Ionic compounds derived from crude glycerol: Thermal energy storage capability evaluation

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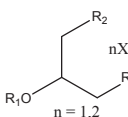
ABSTRACT

Ionic liquids (diimidazol-1-ium esters) prepared from wastes, crude glycerol and carboxylic acids are investigated as potential phase change materials (PCM). The ionic liquids (IL) with best thermophysical properties were those with also better production yield (higher than 75%). The chemical composition of those IL was [structure diagram] with R_1 being $(CH_3)_3CCO$, $CH_3(CH_2)_{14}CO$ or C_2H_3CO; R_2 being BIM^+; R_3 being BIM^+; and X-being 2 Cl^-. Phase change of state (solid-liquid) of this IL was 85 °C, 264 °C and 128 °C, which means potential application in different fields such as domestic hot water, solar cooling and industry, respectively. The measured melting enthalpy 328 kJ/kg, 408 kJ/kg, and 660 kJ/kg is much higher in all cases than the usual found in commercial PCM (100 kJ/kg), therefore, these ILs synthetized in this study are proper candidates to be used as PCM because of the huge amounts of energy that they are able to store and their low cost. Moreover, biobPCM are sustainable materials since its obtaining process is based on oil.

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1. Introduction

Renewable chemicals reduce greenhouse gas emissions, along with other pollutant emissions associated with the supply, processing, and use of petroleum and petrochemicals. Consumer demand for renewable goods and the economic competitiveness of biorefining compared to petroleum refining are beginning to pull the market for new biotechnology applications. By 2021, the global market for biobased chemicals and materials alone is expected to increase to $12.2 billion, accounting for 10.9×10^9 kg of biorefining production [1]. One of its applications is in the preparation of phase change materials (PCM) to be used in thermal energy storage [2,3]. PCM are used in ceiling and wall panels working day and night to stabilize indoor temperatures [4,5] leading to better indoors thermal comfort; and they have been implemented for cold storage [6], domestic hot water (DHW) [7], solar cooling [8], solar concentrated power plants [9], etc. In 2013, the PCM market was quantified in 480.8 million dollars and is expected to reach 1765.8 million in 2020 with an annual compound growth rate of 20.7% [10]. The market can be segmented by three major product categories: paraffin (45%), salt hydrates (33%) and PCM based on biomass (biobPCM) (22%). There are already several commercial products of the above categories, and all of them have advantages and disadvantages, but their main feature is the heat storage capacity. Those with a latent heat storage capacity (ΔH) higher than 100−120 kJ/kg are considered adequate candidates to be used as PCM and this is the typical thermal energy storage capacity of commercial PCM [2,3].

BiobPCM is one of the efficient ways of storing thermal energy from abundant bio-based materials and present higher latent heat values than paraffin [11]. Fatty acids and fatty esters are the main components of these materials [12]. Fatty acids and ester can be obtained from various sources such as by-products and wastes from

oil-crops, fat and oil industries and meat processing companies. By-products and wastes from oil-crops account for 1×10^9 kg/year worldwide, which means producing 5×10^{11} kg/year oil-crops. Moreover, meat waste in Spain accounts for 2×10^9 kg/year containing roughly 1×10^7 kg/year of animal fats [13]. These wastes typically are more homogenous and constant in composition, when compared to the others and they might be used to prepare bio-bPCM. The authors of this paper have already shown that crude glycerol and waste fat and vegetable oils can be used to prepare dihalopropyl esters [14–16].

Recently, ionic liquids (IL) have also been proposed for thermal storage applications [17]. IL are versatile compounds with multiple applications such as solvents [18], in chemical and enzymatic catalysis [19], in carbon dioxide capture and separation, in hydrogen generation, in converting thermal energy into electrical energy, for electrochemical energy storage, and for converting electrical energy into mechanical energy. Moreover, ILs have thermophysical and chemical properties that may be suitable to be used as heat transfer fluid (HTF) in power plants using parabolic trough solar collectors as stated by Van Valkenburg et al. [20]. Moreover, Reddy et al. [21] has studied the thermal stability corrosion effect of ILs when used as HTF. Furthermore, Matic and Scrosati [22], and MacFarlane [17] have recently defined several energy applications of ILs. In addition, depending on the property being investigated, changes in the chemical character of the cation and anion (size, charge distribution, metal complexing, lipophilicity, etc.) and the nature of substituted functional groups can have markedly different effects. This offers various different design points to construct ions with a specific subset of properties [17]. The possibility of performing hydrogen bonds has been proposed as one of the characteristics to consider in the design of IL for thermal storage applications [23]. Recently, we have described the synthesis of the IL 1,1'-(2-hydroxypropane-1,3-diyl)-bis(3-butylimidazol-1-ium) and 1,10-(2-(acryloyloxy)propane-1,3-diyl)-bis(3-butylimidazol-1-ium) salts starting from glycerol derivatives [24].

Joining both concepts, preparation of dihalopropyl esters from crude glycerol and wastes as precursors of IL, and the potentiality of IL in thermal energy storage, led to the aim of the present study: assessing the thermal storage capability of these two ionic compounds described above and a new set of ionic compounds prepared also from crude glycerol and various carboxylic acids described in authors their Spanish patent [25]. A preliminary study on the effect of the chemical character of the cation and anion on the thermal storage capability of these new ionic compounds is also presented. This set of compounds and their use as biobPCM are patent pending.

2. Materials and methods

2.1. Materials and reagents

Acrylic, 1-naphtyl carboxylic, palmitic and pivalic acids were purchased from Sigma-Aldrich (Sigma-Aldrich Quimica, S.A., Madrid, Spain). Chlorotrimethylsilane (CTMS) was also from Sigma-Aldrich (Sigma-Aldrich Quimica, S.A., Madrid, Spain). Hexane, methanol, ethanol, acetone, acetonitrile, ethyl ether, isopropanol, and dichloromethane were supplied by J. T. Baker (Quimega, Lleida, Spain). 1,3-Dichloro-2-propanol, N,N-dicyclohexylcarbodiimide (DCC), and potassium hexafluorophosphate (KPF$_6$) were supplied by Across Organics (Barcelona, Spain). Potassium hydroxide was purchased from Panreac (Barcelona, Spain).

Crude glycerol was obtained from a biodiesel industrial supplier that used an alkali-catalyzed alcoholysis procedure (Raluy S.L., Spain). Crude glycerol was neutralized using sulfuric acid, and most of the residual methanol was removed by distillation under vacuum. Finally, the remaining material was centrifuged at 2600 g and decanted to remove any solids in the suspension. The final product was analyzed using ^{1}H NMR in deuterated dimethylsulfoxide using N,N-dimethylformamide as an internal standard. The final substrate was glycerol rich to c. a. 90%.

2.2. Ionic liquids synthesis procedures

2.2.1. General procedure for the syntheses of 2-chloro-1-(chloromethyl)ethyl esters

Carboxylic acid (1 mmol), glycerol (184 mg, 2 mmol) and chlorotrimethylsilane (CTMS) (540 mg, 5 mmol) were added to a reaction vial fitted with a polytetrafluoroethylene-lined cap. The mixture was stirred and heated at 80 °C for 48 h. After cooling, an organic solvent was added, and the mixture was washed three times with water. The organic layer was dried over anhydrous MgSO$_4$ and the solvent was evaporated under vacuum. The residue was purified by crystallization, distillation, or dry flash column chromatography on silica gel. The corresponding compound was identified by ^{1}H NMR and ^{13}C NMR and yield was calculated. This percentage is a common quantitative method to perform quantitative analysis using ^{1}HNMR where the areas of the peaks of hydrogen atoms observed in the spectrum can be quantitatively compared. Therefore, the purity of a chemical compound can be determined by ^{1}H NMR using internal standards and following Eq. (1). The area of a signal corresponding to given hydrogen atoms can be determined and compared with the signal area of hydrogens present in the internal standard. The purity is commonly calculated by the software that controlled the ^{1}H NMR device.

$$Purity(\%) = \frac{S_{sample}}{S_{st}} \cdot \frac{N_{st}}{N_{sample}} \cdot \frac{m_{st}}{m_{sample}} \cdot \frac{M_{sample}}{M_{st}} \cdot P_{st} \cdot 100 \qquad (1)$$

S = Area of the NMR signal used to perform the quantification.
N = Number of atoms (H) responsible of the NMR signal used to perform the quantification.
m = mass used for performing the analysis.
M = molecular weight.
st = parameter corresponding to the internal standard used.
P$_{st}$ = purity of the internal standard used.

The mentioned compounds were used to prepare N-butylimidazole derivatives, intermediates of the compounds corresponding to samples M1, M5, M7 and M11 in Table 1 as described in 2.2.3.

2.2.2. Procedure for the syntheses of 3-chloro-2-hydroxy-1-propyl 2,2-dimethylpropanoate

A solution of 2-chloro-1-(chloromethyl)ethyl 2,2-dimethylpropanoate (5.08 g, 24 mmol), water (0.7 mL, 38.4 mmol) and sodium carbonate (2.54 g, 24 mmol) in dried 1,4-dioxane (72 mL) was stirred and heated at 115 °C for 48 h in a capped reactor. After cooling to room temperature, dichloromethane was added and the mixture was washed three times with water. The organic layer was dried over anhydrous MgSO$_4$, and the mixture was distilled to yield 2.9 g of the desired compound (62% yield) b. p.: 70 °C/40 Pa. The compound was identified by ^{1}H NMR and ^{13}C NMR and subsequently used to prepare the corresponding N-butylimidazole derivative, entry M3 in Table 1, following the procedure described in 2.2.3.