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OBTAINING EPOXIDIZED MONOALKYL OLEATES OF C2-C4 ALCOHOLS BASED ON WASTE COOKING OIL USING STRONGLY ACIDIC ION EXCHANGE RESINS

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Abstract. The current study is devoted to the synthesis of epoxidized monoalkyl oleates of linear and branched C2-C4 alcohols based on waste cooking oil using commercially available brands of strong acidic ion-exchange resins (non-porous gel Amberlite IR120 and KU-2-8ChS and porous macroreticular Purolite CT275). The process aimed to obtain oleoepoxides as promising bio-based platforms for further chemical modification. At first, corresponding monoalkyl oleates were synthesized via transesterification or esterification. Epoxidation was carried out at 40–60 °C for 4 h using oleate: CH_3COOH : H_2O_2 with a molar ratio of 1 : 0.4 : 2.0. Using 10–11 % (dry basis) of sulfocationites provided 96–100 % conversion and >99 % selectivity. Halving the sulfocationite load resulted in a significant decrease in conversion (83–86 %) for non-porous samples, and the same conversion for porous samples (99 %). The composition of the obtained products (epoxidized oleate content is above 80 %) was determined by gas chromatography; the chemical structure was confirmed by ^1H and ^{13}C NMR spectroscopy.

Keywords: acylglycerol-based biomass, monoalkyl oleates, epoxidation, oleoepoxides, solid acid catalysts, sulfocationites.

1. Introduction

In the developed world, there is a clear trend towards reducing the consumption of fossil hydrocarbons. The exhaustibility of reserves, uneven distribution, and environmental damage are driving humanity to constantly search for alternative renewable energy sources and raw materials. Biomass is a virtually inexhaustible source of renewable carbon. It can be qualified to produce potential "green" functional analogs of practically important materials based on fossil hydrocarbons. Therefore, its chemical transformation is a topical area of modern research[1–3].

Acylglycerol-based biomass, or, more simply, oil and fatty feedstock, being the largest source of renewable carbon after lignocellulosic biomass, has proven to be one of the sustainable alternatives to fossil hydrocarbons. It is most widely used for producing transport biofuels, mainly traditional biodiesel, fatty acid methyl esters (FAME). It is also used to produce surfactants, biolubricants, bioplasticizers, biopolymers, *etc.*[4–8].

The majority of acylglycerol biomass is represented by edible vegetable oils, the use of which as a feedstock is largely limited for both economic and ethical reasons. A more rational and sustainable solution is to process low-cost non-food feedstocks such as waste cooking oil (WCO), refined edible oil by-products (soapstocks, glycerol phosphatides), biodiesel waste materials, *etc.* WCO represents a particularly valuable sustainable source of raw materials for oleochemistry. WCO is produced in large quantities and largely released into the environment without appropriate disposal[7]. Consequently, in the EU, the proportion of WCO in the total volume of oil and fat raw materials processed into transport biofuels (FAME, renewable diesel and sustainable aviation fuel) has reached 29 % and continues to increase[9]. In accordance with the stipulations of the current European Renewable Energy Directive (RED II), the annual expansion of WCO processing volumes is anticipated to be 1.5 %. This is primarily attributable to the reduction in the utilization of biodiesel derived from fresh palm oil[10], which accounts for approximately 9 % of the total[9]. To meet the demand for such raw materials, the import of WCO from outside the EU, including from Ukraine, continues.

Epoxides are currently a significant raw material for the chemical industry, exhibiting a high degree of variability in their modification capabilities through the opening of oxirane cycles. Oleoepoxides exhibit a similar range of chemical modification possibilities to petroleum epoxides and are therefore a sustainable green alternative. It is anticipated that interest in oleoepoxides and their

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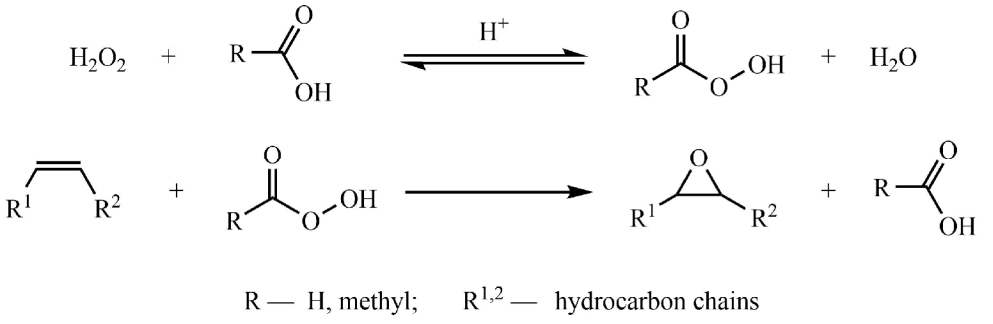
derivatives will continue to grow, due to the simplicity, efficiency, and versatility of oxirane ring formation and their reactions. Furthermore, the ongoing transition of humanity to a sustainable, circular, low-carbon economy will also contribute to this growth. For instance, oleo epoxides are employed in the production of environmentally friendly biolubricants or polyols, which are subsequently utilized in the manufacture of polyurethanes and other materials[11].

It is possible to epoxidize both triglycerides of vegetable oils and any of their derivatives containing unsaturated fatty acid residues, such as esters of monohydric alcohols, diols or polyols, fatty acids, *etc*. The physicochemical and technical characteristics of the resulting oleoepoxides will be determined by the chemical structure of the starting reagents and the degree of unsaturation of their acyl moieties.

The traditional method of epoxidation of double bonds is the so-called Prileschajew reaction[12], which is still widely used in industry (Scheme 1). The formation of the oxirane ring requires the interaction of the double bond with a peroxy acid[11]. The latter is typically formed *in situ* as a result of the oxidation of a carboxylic acid (usually formic or acetic acid) with hydrogen peroxide. The formation of peracid is an equilibrium process[13]. Even small amounts of an acid catalyst significantly intensify the formation of peracid. Traditionally, strong mineral acids are used as acid catalysts. Their effectiveness in this process varies as follows (in descending order): sulfuric acid (H_2SO_4) > phosphoric acid (H_3PO_4) > nitric acid (HNO_3) > hydrochloric acid (HCl)[11]. Hydrogen peroxide is typically employed in the form of an aqueous solution with a concentration of 30–50 %. Consequently, during epoxidation, chemical reactions co-occur in two immiscible phases. In the aqueous phase, peracid formation or perhydrolysis occurs in the presence of a catalyst. In the hydrocarbon phase, the peracid reacts with double bonds and is reduced to the initial acid (Scheme 1)[11].



Scheme 1. A simplified epoxy reaction scheme

The parameters of the epoxidation process in the presence of an acid catalyst determine the occurrence of various side reactions. These include the opening of the oxirane ring with acids, peracids, water, and hydrogen peroxide, as well as epoxy isomerization to ketone, epoxy oligomerization, and others[14].

The conversion of double bonds during epoxidation is influenced by several factors, including the ratio of reagents, temperature, and process duration[15–17]. The efficiency of oxirane ring formation is also affected by many other factors, including mass transfer, diffusion, mixing intensity, fatty acid composition, side reactions, and so on. It is important to note that oxirane rings are much more reactive than stable acyclic esters[11].

The epoxidation methods using strong mineral acids, in addition to the occurrence of side reactions, also possess a number of other typical disadvantages characteristic of homogeneous catalytic systems. These include the complexity of separating the reaction mixture, the necessity to dispose of environmentally damaging mineral acids and epoxidation by-products, high corrosiveness of mineral acids. Consequently, the use of solid acid catalysts in the process is undoubtedly more progressive. A significant amount of researches[18] has been conducted to develop effective alternative catalytic systems for the epoxidation process. It is of particular importance to consider the use of commercially available brands of strong acidic ion-exchange resins, specifically sulfocationites, as solid catalysts. Numerous research studies have demonstrated the catalytic efficiency of such materials in the formation of peroxy acid for the epoxidation reaction of WCO, which is comparable to sulfuric acid. The use of sulfocationites as solid catalysts allows for the epoxidation of vegetable oils to be carried out in a cleaner and more environmentally friendly way[19].

The active sites of sulfocationites are represented by -SO_3H sulfogroups situated on a polystyrene matrix crosslinked with divinylbenzene. A schematic representation of the sulfocationite polymer structure is shown in Fig. 1.

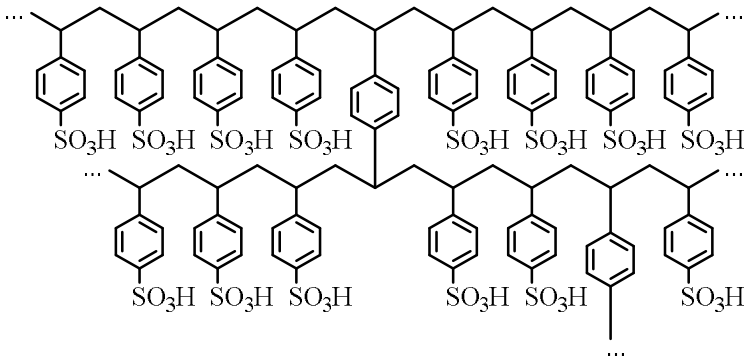


Fig. 1. Schematic representation of sulfocationite polymer structure

Sulfocationites fall into two main categories. The first is gel-type resins with no apparent porosity in the dry state, which limits the access of relatively large reagent molecules to active sites deep within the polymer structure. However, partial access to the latter is made possible by swelling the cationite in the reaction medium. The other group includes macroreticular resins with stable macro and mesopores of 2–200 nm diameter range, which are freely accessible to large reagent molecules.

An important advantage of using acidic cationites in the epoxidation process is the low intensity of side reactions of oxirane cycles. This is due to the fact that the cationite is suspended in a different phase, so the interaction of its active sites with the components of the organic phase is limited. Another obvious advantage is the ease of separation of cationites from reaction products[20,21].

Studying the characteristics of the effective use of acid cationites for producing oleoepoxides is an important subject of modern research. In the study[22], the effectiveness of some strong acid cationites with the various porous structures of the polymer matrix for the epoxidation of sunflower oil was compared. The content of di- and monounsaturated components was 58 % and 32 %, respectively. Epoxidation was carried out with the use of non-porous gel Amberlite IR120 and macroporous Amberlyst 15, Amberlyst 39, Amberlyst 70, Purolite CT275, and Purolite CT269 resins in a mixture with acetic acid and 50 % H_2O_2. Among the porous sulfocationites presented, the authors distinguish between Purolite CT275 and Amberlyst 39. Although both samples have similar characteristics, the latter has a smaller pore diameter, which may restrict the penetration of oil triacylglycerols and, consequently, the probability of side reactions proceeding. The process was carried out at optimum conditions for the porous Amberlyst 39 sample, *i.e.*, 75 °C, with molar ratios of hydrogen peroxide : double bonds of 1.1 : 1 and acetic acid : double bonds of 0.2 :1. A 15 wt. % of catalyst (based on oil) was used. Yield and selectivity were determined by the change in oxirane content. After 24 hours of operation, Amberlyst 39 showed the highest oxirane yield (87 %) with a selectivity of 98 %. It is also the most effective in terms of multiple reuse (at least 10 times without significant loss of efficiency).

Turko *et al.*[23] compared the efficiency of soybean oil epoxidation (C16:0 – 11 %, C18:0 – 4 %, C18:1 – 23 %, C18:2 – 56 %, C18:3 – 5 %) in the presence of solid porous Amberlyst 16, Amberlyst 15, non-porous Amberlite IR 120 with 60 % hydrogen peroxide and formic acid in a semi-batch reactor. Conversion and selectivity were calculated from the change in oxirane and iodine numbers, and the results agreed with the GC analysis. All resin samples after 3 h of reaction (55 °C, 5 wt. % of catalysts, double bonds : formic acid : peroxide molar ratio was 1 : 0.36 : 1.10) gave high conversions (over 90 %) compared to the blank synthesis without a catalyst (about 75 %). The highest conversion was obtained on the porous Amberlyst 16 sample (about 98 %), but the non-porous Amberlite IR120 was not inferior in this respect and surpassed it in the selectivity of epoxy formation (about 87 %). The lowest selectivity (65–70 %) was observed for Amberlyst 15. The authors emphasize that although Amberlite IR 120 is the best in terms of catalytic performance, the high degree of swelling nullifies these advantages as it interferes with catalyst regeneration in a continuous reactor.

The epoxidation of methyl esters of jatropha oil using peracetic acid obtained *in situ* from hydrogen peroxide and acetic acid in the presence of Amberlite IR-120 sulfocationite was studied by Derahman *et al.*[24]. After 6 hours, a conversion of 89.9 % was obtained at a temperature of 70 °C and a molar ratio of acetic acid : hydrogen peroxide : ester of 0.5 : 1.5 : 1. The structure of the products obtained was confirmed by IR spectroscopy and ^{1}H NMR spectroscopy. The authors showed that the use of 20 wt. % sulfocationite allowed to achieve maximum conversion in the shortest time, while the use of 5 wt. % sulfocationite required about 10 hours to achieve the same results.

Rios *et al.*[25] studied the epoxidation of methyl esters of jatropha oil (C18:1 – 34 %, C18:2 – 44 %) using several solid catalysts, including ion-exchange resins

Dowex 50Wx2, Amberlite IR-120, Amberlyst 15 and SAC 13 (a composite material made of Nafion nanoparticles entrapped in a silica matrix), and immobilized Novozym 435 enzyme. The molar ratio of hydrogen peroxide to double bonds was 1.1 : 1, and the catalyst and acetic acid were taken in a mass ratio of 1 : 10 and 1 : 11.9 g/g, respectively, to the ester. The reaction was carried out using toluene as a solvent for 24 h at 57 °C for the cationites and 25 °C for the enzyme. The immobilized Novozym 435 lipase demonstrated near-complete conversion and selectivity for epoxide formation, although it was not suitable for reuse. Among the ion-exchange resin samples, the most effective was the non-porous Amberlite IR-120, which achieved approximately 90 % conversion and 70 % selectivity and was stable for five reuses. The authors posit that the high selectivity observed is a consequence of the reduction in glycol formation, which is facilitated by limiting the access of epoxy to the acid centers of the catalyst. This can be achieved by utilizing resins with a high degree of crosslinking and a low external surface area (*i.e.*, gel type). Conversely, Dowex 50WX2 cationite of gel type and low crosslinking degree exhibited glycol selectivity of over 90 % at a conversion of approximately 90 %. The only porous sample tested, Amberlyst 15, demonstrated unexpected behavior, with epoxidation selectivity dropping significantly within minutes of initiating the process.

The conditions for the synthesis of epoxidized sucrose soyate (soybean oil fatty acids esterified with sucrose) were optimized by Monono *et al.*[15] in the presence of Amberlite IR 120 gel-type sulfocationite. The results of the factorial experiment indicated that the optimal conditions for epoxidation were a molar ratio of double bonds : H_2O_2 : CH_3COOH of 1 : 2.0 : 0.4, a temperature of approximately 60 °C, a reaction time of 4 hours, and use of 20 wt. % cationite. These conditions allowed for a 98 % conversion of double bonds. The authors do not employ the concept of selectivity; however, since the optimization was based on the product epoxy number, its value should be close to 100 %.

A review of the literature reveals that the use of gel-type non-porous sulfocationite samples, such as Amberlite IR-120, typically results in higher selectivity for epoxides. Conversely, the use of porous macroreticular samples has been observed to reduce this parameter due to the occurrence of more intense side reactions of the formed epoxides. It is also noteworthy that in the majority of studies involving sulfocations, double-bond epoxidation is conducted directly on oil triglycerides. Consequently, the resulting products are a mixture of epoxidized triglycerides of varying compositions. The progress of the reaction is quantitatively monitored by changes in general indicators such as iodine number, oxyranic oxygen content, *etc*., or by changes in the signals of the corresponding modes in the NMR spectrum, without consideration of the transformations of individual components of the raw material.

The objective of the present study was to synthesize a series of epoxidized monoalkyl oleates of lower C2-C4 alcohols as a versatile oleochemical platform substances suitable for chemical modification *via* a wide range of oxygen ring-opening reactions. This was done after a preliminary comparison of the common commercial brands of acid cationites efficiency in the epoxidation of fatty acid esters. The raw synthetic feedstock for the preparation of esters was waste cooking high-oleic sunflower oil containing more than 80 % oleic acid in fatty acid composition. The esters obtained from it can rightfully be called oleates, as this term is often applied even to products with a proportion of oleic acid in the range of 60–70 %. Finally, let us emphasize that the chemical nature of the ester substituent (although it should not have a significant impact on the epoxidation of double bonds of acyl moieties) largely determines the physical and chemical properties of esters and their epoxides. The nature of the ester substituent and the reagent employed in epoxide cycle opening reactions offers a wide potential for the directed synthesis of oleochemicals with predictable physical and chemical properties.

2. Experimental

2.1. Materials

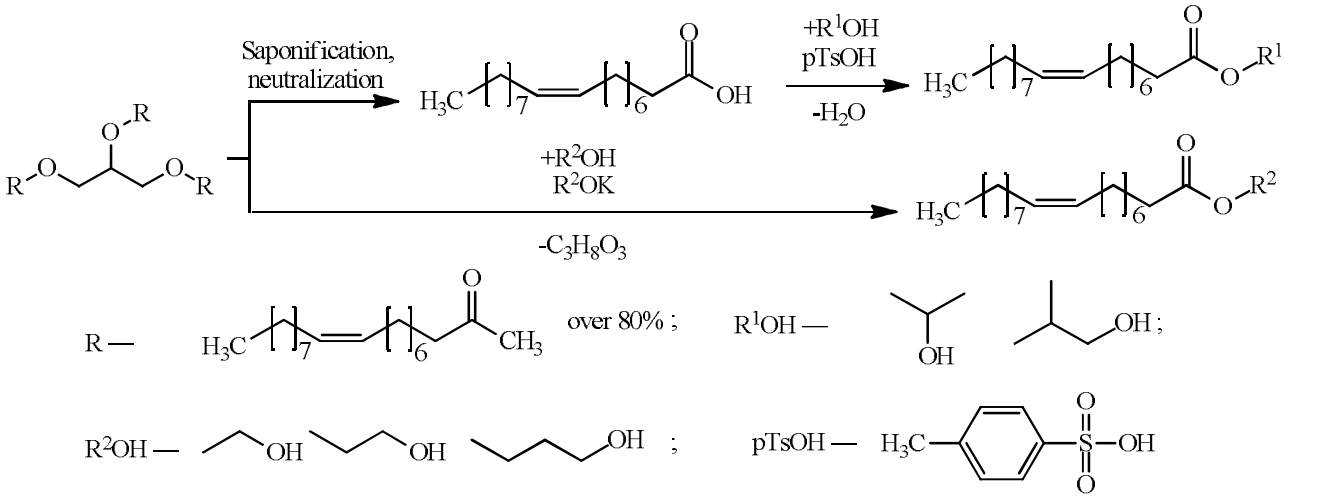
Monoalkyl esters of fatty acids with C2-C4 alcohols were obtained based on waste high oleic cooking sunflower oil. Its characteristics are presented in Table 1.

Table 1. The characteristics of the waste cooking oil sample

Parameter	Value
Acid number, mg KOH/g	1.20
Water content, %	0.05
Fatty acid composition	
Palmitic acid (C16:0), %	4.4
Stearic acid (C18:0), %	2.6
Oleic acid (C18:1), %	81.7
Linoleic acid (C18:2), %	6.1
Other fatty acids, %	5.2

The reaction scheme for the monoalkyl esters synthesis is presented below (Scheme 2). The synthesis of esters with linear substituents was carried out following an effective approach previously developed at the Department of Catalytic Synthesis of the V. P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry NAS Ukraine. This approach involves a one-step alkaline transesterification of oil with alcohols using appropriate

potassium alkoxides as catalytic reagents[26–28]. To obtain esters of branched alcohols, oil triacylglycerols were converted to fatty acids and esterified in the presence of *p*-toluenesulfonic acid. Water, formed *via* esterification, was continuously removed by the Dean-Stark method. In the case of isopropyl alcohol, an azeotropic agent (cyclohexane) was introduced. Following the purification by vacuum distillation, all synthesized transesterification products were light yellow or virtually colorless liquids of 97–99 % purity.



Scheme 2. Reaction scheme for the synthesis of monoalkyl esters based on WCO triglycerides

The sulfocationites of commercially available brands Amberlite IR 120 (USA), CU 2-8ChS (Ukraine), and Purolite CT 275 (USA) in hydrogen form were employed as catalysts for the formation of peracids. The reagents employed in the epoxidation process were acetic acid (98 %) and hydrogen peroxide (50 % aqueous solution). The following auxiliary substances were employed in the purification of epoxides: sodium bicarbonate, sodium sulfate (anhydrous), and cyclohexane. Gas chromatography was used for the analysis, utilizing high-purity helium and hydrogen gases.

2.2. Techniques of Catalysts Characterization

The low-temperature N_2 adsorption / desorption isotherms (–196 °C) of cationite samples were obtained using a Quantachrome Autosorb NOVA 1200e® automatic analyzer. The isotherms were employed to calculate the specific surface area (S^{BET}), the total pore volume (V_Σ), and the average pore size (R^{av}) using the NOVAWin™ software. The S^{BET} was calculated using the multipoint BET method, while the V_Σ was determined based on the volume of adsorbed nitrogen at $p/p_s > 0.991$. Finally, the R^{av} was estimated using the formula $R = 2V_\Sigma/S^{BET}$, assuming the cylindrical shape of pores. The volumetric distribution of pores by radius was determined by the density functional theory (DFT) method.

The infrared absorption spectra were recorded on a Shimadzu IRAffinity-1S infrared spectrometer (Japan) with a Speacac GS 10801-B ATR attachment, using the technique of attenuated total reflection. The spectrum of air was initially recorded as a "zero" sample. Thereafter, a small quantity of powdered dehydrated catalyst was swiftly placed on the surface of the diamond prism of the ATR device, fixed with a special clamp, and the IR spectrum was recorded.

TG/HDSC (thermogravimetry / high-temperature differential scanning calorimetry) studies of the samples were conducted using a Linseis PT 1600 derivatograph in an air atmosphere (12 mg of the sample, 10 °C/min heating rate).

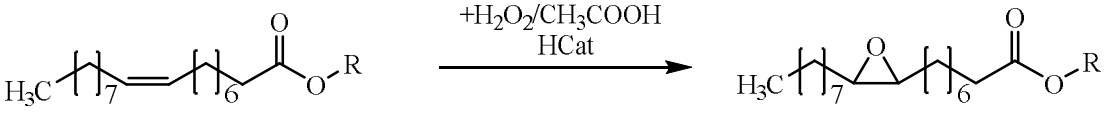
The static exchange capacity of cationites was determined as follows. As the moisture content can be quite uneven throughout the cationite even in the original package, catalyst samples were carefully dehydrated by heat treatment in a drying oven with a gradual temperature increase from room temperature to 110 °C. Calculated loss of samples mass (%) is further referred to as the moisture content of cationites. Thereafter, a dehydrated cationite sample was weighed (0.0001 g accuracy) and placed into a 250 cm^3 flask, and 100 cm^3 of 0.1M NaOH was added. The flask was sealed and left for at least 10 h, stirring occasionally. A 25 cm^3 aliquot of the liquid phase was taken and titrated with 0.1 M HCl using phenolphthalein.

The kinematic viscosity of the epoxy samples at 40 °C was measured using a glass viscometer. The density at 15 °C was determined using an aerometer.

2.3. Synthesis of Epoxides

For the epoxidation of the synthesized monoalkyl esters, we adapted a method known from the literature and optimized for the synthesis of epoxidized sucrose esters of soybean oil fatty acids[15], which consists of the reaction of double bonds with a peracid formed directly during the interaction of acetic acid with hydrogen peroxide in the presence of sulfocationite in hydrogen form (Scheme 3).

The epoxidation was carried out in a three-necked, round-bottomed flask reactor under mechanical stirring. At first, a sample of sulfocationite was placed into the reactor, the calculated mass of monoalkyl esters and acetic acid was added, and heating and stirring were started. At the same time, the calculated mass of H_2O_2 (50 % aqueous solution) was placed in the dropping funnel. When a temperature of 40 °C was reached, the peroxide dropwise addition was started. The rate of addition was controlled in such a way that the temperature of the reaction mixture did not exceed 55–60 °C (due to the exothermic effect of the peracid formation reaction). In our case, the calculated amount of peroxide was added during 30–40 minutes. After this period, the reaction was continued at 60 °C for another 3.5 hours.



R — linear and branched alkyl chains C_2-C_4; HCat — sulfocationite in H-form

Scheme 3. Reaction scheme for epoxidizing double bonds of monoalkyl esters

At the end of the synthesis, the liquid phase was decanted into a separating funnel. The reactor containing cationite was washed with cyclohexane. The cationite was separated by filtration through a paper filter and also washed with cyclohexane to extract the remaining epoxy. The filtrate (cyclohexane with dissolved epoxy) was transferred to a separation funnel with the reaction products. The mixture in the funnel was separated into two phases – the lower aqueous acid phase and the upper phase, which was the oleoepoxide dissolved in cyclohexane. The upper phase was separated and washed first with a 10 % sodium bicarbonate solution to a slightly alkaline or neutral pH and then with distilled water to a neutral pH. The washed product was dried over anhydrous sodium sulfate overnight and filtered. Cyclohexane was distilled out under reduced pressure (water vacuum ejector) with nitrogen bubbling through a capillary tube and heating to 80–90 °C.

2.4. Analysis of Epoxides

Quantitative analysis of epoxy products was performed by gas chromatography (GC) using an Agilent GC 7890A equipped with a split / splitless inlet, a J&W HP-5 high-temperature capillary column (30 m/0.32 mm/ 0.25 μm; (5% phenyl)-methylsiloxane), and a flame ionization detector. 0.2 cm^3 of the sample was placed in a 4 cm^3 vial and diluted by 0.8 cm^3 of n-hexane. Analysis was performed under the following chromatographic conditions: inlet temperature – 250 °C; split ratio – 1 : 25; constant pressure mode, 15 psi (~104 KPa); chromatographic column temperature – heating +5 (°C/min) from 180 °C to 320 °C, then 320 °C for 30 min; sample volume – 1 μL. The content of the components was determined by simple integration as the area ratio of the corresponding peak to all peaks, presented in the high-temperature region of the chromatogram.

The results of chromatographic analyses were employed to calculate the conversion and selectivity of epoxidation, with the sole consideration of the conversion of monoalkyl oleates, as their fraction in sample composition exceeded 80 %. The conversion of C18:2 esters was not quantitatively considered in this work. The conversion of the corresponding monoalkyl oleate ($X_{C18:1E}$, %) was calculated using the following Eq. (1):

$$x_{C18:1E} = \frac{\%^0_{C18:1E} - \%_{C18:1E}}{\%^0_{C18:1E}} \cdot 100\,\% \qquad (1)$$

The percentage of the peak area for each sample, before and after epoxidation, is represented by the values $\%^0_{C18:1E}$ and $\%_{C18:1E}$, respectively.

The selectivity of the conversion of the corresponding oleate to the target epoxide ($X_{C18:1EE}$, %) was calculated using the following Eq. (2):

$$S_{C18:1EE} = \frac{\%_{C18:1EE}}{\sum \%_{C18:1Eall}} \cdot 100\,\% \qquad (2)$$

where $\%_{C18:1EE}$ is the area fraction of epoxide peak and $\sum \%_{C18:1Eall}$ is the sum of the area fractions of epoxide and side products, formed from initial monoalkyl oleate.

The acid number (AN) was determined according to the method described in[29], which involves titrating the sample with a solution of potassium butoxide in *n*-butanol (obtained according to the method described in [30]). The titration was conducted using *n*-butyl alcohol as a solvent, with a bromothymol blue indicator (color change from yellow-hot to blue).

The ^{1}H NMR spectra were recorded using a Bruker AVANCE DRX-500 instrument at an operating frequency of 400 MHz, and the samples were dissolved in deuterated chloroform, $CDCl_3$.

3. Results and Discussion

3.1. Characterization of Catalysts

The solid acid catalysts in the current study were presented by the samples of industrially important and commercially available sulfocationites Purolite CT275 (Pur), CU-2-8ChS (CU), and Amberlite IR120H (Amb) in hydrogen form. By the manufacturer's specifications, the first of these (Pur) is distinguished by a macromesoporous (macroreticular) polymer matrix structure, while the others (CU and Amb) are characterized by a gel-type nonporous structure[31–33]. The identical form of the IR spectra of the cationite samples (Fig. 2) provides evidence of their chemical identity. As discussed earlier, they are the copolymers of styrene cross-linked with divinylbenzene and functionalized with sulfogroups ($–SO_3H$).

In appearance, the sulfocationite samples look like homogeneous spherical grains of gray to brown color, which is generally regulated by manufacturers. The values of the static exchange capacity of the samples are similar, which indicates a close concentration of acid centers potentially capable of catalyzing the formation of superacid (Table 2). All the samples contained a significant amount of moisture, with the highest content in the porous sample Pur. It should be noted that the dehydration of cationite samples was carried out only to determine some of their physicochemical characteristics, while they were used in the syntheses in the wet state as received.

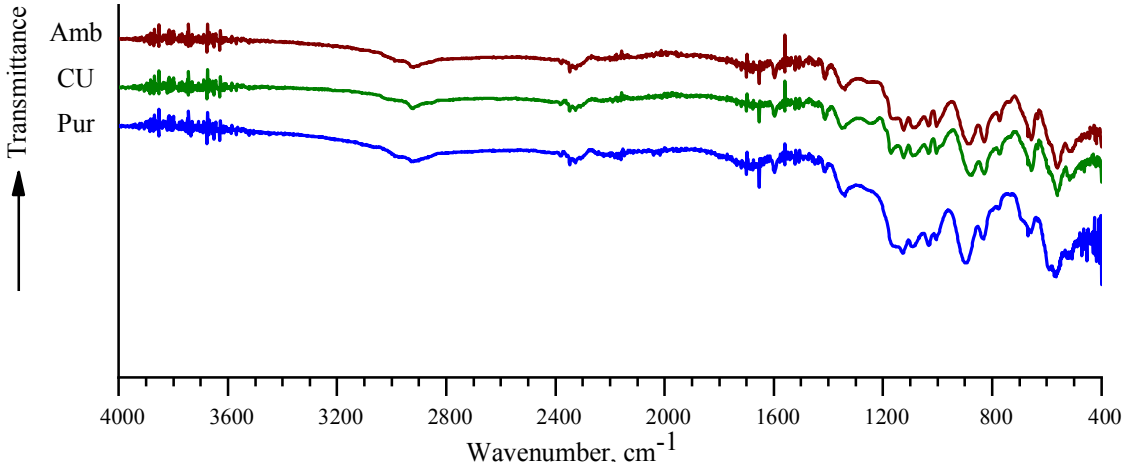


Fig. 2. IR spectra of sulfocationite samples

Table 2. Some characteristics of cationite samples

Characteristics	Sample of cationite		
	Pur	CU	Amb
Appearance	spherical grains of gray color	spherical grains of yellow-brown color	spherical grains of light brown (amber) color
Moisture content, %	59.6	23.0	50.5
Static exchange capacity of the dehydrated sample, mmol/g	5.16	5.03	5.10
Data of low-temperature adsorption/desorption N_2			
S^{BET}, m^2/g	23	6	3
V_Σ, cm^3/g	0.08	0.006	0.003
R^{av}, nm	6.8	2.0	2.0

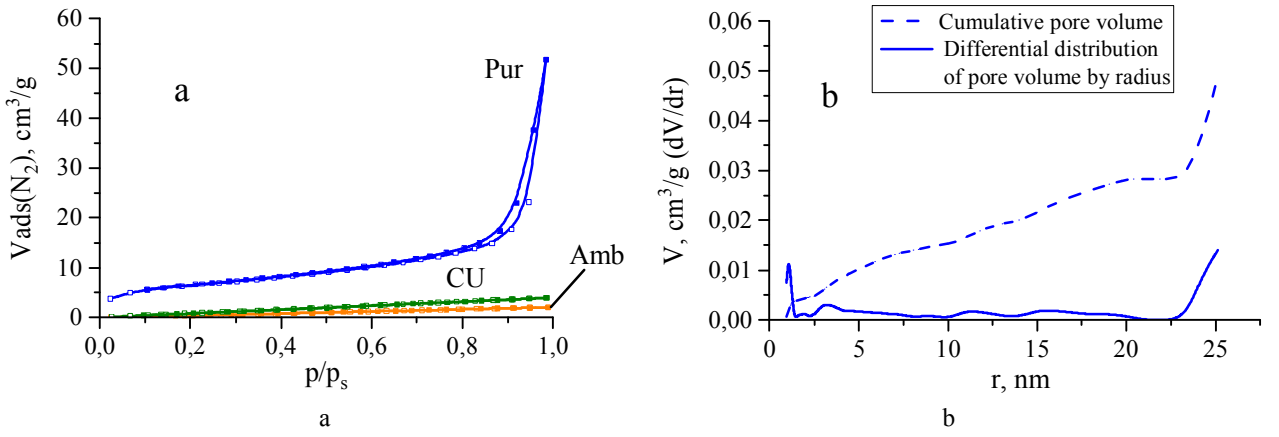


Fig. 3. Low-temperature nitrogen adsorption-desorption isotherms of cationite samples (a) and volume pore radius distribution (DFT) of Pur sample (b)

Fig. 3, *a* illustrates the isotherms of low-temperature nitrogen adsorption-desorption. CU and Amb samples have a linear isotherm, which is characteristic of non-porous materials. In contrast, the isotherm of Pur (Fig. 3, *b*) belongs to type II of the IUPAC [34] classification, indicating its macroporous structure. Additionally, the hysteresis loop indicates the presence of mesopores in the Pur sample. Consequently, the specific surface area of the non-porous samples is several times lower (Table 2). The pore size distribution curve of the porous sample (Fig. 3, *b*) shows a separate minor peak for the narrowest mesopores with a radius of ~1.2 nm, as well as mesopores in the range of 2–20 nm and >22 nm. The latter determines the bulk of the pore volume of the Pur sample, but the presence of pores with a radius of >25 nm, as well as their volume, is not recorded by the method of low-temperature nitrogen adsorption-desorption. Therefore, they are not included in the total pore volume V_Σ calculated from the isotherm point $p/ps \approx 1$. According to the manufacturer, the predominant pores in the Pur sample have a radius of 20–35 nm, and the total pore volume (including macropores) is 0.4–0.6 cm^3/g.[32] This is crucial for the process under investigation, since the possibility of large molecules penetrating the catalyst pores can have a detrimental effect due to side reactions of the epoxy. However, this is unlikely due to the presence of the organic component in a separate phase. It is important to note that the presented isotherms do not show the smallest micropores, which are incapable of penetrating nitrogen molecules. It is also important to note that the isotherms were recorded for samples in a completely dehydrated state, while the syntheses were performed with wet cations in the swollen state. Therefore, the non-porosity of the Cu and Amb samples does not necessarily preclude the possibility of reagent access to acid centers deep within their polymer structure.

Fig. 4 depicts the thermogravimetry TG (sample mass loss) and HDSC curves of cationite samples. Firstly, they show the moisture content of the samples, which removal is reflected by the first area of intense mass loss in the TG curves and the corresponding endothermic effects in the HDSC curves. Despite the higher moisture content, the dehydration of the Pur sample was completed at a temperature 30–40 °C lower than that of the CU and Amb samples, due to its macromesoporous structure.

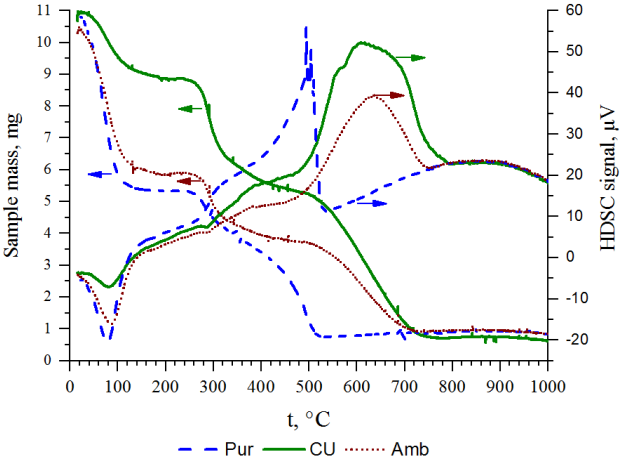


Fig. 4. TG and HDSC curves of cationite samples (10 °C/min, in air)

The mass loss corresponding to the water removal according to the TG curve is somewhat lower than the loss due to drying under steady-state conditions. This discrepancy can be attributed to the partial overlap between the temperature ranges of dehydration and desulfurization. The rapid mass loss of all samples as a result of the latter begins after 235–240 °C. On the HDSC curves of all samples, its low-intensity exothermic effect is transferred to an intense exothermic effect of the poly-

meric matrix oxidation. The nature and temperature limits of the latter are completely different for porous and non-porous samples. It is evident that the open-porous structure of the Pur sample provides free access of air oxygen to the entire internal volume of its grains, which contributes to intensive oxidation at a lower temperature. The oxidation of the Pur polymer matrix begins at a temperature approximately 100 °C lower and ends at a temperature approximately 250 °C lower than in the case of CU and Amb. The exothermic effect on the HDSC curve of the Pur sample, in contrast to CU and Amb, is clearly structured and includes at least three pronounced maxima that can be associated with different chemical processes during oxidation. It is also possible to distinguish subtle endothermic effects at a temperature of approximately 190 °C for the Pur sample and approximately 285 °C for the CU and Amb samples, without any pronounced features on the TG curves. The nature of the TG and HDSC curves generally indicates the complete identity of both non-porous samples (CU and Amb). The disparity in mass loss and intensity of the corresponding thermal effects can be attributed solely to the differing moisture content, which in turn affects the mass of neat cationites. It is also noteworthy that the TG/HDSC data indicates the start of the cationites thermal degradation at temperatures, notably exceeding the thermal stability limits according to the manufacturer's data (120–135 °C).

3.2. Synthesis and Characterization of Epoxides

Table 3 presents the conversion and selectivity of monoalkyl oleates epoxidation in the presence of the corresponding samples of the catalysts, as determined by GC analysis of purified epoxides. The designation of each sample includes "Ep" (epoxy) and an abbreviation, reflecting the alcohol moiety of the corresponding ester (EE – ethyl, PE – *n*-propyl, iPE – isopropyl, BE – *n*-butyl, iBE – isobutyl). As previously stated, we employed a method described in the literature, which involved using Amberlite IR120H sulfocationite (non-porous, gel-type) to form peroxyacetic acid. The original method consists of the use of the cationite in its original as-purchased state. The initial steps of the study's synthetic part commenced with the epoxidation of a sample of ethyl esters using the specified cationite (sample Amb, Table 2), based on the optimal conditions for such systems[15]. It was further assumed that the Amberlite IR120H samples employed in the aforementioned studies exhibited comparable moisture content. Let us underline one more time that cationites were employed in a wet state without preliminary drying, while their load in each synthesis was calculated on a dry basis. The synthesis under the reference conditions (EpEE-2) resulted in the almost complete epoxidation of ethyl oleate double bonds (99.0 % conversion). In the synthesis of EpEE-4 under similar conditions in the presence of the macromesoporous Pur sample, the conversion was at the same level. In contrast, in the synthesis of EpEE-6 using a slightly higher loading of the non-porous CU sample, a completely quantitative conversion (100 % conversion) was achieved.

Table 3. Results of epoxidation of monoalkyl esters samples (molar ratio of monoalkyl ester : CH_3COOH : H_2O_2 – 1 : 0.4: 2.0, 4 h, 40–60 °C)

Epoxy sample	Catalyst, % of moisture	n_{cat}, g/g[1]	X(C18:1E), %	S(C18:1EE), %
EpEE-1	Amb (50 %)	0.05	86.0	100.0
EpEE-2	Amb (50 %)	0.10	99.1	100.0
EpEE-3	Pur (60 %)	0.05	98.9	99.8
EpEE-4	Pur (60 %)	0.10	98.8	99.8
EpEE-5	CU (23 %)	0.05	83.5	100.0
EpEE-6	CU (23 %)	0.11	100.0	99.6
EpPE	CU (23%)	0.11	99.9	99.9
EpiPE	CU (23%)	0.11	100	99.9
EpBE	Amb (50 %)	0.10	96.0	100.0
EpiBE	Amb (50 %)	0.10	98.5	100.0

[1] Catalyst-to-esters mass ratio (on dry cationite basis).

The data obtained indicated the presence of a certain reserve of catalyst efficiency. Consequently, the synthesis was conducted with a reduced catalyst load, maintaining the other process parameters constant. In the case of non-porous cationites CU and Amb, a notable reduction in conversion was observed, with values of 83.5 % and 86.0 %, respectively. Conversely, reducing the loading of the Pur sample did not affect the conversion rate, which may suggest the potential for effective epoxidation with even less Pur sample amount. The high efficiency of the Pur sample is evidently attributable to its macromesoporous structure, which facilitates the access of reagent molecules to a greater number of acid groups within the polymer structure of the sample. This ensures more efficient superacid formation compared to samples of non-porous gel-type cationites Amb and CU. At the same time, high moisture content totally prevents the access of fatty components to the catalyst surface and even inside catalyst pores, filled with water. It is noteworthy that the utilization of macromesoporous caitonite did not cause selectivity dropping issues, as was reported in the literature[22]. In all syntheses, regardless of the porosity of the cationite, this indicator reached almost

100 %. In some instances, the chromatograms exhibited trace components that could be attributed to the occurrence of side reactions, resulting in only a 0.1–0.4 % decrease in selectivity.

Although the porous Pur sample has demonstrated the highest efficiency, epoxidation with the use of gel-type cationite CU-2-8 appears to be a more promising approach. This brand of sulfocationite is the most prevalent in the Ukrainian market, offering the lowest cost. Another disadvantage of Purolite CT275 and similar porous sulfocationite brands is their low mechanical strength. This somewhat limits its potential for multiple reuses in batch reactors with mechanical stirring. In light of the aforementioned considerations, the remaining synthetic tasks of the current study were completed using non-porous samples of CU or Amb. The use of CU for the epoxidation of *n*-propyl and isopropyl esters (under conditions of EpEE-2) confirmed its ability to ensure quantitative conversion. In the case of the epoxidation of *n*-butyl and isobutyl esters using the Amb sample, the conversion rate was slightly lower. Concerning the selectivity of oxirane cycle formation, it remained virtually complete in all cases. It is difficult to definitively identify the factors that contribute most to the complete epoxidation process with the involvement of the CU sample. A slight increase in the catalyst loading may have a beneficial effect on the conversion rate. It is also possible that the lowest moisture content among the tested samples played a role. One might also consider the higher specific surface area of the CU sample (Table 3). However, it should be noted that at such low S^{BET} values, the accuracy of its determination by isotherms is low. Therefore, the given values (3 and 6 m^2/g) should be more correctly interpreted as low specific areas of the same order of magnitude. Additionally, the lengthening of the ester alcohol moiety may also contribute to the reduction in conversion in the experiments with *n*-butyl and isobutyl esters. Consequently, the actual concentration of double bonds in the reagent mixture may be somewhat lower than in the case of epoxidation of ethyl esters. This may result in a slower reaction rate with the superacid.

For instance, the chromatograms of *n*-butyl esters and their epoxides are shown in Fig. 5. The disappearance of the C18:1 *n*-butyl ester peak and the appearance of a proportionally large product peak allow for unambiguous identification of the latter as epoxide at positions 9 and 10 of the acyl moiety. Other peaks on the chromatograms are represented by saturated monoalkyl esters, unconverted unsaturated esters, and epoxidized alkyl esters with other acyl groups in small amounts.

Fig. 6 illustrates ^{1}H-NMR spectra of the epoxidized monoalkyl oleates. It is important to note that the presented spectra do not belong to the pure substances. However, the samples contain more than 80 % of the corresponding epoxidized monoalkyl ester of oleic acid C18:1. The signals of methine protons near carbon atoms forming double bonds (in the range of ~5.4–5.5 ppm) are barely expressed or absent completely. Instead, there are intense signals of oxirane cycle protons (~2.9–3.0 ppm), which indicate that the double bonds of the starting esters are completely and selectively converted into oxirane cycles. Additionally, weak signals in the range of ~3.0–3.2 ppm can be attributed to the methyl protons of the oxirane cycles of the acyl groups of C18:2. There were no other notable changes in ^{1}H NMR spectra after epoxidation, including the appearance of the signals of ring-opening byproducts, expected in the range of 3.0–4.0 ppm. In general, the ^{1}H NMR spectra fully confirm the trends revealed by GC analysis. Complete and selective conversion of double bonds into oxirane cycles is also evident from ^{13}C NMR spectroscopy. As instance, ^{13}C NMR spectrum of epoxidized ethyl oleate (sample EpEE-2) is shown in Fig. 7. Signal, corresponding to oxirane carbon atoms (56.6 ppm) can be clearly identified, while signal of olefinic carbon atoms (around 130 ppm) or any other signals, which can be attributed to the byproducts, are absent.

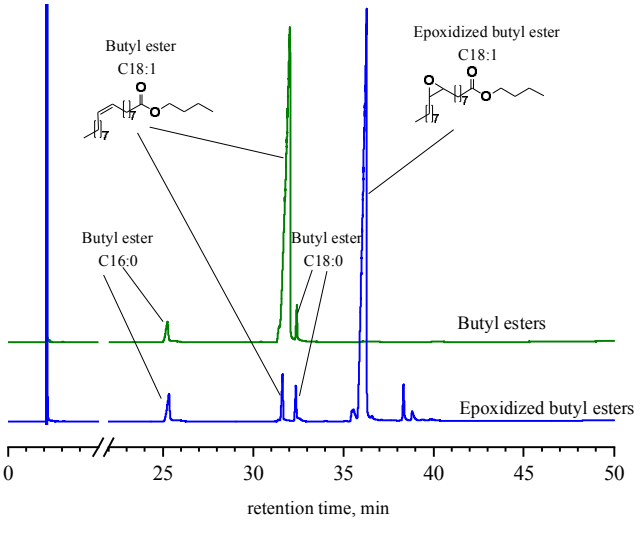


Fig. 5. Chromatograms of *n*-butyl esters and their epoxides

A comparison of the physicochemical parameters of the synthesized oleoepoxides (Table 5) reveals the virtual identity of their density. Contrary, the kinematic viscosity exhibits a considerable degree of variability, with a nonlinear correlation observed between this parameter and the molecular weight of the alcohol moiety. This discrepancy may be attributed to the varying content of non-epoxidized alkyl esters, which exhibit a lower viscosity than their corresponding epoxides. This fact can explain the lower viscosity of the EpBE sample in comparison to the EpPE, EpiPE, and EpiBE samples, as it

exhibited the lowest conversion (Table 3). The content of esters of saturated palmitic and stearic acids in all samples is comparable, as these components did not transform during the process. All epoxy samples exhibit low acidity. This characteristic is highest for the EpiPE sample, which can be attributed to the significant acid value of the initial isopropyl esters, obtained by esterification of fatty acids.

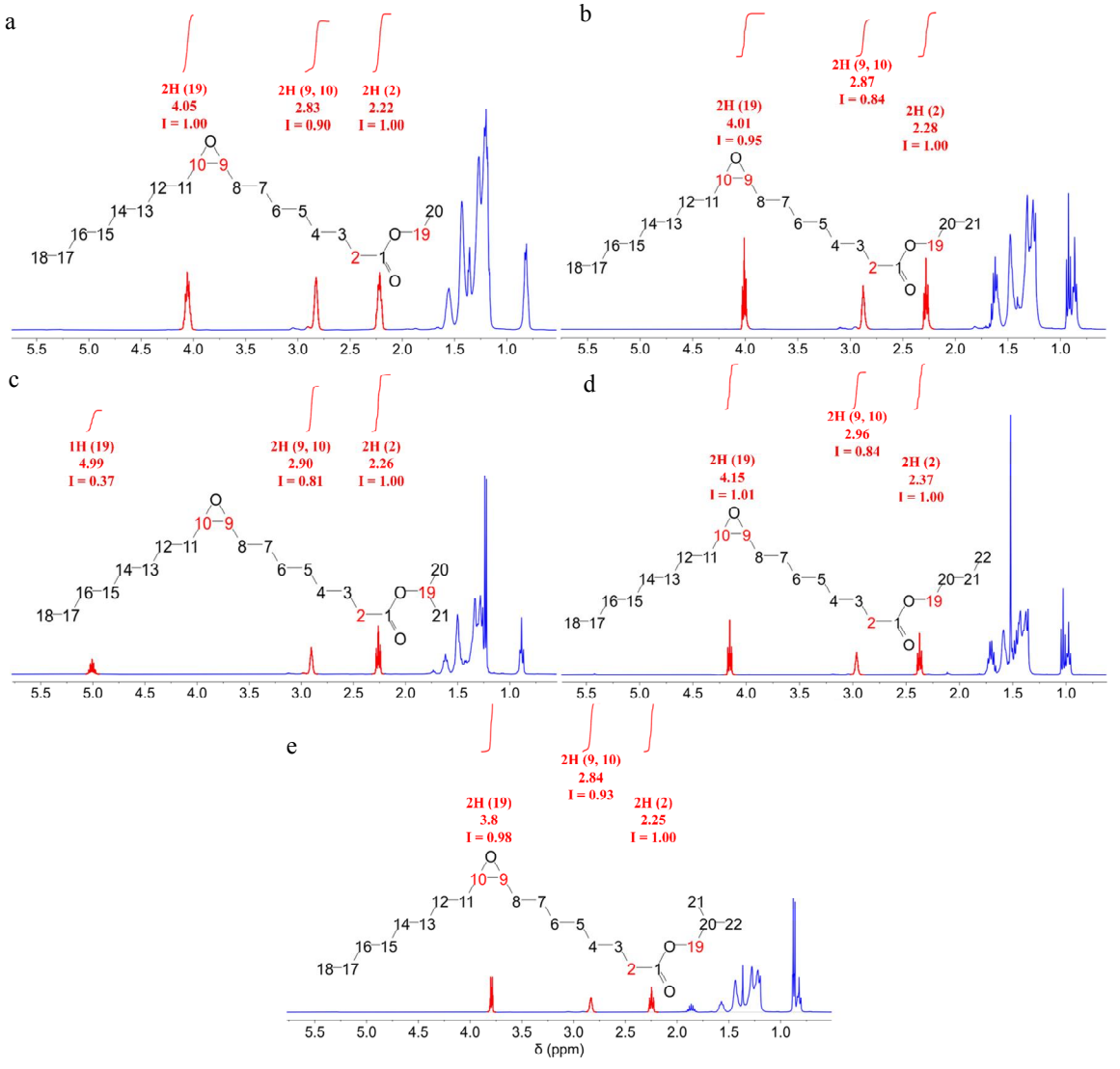


Fig. 6. [1]H NMR spectra of the epoxidized monoalkyl oleates samples: a – EpEE-2, b – EpPE, c – EpiPE, d – EpBE, e – EpiBE

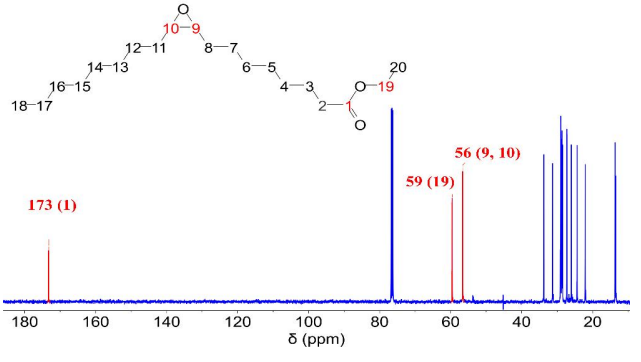


Fig. 7. [13]C NMR spectra of the epoxidized monoalkyl oleate sample EpEE-2

Table 5. Physical and chemical properties and composition of the synthesized fatty epoxides

Parameter	Sample				
	EpEE-2	EpPE	EpiPE	EpBE	EpiBE
Kinematic viscosity (40 °C), mm^2/s	6.99	8.45	8.44	7.91	8.38
Density (15 °C), g/cm^3	0.911	0.911	0.908	0.905	0.899
Acid value, mg KOH/g	0.26	0.24	0.64	0.36	0.22
Content of epoxidized monoalkyl oleate, %	84.1	84.2	83.4	81.4	83.7
Content of unsaturated esters, %	0.9	0.2	0.1	3.9	1.3
Content of saturated esters, %	7.4	7.3	7.4	8.0	7.8

4. Conclusions

This work demonstrates the high efficiency of styrene-divinylbenzene sulfocationites of both gel non-porous (CU-2-8CHs and Amberlite IR120) and macromesoporous types (Purolite CT275) as catalysts for the formation of superacids in the process of monoalkyl oleates double bonds epoxidation. It was shown that the ability of investigated cationites ensured complete or near-complete conversion (96.0–100.0 %) with the absence of side reactions (selectivity of epoxy cycle formation 99.6–100.0 %).

It was demonstrated that the macromesoporous cationite is significantly more efficient in the epoxidation process compared to non-porous samples. This allows for the efficient synthesis of oleoepoxides with at least twice the lower catalyst loading without reducing conversion and selectivity. The Ukrainian-made sulfocationite CU 2-8CHs demonstrated comparable, or even slightly superior, performance compared to the well-known Amberlite IR120 brand.

A series of epoxidized monoalkyl oleates (comprising more than 80 % of the samples composition) of lower alcohols (ethyl, *n*-propyl, isopropyl, *n*-butyl, and isobutyl) were synthesized based on waste cooking high-oleic sunflower oil. The composition and the chemical structure of the obtained products were confirmed by gas chromatography and ^{1}H NMR spectroscopy. The synthesized oleoepoxides are transparent, colorless liquids, exhibiting a density (15 °C) in the range of 0.899–0.911 g/cm^3, kinematic viscosity (40 °C) in the range of 6.99–8.45 mm^2/s, and a low acid number.

The obtained products are promising and versatile platform substances for the targeted green synthesis of oleochemicals with desired physical and chemical properties by means of oxirane ring-opening reactions with a wide range of reagents.

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ОТРИМАННЯ ЕПОКСИДОВАНИХ МОНОАЛКІЛОЛЕАТІВ СПИРТІВ С2-С4 НА ОСНОВІ ВІДПРАЦЬОВАНОЇ КУЛІНАРНОЇ ОЛІЇ З ВИКОРИСТАННЯМ СИЛЬНОКИСЛОТНИХ ІОНООБМІННИХ СМОЛ

Анотація. *Під час дослідження здійснено синтез епоксидованих моноалкілолеатів лінійних і розгалужених спиртів С2-С4 на основі відпрацьованої кулінарної олії з використанням комерційно доступних марок сильнокислотних іонообмінних смол (непористих гелевого типу Amberlite IR120 і KU-2-8ChS і пористої макроретикулярного типу Purolite CT275). Процес здійснено з метою одержання олеоепоксидів як перспективних платформ на основі біовідновлювальної сировини для подальшої хімічної модифікації. Спочатку було синтезовано відповідні моноалкілолеати через переестерифікацію або естерифікацію. Епоксидування виконували з використанням молярного співвідношення олеат : CH_3COOH : H_2O_2 як 1 : 0,4 : 2,0 протягом 4 год за 40–60 °С. Використання 10–11 % сульфокатіоніту (у перерахунку на сухий) забезпечило конверсію 96–100 % і селективність >99 %. У результаті зменшення завантаження сульфокатіоніту вдвічі істотно знизилась конверсія (83–86 %) для непористих зразків і на таке саме значення для пористого зразка (99 %). Склад отриманих продуктів (вміст епоксидованих олеатів понад 80 %) визначено за допомогою газової хроматографії, хімічну структуру підтверджено за допомогою ^1H і ^{13}C ЯМР-спектроскопії.*

Ключові слова: *ацилгліцерольна біомаса, моноалкілолеати, епоксидування, олеоепоксиди, тверді кислотні каталізатори, сульфокатіоніти.*