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# Clean synthesis of biolubricants for low temperature applications using heterogeneous catalysts

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ABSTRACT

Biolubricants derived from vegetable oils are environmentally compatible products due to their low toxicity and good biodegradability. Synthetic esters based on polyols and fatty acids possess suitable properties for lubricant applications, even at extreme temperatures. In this work, synthesis of esters from trimethylolpropane (TMP) and carboxylic acids from C5 to C18 has been studied and compared using different heterogeneous catalysts (silica–sulphuric acid, Amberlyst-15, and immobilised lipase B from *Candida antarctica*). Silica–sulphuric acid was found to be the most efficient catalyst followed by Amberlyst-15, especially when using short chain carboxylic acids. The reaction efficiency decreased with increasing alkyl chain length. On the other hand, the immobilised lipase (Novozym®435) did not exhibit any activity with C5 acid and the activity increased with increase in length of the fatty acid chain. For synthesis of C18-ester, the biocatalytic production turned out to be comparable to silica–sulphuric acid, and moreover led to a better quality of the final product. The products showed suitable cold-flow properties for application at low temperature. A general trend of increasing pour point (−75 °C to −42 °C) and viscosity index (80–208) with increase in alkyl chain of the carboxylic acid from C5 to C18 was observed. The synthesis of TMP-trioleate using the solid acid catalysts and the biocatalyst was compared using the freeware package EATOS (environmental assessment tool for organic synthesis) and showed the enzymatic route to have the least environmental impact.



## 1. Introduction

Lubricants constitute an enormous market worldwide, their consumption being estimated at 37 million metric tonnes per year [1]. Automotive lubricants are the largest group of lubricants followed by hydraulic fluids. Most modern lubricants are complex formulated products consisting of 70–90% base oils mixed with functional additives to modify the natural properties such as cold stability, oxidation stability, hydrolytic stability, viscosity and viscosity index to suit a specific application. The most commonly used base oils are mineral oils.

About 50% of all lubricants sold worldwide end up in the environment via total loss applications (such as two-stroke and chainsaw oils, mould-release agents, lubricant greases and others), spillage, volatility and accidents [1,2]. Losses of hydraulic fluids are claimed to be as high as 70–80%, resulting in severe contamination of soil, groundwater and air [3]. As a result, there has been an increasing demand for environmentally compatible lubricants or biolubricants, particularly in areas where they may come in contact with water, food or people. About 40,000 metric tonnes of biolubricants are sold annually in the European Union and almost similar amount in the United States [4], primarily for use as hydraulic fluids. It has been suggested that a large proportion of the lubricants can be replaced by biolubricants giving a potential market of 5.1 billion dollars [5].

The application range of lubricants is determined by their physico-chemical properties; a basic requirement is to remain in a liquid form over a broad range of temperature. The temperature limits are determined by the pour point at low temperature and flash point at high temperature [6]. During the earlier stage of the development of biolubricants, the focus was on the products based on pure vegetable oils, which in contrast to mineral oils, are rapidly and completely biodegradable and have low ecotoxicity [7]. Although the technical properties of plant oil based fluids are quite comparable with mineral based fluids, they have drawbacks of sensitivity to hydrolysis and oxidation at high temperatures and poor low temperature flow properties, and are hence

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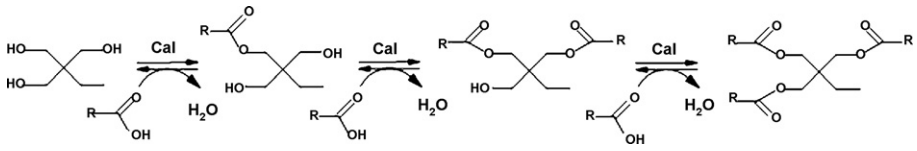


**Scheme 1.** Schematic representation of esterification reaction between trimethylolpropane (TMP) and a carboxylic acid.

limited to total loss applications and those with very low thermal stress [8,9].

Since the 1980s, the trend in biolubricants has been to overcome the limitations of the plant oils, e.g. by chemical modification of oils, or application of synthetic esters that may be partially derived from renewable resources [8]. The various product types include the synthetic esters in which the glycerol has been replaced by other polyols, diesters prepared from dicarboxylic acids and monovalent alcohols, branched-chain fatty acids, and derivatives of epoxidised oils. Synthetic esters of C5–C18 acids with polyols like trimethylolpropane (TMP), neopentyl glycol or pentaerythritol are among the most common biolubricants for different applications. The synthetic esters have been shown to possess high biodegradability under both aerobic and anaerobic conditions [10].

Synthesis of polyol based esters is achieved by esterification or transesterification with fatty acids, fatty acid methyl esters or triglycerides according to Scheme 1, normally catalysed by a homogeneous acid catalyst like p-toluenesulfonic acid in a solvent system [11]. The transesterification with a triglyceride involves two steps, first where the triglyceride is converted to a methyl ester usually at temperatures between 50 °C and 100 °C followed by reaction of the fatty acid methyl ester with the polyol at 110–160 °C [12]. Following the reaction, the product mixture is taken through a number of downstream processing steps to give the ester product [11,13].

There is increasing interest in the use of heterogeneous catalysts as one of the important means of green chemistry. Such catalysts provide simpler, cheaper separation processes and reduced waste generation, and moreover can be recycled for several reaction cycles [14]. This report presents an investigation on comparative assessment of heterogeneous chemical catalysts and biocatalyst for the synthesis of esters of trimethylolpropane (TMP) with C5–C18 acids, with the aim to provide a clean and effective process to produce biolubricant products suited for low temperature applications.

## 2. Materials and methods

### 2.1. Materials

Valeric acid and caprylic acid (both of 99% purity), silica gel 60 (0.040–0.063 mm) and chlorosulfonic acid were obtained from Merck, while oleic acid (95%) and Amberlyst 15 (dry) were from Fluka. Oleic acid (industrial grade 76%) was kindly provided by AarhusKarlshamn, Sweden, and trimethylolpropane (TMP) was from Perstorp AB, Sweden. Novozym®435 (immobilised *Candida antarctica* lipase B) was a kind gift from Novozymes A/S, Bagsvaerd, Denmark. All the solvents used were of analytical grade and were obtained from standard sources.

### 2.2. Preparation of silica–sulphuric acid

Silica–sulphuric acid was prepared according to the method described by Zolfigol [15]. Chlorosulfonic acid (23.3 g) was added dropwise to 60 g silica gel (0.040–0.063 mm particle size, and a pore size above 6 nm) in a 500 mL suction flask, through a dropping funnel at constant flow at room temperature over a period of 30 min. The reaction can be described by the following equation:

$$SiO_2 - OH + ClSO_3H(neat) \rightarrow SiO_2 - OSO_3H + HCl$$

A gas-washing bottle containing water was connected to the suction flask to absorb the HCl gas produced in the reaction. After completion of the reaction, silica–sulphuric acid was collected and stored in a closed flask.

### 2.3. Small-scale reactions for synthesis of trimethylolpropane (TMP) esters with different carboxylic acids

Small-scale reactions were run in 4 mL vials at 70–80 °C with shaking in a temperature controlled thermomixer (HLC BioTech, Bovenden, Germany). A typical reaction was performed in a 1 g reaction mixture containing fatty acid and polyol at a molar ratio of 3:1 (3 mmol of fatty acid and 1 mmol of polyol), and a catalyst at a concentration of 5% (w/w). The vials were kept open to allow the water formed in the reaction to be evaporated easily. Samples (20 mg) were taken at regular intervals with a Pasteur pipette and weighed into 1.5 mL vials, and dissolved in 1 mL of tetrahydrofuran. The solution was diluted 30 fold, and filtered through a glass filter No 3 prior to analysis by chromatography (GC or HPLC).

### 2.4. Synthesis in one-liter reactor

The fatty acid and polyol (molar ratio of 3:1) were mixed with 5% (w/w) silica–sulphuric acid in a final amount of 500 mL in a 1 L reactor, and the reaction mixture was stirred using an overhead propeller at 300 rpm at 70 °C, if not stated otherwise. In the reactions with C18 fatty acids, toluene was added to help the water removal through azeotropic distillation with help of a Dean stark apparatus in order to shift the reaction equilibrium towards the ester synthesis. The solvent was distilled off during the reaction and recirculated at reduced pressure (200 mbar) using a vacuum pump. The reaction was quenched by separating the catalyst from the reaction mixture by filtration or by centrifugation when filtration was not efficient. The solvent remaining in the product was removed by distillation, and the remaining water was removed using molecular sieves 3 Å.

Enzymatic synthesis of TMP-oleate ester was done in a solvent free system using 1.5 mol oleic acid (90%) and 0.5 mol TMP at 70 °C, and 5% (w/w) Novozym®435 was added when the substrate was dissolved. Water removal was done by applying vacuum at 20 mbar. The reaction was stopped by removing the enzyme by filtration.

The reactions were monitored by measuring the total acid number (TAN) and stopped when the TAN was <5, and subsequently by chromatographic analyses.

### 2.5. Analyses

Analysis of fatty acids, TMP, and their ester products were performed by gel permeation chromatography (GPC) on two columns of Shodex GPC KF-801 connected in series using a PerkinElmer HPLC system equipped with a refractive index detector L-2490 (Hitachi) with temperature control and an oven (PerkinElmer series 200), both maintained at 35 °C. Tetrahydrofuran was used as the eluant at a flow rate of 0.5 mL $min^{-1}$. The sample components were separated on the basis of molecular weight, eluting in the order of decreasing size.

Esterification of caprylic acid with trimethylolpropane was followed by capillary gas chromatography [16], on a Varian 3400 with

**Table 1**
Characteristics of the heterogeneous catalysts used in this study.

| Catalyst | Matrix | Active group | Surface ($m^2$/g) | Pore diameter (nm) | Particle size (μm) |
|---|---|---|---|---|---|
| Acid silica | Silica | Sulfonate (5.4 mequiv./g) | 480 | 6 | 40–63 |
| Amberlyst 15 | Styrene-divinylbenzene resin | Sulfonate (4.7 mequiv./g) | 42.5 | 28.8 | 300 |
| Novozym®435 | Lewatit VP OC 1600 (Polymethylmethacrylate) | Lipase B from *C. antarctica* (20% w/w) | 130 | 15 | 315–1000 |

a flame ionization detector (FID) equipped with an autosampler 8200. The detector was maintained at 350 °C, the oven temperature was increased from 80 °C to 300 °C at a rate of 30 °C $min^{-1}$, and the injector was at 310 °C. Helium was used as carrier gas. Samples from the reactor were diluted in THF as described above and 1 μL was injected into a DB1 capillary column (25 m, 0.32 mm id with 0.17 μm film thickness). The retention times of the various reaction components were as follows: caprylic acid 2.02 min, TMP 2.3 min, monoester 5.12 min, diester 7.12 min, and triester 8.84 min.

Esterification of industrial grade oleic acid was monitored by titration of the acid groups remaining in the sample with a base, potassium hydroxide. The total acid number is the quantity of KOH expressed in milligrams per gram of sample, which is required to titrate under the conditions of the international standard.

The free fatty acids in the industrial grade oleic acid were analysed by GC according to the procedure of Lyberg et al. [17]. The sample (12 mg) was pre-treated with 2 mL of dry methanol containing 1% sulphuric acid, and incubated at 50 °C for 2 h after which 5 mL of 5% NaCl solution was added to stop the reaction. Cyclohexane (1 mL) was then added and the tube was vortexed and centrifuged on a table top centrifuge (Wifug) at 6000 rpm for 2 min and the upper phase containing the fatty acid methyl esters was injected into a Supelcowax$^{M}$10 column, (60 m, 0.32 mm id, column film of 25 μm). The temperature program was the same as described earlier [17]. The composition of the industrial oleic acid was 75.9% oleic acid, 5.9% linoleic acid, 5.8% palmitic acid, and 2.3% myristic acid.

The kinematic viscosity of the products was determined according to the ISO method 3104 at 40 °C and 100 °C, respectively. The viscosity index was measured according to ASTM D2270.

The pour point, the lowest point at which a sample (lubricant) continues to flow when cooled under specific standard conditions, was measured according to ISO 3016. The Gardner colour describes the colour of the lubricant, and was measured according to ASTM D6166.

### 2.6. Environmental assessment

The freeware package EATOS (Environmental Assessment Tool for Organic Synthesis) was used for environmental assessment of TMP-oleate production using silica–sulphuric acid (route A), Amberlyst 15 (route B) and Novozym®435 (route C), respectively. The data used to feed EATOS was based on 24 h reactions using 84.7 g (0.3 moles) oleic acid, 13.4 g (0.1 moles) TMP and 5 g catalyst. In the route A, 100 g toluene was used as solvent and 150 g of ethyl acetate for further purification (to break the emulsion formed after stopping the reaction), and the catalyst preparation (5 g) was prepared from 3.6 g silica and 1.4 g chlorosulphonic acid. Recycling of the solvent, catalyst and the auxiliaries was assumed to be 80%. Water was not included in the calculations based on the discussion by Sheldon [18].

## 3. Results

### 3.1. Comparing different catalysts for esterification of TMP with C5-C18 acids

The catalysts used for catalyzing the reaction between TMP and different carboxylic acids included two heterogeneous acidic catalysts – silica–sulphuric acid and Amberlyst 15, and an immobilised lipase B from *C. antarctica* (CALB), commercially available as Novozym®435. Table 1 lists the physico-chemical characteristics of these catalysts. Initial tests were also done with alkali catalysts including Amberlyst A-21 (macroreticular anion exchange resin with dimethylamino-functionality) and potassium carbonate, however no significant esterification was observed. All the catalysts were used at a concentration of 5% w/w.

Fig. 1 shows the profiles of reactions of TMP with valeric (C5:0), caprylic (C8:0) and oleic acid (C18:1), catalysed by silica–sulphuric acid (Fig. 1A), Amberlyst 15 (Fig. 1B) and Novozym®435 (Fig. 1C), respectively, at 70 °C. In the control reactions without any catalyst, spontaneous esterification was observed resulting in TMP conversion of 39%, 17% and 15%, with valeric-, caprylic and oleic acid, respectively, after 24 h. Silica–sulphuric acid turned out to be the most efficient catalyst providing the highest reaction rate with all the acids (Figs. 1A and 2). Maximum TMP conversion achieved was 97% in 3 h in the reaction with valeric acid, 95% in 6.5 h with caprylic acid, and 90% in 24 h with oleic acid. The ester products were separated after 24 h reaction; the valerate product contained 83% of the triester, caprylate product contained less triester (60%) and more of the diester (17%), while oleate product contained mainly triester (90%).

Amberlyst 15 provided a comparable conversion profile to silica–sulphuric acid (although at a lower reaction rate) with valeric acid, and the reaction became slower with increase in the alkyl chain length of the acid leading to significantly lower conversion of TMP (Figs. 1B and 2). On the other hand, the reaction using immobilised *C. antarctica* lipase B, Novozym®435, as the catalyst showed an opposite trend in TMP conversion when moving from C5 to C18-acid. No reaction took place with valeric acid beyond that occurring spontaneously without any catalyst, while TMP conversion on reaction with caprylic acid was 32% after 24 h (Fig. 1C). With oleic acid the reaction rate and degree of conversion (96%) surpassed that of Amberlyst-15 (Figs. 1C and 2). While the biocatalytic reaction rate was lower than that with silica–sulphuric acid, the TMP-oleate product yield was higher and comprises primarily of the triester (96%).

### 3.2. Product characteristics

The TMP-esters with valeric acid, caprylic acid and oleic acid were produced in 500 mL scale using silica–sulphuric acid as catalyst for analysis of some properties. For reaction with oleic acid, toluene was added to help the removal of water by azeotropic distillation, and after the reaction solvent removal was facilitated by washing with ethyl acetate. TMP-oleate product was also synthesised using Novozym®435 in a solvent-free reaction. A general trend observed in the properties of the products was increase in pour point and viscosity index with increase in carboxylic acid chain length (Table 2). In the reactions using acid silica as catalyst, the products obtained with short chain fatty acids were yellow coloured while with oleic acid the product turned dark brown (Gardner Index 5) (Fig. 3). In the lipase catalysed reaction the product exhibited Gardner index of 2 and looked similar to oleic acid. In order to explain the colour development caused by the acid silica, the catalyst was incubated with oleic acid at 70 °C for 24 h in an inert atmosphere (to avoid air oxidation), after which the mix-

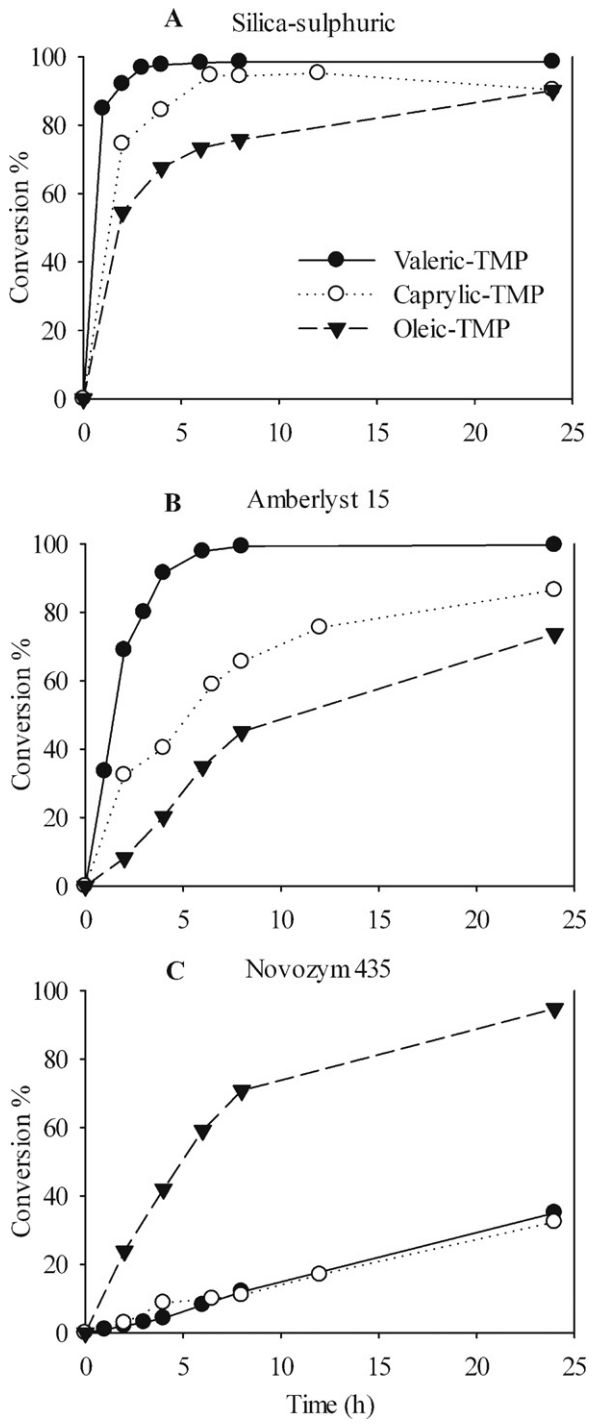


**Fig. 1.** Esterification reaction between different carboxylic acids and trimethylolpropane at molar ratio of 3:1 at 70 °C. The catalysts are 5% w/w (A) silica–sulphuric acid, (B) Amberlyst 15, and (C) Novozym®435.

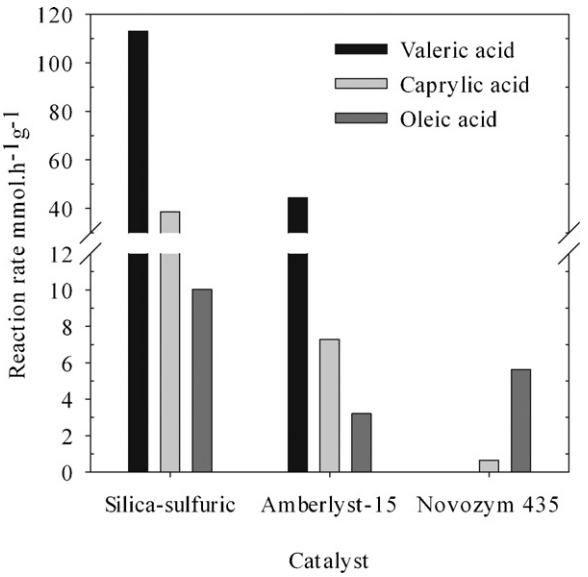


**Fig. 2.** Comparison of the different catalysts in terms of initial reaction rate (mmol $h^{-1}$ $g^{-1}$). The contribution from the spontaneous reaction was subtracted.


**Fig. 3.** TMP-trioleate sample product obtained using (A) silica–sulphuric acid, (B) Amberlyst 15, and (C) Novozym® 435. The Gardner index for the samples was 5, 3–2 and 2, respectively.

ture was analysed by HPLC-GPC. The mixture turned dark as above and the presence of dimeric and trimeric condensation derivatives (estolides) of oleic acid was observed [18] (Fig. 4).

TMP-trioleate ester prepared from the industrial grade oleic acid gave a desirable viscosity index value but relatively high pour point (−24 °C) probably due to low concentration of oleic acid (about 76%) in the raw material. Using technical grade oleic acid (90%) and immobilised lipase as the catalyst, the product obtained was mainly TMP-trioleate and had similar properties as the commercial product (Table 2). It did not require any purification apart from filtration.

**Table 2**
Characteristics of the biolubricant products produced in the current study and a reference TMP-oleate.

| Fatty acid-TMP | Catalyst used | Viscosity (40 °C) $mm^2/s$ | Viscosity (100 °C) $mm^2/s$ | Viscosity index | Pour point (°C) |
|---|---|---|---|---|---|
| Valeric acid | Silica–sulphuric acid | 9.5 | 2.5 | 80 | −75 |
| Caprylic acid | Silica–sulphuric acid | 16.2 | 1.4 | 114 | −45 |
| Oleic acid | | | | | |
| Industrial grade | | 39.6 | 8.7 | 208 | −24 |
| Technical grade | Novozym®435 | 47.1 | 9.1 | 194 | −48 |
| Reference product | | 45.5–46.5 | 9.0–9.3 | 182–187 | −42 |

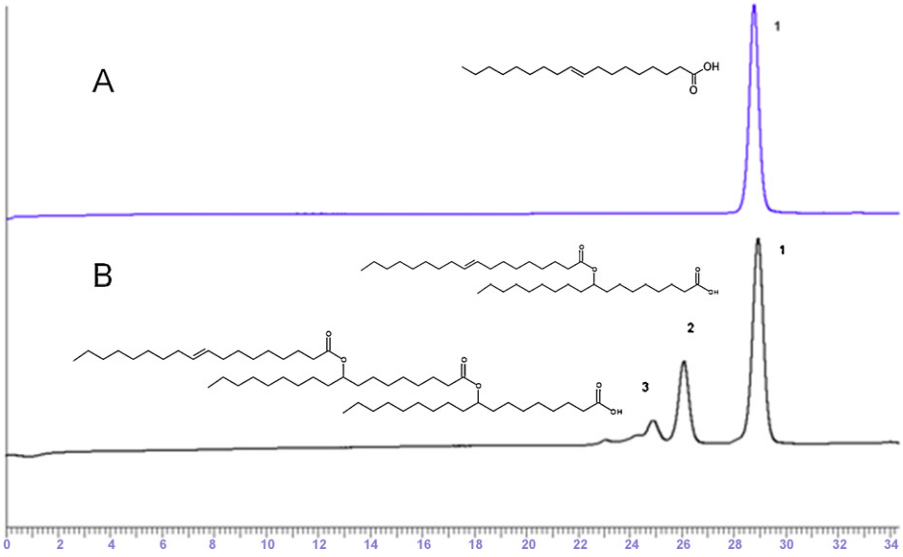


**Fig. 4.** Gel permeation-HPLC chromatogram of oleic acid incubated in the (A) absence and (B) presence of silica–sulphuric acid at 70 °C. The two extra products detected in (B) corresponded to dimer (2) and/or trimer (3) forms of oleic acid.

### 3.3. Environmental assessment of TMP-trioleate ester synthesis using EATOS

A preliminary environmental assessment of the synthesis of TMP-oleate using silica–sulphuric acid (route A), Amberlyst 15 (route B) and immobilised lipase (route C) as catalysts was performed using EATOS [19]. Fig. 5 provides an overview of the different environmental parameters evaluated. The mass index $S^{-1}$ (quantity of input chemicals per one kg of product) shows that the major contribution comes from the substrates, however in route A, solvents (toluene and ethyl acetate) represented 31% of the final mass index value (1.89 kg kg$^{-1}$). On the other hand, the enzymatic route provided the least mass intensive process (1.23 kg kg$^{-1}$) with 34% reduction compared to route A. The potential environmental impact ($EI_{in}$) of the input chemicals is an environmental parameter related to the mass index value; it is calculated based on the following equation $EI_{in} = S^{-1} \times Q_{in}$, where $Q_{in}$ is the unfriendliness quotient of the substrate calculated by EATOS and depends mainly on the risk phrases provided by the material safety data sheet. $EI_{in}$ of the feedstock in route A was seen to be the highest (4.06 PEI kg$^{-1}$ EATOS unit) among the three routes due to the use of toluene (Fig. 5). EATOS assigns a $Q_{in}$ value of 10 to toluene based on its risk phrases, so it contributes to 67% of the feed-in environmental impact expected from using this route of synthesis.

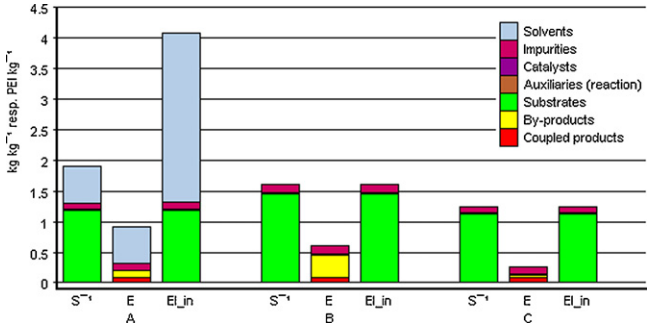


**Fig. 5.** Assessment of the synthesis of TMP-oleate ester by means of the software EATOS. The different routes for synthesis are route A using silica–sulphuric acid as catalyst (toluene and ethyl acetate as solvents), and routes B and C involving Amberlyst 15 and Novozym®435, respectively, as catalysts in a solvent-free system. The parameters evaluated are: mass index $S^{-1}$, environmental factor $E$, and the potential environmental impact of the input $EI_{in}$.

The environmental factor E is the total amount of waste generated per kg of the product. EATOS puts under this item all the by-products other than the main product. The enzymatic route was the least mass intensive synthesis (0.2 kg kg$^{-1}$) followed by route B (0.58 kg kg$^{-1}$) and route A (0.89 kg kg$^{-1}$) (Fig. 5).

## 4. Discussion

Polyol based esters are potential lubricants in a variety of applications. Esters of valeric acid have applications as lubricants in cutting oils and are also useful for low temperature applications as lubricant basestocks when present in a mixture with other esters [20]. TMP-caprylic acid esters are used for biolubricant application requiring high viscosity and high stability, and can also be used as dielectric coolants and as rail/wheel lubricants [21,22], while TMP-oleate is the most widely used biolubricant product for hydraulic fluids.

The choice of acid catalysts for this study was based on the knowledge that sulphuric acid and alkyl sulphonic acids have high acid strengths and are efficient in catalysing the esterification of free fatty acids. Moreover, according to the preliminary screening the alkali catalysts did not catalyse the esterification reaction. Sulphonic acid functionalised solids – both ion exchange organic resins and inorganic supports – are among the commonly reported heterogeneous acid catalysts. Both silica–sulphuric acid and Amberlyst 15 have earlier been used to catalyse a variety of reactions [23,24]; the latter has also been used to catalyse the production of biolubricant basestocks by ring opening of epoxidised vegetable oil and further esterification with shorter chain alcohols [25].

The acid catalysed esterification proceeds by protonation of the carboxylic acid to give an oxonium ion followed by nucleophilic attack of alcohol, resulting in ester bond formation and release of water [26]. The results in this study show silica–sulphuric acid to be a superior proton source and displayed the highest reaction rate with all the carboxylic acids even though the reaction efficiency was declining with increase in alkyl chain length (Fig. 1). Although Amberlyst 15 was less effective, it is possible that change of reaction conditions would improve the performance of the catalyst. For example, increasing the temperature (to 80 °C) resulted in a significant increase in the rate of Amberlyst 15 catalysed reaction (data not shown).

In a lipase-catalysed esterification, the acid substrate binds to the enzyme active site where the hydroxyl group of serine residue acts as a nucleophile to form an ester bond with the acyl group, and subsequently, the alcohol nucleophile attacks the acyl-enzyme complex to give the ester product [27]. Activity of the lipases is affected by nature of both the acyl-donor and -acceptor, and also the water activity of the medium. The rate of the reaction with a polyol is often limited by the size of the active site pocket of the lipase. Immobilised lipases have been used earlier for synthesis of TMP esters. Esterification of TMP with caprylic acid catalysed by immobilised *Rhizomucor miehei* lipase Lipozyme IM 20 in an ether solvent gave a low reaction rate and a conversion yield of 90% in 180 h [16], which was attributed to the detrimental effect of the neopentyl group of TMP on the enzyme activity. Immobilised lipases from *C. rugosa* and *R. miehei* (Lipozyme IM 20) have provided high yields of TMP-oleate in a transesterification reaction with rapeseed methyl ester and at a biocatalyst concentration as high as 20–40% w/w [28,29].

Immobilised lipase B from *C. antarctica* is known to be a versatile catalyst [30,31]. Lack of activity with valeric acid is in agreement with earlier studies that have reported negligible or low activity of *C. antarctica* lipase *B* when exposed to high concentration of short-chain fatty acids [32,33], and is ascribed to enzyme inactivation caused by the short chain acids that are polar and lead to protonation of a critical residue at the enzyme active site [32,34]. The esterification of TMP with oleic acid catalysed by Novozym®435 was quite efficient when compared to the previous studies stated above using the lipase from other sources, and considering that transesterification is a kinetically favourable reaction [28,29]. As in the previous reports, the removal of water from the lipase-catalysed reaction was important for the reaction equilibrium to be shifted to esterification [16,29]. The higher efficiency observed for Novozym®435 than Amberlyst-15 for catalysing esterification with oleic acid is in good agreement with that of an earlier study on production of biodiesel from palm fatty acid distillate [35].

The products obtained with C5, C8 and C18 acids had desirable cold flow properties. A general trend of increasing pour point and viscosity index with increase in alkyl chain of the acid was observed. The main drawback, however, was the coloration of the products obtained in the reactions catalysed by the strong acid silica catalyst. The product obtained with oleic acid showed the presence of significant amounts of estolides. Formation of estolides on treatment of oleic acid with acids has been reported earlier by Isbell et al. [18], and results from the formation of carbocation intermediate at the double bond followed by its capture by another fatty acid molecule to form dimer, and its further reaction with oleic acid to form higher molecular weight products. TMP-oleate obtained from the biocatalytic reaction did not show any development of colour and estolide formation.

Since TMP-oleate could be produced using all the catalysts, the product was used as a model for environmental evaluation of the different catalytic routes. Moreover, TMP-oleate exhibited the most desirable properties with regards the pour point and viscosity index required for application as hydraulic fluid at low temperature applications. The preliminary environmental assessment of organic synthesis becomes affordable with the free EATOS (Environmental Assessment Tool for Organic Synthesis) software. In a previous study, we have employed it to evaluate the enzymatic synthesis of a non-ionic surfactant [36]. The raw materials have a major environmental and economic impact in the production of a specialty or bulk chemical. Besides the raw materials, the use of organic solvent has a significant impact in the process catalysed by silica–sulphuric acid. Moreover, organic solvents in chemical reactions represent the most hazardous contribution and this is clearly highlighted in this example due to the high risk of using toluene (a highly flammable solvent). The amount of waste generated was much lower in the biocatalytic process (route C), which was attributed to higher product yield (as compared to route B) and absence of solvents (as compared to route A).

An important limitation of the biocatalytic process, however, is the much higher cost of Novozym®435 than the chemical catalyst (e.g. the cost is 5 times higher than Amberlyst 15). Reducing the biocatalyst cost has been shown to be possible by optimizing immobilization conditions for CALB [37]. Different approaches for immobilising enzymes like binding to a support, entrapment into a matrix, and cross-linking of enzyme molecules were reviewed by Sheldon [38]. Combining CALB with other immobilization methods (such as cross linked enzyme aggregates) and protein engineering for obtaining a potentially less expensive and robust biocatalyst for biolubricant production are currently being investigated.

## 5. Conclusion

This study shows that silica–sulphuric acid and immobilised lipase to be two promising catalysts for synthesis of biolubricants. Both catalysts are effective under relatively mild conditions; the former was seen to be an efficient catalyst for all the fatty acids and is moreover inexpensive and recyclable. However its use for longer chain fatty acids results in product with unwanted dark colour, which needs further treatment such as bleaching and deodorisation.

Immobilised lipase B from *C. antarctica* seems to be useful for synthesis of biolubricants with longer fatty acid chains that are suitable for hydraulic fluids and provides high yields of a better-quality product. The environmental assessment for synthesis of esters from oleic acid and TMP, has shown the enzyme process to have the least environmental impact. Further studies are ongoing with respect to process optimisation and engineering to improve the process kinetics. Moreover, the biocatalyst recycling and overall costs are issues that need to be addressed for the lipase to be commercially viable as industrial catalyst for bulk chemistry applications.

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