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Abstract

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Keywords

cooling, emulsion, material, change, systems, phase, development, novel

Disciplines

Engineering | Science and Technology Studies

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Abstract

In this paper, a novel phase change emulsion material (PCE-10) consisting of an organic PCM (RT10) and water has been developed. Its thermophysical properties such as heat of fusion, viscosity and sub-cooling temperature have been established. The chemical stability during both storage and discharge periods have also been evaluated. The results indicate low sub-cooling temperature and relatively long period of stability without any sign of segregation but the viscosity was found to be much higher than that of water.

Further improvement and experimental studies into its flow characteristics are therefore being encouraged.

Keywords: PCM emulsion; preparation method; thermo-physical properties; stability

Nomenclature

| | | | |
|-----------|------------------------|--------------|------------------------|
| T_m | Melting point | Δh_f | Latent heat capacity |
| C_p | Specific heat capacity | Δh_e | Heat storage capacity |
| η | Viscosity | Δh_s | Sensible heat capacity |
| φ | Volume fraction | T | Temperature |
| X | Weight fraction | V | Volume |

Subscripts

| | | | |
|---|----------|----------|-----------------|
| e | Emulsion | S | surfactant |
| p | Paraffin | separate | Separated phase |
| w | Water | | |

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18 **1. Introduction**

19 Over last few years, chilled water system powered by environmental friendly energy
20 resources has attracted great attention. However, the availability of renewable energy, such as
21 solar and wind, is uncontinuous. Efficient thermal energy storage (TES) for reducing the
22 mismatch between energy supply and demand for cooling applications is necessary [1]. In
23 addition, chilled water circulation pumps are responsible for roughly 15%-30% of the overall
24 energy consumption [2].

25 To this end, some researchers have suggested replacing water with phase change
26 emulsions (PCMEs) as cooling media which consist of phase change materials (PCMs) and
27 carrier fluids such as water. This is based on the fact that, they possess higher heat capacities
28 and therefore capable of reducing volume flow rates and energy consumption in pumps [4].
29 PCMEs could also act as the thermal storage material simultaneously, reducing the mismatch
30 between energy supply and demand for cooling applications [5].

31 However, most of the commercially available PCMEs do experience high levels of sub-
32 cooling temperatures which tend to affect the performance of refrigeration equipment. For
33 instance Huang et al. [6] observed poor performance in a refrigeration system at high sub-
34 cooling temperatures of 4.3K and 14.7K when tetradecane/water and hexadecane/water
35 PCMEs were used respectively. Royon and Guiffant [7] also observed poor performance at a
36 sub-cooling temperature of 5.6 K when aliphatic hydrocarbons-water emulsion was tested.

37 Another main barrier affecting the application of PCMEs is the thermal instability that
38 they experience after a period of usage and storage. Typically, air conditioning systems
39 operate for a period of six months each year [8]. Therefore the PCMEs should be able to
40 remain stable for at least six months and also not experience any temperature stratification
41 when the air conditioning systems are in operation. Literature review shows that most of the
42 currently available PCMEs fail to meet these requirements. For example, the emulsion

43 developed by Xu et al. [9] with tetradecane and water was stable for only 40-50s. The sample
44 tested by Schalbart et al. [10] achieved a short period of storage stability at room temperature.
45 Vilasau et al. [11] also tested the freeze-thaw stability of a paraffin emulsion and achieved
46 stability for only 5 cycles. The PCME developed by Huang [12] experienced instability after
47 a short storage period of one month and 100 melting/freezing thermal cycling.

48 This study is therefore intended to develop a novel phase change emulsion material that is
49 capable of overcoming these technical barriers.

50 **2. Development of PCME**

51 **2.1 Selection of Paraffin**

52 According to Huang et al [12], selection of PCMEs for air conditioning application should
53 be based on properties such as high heat capacity, low sub-cooling temperature, long term
54 storage stability and low viscosity. Paraffin materials such as tetradecane $\text{CH}_3\text{-(CH}_2\text{)}_{12}\text{-CH}_3$
55 ($T_m=5.8^\circ\text{C}$, $\Delta h_f=227 \text{ kJ}\cdot\text{kg}^{-1}$) and pentadecane $\text{CH}_3\text{-(CH}_2\text{)}_{13}\text{-CH}_3$ ($T_m=9.9^\circ\text{C}$, $\Delta h_f=206 \text{ kJ}\cdot\text{kg}^{-1}$)
56 are typical pure organic PCMs which may be combined with water to form PCMEs for
57 cooling applications within a phase transition temperature range of 7-12°C. However, due to
58 the relatively high cost of pure PCM, commercially available blended paraffin such as RT6
59 and RT10, are widely used for practical application. It should be noted that since the RT
60 series are mixtures of different paraffin their melting/freezing processes do not occur at
61 specific temperatures but rather over a temperature range.

62 The properties of RT10 and RT6 are listed in Tab. 1 [13]. For this development, RT10 was
63 selected as the core material because its melting/freezing temperature falls within the working
64 temperature of air conditioning systems. It also has higher heat of fusion and lower sub-
65 cooling temperature than RT6.

66

67

68
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Table 1: Thermo-physical properties of RT6 and RT10 [14]

| | RT6 | RT10 |
|---|---------|----------|
| Density (g/cm ³) | 0.73 | 0.8 |
| Melting temperature range T _e (°C) | 2.8-8.3 | 2.3-12 |
| Peak melting point T _{p,m} (°C) | 7 | 9 |
| Freezing temperature range T _{p,f} (°C) | 3.5-7.2 | 5.1-11.8 |
| Subcooling (°C) | 1.1 | 0.2 |
| Heat of fusion (kJ kg ⁻¹) | 132 | 135 |
| Conductivity (W m ⁻¹ K ⁻¹) | 0.19 | 0.21 |
| Viscosity (mPas) | 18 | 22 |

70

71 2.1.1 Determination of Paraffin Concentration

72 PCMEs are expected to have at least heat capacity of twice as high as that of water [14]. In
73 the temperature range of 7–12°C, water has a sensible heat capacity of 20.9 kJ·kg⁻¹, and
74 therefore the PCME should have at least a heat capacity of 40 kJ·kg⁻¹.

75 In the temperature range from T₁ to T₂, total heat storage capacity of PCME Δh_e is the sum
76 of latent heat capacity of the emulsion Δh_{f,e}, the sensible heat capacity of water Δh_{s,w} and that
77 of paraffin Δh_{s,p} as follows [15]:

$$78 \quad \Delta h_e = \Delta h_{f,e} + \Delta h_{s,w} + \Delta h_{s,p} = X_p \Delta h_{f,p} + X_w C_{p,w} (T_2 - T_1) + X_p C_{p,p} (T_2 - T_1) \quad (1)$$

79 Where, X_w and X_p are the weight fractions of paraffin and water, Δh_{f,p} is the heat of fusion
80 of paraffin in the temperature range of T₁ to T₂. C_{p,w} and C_{p,p} are the specific heat capacity of
81 water and the average specific heat capacity of the paraffin, respectively.

82 In the temperature range of 7–12°C, 25wt% PCME has a total heat capacity of 41 kJ·kg⁻¹,
83 which is almost 2 times as high as that of water. As indicated in Equ. 1, the heat capacity of
84 PCME is proportional to concentration of paraffin [12]. For paraffin concentration lower than
85 25wt%, the total heat capacity of the sample would fall short of the above criteria hence the
86 limit for this case..

87 Appropriate PCME for application in air conditioning systems should also have low
88 viscosity to ensure an acceptable level of pressure drop in pumps. Zhao [16] proposed the
89 following equation for predicting the kinematic viscosity of a two liquid mixture.

90
$$\eta = \eta_w e^{k\phi} \quad (2)$$

91 Where, η and η_w are the viscosities of emulsion and water respectively, ϕ is the volume
 92 fraction of oil phase and k is a constant which equals to 7 when $\phi \leq 0.74$.

93 For PCM concentrations over 35wt%, the viscosity of emulsions will be 15 times that of
 94 water. PCME is required to have a low viscosity for applications in pump systems. Thus, the
 95 paraffin weight fraction should not be more than 35wt% for this case.

96 Based on the theoretical analysis, different samples of emulsions consisting of 25wt%,
 97 30wt% and 35wt% concentration levels of paraffin were prepared for evaluation as
 98 summarised in Tab. 2. Analysis of the results shows that the sample containing 25wt% of
 99 paraffin is the most appropriate type with the acceptable level of heat of fusion and the
 100 highest thermal conductivity. It also has the lowest viscosity value and therefore suitable for
 101 reducing energy consumption in pumping systems.

102

103 **Table 2: Physical properties of 25-35wt% of RT10/Water emulsion**

| Paraffin (RT 10) Concentration (wt%) | Heat of fusion (kJ·kg ⁻¹) | Heat storage capacity (KJ·kg ⁻¹) | Heat storage ratio PCME-to water ratio | Viscosity (mPas) | Conductivity (W·m ⁻¹ ·K ⁻¹) |
|---|--|--|---|---------------------|---|
| 25 | 30.8 | 42 | 1.99 | 21 | 0.40 |
| 30 | 31.2 | 42.2 | 2.01 | 30 | 0.34 |
| 35 | 31.5 | 42.6 | 2.03 | 36 | 0.33 |
| 0% | - | 21 | - | 1.3 | 0.60 |

104

105 **2.2 Selection of Surfactant**

106 Since paraffin and water are immiscible, the emulsion has to be stabilised with surfactant
 107 to prevent segregation of different components. The Hydrophile-Lipophile Balance (HLB)
 108 method was therefore adopted to determine the appropriate type of surfactants needed to
 109 stabilize the RT10/water emulsion. The principle of this method is to match the specific HLB
 110 requirement (RHLB) of the oil phase against the HLB value of the surfactant in order to

111 obtain an optimum emulsification. HLB values can range from 0 to 20 depending upon the
 112 composition of the surfactant. As the HLB value increases, the surfactant becomes more
 113 hydrophilic and less lipophilic. In a situation where two or more surfactants are mixed
 114 together, the resulting HLB may also be calculated by using the following formula [17, 18]:

$$115 \quad HLB = X_{S,1} \times HLB_{S,1} + X_{S,2} \times HLB_{S,2} + \dots \quad (3)$$

116 **2.2.1 Determination of RHLB**

117 For the required HLB of oil phase, a series of emulsions will be made. Each emulsion will
 118 have the same amount of oil phase, water and surfactants but at a different HLB value. Any
 119 pair of non-ionic surfactants can be used to determine the appropriate values of HLB but one
 120 of them should have a low HLB number (<6) and the other a high HLB number (>14). In this
 121 study, two types of surfactants Brij 52 (HLB=5) and Tween 20 (HLB=16.7) were selected to
 122 produce five different emulsions and Eq. (3) was used to obtain their corresponding HLB
 123 values. The blended samples were then kept in test tubes and observed over a period of time
 124 in order to evaluate their chemical stability levels. As summarised in Tab. 3 sample No. 3
 125 achieved the longest period of chemical stability. Based on this result, the HLB requirement
 126 of the system is closest to 10.9.

127

128 **Table 3: Required HLB values**

| Sample No. | Surfactants | | Calculated HLB | Chemical separation period (min) |
|------------|-------------|----------|----------------|----------------------------------|
| | Brij 52 | Tween 20 | | |
| 1 | 100% | 0% | 5.0 | ≤5 |
| 2 | 60% | 40% | 9.7 | ≤90 |
| 3 | 50% | 50% | 10.9 | >90 |
| 4 | 40% | 60% | 12.0 | ≤30 |
| 5 | 0% | 100% | 16.7 | ≤5 |

129

130 **2.2.2 Optimised blend of surfactants**

131 Even though sample No. 3 appears to be the best candidate, it may not be the best
132 combination as their chemical structures can affect the stability of the emulsions. For instance,
133 surfactants with longer hydrocarbon tails are more effective in stabilizing dispersions than
134 those with shorter carbon chain lengths [19]. For these reasons different types of non-ionic
135 surfactant and an ionic surfactant (HTAB) with mixture HLB values around 10.9 were
136 blended and tested for stability after 48-hour storage period. This was assessed through their
137 separation rates by dividing the sum of the volume of water separated in the test tubes plus
138 that of paraffin ($V_{separate} = V_w + V_p$) by the total sample volume ($V_{total} = V_w + V_p + V_e$). This is
139 explained in Fig. 1 and expressed mathematically in Eq. (4) as:

$$140 \quad V\% = V_{separate} / V_{total} \times 100\% = V_w + V_p / V_w + V_p + V_e \times 100\% \quad (4)$$

141 Analysis of the results in Tab. 4 shows that the blend of Tween 60 and Brij 52 surfactants
142 achieved the highest level of stability without any sign of separation after the monitored
143 period and was attributed to their combined long hydrocarbon tails of 18 and 16 carbon atoms
144 respectively in the alkyl chain. This is further supported by previous research [19] which
145 indicated that long hydrocarbon tail can also act as nucleation centre for activating
146 crystallization and for reducing sub-cooling. To this end, 60% Tween60 and 40% Brij52
147 surfactants were selected for the optimum surfactant blend.

148

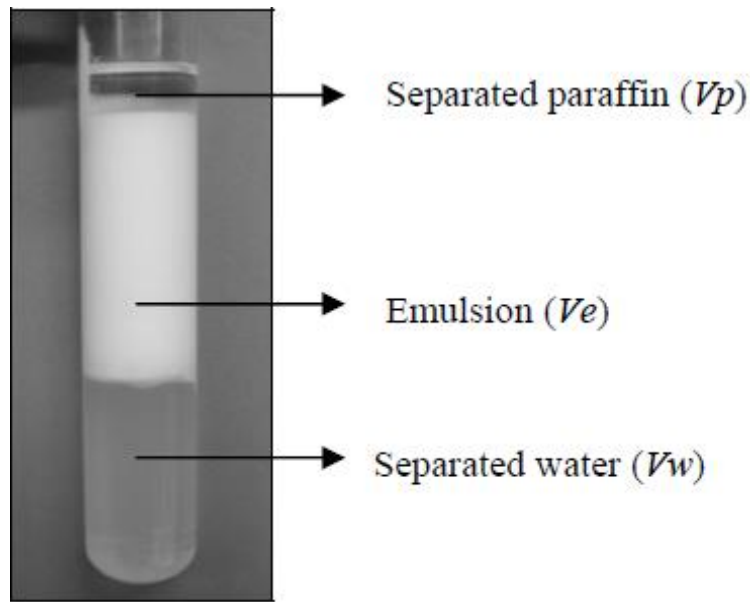


Figure 1: Emulsion separation

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Table 4: Optimised surfactant blends

| Sample No. | Surfactant types | | Calculated HLB | Separation Rate |
|------------|-----------------------|------------|----------------|-----------------|
| | Blends of surfactants | % wt ratio | | |
| 6 | Brij 35/Brij 52 | 50:50 | 11.0 | 60% |
| 7 | HTAB/Brij 52 | 55:45 | 10.9 | 60% |
| 8 | Tween 60/Brij 52 | 60:40 | 10.9 | 0 |
| 9 | Tween 20/Brij 52 | 50:50 | 10.9 | 20% |
| 10 | Brij 58/Brij 52 | 50:50 | 10.5 | 50% |

153

154 2.2.3 Concentration of Surfactant

155 Regarding the level of concentration of surfactant, Wang et al [20] suggested that 10-25%
156 of dispersed phase of surfactant would be effective in ensuring the stability of PCME under
157 either storage or mechanical-thermal cycling condition. However, other investigations
158 revealed that, concentration level should not be lower than 5wt% of total emulsion mixture
159 [21, 22].

160 In order to establish the appropriate level of concentration, 25% RT10 and water
161 emulsions with different mass fractions of the blended surfactant (5-20% of oil phase) were
162 prepared and tested for storage stability over a period of 72 hours. As summarised in Tab. 5,

163 sample No. 4 achieved the best stability result with no sign of chemical separation whereas
 164 samples No. 1-3 suffered from rapid chemical separation of various components before the
 165 end of testing period. Sample No. 5 (20% Surfactant/oil phase ratio) produced the worst
 166 result with large amount of bubbles during the emulsification process and was therefore
 167 considered unsuitable for testing.

168

169

Table 5: Evaluation test results for blended surfactants

| Sample No. | RT10 Concentration | Water Concentration | Blended surfactant Tween 60/Brij 52(3:2) | | Chemical separation period (min) | Separation rate at 72hr |
|------------|--------------------|---------------------|--|----------------------|----------------------------------|-------------------------|
| | | | Concentration of surfactant | Surfactant/oil ratio | | |
| 1 | 25% | 74.75% | 1.25% | 5% | <6 | 60% |
| 2 | 25% | 73% | 2% | 8% | ≤20 | 45% |
| 3 | 25% | 72.5% | 2.5% | 10% | ≤48 | 50% |
| 4 | 25% | 71.25% | 3.75% | 15% | >72 | 0 |
| 5 | 25% | 70% | 5% | 20% | Not applicable | Not applicable |

170

171 **2.3 Preparation of PCME**

172 Phase change emulsion was prepared by the so-called “mixing film synthesis”. All the
 173 constituents were initially weighted by a precision weighing scale as given in Tab. 6. The
 174 lipophilic surfactant Brij 52 was then dissolved in RT10 (Mixture A) while hydrophilic
 175 surfactant Tween 60 was mixed with deionized water (Mixture B). The mixtures were heated
 176 separately to about 50- 55°C before being added together and pre-emulsified using a
 177 magnetic hot plate stirrer at a speed of 500rpm and at 50°C for 15 minutes. Final
 178 emulsification was carried out by passing the coarse emulsion through a rotor-stator machine
 179 type ULTRA-TURRAX T18 at an emulsifying speed of 7200rpm for another 45 minutes.
 180 The developed sample which was named as PCE-10 could be described as a white milky Oil-
 181 in-Water emulsion.

182

183

Table 6: Composition of PCME

| Components | Wt% |
|------------|-------|
| RT10 | 25.0 |
| Tween 60 | 2.25 |
| Brij 52 | 1.5 |
| Water | 71.25 |

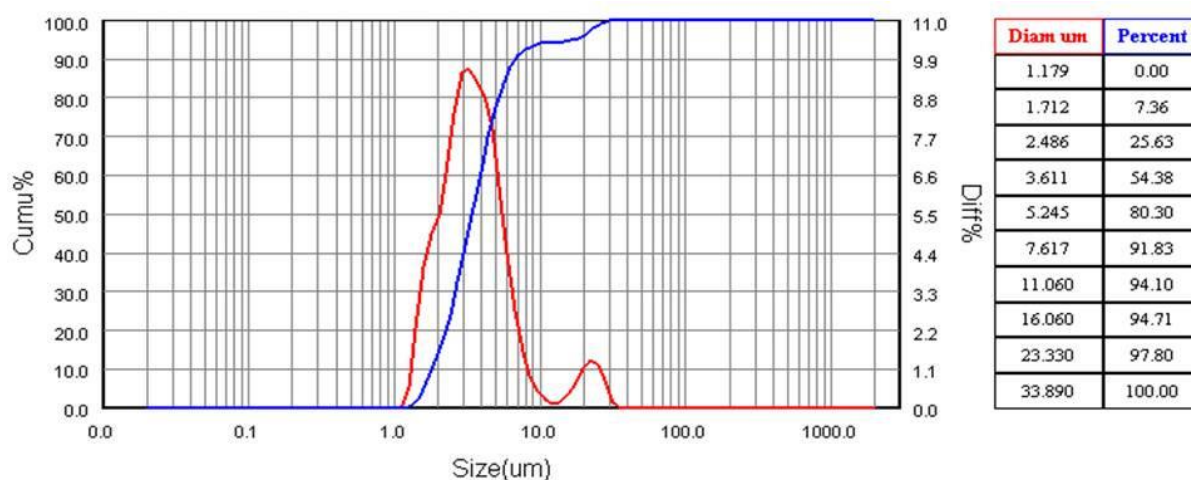
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185 3. Characterisation of developed emulsion (PCE-10)

186 3.1 Particle Sizing

187 Particle sizing and their distribution profiles are important parameters for specifying
 188 emulsions. Normally, dispersions with smaller particle sizes represent increased stability than
 189 those with coarse droplets. On the other hand, viscosity generally increases significantly with
 190 smaller particle sizes for a given mass or volume concentration in the dispersed phase. This is
 191 confirmed by Schramm et al. [23] which reported that the size and characteristics of particles
 192 do affect the stability, viscosity and thermal properties of emulsions. In this regard, a laser
 193 particle size analyser was used to establish the size of the PCE-10 and as a reference for the
 194 stability test. As presented in Fig. 2, the mean particle size was obtained as 3.14µm.

195



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198

Figure 2: Laser Particle sizing of PCE-10

199 3.2 Thermal Conductivity

200 The thermal conductivity of the sample was determined with a KD2 Pro Thermal
201 Properties Analyser, which has the ability to test liquid samples with accuracy of $\pm 5\%$. After
202 repeated tests the average thermal conductivity of the PCE-10 was obtained as $0.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
203 at a temperature of 25°C as summarised in Tab. 7.

204

205 Table 7: Thermal Conductivity Results

| Test No. | Temperature ($^\circ\text{C}$) | Thermal Conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) |
|----------|-------------------------------------|--|
| 1 | 24.94 | 0.409 |
| 2 | 25.00 | 0.406 |
| 3 | 25.22 | 0.400 |
| Average | 25.11 | 0.403 |

206

207 3.3 Phase Transition Temperature and Heat Capacity

208 The phase change temperature and the heat of fusion tests were conducted on 5mg sample
209 of the PCE-10 with a Differential Scanning Calorimetry (DSC) apparatus type EXSTAR SII
210 DSC6220 at a scanning rate of $1 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. DSC enables heat associated with flow in a sample
211 to be evaluated as a function of temperature. This may be achieved by recording the
212 difference in heat flow between a sample and a reference material as a function of
213 temperature as expressed mathematically in Eq. 5 [24].

$$214 \quad \frac{dH}{dt} = \left(\frac{dH}{dt}\right)_{\text{sample}} - \left(\frac{dH}{dt}\right)_{\text{reference}} \quad (5)$$

215 As presented in Fig. 3, an average value for the heat of fusion was obtained as $30.5 \text{ kJ}\cdot\text{kg}^{-1}$
216 ($\Delta h_{f,p}$) within a temperature range of $4 \text{ }^\circ\text{C}$ (T_e) and 11.94°C (T_c). Now by using Eq. (1), the
217 heat storage capacity was calculated as $60.5 \text{ kJ}\cdot\text{kg}^{-1}$ which is 1.8 times of water i.e. 33.4
218 $\text{kJ}\cdot\text{kg}^{-1}$ within the same temperature range.

219

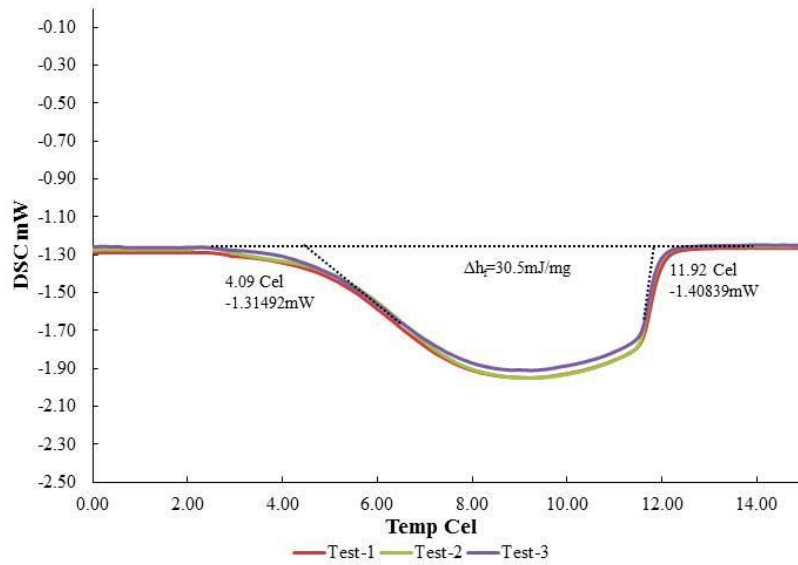


Figure 3: DSC curves of PCE-10

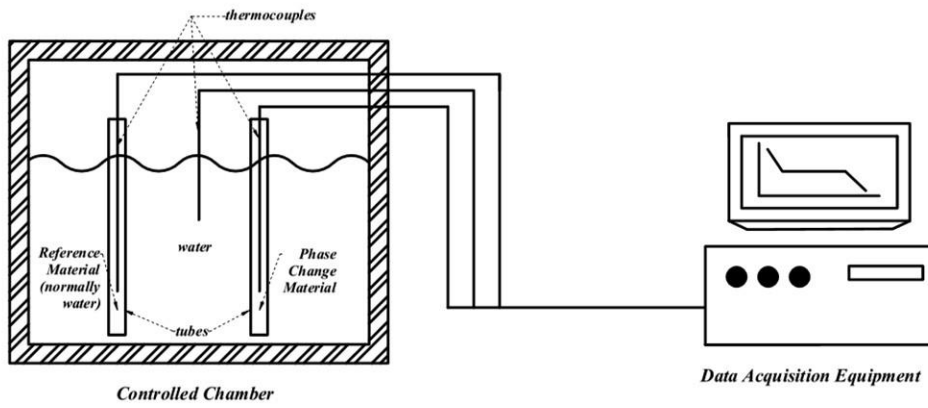
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223 3.4 Sub-cooling temperature

224 Sub-cooling lowers the crystallization temperature of a liquid or a gas, thus latent heat is
225 released at a lower temperature or in a wider temperature range [25]. A large sub-cooling
226 temperature is therefore not acceptable because it would enlarge the operating temperature
227 range of a cooling system and thus affects its performance.

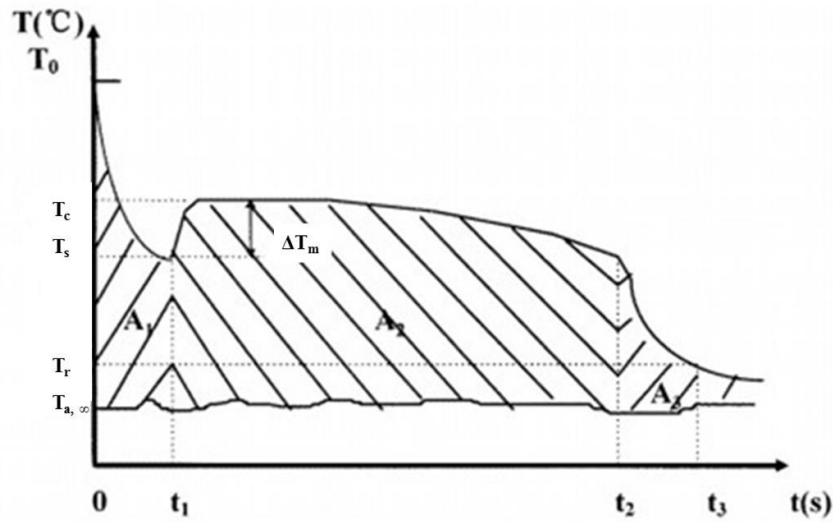
228 The sub-cooling test was conducted with the T-history method which is normally used in
229 measuring the thermal properties of bulk materials [26]. As demonstrated in Fig. 4, one of the
230 test tubes was filled with PCM and the other with a reference material, usually water, due to
231 its well-known thermo-physical properties. The tubes were then preheated above the melting
232 temperature of the PCM and then simultaneously exposed to the ambient temperature to
233 obtain the temperature history (T versus t) curves. A typical T-history curve of PCM with
234 sub-cooling is as presented in Fig. 5. The $\Delta T_m (=T_e - T_c)$ is the sub-cooling degree.

235



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Figure 4: Schematic setup for T-history method



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Figure 5: A typical T-history curve of PCM [26]

242 The T-history curve of PCE-10 was shown in Fig. 6. Analysis of the curves showed a
243 small sub-cooling degree of 0.2°C in the developed sample.

244

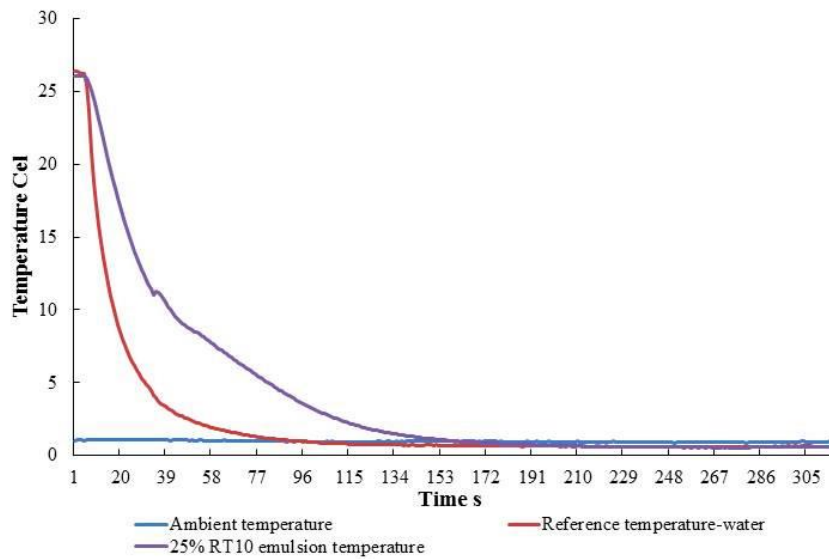


Figure 6: T-history curve of PCE-10

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248 3.5 Viscosity Test

249 Kinexus Lab⁺ Rotational Rheometer was used to determine the viscosity of PCE-10. The
250 plate diameter is 50mm, the cone diameter is 50mm, and the cone angle is 1°. Fig. 7
251 illustrates the relationship between viscosity and shear rate for the developed PCME at 25°C
252 and 10°C. The emulsion is a pseudo-plastic fluid and shows a shear thinning behaviour. The
253 viscosity of the emulsion reduced rapidly with increasing shear rate but stabilised at around
254 13mPas after 600s⁻¹. However, the viscosity appears quite high since it is about 13 times
255 higher than that of water.

256

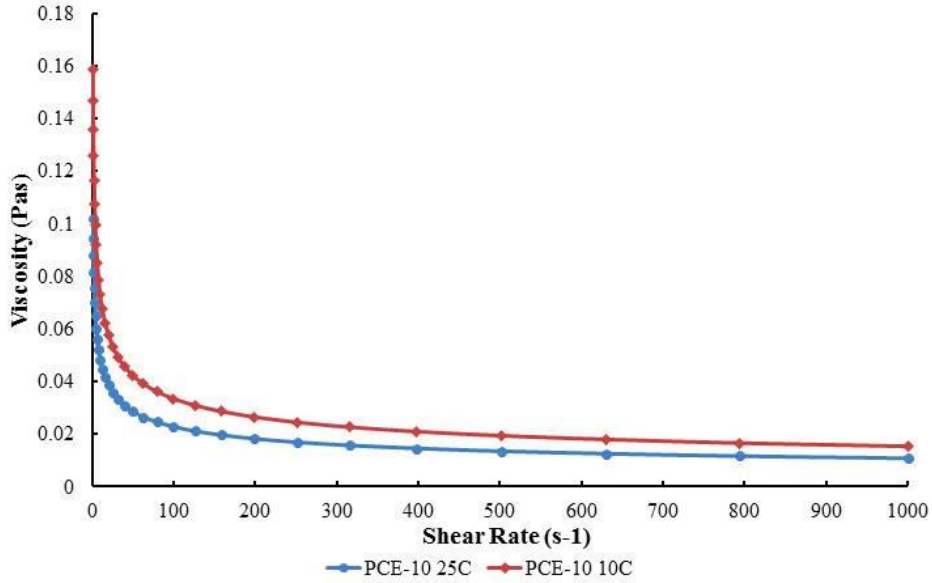


Figure 7: Relationship between viscosity and shear rate for PCE-10 at 10 and 25°C

The non-Newtonian behaviour can be described using Ostwald Equation:

$$\eta = K \times \gamma^{n-1} \quad (5)$$

Where, η is the viscosity, γ is the shear rate. K and n are coefficients which can be determined with a rheometer. The coefficient n is the flow behaviour index of a fluid which characterizes its degree of non-Newtonian behaviour. The greater the divergence of n from unity in either direction, the more non-Newtonian is the fluid. For Newtonian fluids, $n=1$ and for pseudo-plastic fluids $n<1$. The coefficient K, flow consistency index, defines the fluid's consistency. The larger the value of K, the thicker is the fluid.

The coefficients K and n of PCE-10 were obtained by interpreting the curves in Fig. 7 with the Ostwald Equation Eq. (5). The obtained K and n are shown in Tab. 8

Table 8: Coefficients K and n of PCE-10

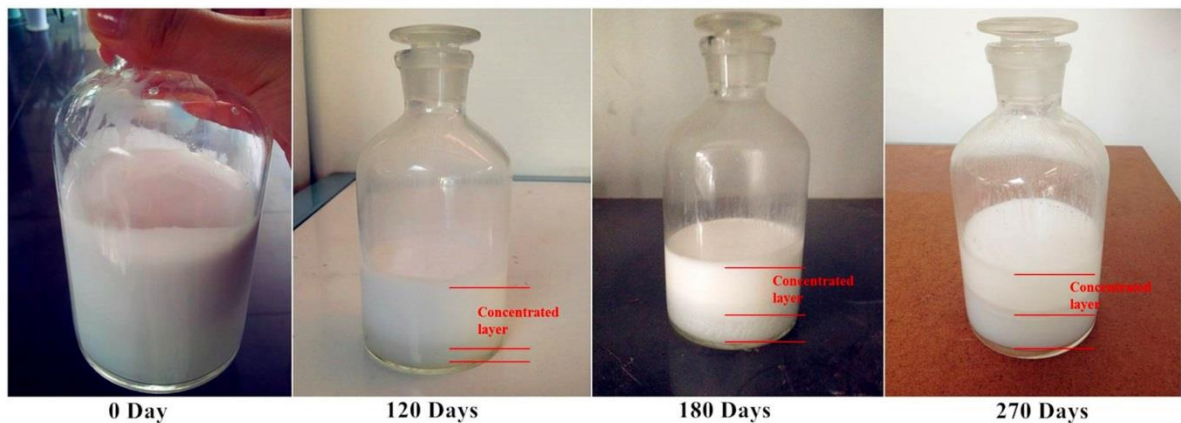
| T (°C) | K | n |
|-----------|--------|-------|
| 10 | 0.1887 | 0.662 |
| 25 | 0.102 | 0.675 |

273 **3.6 Stability Test**

274 *Non-cycling mode*

275 The emulsions were stored in containers made of glass at room temperature. The test was
276 carried out at a room temperature through visual inspection and over periodic number of days.
277 As presented in Fig. 8, separation started to occur after 90 days of storage and by the end of
278 270 days there was a clear separation between the upper and lower layers. This phenomenon
279 is called creaming and it is caused by the fact that paraffin has a lower density than water.
280 Creaming is the movement of oil droplets under gravity or in a centrifuge to form a
281 concentrated layer at the top of an oil-in-water emulsion. Particle size distribution of sample
282 was tested at the end of the storage period. The result shows a value of $3.41\mu\text{m}$ (see Fig. 9) at
283 the end of 270 days storage as compared with the original value of $3.14\mu\text{m}$. This indicates the
284 presence of oil droplets coalescence.

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Figure 8: Phase separation of emulsion

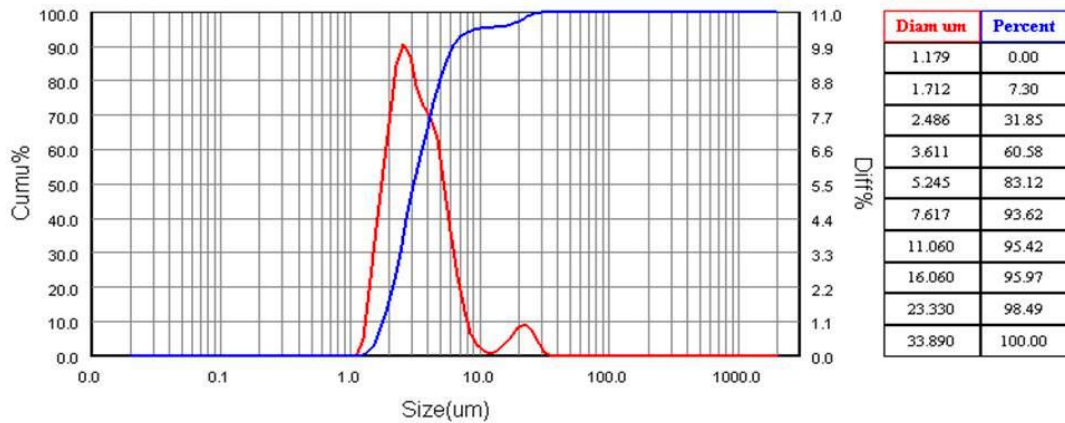


Figure 9: Particle sizing of PCE-10 after 270-day storage

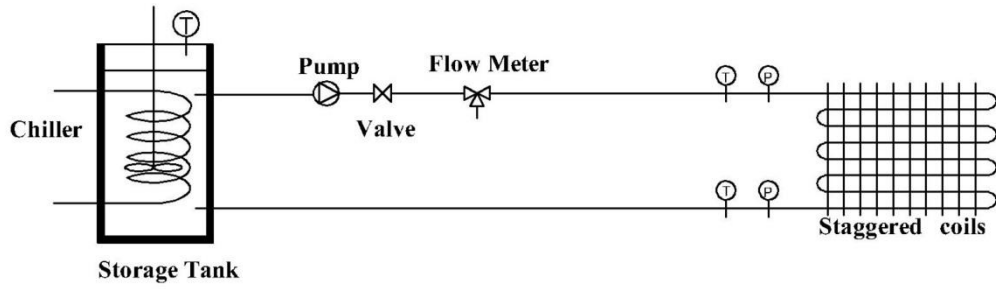
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290
291

292 *Cycling mode*

293 The stability of the sample was examined after being subjected to a number of thermal and
294 mechanical loadings. The test rig as illustrated in Fig. 10, consists of a storage tank, a heat
295 exchanger and a circulating pump. The sample was initially cooled down from 25°C to 5°C
296 and then reheated to 15°C. After 500 cycles, a clear layer of oil was observed (i.e. oiling-off
297 phenomena) as shown in Fig. 11 at the surface of the sample which was a sign of separation
298 of the base material (RT10) from the emulsion.

299 The droplet size distribution, viscosity and thermal properties of the samples were then
300 analysed and compared with the data before cycling. As shown in Fig. 12, there was a slight
301 increase in viscosity from 13mPas to 16mPas at 500rpm. The droplet size also increased
302 slightly from the original size of 3.14µm to 3.93µm (see Fig. 13). The latent heat of fusion
303 was reduced from 30.5 to 29.9 kJ kg⁻¹ as illustrated in Fig. 14. This was attributed to the fact
304 that when the emulsion was heated above the melting point, the crystallized droplets melted
305 and fused together thus leading to coalescence and oiling-off at the surface of the emulsion.
306 Although some changes were observed in the properties, the emulsion remained in dispersion
307 and maintained the heat capacity after the test.

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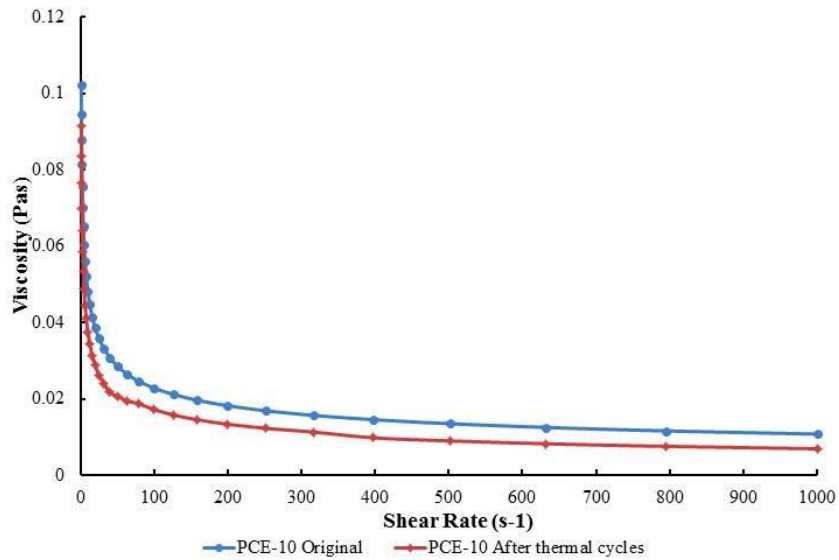
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Figure 10: Schematic diagram of the test rig



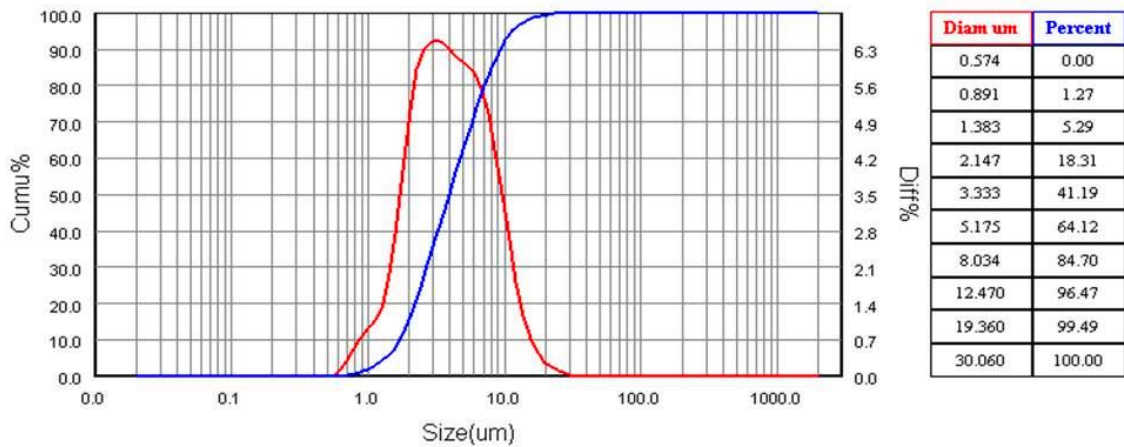
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Figure 11: Oiling-off phenomena of PCE-10



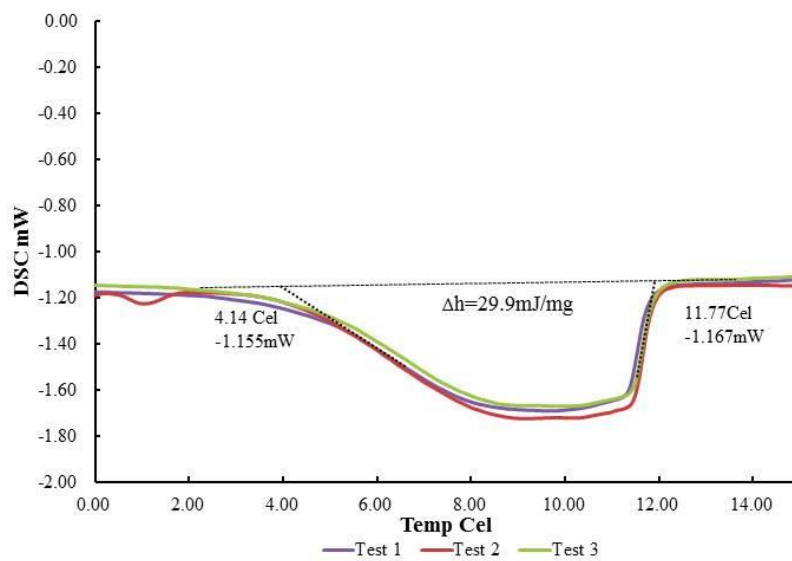
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Figure 12: Rheological behaviour after and before thermal-mechanical cycles



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Figure 13: Laser Particle sizing after 500 thermal mechanical cycles



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Figure 14: DSC curves of PCE-10 after 500 thermal mechanical cycles

4. Conclusion

323 In this paper, a novel paraffin-water emulsion (PCE-10) has been developed based on an
324 organic paraffin material called RT10. In order to achieve good level of stability in the
325 emulsion, the HLB method was used to obtain an optimum surfactant blend consisting of two
326 selected surfactants (Tween 60 and Brij 52). Analysis of the thermophysical properties
327 revealed the particle size of the PCE-10 sample to be 3μm with a storage heat capacity of
328 almost twice as much as that of water and with a negligible level of sub-cooling. The PCE-10
329 also achieved a good level of storage stability for 9 months and was able to withstand over

330 500 freeze-thaw cycles in a pumping system without any significant sign of degradation to
331 particle size and heat storage capacity.

332 However the viscosity of the PCE-10 was found to be much higher than water which could
333 contribute to high pressure drop in a pumping system. Its thermal conductivity was also
334 found to be about 30% lower than the value for water and could influence heat transfer.
335 Further enhancements of these thermophysical properties are therefore recommended.

336 Reference

- 337 [1] T. Hasenöhr, "An Introduction to Phase Change Materials as Heat Storage Mediums,"
338 Sweden2009.
- 339 [2] W. Zhong, "Building air conditioning energy consumption and energy saving measures in
340 China," MSc Master thiese, Environment engineering, MSc Chongqing University
341 unpublished, 2004.
- 342 [3] C. Pollerberg and C. Dotsch, "Phase changing slurries in cooling and cold supply networks,"
343 in *10th International Symposium on District Heating and Cooling*, 2006.
- 344 [4] Y. Xu, "Study the saving energy method for fan-coil unit system," MSc Master thiese,
345 Construction and Civil Engineering, Xi'an University of Architecture and Technology,
346 unpublished, 2005.
- 347 [5] P. Zhang and Z. W. Ma, "An overview of fundamental studies and applications of phase
348 change material slurries to secondary loop refrigeration and air conditioning systems,"
349 *Renewable and Sustainable Energy Reviews*, vol. 16, pp. 5021-5058, 2012.
- 350 [6] L. Huang, E. Günther, C. Doetsch, and H. Mehling, "Subcooling in PCM emulsions—Part 1:
351 Experimental," *Thermochimica Acta*, vol. 509, pp. 93-99, 2010.
- 352 [7] L. Royon and G. Guiffant, "Heat transfer in paraffin oil/water emulsion involving
353 supercooling phenomenon," *Energy Conversion and Management*, vol. 42, pp. 2155-2161,
354 2001.
- 355 [8] J. Wang, "Ruuning cost analysis for water source heat pump air conditioning," *HV & AC*, vol.
356 1, pp. 63-66, 2004.
- 357 [9] H. Xu, R. Yang, Y. Zhang, Z. Huang, J. Lin, and X. Wang, "Thermal physical properties and
358 key influence factors of phase change emulsion," *Chinese Science Bulletin*, vol. 50, pp. 188-
359 193, 2005.
- 360 [10] P. Schallbart, M. Kawaji, and K. Fumoto, "Formation of tetradecane nanoemulsion by low-
361 energy emulsification methods," *International Journal of Refrigeration*, vol. 33, pp. 1612-
362 1624, 2010.
- 363 [11] J. Vilasau, C. Solans, M. J. Gómez, J. Dabrio, R. Mújika-Garai, and J. Esquena, "Stability of
364 oil-in-water paraffin emulsions prepared in a mixed ionic/nonionic surfactant system,"
365 *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 389, pp. 222-229,
366 2011.
- 367 [12] L. Huang, M. Petermann, and C. Doetsch, "Evaluation of paraffin/water emulsion as a phase
368 change slurry for cooling applications," *Energy*, vol. 34, pp. 1145-1155, 2009.
- 369 [13] Rubitherm Technologies GmbH. see: <http://www.rubitherm.com>.
- 370 [14] L. Huang, "Paraffin Water Phase Change Emulsion for Cold Storage and Distribution
371 Applications," PhD, Fraunhofer Institute UMSICHT, Ruhr-University Bochum, Electronic
372 publication, 2009.
- 373 [15] L. Huang, P. Noeres, M. Petermann, and C. Doetsch, "Experimental study on heat capacity of
374 paraffin/water phase change emulsion," *Energy Conversion and Management*, vol. 51, pp.
375 1264-1269, 2010.

- 376 [16] F. Zhao, *Petrol Chemistry*. Beijing: China University of Petroleum Press, 1989.
- 377 [17] I. Americas, *The HLB system a time-saving guide to emulsifier selection*. Wilmington,
378 Delaware, US: chemmunique, 1987.
- 379 [18] K. Zhang, R. Li, Y. Lu, and P. Shang, "HLB and Surfactant selection," *Journal of*
380 *Shijiazhuang Vocational Technology Institute*, vol. 16, pp. 20-22, 2004.
- 381 [19] K. Golemanov, S. Tcholakova, N. D. Denkov, and T. CGurkov, "Selection of Surfactants for
382 Stable Paraffin-in-Water Dispersions, undergoing Soild-Liquid Transition of the Dispersed
383 Particles," *Langmuir*, vol. 22, pp. 3560-3569, 2006.
- 384 [20] B. Wang, Y. Zhang, and D. Sun, "Preparation and application of wax emulsion," *Shandong*
385 *Chemical Industry*, vol. 33, pp. 14-17, 2004.
- 386 [21] J. Wang and T. Zhang, "The anomalous rheological properties of wax miniemulsion with
387 mixed emulsifier," *Journal of Shandong institute of light industry*, vol. 11, pp. 12-14, 1997.
- 388 [22] J. Wang, "Preparation and properties of paraffin miniemulsion," *Journal of Shandong institute*
389 *of light industry*, vol. 11, pp. 24-27, 1997.
- 390 [23] L. L. Schramm, "Emulsion, foams and suspensions," *Weinheim: Wiley-VCH Verlag GmbH &*
391 *Co*, 2005.
- 392 [24] S. D. Sharma and K. Sagara, "Latent Heat Storage Materials and Systems: A Review,"
393 *International Journal of Green Energy*, vol. 2, pp. 1-56, 2005.
- 394 [25] X. X. Zhang, Y. F. Fan, X. M. Tao, and K. L. Yick, "Crystallization and prevention of
395 supercooling of microencapsulated n-alkanes," *Journal of Colloid and Interface Science*, vol.
396 281, pp. 299-306, Jan 15 2005.
- 397 [26] Y. Zhang, Y. Jiang, and Y. Jiang, "A simple method, the T-history method, of determining
398 the heat of fusion, specific heat and thermal conductivity of phase-change materials,"
399 *Measurement and Science Technology* vol. 10, pp. 201-205, 1999.
- 400
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