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Efficient greener methodology for the preparation of bio-based phase change materials from lipids

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ABSTRACT

In the present work, a new, highly efficient and simple strategy has been developed for the synthesis of long chain esters from fatty acids and fatty alcohols as phase change materials. Equivalent amounts of the selected starting compounds were taken to the esterification reaction at 110 °C in a solventless medium. In order to catalyze the esterification reaction, non-hygroscopic triphenylphosphine-sulfur trioxide adduct was used (0.83 mmol%) which is an easily accessible compound. The relevant reaction was completed in a very short time (2 h) and under optimized esterification conditions, excellent conversion were reached. The targeted mono ester compounds (15 examples) were obtained in good to excellent yields even after a simple crystallization step (72–99%). Additionally, a catalyst reuse investigation and study covering the scale-up production of stearyl stearate was also carried out. The triphenylphosphine-sulfur trioxide catalyzed solvent free process can compete with existing processes and proved to be a cheaper, practical and environmentally-friendly method for the esterification of fatty acids and alcohols.

ARTICLE HISTORY

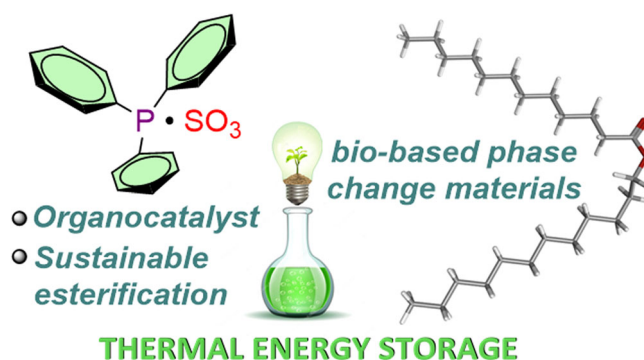
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KEYWORDS

Esterification; renewable resources; green chemistry; triphenylphosphine-sulfur trioxide complex; wax ester; phase change materials

GRAPHICAL ABSTRACT



Introduction

Due to the rapid depletion of fossil resources (which are known as biomass that has undergone transformations over periods of millions of years), as well as increased environmental concerns, an inevitable trend has begun toward biomass-based raw materials with renewable and biodegradable properties.^[1,2] Animal and vegetable originated fats and oils, one of the most important components of these materials, have been considered as important renewable feedstock for the synthesis of versatile oleochemicals.^[3–5] Moreover, catalytic chemical esterification or transesterification reactions of fats and vegetable oils with long chain alcohols to produce ester compounds as bio-based phase change materials (PCM) has become popular both for scientific and industrial community in recent years.^[6–9] In order to accelerate the

esterification reactions between long chain fatty acids and long chain fatty alcohols, several catalytic methods have been employed which have also some drawbacks.^[7,8] Some of these drawbacks are the excessive use of one of the reagents to achieve high ester yields, the preference of metal-based expensive catalysts, the use of toxic organic solvents and the isolation of the product can be rather troublesome.^[6,8] In our recent study, we have developed a highly environmentally friendly method suitable for the synthesis of wax esters using an ionic liquid as a catalyst.^[9]

Due to the high cost of energy production and the rapid increase in energy demand, it is very important to use energy resources efficiently and to store the produced energy properly for later use.^[10] Therefore, in order to store thermal energy effectively and environmentally, advanced

technological studies must be continued.^[11] Substances used for latent heat storage known as phase change materials can be classified mainly as organic, inorganic and eutectics. In order for a substance to be suitable as a phase change material, it must meet various physical and chemical criteria in addition to its economic and environmental characteristics.^[12–14] There are different physical and chemical processes for thermal energy storage, which have been discussed extensively by Jouhara et al.^[14] Recently, Wang et al. reported that, a composite material assembled from a regenerated porous cellulose membrane is a suitable candidate as a thermal energy storage material.^[15] On the other hand, relatively cheaper bio-based phase change materials with desirable biocompatibility and high enthalpy properties were developed by Liu et al.^[16] and Landi et al.^[17] An attractive class of organic phase change materials used for this purpose is fatty acids and their different derivatives such as fatty acid esters and amides.^[18–24] Recently, these organic phase materials have gained great interest in the textile industry.^[25] Fatty acids and their derivatives have a wide range of applications in consumer and industrial markets and some common commercial uses of these valuable renewable materials are schematized in Figure 1.

On the other hand, it is very well known that esters of long chain fatty acids and fatty alcohols, also known as wax esters, have a wide range of industrial uses.^[26–30] Therefore, it is important to synthesize these compounds with high yields through simple and environmentally friendly methods. Herein, triphenylphosphine which is widely used both as a reagent and a catalyst in many organic transformations was chosen as a catalyst component with sulfur trioxide for the esterification reactions.^[31–33] With the present developed

solvent-free method, the targeted long chain fatty acid esters were obtained with good to excellent yields.

Results and discussion

In the esterification reactions carried out in the present work, triphenylphosphine-sulfur trioxide adduct was used as an efficient catalyst. This non-hygroscopic solid which is stable in air was prepared readily according to original procedure given in literature (Scheme 1).^[34] The molecular structure of this complex adduct has been well established by X-ray crystallography.^[35] Moreover, this adduct is an effective coupling reagent in peptide synthesis^[34] but to the best of our knowledge, it has not used previously for esterification or transesterification reactions. Therefore, in this study we investigated the catalytic activity of this compound in esterification reaction of long chain fatty acids and alcohols. As shown in Table 1, in order to optimize the conditions of the performed esterification reaction, stearic acid and stearyl alcohol were chosen as the starting compounds. The conducted studies have shown that the targeted product could not be obtained when the esterification reaction is carried out in a catalyst free medium. In the present solventless process, in order to keep the reaction medium in a molten state and allow it to proceed more safely and smoothly, the minimum reaction temperature value was set to 80 °C. This temperature is slightly above the melting points of stearic acid and stearyl alcohol. As can be seen from Table 1, after several trials, it was determined that increasing the reaction temperature by 10 °C causes slight increases in product yield.

The Table 1 shows the average yields of stearyl stearate (based on two runs) obtained depending on the amount of the catalyst and the reaction time and to the highest product yields was reached under the conditions given in entries 9 and 12. The yield of the ester decreases slightly when the reaction time is kept constant and the catalyst is taken as 10 mg (entry 10). As can be seen from Table 1 the conditions given in entry 12 are the optimal reaction conditions for the general esterification procedure. Therefore, the esterification reactions were carried out with equivalent amounts of fatty acid and fatty alcohol in the presence of 5 mg of the triphenylphosphine-sulfur trioxide adduct in solventless medium for 2 h at 110 °C. The temperature given here belongs to the oil bath and during this 2 h period the TLC (Thin layer chromatography) analysis showed depletion of the starting compounds. According to the conducted procedure the obtained crude esters are pure enough to be used

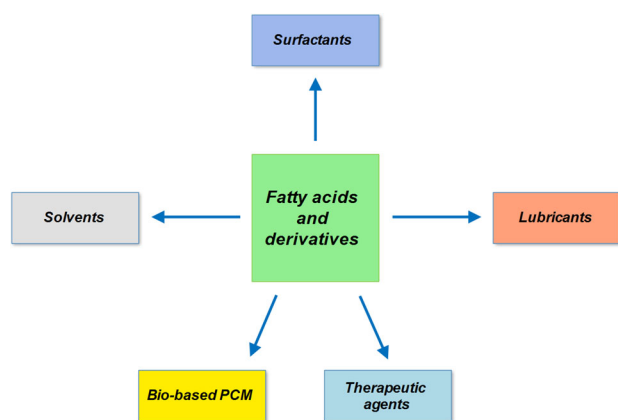
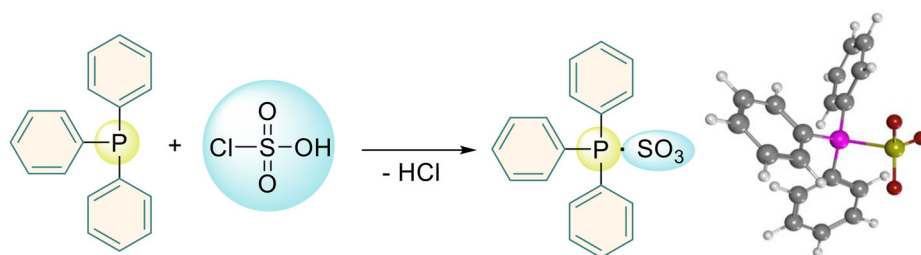
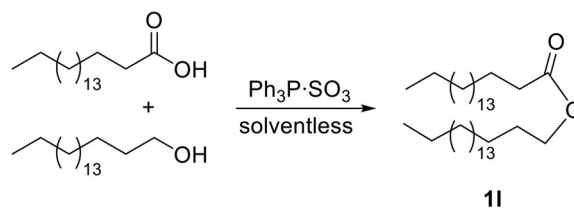


Figure 1. Some common uses of renewable fatty acids and derivatives.



Scheme 1. Preparation of $\text{Ph}_3\text{P}\cdot\text{SO}_3$ adduct.

Table 1. Optimization of the reaction conditions for esterification of stearic acid.

Entry	Catalyst loading (mg)	Catalyst loading (mmol%)	Time (h)	Temperature (°C)	Yield (%) ^a
1	Without catalyst		2	110	No conversion
2	2.5	0.42	0.5	80	70
3	2.5	0.42	0.5	90	71
4	3	0.50	0.5	90	72
5	2.5	0.42	0.5	110	78
6	2.5	0.42	1	110	88
7	2.5	0.42	4	110	97
8	5	0.83	1	110	92
9	5	0.83	4	110	98
10	10	1.66	4	110	95
11	5	0.83	2	90	96
12	5	0.83	2	110	98

^aYields obtained after crystallization from MeOH/Acetone/THF.

Table 2. Wax esters obtained by the esterification procedures.

Entry	Wax ester	Name	Mp (°C) (Lit. Mp [9])	Yield (%) ^a
1	1a	Lauryl laurate	30-31 (29-30)	72
2	1b	Myristyl laurate	41-42 (41-42)	82
3	1c	Stearyl laurate	47-48 (46-47)	89
4	1d	Lauryl myristate	39-40 (38-39)	76
5	1e	Myristyl myristate	44.5-45 (44-45)	85
6	1f	Stearyl myristate	53.6-54.2 (53-54)	99
7	1g	Lauryl palmitate	44.5-45.4 (44-45)	79
8	1h	Myristyl palmitate	53-54 (52-53)	93
9	1i	Stearyl palmitate	61.3-62 (61-62)	91
10	1j	Lauryl stearate	47-48.2 (46-48)	85
11	1k	Myristyl stearate	56-56.8 (54-55)	96
12	1l	Stearyl stearate	62-63 (63-64)	98
13	1m	Lauryl behenate	54.4-55.1 (54-55)	89
14	1n	Myristyl behenate	59-60 (58-59)	96
15	1o	Stearyl behenate	68.2-69.3 (68-69)	97

in industrial applications, but if desired these esters can be crystallized from the appropriate solvent or solvent mixtures which one of them is given in Table 1. The esters synthesized in this study are given with both of their found and literature melting points respectively in Table 2 and as seen in the table, all the esters were obtained in excellent yields.

The progress of the esterification reaction was followed by the depletion of stearic acid. At certain time intervals, the sample of the reaction mixture was analyzed for the remaining stearic acid in the mixture by titrimetric method. In other words, the extent of the esterification reaction can be determined by the acid value and the stearic acid conversion rate. The acid number is directly related to the amount of stearic acid remained in the reaction mixture and the high stearic acid amount corresponds to the high acid number. The acid value is calculated by using the following equation:

$$AV = \frac{M_{KOH} \times V_{KOH} \times 56.1}{m}$$

Where, M_{KOH} is the molarity of the KOH solution (mol/L), V_{KOH} is the volume of the KOH solution (mL), m is the

weight (g) of the analyze sample and 56.1 is the molecular weight of KOH. The stearic acid conversion rate is calculated by using the following equation:

$$SA \text{ conversion } (\%) = \frac{AV_0 - AV_1}{AV_0} \times 100$$

Where, AV_0 is the initial acid value and AV_1 is the acid value after a specific time (the final acid value). The graphs containing these calculated values are given in Figures 2a and 2b respectively. As seen from the both figures, the esterification reaction proceeds very quickly within the first 20 minutes. In this case, the acid value was 30.86 mg KOH g^{-1} , and the degree of esterification was 78%. After 120 minutes, the calculated acid value of the reaction mixture remains constant, which indicating that the esterification process has terminated.

To reveal the synthetic utility of the esterification method developed in the present work, a large scale synthesis of stearyl stearate was carried out. Therefore, for a gram scale preparation of stearyl stearate, 20 g of stearic acid was reacted with 19 g of stearyl alcohol in the presence of 200 mg of the catalyst and as a result of heating at 110 °C for 2 h, the corresponding ester **11** was obtained with a yield of 97%.

Some studies related to triphenylphosphine based catalyst reusability have also been carried out. In order to investigate the reusability of the catalyst, stearic acid and stearyl alcohol were reacted under the optimized esterification conditions depicted in Table 1, entry 12. The crude product stearyl stearate obtained as a result of the reaction was purified by crystallization from acetone/THF/MeOH solvent mixture to give pure wax ester **11** nearly in quantitative yield (98%). The obtained filtrate was concentrated under reduced pressure and the residue containing the catalyst was used for the next esterification reactions. This residue was used in the next similar runs and the results obtained are given in Figure S1 (Supplemental Material). According to the yields obtained (yields of esterification obtained after crystallization

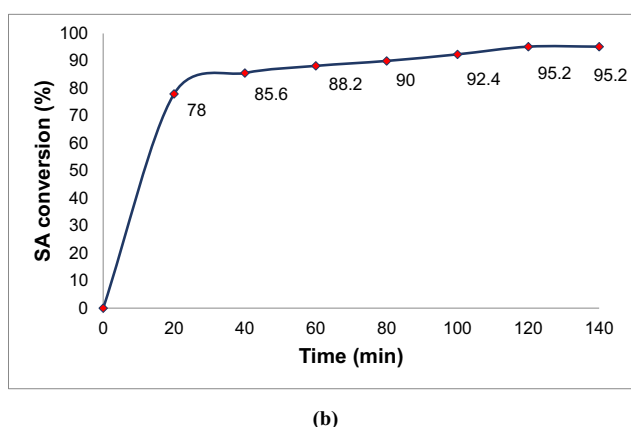
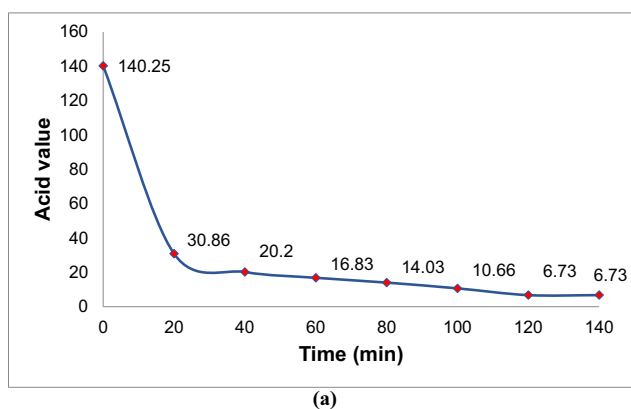


Figure 2. (a) Graph of calculated acid values versus reaction time; (b) graph of calculated stearic acid conversion (%) values versus reaction time.

from acetone/THF/MeOH), it is seen that this catalyst is convenient to use two times without a significant loss in its activity.

The decrease activity of the catalyst might be attributed possibly to the loss of gaseous sulfur trioxide catalyst in the course of esterification. On the other hand, the other possible reason for the catalyst to lose its effectiveness after its use twice is probably due to its degradation in the form of sulfuric acid, as shown in the proposed esterification mechanism given in the subsequent section (Figure 3). Thus, the sulfuric acid molecule released during the progress of the reaction most likely interacts with the fatty alcohol molecule, causing some changes in its structure that reduces the yield of the desired ester (Figure 4). As depicted in this figure, the fatty alcohol may form the relevant decomposition products via these well-known reactions.^[36] However, a comprehensive analysis of the reaction mixture can be carried out in further studies to prove the formation of these products which studies are not performed in the present study yet.

The triphenylphosphine-sulfur trioxide adduct used in this study most likely catalyzes the performed esterification reactions as follows: Under the thermal reaction conditions, sulfur trioxide first released from this adduct, transferred to the molten reaction mixture and forming an intermediate complex with stearic acid molecule by acting as a Lewis acid catalyst.^[34] This action of sulfur trioxide makes it easier for

a weak nucleophile such as fatty alcohol to attack the activated carbonyl functional group of stearic acid molecule (Figure 3). Actually, in the catalytic esterification reaction carried out in this study, triphenylphosphine act as a solid support that contains the sulfur trioxide molecule which has a Lewis acid character. In addition, the sulfuric acid released in the continuation of the reaction may also play a role in catalyzing the esterification reactions by acting as a Brønsted acid catalyst. Thus, under these catalytic conditions, the two voluminous compounds easily interact and forming the corresponding ester in a short reaction time (2 h).

On the other hand, some interpretations can be made through Lewis acid–base interactions supported by some theoretical calculations. The calculated highest occupied molecular orbital (*HOMO*) and lowest unoccupied molecular orbital (*LUMO*) energetics of the stearic acid and the catalyst involved in the esterification with their optimized geometries are given in Figure 5. The geometry optimization was performed using the MM2 force field option through the Chem3D software, PerkinElmer Informatics. As seen from the Figure 5, the *HOMO*_{stearic acid} – *LUMO*_{sulfur trioxide} energy gap is lower than the *HOMO*_{stearic acid} – *LUMO*_{triphenylphosphine sulfur trioxide adduct} (10.158 eV and 11.462 eV respectively). This reveals that in esterification reactions, initially the released SO₃ activates the stearic acid against the nucleophilic attack of the stearyl alcohol molecule. Moreover, the *HOMO*_{stearyl alcohol} – *LUMO*_{sulfur trioxide} energy gap is higher (10.809 eV) than the *HOMO*_{stearic acid} – *LUMO*_{sulfur trioxide} energy gap (10.158 eV) which indicated the more favorable interaction between stearic acid and SO₃.

Experimental

Reagents and chemicals

All reagents and solvents were purchased from either Merck or Sigma–Aldrich (St. Louis, MO) and used without further purification. Thin-layer chromatography was performed using silica gel (60 F254, Merck, Darmstadt, Germany) plates.

Instrumentation

Melting points were recorded by BÜCHI melting point B-540 apparatus (BÜCHI Labortechnik AG in Flawil, Switzerland). The IR spectra were measured by Nicolet FTIR 6700 spectrometer (ThermoFisher Scientific, Massachusetts, USA). The NMR spectra were measured using A600a Agilent DD2 600 MHz NMR spectrometer (Santa Clara, Ca, USA), chloroform-d (CDCl₃) using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are reported in ppm and J values in Hertz. The elemental analyses were performed using an LECO CHNS-932 elemental analyzer (Saint Joseph, MI, USA). The Supplemental Materials contains sample IR, ¹H and ¹³C NMR spectra of the products 1a–o (Figures S2–S46).

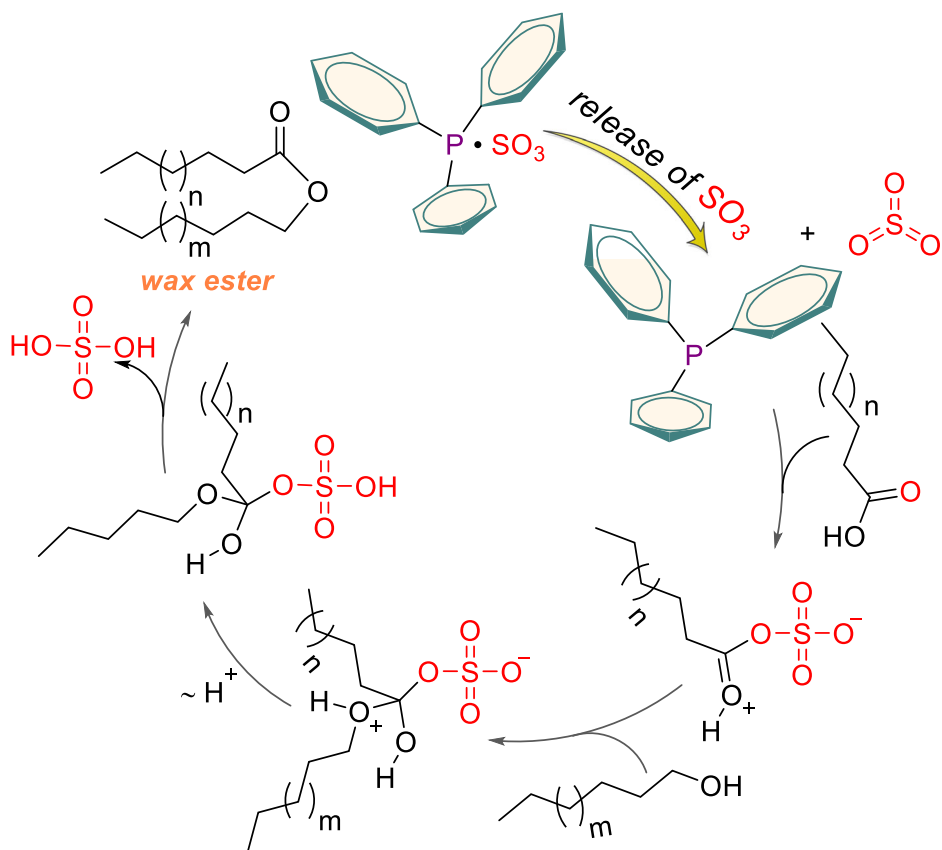


Figure 3. Proposed mechanistic pathway for the $\text{Ph}_3\text{P}\cdot\text{SO}_3$ catalyzed esterification.

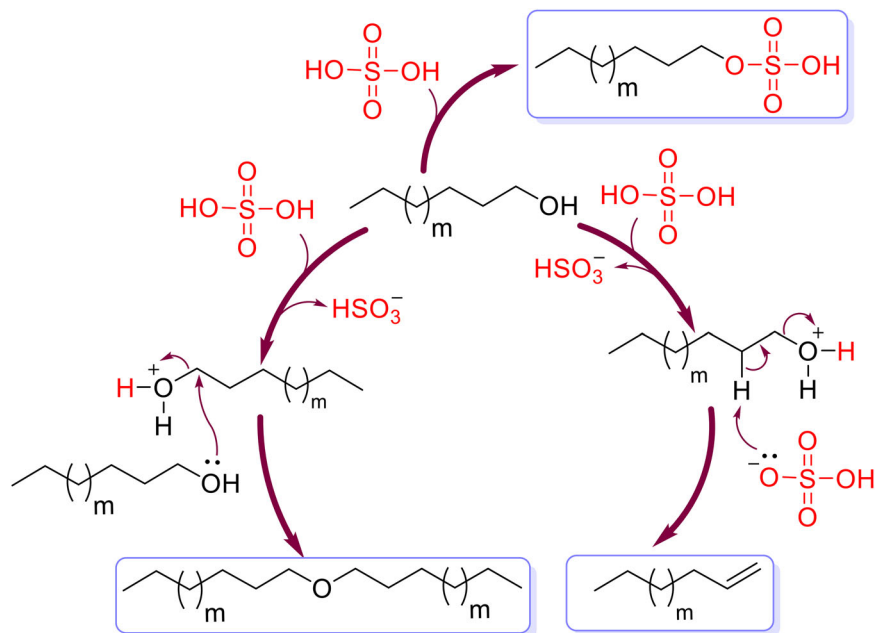


Figure 4. Proposed mechanistic pathways for the formation of decomposition products from fatty alcohol.

Esterification

In order to perform the esterification reaction, into a single-necked reaction flask, at equivalent quantities stearic acid (0.50 g, 1.76 mmol) and myristyl alcohol (0.48 g, 1.77 mmol) were added. After addition of the catalyst (5 mg), the mixture was heated with stirring in an oil bath at 110°C (bath temperature) for 2 h. Finally the reaction mixture was cooled and

the obtained solid was crystallized from methanol/acetone/tetrahydrofuran to afford pure crystalline product.

Method for determination of the acid value

The acid value is determined by titration of the sample (withdrawn with a Pasteur pipette from the reaction flask)

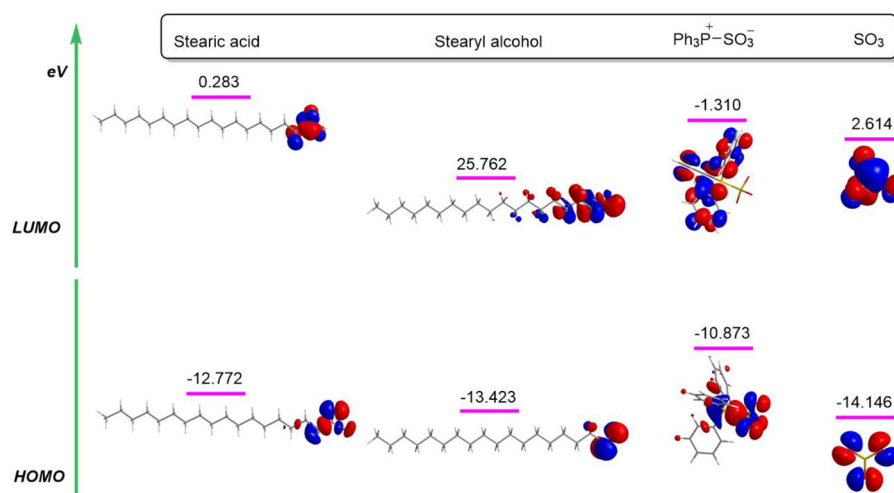


Figure 5. FMO orbitals of stearic acid, stearyl alcohol and catalyst as in the form of $\text{Ph}_3\text{P}^+-\text{SO}_3^-$ and SO_3 .

which is dissolved in 3 mL of EtOH-toluene (1:1 v/v) mixture. The titration process was performed with standard 0.1 M alcoholic KOH solution. In order to estimate the unreacted stearic acid in terms of its acid value one droplet of 1% alcoholic phenolphthalein solution was used as an indicator. 0.2 mL aliquot of samples was withdrawn from the reaction flask for titration at 0, 20, 40, 60, 80, 100, 120 and 140 minute intervals after the onset of the reaction. This sample taken from the reaction flask solidifies immediately and 0.1 gram from this solid is weighed and titrated with the alcoholic base solution. In order to dissolve the solid sample completely, the obtained mixture was heated each time to 40 °C in a water bath and then titrated until the faint pink color persists for at least 30 s.

Conclusion

A highly efficient organocatalyzed sustainable esterification procedure was developed for the preparation of versatile long chain fatty acid esters. The present study is quite successful in that it is compatible with some of the green chemistry principles. The ester preparation procedure was carried out in a solvent-free environment at 110 °C and this procedure does not require the purification of esters for industrial uses. The reaction time is considerably shorter (2 h) than many esterification procedures available in the literature. Moreover, in this work a Lewis acid supported over an organic compound that does not contain any toxic transition metal was used as a catalyst and it is also convenient for large scale esterification. Although the catalyst loses its activity after the second use, the fact that it is used in a small amount (0.83 mmol%) in the reaction medium eliminates this disadvantage. These results show that the esterification procedure developed in this study can compete with the existing esterification procedures.

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