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An environmentally friendly production of ester-biolubricant from oleic acid

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Abstract: The production of oleic-based trimethylolpropane (TMP) esters via the esterification reaction between oleic acid (OA) and TMP in a reactive distillation system, employing the environmentally friendly catalyst methanesulfonic acid, was explored. The homogeneous acid catalyst, the OA/TMP molar ratio within 1.0–3.0, the esterification reaction enhancement and a new purification technique, using choline hydroxide (ChOH), for obtaining choline carboxylate as a subproduct, were studied. It was found that using an OA/TMP molar ratio of 3.0, only unreacted OA remained as an impurity. The deleterious or beneficial effect of intermediate products, unreacted OA and temperature on the kinematic viscosity were unraveled. The kinematic viscosity behavior for the products was practically independent of temperature but an abrupt enlargement of the kinematic viscosity was observed in the presence of functional groups in the intermediate esters, even greater than the Mark–Houwink counterpart effect. On contrary, the presence of OA in the final product decreased the kinematic viscosity attending to its lower molecular weight with respect to the trimethylolpropane trioleate one. It was found that trimethylolpropane monooleate is undesirable for the viscosity index, whereas the presence of trimethylolpropane dioleate could also increase the viscosity index to a small extent, requiring a complex purification process. Finally, it is possible to affirm that the optimal TMP-based lubricant obtained using an OA/TMP molar ratio of 3.0, after OA neutralization presented good marginal benefit and a viscosity index of 208.7, which is applicable for gear lubricants. © 2022 The Authors. *Biofuels, Bioproducts and Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd..

Key words: trimethylolpropane synthesis; biolubricants; triester; methanesulfonic acid; viscosity index

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Introduction

The increase in economic development is putting pressure on the world's capacity to sustain global market demand using environmentally friendly processes and raw materials. Lubricants, which are fluids used to decrease friction, reduce wear, and prevent corrosion and the overheating of various kinds of devices, are considered to be one of the main pollutants at a global level.[1] The replacement of petroleum-based lubricants by biodegradable or natural-occurring substances is the main way to reduce the damaging effects caused by lubricant substances on the environment.[2]

Vegetable oils, animal fats and related products (e.g. free fatty acids, FA) were initially proposed as biobased lubricants.[3,4] However, most of them have deficiencies for specific applications. For example, under high-temperature and oxidative conditions, triglycerides (TG) can be degraded via thermolysis (β-elimination at the ester group) and even autoxidized, which is initiated by hydrogen abstraction from the carbon atoms vicinal to double bonds. Nevertheless, the complete absence of unsaturation leads to poor cold-flow properties. Different approaches such as the development of new or modified crops,[5] the incorporation of appropriate additives in the biolubricant formulation[6] and the chemical modification of vegetable oils[7] have been proposed to overcome these negative properties. The latter is considered the most efficient and environmentally friendly route.

The lubricant properties of vegetable oils can be chemically improved by modifying the ester linkage and the content of unsaturation. Ester reactivity mainly comprises trans- and interesterification;[8] meanwhile the double bond reaction comprises selective hydrogenation,[9] epoxidation,[10] oligomerization[11] and ozonolysis.[12] However, these processes do not eliminate the critical β-CH group relative to the glycerol backbone. The replacement of glycerol with other alcohols which do not contain β-hydrogens to form ester linkages, such as neopentyl glycol, pentaerythriol or trimethylolpropane (TMP), could solve this problem.[13] Among them, TMP is the most convenient since it presents a structure like glycerol.

The synthesis of TMP esters via esterification of oleic acid (OA) as a fatty acid and using acid catalysts has been postulated as one of the most interesting alternative routes for the production of biobased lubricants.[14] Figure 1 shows the schematic reaction to synthesize TMP esters.

As can be observed, the production of TMP-based esters from OA comprises three consecutive esterification reactions with a global consumption of 3 mol of OA per mole of TMP and leading the formation of 3 mol of water. Indeed, trimethylolpropane monooleate (TMPMO) is first formed,

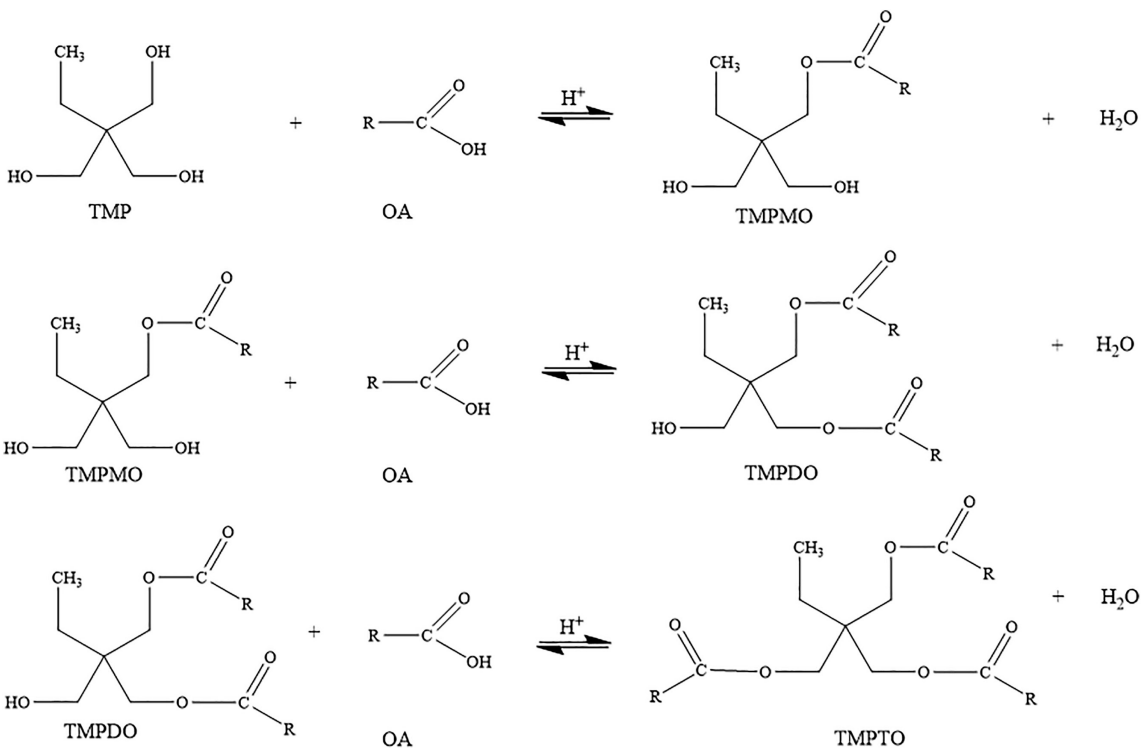

Figure 1. Reaction scheme for the synthesis of trimethylolpropane (TMP) esters from TMP and oleic acid (OA).

followed by trimethylolpropane dioleate (TMPDO) and finally, the desired trimethylolpropane trioleate (TMPTO) is obtained. It is well known that the above esterification reactions are limited by their chemical equilibrium, which undergoes uncompleted reactions. The most studied option for the proposed system consists of shifting the equilibrium using non-stoichiometric amounts of the reactants. Tao *et al.* proposed a FA/TMP molar ratio of up to 10;[15] meanwhile Cavalcanti *et al.* recommended a molar ratio of only 3.75.[16] However, the excess of any reactant is not an efficient approach and implies many complex purification steps. It is possible to shift the reaction toward the higher conversion of reactants by the selective removal of the water formed in the reaction mixture. Various techniques such as membrane processes,[17] ionic liquids,[18] molecular sieves[19] and reactive distillation systems[20] have been proposed. Nevertheless, the latter is the easiest and least expensive option using isooctane as the solvent in a Dean–Stark apparatus.[21]

Different heterogeneous and homogeneous acid catalysts have been reported in the literature to produce TMP esters. Among the heterogeneous ones, various solid acids (SO_4^{2-}/M_xO_y, M = Ti, Zr, Sn) presented a conversion of 96.5% after 3 h of reaction at 220°C.[22] However, their catalytic activity at moderate temperatures is negligible. Immobilized lipases presented high yields (around 97%) toward the formation of TMP triesters. Nevertheless, their low thermal resistance and the long reaction time required (24 h) limit the economic feasibility of these catalysts.[23] Strong cation exchange resins in H^+-form are catalytically active in this reaction, but the TMP conversion was 3 times lower than that achieved with H_2SO_4 using the same operating conditions (120°C for 4 h).[24]

In the literature, homogeneous acid esterification is recognized as the most efficient route to produce TMP esters. Itsikson *et al.* achieved a yield of esters of above 90% in 6 h at 160°C using isovaleric acid as a FA and sulfuric acid as a catalyst.[25] Arbain *et al.* compared five different homogeneous catalysts, namely perchloric, sulfuric, *p*-toluensulfonic, hydrochloric and nitric acids, for the synthesis of TMP esters from a mixture of long-chain FAs. Among them, perchloric and sulfuric acids gave the highest yields (>70%) after a reaction time of 3 h at 150°C.[26] However, Itsikon *et al.* sometimes employed an excessive concentration of catalyst (from 2 to 10 wt%),[25] whereas Arbain and Salimon used an excess of FA over the stoichiometric value (molar ratio FA/TMP = 4) to employ more moderate catalyst concentrations (catalyst/FA mass ratio of 0.02).[26] Furthermore, perchlorate is considered as a persistent inorganic pollutant with high water solubility, diffusivity and stability,[27] and the use of sulfuric acid is avoided owing to its high corrosiveness, even against titanium, which usually presents outstanding corrosion resistance.[28] Environmentally friendly homogeneous catalysts such as methanesulfonic and dodecylbenzene sulfonic acids presented good catalytic activity in other esterification processes for the production of biolubricants,[29,30] exhibiting a reduced environmental impact, being easily degraded in soil[31] and marine environments.[32] Hence, attending to the above properties and the lack of information related to their application for producing TMP esters, these kinds of catalysts must be studied for this purpose.

The presence of byproducts in the biolubricant mixture must be minimized for several reasons. For instance, fatty acids are susceptible to auto-oxidation as they contain acidic carboxylic groups[33] and might cause corrosion problems on the lubricated surfaces and a decrease in the friction coefficient.[34] However, mainly, TMP mono- and diesters and unreacted FA show a deleterious effect on lubricant properties like the viscosity index (VI).[35] Anyway, a purification step is needed to minimize the presence of undesirable byproducts or residues in the final TMP-based biolubricant. This purification process can be performed by molecular distillation[36] or, more conveniently, by neutralization of fatty acids with choline hydroxide (ChOH), producing highly valuable choline carboxylates.[37,38]

Therefore, the precise quantification of mono- and diesters, together with the leftovers of fatty acids, is essential to determine if the synthesized biolubricants satisfy the required viscosity properties, principally expressed as the VI.[39] In this regard, several authors have reported viscosities and VIs for trimethylolpropane triester products for biolubricant applications,[40–42] sometimes obtained from very different vegetable oil sources such as palm oil,[35,43] *Jatropha curcas*,[44] *Calophyllum inophyllum*[45,46] and canola.[47] However, the compositional effect and the contribution of functional groups on the viscosity properties of biolubricant products have not been fully described in the literature previously.

Hence, in this work the viability of using methanesulfonic acid or dodecylbenzene sulfonic acid as catalysts and the feasibility of reactive distillation to produce TMP-based ester lubricants from oleic acid employing OA/TMP molar ratios within 1–3 (values lower than or equal to the stoichiometric one) has been addressed. In addition, the presence of unreacted OA and waste generation have been minimized by using choline hydroxide in the purification step, producing valuable choline carboxylates. The products were characterized by analyzing their composition by gel permeation chromatography (GPC), and obtaining the acid value, the kinematic viscosity and the VI.

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Materials and methods

Materials

Oleic acid ($C_{18}H_{34}O_2$, 90 wt%), 1,1,1-tris(hydroxymethyl) propane (TMP, 97 wt%), sulfuric acid (H_2SO_4, 95–97 wt%), 4-dodecylbenzenesulfonic acid (DBSA, $C_{18}H_{30}O_3S$, a mixture of isomers, >95 wt%), choline hydroxide (ChOH) solution ($C_5H_{15}NO_2$, 45 wt% in methanol), methanol (CH_3OH, >99.8 wt%) and isooctane (synthesis grade) were supplied by Sigma-Aldrich. Methanesulfonic acid (MSA, CH_3SO_3H, 100 wt%) was supplied by BASF. All reactants were used without further purification.

Synthesis and purification of biolubricants

Synthesis of TMP–oleate biolubricants

The synthesis of TMP esters was carried out in a 0.5 L two-necked round-bottom flask heated with an electric heating mantle. The reaction bulk temperature was continuously measured and controlled using a PID controller.

In a typical experiment, 20 g of TMP (0.1491 mol) and the required amount of oleic acid (OA/TMP molar ratio = 1–3) were added to the reactor. When the mixture reached 105°C, the catalyst was added (catalyst/OA mass ratio = 0.035). In this work, a higher value of catalyst/OA mass ratio was employed compared with the one used by Arbain and Salimon (catalyst/FA mass ratio = 0.02).[26] This higher catalyst/OA mass ratio allows a large OA conversion to be reached using OA/TMP molar ratios with only stoichiometric OA, which is lower than the required FA excess used by the above-mentioned authors (FA/TMP molar ratio = 4).[26] The reaction mixture was kept at a constant temperature for 6 h.

For the study of the influence of the OA/TMP molar ratio, a reactive distillation system based on a Dean–Stark apparatus using isooctane as a solvent was employed, permitting the continuous removal of the water produced during the esterification reaction. In these experiments, 150 mL of isooctane were added to the reactor to favor water evaporation, most of the water being removed and collected by means of the Dean–Stark trap owing to its greater density regarding isooctane. The reaction system was kept under reflux at 105°C for 6 h.

Then the reaction mixture was washed with deionized water and transferred to a separatory funnel. The aqueous phase, which comprises the unreacted TMP, the catalyst and the washing water, was discarded. The residual water was separated from the organic phase via rotary evaporation under vacuum at 80°C for 1 h.

Neutralization

To produce the neutralized TMP ester, the unreacted OA was neutralized with ChOH forming choline carboxylates. The neutralization was performed by mixing 1.1 mol of ChOH per mole of carboxylic group in a 1 L flask at room temperature under stirring (700 rpm) for 15 min. After the reaction step between OA and ChOH, the product was split into two phases by centrifugation at 40°C and 156.52 g, obtaining the choline carboxylates as the bottom product, whereas the TMP esters were the main constituents of the upper phase. The upper phase was further washed with Milli-Q water (10 vol%) to eliminate any choline carboxylate trace and dried via rotary evaporation under vacuum at 80°C, so obtaining a product only constituted by the TMP esters.

Characterization

The molecular weight distribution of each reaction product was analyzed using GPC. Measurements were carried out with a Viscotek GPCmax VE-2001 chromatograph equipped with two Waters Stryragel columns HR2 and HR0.5 and a refractive index detector. Tetrahydrofuran was used as the mobile phase under a continuous flow of 1 mL min^{-1} at 40°C.

The determination of the acid value (AV), expressed as mg KOH g^{-1} of product, was developed according to ASTM D974.[48] This standard method details the titration of the sample with ethanolic potassium hydroxide solution using an automatic potentiometric titrator (Metrohm 702 SM Titrino). The conversion of OA after the esterification reaction was determined according to Eqn (1), considering the initial and final acid values (AV_0 and AV_f, respectively).

$$\text{OA conversion}(\%) = \frac{AV_0 - AV_f}{AV_0} \cdot 100 \quad (1)$$

The kinematic viscosity of the obtained products was determined following the ASTM D445[49] standard method using a Canon–Fenske capillary viscometer immersed in a TAMSON TV 2000 bath at 40 and 100°C. The VI was determined from these values according to the ASTM D2270[39] standard method.

Results and discussion

Catalyst selection

In Table 1 the OA conversions achieved using the two previously selected environmentally friendly acid catalysts (DBSA and MSA), H_2SO_4 (a traditional acid catalyst for the synthesis of TMP-based ester lubricants) and without a

Table 1. Oleic acid (OA) conversion using different catalysts (closed system, temperature T = 105°C, time t = 6 h, OA/TMP molar ratio = 3, catalyst/OA molar ratio = 0.1).

Catalyst	OA conversion (%)
H_2SO_4	72.4
MSA	69.2
DBSA	58.2
No catalyst	2.7

MSA, Methanesulfonic acid; DBSA, 4-dodecylbenzenesulfonic acid.

catalyst are shown. This esterification process was carried out in a closed system without water removal, using the stoichiometric OA/TMP molar ratio (OA/TMP = 3) and a catalyst/OA molar ratio of 0.1.

Therefore, attending to the lower environmental impact of MSA,[31] its lower corrosiveness with respect to H_2SO_4[50] and the reduced difference obtained in OA conversion between the MSA and H_2SO_4 catalysts (only 3.2% higher in the case of H_2SO_4), MSA was selected as the catalyst to produce TMP-based ester lubricants from TMP and OA. On the other hand, attending to the low conversion observed without a catalyst (2.7%), it is evident that this esterification reaction is enhanced under acidic conditions.

Influence of the OA/TMP molar ratio employing an open system

Once the catalyst was selected, the OA conversion and the distribution of intermediate products was investigated as function of the OA/TMP molar ratio (ranging from 1 to 3), using an open reactive distillation system based on a Dean–Stark apparatus. The difference between this device regarding the previous close system lies in the elimination of the water formed in the reactor by distillation, using isooctane as the carrier vapor. Figure 2 shows the OA conversion as a function of the OA/TMP molar ratio and using MSA as a catalyst in the open reactive distillation system.

For low OA/TMP molar ratios (1, 1.5 and 2), the OA conversion was almost complete as expected after using a larger catalyst/OA mass ratio with respect to the literature,[26] reaching values higher than 99%. Later, an increase in the molar ratio up to the stoichiometric condition involved a sharp decrease in OA conversion to 81.0%. This abrupt OA conversion decrease can be explained according to Le Chatelier's principle: at low OA/TMO molar ratios when the OA works as the limiting reagent, a minimum amount of OA establishes the equilibrium system with traces of water. Nevertheless, an OA/TMO molar ratio close to the

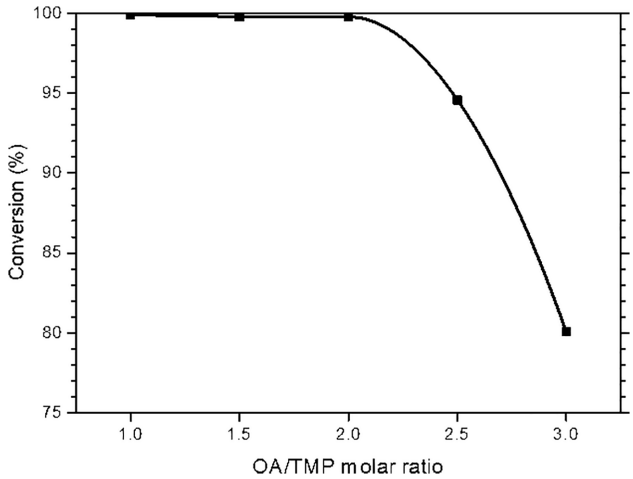

Figure 2. Influence of OA/TMP molar ratio on OA conversion at T = 105°C, time = 6 h and methanesulfonic acid (MSA)/OA mass ratio = 0.035, using a Dean–Stark apparatus.

stoichiometric value implies a fraction of unreacted OA that is able to minimize the presence of the more reactive intermediate compounds TMPMO and TMPDO. Hence, using the Dean–Stark apparatus, the equilibrium control is practically circumvented for OA/TMO values close to 3, transforming the equilibrium mechanism into a single direct reaction that corresponds to the global one. These fatty acid conversions are similar to those previously reported in the literature for traditional catalysts, longer reaction times and conventional closed reaction systems instead of a reactive distillation one.[15,51] Regarding the comparison between closed and open systems, the implementation of the Dean–Stark apparatus has allowed the displacement of the esterification reaction toward products owing to the continuous removal of te formed H_2O. In detail, for the same OA/TMP molar ratio of 3, the OA conversion was increased from 69.2 to 81.0%. Furthermore, the OA conversion achieved by combining MSA as a catalyst together with the reactive distillation procedure was remarkably higher than when using H_2SO_4 in a closed system (81.0 vs. 72.4%). Hence, the use of this open system is an important improvement to accomplish the esterification process by favoring forward reactions rather than reverse ones. In order to facilitate the further characterization of the obtained lubricants, the products obtained were named TMP–ester-x, 'x' being the OA/TMP molar ratio at which they were produced.

To investigate the influence of the OA/TMP molar ratio on the product distribution of the obtained unpurified TMP–ester mixtures, GPC analyses were performed. Additionally, the best product was purified and also characterized through GPC (Fig. 3).

In the chromatograms, four different signals were identified, centered at elution times of 13.75, 14.21, 15.05 and 15.51 min, being attributed to TMPTO, TMPDO, TMPMO and unreacted OA, respectively. These signals were deconvoluted to determine the molar fraction of each component. The detailed compound distribution and the molecular weight of the synthetized TMP–ester products are detailed in Table 2.

Therefore, the distribution of TMP–ester products changes distinctly with the OA/TMP molar ratio, finding the maximum content on TMPTO for TMP–ester-2.5 (up to $x_{TMPTO} = 0.772$). However, this product presented a large amount of TMPDO as a by-product ($x_{TMPDO} = 0.142$) and appreciable contents of TMPMO and unreacted OA. When an OA/TMP molar ratio of 3 was used (i.e. TMP–ester-3), the product was constituted only by TMPTO and the unreacted OA as an impurity. As previously stated in literature, the presence of intermediate reaction products in the final TMP-based lubricant increases its viscosity, normally affecting negatively the quality of the product.[34,35] In order to obtain high-quality biobased lubricants, the TMP–ester-3 product, which only contains TMPTO and unreacted OA, was purified through neutralization of OA with a methanolic solution of ChOH. As can be observed, in the GPC of the neutralized TMP–ester, a single signal corresponding to pure TMPTO was detected. This result confirms not only the complete neutralization of OA, but also the absence of secondary byproducts from the hydrolysis of TMPTO when such a lubricant is treated, following the proposed neutralization procedure with ChOH. After the purification process, a product with an acid value <0.05 mg KOH g^{-1} was obtained, indicating the success of this neutralization technique for removing the unreacted OA, and so reducing the acidity of the biolubricant below the detection limit of the analytical technique.

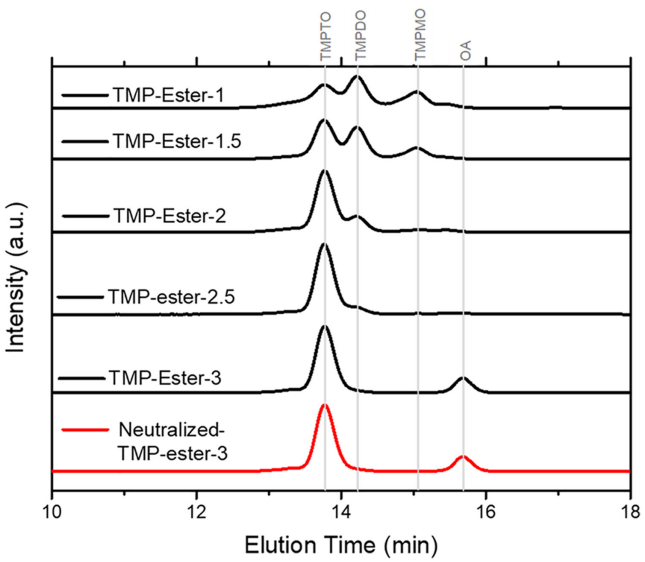

Figure 3. Gel permeation chromatography (GPC) chromatograms of the synthesized TMP–esters.

Furthermore, in Table 3 it is observed that this acid value is even lower than the one reported for a referential TMP–oleate product (<0.05 vs. 0.39 mg KOH g^{-1}).[22]

Hence, attending to the composition, the TMP–ester-3 product is more easily purified by neutralization, allowing it to be effortlessly exploited as a biolubricant after such a neutralization step, when pure TMPTO is obtained. Moreover, the choline carboxylates generated during the neutralization process of OA with ChOH could also be economically profitable, since they are considered as green and harmless biosurfactants.[52]

On the other hand, considering the molecular weight of TMP–esters and observing that the molecular weight of the neutralized-TMP-ester-3 reaches a maximum value that corresponds with the pure TMPTO (926.0 g mol^{-1}), the overall molecular weight of the TMP–esters is greater as the amount of heavier ester oleates (TMPTO) becomes higher. That increasing trend is reduced only for OA/TMP = 3 since there was an excessive quantity of unreacted OA.

Table 2. Composition and molecular weight of the TMP–oleate products without purification and the pure TMPTO after OA neutralization.

Product	OA/TMP	Molar fraction				Molecular weight (g Mol^{-1})
		TMPTO	TMPDO	TMPMO	OA	
TMP–ester	1	0.306	0.252	0.390	0.052	620.1
	1.5	0.342	0.371	0.264	0.023	673.7
	2	0.632	0.231	0.104	0.033	789.1
	2.5	0.772	0.142	0.029	0.057	836.4
	3	0.605	0.000	0.000	0.395	671.6
Neutralized TMP–ester	3	1.000	0.00	0.000	0.000	926.0

TMPTO, trimethylolpropane trioleate; TMPDO, trimethylolpropane dioleate;TMPMO, trimethylolpropane monooleate.

Table 3. Comparison of physicochemical properties of final TMP–oleate product after neutralization and a similar referential one reported in literature.

Property	Neutralized-TMP–ester-3	TMP-based reference product[22]
Acid value (mg KOH g^{-1})	<0.05	0.39
ν_{40} (cSt)	37.9	51.36
ν_{100} (cSt)	8.4	10.11
Viscosity index (a.u.)	208.7	189

Table 4. Kinematic viscosities at 40°C (ν_{40}), at 100°C (ν_{100}) and viscosity index (VI) for the TMP–oleate products without purification and for the pure TMPTO after OA neutralization.

Product	OA/TMP	ν_{40} (cSt)	ν_{100} (cSt)	VI (–)
TMP–ester	1	65.0	9.9	136.0
	1.5	56.1	9.7	159.5
	2	46.2	9.1	184.0
	2.5	37.9	8.3	203.4
	3	34.0	7.5	197.3
Neutralized TMP–ester	3	37.9	8.4	208.7

Nevertheless, to consider the possibility of using these products as biolubricants, assessment of the VI is mandatory.

Influence of the molar fraction of TMP–esters on kinematic viscosity and the viscosity index

The kinematic viscosities of the different TMP–ester lubricants produced, including the neutralized TMPTO (neutralized TMP–ester-3), were measured at 40°°C (ν_{40}) and 100°C (ν_{100}). These results together with the VI obtained using the ASTM D2270 standard method[39] are shown in Table 4.

Attending to the composition of the products previously shown, it can be asserted that the presence of intermediate ester compounds (TMPMO and TMPDO) unequivocally increases the kinematic viscosity of the products. In contrast, the presence of OA as an impurity provokes a reduction of the kinematic viscosity, which can be managed by the neutralization process with ChOH. This behavior is analogous for both the studied temperatures 40 and 100°C, as observed in Fig. 4.

Additionally, it is worth mentioning that the presence of hydroxyl (-OH) and carboxylic acid –COOH) functional

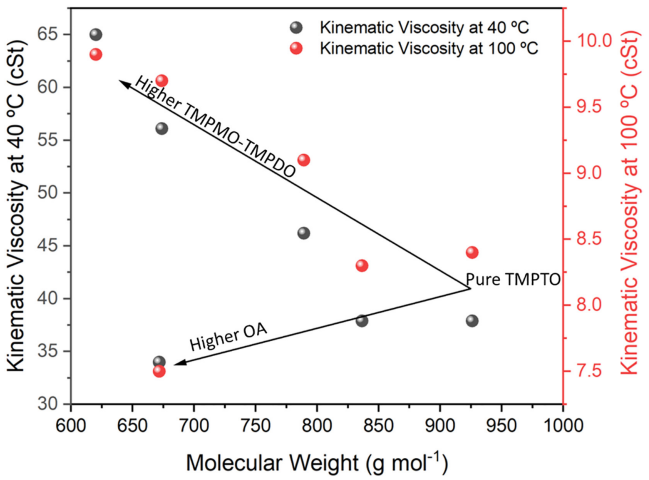

Figure 4. Influence of functional groups and molecular weight on kinematic viscosity in TMP–ester products as a function of their molecular weight.

groups promotes a sudden increase in kinematic viscosity of organic compounds owing to their ability to establish hydrogen bonds with adjacent molecules, whereas only Van der Waals forces are expected in ester (–O–CO–R) functional groups.[53] This viscosity lowering caused by the transformation of hydroxyl groups into ester ones is so important, even considering that the molecular weight of TMPTO is higher than that of its partially reacted counterparts (TMPMO and TMPDO), because the overall effect is a decrease in kinematic viscosity instead of the increase expected by the Mark–Houwink equation attending to the enlargement of the molecular weight. On the other hand, despite the presence of one –COOH functional group from OA, the existence of OA leftovers in the final TMP–ester product provokes a lessening of the kinematic viscosity, since the diminution effect in viscosity driven by much lower molecular weights [only M_w (OA) = 282.5 g mol^{-1}] is, in this case, significantly more important than the presence of one single functional group prone to hydrogen bonding.

Having analyzed the influence of temperature on the viscosity of the products, the VIs were determined. In lubricant applications, a high VI is desired because it indicates a low dependence of viscosity on temperature.[39] Broadly speaking, all of the synthetized TMP–oleate products demonstrate an outstanding capability to be employed for lubricant applications, since their VIs are always higher than 135. In these cases, the observed trend in terms of VI is in good agreement with the previously indicated composition, confirming that the presence of TMPMO not only increases the kinematic viscosity, but also reduces very importantly the VI, in good agreement with the deleterious effect on the VI of

intermediate ester compounds observed by Yunus *et al.*[35] In Fig. 5(a), the product distribution of TMP–ester biolubricants is expressed as function of the OA/TMP molar ratio, whereas Fig. 5(b), illustrates the influence of the OA/TMP molar ratio on the VI.

As can be seen, a linear increment in the VI is observed when the OA/TMP molar ratios of the products increase from 1 to 2.5, with VIs ranging between 136.0 and 203.4. Hence, TMP–ester-2.5 showed the highest VI value before purification. Consequently, the VI of neutralized-TMP–ester-3 was the highest (VI = 208.7), being 5.3 and 11.4 arbitrary units higher than the values for the unpurified TMP–ester 2.5 and TMP–ester-3, respectively, and this VI is even greater than that of other commercial counterparts, being equal to 188.[22] Thus, an abrupt decrease in the VI is observed with the presence of unreacted OA in the final product. This negative effect is even more remarkable than that of the TMPMO and TMPDO ester compounds. However, the purification of TMP–ester-3 becomes quite simple, since OA can be neutralized by ChOH to obtain pure TMPTO, whereas the intermediate oleate byproducts are much more difficult to be removed.

In spite of the presence of TMPDO unambiguously increasing the kinematic viscosity, it does not seem to alter decisively the VI, since TMP–oleate lubricant mixtures with high VI were also obtained for products with a non-minor presence of TMPDO (e.g. TMP–ester-2 and -2.5 with VIs of 184.0 and even 203.4, for TMPDO molar fractions of 0.231 and 0.142, respectively). Thus, the main problem associated with products with high TMPDO concentrations seems to be mainly related to the undesired presence of TMPMO and OA (Fig. 5a).

Therefore, TMP-based ester lubricants made with OA/TMP molar ratios from 1 to 2.5 present moderate interest owing to their substantial dependence of viscosity on temperature, mainly induced by the presence of TMPMO byproducts and OA impurities. In conclusion, it can be stated that not all the impurities present in the TMP–oleate products affect negatively the viscosity index, but the presence of TMPMO in the product TMP–ester-2.5 complicates its purification by a single neutralization.

Preliminary economic assessment

The demand for lubricants is increasing year on year owing to the increasing industrialization of different productive systems. However, several effects such as the variation of petroleum prices and taxes lead to a variation in the marginal benefit of petroleum-based lubricants. Nevertheless, the price of a gear lubricant with lubricant properties similar to those manufactured here has been established at around 13 € kg^{-1}.[54,55] Unlike traditional lubricants, the buying price of raw materials suffers minor variations and it is even financed and supported by different administrations. Generally speaking, FAs are typically obtained by the deodorization of edible vegetable oils. Their price usually depends on the concentration of nutraceutical substances (e.g. tocopherols, sterols, squalene) and the FA profile of the saponifiable fraction.[38] The interval of prices usually goes from 350 € t^{-1} for palm and palm-kernel-based FAs up to 1100 € t^{-1} for olive-oil-based ones. In the proposed process, nutraceutical elements are not required, so an OA buying price can be estimated at around 1660 € t^{-1}, according to previous literature studies based on techno-economical

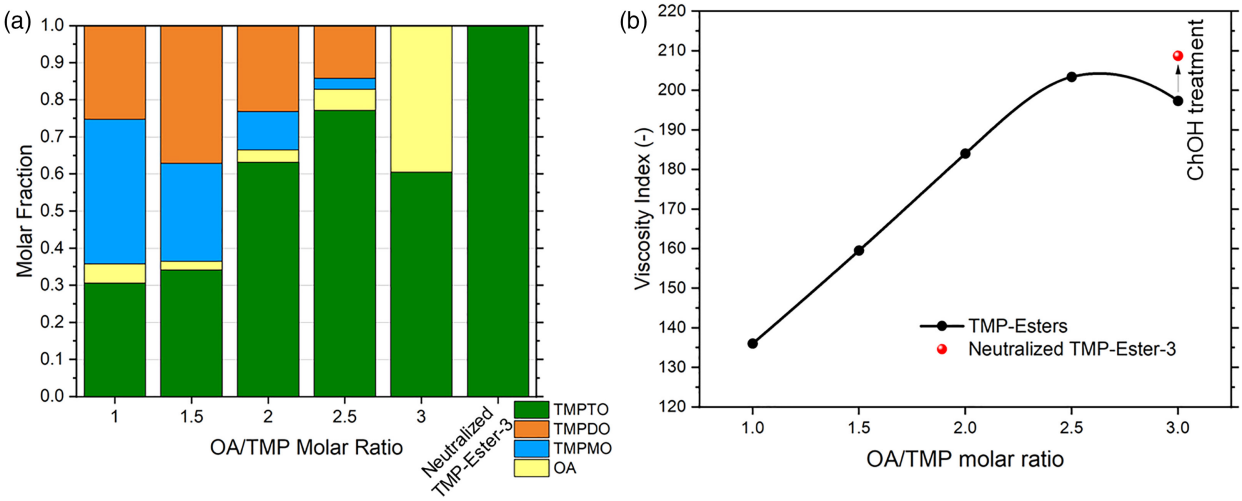

Figure 5. (a) Product distribution as a function of the OA/TMP molar ratio. (b) Viscosity index (VI) of the manufactured TMP–ester lubricants as a function of the OA/TMP molar ratio employed during their synthesis.

assessments for fatty acid production.[56] TMP is a common raw material whose price ranges from 1300 to 1600 € t^{-1}. For this preliminary assessment, a purchase price of 1450 € t^{-1} has been considered.[57] Regarding the choline carboxylate side-products obtained during the neutralization process, they have been commercialized successfully in recent years as biosurfactants. A wide variety of selling prices between 1000 and 3100 € t^{-1} can be found depending on the concentration and the quality of the biosurfactant,[58,59] 1800 € t^{-1} being typical, which can be assigned to the choline carboxylate byproducts obtained here. For the buying price of ChOH, for which it is necessary to carry out neutralization, a price of ~850 € t^{-1} can be considered attending to the purity and the availability of the product.[60] Finally, the buying price of the MSA catalyst is between 2300 and3300 \$ t^{-1},[61] so an average price of 2490 € t^{-1} was chosen.

The marginal benefit per kilogram of final biolubricant product can be assessed considering exclusively the selling/purchase prices of products and raw materials, respectively, the stoichiometry of the chemical reactions, the particular recipe selected for synthesis (i.e. OA/TMP and catalyst/OA relations) and the final product distribution obtained by GPC (Figs 3 and 5a, and Table 2). For instance, the product obtained using a molar ratio OA/TMP of 3 was composed of 60.5% TMPTO and 39.5% OA. The residual OA was totally transformed to choline carboxylates through the proposed neutralization process (using an excess of 10% of ChOH).

In this way, the preliminary assessment of marginal benefit per kilogram of final biolubricant product has been limited only to those with more commercial interest to the lubricant industry. The two products considered for this assessment were the neutralized TMP–esters from OA/TMP molar ratios 2.5 and 3, since the OA leftovers can be easily eliminated from both (purification step with ChOH), and they show interesting VI values. With the neutralized TMP–ester biolubricants from 2.5 and 3, marginal benefits of 11.27 and 10.13 € kg^{-1} of the final product could be attained, respectively, leading to a very profitable process where practically the whole selling price of the product (a referential selling price of 13 € kg^{-1} for the lubricant was considered) can be monetized. It is remarkable that the marginal benefit of using an OA/TMP molar ratio of 2.5 (and subsequent neutralization) is slightly higher owing to the very low amount of OA present in the final product, making the elimination of OA during purification easier and less expensive. On the other hand, it can be stated that the presence of TMPDO not only does not reduce the economic interest of the biolubricant, but also can marginally improve the economic benefit, TMPMO and OA being the only mandatory compounds to be removed. Anyway, these results should be considered with caution since neither fixed capital for the installation nor operation costs were considered. However, this preliminary analysis indicates the potential of this process at an industrial scale, owing to the huge marginal benefits of the process.

Conclusions

The present work demonstrates the technical viability of producing pure TMP-based esters from OA and TMP, using OA/TMP molar ratios limited by its stoichiometric relationship, employing the reactive distillation and the environmentally friendly MSA as catalyst with a slight excess with espect to the catalyst/OA relation used in literature. The OA/TMP molar ratio was found to be a key process variable for the OA conversion and the product composition, finding that TMP–ester-2.5 presented the highest TMPTO content. The effectiveness of the novel purification method based on the neutralization of unreacted OA with ChOH was demonstrated on the TMP–ester-3, which only contained unreacted OA as an impurity, by obtaining a biolubricant with an acid number of <0.05 mg KOH g^{-1} and a VI of 208.7. The presence of the hydroxyl functional groups from the intermediate products presents a deleterious effect on the kinematic viscosity, this behavior being similar to the temperature. On the other hand, the presence of unreacted OA in the biolubricant products decreases the kinematic viscosity attending to its lower molecular weight. Generally speaking, whereas the TMPMO is undesirable for the VI, the presence of TMPDO could be beneficial but requires additional purification steps. The optimal TMP-based lubricant obtained using an OA/TMP molar ratio of 3.0 after OA neutralization presented a VI of 208.7, which is applicable for gear lubricants. This VI is significantly better than the previous ones reported for non-purified TMP–ester based lubricants and, considering the marginal benefit, 77.9 and 86.7% (for neutralized-TMP–ester-3 and neutralized-TMP–ester-2.5, respectively) of the final selling price of the TMP–ester biolubricants with interest can be valued as profit.

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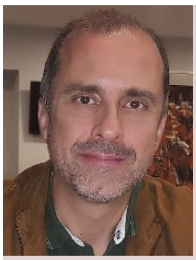

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