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Evaluation of paraffin/water emulsion as a phase change slurry for cooling applications

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A B S T R A C T

A Phase Change Slurry (PCS) is a latent heat storage and transfer medium consisting of a Phase Change Material (PCM) as a dispersed phase and a carrier fluid as a continuous phase. PCSs have a high energy density because they use not only the sensible heat capacity of the carrier fluid, but also the latent heat capacity of the PCM during the phase transition. In this paper, a paraffin/water emulsion has been studied as a PCS for comfort cooling applications in a temperature range of 0–20 °C. A paraffin blend having a melting temperature range of 2–12 °C was used for preparing the emulsion. The properties of the emulsion were studied in view of the application requirements on PCSs. The dependence between the paraffin fraction and emulsion properties was investigated. The stability of the emulsion was examined both during the storage period and under mechanical–thermal loads in a test rig by determining the change in the properties. The results indicate that the paraffin/water emulsion containing a paraffin weight fraction of 30–50 wt.% is an attractive candidate for cold storage and distribution applications.

1. Introduction

The energy demand for cooling applications has been steadily increasing in recent years. There are a number of reasons for this development, e.g. climate change, increasing thermal loads in buildings due to the utilization of light weight construction methods with a poor thermal capacity. The increased cooling demand results not only in a considerable growth in power consumption, but also in a power peak demand during the hottest hours in summer. The distinct increasing peak for electricity consumption will strongly impact the existent power grid. To reduce the increasing electricity consumption for cooling applications and to shift the peak load, thermal energy storage technologies have been developed. Different media have been used or studied for cold storages. Conventional cold storage and distribution systems use water or brines as heat transfer fluids to store or transfer energy by using the sensible heat capacity of water. Due to the typically small temperature differences between forward flow and return flow in cold supply networks, these systems have high volumetric flow rates and low cold capacity of hydraulic buffers. To increase the storage capacity, latent storage systems based on Phase Change Materials (PCMs) have been developed. In a PCM system, energy is stored mainly during a phase change process of the storage material, e.g. solid–liquid transition. A variety of PCMs has been investigated for cooling applications, such as ice/water [1,2], the capric and lauric acid mixtures [3], the manganese (II) nitrate hexahydate [4] and tetradecane and hexadecane binary mixtures [5]. Compared to sensible heat storage materials, PCMs have a high energy storage density with a small temperature swing. However, PCM systems need an additional fluid for the heat transfer between PCMs and heat/cold sources due to the phase transition. The indirect heat transmission results in a decreasing heat transfer rate. Furthermore, most PCMs have a low thermal conductivity, particularly in the solid state.

To avoid these disadvantages of PCM systems, Phase Change Slurries (PCSs) have been recently studied. A PCS is a binary system consisting of a PCM as a dispersed phase and a carrier fluid as a continuous phase. PCS systems store energy not only by using the sensible heat capacity of the carrier fluid, but also by using the latent heat capacity of the PCM. Because PCSs stay pump-able during the phase transition process, a second heat transfer fluid is not necessary for PCS systems. In addition, PCSs have higher heat transfer rates than only PCMs due to the large surface to volume ratio of the dispersed phase. PCSs can be classified into some

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Nomenclature

$c_{p,i}$	specific heat capacity of component *i*, J/(g K)
d_{50}	droplet mean diameter, μm
ΔG	Gibbs free energy, J
ΔG_S	surface Gibbs free energy, J
ΔG_V	volume Gibbs free energy, J
Δh_i	enthalpy change per mass of component *i*, kJ/kg
$\Delta h_{f,i}$	heat of fusion per mass of component *i*, kJ/kg
$\Delta h_{f,v}$	heat of fusion per volume, J/m^3
K, n	coefficient
m_i	mass of component *i*, kg
$\dot{q}$	heat flow per mass, W/g
$\dot{Q}$	heat flow, W
r	nucleus radius, μm
r^*	critical nucleus radius, μm
T	temperature, °C
T_c	extrapolated peak end temperature, °C
T_e	extrapolated peak onset temperature, °C
T_p	peak temperature, °C
ΔT	supercooling, °C
X_i	weight fraction of component *i*, wt.%
Greek letters	
γ	shear rate, s^{-1}
σ	interfacial tension, N/m
τ	shear stress, Pa
Subscripts	
e	emulsion
f	freezing
m	melting
p	paraffin
w	water

groups: ice slurries, hydrate slurries, phase change emulsions, phase change microcapsules, clathrate slurries, shape-stabilized latent heat materials and diphasic slurries of carbon dioxide [6]. There are three kinds of PCSs based on paraffins mentioned in the literature:

- shape-stabilized paraffin-in-water suspensions, where a paraffin is embedded into a support material with a cross-linked structure like high density polyethylene and suspended in water [7–9],
- microencapsulated paraffin-in-water suspensions, where fine paraffin droplets are encapsulated with a thin film of, e.g. PMMA (polymethyl methacrylate) and suspended in water [10–12], and
- paraffin-in-water emulsions, where fine paraffin droplets are directly distributed in water and maintained in dispersion by a surfactant [11–15].

For the first two dispersions, the supporting or coating materials cause additional costs and often increase the viscosity as well as the heat transfer resistance. For paraffin/water emulsions, the heat transfer rate is improved through the direct contact between the paraffin and water. The previous work indicated that the instability and supercooling are the two major problems of preparing paraffin dispersions. The aim of this paper is to study a paraffin/water emulsion for comfort cooling applications and to evaluate its properties in view of the application requirements on PCSs.

2. Emulsion components and formation

Paraffins are a typical organic PCM. The normal paraffins of type C_nH_{2n+2} are a family of saturated hydrocarbons with very similar properties [16]. The melting points and the heat of fusion of paraffins increase with carbon chain length [17,18]. When a PCM is used for comfort cooling applications, it should have a melting temperature between 0 °C and 20 °C. Three pure paraffins have a phase transition point in this temperature range, namely tetradecane CH_3–$(CH_2)_{12}$–CH_3 ($T_m = 5.8$ °C, $\Delta h_f = 227$ kJ/kg), pentadecane CH_3–$(CH_2)_{13}$–CH_3 ($T_m = 9.9$ °C, $\Delta h_f = 206$ kJ/kg) and hexadecane CH_3–$(CH_2)_{14}$–CH_3 ($T_m = 18.1$ °C, $\Delta h_f = 236$ kJ/kg) [5]. Because of the high prices of pure paraffins, blends (mixtures of different paraffins) are usually used for practical applications instead. Blends offer the possibility to shift the melting temperatures towards more applicable temperature levels. Many blends in this temperature range are commercially available, such as RT6, RT10, RT12 and RT20 of Rubitherm Technologies GmbH, Parafol 14-97 and Parafol 16-97 of Sasol Company. These pure paraffins and blends have similar properties and can be used for preparing the emulsion. Here, the experiments with Rubitherm RT10 are presented.

All paraffin emulsions were prepared by the authors at Fraunhofer UMSICHT. The emulsion is composed of water, paraffin, surfactant and nucleating agent. Due to the fact that paraffin and water are immiscible and always tend to separate, a nonionic surfactant was used to stabilize the emulsion. Surfactants are amphipathic molecules consisting of a non-polar hydrophobic part, mostly a hydrocarbon chain, and a polar or ionic part (hydrophilic). The hydrocarbon chain interacts intensively with the oil molecules, whereas the polar or ionic group interacts strongly with water molecules via dipole or ion–dipole interactions [19]. According to the continuous phase, emulsions are distinguished between oil-in-water (O/W) and water-in-oil (W/O) systems. The paraffin/water emulsion is an O/W emulsion where fine paraffin droplets are dispersed in water and surfactant molecules are adsorbed at the interface between the paraffin and water as shown in Fig. 1. Fig. 2 illustrates the external appearance of a paraffin/water emulsion. The emulsion shows a supercooling effect which will additionally increase the operating temperature of the system. Supercooling means that a liquid can be cooled below its melting point without causing crystallisation. Thus, a nucleating agent was used to prevent the supercooling of the emulsion.

To make an emulsion, mechanical energy is supplied for premixing and breaking up droplets. Premixing the emulsion components is mostly accompanied by stirring. The droplet break-up is carried out by emulsifying machines. To study the dependence between the paraffin fraction and the emulsion properties, 13 samples of each weighing 200 g and containing a paraffin fraction from 15 wt.% to 75 wt.%, 2.5 wt.% surfactant and 2.5 wt.% nucleating

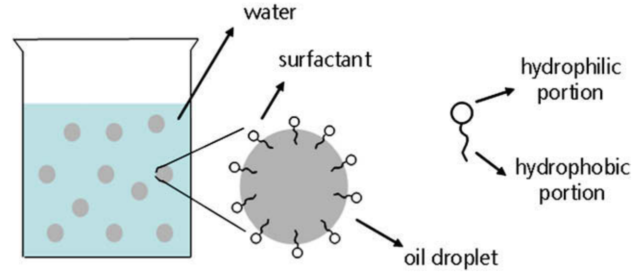

Fig. 1. Illustration of an O/W emulsion.