

## Sustainable process for the production of symmetrical dibasic acid ester-based thermal energy storage materials from lipids

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**Abstract:** Oleochemical-based long-chain diesters are potential organic phase change materials convenient for thermal energy storage. The development of efficient and green methods is an important requirement for the preparation of these environmentally friendly compounds, which also are finding wide industrial application. Thus, in the present work, a series of dibasic acid esters were synthesized through ionic liquid catalyzed scalable chemical esterification or transesterification reactions in a solvent-free medium. The starting compounds, dicarboxylic acids or their methyl esters and fatty alcohols or cholesterol, were reacted in the ratio of 1:2 respectively and the synthesized esters were characterized by FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR.

**Key words:** Diester, green chemistry, ionic liquid, organic phase change materials, thermal energy storage

### 1. Introduction

Along with the rapid political, economic, and technological developments observed worldwide, the demand for energy is increasing day by day.<sup>1,2</sup> Therefore, it is important to meet this demand and generate energy by more environmentally friendly processes. In many countries today, a large part of energy production is from fossil fuels. However, this method has several disadvantages, the most important of which is that fossil fuels are very costly and not renewable resources. On the other hand, the negative effects of nuclear power plants on the environment and human health are well known. Therefore, one of the ways to overcome these problems encountered in energy production is to reduce the loss and excess consumption by storing energy.

As it is essential to explore new energy sources, it is also important to develop cheap and effective energy storage materials. Recently, many materials capable of storing thermal energy have been researched and developed.<sup>3</sup> While some of these materials are suitable for use as energy storage materials, some are not suitable due to their low chemical stability and high cost. Among these materials, some specific nonparaffin organic compounds are particularly notable. Fatty acids as well as their derivatives are significant renewable raw materials for the chemical industry.<sup>4</sup> Recently, the latent thermal energy storage potential of these compounds has been reported.<sup>5–12</sup> As is known, phase change materials (PCMs) are inorganic or organic compounds that absorb and release latent thermal energy during melting and freezing processes.<sup>13</sup> Fatty acids and their derivatives possess some superior properties among such organic compounds. The preparation methods of these compounds are inexpensive and generally fatty acids and their derivatives have no toxic properties. In addition, these compounds have low corrosive effects and they are highly resistant to chemical degradation under storage conditions.<sup>14</sup>

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Several studies have reported that diesters derived from fatty acids and fatty alcohols can be used as thermal energy storage materials.<sup>15,16</sup> Figure 1 shows the principle of PCMs. In this context, developing suitable methods for the synthesis of these compounds is an important goal. To prepare long-chain diesters, there are only a few methods available in the literature and they have certain disadvantages.<sup>17–20</sup> The use of aromatic toxic solvents such as toluene and azeotropic removal of water formed in the reaction, use of aggressive reagents such as  $\text{SOCl}_2$ , and difficult stages in product purification are only some of them. On the other hand, in the transesterification reactions carried out in basic medium, the formation of by-products decreases the diester yield. Therefore, it is important to investigate the synthesis of these esters with efficient and environmentally friendly methods.

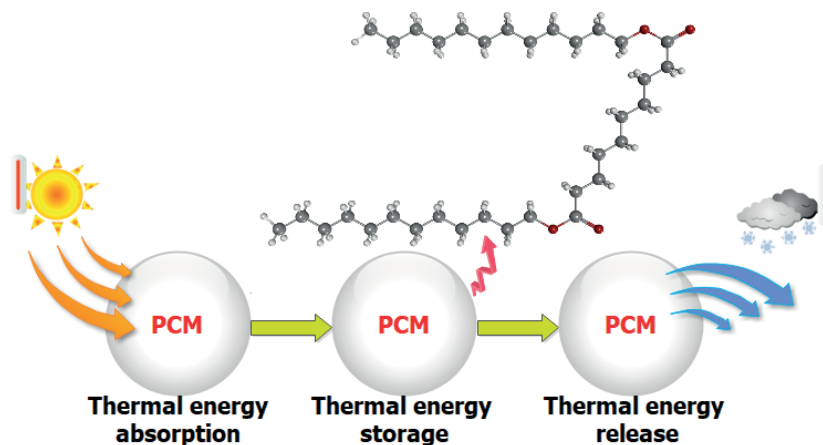


Figure 1. Principle of PCMs.

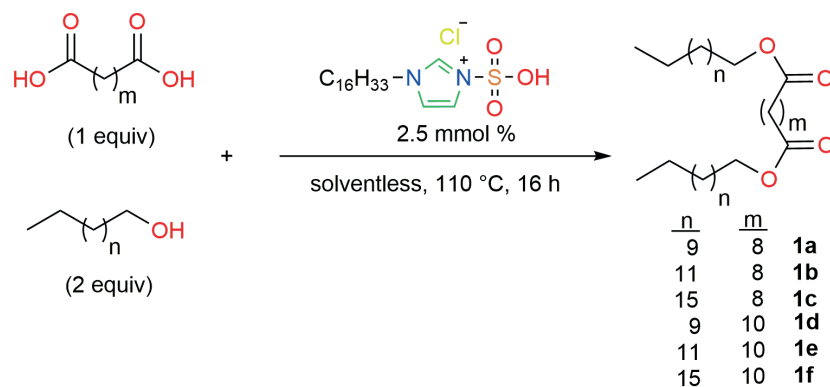
## 2. Results and discussion

In order to achieve maximum yield in esterification reactions, usually one of the reagents is used in excessive amounts. Another method is to remove the water formed during the reaction by Dean–Stark apparatus azeotropically from the medium. In this case, however, it is generally necessary to use toxic aromatic solvents such as toluene, xylene, or mesitylene.<sup>17,18</sup> In alternative methods, more active derivatives of carboxylic acids are used in the esterification reactions.<sup>19</sup> It is therefore necessary to develop more environmentally friendly and practical methods of esterification and transesterification reactions.

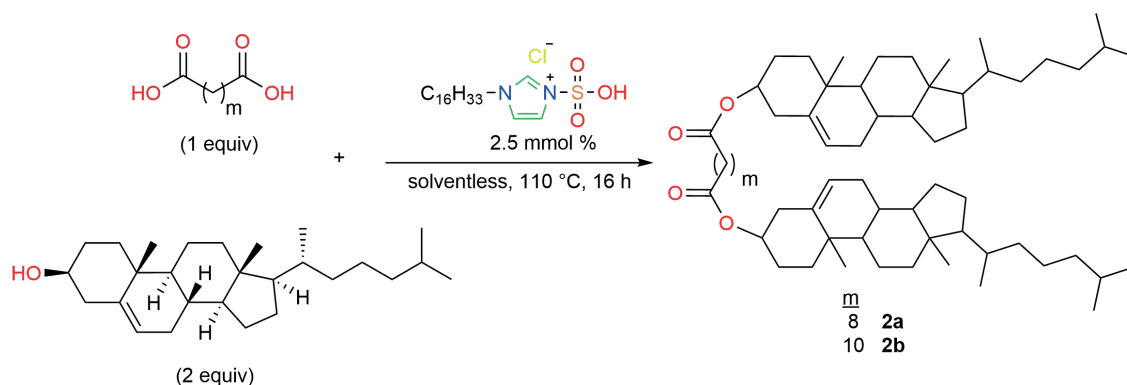
In the present study, some long-chain dibasic carboxylic acid esters that may be potent PCMs were prepared from long-chain dicarboxylic acids or dimethyl esters thereof and fatty alcohols or cholesterol by esterification or transesterification reactions (Schemes 1 and 2).

The IR spectrum of **1a** shows the characteristic band for the ester group at  $1733\text{ cm}^{-1}$ . Some of the characteristic  $^1\text{H}$  NMR peaks of **1a** are a triplet at  $\delta$  4.07 ppm for the  $2x\text{CH}_2\text{O}$  protons, a triplet at  $\delta$  2.30 ppm for the  $2x\text{CH}_2\text{CO}$  protons, and a quintet at  $\delta$  1.61 ppm for the  $2x\text{CH}_2\text{CH}_2\text{O}$  and  $2x\text{CH}_2\text{CH}_2\text{CO}$  protons (Figure 2). On the other hand, the  $^{13}\text{C}$  NMR spectrum showed a peak at  $\delta$  173.98 ppm for the carbon atom of the ester functional group.

The IR spectrum of **2a** shows the characteristic band for the ester group at  $1733\text{ cm}^{-1}$ . Some of the characteristic  $^1\text{H}$  NMR peaks of **2a** are a triplet at  $\delta$  5.39 ppm for the cholesteryl  $\text{CH}=\text{}$  protons, a multiplet at  $\delta$  4.66–4.60 ppm for the cholesteryl  $\text{CHO}$  protons, a triplet at  $\delta$  2.30 ppm for  $\text{CH}_2\text{CH}_2\text{COO}$  protons of the



**Scheme 1.** Synthesis of fatty alcohol-based diesters.



**Scheme 2.** Synthesis of cholesterol-based diesters.

acid chain, and a doublet of doublets at  $\delta$  0.89 ppm for the cholesteryl  $\text{CH}(\text{CH}_3)_2$  protons. The  $^{13}\text{C}$  NMR spectrum showed characteristic peaks at  $\delta$  173.30 ppm for the carbon atom of the ester functional group, and at  $\delta$  139.73 and 122.61 ppm for the cholesteryl olefinic carbon atoms. Cholesterol found in living cells has many functions, mainly as hormones. Symmetric liquid crystals based on cholesterol can find different uses due to their unique structure<sup>21–25</sup> (Figure 3).

As is well known, ionic liquids, especially those functionalized with a  $-\text{SO}_3\text{H}$  group, are widely used as catalysts in organic synthesis.<sup>26</sup> The Brønsted acid ionic liquid catalyst used in the present study was previously synthesized and characterized in our laboratory.<sup>27</sup> The optimum reaction conditions for the esterification reactions performed are given in Table 1. The highest diester yield was achieved under the conditions given in entry 3. While extension of the reaction time did not change the yield of the product, a reduction in the amount of catalyst by half resulted in a slight increase in yield. On the other hand, transesterification reactions were also carried out under similar conditions of esterification, but with slightly lower yields of diesters (Table 2). In both ester synthesis methods, cholesterol esters were obtained at lower yields than fatty alcohol esters, because the cholesterol molecule is a sterically hindered molecule. The minimum amount of toluene was used as the solvent in order to reduce the amount of colored impurities formed in the esterification and transesterification reactions of cholesterol.

In order to investigate the synthesized catalyst's reusability, sebacic acid and lauryl alcohol were esterified under solventless conditions in the presence of catalyst at 110 °C for 16 h. The crude diester dilauryl sebacate

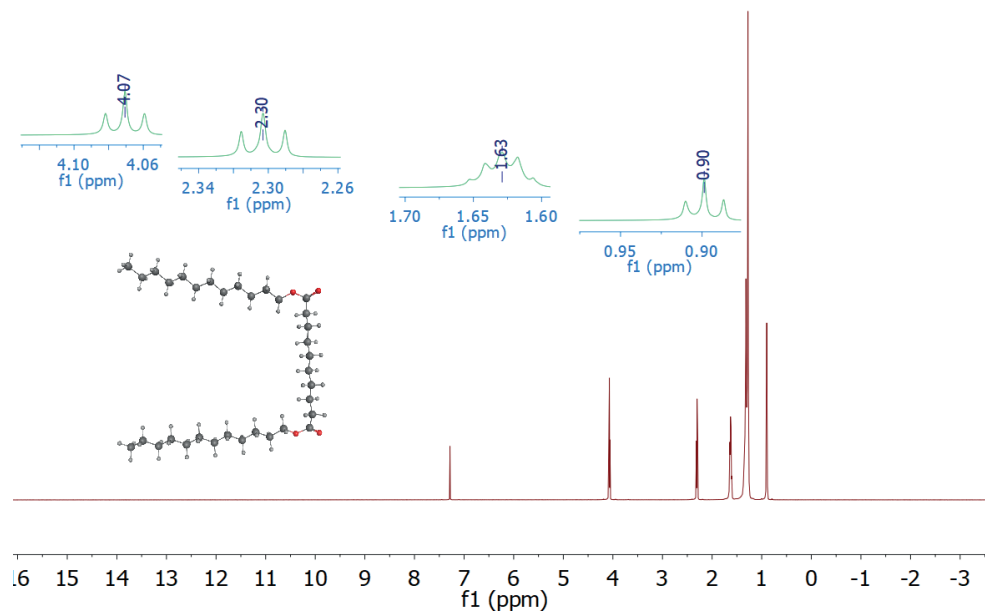


Figure 2.  $^1\text{H}$  NMR spectrum of **1a**.

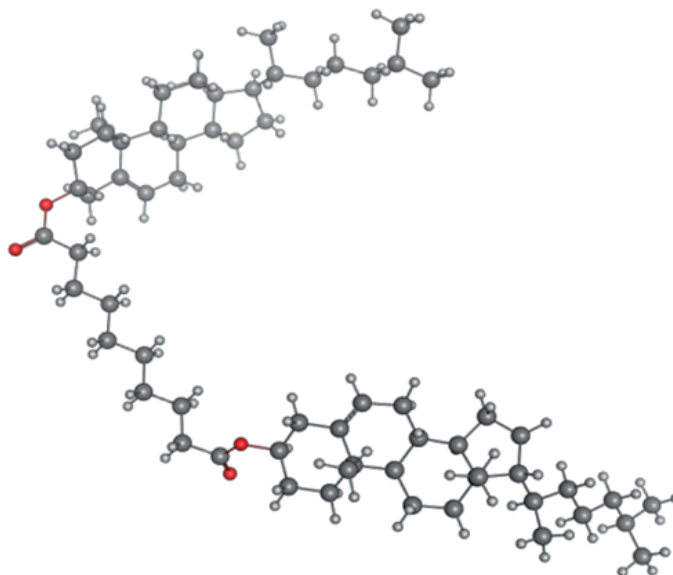


Figure 3. Molecular structure of cholesterol-based diester **2a**.

obtained as a result of the esterification reaction was purified by crystallization from THF/MeOH to give pure diester **1a** with 83% yield. The resulting filtrate was concentrated under reduced pressure and the residue was dissolved in a minimum amount of diethyl ether and then the catalyst was precipitated with hexane and used without further purification for the next esterification procedure under the same reaction conditions. The experimental results obtained are given in Figure 4. According to the yields of the esterification reaction obtained after crystallization from MeOH/THF, it is seen that the efficiency of the catalyst after three uses is reduced.

**Table 1.** Optimization of conditions for the esterification reaction.

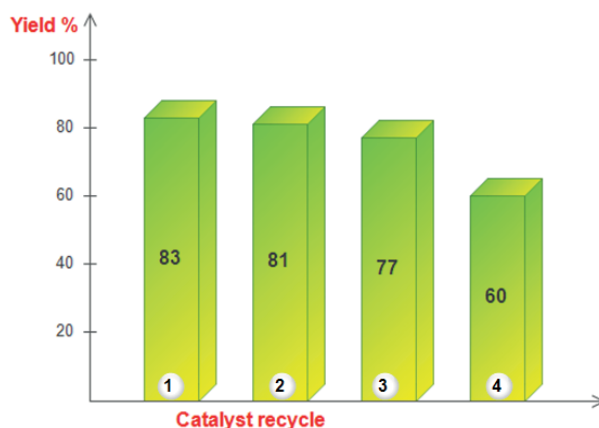
Entry	Catalyst loading	Time (h)	Temperature (°C)	Yield (%) <sup>a</sup>
1	5 mmol %	16	110	81
2	5 mmol %	24	110	81
3	2.5 mmol %	16	110	83

<sup>a</sup>Yields obtained after crystallization from THF/MeOH.

**Table 2.** Diesters obtained by the esterification or transesterification procedures.

Entry	Diester	Name	Yield (%) <sup>a</sup> (Esterification)	Yield (%) <sup>a</sup> (Transesterification)
1	<b>1a</b>	Dilauryl sebacate	83	43
2	<b>1b</b>	Dimyristyl sebacate	90	68
3	<b>1c</b>	Distearyl sebacate	70	84
4	<b>1d</b>	Dilauryl dodecanedioate	81	53
5	<b>1e</b>	Dimyristyl dodecanedioate	88	64
6	<b>1f</b>	Distearyl dodecanedioate	99	94
7 <sup>b</sup>	<b>2a</b>	Dicholesteryl sebacate	60	58
8 <sup>b</sup>	<b>2b</b>	Dicholesteryl dodecanedioate	56	51

<sup>a</sup>Yields obtained after crystallization from THF/MeOH. <sup>b</sup>Small amounts of toluene were used as a reaction solvent.

**Figure 4.** Reusability of the ionic liquid catalyst in the esterification reaction.

On the other hand, it was also investigated whether the developed methods are suitable for large-scale preparation of related diesters. Therefore, 15 g of sebacic acid was reacted with 27.6 g of lauryl alcohol in the presence of 2.5 mmol % of the catalyst. For the esterification reaction, the above reagents were heated at 110 °C for 16 h, and 32.1 g of dilauryl sebacate diester was obtained (81% yield).

## 2.1. Conclusions

For the synthesis of a series of long-chain diesters as potential PCMs, long-chain dicarboxylic acids and fatty alcohols or cholesterol at a ratio of 1:2 and in the presence of an ionic liquid catalyst were chemically esterified in a solvent-free medium. Relevant products were obtained in fairly good yields even after crystallization. The

corresponding compounds were also synthesized from dicarboxylic acids or dimethyl esters and fatty alcohols or cholesterol under similar conditions via transesterification reactions. In addition, catalyst reuse studies and large-scale synthesis of diesters were carried out and as a consequence the catalyst used in this work is also suitable for scale-up synthesis.

### 3. Experimental

#### 3.1. Reagents and chemicals

All reagents and solvents were purchased from either Merck or Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Thin-layer chromatography (TLC) was performed using silica gel plates (60 F254, Merck, Darmstadt, Germany). The catalyst 1-hexadecyl-3-sulfo-1*H*-imidazol-3-ium chloride [ $C_{16}ImSO_3H$ ]Cl was prepared according to the procedure given in the literature.<sup>27</sup>

#### 3.2. Analytical techniques

Melting points were recorded by BÜCHI melting point B-540 apparatus (BÜCHI Labortechnik AG, Flawil, Switzerland). The IR spectra were measured using a PerkinElmer Spectrum 100 spectrometer, while the NMR spectra were measured using a Bruker Avance NEO 600 MHz NMR spectrometer (Santa Clara, CA, USA) using tetramethylsilane (TMS) as internal standard. Chemical shifts ( $\delta$ ) are reported in ppm and *J* values in Hertz. The elemental analyses were performed using an LECO CHNS-932 elemental analyzer (St. Joseph, MI, USA).

#### 3.3. General esterification procedure

Into a reaction flask dicarboxylic acid and fatty alcohol or cholesterol were added at the ratio of 1:2, respectively. After addition of the ionic liquid catalyst (2.5 mmol %) the resulting mixture was heated with stirring at 110 °C for 16 h. At the end of this, the flask was cooled to room temperature and the resulting solid reaction mixture was crystallized from THF/MeOH to afford pure crystalline product.

#### 3.4. General transesterification procedure

Into a reaction flask dicarboxylic acid dimethyl ester and fatty alcohol or cholesterol were added at the ratio of 1:2, respectively. After addition of the ionic liquid catalyst (2.5 mmol %) the resulting mixture was heated with stirring at 110 °C for 16 h. At the end of this, the flask was cooled to room temperature and the resulting solid reaction mixture was crystallized from THF/MeOH to afford pure crystalline product.

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