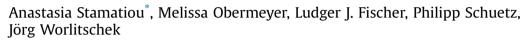
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# Investigation of unbranched, saturated, carboxylic esters as phase change materials



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# A R T I C L E I N F O

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## ABSTRACT

This study evaluates unbranched, saturated carboxylic esters with respect to their suitability to be used as storage media for latent heat storage applications. Therefore, important thermophysical properties are gathered both by means of literature research as well as by experimental measurements. Additionally esters are critically evaluated against other common phase change materials in terms of their environmental impact and their economic potential. The experimental investigations are performed for eleven selected ester samples with a focus on the determination of their melting temperature and their enthalpy of fusion using differential scanning calorimetry. Transient Hot Bridge was used to determine the thermal conductivity of the liquid samples while thermogravimetric analysis was employed for the evaluation of the 5% weight loss temperature as well as of the decomposition temperature of the nonvolatile samples.

Both experimental results and literature data reveal that the highest potential of esters against other phase change materials lies in low temperature applications where the main alternative is using salt hydrates.

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# 1. Introduction

In the course of the energy transition, the use of renewable energy resources is of growing interest for applications in the industry as well as in the building sector. In order to account for the fluctuating supply of renewable energies, storage systems will be of major importance for future energy supply systems [1]. More than 50% of the energy used in the European Union is dedicated to heating and cooling applications [2]. A big part of this energy consumption occurs at low and medium temperatures for space heating applications, production of domestic hot water as well as conditioning systems for offices, households or production and cooling processes in the industry [3–5]. The development of sustainable storage technologies at relevant temperature levels, that are associated with low costs in production and maintenance, and low environmental impact, is therefore an important research topic. Latent Heat Storage technologies (LHS), using Phase Change

\* Corresponding author. *E-mail address:* anastasia.stamatiou@hslu.ch (A. Stamatiou). Materials (PCM) allow for compact and reliable storage of thermal energy for a wide variety of applications [6,7].

A rough classification of PCMs can be made in terms of organic and inorganic substances [3]. The most widely considered inorganic PCMs, are salt hydrates which are generally characterised by a broad melting temperature range and relatively low purchase prices. However, salt hydrates show some disadvantages such as phase segregation and considerable supercooling effects which do not occur with pure substances [8]. The most commonly used organic PCMs are paraffin waxes which are generally characterised by high flammability and higher prices in a relatively limited melting point range. However, they present a high cyclability, low corrosiveness and low supercooling [3,9]. Carboxylic esters have been only briefly discussed as PCMs. They are expected to have similar thermal properties as paraffin waxes due to chemical similarity but very limited studies have been dedicated in the systematic evaluation of esters. In comparison to other PCMs, little research has been conducted in order to assess the suitability of carboxylic esters as PCMs for LHS applications. Table 1 compares some of the most common commercial PCMs with esters in terms of their thermal and physical properties based on the given references and own experience with





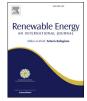


Table 1
Comparison of important PCM groups according to [3,8–10].

	Paraffin waxes	Salt hydrates	Carboxylic acids	Esters
Formula	$C_n H_{2n+2} (n = 12 - 38)$	AB*H <sub>2</sub> O	R-COOH	R-COO-R'
Phase change temperature	$T_{PC} = 12-71$ °C, increases with the amount of atoms	$T_{PC} = (-30) - 120 \ ^{\circ}C$	$T_{PC} = 0-150$ °C, increases with the amount of atoms	$T_{PC} = (-100)  200 \ ^{\circ}\text{C}$
Phase change enthalpy	$\Delta H_{PC} = 100{-}250 \text{ J/g}$	$\Delta H_{PC} = 200{-}400 \text{ J/g}$	$\Delta H_{PC} = 190230 \text{ J/g}$	$\Delta H_{PC} = 100{-}250 \text{ J/g}$
General characteristics	Organic, mixture of saturated hydrocarbons (i.e.: alkanes); most used commercial PCM	Inorganic salts with crystal water, mostly used at high T, probably most investigated PCM	Organic fatty acids, short-chain $(, long-chain (>C_6), acidic character decreases with increasing chain length$	Organic, synthesised from carboxylic acids and alcohols, little research on use as PCM to date
Advantages	Low toxicity, odourless, compatible with metal containers, chemically stable, no segregation, low supercooling, paraffin mixtures can be cheap	High heat capacity, high density, high conductivity, sharp $T_{PC}$ , in many cases low cost, soluble in water, not flammable	Low supercooling, low $\Delta V$ , chemically stable, molecules with C > 6 are non-toxic, in some cases produced from natural oils, relatively sharp T <sub>PC</sub>	In some cases produced from natural sources, low supercooling, high $\Delta H_{PC}$ , odourless, low $\Delta V$ , chemically stable, can form eutectic systems
Disadvantages	High price of pure paraffins, flammable, hydrophobic, problematic with plastics, high $\Delta V ~(\approx 10\%)$ , low $\lambda$ , low $\rho$ , low viscosity, non-congruent phase change in case of mixtures	Corrosive for many metals, high supercooling, phase- segregation, often toxic, high $\Delta V ~(\approx 10\%)$	Low conductivity, incompatible with many materials, short- chained are often odour- intensive and corrosive, relatively expensive, long- chained are problematic with plastics	Often low availability, flammable, limited information on properties available, low conductivity, short-chained are odour intensive and corrosive, long-chained are problematic with plastics, low density

the listed PCMs. The properties of esters compare well with the properties of commonly used PCMs. One of the main barriers for their further investigation and implementation is the lack of high purity commercial esters and, in the few cases where they can be commercially purchased, their high price.

Carboxylic esters belong to the carbonyl compounds, i.e. they contain a carbon-oxygen double bond within their structure. This carbonyl group is highly polarised due to the difference in electronegativity present between the oxygen atom and the carbon atom [11]. The degree of polarisation as well as the chain length of the carbon chain influence the reactivity of the molecule: nevertheless it can be stated that esters are of medium reactivity. They are synthesised from carboxylic acids and alcohols mostly with a balanced, catalytic reaction called esterification or alcoholysis [12]. The catalyst usually is a strong, inorganic acid such as sulphuric acid. The yield of the synthesis can be shifted towards the ester by using the alcohol in excess and by continuous removal of the produced water from the reaction mixture. Carboxylic esters exist in a wide range of different configurations such as:

- Mono-, Di-, Tri-, and Polyesters
- Unbranched and branched esters
- Saturated and Mono-, Di-, Tri-, and Polyunsaturated esters
- Cyclic or linear esters

Riemenschneider and Bolt [13], give an extensive review of the properties, production methods and applications of esters stating that certain types of esters can be found in nature. Similar to paraffins, most organic esters are flammable (moderately flammable according to [14]). They further have limitations in terms of storage and transportation materials made of plastic, as mainly long-chained esters are highly lipophilic. On the other hand, the compatibility of esters is ensured with all types of metals and their alloys. Shorter esters frequently occur in fruits leading to their distinct odour and longer esters are found, amongst others, in fats and oils [11]. Nevertheless, carboxylic esters are considered toxic in larger quantities and they may cause harm to human health [15].

Esters formed from lower alcohols (up to  $C_5$ ) have been investigated with respect to their thermochemical properties and a series of experimental data on melting- and boiling temperatures as well as on densities is readily available from different sources [16–19]. Esters formed of longer alcohols, however, have been barely characterised by experimental data to this date. Limited previous studies have been conducted on the topic of esters as PCMs. Feldman, Banu and Hawes [20] considered esters to be promising storage media candidates for LHS systems as they show little to no supercooling, high chemical and thermal stability and no corrosiveness. This is supported by Karaipekli and Sari [21] who attribute good thermal and physical properties to esters. Aydin et al. [22,23] declare fatty acid esters (i.e.: long-chained carboxylic esters) as a rather new type of organic PCMs and recognise the lack of data availability in the literature. Their latter study mainly focused on a few representatives of high chain fatty acid esters formed of 1-octadecanol and myristyl alcohol.

This paper aims to expand the set of data available for esters, to enable an educated assessment of their suitability as novel phase change materials for latent heat storage technologies. For this first study, one of the least complex configurations of carboxylic esters was considered, which are linear, unbranched and saturated monoesters. A set of eleven esters was chosen based on their commercial availability in high purities and their distribution across different phase change temperatures. These eleven esters covered molecular weights from 88 g/mol to 510 g/mol and melting temperatures from -78 °C to 55 °C. Beside the assessment of the thermal properties of these materials, their environmental impact was evaluated and some economic data were collected.

### 2. Materials and methods

#### 2.1. Materials

The materials used were purchased from Sigma-Aldrich in purities ranging between 95% and 99%. The eleven selected esters are presented in Table 2. They were used for the analyses applied in this study without further processing and purification.

#### 2.2. Experimental methods

Fourier transform infrared spectroscopy (FTIR) spectra of the purchased carboxylic esters were collected to test the purity of the purchased substances [22]. An Agilent Cary 630 with an attenuated total reflection attachment was used. The spectra were recorded between wavelengths of 4000 and 600 cm<sup>-1</sup>.

Thermal conductivity measurements were conducted using a

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