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Thermophysical properties of $Ca(NO_3)_2$-$NaNO_3$-KNO_3 mixtures for heat transfer and thermal storage

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ABSTRACT

In this study calcium nitrate, sodium nitrate, and potassium nitrate were mixed to form cheap ternary molten salts based on different weight ratios. These molten salts can be used as both sensible heat storage materials and latent heat storage materials. In addition, they can be directly used as heat transfer fluids due to their low freezing temperatures. The results indicated that the mixture ($Ca(NO_3)_2$:$NaNO_3$:KNO_3 = 32:24:44 wt%) had the best performance for latent heat storage with its enthalpy of 67 J/g and melting point of about 80 °C. The specific heat capacity (1.7 J/(g °C) for the solid phase and 1.2 J/(g °C) for the liquid phase), viscosity (next to zero at 200 °C), thermal conductivity (about 1–3 W/(m K)), thermal decomposition, and cycle stability of the molten salts were measured by DSC, Malvern Kinexus Ultra+, a transient plane thermal conductivity meter, STA, and XRD, respectively. The thermophysical properties including the low manufacturing cost showed that the molten salts have great potential applications in thermal storage systems.

1. Introduction

Because of the disparity between energy supply and demand, thermal storage plays a crucial role in renewable energy and industrial waste heat recovery. Heat storage technology and heat transfer fluids are very important components in thermal storage. Heat storage technology, can be classified as latent heat storage, sensible heat storage, thermochemical heat storage, and adsorptive heat storage (Sharma et al., 2009; Zhao and Tian, 2013). Among the four kinds of technology, latent heat storage has received much attention in recent decades because it has merits such as large heat capacity, and no significant temperature variation in the process of phase transition (Zuo et al., 2005). Heat transfer fluid (HTF), is an important component of thermal-energy storage (TES) systems. The main energy storage system is based on a sensible energy storage system, which is equipped with two tanks: a "cold" tank to collect solar heat and a "hot" tank to store thermal energy (Kearney et al., 2002; Kearney, 2004). If the storage system in these tanks is direct, the heat transfer fluid can also be used as a storage medium (Javier Ruiz-Cabarias et al., 2017).

For both latent heat storage and heat transfer technology, the materials have a predominant effect on their use. In the case of latent heat storage, phase-change material selection is very crucial (Yan et al., 2015) and preparation and characterization of phase-change materials have been investigated by many researchers. Paul et al. (2015)studied a eutectic mixture of galactitol and mannitol. When the molar ratio of galactitol and mannitol is 3:7, they have a melting point of 153 °C and a high latent heat of fusion (292 J/g). Warzoha et al. (2015) implemented random HGNF(herringbone style graphite nanofibers) into paraffin (IGI 1230A) and quantified the effect of HGNF on the paraffin in both solid and liquid phases. Lee et al. (2014) investigated the thermal characterization of EG (expanded graphite) and the composition of EG and erythritol. They found that the latent heat and thermal conductivity improved with an increase of the EG interlayer distance under the assistance of the thermal equilibrium technique. Zhao et al. (2015) studied binary nitrate salt mixtures consisting of $NaNO_3$ and $Ca(NO_3)_2$ with different molar ratios. They found that when the molar ratio is 3:7 ($Ca(NO_3)_2$:$NaNO_3$), the sample has the best heat storage performance and this ratio is considered as the best eutectic composition. Roget et al. (1980) investigated a binary molten salt ($LiNO_3$-$NaNO_3$) and a ternary molten salt ($LiNO_3$-KNO_3-$NaNO_3$). They measured their physical properties such as thermal cycle stability, corrosion, and enthalpy. Judith and Calvet (2013) investigated a molten salt mixture which combined KNO_3, $NaNO_3$, and $Ca(NO_3)_2$ and the best composition was considered to be 36 wt % $Ca(NO_3)_2$, 16 wt% $NaNO_3$, and 48 wt% KNO_3. In t most of the commercial solar thermal power plants, synthetic oil is used as the heat transfer fluid. But the high price of synthetic oil poses a huge limitation on its utilization. In order to remedy this, recent heat transfer fluids use inorganic molten salts. From the 1980s, a molten

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nitrate salt mixture which is 60% $NaNO_3$ and 40% KNO_3(Solar Salt) has been used as an attractive candidate for heat transfer fluid in the Concentrating Solar Power (CSP) pilot plant (Kearney, 2004; Mar and Kramer, 1981; Herrmann et al., 2004) because of its great thermal stability, the lowest cost, and highest melting point. The second commercial salt is Hitec Salt, which is a mixture of 53 wt % KNO_3, 40 wt% $NaNO_2$, and 7 wt% $NaNO_3$ with a melting point of 142 °C (Gil, 2010). The third salt mixture is comprised of 28 wt% $NaNO_3$, 52 wt% KNO_3, and 20 wt% $LiNO_3$, and this mixture's thermal property was studied by Olivares and Edwards (2013) and Fernandez et al. (2014). The working temperature range of this mixture is 130–600 °C, and its viscosity is 0.03 Pa S at 300 °C (Olivares et al., 2012), which is good for fluid flow properties. But the high price of $LiNO_3$ ($4.32/kg) poses a huge limitation on its development. The fourth salt mixture is Carbonate salt (Vignarooban et al., 2015) with 32.1 wt% Li_2CO_3, 33.4 wt% Na_2CO_3, and 34.5 wt% K_2CO_3, which was proposed to replace the nitrate salt to increase the thermal stability temperature limit. The melting point of this mixture is 400 °C and the decomposition temperature is 800–850 °C.

Among the mentioned materials which are used for both latent heat storage and heat transfer fluid, nitrate salts have wide use in actual practice due to their merits such as high heat storage capacity (enthalpy), favorable thermal stability, satisfactory compatibility with containers, low corrosion (Javier Ruiz-Cabarias et al., 2017), low vapor pressure, low viscosity in most cases, and chemical inertness (Zhao and Wu, 2011). Reviewing relevant references (Paul et al., 2015; Warzoha et al., 2015; Lee et al., 2014; Zhao et al., 2015; Roget et al., 1980; Judith and Calvet, 2013; Mar and Kramer, 1981; Herrmann et al., 2004; Gil, 2010; Olivares and Edwards, 2013; Fernandez et al., 2014; Olivares et al., 2012; Vignarooban et al., 2015; Zhao and Wu, 2011; Li et al., 2016; Fernandez and Perez, 2016; Prieto et al., 2016; Brandon and Davidson, 2017; Myers and Yogi Goswami, 2016; Zhou and Eames, 2016), $Ca(NO_3)_2$, $NaNO_3$, and KNO_3 are eligible as both phase change materials and heat transfer fluid due to their insignificant corrosion, no toxicity, and low price. Although several reports mentioned $Ca(NO_3)_2$, $NaNO_3$ or KNO_3 as an additive in the mixtures, the study remains incomplete. For example, Judith and Calvet (2013) used $Ca(NO_3)_2$-$NaNO_3$-KNO_3 as phase-change materials, but the data was incomplete (only 6 groups) and the thermal conductivity was not presented in his study. Roget et al. (1980) prepared a ternary molten salt ($LiNO_3$-KNO_3-$NaNO_3$), but the price of $LiNO_3$ is much higher than that of $Ca(NO_3)_2$, which is not economical in solar plants. Moreover, Zhao et al. (2015) used $Ca(NO_3)_2$ as an additive in $NaNO_3$, but its' melting point (220 °C) isn't suitable for low or medium temperatures.

The present study prepared a ternary molten salt consisting of KNO_3, $NaNO_3$, and $Ca(NO_3)_2$ based on different weight ratios. Experiments showed that this mixture has a melting point of 80 °C and the maximum stable temperature is 600 °C. However, this mixture focuses mainly on low and medium temperatures (less than 200 °C). Hence, other thermophysical properties such as thermal conductivity and viscosity were measured in the temperature range of 50–200 °C. Further study indicated a correlation between the heating rate and heat enthalpy, and the economic impact id discussed at the end of this study. Overall, the experimental results showed that these ternary molten salts are suitable candidates as thermal storage materials and heat transfer fluids.

2. Material preparation and experimental methods

2.1. Material preparation

The molten salt was prepared from $Ca(NO_3)_2{\cdot}4H_2O$(purity > 99%), $NaNO_3$(purity > 99%), and KNO_3(purity > 99%) manufactured by Sinopharm Chemical Reagent Co. Ltd. The method of preparing the formulations was to mix the anhydrous form of the single components at room temperature. In order to produce the anhydrous form of calcium nitrate, the tetrahydrate form was heated in two stages: (i) at 150 °C for 10 h and (ii) at 350 °C for 20 h. Then the anhydrous salts were put in a muffle furnace at 150 °C to ensure drying. In order to avoid water absorption, especially for the extremely anhydrous calcium nitrate, the handling and mixing of the salts, as well as putting samples in the testing pan, were performed in a box under dry nitrogen. To weigh the samples based on 32 sets of data, an analytical balance with a resolution of 0.1 mg was used.

2.2. Simultaneous Thermal Analyzer

Fusion heat, cycle stability, and the endothermic peak's property under different heat rates were measured by a Simultaneous Thermal Analyzer (STA 8000, Perkin Elmer) which provides real-time analysis of sample weight change and heat flux. The weight and temperature accuracy of the STA were 0.0001 mg and 0.01 °C, respectively. The temperature accuracy of the oven was 0.1 °C.

To measure the fusion heat, the 32 groups of samples were heated from 50 °C to 250 °C at a rate of 10 °C/min under N_2 purging of 20 L/min. The samples were heated 33 times in three stages for the cycle stability test: (i) from 50 °C to 250 °C at a rate of 10 °C/min, (ii) at 250 °C for 1 min, and (iii) from 250 °C to 50 °C at the rate of 10 °C/min. In order to determine the endothermic peak's property at different heating rates, the sample was measured at different heating rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC 8000, Perkin Elmer) was used to determine the specific heat capacity of the mixtures. The temperature calibration was performed with benzophenone and caffeine. The heat flow calibration was carried out by indium. After the aforementioned calibration, the samples were heated from 50 °C to 80 °C and from 200 °C to 250 °C, respectively, in order to measure the samples' solid and liquid specific heat capacity.

2.4. X-ray diffraction

X-ray diffraction (XRD) measurements were carried out to investigate the remnants after thermal decomposition. The sample was heated by STA from 200 °C to 950 °C at a rate of 10 °C/min, and then, XRD was used to investigate the remnants at ambient temperature.

2.5. Transient plate method

The transient plate method was performed to measure the sample's thermal conductivity. This methods measure the transient thermal conductivity and the instrument's uncertainty was about 10%.

2.6. Malvern Kinexus Ultra$^+$

Malvern Kinexus Ultra$^+$ was used to test the sample's viscosity and the apparatus's uncertainty was about 10%. In order to avoid the water absorption, the experiments were performed under a flow of either dry nitrogen or dry synthetic air. The viscosity was measured with a 40 mm diameter stainless steel parallel plate.