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Ternary mixture of fatty acids as phase change materials for thermal energy storage applications

Karunesh Kant *, A. Shukla, Atul Sharma

Non-conventional Energy Laboratory, Rajiv Gandhi Institute of Petroleum Technology, Rae Bareli-(UP), India

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ABSTRACT

The present study deals with the development of ternary mixtures of fatty acids for low temperature thermal energy storage applications. The commercial grade fatty acids such as Capric Acid (CA), Lauric Acid (LA), Palmitic Acid (PA) and Stearic Acid (SA), have been used to prepare stable, solid–liquid phase change material (PCM) for the same. In this regard, a series of ternary mixture i.e. CA–LA–SA (CLS) and CA–PA–SA (CPS) have been developed with different weight percentages. Thermal characteristics of these developed ternary mixture i.e. melting temperature and latent heat of fusion have been measured by using Differential Scanning Calorimeter (DSC) technique. The synthesized materials are found to have melting temperature in the range of 14–21 °C (along with adequate amount of latent heat of fusion), which may be quite useful for several low temperature thermal energy storage applications.

1. Introduction

Due to the fast depleting fossil fuel resources and ever increasing global energy requirement, the efficient usage of solar energy has become more than essential. The availability of solar energy is quite abundant, though intermittent in nature. Due to its intermittent nature solar energy can be stored in form of thermal energy as well for various domestic as well as industrial requirements. The thermal energy thus received through solar radiations can be stored by several methods such as sensible heat storage and latent heat storage (LHS) (Kant et al., 2016b). These LHS materials are commonly known as phase change materials (PCM). The importance of using fatty acid as PCM for thermal energy storage has risen in recent times as; they have desired thermodynamic and kinetic criteria for low-temperature LHS (Feldman et al., 1989) such as solar drying (Kant et al., 2016b), solar desalination etc. (Al-Hamadani and Shukla, 2012). Fatty acids have few superior properties over many other available PCMs, namely—good chemical stability, melting congruency, non-toxicity and most important is their smaller volume change in the course of phase transition. There is a further value addition in the use of fatty acids due to high latent heat of fusion per unit mass and appropriate melting temperature range for solar passive heating applications (i.e. solar dryer, solar greenhouse and solar desalination etc.). Moreover, since fatty acids are mainly derived from common vegetable and animal oils hence these are abundantly available and offer an assurance of continuous supply (Al-Hamadani and Shukla, 2012; Cedeño et al., 2001; Feldman et al., 1989; Kant et al., 2016b). Amongst the majorly studied fatty acids, the Capric acid, Lauric acid, Palmitic acid and Stearic acid are possible materials for heat storage in solar space and water heating systems (Chen et al., 2008; Kant et al., 2016a; Sari and Kaygusuz, 2002).

Yang et al. (2014) prepared ternary eutectic mixture using Myristic acid, Palmitic acid and Stearic acid (MA–PA–SA) with a mass ratio of MA:PA:SA = 52.2:29.4:18.4 and further MA–PA–SA/expanded graphite (EG) composite PCM with an optimum mass ratio of MA–PA–SA: EG = 13:1 and characterized by DSC. Li et al. (2011) prepared a chain of binary PCM by mixing Decanoic (Capric) acid, Dodecanoic (Lauric) acid, Hexadecanoic (Palmitic) acid and Octadecanoic (Stearic) acid and observed that the Decanoic–Dodecanoic acid is uniformly adsorbed into diatomite and formed stable PCM. He et al. (2013) investigated the effect of the compounding condition of Stearic Acid and Myristic acid at different weight ratios. Shilei et al. (2006) prepared eutectic mixtures of Capric acid and Lauric acid for application of building wallboard and found that Capric acid; Lauric acid with mass ratio 65.12% and 34.88% respectively were suitable for this application. Sharma et al. (2014) developed binary eutectics mixture of fatty acids i.e. Lauric, Myristic, Palmitic and Stearic acid in different ratio.

* Corresponding author. Fax: +91 535 2211 888.
E-mail addresses: k1091kant@gmail.com (K. Kant), amritanshu.shukla@gmail.com (A. Shukla).

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The major concern regarding TES systems (such as solar thermal energy storage, central air-conditioning systems, energy-efficient buildings, industrial waste heat recovery, temperature-adapted greenhouses and thermo-regulating fibers) is the limited availability of suitable PCMs for low-temperature applications along with their long-term thermal stability (Shukla et al., 2016). In last few decades, a lot of research has been devoted in this area, but still, there is a large need of developing more commercially viable PCMs, having low melting temperature in the range of 15–25 °C with high latent heat of fusion for the application of biomedical usage, central air condition systems etc. Such materials should be easily available in the market and cost effective too. The production cost of binary or ternary fatty acids as PCMs is affected mainly by the practical compounding conditions and constituent material costs and these materials could be high in demand (Hasan et al., 2014, 2010; Huang et al., 2011; Sharma et al., 2013).

The phase change temperatures of fatty acids can be adjusted by mixing fatty acids in suitable proportion. Appropriate phase change temperature and a high latent heat of fusion are two essential requirements for developed mixture to be a useful PCM. Therefore, in recent times, research work is mainly focused towards the synthesis of solid–liquid PCMs which could develop high quality PCMs. For the present study, commercial grade CA, LA, PA and SA were identified due to their high latent heat capability, suitable heat transfer characteristics during the melting and solidification process and low cost. However the phase changes temperatures of these PCMs does not allow these materials to be employed directly for many thermal energy storage applications. Hence, the ternary mixtures based on commercial grade fatty acids (CA, LA, PA and SA) were developed with different weight percentages as specified in Tables 2 and 3 and their thermal properties were measured through the DSC method. The PCMs thus developed can be used for low-temperature thermal energy storage applications and may easily be made commercially available.

2. Materials and methods

For the present study, commercial grade (purity >98%) CA, LA, PA and SA, supplied from the Burgoyne Pvt. Ltd. Kanpur company were used without sanitization. To develop novel PCMs, a series of ternary mixtures, i.e., (CA–LA–SA, CA–PA–SA) were prepared with different weight percentages. The materials with different weight ratios according to sample were taken in the beaker and heated up to 80 °C and kept at the same temperature for 15 min for proper mixing. Forty-three samples (100 g each) were prepared by mixing in melted state, retained at room temperature for half an hour. A semi-analytical digital balance (accuracy ±0.0001 g) was used to weigh up the samples (g).

3. Measurement techniques of latent heat of fusion and melting temperature

The main thermal properties of PCMs are the latent heat of fusion, melting and solidification temperatures. The DSC method is used for measurement of melting temperature and latent heat of fusion of fatty acids and their ternary mixtures. In DSC, sample (to be measured) and reference materials both are heated at a constant rate. The temperature difference between the both is proportional to the variance in heat flow between the two materials and is recorded in the DSC curve. The latent heat of fusion of the material is measured by using the area below the peak and melting temperature is measured by the tangent at the point of maximum slope on the face part of the peak. Thermal properties of the developed ternary mixture were measured by DSC 4000 supplied by Perkin Elmer at 2 °C min^{-1} under a continuous stream of nitrogen with a flow rate of 20 ml min^{-1}. The largest variation in enthalpy measurements was found to be ±2% (Sharma et al., 2014) and the maximum deviation in temperature measurements was ±0.10 °C. A semi-analytical digital balance was used to measure the mass of the ternary mixture in milligram for the DSC study. Thermal properties i.e. melting point (T_m), according to ICTAC standards onset of the melt peak is melting point for metals, organics, and similar materials, but the peak value should be used for polymers (PerkinElmer, 2014), melting peak (ˆ represents peak temperature, which corresponds to complete melting in organics (PerkinElmer, 2014).) latent heat of fusion (λ_m) and crystallization (λ_f) of fatty acids obtained from market measured by DSC for thermal energy storage applications and data as provided by the manufacturers are given in Table 1.

4. Results and discussion

As discussed in previous section, four different fatty acids with thermo-physical properties as following, i.e., CA (T_m = 30.61 °C, λ = 154.42 kJ/kg), LA (T_m = 43.5 °C, λ = 175.77 kJ/kg), PA (T_m = 61.62 °C, λ = 206.11 kJ/kg) and SA (T_m = 54.83 °C, λ = 180.79 kJ/kg) were used in this research work for developing the ternary mixture samples. Total of forty three ternary mixture samples were prepared in the laboratory for CA–LA–SA and CA–PA–SA composition to find out their onset melting temperature and latent heat of fusion through DSC analysis technique with a scan rate of 2 °C/min and data obtained from the DSC for CA–LA–SA and CA–PA–SA is also given in Tables 2 and 3 respectively. In the same table the estimated cost of the PCMs in US$ has also been given so as to see the commercial viability of the developed PCMs. As occurs with fatty acids and Acetamide, it was difficult to find approaches to estimate melting temperature and latent heat of fusion in mixtures. It was also observed that melting temperature of a mixture of fatty acids is always lower in the fatty acid (Rathod and Banerjee, 2013). The behavior of temperature versus composition in binary mixtures of fatty acids, where the presence of minimum melting points is observed; it is demonstrated that the behavior of fatty acid mixtures was completely non-ideal. The same was observed in this research work also. The present research work also demonstrates the heterogeneity of fatty acid mixtures and find out the different T_m and λ_m value of heterogeneous mixture.

4.1. Melting temperature and latent heat for ternary mixture of Capric, Lauric and Stearic acid

Twenty two samples of the ternary mixture of fatty acids were prepared with different weight ratio of CA, LA and SA. The first peak of the ternary mixture of CLS-316, CLS-325, CLS-334, and CLS-343 is found at the onset melting temperature of 13.64 °C, 14.56 °C, 15.85 °C and 15.48 °C and second was at 43.60 °C, 38.31 °C, 29.39 °C and 28.65 °C respectively. From the results displayed in the tables, it can also be seen that the secondary peak of the mixtures was shifted towards the lower melting temperature with the increase in the weight ratio of Lauric Acid and decreasing weight ratio of the Stearic acid. It was also seen that the latent heat of fusion for secondary peak was decreasing as the weight fraction of the Lauric Acid increases. The reason for this happening is the merging of the second peak into the first peak; therefore the value of the latent heat of fusion gets shifted to lower value.

For the CLS-352 and CLS-361, the secondary peak was completely disappeared and melting temperature and latent heat of fusion was measured 16.88 °C, 16.41 °C and 129.60 kJ/kg, 174.99 kJ/kg respectively. For, CLS-343, CLS-334 two peaks were found in the DSC curve, however, both melting temperature range can be utilized for the cooling application, therefore, CLS-343, CL-334, CLS-352, CLS-361 can be used for LHS.

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