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V.V. Zinin^{a, b}, *O.V. Shkutkova*^c, *I.V. Kornienko*^c, *Yu.V. Polishchuk*^a, *A.S. Makarov*^c**RHEOLOGICAL PROPERTIES OF COMPOSITE SUSPENSIONS BASED ON PYROLYSIS PRODUCTS OF TIRES OBTAINED BY WET GRINDING METHOD**^a Ukrainian State University of Science and Technologies, Dnipro, Ukraine^b LIQUID CARBO LLC, Kyiv, Ukraine^c A.V. Dumansky Institute of Colloid and Water Chemistry of NAS of Ukraine, Kyiv, Ukraine

A promising approach to addressing the shortage of traditional energy carriers in Ukraine is the development of suspension fuels based on secondary raw materials. One such resource is waste automobile tires, the accumulation of which has become a serious global environmental problem. Pyrolysis is considered the most effective method for tire recycling, producing gaseous products, liquid pyrolysis products (LPP), pyrocarbon, and metal cord. In this study, composite suspension fuels were prepared by wet milling of pyrocarbon obtained from tire pyrolysis with the addition of 10 wt.% LPP. The rheological and sedimentation properties of the suspensions were investigated at various concentrations of dispersant C-3, stabilizer OP-10, and solid pyrocarbon phase. The results showed that optimal apparent viscosity was achieved at 1.5–2.0 wt.% C-3 and 0.5 wt.% OP-10 for both types of suspensions. The most favorable viscosity characteristics were observed for suspensions containing 50–56 wt.% solid phase and 10 wt.% LPP. A maximum solid loading of up to 60 wt.% was obtained in suspensions without LPP. Sedimentation stability exceeded 20 days for suspensions with 50–52 wt.% solid phase and reached up to 47 days for the obtained formulations. The findings indicate that pyrocarbon-based suspension fuels are suitable for application in liquid-fuel boiler systems.

Keywords: apparent viscosity, composite suspensions, pyrocarbon, rheological properties, sedimentation stability.

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Introduction

In modern conditions, where environmental protection is a crucial factor for the existence and development of civilization, an urgent problem is the disposal of waste and its conversion into secondary raw materials. Particular attention should be paid to used automobile tires, the accumulation volumes of which have reached significant levels worldwide. At the same time, this type of waste represents a valuable resource, since tires are manufactured from vulcanized natural and styrene-butadiene rubber (accounting for 41–45%), steel (13–15%), carbon black (about 28%),

and polymer fibers, as well as organic and inorganic compounds (14–17%), namely accelerators and antioxidants such as sulfur, zinc oxide, and silicon dioxide [1].

The most promising method of tire recycling is pyrolysis – a process of decomposition at temperatures of 450–600°C in the absence of air. This method not only enables the utilization of tires and polymeric materials but also significantly reduces emissions of toxic oxides of sulfur, nitrogen, and carbon into the atmosphere [2]. As a result of pyrolysis, intermediate products are formed: gas, liquid pyrolysis product

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(LPP), carbonaceous solid residue (pyrocarbon), and metal cord [3]. The further use of these products in various industrial sectors is a key element of an integrated approach to reducing the toxic burden on the environment.

Pyrocarbon, as an energy carrier, represents a real alternative to traditional coal, liquid fuels (fuel oil, diesel), and gaseous fuels. For the formation of fuel compositions, a promising approach is its dispersion in various liquid organic-containing wastes, such as used lubricants [4], effluents from the food [5] and pharmaceutical industries, wash waters containing surfactants and solvents [6]. The use of these secondary resources not only increases the energy value of composite suspension fuel (CSF) but also simultaneously addresses the problem of disposing of harmful organic-containing effluents. An important advantage of CSF is the possibility of its application in existing liquid-fuel boilers, which is particularly relevant for Ukraine under conditions of shortage of traditional energy carriers.

The aim of this study was to obtain composite suspension fuel from secondary products of tire pyrolysis—solid (pyrocarbon) and liquid (LPP) by wet grinding in a ball mill, and to investigate the rheological properties and sedimentation stability of composite suspensions based on pyrocarbon with the addition of LPP.

Experimental

Pyrocarbon was obtained by low-temperature pyrolysis of passenger car tires at a pyrolysis temperature of 400–450°C. The pyrolysis was carried out in a vertical-type furnace with a retort volume of 1200 kg of rubber. The tires were preliminarily cut into four parts. The heating rate was 2.5 hours, the duration of the pyrolysis process was 8 hours, and cooling of the retort took 6 hours. As a result, the final pyrolysis products were obtained: up to 5 wt.% pyrolysis gas, 35–40 wt.% pyrocarbon, 35 wt.% liquid pyrolysis product (LPP), 20 wt.% metal cord, and traces of pyrolytic water.

Technical and elemental analysis of pyrocarbon was performed according to the state standards DSTU EN 14774-1, DSTU EN 15403, ISO 1171, DSTU EN 15148:2012, DSTU ISO 1928, DSTU EN 15289:2013, DSTU EN 15104:2013, and DSTU 9045:2020.

To study the chemical nature of pyrocarbon, the number of surface functional groups was determined by potentiometric titration according to Boehm [7]: COOH, OH, >C=O, using reagents such as 0.05 M NaOH, Na₂CO₃, and NaHCO₃. The amount of basic NH₂ groups was determined according to the method described in ref. [8].

Micrographs of pyrocarbon were obtained using

a scanning electron microscope (SEM) MIRAZ TESCAN (Czech Republic), which provides high-precision probing.

The chemical composition of pyrocarbon surface groups was determined by IR spectroscopy using the «Avatar 370 FT-IR, Thermo Nicolet» instrument in the range of 4000–400 cm⁻¹. For analysis, three samples were prepared by pressing pre-ground pyrocarbon mixed with KBr powder in a ratio of 1:100 in an agate mortar.

For component identification, the obtained spectra were compared with reference and standard spectra from the instrument database (EZ Omnic v. 7.0 software) and with spectra reported in the literature [9]. The spectra of all three samples were identical.

Structural–sorption characteristics of pyrocarbon: specific surface area (S_{sp} , m²·g⁻¹), specific pore volume (V_{pore} , cm³·g⁻¹), and effective pore diameter (d_{pore} , nm), were determined using density functional theory (DFT) based on low-temperature nitrogen adsorption data (77 K) obtained with a Quantachrome Autosorb surface analyzer. Data processing was performed using Quantachrome Instruments software v. 3.2.

The apparent viscosity (η) of the samples was measured using a Rheotest-2 instrument at $t=20^{\circ}\text{C}$ and shear rate $Dr=9\text{ s}^{-1}$. The measurement range of shear rates Dr was limited to 1–450 s⁻¹.

Sedimentation stability (St) was studied by monitoring the stratification time of CSF samples in a graduated cylinder.

Grinding of the initial pyrocarbon ($d=1\text{ mm}$) was carried out in a roller mill with a porcelain drum of 2 dm³ capacity using ceramic balls. To standardize the sample and eliminate the influence of particle size distribution on rheological properties, the ground product was classified by sieving through SLM 300 sieves. The pyrocarbon fraction contained particles up to 300 μm .

For the preparation of CSF, mechanochemical treatment of pyrocarbon was carried out by wet grinding in a ball mill with a capacity of 2 dm³. Mechanochemical activation was performed in distilled water with the addition of chemical reagents C-3, OP-10, and liquid pyrolysis product (LPP).

The following chemical reagents were used: C-3 – product of polycondensation of β -naphthalene sulfonic acid and formaldehyde (technical specifications TU 5870-005-58042865-05); OP-10 – product of ethoxylation of a mixture of mono- and dialkylphenols with a degree of ethoxylation of 10 (UCGFE code 3402 90 10 00); LPP – is characterized by $\eta=0.0046\text{ Pa}\cdot\text{s}$, $\rho=0.936\text{ g}\cdot\text{cm}^{-3}$, and $Q=7.6\text{ MJ/kg}$.

Two types of CSF compositions were obtained: Composition 1 containing 2 wt.% C-3; 0.5 wt.% OP-10, with a solid phase concentration of 50–62 wt.% and Composition 2 containing 2 wt.% C-3; 0.5 wt.% OP-10; 10 wt.% LPP, with a solid phase concentration of 50–56 wt.%.

Results and discussion

The technical characteristics of pyrocarbon were determined and are presented in Table 1. The analysis revealed that the sample belongs to medium-ash materials, with a specific surface area of $35.3 \text{ m}^2\cdot\text{g}^{-1}$, a high content of volatile matter, and high calorific value.

Among the identified inorganic compounds, the highest content corresponds to oxides: SiO_2 , ZnO , and MgO . Zinc in the form of oxide is used in tire production as an activator of sulfur vulcanization and to prevent rubber degradation. Calcium and magnesium are applied in the form of oxides as fillers, while SiO_2 is known as a technogenic «white carbon black». Iron most likely enters pyrocarbon from the residual metal

cord of worn tires. However, considering that metal cord removal was carried out by magnetic separation, the Fe content in pyrocarbon is insignificant. A somewhat elevated concentration was observed for sulfur, which is explained by its participation in the vulcanization process.

The micrograph shows the surface of pyrocarbon obtained during pyrolysis of used tires at a pyrolysis temperature of 400–450°C (Fig. 1). Particles of irregular shape with varying dispersity were observed. The majority of particles ranged in size from several micrometers up to 100 μm . A small number of particles with sizes up to 200–300 μm was also present.

Pyrocarbon particles are characterized by lamellar and fragmentary morphology. The particle surface is rough, with a developed microrelief and the presence of small pores and cracks formed as a result of intensive release of volatile products during thermal decomposition of rubber. As shown by the technical analysis (Table 1), pyrocarbon contains 23.5% of volatile compounds.

Table 1

Characteristics of pyrocarbon from tire pyrolysis

Characteristic	Parameter	Value	Ukrainian state standard (DSTU) or ISO
Technical parameters	Humidity, W_a , %	2.5	EN 14774-1
	Ash content, A_d , %	16.4	EN 15403, ISO 1171
	Volatile substances, V_{daf} , %	23.5	EN 15148:2012
	Higher heating value (HHV) on a dry basis, Q_{HHV} , $\text{kJ}\cdot\text{kg}^{-1}$	37200	ISO 1928
	Lower heating value (LHV) on a dry basis, Q_{VLHV} , $\text{kJ}\cdot\text{kg}^{-1}$	29500	
Elemental composition (dry sample), %	C	77.39	EN 15289:2013, EN 15104:2013
	H	2.81	
	N	0.12–0.17	
	O	2.6–3.5	
	S	2.19	
Component content expressed as oxides, wt.%	SiO_2	51.51	EN 9045:2020
	Al_2O_3	3.19	
	Fe_2O_3	1.50	
	MgO	13.36	
	CaO	4.91	
	Na_2O	0.80	
	K_2O	0.90	
	PbO	0.10	
	SO_3	5.85	
	ZnO	16.5	
	CuO	1.23	

The presence of sharp-edged fragments indicates the grinding of the solid residue after pyrolysis. The absence of spherical aggregates, which are characteristic of carbon black contained in tires, points to an amorphous or weakly structured state of carbon. In some areas, light inclusions were observed, which may correspond to residual inorganic impurities (ash, metal oxides of Zn, Si, Ca, Fe), the quantitative composition of which is presented in Table 1.

The morphological features of the particle surface are consistent with literature data [10], which state that pyrocarbon obtained at a pyrolysis temperature of 400–600°C has a predominantly amorphous structure and high porosity, whereas an increase in pyrolysis temperature to 800–900°C promotes densification and partial graphitization of the surface layers.

To study the chemical nature of pyrocarbon, the number of surface functional groups was determined by potentiometric titration according to Boehm. It was shown that pyrocarbon has a heterogeneous surface, where basic NH_2 groups predominate (Table 2).

Structural–sorption characteristics of pyrocarbon

were investigated using low-temperature nitrogen adsorption (77 K). It was demonstrated that pyrocarbon has a porous structure with mesopores (2–50 nm) and a developed specific surface area of $35.3 \text{ m}^2\cdot\text{g}^{-1}$ compared to fossil coal (specific surface area of non-activated anthracite 2–3 $\text{m}^2\cdot\text{g}^{-1}$).

Functional groups on the surface of pyrocarbon were studied by IR spectroscopy. The pyrocarbon spectrum was reported in previous studies [11]. The IR spectrum recorded absorption bands characteristic of aliphatic compounds (2925 cm^{-1} , 2856 cm^{-1} , 1456 cm^{-1} , 1376 cm^{-1} , and 754 cm^{-1}); carbonyl compounds (1703 cm^{-1}); and aliphatic sulfides (1076 cm^{-1} , and 699 cm^{-1}). In addition, weak bands corresponding to aromatic compounds (1630 cm^{-1} , 1032 cm^{-1} , and 877 cm^{-1}) were observed.

The rheological properties of composite fuels, in particular viscosity and flowability, together with granulometric composition, sedimentation stability, and dispersity of the solid phase, are decisive factors determining the technology of their transportation, storage, ignition, and combustion. A characteristic feature of pyrocarbon is its hydrophobicity, combined

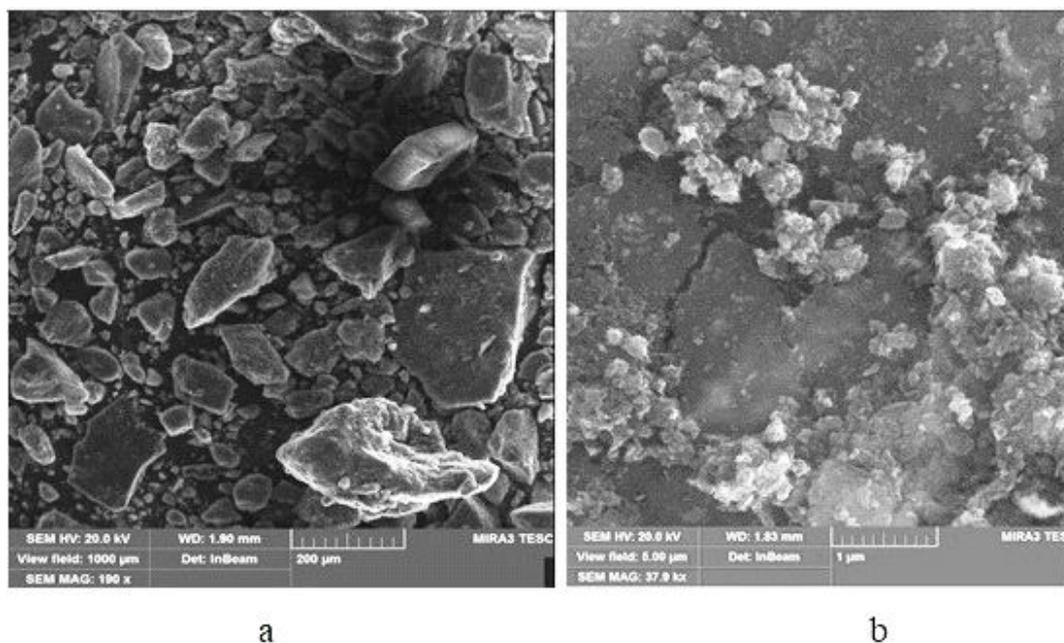


Fig. 1. Micrograph of pyrocarbon particles with $<300 \mu\text{m}$ (a) and $1\text{--}5 \mu\text{m}$ (b) view field

Table 2

Structural–sorption characteristics of pyrocarbon

Surface functional groups concentration (C), $\text{mg}\cdot\text{eq}\cdot\text{g}^{-1}$				Sorption characteristics		
–COOH	–OH	>C=O	–NH ₂	$S_{\text{sp}}, \text{m}^2\cdot\text{g}^{-1}$	$V_{\text{pore}}, \text{cm}^3\cdot\text{g}^{-1}$	$d_{\text{pore}}, \text{nm}$
0.0085	0.0206	0.00955	0.053	35.3	0.0365	26.8

with the ability to sorb oil and petroleum products [12]. It was established that pyrocarbon more effectively absorbs low-molecular fractions of petroleum products, such as gasoline. To improve the wettability of the pyrocarbon surface and increase its energy potential, 10 wt.% LPP was added to the dispersion medium.

The hydrophobicity of the pyrocarbon surface necessitates consideration of three key physicochemical processes when selecting additives for the formation of stable and flowable high-concentration suspensions: wetting of the solid surface; dispersion of the solid phase during mechanochemical activation; stabilization of the dispersed system.

To select optimal plasticizers and stabilizers for CSF, the effect of various reagents (at concentrations of 0.5–2.0 wt.%) on the rheological properties of suspensions was studied. As shown in previous works [13], the lowest apparent viscosity of CSF based on pyrocarbon was observed when using dispersants such as sodium lignosulfonate (LSTNa), naphthalene–formaldehyde (NF), and the polycondensation product of β -naphthalene sulfonic acid and formaldehyde (C-3). A common structural feature of these substances is the presence of aromatic nuclei with sulfo groups, which impart amphiphilic properties and promote the dispersion of hydrophobic particles in water.

The plasticizing effect of these reagents is due to the formation of thin monomolecular adsorption layers on the particle surface, which reduce internal friction in the colloidal system. In addition, the peptizing action of the additives prevents the formation of flocules from pyrocarbon particles. The phenomenon of peptization leads to an increase in the specific surface area of particles and positively influences the intensity of hydration and structure formation in hydrosuspensions.

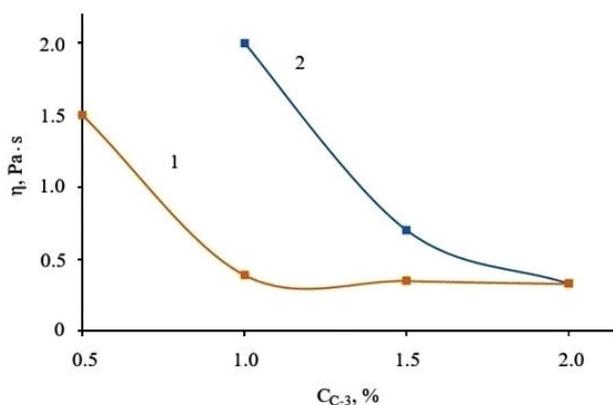


Fig. 2. Dependence of apparent viscosity of CSF on the concentration of dispersant C-3: 1 – CSF composition 1; 2 – CSF composition 2

To study the rheological properties of CSF based on pyrocarbon obtained by wet grinding, a graphical dependence (Fig. 2) of apparent viscosity (η) on the concentration of dispersant C-3 in the range of 0.5–2 wt.% was obtained. The amount of stabilizer OP-10 was constant at 0.5 wt.%.

As seen in Fig. 2, optimal viscosity is demonstrated by CSF samples without (curve 1) and with the addition of 10 wt.% LPP (curve 2) at a dispersant C-3 concentration of 1.5–2 wt.%. For CSF with LPP addition, the values of apparent viscosity are higher, and when the dispersant concentration decreases to 1 wt.%, the value of $\eta > 2$ Pa·s exceeds the limiting values (the technological parameter of apparent viscosity equals 1.5 Pa·s at $Dr=9$ s⁻¹).

Electrokinetic studies of the pyrocarbon surface conducted in previous work [13] showed that the addition of LPP to pyrocarbon does not recharge the surface, which remains positive throughout the pH interval. The introduction of dispersants with anion-active forms into the dispersion medium causes surface recharging of pyrocarbon, which becomes more pronounced with increasing pH. This is associated with the enhanced dissociation of anion-active surfactants and the increased surface activity of anions. Dispersant C-3 belongs to anionic polyelectrolytes. Its plasticizing effect is based on the mechanism of electrostatic dispersion, which under mechanical activation leads to a significant shift of the ζ -potential of pyrocarbon particles into the negative region. By adsorbing onto the particle surface, C-3 molecules, due to negatively charged sulfo groups, induce mutual repulsion of the particles.

As reported in the literature [14], the key mechanism of interaction of such dispersants with coal surfaces is the formation of hydrogen bonds. Elemental analysis of pyrocarbon (Table 1) showed a sufficient hydrogen content of 2.8%, enabling hydrogen bond formation. For comparison, coal of DG grade contains 4.9% hydrogen [15]. The strength of fixation and the amount of adsorbed dispersant determine the key operational parameters of the fuel: rheological properties, maximum concentration of structure formation, as well as the aggregative and sedimentation stability of CSF. Thus, any changes in the hydrophilic–lipophilic balance on the particle surface caused by fixation of an apolar reagent (in our studies, LPP) can significantly affect the quality of the final composite fuel.

In addition to the processes described above, in such a multicomponent heterogeneous system as CSF, competition occurs between different reagents (dispersant C-3, apolar reagent LPP, and stabilizer OP-10) for adsorption sites on the particle surface.

Experimental data (Fig. 2) indicate that adsorption of dispersant C-3 on the pyrocarbon surface modified with LPP is lower compared to the clean surface at low C-3 dosage (0.5 wt.%). This difference is leveled out as the concentration of C-3 increases to 2 wt.%. This phenomenon can be explained by screening of active functional groups on the pyrocarbon particle surface by the apolar reagent or by particle flocculation at low dispersant concentrations. With increasing C-3 concentration, its competitive redistribution at the phase boundary ultimately ensures the predominance of its adsorption process [14].

To study the rheological properties of CSF as a function of C-3 concentration, dependencies of apparent viscosity on shear rate were obtained (Fig. 3).

As shown in Fig. 3, increasing shear rate is accompanied first by a sharp, then by a more gradual decrease in viscosity to certain shear rate values (Dr), at which viscosity becomes minimal and then remains constant. At Dr values of $15\text{--}20\text{ s}^{-1}$, the viscosity of the suspension decreases sharply, indicating that all systems exhibit pseudoplastic flow behavior. This inflection is characterized by intensive destruction of bonds within the structure. At Dr values of $30\text{--}60\text{ s}^{-1}$, the system behaves as a Newtonian fluid with constant viscosity, corresponding to complete destruction of the structural network of suspensions. In this region, ultimate structural breakdown occurs during flow with only minor recovery. This pattern is observed for all types of CSF compositions 1 and 2 at the studied dispersant concentrations of 0.5–2 wt.%.

With increasing concentration of the dispersed phase in the system, a regular change in the properties of highly dispersed suspensions is observed. This change occurs until a certain critical concentration is reached, at which a qualitative transformation of the rheological characteristics of the system takes place.

An increase in the solid phase content leads to a

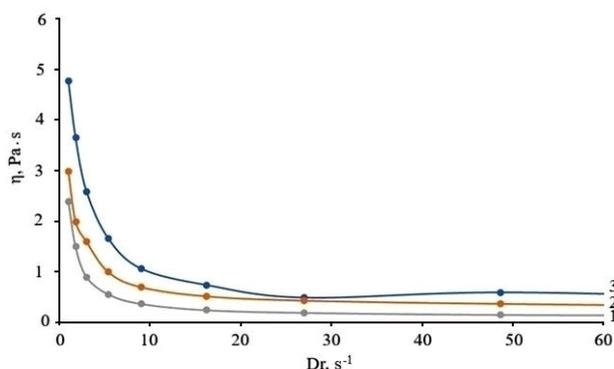


Fig. 3. Dependence of apparent viscosity on the shear rate for CSF composition 2 at different concentrations of dispersant C-3: 1 – 2 wt.%; 2 – 1.5 wt.%; 3 – 1 wt.%

rise in the structural viscosity of the suspension, which is determined by two main factors:

- an increase in the number of interparticle contacts;
- strengthening of adhesive interactions between dispersed particles.

These processes contribute to the formation of a spatially structured network (framework) throughout the system volume. A clear correlation is observed: the higher the concentration of the solid phase, the more intensive the interparticle interactions become, ultimately resulting in significant complications in deformation and flow of the dispersed system.

The graphical dependence of apparent viscosity (η) on the concentration of pyrocarbon solid phase (C , wt.%) for CSF based on pyrocarbon with the addition of 10 wt.% LPP compared to the original (Fig. 4) shows that with increasing solid phase concentration, the apparent viscosity increases for all samples. For CSF based on pyrocarbon without the addition of liquid pyrolysis product (curve 1), the maximum solid phase filling can reach 62 wt.% while maintaining the limiting viscosity value of 1.5 Pa·s. Suspensions of composition 2 exhibit higher apparent viscosity values (curve 2). Therefore, the maximum solid phase filling for such systems can be achieved at up to 56 wt.%, after which a sharp increase in apparent viscosity occurs. However, systems with LPP addition demonstrated higher sedimentation stability at low solid phase concentrations compared to CSF without LPP.

The apparent viscosity of CSF without LPP addition gradually increased after 7 days with increasing pyrocarbon solid phase concentration. For CSF composition 1 (Fig. 5), at a solid phase concentration of 62 wt.% the limiting value of 1.5 Pa·s was reached (curve 1).

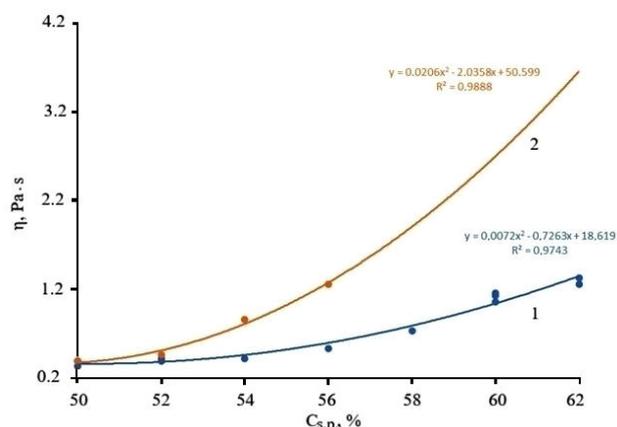


Fig. 4. Dependence of apparent viscosity on the solid phase concentration: 1 – CSF composition 1; 2 – CSF composition 2

With the addition of LPP (curve 2), the sedimentation stability of CSF increased at lower concentrations of the solid energy carrier, while the apparent viscosity remained within normative values. Thus, for CSF composition 1 at a solid phase concentration of 50–52 wt.%: on the first day the apparent viscosity was $\eta=0.66\text{--}0.73$ Pa·s; on day 14 $\eta=0.86\text{--}0.90$ Pa·s; on day 47 $\eta=1.19$ Pa·s. The parameters of sedimentation stability met technological requirements (for liquid fuel supply through pipelines, sedimentation stability should be at least 30 days, and for tank transport at least 2 weeks), with viscosity increasing gradually.

The study of sedimentation stability for CSF composition 2 at a solid phase concentration of 50 wt.% showed that on the first day, the effective viscosity did not differ from CSF composition 1 and was $\eta=0.66$ Pa·s; on day 19 the apparent viscosity increased to $\eta=1.1$ Pa·s, while on day 47 the apparent viscosity exceeded the limiting values, reaching $\eta>2$ Pa·s.

To investigate the influence of solid phase concentration on the flow processes of composite suspensions based on pyrocarbon, complete rheological curves were constructed (Fig. 6). As shown in Fig. 6, with increasing concentration of the dispersed system, the character of the flow curves changes. As noted above, the change in CSF flow behavior with increasing solid phase concentration is associated with the growth in the number and strength of contacts within the structural network. As a consequence, the non-Newtonian character of the system is enhanced, with a transition from viscoplastic (50–58 wt.%) to pseudoplastic behavior (60–62 wt.%).

The presence of thixotropy in the studied systems was identified by the characteristic dynamics of

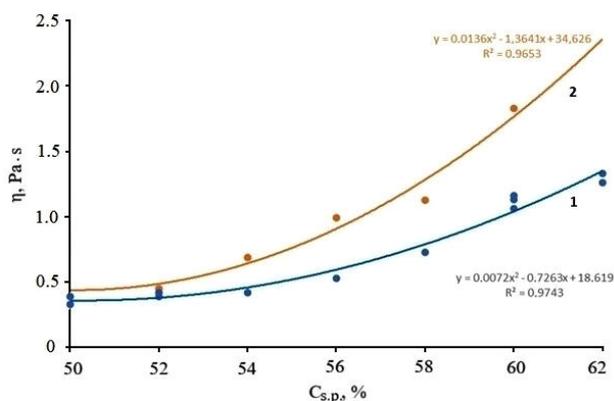


Fig. 5. Dependence of apparent viscosity on the solid phase concentration for CSF composition 1:
1 – 1 day; 2 – after 7 days storage

viscosity: its decrease under mechanical influence and subsequent gradual increase after cessation of the load. The study of rheological curves «shear stress vs. shear rate» for pyrocarbon suspensions demonstrated the phenomenon of structural recovery of the coagulated system. During shear deformation, the bulk structure is destroyed into separate aggregates, which restructures after the load is removed. A visual manifestation of this process is the formation of a hysteresis loop, which is a clear indicator of system structuring and thixotropic properties. The area of this loop serves as a quantitative measure of thixotropy.

It was found that for highly concentrated suspensions with pronounced thixotropy, the flow curve obtained under increasing shear stress does not coincide with that obtained during decreasing stress. As shown in Fig. 7, increasing the solid phase concentration from 50% to 62% leads to a reduction in thixotropy, as evidenced by the increase in the area of the hysteresis loop. This indicates a diminished ability of the system to restore its structure as the solid phase concentration increases, which is attributed to the excessive growth in the number of interparticle contacts within the suspension.

Conclusions

Potentiometric analysis of the pyrocarbon surface revealed its heterogeneous nature, with acidic groups $-\text{COOH}$, $>\text{C}=\text{O}$ and basic groups $-\text{OH}$, $-\text{NH}_2$. IR spectra of pyrocarbon confirmed the presence of aliphatic and carbonyl compounds, aromatic hydrocarbons, and aliphatic sulfides.

SEM imaging and elemental analysis showed that pyrocarbon particles exhibit lamellar and fragmentary morphology. Their surface is rough, with a developed microrelief, fine pores and cracks, and residual inorganic inclusions (metal oxides of Zn, Si,

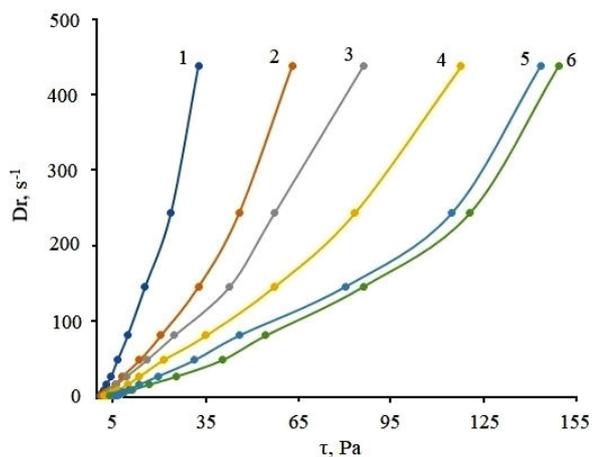


Fig. 6. Flow behavior dynamics of CSF based on pyrocarbon composition 1 at different solid phase concentrations:
1 – 50%; 2 – 52%; 3 – 56%; 4 – 58%; 5 – 60%; 6 – 62%

Ca, Fe, Al, Cu, Pb, Na, K, Mg, etc.).

Structural–sorption studies confirmed that pyrocarbon has a porous structure with mesopores (2–50 nm) and a developed specific surface area of $35.3 \text{ m}^2\cdot\text{g}^{-1}$, significantly higher than that of non-activated anthracite ($2\text{--}3 \text{ m}^2\cdot\text{g}^{-1}$).

Rheological properties of CSF based on pyrocarbon were studied using wet grinding. It was shown that optimal viscosity was achieved in samples both with and without the addition of 10 wt.% LPP, at a dispersant C-3 concentration of 1.5–2 wt.%.

For CSF composition 1, containing 1.5 wt.% C-3 and 0.5 wt.% OP-10 at a solid phase concentration of 50–52 wt.%, viscosity increased gradually, reaching $\eta=1.19 \text{ Pa}\cdot\text{s}$ on day 47. For CSF composition 2, containing 1.5 wt.% C-3, 0.5 wt.% OP-10, and 10 wt.% LPP, the apparent viscosity exceeded the limiting value on day 47. Increasing the solid phase concentration led to reduced sedimentation stability in both CSF types.

The best viscosity results were obtained for CSF composition 2 with a solid phase concentration of 50–56 wt.% and LPP addition. Further increases in solid phase concentration caused a sharp rise in effective viscosity. The maximum solid phase loading for composition 1 without LPP addition was observed at 60 wt.%, which meets the technological requirements for CSF.

Rheological studies of the hysteresis loop confirmed the ability of both CSF types to restore their structure after mechanical disruption. Increasing the solid phase concentration led to a decrease in thixotropy.

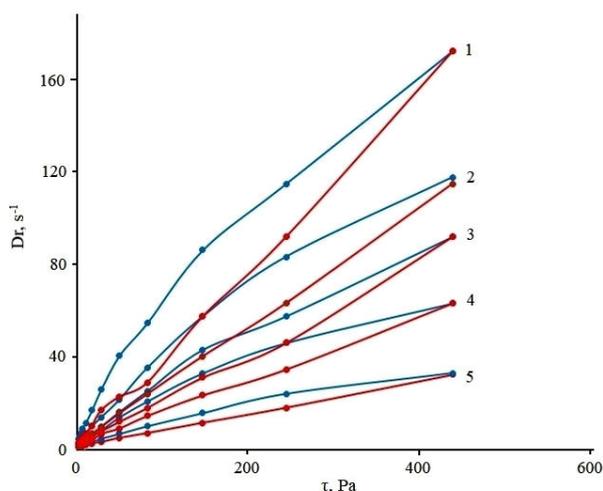


Fig. 7. Flow hysteresis dynamics of CSF based on pyrocarbon composition 1 at different solid phase concentrations (blue curves show increasing D_r , and red curves show decreasing D_r):
1 – 62%; 2 – 58%; 3 – 56%; 4 – 54%; 5 – 50%

The conducted studies demonstrated that the viscosity and sedimentation stability parameters meet normative requirements. Composite suspensions based on pyrocarbon are recommended for use as liquid suspension fuel for combustion in liquid-fuel boilers.

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РЕОЛОГІЧНІ ВЛАСТИВОСТІ КОМПОЗИЦІЙНИХ СУСПЕНЗІЙ НА ОСНОВІ ПРОДУКТІВ ПІРОЛІЗУ ШИН МЕТОДОМ МОКРОГО ПОМЕЛУ

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Перспективним напрямом подолання дефіциту традиційних енергоносіїв в Україні є розроблення суспензійних палив на основі вторинної сировини. Одним із таких ресурсів є відпрацьовані автомобільні шини, накопичення яких становить серйозну глобальну екологічну проблему. Найефективнішим методом перероблення шин є піроліз, у результаті якого утворюються газоподібні продукти, рідкий піролізний продукт (РПП), пірокарбон та металокард. У даній роботі композитні суспензійні палива одержували шляхом мокрого помелу пірокарбону, одержаного з піролізу шин, з додаванням 10 мас.% РПП. Досліджено реологічні та седиментаційні властивості суспензій за різних концентрацій диспергатора С-3, стабілізатора ОП-10 та твердої фази пірокарбону. Встановлено, що оптимальна уявна в'язкість досягається за вмісту 1,5–2,0 мас.% С-3 та 0,5 мас.% ОП-10. Найкращі реологічні характеристики спостерігалися для суспензій із концентрацією твердої фази 50–56 мас.% і 10 мас.% РПП. Максимальне наповнення твердої фази до 60 мас.% досягнуто без додавання РПП. Седиментаційна стійкість одержаних суспензій становила 47 діб. Отримані результати свідчать про доцільність використання пірокарбонних суспензій як палива для рідкопаливних котлів.

Ключові слова: ефективна в'язкість, композиційні суспензії, пірокарбон, реологічні властивості, седиментаційна стійкість.

RHEOLOGICAL PROPERTIES OF COMPOSITE SUSPENSIONS BASED ON PYROLYSIS PRODUCTS OF TIRES OBTAINED BY WET GRINDING METHOD

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A promising approach to addressing the shortage of traditional energy carriers in Ukraine is the development of suspension fuels based on secondary raw materials. One such resource is waste automobile tires, the accumulation of which has become a serious global environmental problem. Pyrolysis is considered the most effective method for tire recycling, producing gaseous products, liquid pyrolysis products (LPP), pyrocarbon, and metal cord. In this study, composite suspension fuels were prepared by wet milling of pyrocarbon obtained from tire pyrolysis with the addition of 10 wt.% LPP. The rheological and sedimentation properties of the suspensions were investigated at various concentrations of dispersant C-3, stabilizer OP-10, and solid pyrocarbon phase. The results showed that optimal apparent viscosity was achieved at 1.5–2.0 wt.% C-3 and 0.5 wt.% OP-10 for both types of suspensions. The most favorable viscosity characteristics were observed for suspensions containing 50–56 wt.% solid phase and 10 wt.% LPP. A maximum solid loading of up to 60 wt.% was obtained in suspensions without LPP. Sedimentation stability exceeded 20 days for suspensions with 50–52 wt.% solid phase and reached up to 47 days for the obtained formulations. The findings indicate that pyrocarbon-based suspension fuels are suitable for application in liquid-fuel boiler systems.

Keywords: apparent viscosity; composite suspensions; pyrocarbon; rheological properties; sedimentation stability.

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