною моделлю Гершеля–Балклі в діапазоні температур 10–50°C. Виявлено аномальний ефект терморепексії (антитиксотропії) при нагріванні вище 42°C, що супроводжується різким зростанням границі текучості та коефіцієнта консистентності. Розрахунок енергії активації в'язкої течії за рівнянням Арреніуса підтвердив зміну термодинамічного режиму практично для всіх виміряних швидкостей: від термічного розрідження (10–42°C,  $E_a=9,87$  кДж/моль) до термоіндукованої флокуляції (42–50°C,  $E_a=-18,18$  кДж/моль). Встановлено, що механізм аномального згущення зумовлений дестабілізацією адсорбційних шарів неіоногенної поверхнево активної речовини при наближенні до точки помутніння, що підсилюється високою іонною силою розчину та наявністю гідрофобних центрів агрегації у формі мікро і наночасток ZnS. Отримані результати дозволяють оптимізувати температурні режими транспортування та спалювання пірокарбонівих суспензій.

**Ключові слова:** терморологія, терморепексія, модель Гершеля–Балклі, енергія активації, ефективна в'язкість, композиційні суспензійні палива, пірокарбон.

## THERMORHEOPEXY AND STRUCTURAL STABILITY OF CARBONACEOUS SUSPENSIONS BASED ON PYROCARBON

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The thermo-rheological behavior of composite suspension fuels based on pyrocarbon obtained by low-temperature pyrolysis of waste automobile tires was investigated. Pyrocarbon is characterized by a specific nanoglobular structure and high hydrophobicity, which distinguishes it from traditional fossil coal. Using scanning electron microscopy and energy-dispersive X-ray spectroscopy, the multiphase structure of the material was established, including a carbon matrix and nanodispersed inclusions of zinc sulfide (ZnS). The rheological parameters of the system (58 wt.% solid phase) were calculated using the three-parameter Herschel–Bulkley model in the temperature range of 10–50°C. An anomalous thermorhepepy (anti-thixotropy) effect was revealed upon heating above 42°C, accompanied by a sharp increase in yield stress and consistency coefficient. Calculation of the viscous flow activation energy according to the Arrhenius equation confirmed a change in the thermodynamic regime for almost all measured shear rates: from thermal thinning (10–42°C,  $E_a=+9.87$  kJ·mol<sup>-1</sup>) to thermo-induced flocculation (42–50°C,  $E_a=-18.18$  kJ·mol<sup>-1</sup>). It was established that the mechanism of anomalous thickening is caused by destabilization of the adsorption layers of the non-ionic surfactant near its cloud point, intensified by the high ionic strength of the solution and the presence of hydrophobic aggregation centers in the form of micro- and nanoparticles of ZnS. The obtained results make it possible to optimize the temperature regimes for transportation and combustion of pyrocarbon-based suspensions.

**Keywords:** thermorheology; thermorheopepy; Herschel–Bulkley model; activation energy; effective viscosity; composite suspension fuels; pyrocarbon.

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