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Regularities of epoxidized alkyl oleates ring-opening reactions with alcohols, water and organic acids in the presence of commercial sulfonated resins as catalysts

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Current paper deals with the use of sulfonated resins, distinguished by the porous structure (macroreticular Purolite CT275 and gel-type CU-2-8ChS), as solid acid catalysts for syntheses of perspective components of biolubricants via oxirane ring-opening reactions of fatty epoxides with water (hydrolysis), ethanol and i-propanol (alkoxylation), and levulinic and oleic acids (acylation). Epoxidized ethyl and i-propyl oleates as ring opening substrates were synthesized from used cooking oil. Reactions were carried out in batch reactor for 3 h at 100 °C under stirring with epoxide: resin acid sides molar ratio 1 : 0.05. Reagent to epoxide ratio was 10 : 1 (alkoxylation, hydrolysis) or 1.5 : 1 (acylation). Products composition was determined by GC, conversion and selectivity were calculated. Number of side ring-opening reaction were revealed, main of which were isomerization to ketone and dimerization. General observation is that porous Purolite CT275 provides higher conversion, but facilitates side processes. Non-porous CU-2-8-CHs provided notably higher selectivity (up to 90 % for hydroxyl esters in ethoxylation), but with many-times slower conversion, especially in case of alkoxylation with secondary alcohol. In hydrolysis, water soaked cationites did not provide any conversion, while epoxide introduction first on catalyst made transformation possible. Acylation proceeded in a great extent without separate catalyst and was accompanied by dimerization, while isomerization was not observed. Gel-type resin provided only negligible growth of conversion and selectivity. Porous resin enhanced the conversion, but mainly by side reactions intensification. Cyclohexane as solvent facilitated slightly selective catalyst-free acylation, but with significant conversion drop. Purolite CT275 in ethyl levulinate media favored the ring opening of epoxide with ketone function, yielding ketal-type product.

Keywords: fatty epoxide, oxirane ring-opening, sulfonated resins, solid acid catalyst, alkoxylation, hydrolysis, acylation, isomerization

Introduction

Epoxidation of double bonds of fatty feedstock and ring opening (RO) reactions of the formed oxirane cycles is topical area of modern researches [1-2]. Fatty epoxides and their derivatives present the valuable eco-friendly bio-based alternative for a number of fossil hydrocarbon-based chemicals and functional materials. Generally, terms “fatty epoxides” (FE) or “oleoepoxides” are used both for epoxidized vegetable oils (EVO) or animal fats and a range of their derivatives, including fatty acid esters and fatty acids [1]. The most important direct applications of FE are plasticizers and stabilizers for polyvinyl chloride to replace nonrenewable phthalates [1, 3-6]. They also find applications, such as reactive diluents for paints, viscosity modifiers, lubricant additives, acid scavengers, corrosion inhibitors, etc. [1-2, 5-7]. Variety of oxirane RO reactions offers wide opportunities for FE transformation into biopolymers, biolubricants and other materials. Neat epoxides as monomers may serve for thermosetting resins production, while polyols originating from RO can be used for to obtain plant-based polyurethanes [1, 8-12]. The number of RO reactions with various nucleophilic reagents can be carried out to produce biolubricants and other valuable functionalized fatty derivatives. It is anticipated the continuous growth of interest in FE and their consequent products due to the simplicity, efficiency, and versatility of oxirane formation and RO reactions [1]. Used cooking oils (UCO) are sustainable and economical raw staff choice for biofuels and oleochemicals production. UCO worldwide generation is estimated within 41-67 Mt/yr (between 20 % and 32 % of global vegetable oil consumption) and majority of these volumes are still end up in the environment. [2, 13].

Oxirane ring opening needs electrophilic activation of the epoxide by proton or other acid on the first step, followed by regioselective nucleophilic. FE, having no chemical difference between the carbons of oxirane cycle, reacts yielding near equal mixture of two possible regioisomers [1]. In current study we focused on the acid-catalyzed oxirane RO reactions with common and abundant reagents, including water (hydrolysis), lower monohydric alcohols (alkoxylation) and biomass-derived carboxylic acids (acylation). These processes can be carried out in the presence of liquid or organic-soluble acid catalysts, such as H_2SO_4 [14-20], HCl [21], H_3PO_4 [22], $HClO_4$ [23-24], HBF_4 [25-27], *p*-toluenesulfonic [28-30], methanesulfonic or sulfamic [20], formic [31] and acetic [32] acids, as well with the use of solid acid catalysts [17, 28, 33-43]. Development of practically important heterogeneous-catalytic processes for substitution of environmentally and technologically non-excellent homogeneous-catalytic ones, continues to be important subject of modern-day researches [1, 44-48]. Among solid acid catalysts under investigation, strong acid ion-exchange resins (sulfocationites), is of particular importance, as they are commercially available, large-scale produced, widespread materials. Their strong acidic properties is carried by $-SO_3H$ sulfogroups, situated on a polystyrene matrix crosslinked with divinylbenzene (DVB). There are two main types of sulfocationites, distinguished by the porous structure of polymer matrix. The first is gel-type polymer, having no apparent porosity in the dry state. The lack of porosity restricts the access of reactant molecules to the acid sites in the depth of polymer structure, which is may still be possible due to swelling of the resin in the reaction media. The second type is macroreticular resins, bulk of which structure is also presented by gel-type polymer, but containing also a network of the stable macro and mesopores [44, 49-50].

Alongside with liquid acids, sulfocationites use for FE preparation via Prilezhaev's double bond epoxidation method was recently investigations [1, 49-50]. Acid catalyst in this particular case promotes the *in situ* formation of peroxy acid by the reaction of carboxylic acid (usually formic or acetic) with H_2O_2. Aroused peracid oxidizes the double bounds, yielding oxiranes. The latter may react via several RO pathways, causing decrease in selectivity for epoxide. If the final synthetic goal is to obtain vicinal diols, one-pot modified Prilezhaev epoxidation-hydrolysis procedure may be carried out [1, 21, 33-34]. Azzena et al. [33] investigated the selectivity of epoxide/vicinal diol formation in modified Prilezhaev's oxidation (24 h, 57 °C, $C{=}C / H_2O_2 / CH_3COOH = 1.00 : 1.10 : 0.38$ mole ratio) of monounsaturated C18-C22 monoalkylesters using gel-type AmberliteIR120 (8 % DVB) and Dowex50WX (2 % DVB), and macroleticular Amberlyst15 (20 % DVB) sulfonated resins. It was revealed the great difference in catalytic properties of wet as-received and dried samples of resins. For wet cationites conversion was slightly lower and epoxide was the primary product (88-99 %), while dried samples facilitated to diols formation (69.4->99 %). Dried Dowex50WX with lowest crosslinking provided the highest conversion and selectivity for diol (>99 %). Dowex50WX dry sample use for different fatty substrates revealed the clear tendency for decreasing of the diol/epoxide ratio with enlarging of fatty substrates molecules. In case of oils conversion, selectivity for diols was very low. Discussed results is in a good agreement with the earlier work [34], dealing with jatropha oil methyl esters epoxidation/hydrolysis (57 °C, 24 h) with use of the same set of sulfonated resins (dehydrated). Gel-type mid-DVB resin use resulted in the lowest selectivity for glycols (about 30 %), while both gel-type low-DVB and macroreticular high-DVB samples provided similarly high final selectivity around 90 %. Although conversion rate and selectivity for glycols in course of reaction with Amberlyst15 were lower, it was preferred for potential industrial use for its better mechanic stability and better morphology.

Alkoxylation (alcoholysis) of FE in the presence of acid catalyst is accompanied by side transesterification (TE), which may lead to the formation of the complex mixture of products. But since reaction rate of the acid catalyzed TE is low comparing with RO of high-reactive oxiranes, it is does not always taken into account [1]. However, various possible side oxirane reaction are also not often considered by researchers. In classical works [14-16, 18-19] FE alkoxylation was carried out using concentrated sulfuric acid. Hwank et al. [14] alkoxylated epoxidized soybean oil (ESBO) with two-time stechiometric excess of alcohol (methanol, 1-butanol, 2-butanol, 1-hexanol, cyclohexanol, 2,2-dimethyl-1-propanol and 1-decanol) at 80-110 °C. Depending on the reagent, full conversion of oxiranes was achieved after 3-7 h. Significant TE (up to 85 %) was also reported. In the next work [15] of the same authors, alkoxylation of ESBO with 2-ethylhexanol was carried out in similar way. Although authors mentioned formation of side minor products, such as oligomers from epoxy-epoxy reactions, TE and RO were referred as the major products yielding processes. Besides H_2SO_4, other catalysts were also tested. Surprisingly, *p*-toluenesulfonic acid provided very slow RO (82 %) and no TE after 22 h at 130 °C, while solid catalyst Dowex 50W-8X (gel-type sulfonated resin, 8 % DVB) provided 100-% conversion of epoxide and 83 % TE (24 h, 130 °C). In another following paper [16] authors managed to obtain both 100-% RO/0-% TE and 100-% RO/100-% TE products by means of varying of the conditions applied in the ESBO reaction with Guebert alcohols. Moser at al. [18] used other approach for FE alkoxylation in presence of H_2SO_4. Reaction of epoxidized *i*-propyl oleate with monohydric alcohols C2-C10 was carried out at room temperature, which enabled to avoid side TE. Moderate yields of hydroxyl ethers (80-85 %) was obtained after long reaction time (from 24 h for ethanol to 240 h for *n*-decanol). Later, the described approach was extended by to alkoxyalion of the various epoxidized monoalkyl oleates (EMAO) [19]. Issues with the unwanted TE was reported for reaction with methanol. Generally, it was observed, that reactivity of alcohols in RO decreases with lengthening of alkyl chain and with its branching. Also, low reactivity of secondary alcohols (1-propanol, 2-butanol) was reported.

Borugadda et al. [17] tried to use AmberliteIR120 as solid acid catalyst for alkoxylation of epoxidized UCO and methyl esters with methanol. At 70 °C, using 5 % of catalyst load and high excess of alcohol, only 61 % RO was achieved after 9 h of reaction. Switching for sulfuric acid enabled >90 % RO at room temperature after <30 min. For some reason, authors did not try to carry out alkoxylation over Amberlyst15, which was applied on the next synthetic step for esterification. Amberlyst15 (macroreticular, 20 % DVB) is most widely used resin for RO reaction with alcohols [36-42]. Lathi et al. [37] applied Amberlyst15 (2 %) for ESBO alkoxylation with *n*-butyl, *i*-amyl and 2-ethylhexyl alcohols (two-fold excess over stoichiometry) and achieved full epoxides conversion at 90-120 °C after 15-24 h. Longer or bulkier alcohols required longer reaction time and higher temperature to complete reaction. Authors confirmed the retention of triacylglycerol backbone of the alkoxylated products, but no quantitative assessment of the side RO and TE reaction was provided. In paper [40] RO of partially epoxidized camelina oil with methanol in the presence of 10 % of catalyst Amberlyst15(dry) was carried out at 60 °C. Full oxirane conversion was achieved after 6 h of reaction. Authors did not consider possible side TE, but underlined the importance of the avoiding of oligomerization, leading to low hydroxyl functionality and increased viscosity. Use of excess methanol prevented formation of the oligomeric compounds. It was shown, that polyol produced contained less than 10 % dimers and no trimers and higher oligomers. Marques et al. [39] used Amberlyst15 for alkoxylation of deoxidized *n*-octyl oleate with *n*-hexyl, cyclo-hexyl, *n*-octyl and 2-ethylhexyl alcohols (molar ration 3 : 1, 70 °C, 4 h). Provided ^{1}H NMR spectra of the RO products confirms the full epoxide conversion, but also contains the evidence of extensive fatty ketones formation via epoxide isomerization. The latter is known as Meinwald reaction, which is the intramolecular rearrangement of an epoxide to an aldehyde or ketone in the present of Bronstead or Lewis acid [1].

Unlike hydrolysis and alkoxylation, in general case FE acylation does not necessary need separate catalyst. Carboxylic acid reactant, being weak Bronsted acid, is able to autocatalyze the reaction [1]. However, introduction of catalyst may be useful for enhancing the conversion rate and/or to modify a selectivity patterns. In work [51] catalyst and solvent free acylation of epoxidized jojoba-like esters (i.e. oleyl oleate) with propionic acid at 95 °C needed reaction time 16-24 h. Caillol et al. [52] synthesized polyester polyols from ESBO by catalyst free acylation with acetic (100 °C, 40 h, 5 : 1 epoxide/acid ratio), glycolic and lactic acids (80 °C, 4 h, 5 : 1 epoxide/acid ratio). Presence of hydroxyl function in alpha position to carboxylic seemed to activate RO reaction. Side reactions were evidenced, whose explanation is complex. Reaction pathways of oligomers formation were included RO with hydroxyls of formed polyols. Earlier Moser et. al [53] acylated the various alkyloleates epoxides with propionic and octanoic acid at 100 °C for 8-9 h before reaction completed and did not reported the oligomers formation. Dehghan et. al. [54] synthesized vegetable oil based polyols by catalyst free acylation of epoxidized canola oil with fatty acids of castor oil (mainly hydroxysteric acid) for 8.5 h at 180 °C. No oligomerization or other possible side reaction were discussed. Dai et. al. [55] prepared polyols by ESBO acylation with ricinoleic (hydroxystearic) acid for 8 h at 170 °C. Proposed structure of produced soy-based triglyceride polyol assumed also occurrence of the alkoxylation of epoxy with hydroxyl group of the acylation reagent. No other reaction pathways were considered. In work [56] authors demonstrated, that magnesium stearate was a highly efficient catalytic reagent for solvent-free ring-opening epoxy methyl oleate. It resulted in the highest yield (95 %) and conversion rate (99 %) toward alkoxyesters under the same conditions (160 °C, 12 h) superior to lithium and sodium stearates and stearic acid. In case of the latter conversion was 96 %, but alkoxyester yield was only 47 %. Side product (20 % yield), which is dimer from epoxide coupling with secondary alcohol, was observed. In work [28] acylation of epoxidized broccoli oil with benzoic acid (110 °C, 4-24 h, toluene) was carried out as model reaction using Bronsted and Lewis acids (*p*-toluensulfonic acid and $ZnCl_2$) and sodium methoxide. Lewis catalyst provided slowest conversion with highest side reactions rate. Bronsted catalyst also tended for side reactions promotion at prolonged reaction times. MeONa, which indeed immediately reacts with benzoic acid to form sodium benzoat, was found to favor the formation of ester linkage. Schuster et al. [43] evaluated a number of acid solid catalysts, including sulfonated resins (AmbeliteIR120, Amberlyst15, Nafion NR50 and its composites with silica), montmorillonites K10 and KSF, zeolite HY (as received and modified via steaming and dealumination with HCl) in acylation of epoxidized methyl oleate with various carboxylic acids. After 24 h of reaction at 30 °C with butiric acid (5 : 1 to epoxide, catalyst load - 0.1 g per 1 g of epoxide) montmorillonite K10 provided highest (80 %) conversion, while HY samples was least active (9-13 %). Sulfonated resins showed intermediate activity. It was also shown, that reactivity of acids in RO decreased in a raw formic – acetic – benzoic – 2,2-dimethylpropanoic (pivalic) – 2-methyl-propanoic (isobutiric). However, such observation was made for reaction over microporous HY catalyst and its universality is doubtful. Selectivity for hydroxy ethers over Amberlyst15 at prolonged reaction time (24-72 h) and higher temperatures (30-60 °C) was in a range between >95 % for formic and 80 % for pivalic and isobutiric acids. Use of levulinic acid, which is one of the most important renewable chemicals, producing from biomass [47-48], may be complicated by the reaction of ketone function, yielding five-membered heterocyclic ketals (ketalization) In general, the analysis of literary sources showed the lack of the systematic studies of the solid catalysts use in processes under investigation. Researches, as the rule, set as the objective to synthesize a product for certain application and investigate its relevant characteristics, while occurrence of the side transformation and their influence on the product properties are not covered in full. Transformation of EVO triglycerides also does not allow to observe the reactions of individual components due to the complexity of the products formed. Regularities, observed for RO reaction of EVO may be not relevant to the same reaction of the less bulk epoxidized fatty substrates. Studies of various type of solid acid catalyst use in FE reaction and targeted development of new effective ones is promising perspective area of the modern-day green chemistry agenda.

The objective of current study was to synthesize perspective used cooking oil based components for biolubricants formulation via ring-opening alkoxylation and acylation of epoxidized monoalkyl oleates, using sulfonic resins as catalysts. Whole synthetic sequence included obtaining of the high-pure monoalkyl esters from high-oleic used cooking oil on the first stage, epoxidation of the double bonds of monoalkyl oleates on the second stage, and alkoxtylation or acylation of oleoepoxides on the third stage. Purolite CT275 (macroreticular) and CU-2-8ChS (gel) commercial brands of resins were chosen for investigation as catalysts.

Materials and methods

Materials

Initial synthetic source for preparation of oleoepoxides was wasted high oleic cooking sunflower oil, having acid value 1.20 mg KOH/g and water content 0.05 %. Fatty acid composition was the following: 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 %. Wasted oil was kindly provided by representative of the company “Bio-OIL” that collects and supplies such raw materials to its own industrial biodiesel facilities in EU countries.

Technical grade anhydrous ethyl alcohol and reagent grade anhydrous *i*-propyl alcohol (Germany), as well as technical grade potassium hydroxide (China, 89 %), technical grade sodium hydroxide (China, 99 %), molecular sieves 3A (China), diluted sulfuric acid (45-% aqueous solution), reagent-grade *p*-toluenesulfonic acid monohydrate (97.5 %, India) and lab-grade cyclohexane were used for monoalkylesters preparation.

Epoxidation of ester double-bonds was carrying out using acetic acid (98 %) and hydrogen peroxide (50 % aqueous solution) as reactants and sodium bicarbonate, anhydrous sodium sulfate and cyclohexane as auxiliary substances. Sulfocationites of common commercially available brands, CU-2-8ChS (Ukraine) and Purolite CT 275 (USA) in H-form were employed as catalysts for the epoxides RO reactions. CU-2-8ChS also was employed on the stage of epoxides preparation. In RO reactions, the same ethanol and *i*-propanol, distilled water, formic acid (99 %, Germany), levulinic acid (99.8 %, Italy) and oleic acid (about 80 %, prepared from the high-oleic wasted oil sample) were used as reagents. Lab-grade cyclohexane and ethyl acetate, as well as ethyl levulinate (99.2 %), synthesized via esterification of levulinic acid over pTsOH, were used as solvents in epoxides acylation. Samples for GC were dissolved in *n*-hexane (reagent grade) or pyridine (analytic grade).

Catalysts characterization methods

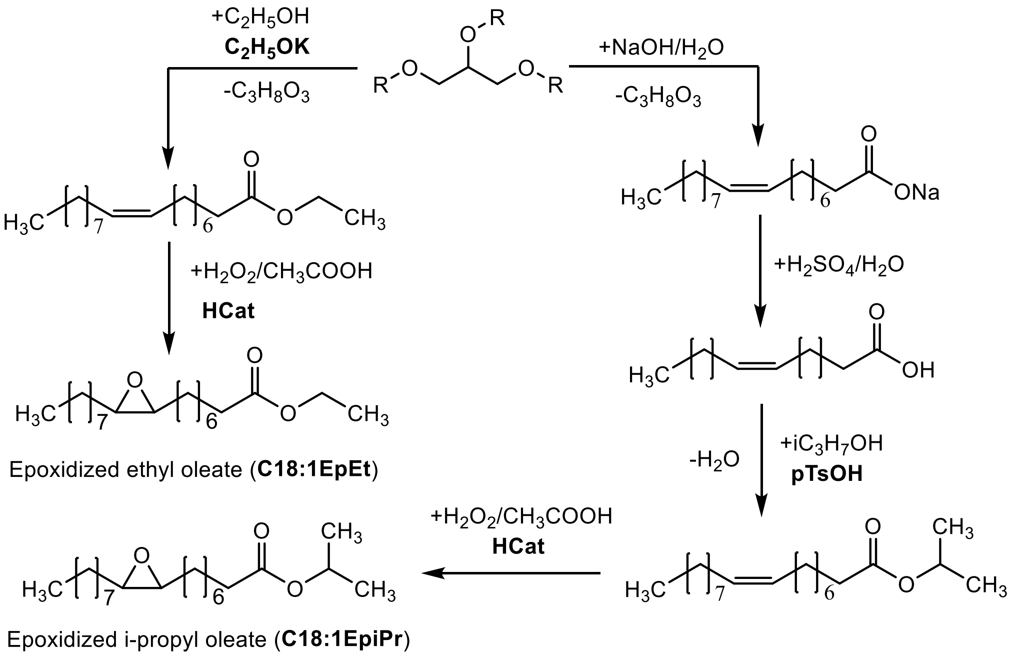
In current study, sulfonated resins were used in dehydrated state. Dehydration was carried out by means of heat treatment in a drying oven with a gradual temperature increase from room temperature to 110 °C. The loss of sample mass (%) was regarded as the moisture content of the initial wet resin.

Static exchange capacity of was determined via acid-base reverse titration. About 1 g of dehydrated sample (four digit weighting) was placed into a 250 cm^3 flask and 100 cm^3 of 0.1 M NaOH was added. Then the flask was sealed and left for at least 10 h, stirring occasionally. Thereafter, 25 cm^3 aliquot of the liquid phase was taken and titrated with 0.1 M HCl using phenolphthalein as indicator.

The low-temperature nitrogen adsorption/desorption isotherms (-196 °C) of cationites samples were recorded using a Quantachrome Autosorb NOVA 1200e® automatic analyzer. The specific surface areas (S^{BET}) were calculated according to the BET theory.

Synthesis of the epoxidized materials as oleochemical platform substances

Scheme 1 demonstrates the reaction sequence of the EMAO synthesis. At first, corresponding monolalkyl esters (ethyl or *i*-propyl) were synthesized. As fatty acid composition of the initial oil is composed predominantly by C18:1 acyl moieties, obtained products can be rightfully regarded as alkyl oleates. To obtain ethyl oleate, direct oil TE with ethanol at ambient temperature, using KOC_2H_5 as alkaline catalyst was carried out. In more details, alkaline synthesis of ethyl esters is discussed in [57-58]. To obtain *i*-propyl oleate, oil was converted into sodium soaps, which where decomposed using water solution of sulfuric acids. Obtained fatty acids were washed, dried over sodium sulfate and finally purified via vacuum distillation under nitrogen gas bubbling. Purified fatty acids were esterified with *i*-propyl alcohol, using *p*-toluenesulfonic acid as soluble catalyst. In order to enhance the efficiency of the esterification, reaction was carried out under reflux condition with removal of the forming water by the Dean-Stark method. Cyclohexane was added as azeotrope-forming agent. The excess of alcohol was removed from products of transesterification (ethyl esters) or esterification (*i*-propyl esters) under mild vacuum (waterjet pump) and continuous stirring at 80 °C. Resulting crude esters were finally purified by vacuum distillation under bubbling of nitrogen gas. Samples of distilled monoalkyl oleates were clear, virtually colorless liquids, containing 97-99 % of monoalkyl esters (>80 % of oleates).



Scheme 1. Reaction scheme of EMAO synthesis: R – fatty acyls (over 80 % C18:1), HCat – sulfocationite CU-2-8ChS (hydrogen form), pTsOH – *p*-toluenesulfonic acid

For epoxidation, the method [59] was adapted. At first, CU-2-8ChS (wet), ethyl or *i*-propyl esters (about 100 g) and acetic acid were placed in the three-necked reactor and heated to 40 °C under stirring. Then, the predetermined H_2O_2 was added dropwise during 0.5 h and reaction was continued for another 3.5 h at 60 °C. Esters : CH_3COOH : H_2O_2 molar ratio accounted for 1 : 0.4 : 2.0. The load of cationite was about 14 g (wet) per 100 g of esters. Products was filtered, catalyst and reactor were poured with cyclohexane. Organic phase was separated and washed with sodium bicarbonate (10-% water solution), distilled water and dried over sodium sulfate. Cyclohexane was removed by distillation under reduced pressure.

Ring-opening reaction of fatty epoxides

Ring-opening reaction of EMAO were carried out in 35 cm^3 (30×100 mm) glass screw pressure bottles with PTFE stoppers using magnetic stirrer. All catalytic tests were carried out for 3 h at 100 °C, with 25-30 % reactor filling. Reagents and catalyst ratio depended on the process. At first, the known mass of the dry cationite was placed in the reactor. Thereafter, ring opening reagent was added and allowed to soak the cationite for 1 h (porous Purolite CT275) or overnight (about 15 h, non-porous CU-2-8ChS). In case of acylation in the organic solvents media, the corresponding solvent (cyclohexane – C-hex, ethyl acetate – EtAc or ethyl levulinate – EtLev) were added together with carboxylic acid. Soaking of the cationites with levulinic acid, normally melting at 33 °C, was carried at 40 °C. Obtained liquid reaction products were filtered through paper filter to remove cationite and subjected to analysis via GC with any additional purification. Selected samples of perspectively practically valuable alkoxylation and acylation products were isolated, purified and analyzed by GC and NMR. Product of epoxidized *i*-propyl oleate alkoxylation were washed stepwise with water solution of sodium bicarbonate and distilled water, followed by drying over anhydrous potassium sulfate. In case of product of alkoxylated ethyl oleate alkoxylation, excess of ethanol was rotary evaporated (80-90 °C) and only than treated in the same way. Products of epoxide acylation with levulinic was firstly washed with neutral water and then treated under vacuum at elevated temperature (90-100 °C).

Analytic methods

EMAO and RO products were analyzed via GC using Agilent 7890A Series gas chromatograph equipped with split/splitless inlet, flame-ionization detector and J&W HP-5 capillary column (30 m, 0.32 mm, 0.25 μm) with ((5 % phenyl)-methyl polysiloxane stationary phase, nitrogen was as carrier gas. About 0.1 cm^3 of epoxide, alkoxylation or acylation products were dissolved in 1.0 cm^3 of *n*-hexane. In case of hydrolysis, sample (~0.1 g) were dissolved in 1.0 cm^3 of pyridine. Chromatographic conditions were the following: inlet temperature – 250 °C; split ratio – 64 : 1; constant pressure mode, 14.7 psi (103 kPa); column thermostat temperature – 110 °C for 7 min, heating +5 (°C/min) up to 320 °C, 320 °C for 30-60 min; FID temperature – 300 °C; sample volume – 1 μl. Using GC-analyses data, conversion of corresponding EMAO (X(C18:1EpAlc), %) and selectivity for corresponding ring-opening products (S(X), %) were calculated as follows:

$$\mathrm{X(C18{:}1EpAlc)} = \frac{\%^0\mathrm{(C18{:}1EpAlc)} - \%\mathrm{(C18{:}1EpAlc)}}{\%^0\mathrm{(C18{:}1EpAlc)}} \cdot 100\%, \tag{1}$$

$$\mathrm{S(X)} = \frac{\%\mathrm{(X)}}{\sum \%\mathrm{(C18{:}1Ep)}} \cdot 100\%. \tag{2}$$

In formula (1) $\%^0(\mathrm{C18{:}\,EpAlc})$ and $\%(\mathrm{C18{:}\,EpAlc})$ are defined as GC area assay of the epoxidized oleate before and after reaction. In reaction (2) $\%(\mathrm{X})$ is GC area assay of the corresponding reaction product and $\sum\%(\mathrm{C18{:}\,1Ep})$ is the sum of the GC area assays of all products, formed from epoxidized oleate.

Acid value (AV) was measured as described in [60].

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE DRX-500 instrument at an operating frequency of 400 MHz and 125 MHz respectively. Samples were dissolved in deuterated chloroform $CDCl_3$.

Results and discussions

Samples of sulfocationites

As said early, the chemical composition of different brands of sulfonated resins are roughly identical, since all of them are the polystyrene copolymers, cross-linked with divinylbenzene and functionalized with sulfonic group. Both cationites, studied in this work (Table 1) have close static ion exchange capacity per unit of mass (Table 1). Slightly higher exchange capacity of Pur sample is more likely due to the higher degree of functionalization. The key difference between the samples is the structure of their polymer matrix. CU is a typical gel-type (non-porous) cationite, while Pur is macroreticular (macro-mesoporous) one [61-62]. Consequently, the specific surface area of the Pur sample is several times higher. Its low-temperature nitrogen adsorption-desorption isotherm (Fig. 1) indicating its macroporous structure, while hysteresis loop indicates the presence of mesopores. Isotherm of CU sample is linear, which is characteristic for non-porous materials.

Table 1. Chararcteristics of the sulfocationites samples

Chararcteristic	Sample name (full name of the commercial brend)	
	Pur (Purolite CT275)	CU (CU-2-8CHs)
Appearance	grey spherical grains	yellow-brown spherical grains
Polymer matrix type	macroreticular	Gel
Crosslinking, %	8	8
Moisture content, %	56.8	23.0
Static exchange capacity[1], mmol/g	5.43	5.03
S^{BET}, m^2/g	23	6

[1] measured for dehydrated sample

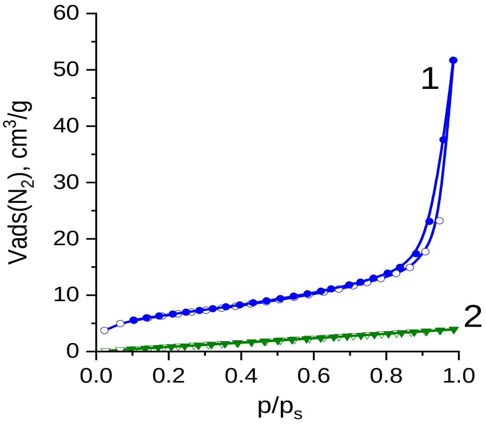


Fig. 1. Low-temperature nitrogen adsorption-desorption isotherms of sulfocationites: 1 – Pur, 2 – CU

Let us also note, that CU-2-8ChS sample, studied in this work, was produced by “Azot” (Cherkasy), which is now PrJSC “Azot” (OSTCHEM Holding AG). But at the current moment, cationites under brand CU-2-8, which are widely presented in Ukrainian market, are exclusively originated from PRC.

Samples of epoxidized monoalkyl oleates

Synthesized fatty epoxides were clear colorless liquids. Composition of the samples according to GC-analyses is given in the Table 2. Almost all double-bounds of initial alkyl oleates were converted into epoxides, while unsaturated esters remained unaltered. Chromatograms of epoxidized samples and initial esters is presented in Fig. 2. Slightly higher acid value of EpiPr sample is due to the synthetic pathway of its preparation via fatty acid esterification. This value is roughly equal to only 0.3 % concentration of free fatty acids.

Table 2. Composition of the samples of epoxidized monoalkyl oleates

Chararcteristic	Sample	
	EpEt	EpiPr
Content of EMAO, %	84.1	83.4
Content of other epoxidized esters, %	7.1	7.0
Content of unsaturated esters, %	0.9	0.1
Content of saturated esters, %	7.4	7.4
Acid number, mg KOH/g	0.26	0.64

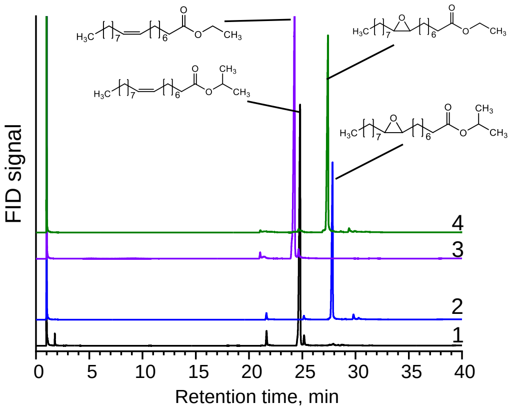


Fig. 2. Chromatograms of epoxidized samples and initial esters (J&W HP-5 column; +5 °C/min from 110 to 320 °C; constant pressure 101,3 kPa): 1 – ethyl esters; 2 – EpEt; 3 – *i*-propyl esters; 4 – EpiPr

^{1}H NMR-spectra of epoxidizied esters (Fig. 3) contain intense signal of methine protons of oxirane cycle carbon atoms (~2.9-3.0 ppm), while the signals of the methine protons near carbon atoms forming double bonds (~5.4-5.5 ppm) are almost absent. Actually full conversion of double bonds is also strictly evident from ^{13}C NMR-spectra (Fig. 4), containing signal of oxirane cycle carbon atoms (56.6 ppm) and no signals in area around 130 ppm. The spectral peaks and assignments are close to the computed chemical shifts and their order.

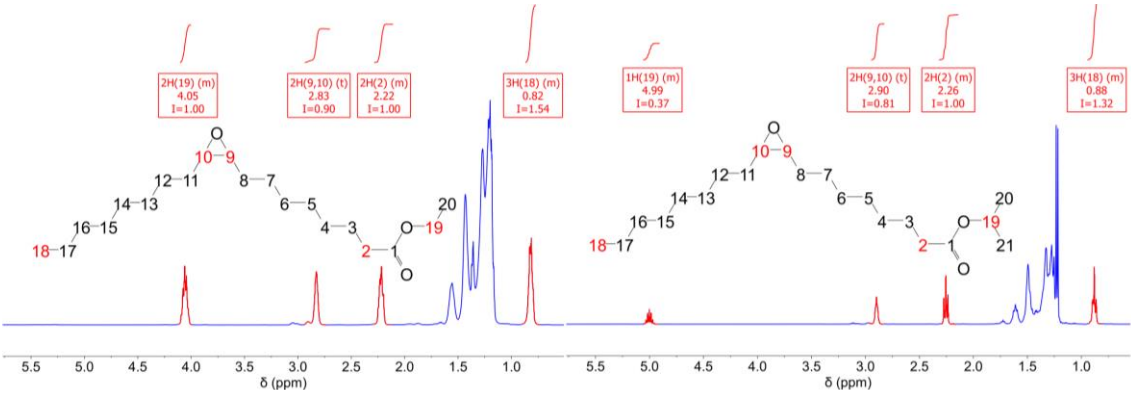


Fig. 3. ^{1}H NMR-spectra of the epoxides samples ($CDCl_3$, 400 MHz): a - epoxidized ethyl oleate (EpEt); b - epoxidized *i*-propyl oleate (EpiPr)

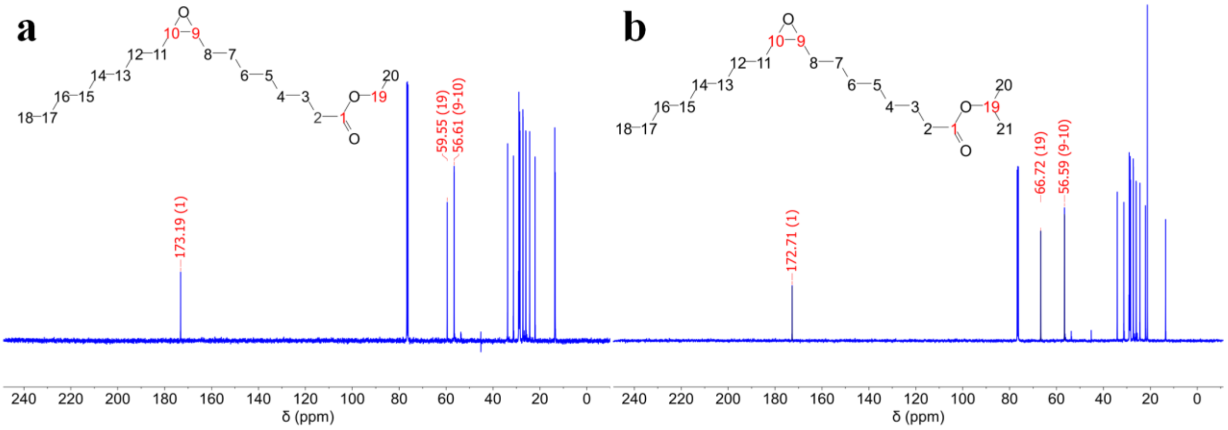
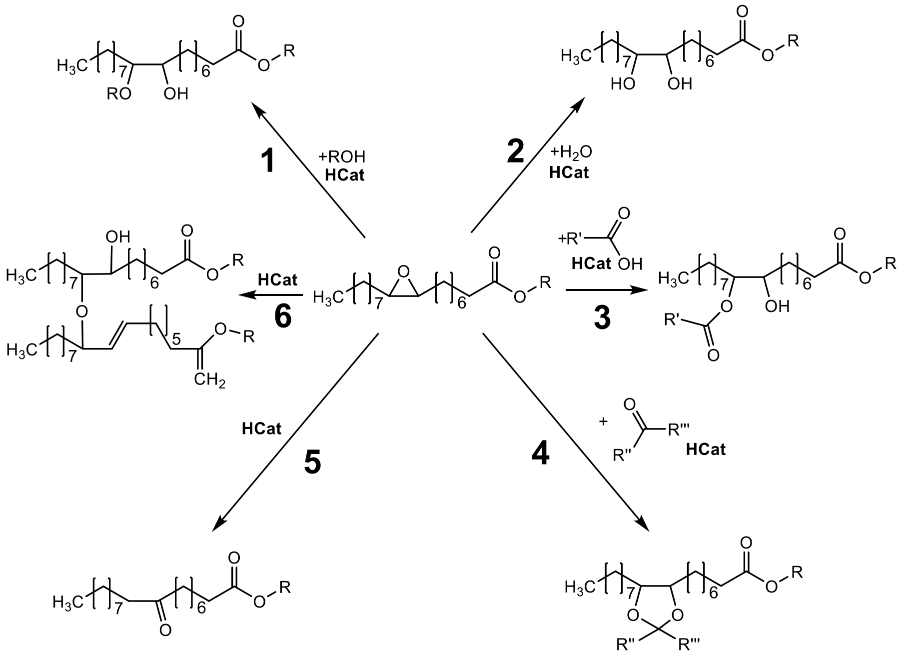


Fig. 4. ^{13}C NMR-spectra of the epoxides samples ($CDCl_3$, 125 MHz): a - epoxidized ethyl oleate (EpEt); b - epoxidized *i*-propyl oleate (EpiPr)

Catalytic oxirane ring-opening reactions

Scheme 2 shows the key RO reaction of the EMAO, that were observed in current study, including hydrolysis (1), alkoxylation (2), acylation (3), ketalization (4), isomerization (5), and dimers formation (6). Each of the RO products indeed forms as near equal amounts of (9,10) and (10,9) regioisomers. Also, reactions of epoxidized esters with alcohols is accompanied with TE of their ester functions. In order to avoid additional side reactions, alkoxylation was carried out only using corresponding alcohols (i.e. *i*-propanol for epoxidized *i*-propyl oleate).



Scheme 2. Reactions of epoxides in the presence of acid catalyst: 1 - alkoxylation; 2 - hydrolysis; 3 - acylation; 4 - ketalization; 5 - isomerization; 6 - dimerization

When investigating the efficiency of the catalysts and catalytic processes, it is essentially to understand the possibility and the rate of target and side processes, occurring at the same synthetic conditions without catalyst. So, the number of blank syntheses without catalyst were carried out (Table 3). No signs of chemical alterations were observed after 3 h at 100 °C in case of neat epoxide, as well as epoxide mixtures with alcohols and water. In presence of porous cationite sample Pur, epoxide was totally converted into ketone and dimers, while in case of non-porous CU conversion was almost negligible.

Completely different observations were made for the carboxylic acids. Significant or even full conversion was achieved. This fact confirms, that RO reactions of epoxides may be catalyzed by even such kind of weak acids at applied reaction conditions. In case of formic acid, which is the strongest among the one-base carboxylic ones ($pK_a = 3.75$), epoxide was converted totally, yielding hardly-to-identify set of products. Besides target acylation product, vicinal diol was found among them in significant amount. Let us emphasized, that reactions were carried out carefully avoiding introduction of any moisture. The only possible source of water for hydroxylation is admixtures in the formic acid, although it was purchased as 99-% pure reagent. Therefore, the further investigations of acylation over cationites was carried out with levulinic and oleic acids.

Introduction of the H-form of the gel type non-porous cationite CU resulted in almost negligible growth of conversion and acylation selectivity (Fig. 5). Also, insignificant epoxide isomerization (~1-2 % selectivity) was observed. When using macro-mesoporous Pur sample, conversion increased significantly. But the growth was provided mainly by side isomerization reaction, while selectivity of acylation notably dropped. Also, trace amount of the side product, which is more likely can be identified as ketal-type compound (Scheme 2, reaction 4) was found in case of epoxide reaction with levulinic acid over Pur sample.

Table 3. Blank reactions of the epoxides (100 °C, 3 h, 500 rpm)

Epoxide sample	Ring-opening reagent	Catalyst	Molar ratio epoxide : reagent : ^{1}catalyst	X(C18:1EpAlc), %	^{2}S, %
EpEt	-	-	1 : (-) : (-)	0	-
EpEt	-	Pur	1 : (-) : 0.05	100	44 (isomerization)
EpEt	-	CU	1 : (-) : 0.05	4	23.5 (isomerization)
EpEt	ethanol	-	1 : 10 : (-)	0	- (alkoxylation)
EpiPr	*i*-propanol	-	1 : 10 : (-)	0	- (alkoxylation)
EpiPr	water	-	1 : 10 : (-)	0	- (alkoxylation)
EpEt	formic acid	-	1 : 1.5 : (-)	100	38 (acylation)
EpEt	levulinic	-	1 : 1.5 : (-)	56	57.3 (acylation)
EpEt	oleic acid	-	1 : 1.5 : (-)	45	71.9 (acylation)

[1] amount of the cationite acid sites (based on exchange capacity)
[2] selectivity of the main reaction (mentioned in brackets)

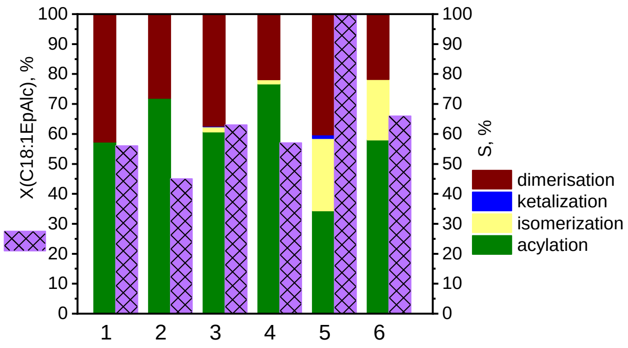


Fig. 5. Conversion and selectivity of epoxidized ethyloleate (EpEt) RO reactions with carboxylic acids (100 °C, 3 h, 500 rpm, molar ratio epoxide : acid : catalyst 1 : 1.5 : 0.05): 1 - levulinic acid/no catalyst; 2 - oleic acid/no catalyst; 3 - levulinic acid/CU; 4 - oleic acid/CU; 5 - levulinic acid/Pur; 6 - oleic acid/Pur

Next step of the current study was carrying out epoxides acylation in the environment of organic solvents. The expectations from the solvents consisted in the dilution of the reactants, which limits the probability of dimers formation. Additionally, solvent molecules, adsorbing on the catalyst surface, may restrict the access of the epoxides molecules to the acid sites, potentially preventing undesirable chemical transformations. Indeed, in case of catalyst-free epoxide reaction with levulinic acid in C-hex (Fig. 6), selectivity of acylation notably grew, while conversion value decreased about one-and-half time. In case of ethyl esters (EtAc and EtLev) use as solvents, conversion drop was about an order of magnitude, but some tendency to acylation selectivity enhancing preserved. Also, carrying out the reaction in EtLev facilitated to formation of ketal (Scheme 2, reaction 4). In case of non-porous CU use, observed conversion and selectivity regularities were roughly the same as in catalyst-free experiments. This fact indicates the minor participation of the CU as the catalyst of the oxirane reactions. Use of porous cationite Pur enhanced the conversion rate, but in major part, due to the activation of the side reaction of epoxide isomerization. In case of EtLev environment, intense formation of the ketal over porous sample was observed. Selectivity for ketal was even twice higher, than selectivity of acylation. As for the term "solvent-specific", we applied it for the products, which were not observed in syntheses in other solvents or in solvent-free conditions. For example, solvent-specific product in case of EtAc was presumably originated from transacylation of ethyl acetate with levulinic acid, followed by reaction of the formed acetic acid with epoxide.

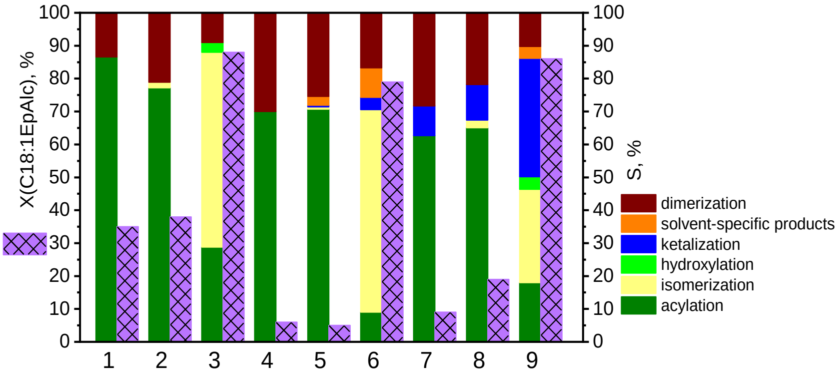


Fig. 6. Conversion and selectivity of epoxidized ethyl oleate (EpEt) RO reactions with levulinic acid in the solvents environment (100 °C; 3 h; 500 rpm; molar ratio epoxide : acid : catalyst 1 : 1.5 : 0.05; solvent-to-reagents volume ratio – 2 : 1): 1 - no catalyst/C-hex; 2 - CU/C-hex; 3 - Pur/C-hex; 4 - no catalyst/EtAc; 5 - CU/EtAc; 6 - Pur/EtAc; 7 - no catalyst/EtLev; 8 - CU/EtLev; 9 - Pur/EtLev

Generally similar observations were made for the acylation of epoxides with oleic acid in solvents media (Fig. 7). Even lower conversion of epoxide can be attributed to the actually lower concentration of carboxylic group, acting as acid catalyst, in the reaction media. Reaction with levulinic and oleic acids were carried out at the same reagents molar ratio (epoxide : acid – 1 : 1.5 mol/mol), while oleic acid acyl chain is several time longer. Also, no enhancing of the selectivity in catalyst-free experiment were observed. The same observation of the negligible catalytic activity of non-porous cationite CU, as in the case of levulinic acid, was made. Use of porous sample Pur majorly contributed into epoxides isomerization, resulting in notable conversion growth, but selectivity for target acylation dropped significantly. Interest observation is the finding of the significant peak of the same compound, which was early identified as ketal (Scheme 2, reaction 4) in the products over Pur in EtLev media. In Fig. 7 it is included to "solvent-related products", since possible explanation of its formation consists in the transacylation of EtLev with oleic acid. The product of acylation with levulinic acid was also fixed (included to “solvent-related products”), but selectivity for it was only around 4 %. Hence, even in such indirect case, ethyl levulinate as reaction media strongly facilities to the reaction of the levulinic acid ketone moiety with oxirane, but not to the acylation.

More straightforward and encouraging catalytic results were obtained for epoxide RO reactions with monohydric alcohols (ethanol and *i*-propanol). Let us emphasized, that reactions were carried out using great excess of ring-opening reagent (ten-fold excess over stoichiometry). Unlike biomass derived carboxylic acids, low-boiling monohydric alcohols can be easily removed from products by distillation and recycled in the process. In current study alcohols acted both as ring-opening reagent and organic solvent media.

As was shown earlier, EMAO does not react with alcohols at the conditions of catalytic testing. In the presence of the macromesoporous cationite, conversion of epoxide after 3 h was 100 % both for reactions with ethyl and *i*-propyl alcohols (Fig. 8). Relatively high selectivity was observed for ethoxylation (about 75 %), but in the case of *i*-propanol it was almost twice lower. As in the case of acylation, the main side reaction was epoxide isomerization to ketone (Scheme 2, reaction 5). Also, insignificant dimerization and hydroxylation were observed. Again, there was no enough water in the initial materials to provide such level of selectivity for diol compound. The most obvious explanation is water formation by the reaction of alcohol etherification, proceeding on the cationite acid sites, and its immediate reaction with epoxide. Such explanation is supported by fact, that strong acidic macroreticular ion-exchange resin Purolite CT275 is developed as the catalyst for production of ethers, such as MTBE and TAME [62].

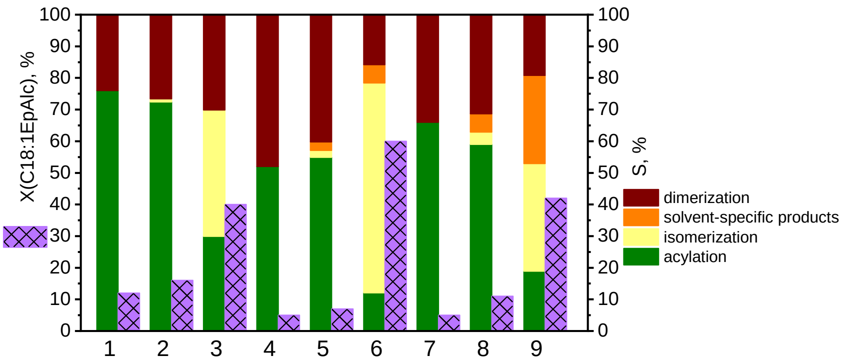


Fig. 7. Conversion and selectivity of epoxidized ethyloleate (EpEt) RO opening reactions with oleic acid in the solvents environment (100 °C; 3 h; 500 rpm; molar ratio epoxide : acid : catalyst 1 : 1.5 : 0.05; solvent-to-reagents volume ratio – 2 : 1): 1 - no catalyst/C-hex; 2 - CU/C-hex; 3 - Pur/C-hex; 4 - no catalyst/EtAc; 5 - CU/EtAc; 6 - Pur/EtAc; 7 - no catalyst/EtLev; 8 - CU/EtLev; 9 - Pur/EtLev

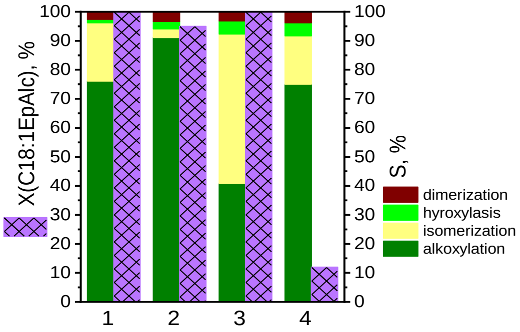


Fig. 8. Conversion and selectivity of EMAO reactions with alcohols in the presense of the sulfocationites (100 °C; 3 h; 500 rpm; molar ratio epoxide : alcohol : catalyst 1 : 10 : 0.05): 1 - EpEt/EtOH/Pur; 2 - EpEt/EtOH/CU; 3 - EpiPr/iPrOH/Pur; 4 - EpiPr/iPrOH/CU

Gel type sample CU provide quite promising efficiency of epoxide alkoxylation. In case of the reaction with ethanol, almost full conversion (95 %) was achieved with high selectivity for the target alkoxylation (about 90 %). Contrary, in case of *i*-propanol conversion was almost an order of magnitude lower, than after reaction over porous Pur, but trend for higher selectivity preserved. The lower conversion and selectivity in case of *i*-propanol is caused by its secondary structure, unlike primary ethyl alcohol. The lower reaction ability of secondary alcohols is generally known fact. It was also the reason for *i*-propyl esters preparation via multi-step saponification-neutralization-esterification sequence instead of one-step TE (as ethyl esters). From the other hand, lower polarity of *i*-propyl alcohol reaction media due to actually lower concentration of hydroxyls may also contribute to lower alkoxylation rate and, hence, higher selectivity for side reactions.

The same approach of the cationite swollening with RO reagent before epoxide addition appeared to be totally ineffective for hydroxylation. No reaction was observed both in case of the same reagents and catalyst molar ratio as in alkoxylation, and even in case of ten times bigger amount of catalyst (Table 4). Unlike alcohols, water is totally immiscible with low-polar fatty epoxides phase. So, the water-swollen cationite appeared to be reliably screened from fatty epoxides molecules, which fully prevented their access to the catalyst acid sites. Vice versa reagents introduction sequence (epoxide first) maid reaction proceeding possible, but selectivity for vicinal diol was not high. In case of porous sample Pur at molar ratios 1 : 10 : 0.05 (epoxide : water : H-sites of catalyst) conversion was close to full (86 %). The main side reaction was dimers formation, while isomerization rate was insignificant. In the case of the higher water and catalyst excess (ratio 1 : 20 : 0.50), conversion was full, while hydroxylation selectivity remained at the same level. Interestingly, selectivity for dimers and ketone at such components ratio swopped and isomerization became the primary reaction. In case of non-porous CU conversion was several times lower (almost negligible with low catalyst amount), while selectivity of alkoxylation tended to be insignificantly higher than in case of Pur.

Table 4. Efficiency of *i*-propyl oleate hydrolysis over sulfocationites (100 °C, 3 h, 1500 rpm)

Catalyst	[1]Molar ratio E : W	[2]Sequence of the reactants addition	X(C18:1EpiPr), %	S, %		
				hydrolysis	isomerization	dimerization
-	1 : 10	-	0	-	-	-
Pur	1 : 10 :	water (1 h) +	0	-	-	-
Pur	1 : 20 :	water (1 h) +	0	-	-	-
Pur	1 : 10 :	epoxide (1 h) +	86	38.0	7.1	54.9
Pur	1 : 20 :	epoxide (1 h) +	100	36.6	51.2	12.2
CU	1 : 10 :	water (15 h) +	0	-	-	-
CU	1 : 20 :	water (15 h) +	0	-	-	-
CU	1 : 10 :	epoxide (15 h) +	3	60.1	15.3	24.7
CU	1 : 20 :	epoxide (15 h) +	38	46.9	14.0	49.1

[1] Epoxide : H_2O : catalyst acid centers ratio
[2] after catalyst was placed into the reactor

All observed regularities of the fatty epoxides reactions are based on the GC data. The evidence of all discussed reactions occurrence and corresponding compounds formation is supported by ^{1}H and ^{13}C NMR spectra (not shown) of selected finalized products. Composition of some of the alkoxylation and acylation products are given in Table 5. Remained 6-10 % of unspecified components accounts for various RO products of epoxidized linoleates and small amounts of low-molecular components and unconverted unsaturated esters. The composition of finalized products may to some extend alternated in course of purification. For example, sample of alkoxylated ethyl esters EtEtpEt/Pur does not contain vicinal diol. It most likely transformed into dimers during alcohol removal at elevated temperature. The latter was carried out without preliminary neutralization, while mixture of reagents may still content some residual acid material even after catalyst removal. At the same time, alkoxylated *i*-propyl esters iPrEpiPr/Pur, purified via neutralization and washing, still contains vicinal diol. If unconverted epoxide and acid remain in acylation products, its transformations may slowly continue after syntheses, causing the alterations in the storing sample composition.

Table 5. Composition of some isolated alkoxylation and acylation products according to GC analysis

Sample	Content of component(s), %						
	Saturated	Epoxidized	Ketone	Dihydroxy	Alkoxy/	Acyloxy/	Dimers
EtEtEp/Pur	7.4	0	16.2	0	62.7	0	5.9
iPrEpiPr/Pur	7.9	0	39.4	4.2	36.9	0	2.2
LAEpEt/no catalyst	4.5	8.2	0.4	0	0	23.0	58.2
LAEpEt/Pur	5.2	0	17.4	0	0	18.8	50.9

As can be seen from the Table 5, the target reaction (alkoxylation or acylation) products are not necessary the major components of the obtained samples. This is the case only for alkoxylated ethyl esters, containing more than 60 % of target alkoxy/hydroxy component. Alkoxylated ethyl esters indeed contains more than half of dimers, having quite complex composition, and only limited fraction of acyloxy/hydroxy monomer product. Significant fraction of complex dimers mixture is presented by the component, which is more likely acyloxy/hydroxy dieester formed via epoxide reaction with hydroxy function of acylated ester. Formation of such type of compounds were observed in work [56]. In practice, high content of dimeric compounds may be beneficial for use of obtained products as components and/or additives for biolubricants formulations for machines and mechanisms. Similar alkoxylation products, synthesized by the authors, was earlier reported by authors as the promising sulfur-free tribological additives to diesel fuel [63-64]. The important advantage of such compounds over hydrocarbon-based counterparts is that they are produced from biorenewable plant-based materials, and thus have a much better biodegradability. Physico-chemical properties of similar oleochemicals would be greatly influenced by the way, how synthesis was carried out. On the other hand, ability to synthesize the oleochemicals, having predetermine ring-opening products composition, may by useful for the achieving the properties, needed for certain practical applications.

Conclusions

The number of alkoxylated and acylated monoalkyl esters as perspective components for biolubricants formulation were synthesized via sulfonated resins catalyzed ring-opening reactions of epoxidized monoalkyl oleates, obtained from used cooking oil based monoalkyloleates via modified Prilezhaev’s double bonds epoxidation method with use of gel-type CU-2-8ChS sulfonated resin. It was shown, that fatty epoxides ring-opening reactions over sulfocationites is significantly sophisticated by number of possible side processes. As result, the composition of obtained oleochemicals was shown to be rather complex and dependent on the type of sulfonated resin, used as catalyst. Porous macroreticular resin Purolite CT275 was shown to be highly effective in terms of epoxide conversion, but limited selectivity for target reactions caused the presence of significant amounts of side products, such as fatty ketones, dimers, ketals, and vicinal diols in oleochemicals obtained. Non-porous gel-type CU-2-8Chs provided notably higher selectivity in the same reaction conditions, but conversion rate was slow in most cases. Namely, in epoxides acylation with carboxylic acids non-porous resin almost did not show catalytic action comparing with catalyst free conditions.

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Особливості реакцій розкриття циклів епоксидованих алкіл олеатів спиртами, водою та органічними кислотами у присутності комерційних сульфокатіонітів як каталізаторів

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Стаття присвячена використанню сульфокатіонітів, що відрізняються за пористою структурою (макроретикулярний Purolite CT275 і гелевий КУ-2-8Чс), як твердих кислотних каталізаторів для синтезу перспективних біомаститльних компонентів шляхом розкриття оксиранових циклів жирних епоксидів водою (гідроліз), етанолом та і-пропанолом (алкоксилювання), і левуліновою та олеїновою кислотами (ацилювання). Епоксидовані етил- та і-пропіл олеати як субстрати для реакцій розкриття оксиранів було синтезовано на основі використаної кулінареної олії. Реакції проводили в реакторі періодичної дії протягом 3 годин за 100 °C з перемішуванні, молярне співвідношення епоксид : кислотні центри каталізатора становило 1 : 0.05. Співвідношення реагент : епоксид становило 10 : 1 (алкоксилювання, гідроліз) або 1.5 : 1 (ацилювання). Склад продуктів визначали методом ГХ, розраховували конверсію та селективність. Виявлено ряд бічних реакцій розкриття кільця, основними з яких є ізомеризація до кетону та димеризація. Загальним спостереженням було те, що пористий Purolite CT275 забезпечує більш високу конверсію, але сприяє побічним процесам. Непористий CU-2-8-CHs забезпечував помітно вищу селективність (до 90 % для гідрокси етерів при етоксилюванні), але з у багато разів повільнішим перетворенням, особливо у випадку алкоксилювання вторинним спиртом. При гідролізі просочені водою катіоніти не забезпечили жодного перетворення, тоді як введення епоксиду спочатку на каталізаторі робило перетворення можливим. Ацилювання значною мірою протікало без окремого каталізатора і супроводжувалося димеризацією, а ізомеризації не спостерігалося. Катіоніт гелевого типу забезпечував лише зникомо мале зростання конверсії та селективності. Пористий катіоніт підвищував конверсію, але головним чином за рахунок інтенсифікації побічних реакцій. Циклогексан як розчинник дещо сприяв селективному ацилюванню без каталізатора, але зі значним зниженням конверсії. Purolite CT275 у середовищі етиллевулінату сприяв розкриттю епоксиду кето-групою левулінової кислоти з утворенням продукту типу кеталю.

Ключові слова: жирний епоксид, розкриття оксиранового циклу, сульфокатіоніти, твердий кислотний каталізатор, алкоксилювання, гідроліз, ацилювання, ізомеризація