



Study on solidification process of sodium acetate trihydrate for seasonal solar thermal energy storage



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ABSTRACT

The phase change of sodium acetate (SA) aqueous solution to sodium acetate trihydrate (SAT) requires large supercooling degree, then the aqueous solution can be at liquid state at fairly low temperature without releasing the stored latent heat. Such a feature makes SAT a promising material for seasonal solar thermal energy storage. The present study firstly summarized the thermo-physical properties of the solid SAT and liquid SA aqueous solution at different temperatures and concentrations, including equilibrium temperatures, densities, specific heats and thermal conductivities. The calculation methods of these properties have been established. Secondly, with the aid of the above properties, a mathematic model of the thermal discharge process of the storage system, i.e. the solidification process of supercooled SA aqueous solution, was built based on the heat transfer between the phase changing material within a single storage tube and the external flowing heat transfer fluid (HTF). The experimentally obtained SAT crystal growth rate and the enthalpy change of solidifying supercooled SA aqueous solution were employed to aid the modelling. The discharge temperature and thermal power of the storage system were numerically obtained and analysed. The influence of the ambient temperature, the mass flow rate as well as the heat transfer coefficient of the HTF on the thermal discharge performance were discussed. Finally, the seasonal thermal storage density of SAT was given and compared to that of water and some sorption materials.

1. Introduction

Space heating and domestic hot water consumes the majority energy demanded by residential buildings, e.g. about 82% in Europe [1]. On the other side, the amount of solar radiation projected to a typical house roof normally exceeds the total amount of heat needed for the house heating over a year. That implies that the seasonal solar thermal energy storage seems to be the most feasible way to achieve completely 'free' house heating. The well-known three types of thermal energy storage technologies, i.e. sensible heat storage, latent heat storage and chemical reaction heat storage, are all available for seasonal solar thermal energy storage [1–3].

The latent heat storage by phase change material (PCM) provides larger thermal energy storage density than that of sensible heat storage; although its storage density is not competitive to chemical reaction storage, the system is simpler, more robust and reliable than chemical reaction system. Salt hydrate as PCM distinctively features large supercooling degree, which is regarded as one of the drawbacks that impedes latent heat releasing at desirable temperature level. However, this drawback can be treated as a valuable merit for a different purpose – the long-term thermal energy storage; because of the large

supercooling degree, the melted salt hydrate can remain at liquid state at relatively low temperature without losing any stored latent heat, only sensible heat is lost throughout the storage period, therefore the system is not necessarily thermal insulated but can still discharge the majority of the stored thermal energy.

Sodium acetate trihydrate (SAT) is one of the typical salt hydrate PCMs, which has the melting temperature of 58.0 °C and latent heat of 264.0 kJ/kg [4]. These properties and the low cost make it a suitable PCM for residential heating. Furthermore, the melted SAT can be easily supercooled to below 0 °C with a supercooling degree as large as 80 °C [5], so that the latent heat can be preserved during long-term storage. Recently, Dannemand et al. have reported a series of study on using SAT for seasonal solar thermal energy storage [6–9]. The authors simulated the storage system using TRNSYS and concluded that the seasonal solar thermal energy storage with 7 PCM modules of 150 L each can satisfy 80% of annual space heating and hot water of a house in Danish climate [6]. The solidification behavior of SAT with thickening agent, including carboxymethyl cellulose (CMC) and xanthan rubber, and the thermal conductivity enhancement by adding graphite powder were experimentally tested and discussed in the work [7], where liquid CO₂ was used to initiate the crystallization of supercooled

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Nomenclature

A, B, C, D, E, F, G	equation constant (-)
c	molar density (mol/dm ³)
c_p	specific heat (J/(kg K))
D	diameter (m)
D_e	hydraulic diameter (m)
h	enthalpy (J/kg)
Δh	enthalpy change (J/kg)
ΔH	latent heat (J/kg)
L	total length (m)
Nu	Nusselt number (-)
M	molecular weight (kg/mol)
m	mass (kg)
\dot{m}	mass flow rate (kg/s)
Pr	Prandtl number (-)
Re	Reynolds number (-)
r	radius (m)
T	temperature (°C)
ΔT	temperature difference (°C)
t	time (s)
Δt	time interval (s)
u	flow velocity (m/s)
v_c	crystallization speed (mm/s)
w	mass fraction/concentration (-)
z	axial coordinate (m)
Δz	length (m)

Greeks

α	heat transfer coefficient (W/(m ² K))
λ	thermal conductivity (W/(m K))
ρ	density (kg/m ³)
φ	volume fraction (-)

Subscripts

0	initial
amb	ambient
eq	equilibrium
f	heat transfer fluid
fin	heat transfer fluid inlet
fout	heat transfer fluid outlet
i	inner
l	liquid
p	PCM
pre	preliminary
s	solid
sup	supercooled
tp	two phase
w	wall
wat	water
wb	wall boundary

sodium acetate solution. Two different treatment methods were applied to SAT to prevent the phase separation during the phase changing, one was to add extra water and the other one was to add thickening agents. The test of SAT with 9% extra water (199.5 kg) in flat rectangular container showed the reduction of discharged thermal energy from 194 kJ/kg to 179 kJ/kg after 20 test cycles; while SAT with 1% CMC (220 kg) can maintain the discharge thermal energy at 205 kJ/kg over six test cycles. Both additions led to 45 °C discharge temperature when the heat transfer fluid flow rate at 2 L/min, and the discharge power reduced from 4.5 to 5.0 kW at the beginning to about 1.0 kW within about 4 h [8]. Similar performance was found when using a cylindrical shell-and-tube heat exchanger [9], spontaneously crystallization was noticed regardless of either addition of extra water or thickening agent when using this heat exchanger. The thermal conductivity of SAT was improved from 0.17 to 0.70 W/(m K) to 1.1 W/(m K) due to the presence of graphite powder.

The interesting discoveries in above studies encourage more efforts to explore such a promising material for seasonal solar thermal energy storage. The present paper modelled and simulated the solidification process of the supercooled SA aqueous solution to evaluate the thermal discharge performance of the storage system. Thermo-physical properties of liquid SA aqueous solution and solid SAT were both summarized, and the experimentally determined SAT crystal growth rate and the enthalpy change of the solidifying SA aqueous solution were introduced to the model in this paper for elaborating modelling.

2. Thermo-physical properties

2.1. Phase diagram

The solubility of SA in water and the melting points of SAT were experimentally measured by Green [10]. The phase diagram of sodium acetate aqueous solution is presented in Fig. 1. SAT has the salt mass fraction of 0.603 and the congruent melting point at 58.0 °C. The phase diagram was divided into six areas, including liquid SA aqueous solution area, liquid SA aqueous solution and solid SA area, liquid SA

aqueous solution and solid SAT area, solid SAT and solid SA area, liquid SA aqueous solution and solid ice area, solid SAT and solid ice area. To avoid the presence of un-dissolved solid SA in the aqueous SA aqueous solution during heat charge process, the heating temperature for the pure SAT must be high enough, i.e. higher than 77.6 °C as indicated in the phase diagram. Otherwise phase separation occurs due to the larger density of solid SA. Alternatively, using leaner SA aqueous solution (< 0.58 by weight) can avoid this problem. For SAT with extra water (SA aqueous solution with concentration lower than 0.603 by weight), the phase equilibrium temperature reduces as the decrease of solution concentration, and the lowest equilibrium temperature is the eutectic melting point of ice-SAT binary system, which is -18.0 °C at the SA concentration of 0.233 by weight as shown in the phase diagram.

The measured equilibrium temperature of SA aqueous solution as the function of the solution concentration w_1 were fitted by polynomial equations, Eqs. (1)–(3).

$$T_{eq} = -55.355w_1 + 59.1244w_1^2 - 655.7453w_1^3 \quad 0 \leq w \leq 0.233 \quad (1)$$

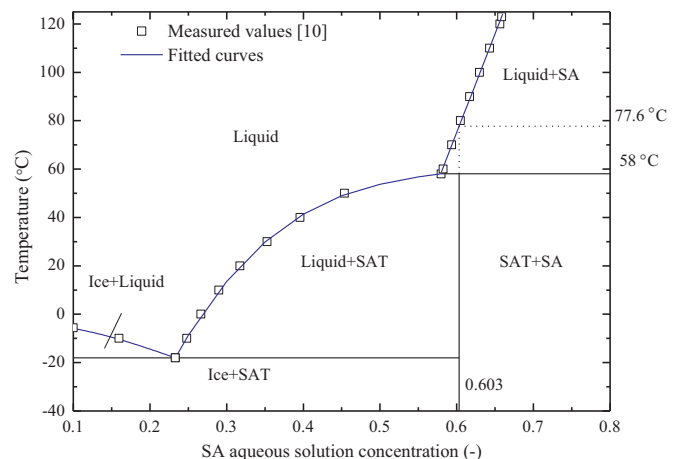


Fig. 1. Phase diagram of sodium acetate aqueous solution.

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