

Statistical optimization of the synthesis of plant-derived fatty acid esters of TMP over homogeneous organometallic tin catalyst

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A class of very important industrial-grade biolubricants was synthesized from plant-derived fatty acids (oleic and isostearic acid) by direct esterification of trimethylolpropane according to novel effective and high selective method using Sn bis(2-ethylhexanoate) as catalyst. Model transesterification reactions were performed with oleic and isostearic acids to optimize the reaction conditions to obtain maximum content of TMP triesters. Used specific homogeneous Sn catalyst allows to obtain TMP esters with very high content of triesters, above of 94 wt% without deep vacuum purifying distillation. Both TMP esters were evaluated for their physicochemical and tribological properties using ASTM standards. Both TMP esters exhibited high viscosity indexes and excellent low temperature properties.

Keywords: tin catalyst, trimethylolpropane esters, statistical optimization, tribology.

INTRODUCTION

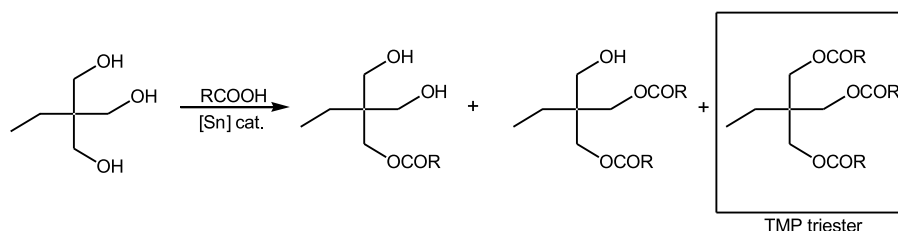
Due to the higher environmental requirements and more restrictive regulations the development of biodegradable modern lubricants is observed^{1, 2}. The modern lubricants should be more environmentally friendly and should be characterized by a higher level of performance and lower total life-cycle costs than the commonly used lubricants³. Synthetic esters biolubricants derived from renewable raw materials have been developed for applications in environmentally sensitive areas, such as forests, agriculture and aqueous areas due to their high biodegradability, low toxicity, and environmentally friendly nature. Synthetic esters biolubricants exhibit also good lubricity, excellent viscosity index, and lower volatility than common petroleum-based lubricants^{4, 5}. Most of the synthetic esters biolubricants are manufactured based on branched polyols, especially neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE)^{5–10}. Among them TMP esters are especially important. Trimethylolpropane esters of sunflower and rapeseed oil-derived fatty acids can be used in the production of hydraulic fluids^{11, 12}. Trimethylolpropane esters of low viscosity and high temperature stability have long been used as lubricants for aircraft, and a method has been patented to produce esters of the high thermal stability required for lubricants used in high-performance jet turbine engines¹³. It has also been shown that mixtures containing trimethylolpropane esters having a sufficiently high viscosity as well as low pouring point for car engine oils can be prepared^{14, 15}.

Esters of higher fatty acid and higher polyols (neopentyl glycol, trimethylolpropane, pentaerythritol) are commercially available. Despite the important role of oleic acid esters of polyols, particularly TMP esters, in the market, the literature on the methods for their synthesis is very limited. Conventional methods of manufacturing trimethylolpropane esters of fatty acids are based on esterification processes conducted in the presence of strong acidic catalysts. The most commonly used are homogeneous sulfonic acids, such as sulfuric acid, methanesulfonic acid or p-toluenesulfonic acid¹⁶. The yield of the product does not usually exceed 95% and the crude ester require careful purification. Fatty acid

esters of TMP can be also obtained by transesterification of fatty acid methyl esters (FAME) using conventional homogeneous basic catalyst^{17–21}.

An alternative to the homogeneous catalysts are various types of heterogeneous catalysts such as acidic phosphates, metal oxides, synthetic silicates or acidic ion exchange resins^{22–28}. Their main advantage is a very convenient separation from the post-synthesis mixture, but the great disadvantage of heterogeneous catalysts is the gradual loss of their activity, which is associated with the formation of a very troublesome waste. Acidic heterogeneous catalysts are also characterized by relatively low selectivity to the desired triester. In this context heterogeneous enzyme catalysts may be of interest^{4, 29–31}. Enzyme catalysts, despite the high yield and selectivity, are of lesser significance from the industrial point of view.

In the processes of manufacturing synthetic ester-type biolubricants, particularly TMP fatty acid esters, organometallic Ti, Zr and Sn compounds may be used. They have been widely used as catalysts in synthetic polyester technologies. In the processes of esterification they exhibit high activity with relatively small amounts are required to effectively catalyze the reaction, generally not exceeding 1 wt%. Thereby they not need to be removed from the post-synthesis mixtures. Method of the synthesis TMP oleate with the use of Sn oxalate as catalyst has been claimed German patent³². The described method allows to obtain a product characterized by good physicochemical and lubricant properties (viscosity and pour point), which can be acceptable for technical applications. Unfortunately, according to the described method it is possible to obtain ester characterized by low content of very important TMP triester (only 80 wt%). In this paper the novel more effective and more selective method of the synthesis of TMP fatty acid esters using homogeneous Sn bis(2-ethylhexanoate) as catalyst was described (Scheme 1). The use of Sn catalyst allows to obtain product contains above 94 wt% of TMP triester. Developed method has been also optimized according to common adopted statistical procedure.



Scheme 1. Highly selective synthesis of trimethylolpropane fatty acid esters

MATERIALS AND METHODS

Materials

Tallow based oleic acid was purchased from Oleon as Radiacid 0212. Isostearic acid was purchased from Oleon as Radiacid 0908. This product contains ca. 83 wt% of branched and saturated acids C16-C22 and 16 wt% cyclic derivatives. Trimethylolpropane was purchased from Perstorp (Sweden). As catalysts was used a commercially available homogeneous Sn bis(2-ethylhexanoate) purchased as Fascat 2003 from PMC Organometallic.

Analytical method

Products were analyzed by gas chromatography with head-space system using HP 5890 Series II chromatograph equipped with flame ionization detector, 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 temp. -360°C , detector temp. -380°C . Temperature programming: initial isotherm $100^{\circ}\text{C} - 1$ min., $100-380^{\circ}\text{C} - \text{gradient } 15^{\circ}\text{C}/\text{min.}$, final isotherm $380^{\circ}\text{C} - 3$ min. Carrier gas: 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. The conversion rate of acid was calculated as the ratio between the amount of the acid consumed in the synthesis to a total amount of the acid used in the synthesis. Resultant ratios were then converted to percentages.

Synthesis procedure

A 200 mL glass reactor, equipped with a mechanical stirrer, an electronic temperature control system, a nitrogen purge glass capillary and a receiver to collect esterification water was charged with 180 g (0.6 mol) of oleic or isostearic acid and required amount of trimethylolpropane (according to planned COOH : OH molar ratio). The reactor was heated up to 150°C and then a proper amount of the catalyst was poured into the reactor. After stabilizing the flow of nitrogen, the temperature was raised to required temperature. The reaction mixture was stirred for 6 hours. During the synthesis, the esterification water was collected in the receiver. The crude ester was first washed with 5 wt% K_3PO_4 water solution and water to remove residual acidic impurities, and then it was dehydrated under slightly reduced pressure to remove residual water.

Experimental design

The optimization studies were conducted according to 3-level 3-factor plan of experiments based on common Box-Behnken statistical methodology, in order to

determination the effects of the catalyst amount and process temperature on the triester content in post-synthesis mixtures^{33,34}. Fifteen runs of experiments (three repetitive experiments) have been conducted for three levels of three independent variables: X1 – COOH : OH molar ratio; X2 – reaction temperature ($^{\circ}\text{C}$) and X3 – catalyst concentration (wt%) to study the effect of the TMP triesters content (wt%) in post-synthesis mixture (Y). Independent variables and their levels for TMP oleic acid ester are presented in Table S1 and for TMP isostearic acid in Table S3 (see Supporting Informations).

Other than for oleic acid molar ratios adopted for the calculation of the isostearic acid due to lower content of carboxylic groups in the product. Acid number adopted for oleic acid was 200 mg KOH/g and for isostearic acid 180 mg KOH/g.

Statistical analysis

A general linear interaction model (Eq. 1), which accounts for the independent parameters with their interaction effects was considered in this study.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_{ij}$$

where X_{ij} – the levels of the factors adopted in this under study ($i, j = 1, \dots, k$)

Y – the predicted response of the process (TMP triesters contents, wt%),

n – the number of factors,

β_i and β_{ij} – the linear and interactive coefficients, respectively ($i, j = 1, \dots, k$)

The method of least squares was employed as certain values of the model parameters and analysis of variance (ANOVA) was applied to establish their statistical significance at a confidence level of 95%. The optimum values of the selected explanatory variables (X_i) were determined using STATGRAPHICS CENTURION 15 software for mathematical optimization and regression analysis. Microcal Origin 9.0 software was used for plot the response 3D plots and 2D surface plots.

Physicochemical properties of polyol esters

Kinematic viscosity measurements were made at 40 and 100°C using calibrated Ubbelohde Viscometer tubes. Viscosity and viscosity index (VI) were calculated using ASTM D 445 and ASTM D 2270 methods, respectively. All viscosity measurements were run in duplicate and the average value was reported. Pour points were determined according to standard ISO 3104. All runs were carried out in duplicate. Sample temperature was measured in 3°C increments at the top of the sample until it stopped pouring. Acid value was determined according to standard ISO 660:1996. Saponification value was determined according to standard ISO 3657:2013-10.

Hydroxyl value was determined according to standard DIN 53240-1. Color of esters (Gardner) was determined on Hach-Lange Lico 100 colorimeter.

Tribological properties of polyol esters

Lubricating properties of the base oil and the influence of the modifiers on these properties were assessed using the T-02U universal machine. T-02U universal four-ball testing machine is intended for determination of antiwear (AW) properties of lubricants and engineering materials, as well as determination of the tendency of lubricants and engineering materials to produce surface fatigue failures (pitting). All the tests may be carried out at an elevated temperature. T-02U machine determines AW properties in accordance with the standards: ASTM D 2783, ASTM D 2596, ASTM D 4172, ASTM D 2266, IP 239.

The wear standardized measurements, the average wear scar diameter (d), was determined. The average wear scar diameter and limiting load of the wear, which characterizes the antiwear (AW) properties of the tested oils, were determined after the 3600-s runs at a constant rotational speed (1450 rpm) and constant load (392.4 N). Assessment of the antiseizure based on scuffing load (P_t) was determined according to the standardized methods. The scuffing load was determined after the 18 sec. runs at a constant rotational speed (500 rpm) and a step-wise increasing load that were performed until seizure of the test balls was observed. Determining the value of scuffing load for steel-steel friction joint (100Cr6/100Cr6) lubricated with investigated oils. Taken as a measure of resistance to scuffing load P_t at which a sharp increase in friction torque and limiting pressure of seizure p_{oz} characterized by the value of the loading force at which there has been a seizure of friction. The parameters values adopted in the tribological test are given in Table 1.

For tribological test steel balls 12.7 mm in diameter, with 60–65HRC hardness were used. The sample volume required for each test was 8 ± 2 ml. The wear produced on the three stationary balls was measured under a calibrated microscope and reported as the WSD (wear scar diameter) or calculated wear.

RESULTS AND DISCUSSION

Preliminary evaluation the synthesis of trimethylolpropane fatty acid esters

Esterification reaction of polyols such as trimethylolpropane (TMP) and fatty acids in the presence of Ti, Zr, or Sn organometallic catalysts is similar to well-known polyesterification processes leading to synthetic polyester resins. The esterification process catalyzed by homogeneous organometallic catalysts is characterized by relatively low requirements with respect to the amount of

added catalyst and the temperature of 200–230°C, which is related to required activation temperature for this type of catalysts. Our previous experience in the esterification process of fatty acids and polyols, particularly pentaerythritol, leading to determine the reaction conditions allow to obtain products with the desired composition³⁵. The quality of synthesized TMP fatty acid ester depends on four key factors: reaction temperature, reagents molar ratio, amount of catalyst and reaction time. The use of organometallic tin catalyst in the synthesis of polyol esters was studied in more detail and we found that the high conversion of fatty acid (>95%) is obtained after 4–5 hours of the synthesis³⁵. In this study we have adopted 6 hours as effective reaction time and three other reaction parameters were further optimized. From several evaluated organometallic Lewis-type catalysts (Ti, Zr and Sn) in studied process Sn bis(2-ethylhexanoate) was characterized by the highest activity and selectivity to desired products. The reaction conditions adopted for the synthesis of trimethylolpropane ester were analogous to the initial testing used in the esterification of pentaerythritol with oleic acid and isostearic (molar ratio COOH : OH = 1 : 1, reaction temperature –220°C, the amount of catalyst – 0.9 wt%). After 6 hours the reaction yielded a product comprising 94.4 wt% of triester. Similar results were achieved also for isostearic acid ester. Content of diesters in crude product was below 5 wt% and monoesters <1 wt%. Content of unreacted fatty acids was 1.0–1.5 wt%.

Regression model analysis

The data obtained from Box-Behnken experimental plan were analyzed by linear multiple regression using STATGRAPHICS 15 software. Due to the different assumptions in the construction of plans for the experiments for oleic acid and isostearic esters both processes have been described separately.

Trimethylolpropane oleic acid ester.

Tables S1 and S2 (Supporting Informations) showed designed matrix of experiments and responses of trimethylolpropane oleic acid triester contents in post-synthesis mixtures. The data obtained from Box-Behnken experiments were analysed by linear multiple regression using STATGRAPHIC 15 software. Based on this statistical model analysis the process was set for two factors: COOH : OH molar ratio (for oleic acid and tromethylolpropane respectively) (X1), reaction temperature (X2) and COOH : OH molar ratio (X1), amount of added catalyst (X3) was performed. Analysis of variance (ANOVA) was applied to establish the statistical significance of the model parameters. The significance of each parameter (coefficient) was determined by F-values and P-values (Table 2 and 3).

Table 1. The Values of parameters values of the tribological test adopted in this Study

Parameter	G_{oz} , Nmm ⁻²	P_t , N	p_{oz} , Nmm ⁻²
Rotational velocity of the upper ball	1450 rpm	500 rpm	500 rpm
Time	1 hour	18 s	18 s
Test temp., [°C]	20 ± 5	20 ± 5	20 ± 5
Initial load of the test couple	392.4 N	0 N	0 N
Final load of the test couple	–	7200 N	7200 N
Speed of load increase	–	409 N/s	409 N/s
Measurement	Wear scar diameter, Limiting load wear, G_{oz}	Scuffing load P_t	Scar diameter, Limiting seizure pressure p_{oz}

Table 2. Significance of regression parameters for TMP oleate synthesis (X_1 i X_2)

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value	Degree of significance
A:X1	22.4832	1	22.4832	88.00	0.0000	high significant
B:X2	0.00274087	1	0.00274087	0.01	0.9198	not significant
AA	1.68335	1	1.68335	6.59	0.0303	possibly significant
AB	1.01937	1	1.01937	3.99	0.0769	not significant
BB	1.12204	1	1.12204	4.39	0.0656	not significant
Total error	2.29934	9	0.255482			
Total (corr.)	36.916	14				$R^2 = 0.9377$; R^2 (adjusted for D.f.) = 0.9031

Table 3. Significance of regression parameters for TMP oleate synthesis (X_1 i X_3)

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value	Degree of significance
A:X1	21.0021	1	21.0021	87.94	0.0000	high significant
B:X3	0.284269	1	0.284269	1.19	0.3036	not significant
AA	1.63699	1	1.63699	6.85	0.0279	possibly significant
AB	1.12859	1	1.12859	4.73	0.0577	not significant
BB	1.42936	1	1.42936	5.99	0.0570	not significant
Total error	2.1493	9	0.238811			
Total (corr.)	36.916	14				$R^2 = 0.9417$; R^2 (adjusted for D.f.) = 0.9094

The larger magnitude of the by F-values and smaller P-values (< 0.01) prove that, the corresponding coefficient is more significant. The T-test was used to determine the significance of the regression coefficients of variables, and P-value was the indicator of the significance of the statistical test, whose value below 0.001 means the variable is very significant and almost (probably) significant below 0.05. It was noticed that the COOH : OH molar ratio is highly significant followed the esterification temperature and catalyst amount.

To test the fit of the model, the determination coefficients R^2 were evaluated. In case of X_1 and X_2 as function of Y the value of $R^2 = 0.9377$. This indicates that the model could explain 93.77% of variability. That is only 6.23% of total variation are not explained by the model, which ensures the high compatibility of fit and confirming the adequacy of the adopted regression model. In case of X_1 and X_3 as function of Y the value of $R^2 = 0.9417$. This indicates that the model could explain 94.17% of variability and also ensures the high compatibility of fit and confirming the adequacy of the adopted regression model.

Based on the statistical analysis described above, it can be concluded that the adopted model is characterized by a very good degree of fit. The parameter describing the degree of fit of the model to experimental results reached 88.8%. For most processes the value of this index $> 85\%$ is considered to be satisfactory. The re-

sults in Tables 3 and 4 also indicate, as expected, that on the value of the parameter a function of response Y (content triesters reaction mixtures), the strongest effect has COOH : OH molar ratio.

Trimethylolpropane isostearic acid ester.

Tables S3 and S4 (Supporting Informations) showed designed matrix of experiments and responses of trimethylolpropane isostearic acid ester contents in post-synthesis mixtures.

Analogously to trimethylolpropane oleate the analysis of variance (ANOVA) was applied to establish the statistical significance of the model parameters. The significance of each parameter (coefficient) was determined by F-values and P-values (Table 4 and 5).

The T-test was used to determine the significance of the regression coefficients of variables, and P-value was the indicator of the significance of the statistical test, whose value below 0.001 means the variable is very significant and almost (probably) significant below 0.05. It was noticed that in the synthesis of trimethylolpropane isostearate the COOH : OH molar ratio is also highly significant followed the esterification temperature and catalyst amount. To test the fit of the model, the determination coefficients R^2 were evaluated. In case of X_1 and X_2 as function of Y the value of $R^2 = 0.8834$. This indicates that the model could explain 88.34% of variability. That is only 11.66% of total variation are not

Table 4. Significance of regression parameters for TMP isostearate synthesis (X_1 i X_2)

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value	Degree of significance
A:X1	29.861	1	29.861	57.51	0.0000	high significant
B:X2	4.5586	1	4.5586	8.78	0.0159	possibly significant
AA	0.319214	1	0.319214	0.61	0.4531	not significant
AB	0.0151789	1	0.0151789	0.03	0.8680	not significant
BB	0.18101	1	0.18101	0.35	0.5694	not significant
Total error	4.67274	9	0.519193			
Total (corr.)	40.064	14				$R^2 = 0.8834$; R^2 (adjusted for D.f.) = 0.8186

Table 5. Significance of regression parameters for TMP isostearate synthesis (X_1 i X_3)

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value	Degree of significance
A:X1	32.7772	1	32.7772	68.74	0.0000	high significant
B:X3	5.5364	1	5.5364	11.61	0.0093	possibly significant
AA	0.303876	1	0.303876	0.64	0.4477	not significant
AB	0.684968	1	0.684968	1.44	0.2650	not significant
BB	1.34768	1	1.34768	2.83	0.1312	not significant
Total error	3.81446	8	0.476807			
Total (corr.)	40.0636	13				$R^2 = 0.9048$; R^2 (adjusted for D.f.) = 0.8453

explained by the model, which ensures the high compatibility of fit and confirming the adequacy of the adopted regression model. In case of X1 and X3 as function of Y the value of $R^2 = 0.9048$. This indicates that the model could explain 90.48% of variability and also ensures the high compatibility of fit and confirming the adequacy of the adopted regression model.

Effect of reaction parameters on TMP oleic acid ester synthesis

The 3D plots and 2D contour plots were developed with trimethylolpropane triester contents in post-synthesis mixtures. This parameter of crude trimethylolpropane fatty acid esters is crucial for most of application properties, especially lubricant properties and pour point.

Figures 1A and 2A show the effect of COOH : OH molar ratio and reaction temperature on TMP trioleate content in post-synthesis mixture formed in esterification reaction of oleic acid with trimethylolpropane catalysed by Sn di(2-ethylhexanoate) at a resident reaction time of 6 hr. The TMP trioleate content increased as the COOH : OH molar ratio increased to close to equimolar. Figures 1B and 2B show the effect of COOH : OH molar ratio

and amount of added catalyst on TMP trioleate content in post-synthesis mixture. The TMP trioleate content increased also as the reaction temperature increased from 210 to 230°C. The maximum of TMP trioleate content (94.8 wt%) can be obtained for the molar ratio from 0.99 : 1, reaction temperature 220–230°C. A similar effect was also observed in effect of COOH : OH molar ratio and amount of added catalyst. The maximum of TMP trioleate content can be obtained for the molar ratio from 0.98 : 1 to 0.99 : 1 and amount of added catalyst from 0.8 to 0.9 wt%. (see Figure 1B and 2B).

This study did not evaluate the effect of reaction time on the TMP triester content in post-synthesis mixtures. From our preliminary studies on the esterification of polyols with fatty acids shows, that esterification reaction catalysed by Sn, Ti and Sn organocatalysts was only slightly influenced by residence reaction time at the studied levels of reaction variables³⁵. The main driving force of this reaction is associated with two other process parameters: resistant rotation speed (350 rpm and N2 stream at constant level).

According to the adopted model, the estimated optimum conditions for esterification of trimethylolpropane

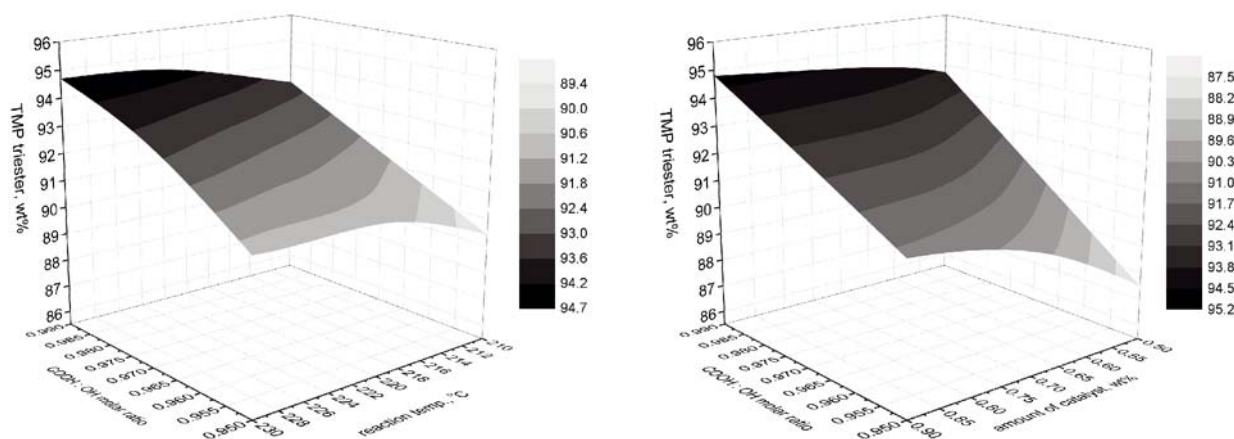


Figure 1. 3D surface plots for the trimethylolpropane trioleate content in post-synthesis mixtures. Change variables were (A) COOH : OH molar ratio and reaction temperature (reaction time – 6 hr; catalyst – 0.7 wt%), (B) COOH : molar ratio and amount of catalyst (reaction time – 6 hr; reaction temperature – 220°C)

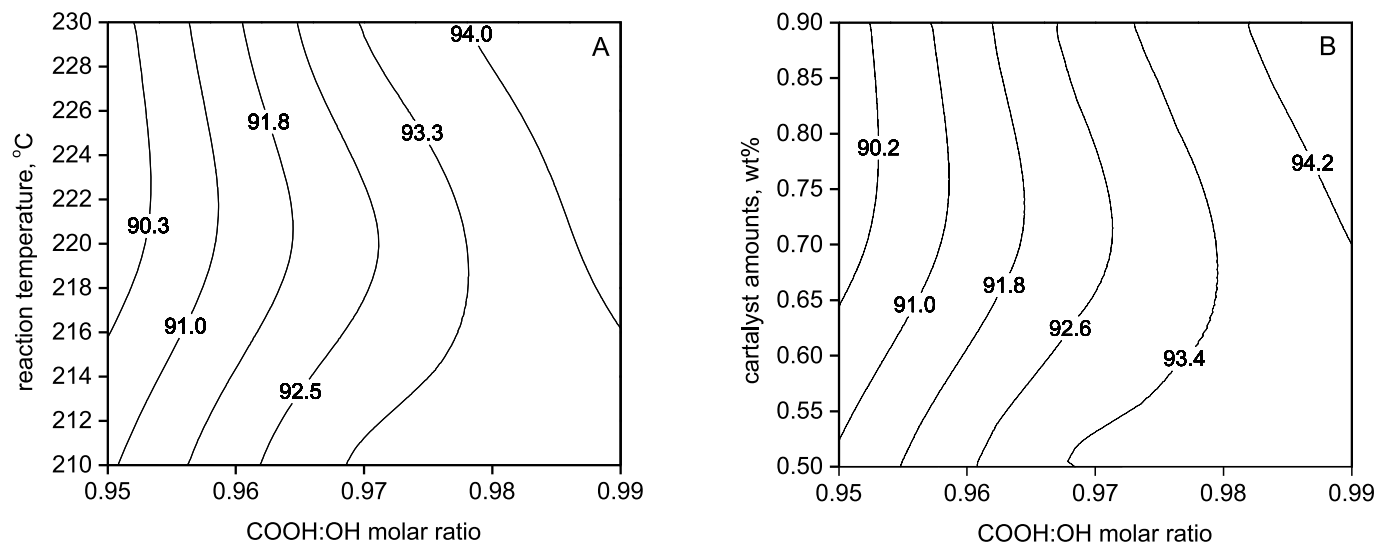


Figure 2. Contour plots for the trimethylolpropane trioleate content in post-synthesis mixtures. Change variables were (A) COOH : OH molar ratio and reaction temperature (reaction time – 6 hr; catalyst – 0.7 wt%), (B) COOH : molar ratio and amount of catalyst (reaction time – 6 hr; reaction temperature – 220°C)

with oleic acid were: COOH : OH molar ratio, 0.99 : 1; reaction temperature, 230°C; amount of added catalyst, 0.7–0.9 wt%. Under this reaction conditions TMP trioleate content in post-synthesis mixture above of 94 wt% was achieved.

Effect of reaction parameters on TMP isostearic acid ester synthesis

The 3D plots and 2D contour plots were developed with trimethylolpropane triester contents in post-synthesis mixtures. Figures 3A and 4A show the effect of COOH : OH molar ratio and reaction temperature on TMP triisostearate content in post-synthesis mixture formed in esterification reaction of oleic acid with trimethylolpropane catalysed by Sn bis(2-ethylhexanoate) at constant reaction time of 6 hr. The analogously to TMP trioleate the TMP triisostearate content also increased as the COOH : OH molar ratio increased to close to equimolar. Figure 3B and 4B show the effect of COOH : OH molar ratio and amount of added catalyst on TMP triisostearate content in post-synthesis mixture. Similarly to TMP trioleate the TMP triisostearate content increased

also as the reaction temperature increased from 210 to 230°C. The maximum of TMP triisostearate content in post-synthesis mixture (> 94 wt%) can be obtained for the molar ratio from 0.92 : 1 to 0.94 : 1, reaction temperature from 220 to 230°C. A similar effect was also observed in effect of COOH : OH molar ratio and amount of added catalyst. The maximum of TMP triisostearate content can be obtained for the molar ratio 0.94 : 1 and amount of added catalyst from 0.8 to 0.9 wt%. (see Figure 3B and 4B).

According to the adopted model, the estimated optimum conditions for esterification of trimethylolpropane with isostearic acid were: COOH : OH molar ratio, 0.94 : 1; reaction temperature, 230°C; amount of added catalyst, 0.9 wt%. Under this reaction conditions TMP triisostearate content in post-synthesis mixture above of 94 wt% was achieved.

Physicochemical characteristics of TMP fatty acid esters

Under the optimal reaction conditions the synthesis of oleic acid and isostearic acid esters of trimethylolpropane were performed. The crude TMP ester was washed with

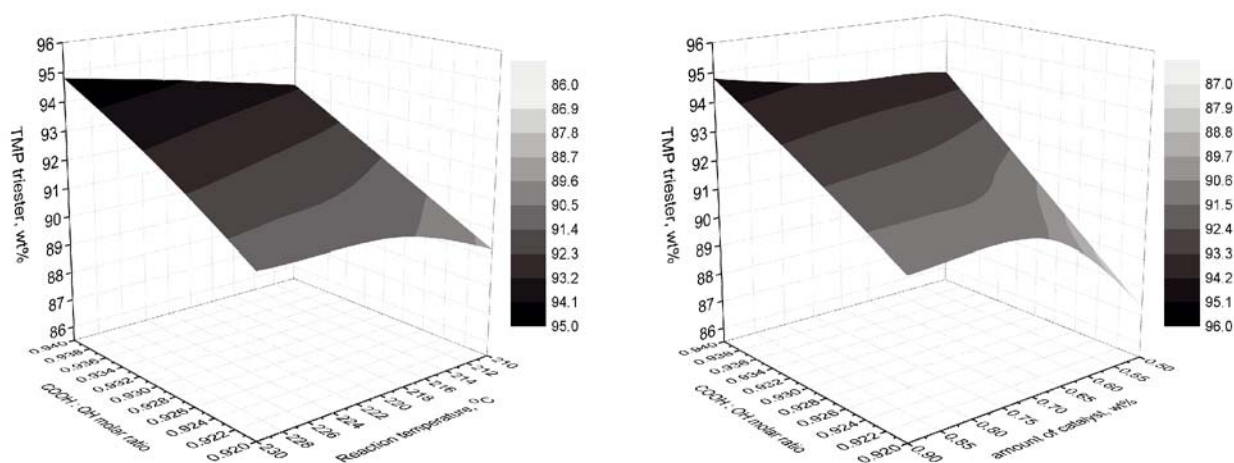


Figure 3. 3D surface plots for the trimethylolpropane triisostearate content in post-synthesis mixtures. Change variables were (A) COOH : OH molar ratio and reaction temperature (reaction time – 6 hr; catalyst – 0.7 wt%), (B) COOH : molar ratio and amount of catalyst (reaction time – 6 hr; reaction temperature – 220°C)

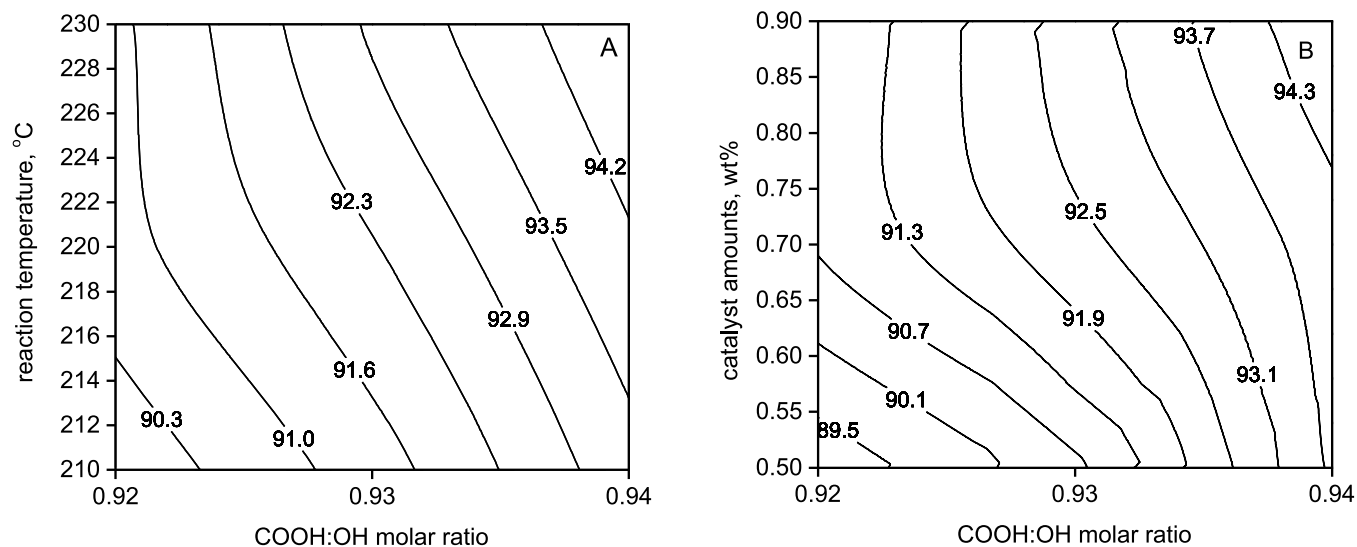


Figure 4. Surface plots for the trimethylolpropane triisostearate mixtures. Change variables were (A) COOH : OH molar ratio and reaction temperature (reaction time – 6 hr; catalyst – 0.7 wt%), (B) COOH : molar ratio and amount of catalyst (reaction time – 6 hr; reaction temperature – 220°C)

the use of 5 wt% water solution of K_3PO_4 (10 wt% in relation to crude ester). The amount of K_3PO_4 used for washing was calculated as a three-fold molar excess relative to the acid number of the crude product. The purification washing was performed at 50°C for 30 min. After phase separation, the ester was washed twice with water to neutral pH and finally dried under reduced pressure. Table 6 summarizes the compositions of the purified TMP oleic and isostearic acid esters.

Table 6. Compositions of purified trimethylolpropane ester of oleic and isostearic acid (GC, wt%)

Fatty acid	oleic acid	isostearic acid
TMP	–	–
FA	0.2	0.2
Monoesters	0.4	0.9
Diesters	3.0	4.0
Triesters	95.7	94.1
Other	0.7	0.8
Σ di- and triesters	98.7	98.1

The composition of the purified TMP oleate obtained in this study was significantly better than commercially available TMP oleate. The content of oleic acid triester was 95.7 wt% and sum of di- and triesters was 98.7 wt%. The composition of TMP isostearate was similar to the corresponding ester of oleic acid. The content of triester

was 94.1 wt% and the content of the sum of di- and triesters was 98.1 wt%.

In Figure 5 and 6 FTIR spectra of both TMP esters are presented.

FTIR spectroscopy confirms the high purity of synthesized esters. In particular, the appearance and intensity of absorption peaks corresponding to the stretching vibration of C=O of carboxylic ester groups at around 1730–1745 cm^{-1} and OH hydroxyl polyol groups at 3440–3480 cm^{-1} . The formation of carboxylic ester can be also confirmed by appearance of the peaks assigned to ester C–O stretching band at ca. 1150 cm^{-1} and ester C=O band at ca. 1740 cm^{-1} . Moreover, the disappearance of peak corresponding to the stretching of polyols O–H groups at ca. 3460 cm^{-1} has also confirmed the formation of esters. All FTIR spectra recorded for synthesized esters show the appearance of characteristic ester peaks (1162 and 1740 cm^{-1}) and peaks assigned to hydroxyl O–H groups which are significantly reduced.

For the obtained esters of oleic acid, the basic physico-chemical properties were determined including viscosity characteristics, viscosity index, acid number and pour point. The results were compared with the values of the corresponding parameters for a commercial grade TMP oleic acid and isostearic acid esters (Table 7).

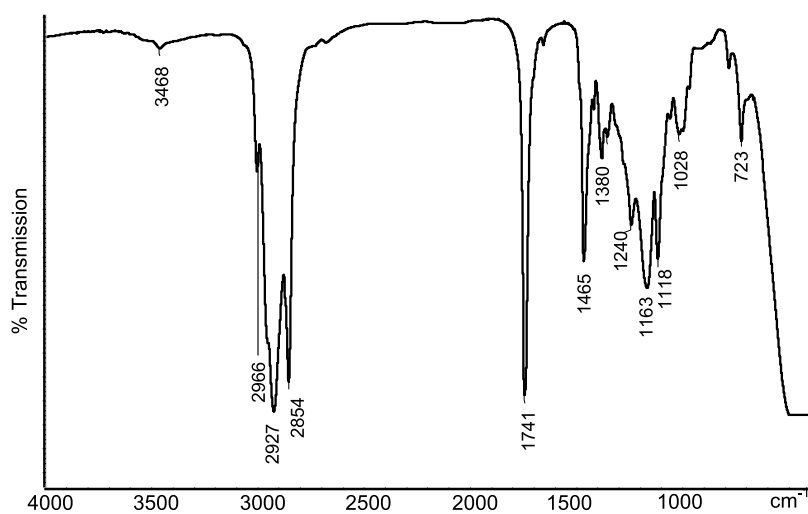


Figure 5. FTIR spectrum of trimethylolpropane trioleate

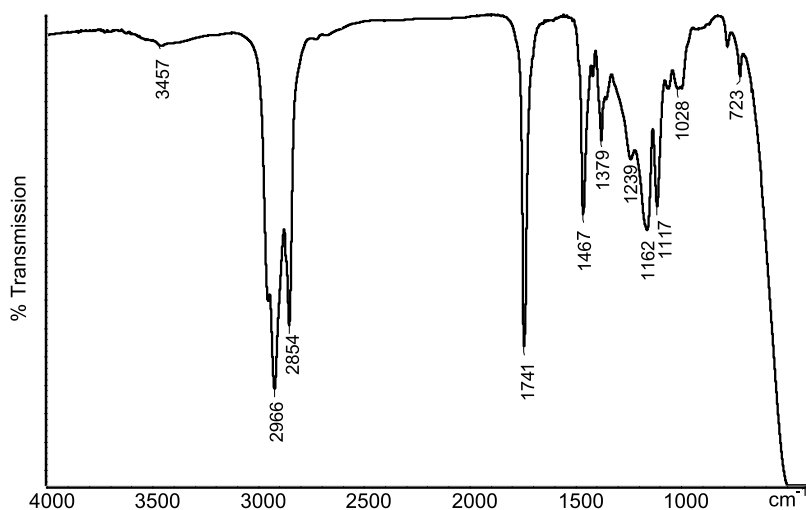


Figure 6. FTIR spectrum of trimethylolpropane triisostearate

Table 7. Physicochemical characteristics of oleic and isostearic acid esters of TMP

Product	TMP trioleate comm. grade ¹⁾	TMP oleate	TMP isostearate comm. grade ²⁾	TMP isostearate
Appearance	yellowish, clear liquid	yellowish, clear liquid	colorless, clear liquid	colorless, clear liquid
Color (Gardner)	5	5	2–5	3
Viscosity, m ² /s, 40°C	47	47	90	92
100°C	9.8	9.8	14	15
Viscosity index	185	185	144	157
L _A , mg KOH/g	0.5	0.2	0.2	0.2
L _S , mg KOH/g	175	175	172	175
L _{OH} , mg KOH/g	≤ 10	7	13	9
Pour point, °C	-51	< -55	-26	-26

LA – acid value; LS – saponification value; LOH – hydroxyl value;
1, 2) Industrial Quimica Lasem Technical Data (Spain)

The results summarized in Table 7 show, that trimethylolpropane trioleate obtained with the use of homogeneous organotin catalyst is characterized by similar physicochemical data compared to commercial trimethylolpropane trioleate. However, commercial TMP ester is manufactured by using a more onerous technology, that requires purification distillation under very high vacuum. The new and convenient method described in this paper is free of this problem. Lower hydroxyl value proves also, that the use of Sn bis(2-ethylhexanoate) as catalyst leads to a product having a lower content of undesirable TMP mono- and diesters.

Table 6 presented also the chemical composition of purified TMP isostearic acid ester. In our studies we used isostearic acid obtained from oleic acid, so it can also be considered as a raw material derived from renewable sources. Both oleic and isostearic acid esters of trimethylolpropane are used as lubricants for hydraulic and metalworking oils, plastics, textiles; in the cosmetic industry as emollients and also as replacements for petroleum-based lubricants in metalworking³⁶. The chemical compositions of isostearic acid esters shown in Table 8 does not significantly differ from the corresponding of oleic acid esters. Table 7 presents the results of determinations of physicochemical properties of isostearic acid esters. TMP isostearic acid ester is characterized by significantly higher kinematic viscosity values, but also by lower, compared to the corresponding oleic acid ester, values of the viscosity index (V.I.). Obtained TMP isostearic acid ester is also characterized by lower, compared to commercial product, hydroxyl value.

Tribological characteristics of TMP fatty acid esters

The results of the performed four-ball test of obtained esters show that esters of fatty acids (oleic and isostearic) and TMP synthesized according to the adopted method, which used easily accessible homogeneous organotin catalyst, are characterized by good lubrication properties. The results of four-ball test of synthesized esters were presented in Table 8.

Table 8. Tribological properties of trimethylolpropane fatty acid esters

	TMP oleate	TMP isostearate
Wear scar d, mm	0.73	0.71
Limit. wear load, G _{oz} , N/mm ²	382.9	404.8
Scuffing load, P _i , N	1850	1300
Limit. pressure of seizure, p _{oz} , N/mm ²	355.5	318.1

Measured scuffing load of esters were at the level of 1850–1300 N and wear scar diameter of 0.73 and 0.71 mm respectively can be considered as good and similar to published data for pentaerythritol oleate (1600 N and 0.79 mm respectively), in particular wear scar diameter²². As can be seen in Table 10 lubrication properties of TMP isostearic ester are significantly better compared to the corresponding oleic acid esters. Physicochemical and tribological properties of TMP esters indicated in Tables 9 and 10 clearly show that the described method for the synthesis of polyol esters using the specific homogeneous organotin catalyst provides a convenient way to obtain products which are potentially useful for tribological and cosmetic applications.

CONCLUSIONS

The esterification of trimethylolpropane with oleic acid and vegetable-derived isostearic acid was carried out using homogenous organometallic catalysts – Sn bis(2-ethylhexanoate). For this catalyst the optimal synthesis parameters were determined, in particular, the fatty acid-polyol molar ratio, the reaction temperature, the reaction time and the amount of added catalyst. Based on the preliminary studies on the synthesis of fatty acid esters of polyols we have adopted 6 hours as an effective reaction time and three other reaction parameters were further optimized. The optimization studies were conducted according to 3-level 3-factor plan of experiments based on Box-Behnken statistical methodology. Under the adopted reaction conditions the highest conversion of fatty acid, close to 99 % was achieved and additionally the sum of di- and triesters in post-synthesis mixtures was above 98 wt%, significantly better compared to commercial available TMP ester without deep vacuum purifying distillation. The described method of the synthesis is suitable for industrial scale and allows to obtain high-quality products fully suitable for many technical applications. A systematic evaluation of basic physicochemical and lubricating properties of the synthesized esters was also carried out and their good properties as biolubricants were confirmed.

SUPPORTING INFORMATIONS

Table S1. Independent variables and their levels used in the experimental design for trimethylolpropane oleic acid ester synthesis

Level	X_1	X_2	X_3
1	0.99 : 1	230	0.9
0	0.97 : 1	220	0.7
-1	0.95 : 1	210	0.5

Table S2. Design of experiments and response of TMP triester content for trimethylolpropane oleic acid ester synthesis

Run	molar ratio COOH:OH X_1	reaction temperature [°C] X_2	catalyst amounts [wt%] X_3	TMP triester content [wt%] Y
1	0.99 : 1	230	0.7	94.3
2	0.99 : 1	210	0.7	93.3
3	0.95 : 1	230	0.7	90.9
4	0.95 : 1	220	0.7	90.8
5	0.97 : 1	220	0.7	92.2
6	0.99 : 1	220	0.9	94.2
7	0.99 : 1	220	0.5	94.6
8	0.95 : 1	220	0.9	90.8
9	0.97 : 1	220	0.9	92.7
10	0.97 : 1	230	0.9	93.6
11	0.97 : 1	210	0.5	90.5
12 ¹⁾	0.97 : 1	210	0.5	90.7
13	0.97 : 1	230	0.7	93
14	0.97 : 1	210	0.9	92.9
15 ²⁾	0.97 : 1	220	0.7	92.2

1,2) – repetitive runs

Table S3. Independent variables and their levels used in the experimental design for trimethylolpropane isostearic acid ester synthesis

Level	X_1	X_2	X_3
1	0.94 : 1	230	0.9
0	0.93 : 1	220	0.7
-1	0.92 : 1	210	0.5

Table S4. Design of experiments and response of TMP triester content for trimethylolpropane isostearic acid ester synthesis

Run	molar ratio COOH:OH X_1	reaction temperature [°C] X_2	catalyst amounts [wt%] X_3	TMP triester content [wt%] Y
1	0.94	230	0.7	94.8
2	0.94	210	0.7	93.3
3	0.92	230	0.7	90.8
4	0.92	220	0.7	90.7
5	0.93	220	0.7	92
6	0.94	220	0.9	94.4
7	0.94	220	0.5	93.8
8	0.92	220	0.9	90.7
9	0.93	220	0.9	92.5
10	0.93	230	0.9	93.2
11	0.93	210	0.5	90.5
12 ¹⁾	0.93	210	0.5	90.6
13	0.93	230	0.7	92.8
14	0.93	210	0.9	91.8
15 ²⁾	0.93	220	0.7	92.1

1,2) – repetitive runs

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LITERATURE CITED

- Erhan, S.Z. & Asadauskas, S. (2000) Lubricant basestocks from vegetable oils. *Ind. Crop. Prod.* 11, 277–282. DOI: 10.1016/S0926-6690(99)00061-8.
- Alias, N.H., Yunus, R., Idris, A. & Omar, R. (2009) Effects of additives on oxidation characteristics of palm oil-based trimethylolpropane ester in hydraulics applications. *Eur. J. Lipid Sci. Technol.* 111, 368–375. DOI: 10.1002/ejlt.200800136.

3. Pettersson, A. (2007) High-performance base fluids for environmentally adapted lubricants. *Tribol. Int.* 40, 638–645. DOI: 10.1016/j.triboint.2005.11.016.
4. Kiriliauskaite, V., Bendikiene, V. & Juodka, B. (2011) Synthesis of trimethylolpropane esters of oleic acid by Lipoprime 50T. *J. Ind. Microbiol. Biot.* 38, 1561–1566. DOI: 10.1007/s10295-011-0946-3.
5. Willing, A. (2001) Lubricants based on renewable resources – an environmentally compatible alternative to mineral oil products. *Chemosphere* 43, 89–98. DOI: 10.1016/S0045-6535(00)00328-3.
6. Nagendramma, P. (2011) Study of pentaerythritol tetraoleate ester as industrial gear oil. *Lubr. Sci.* 23, 355–362. DOI: 10.1002/lis.161.
7. McNutt, J. & He, Q. (2016) Development of biolubricants from vegetable oils via chemical modification. *J. Ind. Eng. Chem.* 36, 1–12. DOI: 10.1016/j.jiec.2016.02.008.
8. Syahir, A.Z., Zulkifli, N.W.M., Masjuki, H.H., Kalam, M.A., Alabdulkarem, A., Gulzar, M., Khuong, L.S. & Harith, M.H. (2017) A review on bio-based lubricants and their applications. *J. Clean. Sci.* 168, 997–1016. DOI: 10.1016/j.jclepro.2017.09.106.
9. Panchal, T.M., Patel, A., Chauhan, D.D., Thomas, M. & Pate, J.V. (2017) A methodological review on bio-lubricants from vegetable oil based resources. *Renew. Sustain. Energ. Rev.*, 70, 65–70. DOI: 10.1016/j.rser.2016.11.105.
10. Zainal, N.A., Zulkifli, N.W.M., Gulzar, M. & Masjuki, H.H. (2018) A review on the chemistry, production, and technological potential of bio-based lubricants. *Renew. Sustain. Energ. Rev.*, 82, 80–102.
11. Bongardt, F., Bossmann, B., Westfechtel, A. & Giede, W. (1996) Synthetische ester aus alkoholen und fettsäuregemischen aus ölsäurereichen, stearinsäurearmen pflanzenölen. German Pat. DE 4444137.
12. Lämsä, M. (1996) Process for preparing a synthetic ester from a vegetable oil. World Pat. WO 1996007632 A1.
13. Leleu, G., Bédague, P. & Sillion, S. (1977) Trimethylolpropane esters useful as base lubricants for motor oils. USA Pat. US 4061581.
14. Tsai, M., Laemmler JT (1987) Metalworking with a trimethylolalkane ester lubricant. USA Pat US 4655947.
15. Mattei, L., Pacor, P. & Piccone, A. (1995) Oils with Low Environmental Impact for Modern Combustion Engines. *Synth. Lubr.* 26,49–52. DOI: 10.1007/s11746-998-0094-8.
16. Lawate, S.S. & Lal, L. (1998) High oleic polyol esters, compositions and lubricants, functional fluids and greases containing the same. USA Pat. US 5773391 .
17. Yunus, R., Fakhru'l-Razi, A., Ooi, T.L., Biak, D.L. & Iyuke, S.E. (2004) Kinetics of transesterification of palm-based methyl esters with trimethylolpropane. *J. Am. Oil Chem. Soc.* 81, 497–503. DOI: 10.1007/s11746-004-0930-7.
18. Uosukainen, E., Linko, Y.Y., Lämsä, M., Tervakangas, T. & Linko, P. (1998) Transesterification of trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants. *J. Am. Oil Chem. Soc.* 75, 1557–1563. DOI: 10.1007/s11746-998-0094-8.
19. Wang, E., Ma, X., Tang, Sh., Yan, R., Wang, Y., Riley, W.W. & Reaney, M.J.T. (2014) Synthesis and oxidative stability of trimethylolpropane fatty acid triester as a biolubricant base oil from waste cooking oil. *Biomass Bioenerg.* 66, 371–378. DOI: 10.1016/j.biombioe.2014.03.022.
20. Chang, T., Yunus, R., Rashid, U., Choong, T. S.Y., Biak, D.R.A. & Syam, A.M. (2015) Palm Oil Derived Trimethylolpropane Triesters Synthetic Lubricants and Usage in Industrial Metalworking Fluid. *J. Oleo Sci.* 64, 143–151.
21. Hamid, H.A., Yunus, R., Rashid, U., Choong, T. S.Y., Ali, S. & Syam, A.M. (2016) Synthesis of high oleic palm oil-based trimethylolpropane esters in a vacuum operated pulsed loop reactor. *Fuel*, 166, 560–566.
22. Srinivas, D. & Kotwal, M. (2013) Process for preparing biodegradable lubricant base oils World Pat. WO 2013175509.
23. Brini, S., Psaro, R., Zaccheria, F. & Ravasio, M.N. (2014) Process or the synthesis of esters of fatty acids in the presence of catalyst. World Pat. WO 201400659.
24. Zaccheria, F., Mariani, M., Psaro, R., Bondioli, P. & Ravasio, N. (2016) Environmentally friendly lubricants through a zero waste process. *Appl. Catal. B: Environ.* 181, 581–586. DOI: 10.1016/j.apcatb.2015.08.032.
25. Kotwal, M., Kumar, A. & Darbha, S. (2013) Three-dimensional, mesoporous titanasilicates as catalysts for producing biodiesel and biolubricants. *J. Mol. Catal. A, Chemical* 377, 65–73. DOI: 10.1016/j.molcata.2013.04.029.
26. Varhadi, P., Kotwal, M. & Srinivas, D. (2013) Zirconium phenyl phosphonate phosphite as a highly active, reusable, solid acid catalyst for producing fatty acid polyol. *Appl. Catal. A: General* 462–463, 129–136. DOI: 10.1016/j.apcata.2013.04.043.
27. Oh, J., Yang, S., Kim, Ch., Choi, I., Kim, J. & Lee, H. (2013) Synthesis of biolubricants using sulfated zirconia catalysts. *Appl Catal A: General* 455, 164–171. DOI: 10.1016/j.apcata.2013.01.032.
28. Nagendramma, P., Kaul, S. & Bisht, R.P.S. (2010) Study of synthesized ecofriendly and biodegradable esters: fire resistance and lubricating properties. *Lubr. Sci.* 22,103–110. DOI: 10.1002/lis.108.
29. Linko, Y.Y., Tervakangas, T., Lamsa, M. & Linko, P. (1997) Production of trimethylolpropane esters of rapeseed oil fatty acids by immobilized lipase. *Biotechnol. Tech.* 11, 889–892. DOI: 10.1023/A:1018410316231.
30. Åkerman, C.O., Gaber, Y., Ghanid, N.A., Lämsä, M. & Hatti-Kaul, R. (2011) Clean synthesis of biolubricants for low temperature applications using heterogeneous catalysts. *J. Mol. Catal. B. Enzym.* 72 263–269. DOI: 10.1016/j.molcatb.2011.06.014.
31. Åkerman, C.O., Hagström, A.E.V., Mollaahmad, M.A., Karlsson, S. & Hatti-Kaul, R. (2011) Biolubricant synthesis using immobilised lipase: Process optimization of trimethylolpropane oleate production. *Process. Biochem.* 46, 2225–2231. DOI: 10.1016/j.procbio.2011.08.006.
32. Bongardt, F., Bossmann, B., Westfechtel, A. & Giede, W. (1996) Synthetische Ester aus Alkoholen und Fettsäuregemischen aus ölsäurereichen, stearinsäurearmen Pflanzenölen. German Pat. DE 4444137.
33. Dai, J., Li, D., Zhao, Y. & Xiu, Zh. (2014) Statistical Optimization for Biodiesel Production from Soybean Oil in a Microchannel Reactor. *Ind. Eng. Chem. Res.* 53 9325–9330. DOI: DOI: 10.1021/ie4037005.
34. El-Gendy, N.S., Deriase, S.F. & Hamdy, A. (2014) Statistical optimization of biodiesel production from sunflower waste cooking oil using basic heterogeneous biocatalyst prepared from eggshells. *Egypt J. Petrol.* 24, 37–48. DOI: 10.1016/j.ejpe.2015.02.004.
35. Nowicki, J., Stańczyk, D., Drabik, J., Mosio-Mosiewski, J., Woszczyński, P. & Warzała, M. (2016) Synthesis of Fatty Acid Esters of Selected Higher Polyols Over Homogeneous Metallic Catalysts. *J. Am. Oil Chem. Soc.* 93, 973–981. DOI: 10.1007/s11746-016-2840-7.
36. Ash, M. & Ash, I. (2004) Handbook of Green Chemicals, Endicott NY, USA: Synapse Info Resources Inc.,