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New sugar alcohols mixtures for long-term thermal energy storage applications at temperatures between 70 °C and 100 °C

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ABSTRACT

Sugar alcohols (SA) are attractive phase change materials for long-term thermal energy storage (TES) applications at low-to-medium temperatures, as i.e. solar seasonal energy storage. Most of them undergo severe undercooling, thus allowing energy storage at temperatures far below the melting point with thermal losses reduction. Besides, some of them could provide very high volumetric energy density at affordable cost. However, sugar alcohols with high latent heat of fusion often exhibit melting temperatures above 100 °C. The objective of this work was to found out new sugar alcohol eutectic mixtures that display lower temperatures without significant reduction of the latent heat. A comprehensive analysis of SA relevant properties for TES has been carried out in order to select the most appropriate single SA for mixtures analysis. Sixteen SA-based binary systems have been investigated. Their corresponding phase diagrams have been experimentally and theoretically established. Four eutectic mixtures with potential for long-term TES at temperature around 80 °C have been identified. They are: 1) adonitol-erythritol at 30 mol% of erythritol, with melting temperature of 87 °C and latent heat of fusion of 254 J/g; 2) arabitol-erythritol at 40 mol% of erythritol, with melting temperature of 86 °C and latent heat of fusion of 225 J/g; 3) xylitol-erythritol at 36 mol% of erythritol, with melting temperature of 82 °C and latent heat of fusion of 270 J/g; and 4) arabitol-xylitol at 56 mol% of xylitol, with melting temperature of 77 °C and latent heat of fusion of 243 J/g.

1. Introduction

Phase change materials (PCMs) used for the storage of thermal energy as latent heat are an important class of modern materials which substantially contribute to the efficient use and conservation of waste heat and solar energy. The storage of latent heat provides a greater density of energy storage with a smaller temperature difference between storing and releasing heat than the sensible heat storage method. Many different groups of materials have been investigated during the technical evolution of PCMs, including inorganic systems (salt and salt hydrates), organic compounds such as paraffin waxes, fatty acids or sugar alcohols and polymeric materials, e.g. poly(ethylene glycol). Extensive work has been reported in the literature on the selection, characterization and applications of PCMs. For comprehensive details, readers are referred to recent review articles [1–6].

Sugar alcohols (SA), also called polyalcohols or polyols, have received less attention than other organic materials in the thermal energy storage (TES) literature. The reason is that the majority of SA have melting temperatures between 90 and 200 °C putting them outside the range of the main applications that have been considered so far, including solar heating (or cooling) of buildings, thermal comfort in dwellings/workspaces and domestic hot water (DHW) production. Some of the first proposed uses of polyalcohols as PCMs are described in a patent by Guex et al. (1981) on the use of xylitol as heat storage material [7] and in a patent by Hormansdorfer (1989) on the use of pure or blended polyols for tailored TES [8]. They noted that some of the polyalcohols have volumetric latent heat values as much as twice that of other organic materials, while still possessing the non-toxic and non-corrosive properties of paraffins. Besides, SA are bio-sourced and non-flammable materials.

Recently, much attention has been paid to the development of new PCMs for storage applications at medium temperatures (100–200 °C). Therefore, the use of SA as a TES materials has regained interest. Among sugar alcohols, erythritol has received the most attention so far. It is characterized by a melting temperature

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around 118 °C and relatively large latent heat of 340 J/g, which is almost equivalent to that of the phase change of ice to water [9,10]. It has been used in various applications such as waste-heat transportation [10–12], solar cookers [13,14], absorption chillers [15], and as an automotive coolant waste heat storage system [16]. The thermal stability of erythritol under repeated phase change cycles has been studied by several authors and proved to be excellent [11,17]. As many other SA, erythritol may undergo severe undercooling. However, Ona et al. [18] reported that ultrasound was effective to relax supercooling. Erytritol-based composite PCMs with improved thermal conductivity were also recently proposed [19,20].

Because the melting point of erythritol is relatively low to utilize heat sources at around 200 °C, other sugar alcohols have also been studied as new PCM candidates, including mannitol [11,21–26], dulcitol [24–26], myo-inositol [24,26]. The major concerns with these SA is thermal and chemical stability. Myo-inositol was found to have a relatively high cyclic thermal stability when analyzed between 150 °C and 260 °C [24]. On the contrary, dulcitol and mannitol show poor thermal cyclic stability [24] and poor thermal endurance [26]. Significant improvement of mannitol thermal endurance has been recently achieved by impregnation into nanosized pores of porous SiO_2 grains [27]. Mixtures of mannitol and dulcitol were explored as potential phase change materials for use in medium temperature by Paul et al. [25] and Nomura et al. [27]. The SA were found to form a eutectic mixture at dulcitol to mannitol molar ratio of 30:70, which melts at around 155 °C with latent heat of 290 J/g. Besides, the eutectic mixture displayed good cyclic, thermal, and chemical stability compared to its individual components under nitrogen or air. Inositol/Mannitol and Inositol/Dulcitol/Mannitol mixtures were also investigated by Nagasaka [28] and Nomura et al. [27]. Eutectic mixtures with melting point and latent heat of (160 °C, 241 J/g) and (150 °C, 222 J/g) were identified respectively in Inositol/Mannitol and Inositol/Dulcitol/Mannitol systems. As before, the degradation rates of eutectic mixtures were significantly smaller than those of single-component sugar alcohols.

Another promising direction of research consists in developing new SA mixtures for storage application at temperatures below 100 °C (e.g. solar heating and DHW, district heating). In general, sugar alcohols with high heats of fusion often exhibit high melting temperatures (> 100 °C), which limits the choice of heat transfer fluids to be used in conjunction with sugar alcohol based thermal storage media. This is particularly annoying in solar heating and DHW applications, where cheap water-based solar collectors are required. Hence, there is a need to develop SA-based PCMs that display relatively low melting temperatures without significant reduction of the heats of fusion. The phase diagrams of the following binary systems have been investigated for their use in the pharmaceutical and food industries: xylitol/sorbitol [29], xylitol/mannitol [29], sorbitol/mannitol [29–31] and sorbitol/maltitol [30]. Only xylitol/sorbitol seems to have potential interest for TES applications. Indeed, xylitol and sorbitol form an eutectic mixture (molar ratio of 50:50) at 76 °C with latent heat of melting of 196 J/g [29]. In the TES field, Hidaka et al. [32] investigated different erythritol-polyalcohol mixtures for heat storage in the temperature range between 80 °C and 100 °C. Two mixtures containing erythritol, trimethylethane (TME) and trimethylpropane (TMP) with suitable range of melting temperature and relatively high latent heat (231/246 J/g) were found out. However, both mixtures show non-congruent melting. Nakada et al. [33] established the phase diagrams of erythritol/TME, erythritol/TMP, erytritol/EMPD and erythritol/xylitol systems. Erythritol and Xylitol were found to form a eutectic mixture at 0.67 of xylitol molar fraction, which has melting point of 87 °C and latent heat of melting of 263 J/g. Diarce et al. [34] studied erythritol/xylitol, erythritol/sorbitol and xylitol/sorbitol systems as well. The corresponding eutectic composition, eutectic melting temperature and latent heat of melting values are consistent with previous results by Hidaka et al. [32] and Nakada et al. [33]. Regarding melting temperatures (84 °C, 87 °C and 75 °C respectively), enthalpies of fusion (248 J/g, 173 J/g and 169 J/g) and market prices (5.2 €/kg, 1.5 €/kg and 3 €/kg), the three eutectic mixtures seem suitable TES materials for heating and DHW applications. However, experimental measurements performed by polarized thermomicroscopy showed that the mixtures presented a low crystallization rate, which limits their use in short term TES systems.

In the recent European project SAM.SSA (FP7 2012–2015; www.samssa.eu/) new sugar alcohol-based materials for solar thermal seasonal storage applications in the range of temperatures between 80 °C and 100 °C have been developed and studied in-depth. Contrary to short-term TES, long term storage requires PCMs undergoing stable and severe undercooling like most of SA. This allows reducing thermal losses by storing the energy at temperatures far below the melting point while minimizing the risk of spontaneous crystallization during the long period of storage. SAM.SSA developments include new SA-based eutectic mixtures lowering the original high temperatures of the single materials, low-cost tailor-made carbon porous structures and corresponding carbon/SA composites with enhanced thermal conductivity, and SA micro-encapsulation [35]. A new appealing solution for efficient SA crystallization was also established [36].

Herein, we report the work carried out in SAM.SSA project regarding SA mixtures selection. In general, adjustment of the melting point of a PCM can be achieved by disrupting the crystal arrangement and weakening the intermolecular interactions by adding impurities. Another way of controlling the melting point is by single compounds mixing. It is well-known that an eutectic mixture exhibit a lower melting point than either of its constituents while still melting congruently. The ultimate objective of this study was hence to propose SA-based eutectic mixtures with melting point bellow 100 °C, high latent heat and severe and stable undercooling. Section 2 provides a comprehensive analysis of SA relevant properties for TES and leads to the selection of single SA for mixtures analysis. The materials, the methodology and the experimental and theoretical methods used in the search of eutectic mixtures are described in Section 3. Sixteen SA-based binary systems have been investigated. Their corresponding phase diagrams have been experimentally and theoretically established. Four eutectic mixtures with potential for long-term TES at temperatures between 80 °C and 100 °C have been identified. The results achieved are presented and discussed in Section 4. Full-characterization of the selected mixture, including measurement of key thermodynamics and physical properties as well as crystallization kinetics analysis, will be published elsewhere.

2. Selection of single sugar alcohols for mixtures

2.1. Data base employed

Sugar alcohols are a sub-class of carbohydrates whose defining characteristic is the occurrence of an alcohol group (> CH–OH) in place of the carbonyl group (> C=O) in the aldose and ketose moieties of mono-, di-, oligo- and polysaccharides. Some polyols are found naturally in various fruits and vegetables. However, most of them are produced by chemical reduction of carbohydrates. Most commonly used carbohydrate sources are corn starch, sugarcane/beets, plant gums and whey. The production of polyurethane is the largest and the oldest industrial application of SA. They are also widely used nowadays in the pharmaceutical and food industries. More than 900 polyols are listed in the dictionary