



Paraffin wax–water nanoemulsion: A superior thermal energy storage medium providing higher rate of thermal energy storage per unit heat exchanger volume than water and paraffin wax



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ABSTRACT

Experimental investigations have been carried out to identify an appropriate concentration of paraffin wax in paraffin wax–water nanoemulsions, for use as thermal energy storage media. For this purpose, paraffin wax–water nanoemulsions containing different concentrations of paraffin wax (10 wt%, 20 wt%, 33 wt% and 50 wt%) were prepared, with the size of dispersed phase ranging between 200 and 600 nm. Specific heat of nanoemulsions increased with paraffin wax concentration, with 50% paraffin wax–water nanoemulsion possessing 47% higher specific heat than that of water. The variation of viscosity of paraffin wax–emulsions was similar to that of pure liquid, with a reduction in viscosity at elevated temperatures. The performances of paraffin wax–water emulsions and those of water and pure paraffin wax were evaluated during charging cycle of thermal energy storage in an experimental setup. The experiments revealed that the energy stored per unit time per unit heat exchanger volume was the highest for paraffin wax–water emulsion containing 10% paraffin wax, exceeding those of water and pure paraffin wax by 11% and 23% respectively.

1. Introduction

Thermal energy storage systems bridge the gap between energy supply and energy demand, thereby making solar thermal energy available on-demand. Thermal energy storage systems based on latent heat storage have the benefits of higher energy density and capability to deliver heat at a constant temperature. While the former ensures lower foot-print of thermal energy storage system, the latter ensures the availability of thermal energy for a constant temperature process heating. The most commonly used phase change material category, the organic phase change materials, are impaired by their low thermal conductivity. Efforts to improve effective thermal conductivity include the addition of nanoparticles, use of finned heat exchangers, use of metal foam heat exchangers, macro/micro/nano-encapsulation, etc. Water can be considered as an alternative to phase change materials for thermal energy storage due to its higher heat capacity than other coolants and capability of higher rates of charging and discharging.

When a phase change material is dispersed in liquid coolant through either surfactant encapsulation or microencapsulation, phase change emulsions are formed. In the last five years, preparation and characterization of phase change emulsions comprising organic phase

change materials in water have been widely reported [1–4]. Phase change emulsions can be prepared by high energy methods [5] or by D-phase emulsification [2,4,6]. Sakai et al. [1] investigated the colloidal stability and fluidity of hexadecane-in-water emulsions that contained droplet sizes ranging from 2 to 13 μm . The use of surfactant with long hydrocarbon chain was suggested to minimize supercooling. Chen and Zhang [2] reported the thermophysical characteristics of n-hexadecane-water and n-octadecane-water nanomemulsions prepared by D-phase method. The average size of dispersed phase was 290 nm and 320 nm respectively. The viscosity of phase change emulsions containing 30 wt % dispersed phase was 20 times higher than that of pure water [2]. Kawanami et al. [4] too reported that the phase change emulsions prepared by D-phase emulsification exhibited better colloidal stability.

The specific heat of phase change emulsion is greater than that of the liquid coolant [7]. For instance, the dispersion of 20 wt% of silica encapsulated polyalcohol phase change material in polyalphaolefin (PAO) resulted in 56% increase in specific heat capacity [8]. A review of the applications of PCM slurries under natural and forced convective heat transfer conditions is available, wherein PCM slurries are considered as an alternative to single phase liquid coolant or for refrigeration and air conditioning applications [9]. Phase change

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Nomenclature		Greek symbol	
Symbol	Meaning	λ	latent heat for phase change (J/kg)
A	heat transfer area (m ²)	Θ	time (s)
C_p	specific heat or apparent specific heat (J/kg K)		
dT	temperature interval		
E'	energy stored per unit time per unit volume (W/m ³)		
h_i	storage media side heat transfer co-efficient (W/m ² K)		
h_o	bath side heat transfer co-efficient (W/m ² K)		
m	mass of storage media (kg)		
T	temperature of bath fluid (°C)		
t	temperature of storage media (°C)		
U	overall heat transfer co-efficient (W/m ² K)		
V	volume of heat exchanger (m ³)		
x	mass fraction of paraffin wax (–)		
		Subscript	
		e	emulsion
		f	freezing
		i	run number
		m	melting
		p	paraffin wax
		SL	solid-liquid
		W	water

emulsions can also be used as heat transfer fluid in direct absorption solar collector [10] and for cooling applications [11]. The high viscosity of phase change emulsions, insufficient thermal stability and super-cooling were identified as the problems that need to be overcome to ensure the use of phase change emulsions for real-time applications [12]. Shao et al. (2016) reported 200% enhancement in heat capacity of 35 wt% RT10-water emulsion, over that of water [11]. However, the viscosity was 25 times higher than that of water, which when compounded with 30% reduction in thermal conductivity could impede the rate of heat transfer [11]. Fischer et al. (2016) have emphasized the importance of drop size and viscosity on the emulsion stability, pressure drop and heat transfer [13]. A combination of lower droplet size and lower viscosity is advantageous from the aspects of emulsion stability, pressure drop and heat transfer while higher droplet size and lower viscosity are likely to deter emulsion stability through foaming [13].

The uniqueness of this manuscript stems from the use of phase change nanoemulsion as an alternative to organic phase change material and water for thermal energy storage. A model phase change nanoemulsion involving paraffin wax and water has been developed for this purpose. Phase change nanoemulsion has been designed in such a way that the same contains a low viscous liquid (water) as one component and an organic phase change material (paraffin wax) as another component, with paraffin wax undergoing solid-liquid phase transition during all periods of charging and discharging. The presence of low viscous liquid during the entire charging-discharging cycle will ensure higher heat transfer rates due to natural convection effects (in addition to conduction). The presence of organic phase change material ensures higher storage density than pure liquid.

This work assumes importance due to absence of experimental prior art with heat transfer experiments, on the use of phase change emulsion as an alternative to the phase change materials for latent heat storage. This manuscript reports the identification of an appropriate composition of paraffin wax–water nanoemulsion for use as thermal energy storage media. For this purpose, paraffin wax–water nanoemulsions containing paraffin wax at concentrations as high as 50 wt% were prepared, characterized and thermal energy storage performance tested and compared with those of water and paraffin wax, in a first-of-its-kind experimental study. This work has also demonstrated that the conduction limitation for heat transfer in conventional latent heat thermal energy storage systems could be overcome by employing phase change emulsions as storage media. A new metric for assessment of thermal energy storage media has also been introduced.

2. Experimental

2.1. Preparation and characterization of paraffin wax–water nanoemulsion

Paraffin wax, with the melting point range of 58–60 °C was chosen

Table 1
Values/Range of values for different variables.

Variable	Values/Range of values
Concentration of paraffin wax in paraffin wax–water nanoemulsion (wt.%)	10, 20, 33, 50
Temperature range for differential scanning calorimetry, viscosity measurement and assessment of charging performance (°C)	30–60
Test storage media	Water, paraffin wax, paraffin wax–water nanoemulsion

as the dispersed phase. A mass of paraffin wax corresponding to the required concentration (as shown in Table 1), was heated to 70 °C and was added to surfactant solution drop-wise along with continuous stirring and probe ultrasonication. The magnetic stirrer used for stirring was operated at 500 rpm. The 700 W power probe ultrasonicator delivered ultrasound at 20 kHz, with intensity being 20%. The probe ultrasonication was carried out for 1 h using 13 mm diameter probe, with both on-cycle and off-cycle of 9.9 s in duration.

The use of surfactant was necessitated due to the intended preparation of a dispersion of hydrophobic paraffin wax in the aqueous phase. Pluronic P-123 has been used as the surfactant with the surfactant: paraffin wax mass ratio being 0.05:1 [14,15]. Owing to the ease of preparation of liquid-liquid dispersion, the paraffin wax was dispersed in water while it was in liquid form. After the completion of paraffin wax addition and probe ultrasonication, the mixture was rapidly cooled by placing in a water bath maintained at 10 °C.

The shape and size of paraffin wax particles in the paraffin wax–water emulsion were observed using a scanning electron microscope (VEGA3, TESCAN, Czech Republic). A couple of drops of paraffin wax–water emulsion was placed on a glass slide and dried, before being exposed to electron beam in the electron microscope. Paraffin wax–water emulsions were imaged before and after thermal cycling. The particle size distribution of paraffin wax in paraffin wax–water emulsion was determined by dynamic light scattering (NanoZS, Malvern Instruments, USA). The thermal conductivity of water and paraffin wax–water emulsion was measured using transient hot-wire technique. A digital thermal conductivity meter (KD2 Pro, Decagon Devices, USA) employing a thin stainless sensor of diameter 1.27 mm and length 60 mm was used. The sensor carried out the function of a line heat source and that of temperature measurement. The measurements were carried out for 1 min, with heating time being 30 s, in accordance with the manufacturer's guidelines [16]. The accuracy of thermal conductivity meter was ascertained through measurement of thermal conductivity of standard sample (glycerol) provided by the manufacturer. The deviation between measured and manufacturer-specified values was less than 2%. The viscosity of paraffin wax–water

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