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Esterification of fatty acids with C_8-C_9 alcohols over selected sulfonic heterogeneous catalysts

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A study on the synthesis of esters of fatty acids of natural origin (oleic acid from rapeseed oil) and branched synthetic isostearic acid with commercially available alcohols C_8-C_9 i.e. 2-ethylhexanol (2-EH) and 3,5,5-trimethylhexanol (TMH) in the presence of selected heterogeneous catalysts containing active sulfonic groups has been made. The catalysts were obtained using ready available amorphous silicas with different textural characteristics. The influence of catalyst porosity on the catalytic properties in the esterification of fatty acids has been investigated. The effect of the synthesis temperature has also been studied. The results were compared with the results of esterification with the use of acidic ion exchange resins. It was shown that catalysts obtained on the basis of amorphous silicas are good and reusable catalysts for the esterification of fatty acids with higher alcohols.

Keywords: esterification of fatty acids, C_8-C_9 alcohols, sulfonic acid catalysts.

INTRODUCTION

Esters of C_{12}–C_{20} fatty acids are among major groups of products derived from fatty acids coming from vegetable oils or animal fats as well as acids produced through the chemical synthesis. In this group the most important products for industrial applications are methyl and ethyl esters of fatty acids derived from vegetable oils of different species. The basic method of their synthesis is transesterification of oils with methanol or ethanol in the presence of alkaline catalysts. Direct esterification of an acid by an alcohol in this case is unprofitable from the economic point of view. A direct esterification method is the most commonly used in the case of esters of higher alcohols ($> C_4$). These esters can also be obtained by transesterification of fatty acids methyl esters (FAME) with suitable and easily accessible higher alcohols[1]. This approach is often applied to the present on the market in large quantities various types of methyl esters derived from vegetable oils. This method, however, cannot be applied to esters of petrochemical origin due to the unavailability on the market of relevant methyl esters. Thus, esters of fatty acids of petrochemical origin are obtained only by direct esterification of fatty acids with corresponding alcohols.

Esters of C_8–C_{18} aliphatic alcohols and fatty acid are widely used in cosmetics, pharmaceuticals and also as components of oil bases and lubricants[2–4]. Due to the specific requirements for the esters used in cosmetic or pharmaceutical products they are usually produced using enzymatic catalysis[5, 6]. The basic method of preparation of such esters, however, is the direct esterification of alcohol with acid in the presence of homogeneous acid catalysts, such as H_2SO_4, RSO_3H or H_3PO_4[7–11].

Esterification is a reversible reaction so in order for it to progress toward the desired product an excess of one of the reactants, usually alcohol, is necessary. In addition, the reaction is favored by removal of water made in the course of the reaction. In the case of higher alcohols the use of additional solvents such as toluene or xylene is not necessary because these alcohols typically form heteroazeotropic mixtures with water and that facilitates water removal. Reactivity between alcohols and fatty acids is dependent on their structure. The rate of esterification varies in the following order[1]:

CH_3OH > primary alcohols > secondary alcohols > tertiary alcohols and:

$HCO_2H > CH_3CO_2H > RCH_2CO_2H > R_2CHCO_2H > R_3CCO_2H$

The acid strength has smaller effect on the rate of esterification. These dependencies are important in the synthesis of fatty acid esters of petrochemical origin, especially those with a secondary carboxyl group (eg. Guerbet acids).

Homogeneous esterification catalysts are very effective, but require their careful removal from the reaction mixture. In addition, they can adversely affect the color of the product. This is especially noticeable in the case of polyunsaturated fatty acids. More often for the esterification reaction heterogeneous catalysts are used. A number of zeolites such as H-Y, H-Beta and H-ZSM-5 were studied in reactions of esterification of fatty acids with polyols, among them glycerol was the most common[2, 12, 13].

The study has shown that for an efficient removal of the produced water a very important factor is the hydrophobicity showed by this type of catalysts. Therefore, MCM-type mesoporous materials were proven to be poor catalysts for the esterification. Only the modification of their surface by sulfonic groups leads to a stable and active catalyst, suitable for the esterification process. Esterification of fatty acids by glycerol was the subject of many studies, whose results were published in literature[14–19]. In the temperature of 120°C, after 6 h lauric acid conversion reaches 97% and 95% for oleic acid. Conversion of > 96% were obtained also for sieve SBA-15 modified with sulfonic groups[20]. Worse results were obtained for MCF mesoporous silica foams containing sulfonic groups. In the esterification of acetic acid with butanol conversion has reached only 65%[21].

For the synthesis of a catalysts containing sulfonic groups, in addition to synthetically produced materials with mesoporous structure, also widely used is the commercially available amorphous silica. Average porosity of these materials is usually in the range of 20–150 Å. These types of catalysts were used in the esterification reactions of fatty acids with ethanol and butanol. Conversion of acid was 98–99%, which is clearly better than the result of action by the above mentioned catalysts with mesoporous structure[22]. Heterogeneous catalysts have not yet been applied for the processes of esterification of alcohols C_8–C_9. The high boiling point of those alcohols causes that such a process would require the use of higher temperatures in the synthesis or the use of additional solvents to remove water, and also a catalysts of high activity.

This work presents the results of studies on the synthesis of fatty acid esters, of plant and chemical origin through their esterification with commercially available C_8–C_9 alcohols i.e., 2-ethylhexanol and 3,5,5-trimethylhexanol in the presence of heterogenous sulfonic catalysts based on the amorphous SiO_2. Fatty acid esters of 2-ethylhexanol have been known as components of oil bases, but there are no reports on the use for this purpose esters of 3,5,5-trimetylhexanol. Derivatives of this alcohol are primarily used in is the cosmetics industry.

MATERIAL AND METHODS

Materials

Oleic acid was purchased from Brenntag (Poland). This product is a mixture of distilled fatty acids and contains 9.2 wt.% of $C_{14–16}$ acids, 77.3 wt.% of $C_{18:1}$ acid, 12.1 wt.% of $C_{18:2}$ acid, 1.1 wt.% of $C_{18:3}$ acid and < 1 wt.% of C_{20+} acids (GC). Isostearic acid was purchased from Unichema (UK) as Prisorine 3603. This product contains ca. 83 %wt. of branched and saturated (Iodine No. ~6) acids C_{16}–C_{22}. 2-Ethylhexanol was purchased from Grupa Azoty ZAK S.A., (Poland) and 3,5,5-trimethylhexanol was purchased from Sigma-Aldrich.

For the studies two types of amorphous silicas (SiO_2) were used. Silica with the porosity of 150 Å was purchased from SilyCycle (Quebec) as SilaFlash B150. Silica with the porosity of 22 Å was purchased from Sigma-Aldrich as Silicagel Grade 12. Cation exchange resin Amberlyst 15 was purchased from Rohm & Haas and Purolite CT124 and CT169 were purchased from Purolite Ion Exchange Resins. Before the first application all resins were washed several times with distilled water to remove water-soluble mineral acids, and then they were dried at 60°C. Table 1 shows the physicochemical characteristics of the silicas and cation exchange resins. All physicochemical data was derived from the suppliers. 3-Mercaptopropyltrimethoxysilane was purchased from Alfa-Aesar. Hydrogen peroxide (30 wt.% water solution) and analytical grade toluene was purchased from POCh (Poland).

Methods

Synthesis of silica-based sulfonic acid catalyst

A 500 mL glass reactor, equipped with a mechanical stirrer, reflux condenser and electronic temperature control system, was charged with 22 g of dried at 105°C silica (Silica 1) and 200 mL of toluene. Suspension of silica in toluene was stirred while heating to reaching the boiling point (110°C). Then, through the funnel, 20 g of 3-mercaptopropylotrimethoxysilane was continuously added. Addition of silane was continued for 1 h in boiling temperature of reaction mixture. After completion of dosing resulting suspension was stirred for another 5 h at boiling temperature. After cooling, the silica was filtered off, the resulting precipitate was washed three times with toluene and then dried at 105°C to obtain 26.3 g of light brown powder. The resulting pre-catalyst was placed into the reactor containing 200 g of 30 wt.% H_2O_2 solution. The resultant suspension was stirred for 3 h at 24°C and another hour at 60°C. The crude catalyst was then decanted and poured into the reactor a 200 mL of 10 wt.% solution of H_2SO_4. The resultant suspension was stirred at room temperature for 1 h. Catalyst precipitate was filtered off, washed three times with water and dried at 105°C to obtain 27 g of the catalyst in the form of light-gray powder.

General procedure for esterification of oleic acids with alcohols

A 200 mL glass reactor, equipped with a mechanical stirrer, an electronic temperature control system, a glass capillary to introduce nitrogen and a receiver to collect esterification water was charged with 72 g (0.25 mol) of oleic acid and 54 g (0.41 mol) of 2-ethylhexanol, or 57 g (0.41 mol) of 3,5,5-trimethylhexanol. The reactor content was heated up to 100°C and then 9 g of catalyst was poured into. After stabilizing the flow of nitrogen, the temperature is raised to 120°C. The reaction mixture was stirred for 6 hours. During synthesis esterification water was collected in the receiver. The crude ester was washed with water to remove residual acidic impurities, and then distilled under reduced pressure to remove water and excess alcohol.

Analysis of esterification products by gas chromatography

The products were analyzed by GC chromatography with head-space system using chromatograph HP 5890 Series II equipped with flame ionization detector (FID), capillary column, Ultra-high-2 (5HT), l = 15 m, d = 0,32 mm. All samples were transformed into silane derivatives with BSA (*N,O*-bis(trimethylsilyl)acetamide). Instrument settings: injector temperature – 360°C, detector temperature – 380°C. Temperature programming: initial isotherm 100°C – 1 min., 100–380°C – gradient 15°C/min., final isotherm 380°C – 3 min. Carrier gas:

Table 1. Physicochemical characteristics of catalysts used in the study1)

Catalyst	Silica 1	Silica 2	Purolite CT124	Purolite CT169	Amberlyst A15
Particle size	100 mesh2)	70 mesh2)	1–1.2 mm	1–1.2 mm	1–1.2 mm
Pore size, Å	22	150	–	350	300
Surface area, m^2/g	800	270	–	50	53

1) all physicochemical data derived from suppliers,
2) average values.

argon – 1.8 ml/min. Quantitative interpretation of the results was performed by internal standardization for all components assuming a correction factor equal to 1. All results are given with an accuracy of the decimal values Conversion of acids was calculated as the ratio between the amount of acid consumed in the synthesis to total amounts of acid used in synthesis. The resultant ratios were then converted to percentages values. In calculations, for simplification, as oleic acid $C_{18:1}$ acid was adopted and as isostearic acid $C_{18:0}$ acid was adopted.

Analysis of the physicochemical properties of catalysts

N_2 sorption/desorption were carried out on QUANTACHROME Autosorb Gas Sorption Analyzer in the pressure range p/p0 = 0–1. Determination of adsorption and desorption isotherms of nitrogen were performed at 77 K. The specific surface area was determined by adopting the assumptions of theory of Brunauer, Emmett and Teller (BET) and the pore distribution of the desorption curve based on the method of Barrett, Joyner and Halendy (BJH). FTIR spectra were obtained on Mattson 3000 spectrometer with Galaxy 3020 (Unicam) software. Determination of sulfonic groups (acidity) was performed through ion exchange. For this purpose, catalyst sample in an amount of about 0.2 g was placed in a beaker containing 50 mL of 2N NaCl solution. The resultant suspension was stirred at room temperature for 24 h. The released HCl was titrated with 0.1N solution of KOH against phenolphthalein indicator.

Analysis of the physicochemical properties of esters

Density at 20˚C was determined by aerometric method according to standard PN-EN ISO 12937:2005. Kinematic viscosity was determined according to standard PN-EN ISO 3104:2004. Measurements were made by Ubbelohde's method at 40ºC and 100ºC. The pour point was determined according to standard PN-ISO 3016:2005. Determination of border four ball wear test Pz was performed on 4-ball apparatus according to standard PN-76/C-04147.

RESULTS AND DISCUSSION

Catalysts characterization

Preparation of sulfonic functionalized amorphous silicas was performed using the method described by the literature[23, 24]. Table 2 lists the physicochemical characteristics of the catalysts. Figure 1 shows the pore size distribution for catalyst SiO_2-PSO_3H/1 catalyst and in Fig. 2 for the SiO_2-PSO_3H/2 catalyst. The characteristics of the catalysts is consistent with the physicochemical parameters of the silicas used in their synthesis. Figure 3 shows the FT-IR spectrum for the SiO_2-PSO_3H/1 catalyst. The bands at 798 cm^{-1} and 1200–1000 cm^{-1} are the characteristic bands of SiO_2 assigned to the Si-O streching vibrations while the band at 951 cm^{-1} is assigned to the bending vibrations of the surface silanols. The propyl group attached to the silicon framework are identified by the methylene streching bands in the 2945–2895 cm^{-1} region. The deformations bands of methylene group are also observed at 1410 and 3448 cm^{-1}. The absence of band at 2580^{-1} indicates the full oxidation of SH groups into SO_3H.

Table 2. Physicochemical data of sulfated silicas

	SiO_2-PSO_3H/1	SiO_2-PSO_3H/2
BET, $m^{2/}g$	381.3	276.7
Total pore volume,	0.2	0.84
cm^3/g	21.7	122
Average pore	1.7	1.0
diameter, Å		
Acidity, mmol/g		
SO_3H		

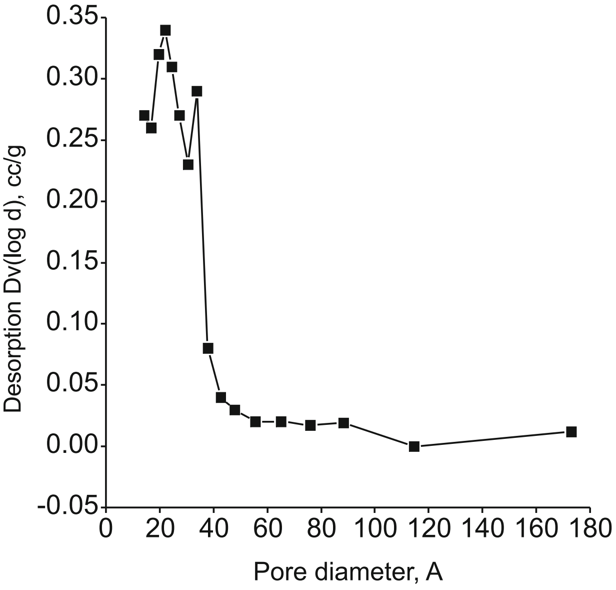

Figure 1. Pore size distribution for sample SiO_2-PSO_3H/1

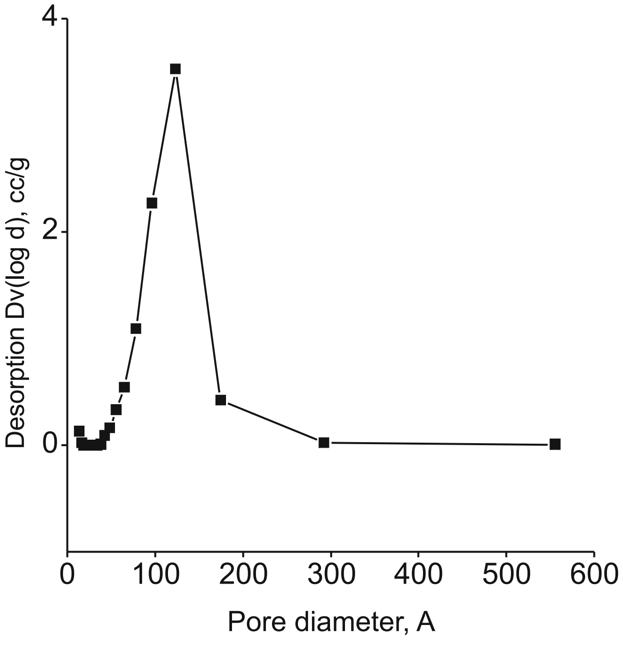

Figure 2. Pore size distribution for sample SiO_2-PSO_3H/2

Esterification of fatty acids

Esterification of fatty acids with higher alcohols depends on the removal of water being produced during reaction. Also important is high enough reaction temperature in order not to prolong the reaction, which may adversely affect the color of the final product. This can be achieved by, for example, running the synthesis in the presence of a neutral solvent, usually toluene or xylene, which creates a heteroazeotropic mixture with water. C_8–C_9 alcohols

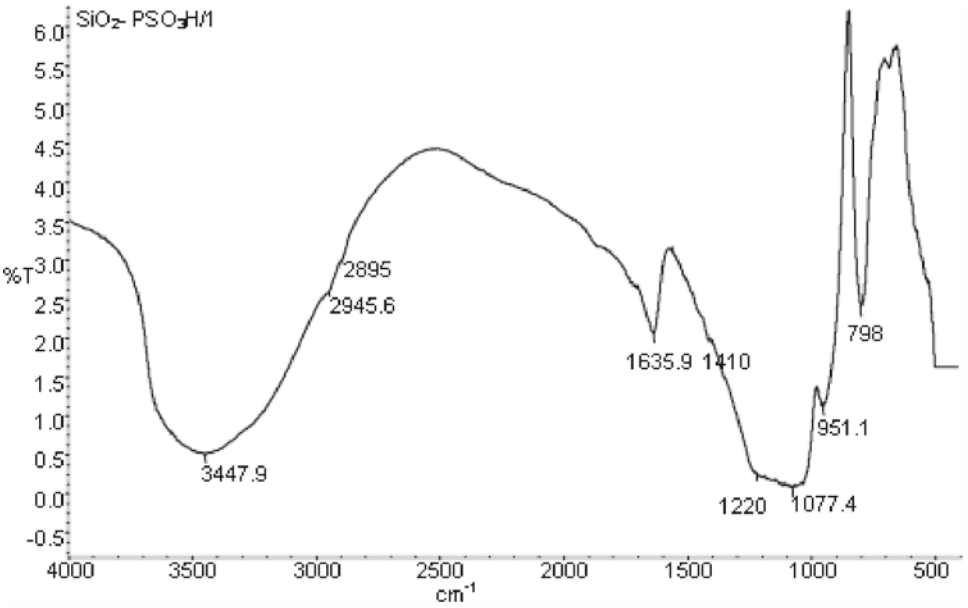

Figure 3. FTIR spectrum of sample SiO_2-PSO_3H/1

have this advantage that they form heteroazeotropic mixtures with water whose boiling points exceed 90°C. Under the reaction conditions these alcohols can act as both reagent and solvent eliminating water. In order to utilize such conditions one should use for the synthesis an excess of alcohol. In the studies, the excess of alcohol in relation to the fatty acid was taken at 60 %mol. After the synthesis, that excess is removed under the reduced pressure.

Table 3 shows the results of the esterification of oleic acids with 2-ethylhexanol and 3,5,5-trimethylohexanol in the presence of sulfonic acid catalysts based on two different types of amorphous silicas. As shown in table a more effective catalyst for the esterification of oleic acid is a catalyst prepared from small pore silica which has high specific surface area. Reaction runs on the surface, on which propylsulfonic groups were immobilized. Conversion of oleic acids exceeded 99%, while for the catalyst based on macroporous silica conversion reaches 95%, and the corresponding ester content in the product is only 88%. The content of unreacted oleic acid (as sum of C_{14}–C_{22} acids) for SiO_2-PSO_3H/1 did not exceed 0.5 wt.% while for SiO_2-PSO_3H/2 was 3–4 wt.%. No significant differences in the esterification process for both of the used alcohols were found. Figure 4 shows the GC chromatogram of reaction product of esterification of oleic acid with 3,5,5-trimethylhexanol. The main component is C_{18} ester (as sum of esters of $C_{18:0}$, $C_{18:1}$, $C_{18:2}$ and $C_{18:3}$ acids). In addition, small amounts of esters of C_{16} and C_{14} are present in product.

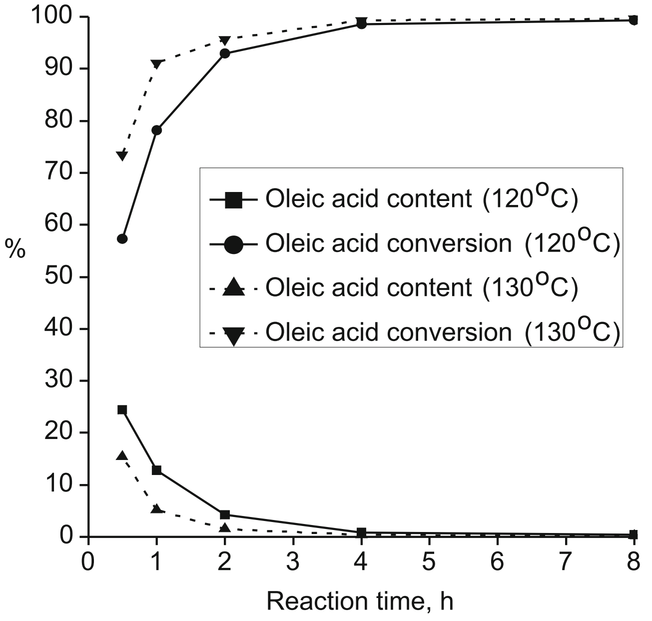

Figure 4. Influence of the reaction temperature on the content of oleic acid in the reaction mixture and the conversion of oleic acid during the synthesis of TMH oleate

Table 4 contains corresponding results for esterification of synthetic isostearic acid. Just as it was in the case of rapeseed oleic acid also in this case the SiO_2-PSO_3H/1 catalyst showed higher activity. Conversion of fatty acid was 94–95.4%, while for the SiO_2-PSO_3H/2 catalyst it was 90–91.8%. As compared to oleic acid in the case of isostearic acid lower amounts of unidentified byproducts (NI), i.e. 1.2–1.6 wt.% were observed, while in the case of oleic acid, it exceeded 6 wt.% (catalyst SiO_2-PSO_3H/2). The content of unreacted fatty acid was higher than for

Table 3. The results of the esterification of oleic acid with C8-C9 alcohols (wt.%, GC)

Catalyst	Ester 2-EH	Ester TMH	Ester 2-EH	Ester TMH
	SiO_2-PSO_3H/1	SiO_2-PSO_3H/1	SiO_2-PSO_3H/2	SiO_2-PSO_3H/2
Alcohol	1.5	1.7	1.6	1.3
Oleic acid	0.4	0.3	3.0	4.3
Ester	95.2	94.6	88.7	88.1
NI	3.0	3.4	6.7	6.7
FA conv.	99.6	99.7	96.6	95.6

Reaction conditions: 120°C, 6 hr,; 2-EH – 2-etylhexanol; TMH – 3,5,5-trimethylhexanol,
NI – unidentified byproducts (non-ester type).

Table 4. Intraparticle diffusion, Boyd kinetic and SCM Model for Zn(II) ions adsorption onto the SMSP

	Ester 2-EH	Ester TMH	Ester 2-EH	Ester TMH
Catalyst	SiO_2-PSO_3H/1	SiO_2-PSO_3H/1	SiO_2-PSO_3H/2	SiO_2-PSO_3H/2
Alcohol	0.1	0.7	1.9	2.3
Fatty acid	3.2	3.9	4.7	6.4
Ester	95.4	94.1	91.8	90.1
NI	1.3	1.4	1.6	1.2
FA conv.	96.8	96.1	95.3	93.5

Reaction conditions: 120°C, 6 hr,; 2-EH – 2-etylhexanol; TMH – 3,5,5-trimethylhexanol
NI – unidentified byproducts (non-ester type).

oleic acid and was 4–6 wt.%. Taking into account the results shown in tables 3 and 4, further studies were conducted only with the SiO_2-PSO_3H/1 as catalyst.

Figure 5 shows the changes of the concentrations of oleic acid in reaction mixtures and oleic acid conversion during the esterification of oleic acid with 3,5,5-trimethylhexanol conducted at the temperatures of 120 and 130°C. The figure shows that conversion of 90% is achieved already after 2 h of synthesis. Raising the temperature from 120 to 130°C has a positive but relatively small impact.

A possibility of reuse of the catalyst has also been examined for the esterification of oleic acid with 3,3,5-tromethylhexanol. For this purpose, after the completion of the synthesis the catalyst was centrifuged from the reaction mixture and used without further washing in the next run. Thus, the recovered catalyst and appropriate amounts of oleic acid and 3,3,5-trimethylhexanol was placed into the reactor. Esterification was carried out in the same way as described previously. Table 5 shows the changes in the conversion of fatty acids in the subsequent reruns of the catalyst. As shown in the figure conversion decreases very slightly, but is still high, thereby providing evidence of the activity of the catalyst employed.

For comparison, a series of esterification reactions of oleic acid with 3,5,5-trimethylohexanol has been run in the presence of acidic ion exchange resins, which were either of gel-type (Purolite CT124) or skeletal (Purolite CT169 and Amberlyst 15). The results were collected in Table 6. The conversions of fatty acid in the case of sulfonic cation exchangers used as esterification catalysts were high and exceeded 99%. However, the drawback of these catalysts is the formation of relatively large amounts of by-products. As it can be supposed they are mainly the products of etherification of alcohols.

As indicated in the introduction, one of the most important directions of application of this type of ester is using it as a component of oil biobases. Table 7 summarizes some physicochemical data of esters of oleic acid and 2-ethylhexanol or 3,5,5-trimethylohexanol. The results in Table 7 show that these esters have good tribological properties in particular a high viscosity index and good low temperature properties. Ester obtained from 3,5,5-trimethylohexanol in this respect looks better than the corresponding ester obtained from 2-ethylhexanol.

CONCLUSIONS

Using commercially available amorphous silica varieties a series of active catalysts containing sulfonic groups has been synthesized. The catalysts have been used in the esterification reactions of fatty acids with the available on industrial scale C_8–C_9 alcohols such as 2-ethylhexanol and 3,5,5-trimethyloheksanol. The catalysts which have been synthesized on the basis of a small pore silica with high expanded specific surface have shown higher activity. The

Table 5. Esterification of oleic acid with 3,3,5-trimethylhexanol over reused catalyst (wt.%, GC)

Run	1	2	3	4
Alcohol	1.6	2.1	2.2	2.2
Oleic acid	0.8	1.8	1.8	1.9
Ester	94.6	93.4	93.1	93.0
NI	3.0	2.7	2.9	2.8
FA conv.	99.8	98.1	98.0	97.9

Catalyst: SiO_2-PSO_3H/1; reaction conditions: 120°C, 6 hr; NI – unidentified byproducts (non-ester type)

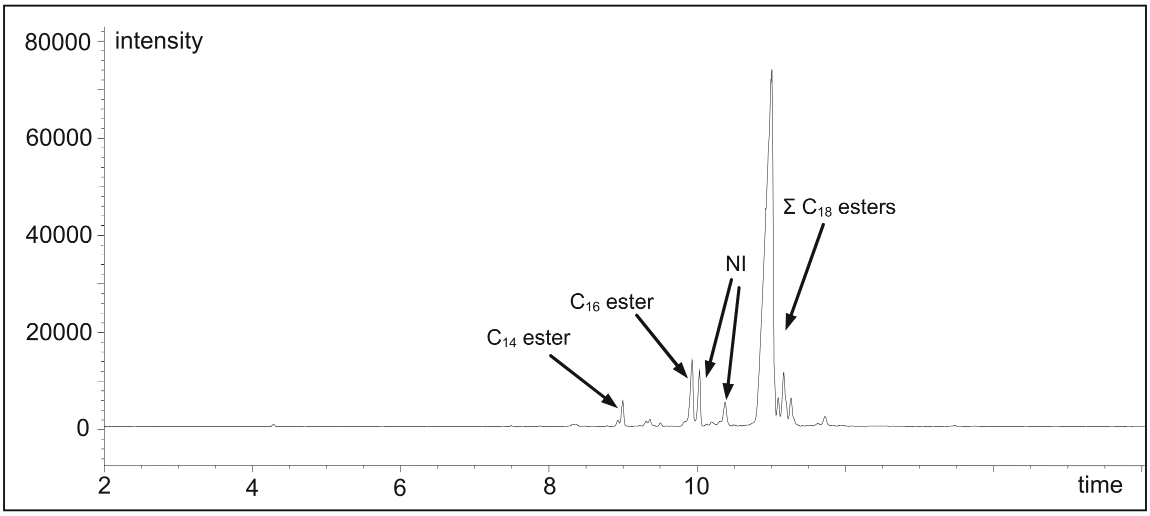

Figure 5. GC chromatogram of the product of esterification of oleic acid with 3,5,5-trimethylhexanol (120°C, 6 h, $SiO_2PSO_3H/1$)

Table 6. Esterification of oleic acid and 3,3,5-trimethylhexanol over selected acidic resins as catalysts (wt.%, GC)

Catalyst	Purolite CT124	Purolite CT169	Amberlyst A15
Alcohol	1.1	0.4	2.0
Oleic acid	0.1	0.1	0.1
Ester	89.6	92.5	91.6
NI	9.2	6.7	6.7
FA conv.	99.8	99.8	99.8

Reaction condition: 120°C, 6 hr; NI – unidentified byproducts (non-ester type).

Table 7. Physicochemical data of 2-EH and TMP oleate

Ester	2-EH oleate	TMH oleate
Viscosity., 40°C	8.1	9.3
Viscosity, 100°C	2.7	3.0
Viscosity index	202	205
Density, g/cm^3	0.869	0.895
Pour point, °C	–20	–27
Four ball wear test, kG	120	120

resulting fatty acid conversion exceeded 99% and during the subsequent reuses of the catalyst, this value has not undergone significant changes. The resulting esters, in particular oleic acid ester of 3,5,5-trimethyloheksanol, have interesting tribological properties such as viscosity index and low temperature properties and can be used as components of oil bases. The described method of synthesis of fatty acid esters and higher alcohols is "clean", sustainable and does not generate any waste chemicals.

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