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Evaluation of thermophysical properties of refrigerant clathrates with additives

Sayem Zafar[a,*], Ibrahim Dincer[b], Mohamed Gadalla[c]

[a] Faculty of Engineering and Technology, Higher Colleges of Technology, Center of Excellence in Research and Training, Abu Dhabi, United Arab Emirates
[b] Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario L1H 7K4, Canada
[c] Department of Mechanical Engineering, American University of Sharjah, Sharjah, United Arab Emirates

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ABSTRACT

A modeling study is conducted to evaluate the heat transfer properties of novel refrigerant clathrate-based phase change materials (PCMs). Novel PCMs with large specific energy densities are formed by using different additives in the refrigerant clathrates. Refrigerant clathrates of R134a, R1234yf and R32 are investigated at different refrigerant mass percentages with water. Glycols, sodium chloride, magnesium nitrate hexahydrate, nanoparticles of pure aluminum, copper and graphene are used as additives. Empirical correlations are used to predict the liquid-phase thermal conductivities of refrigerant clathrates and the improvement obtained with the addition of different additives. The results show that an increase in refrigerant mass percentage lowers the thermal conductivity of the refrigerant clathrate but not extensively. The addition of salt results in a minor improvement in thermal conductivity while addition of glycols as liquid additives greatly improves the liquid-phase thermal conductivity. The inclusion of nanoparticles significantly improved the thermal conductivity of the phase change material. The liquid-phase specific heat capacity, however, is not generally improved by the nano-particles as it depended on the additive used.

1. Introduction

The ability to utilize energy was a great scientific achievement of the human recent-past and it continues to reform at a gradual pace. The recent global trend has changed from rudimentary energy production to precisely manage and absorb energy. Energy management has been a key challenge that needs to be dealt with in order to achieve the goal of sustainable growth. A bridge from conventional energy use to sustainable energy utilization is the concept of the temporary storage of high or low temperature energy for later use. Thermal energy storage (TES) refers to the storage of heat/cool by increasing or decreasing the temperature of a substance or by changing the phase of a substance [1]. The study related to energy storage systems is divided into the analysis of the heat exchanger while the other aspect looks at the materials to be used to store the energy. This paper investigates the materials to be used in cold energy storage systems.

Applicable materials for the cold energy storage come in all shapes, varieties and sizes. Materials that change their phase, liquid to solid to gas or vice versa appear more feasible for energy storage applications due to their latent heat capability. One of the ways to form a useable phase change material (PCM) is by introducing refrigerant gas/liquid into the water molecules, called clathrate hydrates. Refrigerant clathrate has appeared to be a promising way to store thermal energy for cooling applications. Clathrate is a solidified inclusion compound that contains gas molecules in water molecular cavities [2,3]. Clathrates form when water and gas combine in a lattice structure under low temperatures and moderate pressures [4]. Since the phase change temperature of clathrate is above the freezing point of water, yet low enough to be used for comfort cooling, its use in air conditioning has been studied and found to be useful and applicable [5]. Refrigerant clathrates are considered to be more effective, for cooling applications, compared with other type of PCMs such as ice as they can be used through refrigerant loops and easily be circulated [6,7].

Note that refrigerant clathrates have certain properties that make them very attractive PCMs for cold storage applications as follows:

- They have high heat of fusion which means that they can store higher amount of energy.
- They have high energy density which means the storage size can be smaller per unit energy rate.
- They are non- corrosive or non-toxic, and hence the conventional refrigeration unit can be used to form clathrates of refrigerants.

* Corresponding author.
E-mail addresses: szafar@hct.ac.ae (S. Zafar), ibrahim.dincer@uoit.ca (I. Dincer), mgadalla@aus.edu (M. Gadalla).

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Nomenclature

A	area m^2
B	empirical constant -
Cp	specific heat capacity J/kg K
d_p	particle diameter m
k	thermal conductivity coefficient W/m K
l	length m
m	mass kg
n	empirical constant -
Pr	Prandtl number; $(\frac{\mu C_P}{k})$ -
Q	heat J
$\dot{Q}$	heat rate W
Re	Reynolds number; $(\frac{\rho v d_p}{\mu})$ -
R_b	interfacial thermal resistance K m^2/W
T	temperature K

Greek letters

α	Biot number -
Δ	difference -
ρ	density kg/m^3
λ	specific latent heat of fusion J/kg
φ	volume fraction -

Subscripts

f	base fluid -
p	additives -

Acronyms

CFC	chlorofluorocarbons -
HCFC	hydro-chlorofluorocarbons -
HFC	hydrofluorocarbons -
PCM	Phase Change Material -
TES	thermal energy storage -

- They are essentially a mixture of water and refrigerant only which makes them more efficient and more cost effective.

Many chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydro-fluorocarbons (HFCs) can form clathrates of refrigerant [8]. In order to be used for cold thermal energy storage, an effective refrigerant clathrate should form at close to atmospheric pressure and between temperature range of 278 K to 285 K [9]. Several refrigerants form the clathrates, but only few are commercialized. Due to the stratospheric ozone layer depletion concerns, CFC clathrates are forbidden. This constrain leaves only the hydro-chlorofluorocarbon and hydrofluorocarbons to be used for PCM. Refrigerant clathrates with R-134a have been proposed as a PCM which demonstrated to be the most promising candidates for this goal [9]. R-134a has been widely studied for its clathrate formation and performance with thermal energy storage systems [10,11]. Another refrigerant considered feasible for refrigerant clathrates is R141b due to its available engineering applications, low saturated vapor pressure, low cost, and its low pressure character [12,13]. In spite of having such positive attributes, R141b refrigerant requires long charging time to form clathrates when compared with other commonly used refrigerants. Refrigerant R1234yf is also of interest as it has low global warming potential and recently commercialized as an alternative to R134a [14].

Conventional PCMs, especially the ones based on refrigerant clathrates, have poor heat transfer properties. In order to enhance the performance of refrigerant clathrates, to be effective PCMs, additives of different materials have been studied. For instance, adding calcium hypochlorite or benzenesulfonic acid sodium salt improved the cold energy storage capacity and the cold energy transfer rate of R141b based clathrate [12]. For organic materials, adding alcohol in R-134a based clathrate accelerates the cool storage rate and eliminates the floating foam-clathrate during the hydration process [15].

In order to increase thermal conductivity of inclusion compounds, metallic nano-particles have also been added to improve the thermal conductivity of the PCM. It has been reported that even a small fraction of nano-particles of low thermal conductivity metallic oxides can favorably increase the thermal conductivity of pure a substances, such as water [16,17]. Even for organic compounds such as monoethylene glycol and paraffin fluids, copper oxide nano-particles can improve the thermal conductivity [18]. Addition of pure copper nanoparticles in ethylene glycol increases the thermal conductivity by 40% [19]. Studies with refrigerant clathrate and nano-particles of copper show improvement in the heat transfer rate [20]. This improvement in thermal transport properties depends on the particle size, dispersion and the operating temperature [21–26].

Liquid additives have also been studied as they do not pose significant hindrance when used for active cooling/heating applications. Liquid additives are of interest as they can easily run through pumps and compressors, without causing any significant damage or loss of efficiency. However, liquid additives namely propylene glycol and ethylene glycol have been used for passive cooling applications as well [27]. Ethylene glycol is commonly used as automotive engine coolant hence presents itself as a strong candidate for liquid additive [28]. Apart from thermal properties improvement, additives help enhance the performance and usability of PCMs. The melting temperature of some refrigerant clathrates is a little higher than what is generally required for comfort, food or electronics cooling. It is believed that this phase change temperature can be lowered by using additives such as salt, alcohol and ethylene glycol to make clathrates more suitable for cooling applications [12].

This paper aims to calculate the specific heat and thermal conductivities of different refrigerant clathrates with additives. It describes the model study to investigate the effects of adding additives in the selected refrigerant clathrates to enhance their thermal properties. Refrigerant clathrates of R134a, R1234yf and R32 are studies with copper, aluminum and graphene nanoparticles as additives. Some parametric studies are also conducted, varying the percentage of refrigerant and nanoparticles fraction, to study its effect on the thermal properties. At a preliminary level, the most appropriate refrigerant clathrates are proposed, and the use of suitable additives is also evaluated and discussed.

2. Methods

In order to assess the heat to or from a PCM, an appropriate knowledge of heat of fusion and specific heat of both the phases are required. Predicting the behavior of phase-change systems is difficult due to its inherent non-linear nature at moving interfaces, for which displacement rate is controlled by the latent heat lost or absorbed at the boundary [29]. The governing equation for heat can be written as follows:

$$Q = (mC_p\Delta T)_{Solid} + m\lambda + (mC_p\Delta T)_{liquid} \quad (1)$$

where m is the mass of the PCM, C_P is the specific heat, T is the temperature, and λ is the heat of fusion of PCM. Subscripts “solid” and “liquid” are for solid and liquid phase respectively. Specific heat can be