

OLEOCHEMICAL SYNTHESIS OF SULFANES, THEIR STRUCTURE
AND PROPERTIES

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Abstract. For the first time, oleochemical sulfanes were synthesized *via* sequential vulcanization of fatty acid alkyl esters from rapeseed oil by benzoyl peroxide and elemental sulfur. Their structure and properties were established by the methods of instrumental analysis and it was shown that oleochemical sulfanes are complex structures with different cross-linking degrees, which provide excellent antioxidant and tribological characteristics and do not cause steel or copper corrosion under harsh test conditions.

Keywords: rapeseed oil, organic sulfanes, synthesis, reaction mechanisms, lubricant additives.

1. Introduction

Organic sulfanes (OS) are covalent compounds of the type $R-S_n-R$ (R – organyl) that contain divalent sulfur ($n = 1$), or polysulfide groups ($n \geq 2$) [1]. Due to the specific structure and, as a consequence, properties of OS, they play an important role in science and technology. Primarily, these sulfur-rich compounds are used as lubricant additives which improve extreme pressure and antioxidant characteristics [2]. Moreover, in contrast to phosphorous or chlorine-containing analogues, OS have a high degree of biodegradation and do not cause harm to the natural environment [3].

Despite all of the given benefits, industrial techniques of OS manufacturing still base on sulfuration of non-renewable petrochemicals, such as alkenes, and demand applying of high pressure, valuable catalysts, or even utilization of noxious byproducts [4-6]. The combination of these factors led to the investigation of new methods of sulfuration with the involvement of ecologically favorable renewable bioresources.

Among variety of bioraw materials suitable for producing of OS, vegetable oils occupy a prominent place. Sulfurized oils are well-known in the field of lubricants and are widely used as components for cutting fluids, for instance [7]. However, modified oils contain a high percentage of active sulfur that cause copper corrosion and deterioration of the product quality during storage. On the other hand, sulfuration of oils is carried out under comparably severe reaction conditions, which may be accompanied by release of hydrogen sulfide, or formation of factice structures, especially, at high concentration of sulfur.

In our previous studies, we proved that products of oils chemical transformation are the most perspective feedstock for OS synthesis [8, 9]. In particular, it was established that sulfur-containing additives may be easily obtained by the interaction of fatty acid ethyl esters with elemental sulfur, without application of high pressure and catalysts, release of H_2S , or formation of substances which are insoluble in hydrocarbons. In contrast to oils, OS from fatty esters do not induce copper corrosion and are stable for a long-term storage, however, have worse tribological properties.

In a given article our goal is developing a new method of oleochemical synthesis of multifunctional OS on the basis of fatty acid alkyl esters (FAAE), exploration of their structure and operating properties in lubricating systems.

2. Experimental

2.1. Materials

We used unrefined rapeseed oil for OS synthesis provided by JSC “Nizhynsky Zhyrocombinat” (Nizhyn, Ukraine) with properties and fatty acid composition given in Table 1. Alcohols (methanol, ethanol, *n*-propanol and *n*-butanol) were received from local commerce (Kyiv, Ukraine), and were dehydrated over molecular sieves 3A. Potassium hydroxide, benzoyl peroxide (BP), elemental sulfur and all of the other reagents were purchased in

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Chemlaborreactiv Ltd. (Brovary, Ukraine). Tradable BP was supplied as a white powder with a mass fraction of base material 75 % and additional water as a phlegmatizer. Therefore, before synthesis it was recrystallized from diethyl ether via technique described in [10]. Sulfuration reaction was performed with application of the precipitated sulfur powder with a mass fraction of S – 99.90 %.

Table 1

Properties and fatty acid composition of rapeseed oil

Property	Value
Acid value, mg KOH·g ⁻¹	2.63
Iodine value, g I ₂ ·100 g ⁻¹	107.00
Kinematic viscosity at 40 °C, mm ² ·s ⁻¹	34.90
Fatty acids (C _{carbon atoms} : double bonds), %	
C ₁₄	1.35
C ₁₆	4.89
C _{18:0}	–
C _{18:1}	86.75
C _{18:2}	2.20
C _{18:3}	0.39
C ₂₀	–
C ₂₂	3.34
C ₂₄	1.08

2.2. Methods

Synthesis of oleochemical OS was performed by multistep procedure, according to Fig. 1.

Firstly, FAAE were produced *via* base-catalyzed transesterification (Fig. 1, step 1), by a technique as described in [11, 12]. For this purpose, unrefined RO and alcohol, with molar ratio 1:6, were mixed with a potassium hydroxide (1.8 wt % from oil) and were agitated vigorously for 30 min, at room temperature. After completion of the process, the excess alcohol was evaporated under reduced pressure and the mixture was

transferred to a separation funnel for glycerol removing. Content of FAAE in the top phase were 90, 93, 85, 88 % for methyl, ethyl, *n*-propyl and *n*-butyl esters, respectively. Resulted esters were further distilled off from the top phase under pressure 0.67–2.67 kPa for obtaining the purified product.

Next, BP (1–10 wt %) and obtained FAAE (80–89 wt %) were introduced in a reactor equipped with a mechanical stirrer, thermometer and colonic tube. Resulted mixture was heated at 353–363 K for 30 min, until the full conversion of BP that we ascertained by cessation of CO₂ evolution and kinematic viscosity measurements. Further, the system was cooled to 343 K and additional 10 wt % of sulfur was introduced. After this procedure, the temperature of reaction media was heightened to 438–448 K and maintained for 15–35 min, till complete disappearance of free sulfur (step 3). Ratio of initial reagents, conditions of the reaction and results of the vulcanized FAAE (*a*BP-*b*S-FAAE, where *a* – wt % of BP, *b* – wt % of S) synthesis are reflected in Table 2.

Standard GC test EN14103 was used for determination of FAAE concentration. Analysis was conducted with application of a capillary column HP-5 (30 m/0.32 mm/0.25 μm) on an Agilent 7890A chromatograph. Structure of the *a*BP-*b*S-FAAE was determined by elemental analysis, FTIR spectrometry, ¹H NMR and modulated differential scanning calorimetry (MDSC). FTIR spectra were recorded in a thin layer on a Bruker Vertex-70 spectrometer. ¹H NMR spectra were obtained on a Bruker AVANCE DRX-500 spectrometer, using dimethyl sulfoxide (DMSO-*d*₆) as a solvent, and tetramethylsilane (TMS) as an internal standard. MDSC curves were measured on a Q2000 TA calorimeter, in a temperature range from 183 to 285 K, at a heating rate 5 K/min. All of the other properties of the *a*BP-*b*S-FAAE were tested by standard procedures.

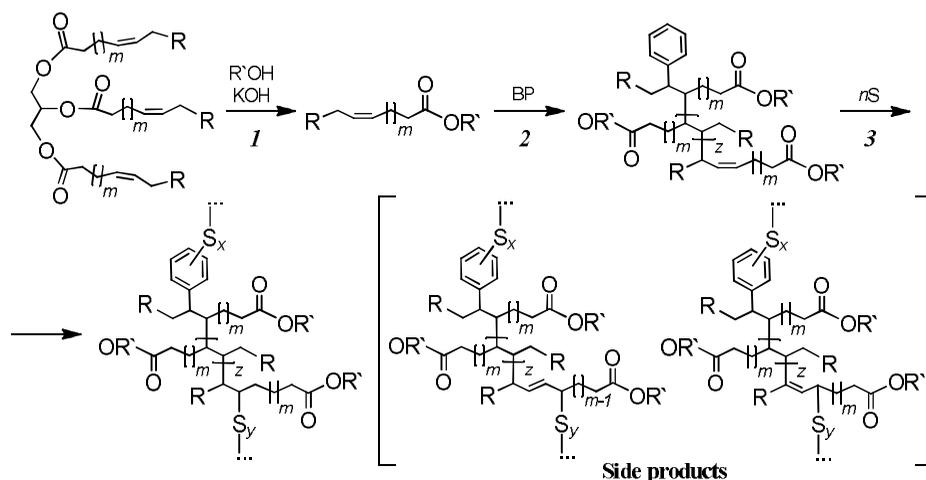


Fig. 1. Scheme of multistep transformation of rapeseed oil: R – alkyl or alkenyl; R' – methyl, ethyl, *n*-propyl, or *n*-butyl; *m* – 6, 9, 10, 12; *z* – integer; *n* = *x* + *y*

Table 2

Ratio of initial reagents, conditions and results of OS synthesis from FAAE

Sample No	Initial reagents			Conditions		Results		
	FAAE – wt. %	BP, wt. %	S, wt. %	Temperature, K	Duration, min	Yield, %	S content, %	Viscosity, mm ² ·s ⁻¹ (313 K)
1	FAME – 89	1	10	363–368 438–443	30 15	99.6	9.96	17.21
2	FAEE – 89	1	10	363–368 438–443	30 15	99.1	9.91	17.98
3	FAPE – 89	1	10	363–368 438–443	30 15	98.8	9.88	19.64
4	FABE – 89	1	10	363–368 438–443	30 15	97.5	9.75	21.17
5	FABE – 88	2	10	363–368 438–443	30 20	97.7	9.77	25.02
6	FABE – 85	5	10	363–368 438–443	30 25	98.4	9.84	30.97
7	FABE – 80	10	10	363–368 438–443	30 35	100.0	10.00	69.50

Notes: FAME – fatty acid methyl esters; FAEE – fatty acid ethyl esters; FAPE – fatty acid propyl esters; FABE – fatty acid butyl esters.

Quantum chemical calculations were carried out using Gaussian 09 software package [13], with the application of density functional theory (DFT) at the level 6-31+G(d). All computations were conducted considering solvation effect by the *n*-heptane, and temperature of the system 368 K.

Lithium plastic lubricants with addition of the *a*BP-*b*S-FAAE (2.5 wt %) were developed by a standard technique given in [14]. Their tribological properties, such as weld and critical load (*P_w* and *P_c* appropriately), were evaluated using a four-ball tester; antioxidant stability and corrosiveness were determined according to the standards.

3. Results and Discussion

Alcoholysis of the rapeseed oil, conducted by typical base-catalyzed procedure, allowed us to obtain fatty acid esters of various alcohols in a good yield (85–93 %). Significant step was FAAE purifying by vacuum distillation that prevents from the residue of the waste glycerol, acyl glycerides, soaps, phospholipids, or potassium hydroxide. However, even after distillation these compounds may remain in small quantities and accelerate decomposition of BP at step 2 (Fig. 1). For instance, in monography [15] the authors mentioned that alcohols significantly increase the rate of organic peroxides breakup.

From analysis results of OS synthesis given in Table 2, it is clearly seen that yields slightly decrease with lengthening of alcohol alkyl chain from methyl to butyl (samples 1-4). However, with growing of the BP concentration, yields of sulfanes from modified FABE

going up to 100 % (samples 4-7), apparently, as a consequence of appearing the new reaction centers at aromatic rings. On the other hand, we supposed that remaining BP and free radicals after the second step of the modification induce activation of sulfur and its further interaction. At the same time, duration of sulfur conversion increases at high concentration of BP that might be caused by the raise of vulcanized esters viscosity. The similar patterns were detected for fatty acid methyl, ethyl and propyl esters.

From FTIR-spectra of synthesized OS, which are depicted in Fig. 2, we could observe that band ν =CH (stretching, 3005 cm⁻¹) inherent to double bonds of the initial FAAE disappears after vulcanization *via* BP and elemental sulfur. In contrast, the absorption characterizing ν S–S (stretching, 550–450 cm⁻¹) of polysulfane bonds arises, as well as vibrations C–C (in-plane, 1610–1590 cm⁻¹), δ C–H (in-plane bending, 1270–1250 cm⁻¹), δ C–H (out-of-plane bending, 680 cm⁻¹) native to arenes and δ =CH (out-of-plane bending, 965, or 800 cm⁻¹) typical for *trans*-disubstituted, or trisubstituted alkenes [16]. Also we noticed increase in intensity of bands δ_s CH₃ (symmetric bending, 1375–1355 cm⁻¹), γ CH₃ (skeletal vibrations, 1250–1245 cm⁻¹), γ CH₂ (skeletal vibrations, 1070–1065 cm⁻¹), δ C–H (in-plane bending, 1310–1295 cm⁻¹), ν C=O (stretching, 1740 cm⁻¹), ν C–O (stretching, 1175, 1115 cm⁻¹) and ν_{as} C–O (asymmetric stretching, 1025 cm⁻¹) with rising of BP concentration. This tendency might indicate the growing of molecular mass, or, as we established in our previous work, inclusion of electronegative substituents in the structure of fatty esters [8].

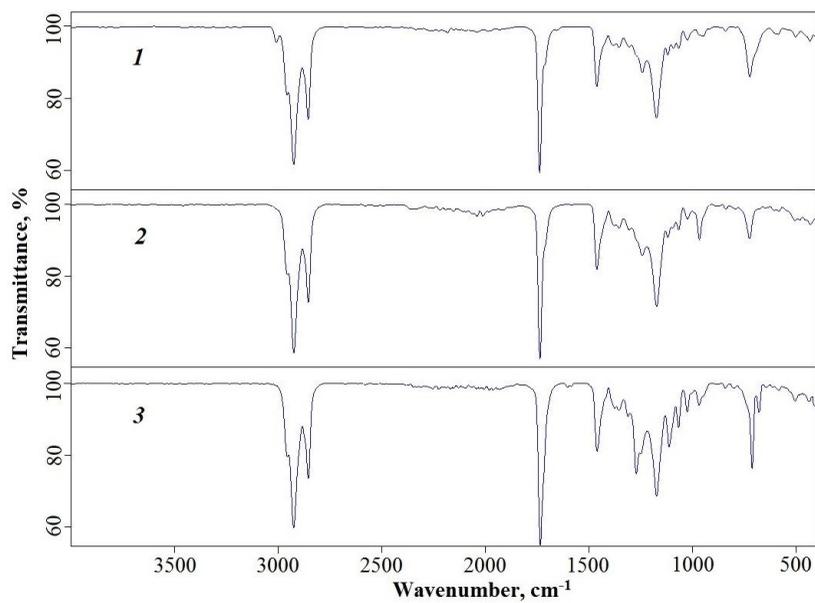


Fig. 2. FTIR spectra of Fabe (1); 1BP-10S-Fabe (2) and 10BP-10S-Fabe (3)

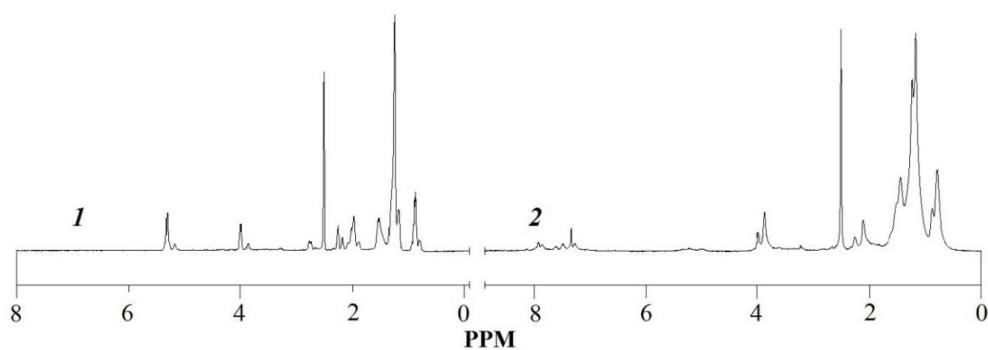


Fig. 3. ^1H NMR spectra of Fabe (1) and 10BP-10S-Fabe (2)

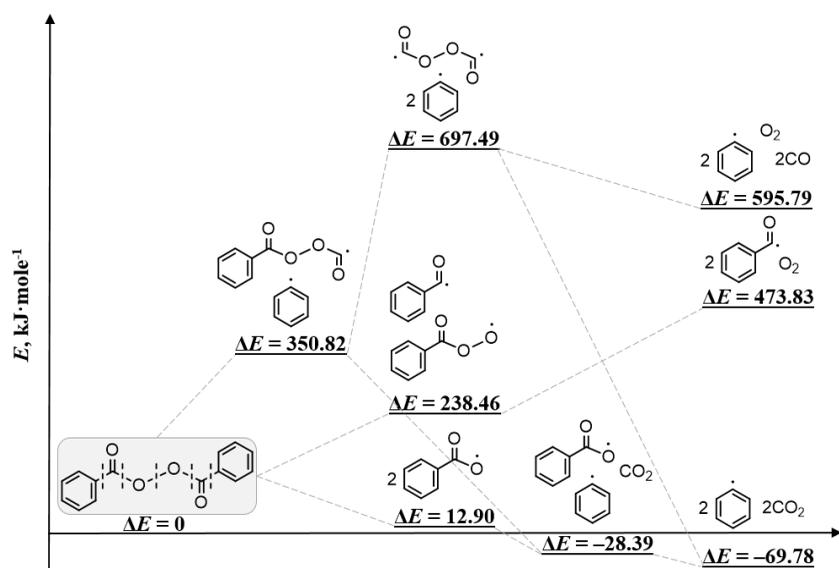


Fig. 4. Scheme and free energy values of radical decomposition of BP

Alike regularities can be observed from ^1H NMR spectra in Fig. 3. Multiplet characteristic of protons near double bonds at 5.45–5.25 ppm (m, $\text{CH}=\text{CH}$) decreases with the growth of BP concentration and almost disappears for 10BP-10S-FAAE. Instead, a number of bands in the range of 8.20–7.00 ppm (m, CH_{Ar}) arises, which are typical for aromatic and heterocyclic derivatives. Also moderate diminish of peaks at 2.25–2.00 ppm (m, $\text{CH}_2-\text{CH}=\text{CH}$), inherent to methylene groups near double bonds, is remarkable [16].

Conducted analysis of IR and NMR spectra points out that a multistep vulcanization induced a number of FAAE transformations. We suppose that, primarily, BP decomposes to free radicals, which are likely to interact with double bonds, instead of allyl hydrogen abstraction by benzoyloxyl radical, as per earlier conceptions [17]. This is evidenced by decreasing of frequencies intrinsic to double bonds in IR and NMR spectra after the second step of modification. In addition, we did not fix any band, which characterizes carboxylic acids. However, the structure of original radicals is still disputable, so we concentrated our attention to the initiation step of esters vulcanization by BP.

In recent literature different ways of BP thermal decomposition are suggested [15, 18-21]. Generally, they are based on formation of various radicals and biphenyl, as a resulting product. Especially in articles [20, 21] the authors conducted *ab initio* calculations for reasoning the mechanisms of BP decomposition and provided reliability and appropriateness of theoretical methods by experimental results. We summarized conducted investigations and calculated energetic parameters of various paths of BP breakup, with consideration of the temperature factor and solvation effect which are maximally adjusted to synthesis condition. As it could be seen from Fig. 4, among the number of active particles, phenyl radicals are the most thermodynamically favorable product, because their formation is accompanied by the lowest change of free energy ($\Delta E = -69.78 \text{ kJ}\cdot\text{mol}^{-1}$). Also, it was established that formation of benzoyloxyl radicals might occur, but under less favorable conditions ($\Delta E = -28.39 \text{ kJ}\cdot\text{mol}^{-1}$) and obtained particles are likely to decompose to phenyl radicals and CO_2 . Summarizing experimental data and results of theoretical modeling, we believe that generated radicals interact with double bonds and lead to the formation of dimers and further cross-linking, as depicted in Fig. 1. However, at high concentration of BP recombination of radicals and formation of biphenyl may take place, due to the appearance of cage effect [15].

Spectral analysis also revealed that during sulfuration, besides addition to double bonds, substitution of hydrogen at the α -methylene groups near these bonds occurs (Fig. 1, side products). Among other reactions,

generation of linear sulfur-rich trisubstituted alkenes and heterocyclic compounds was observed. All of these side reactions were described in our previous papers [8, 9]. For derivatives, which were obtained at high concentration of BP, substitution at C–H σ -bonds of phenyl ring also took place. However, these interactions were unselective and led to the formation of various positional isomers, which were confirmed by a multitude of peaks in the aromatic region in NMR spectra (Fig. 3(2)).

Research results of oleochemical sulfanes phase transitions are represented in Fig. 5.

Primarily, it could be seen that endothermic peaks on the FAE curve (Fig. 5(1), maxima at 195, 207, 222, 227, 250 and 257 K for the heat flow, and at 195, 207, 225, 250 and 257 K for the reversing heat flow), which specify melting of fatty esters with various unsaturation degree, disappear after complex vulcanization. It indicates the transition in the structure from comparably ordered esters crystals to disordered amorphous cross-linking solids [22]. Significantly that this tendency is going up with the increase of BP concentration. For instance, in the case of 1BP-10S-FABE (Fig. 5(2)) glass transition is observed at 189 K and maximum of melting endotherm at 237 K, in contrast to 10BP-10S-FABE, for which glass transition visualizes at 195 K and melting endotherm at 262 K. This temperature shift undoubtedly evidences growing of molecular mass and cross-linking degree of esters [8, 22].

Despite glass transition and melting endotherms, broad exothermic peak might be detected on the plot of heat flow from the temperature for the vulcanized esters (Fig. 5(2)). Moreover, at the BP mass fraction 1 % maximum of the exotherm appears at 211 K with a peak area of 1.36 J/g, as opposed to the product with 10 wt % with the maximum at 204 K and a peak area of 1.06 J/g. We consider that exothermic peaks are the consequence of conglomerates formation, which includes ordered crystals and more disordered amorphous solids of OS. These partially crystallized structures induce the effect of cold crystallization, which is noticeably, less observable at high concentration of BP.

Synthesized OS were approved as functional additives for lithium lubricants. Comprehensive investigations of the properties of the developed lubricants revealed a number of patterns, which allow purposefully to manage operating characteristics and accelerate their practical implementation. It was established that under harsh conditions – after holding of samples at 393 K during 10 h, acid values (AV) of lubricants do not change (Fig. 6(1)), so, it indicates their high antioxidant stability. On the other hand, we found that all samples provide protective properties on steel surface and do not cause copper corrosion after a three-hour endurance of metal plates in lubricants at the temperature of 373 K.

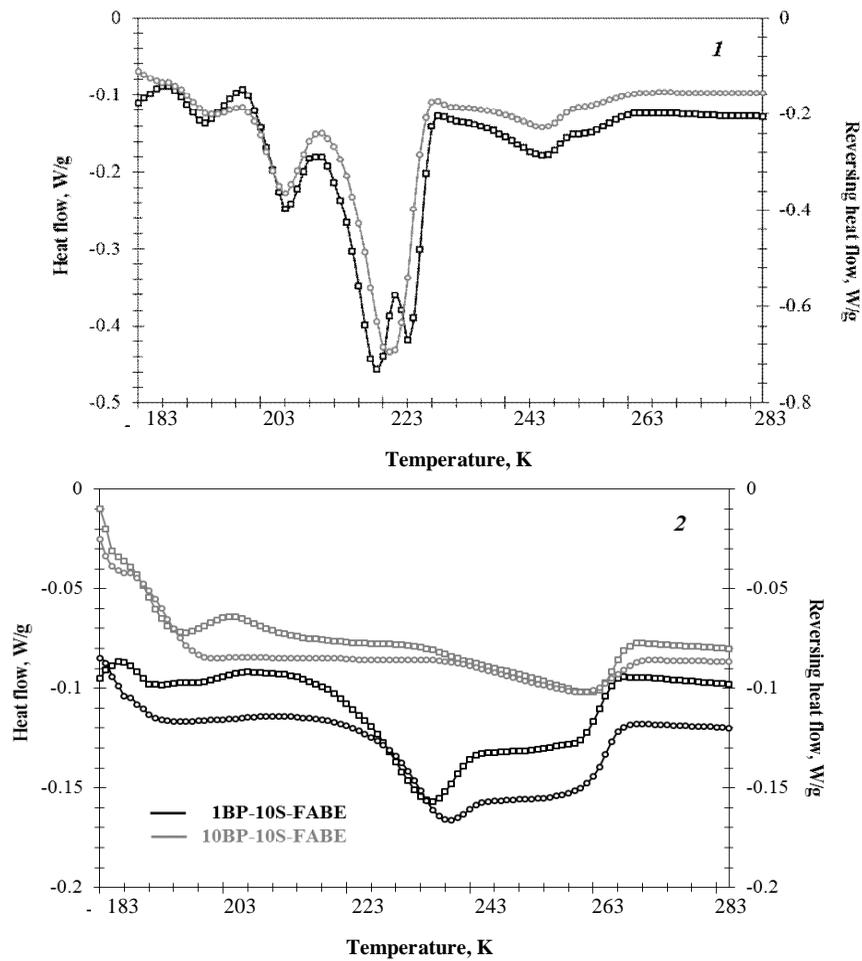


Fig. 5. MDSC curves of FAE (1) and vulcanized FAE (2): □ – heat flow; ○ – reversing heat flow

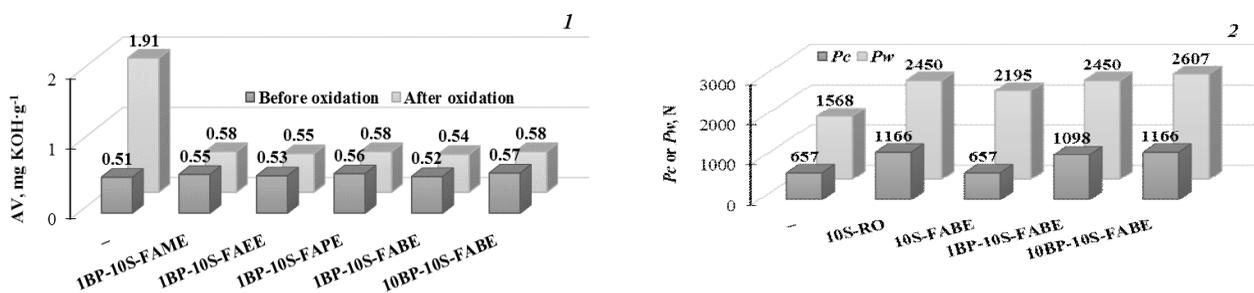


Fig. 6. Properties of lithium lubricants with application of oleochemical sulfanes: antioxidant (1) and tribological (2)

Test results of tribological properties illustrated in Fig. 6(2) showed that lubricants with the application of synthesized OS have higher values of P_c and P_w , in comparison with a base lubricant and lubricant on the basis of sulfurized butyl esters (10S-FABE). In addition, their extreme pressure characteristics do not concede to the quality of sulfurized rapeseed oil (10S-

RO), and at high concentration of BP surpass them. It should be mentioned that we did not find any difference between extreme pressure properties of vulcanized FAE obtained with various alcohols. As for anti-friction properties, there is no single answer for now. The problem is still open and needs further deep exploration.

4. Conclusions

For the first time, the method of synthesis of oleochemical sulfanes was developed via complex transformation of rapeseed oil by transesterification with methyl, ethyl, *n*-propyl, or *n*-butyl alcohols and further sequential vulcanization of esters by benzoyl peroxide and elemental sulfur. The structure of synthesized OS was discovered by the methods of elemental analysis, IR spectrometry, NMR and DSC. In combination with quantum chemical models, reasonable mechanism of benzoyl peroxide decomposition and further reaction were proposed. It was established that oleochemical sulfanes from vulcanized FAAE do not cause corrosion of steel or copper, provided high antioxidant and tribological properties, thereby, recommended as effective multifunctional additives for lubricants.

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ОЛЕОХІМІЧНИЙ СИНТЕЗ СУЛЬФАНІВ, ЇХ БУДОВА ТА ВЛАСТИВОСТІ

Анотація. Вперше внаслідок послідовної вулканізації алкілових естерів вищих жирних кислот ріпакової олії пероксидом бензоїлу та елементним сульфуром синтезовано олеохімічні сульфани. Методами інструментального аналізу встановлено їх будову і властивості. Показано, що олеохімічні сульфани – комплексні структури різного ступеню зшивання, характеризуються відмінними антиокиснювальними й трибологічними властивостями і не викликають корозії міді та сталі у жорстких умовах тестування.

Ключові слова: ріпакова олія, органічні сульфани, синтез, механізми реакцій, добавки до мастильних матеріалів.