Development of a novel phase change material emulsion for cooling systems

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

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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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_m )</td>
<td>Melting point</td>
</tr>
<tr>
<td>( C_p )</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Viscosity</td>
</tr>
<tr>
<td>( \varphi )</td>
<td>Volume fraction</td>
</tr>
<tr>
<td>( X )</td>
<td>Weight fraction</td>
</tr>
<tr>
<td>( \Delta h_f )</td>
<td>Latent heat capacity</td>
</tr>
<tr>
<td>( \Delta h_e )</td>
<td>Heat storage capacity</td>
</tr>
<tr>
<td>( \Delta h_s )</td>
<td>Sensible heat capacity</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
</tr>
<tr>
<td>( V )</td>
<td>Volume</td>
</tr>
</tbody>
</table>

Subscripts

- e: Emulsion
- p: Paraffin
- w: Water
- S: Surfactant
- separate: Separated phase

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1. Introduction

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

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

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

Another main barrier affecting the application of PCMEs is the thermal instability that they experience after a period of usage and storage. Typically, air conditioning systems operate for a period of six months each year [8]. Therefore the PCMEs should be able to remain stable for at least six months and also not experience any temperature stratification when the air conditioning systems are in operation. Literature review shows that most of the currently available PCMEs fail to meet these requirements. For example, the emulsion
developed by Xu et al. [9] with tetradecane and water was stable for only 40-50s. The sample tested by Schalbart et al. [10] achieved a short period of storage stability at room temperature. Vilasau et al. [11] also tested the freeze-thaw stability of a paraffin emulsion and achieved stability for only 5 cycles. The PCME developed by Huang [12] experienced instability after a short storage period of one month and 100 melting/freezing thermal cycling.

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

2. Development of PCME

2.1 Selection of Paraffin

According to Huang et al [12], selection of PCMEs for air conditioning application should be based on properties such as high heat capacity, low sub-cooling temperature, long term storage stability and low viscosity. Paraffin materials such as tetradecane CH₃-(CH₂)₁₂-CH₃ (T_m=5.8°C, Δh_f=227 kJ·kg⁻¹) and pentadecane CH₃-(CH₂)₁₃-CH₃ (T_m=9.9°C, Δh_f=206 kJ·kg⁻¹) are typical pure organic PCMs which may be combined with water to form PCMEs for cooling applications within a phase transition temperature range of 7-12°C. However, due to the relatively high cost of pure PCM, commercially available blended paraffin such as RT6 and RT10, are widely used for practical application. It should be noted that since the RT series are mixtures of different paraffin their melting/freezing processes do not occur at specific temperatures but rather over a temperature range.

The properties of RT10 and RT6 are listed in Tab. 1 [13]. For this development, RT10 was selected as the core material because its melting/freezing temperature falls within the working temperature of air conditioning systems. It also has higher heat of fusion and lower sub-cooling temperature than RT6.
Table 1: Thermo-physical properties of RT6 and RT10 [14]

<table>
<thead>
<tr>
<th></th>
<th>RT6</th>
<th>RT10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.73</td>
<td>0.80</td>
</tr>
<tr>
<td>Melting temperature range Tₑ (°C)</td>
<td>2.8-8.3</td>
<td>2.3-12</td>
</tr>
<tr>
<td>Peak melting point Tₚ,m(°C)</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Freezing temperature range Tₚ,f (°C)</td>
<td>3.5-7.2</td>
<td>5.1-11.8</td>
</tr>
<tr>
<td>Subcooling (°C)</td>
<td>1.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Heat of fusion (kJ kg⁻¹)</td>
<td>132</td>
<td>135</td>
</tr>
<tr>
<td>Conductivity (W m⁻¹K⁻¹)</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>Viscosity (mPas)</td>
<td>18</td>
<td>22</td>
</tr>
</tbody>
</table>

2.1.1 Determination of Paraffin Concentration

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

In the temperature range from T₁ to T₂, total heat storage capacity of PCME Δhₑ is the sum of latent heat capacity of the emulsion Δhₑ,e, the sensible heat capacity of water Δhₛₕ, and that of paraffin Δhₛ,p as follows [15]:

\[
Δhₑ = Δhₑ,e + Δhₛₕ + Δhₛ,p = X_pΔh_p + X_wC_p,W(T₂−T₁) + X_pC_p,p(T₂−T₁)
\] (1)

Where, X_w and X_p are the weight fractions of paraffin and water, Δhₑ,e is the heat of fusion of paraffin in the temperature range of T₁ to T₂, C_p,W and C_p,p are the specific heat capacity of water and the average specific heat capacity of the paraffin, respectively.

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

Appropriate PCME for application in air conditioning systems should also have low viscosity to ensure an acceptable level of pressure drop in pumps. Zhao [16] proposed the following equation for predicting the kinematic viscosity of a two liquid mixture.
Where, $\eta$ and $\eta_w$ are the viscosities of emulsion and water respectively, $\varphi$ is the volume fraction of oil phase and $k$ is a constant which equals to 7 when $\varphi \leq 0.74$.

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

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

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

2.2 Selection of Surfactant

Since paraffin and water are immiscible, the emulsion has to be stabilised with surfactant to prevent segregation of different components. The Hydrophile-Lipophile Balance (HLB) method was therefore adopted to determine the appropriate type of surfactants needed to stabilize the RT10/water emulsion. The principle of this method is to match the specific HLB requirement (RHLB) of the oil phase against the HLB value of the surfactant in order to
obtain an optimum emulsification. HLB values can range from 0 to 20 depending upon the composition of the surfactant. As the HLB value increases, the surfactant becomes more hydrophilic and less lipophilic. In a situation where two or more surfactants are mixed together, the resulting HLB may also be calculated by using the following formula [17, 18]:

\[ HLB = X_{S,1} \times HLB_{S,1} + X_{S,2} \times HLB_{S,2} + \ldots \]  

(3)

### 2.2.1 Determination of RHLB

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

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Surfactants</th>
<th>Calculated HLB</th>
<th>Chemical separation period (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Brij 52 100%, Tween 20 0%</td>
<td>5.0</td>
<td>≤5</td>
</tr>
<tr>
<td>2</td>
<td>Brij 52 60%, Tween 20 40%</td>
<td>9.7</td>
<td>≤90</td>
</tr>
<tr>
<td>3</td>
<td>Brij 52 50%, Tween 20 50%</td>
<td>10.9</td>
<td>&gt;90</td>
</tr>
<tr>
<td>4</td>
<td>Brij 52 40%, Tween 20 60%</td>
<td>12.0</td>
<td>≤30</td>
</tr>
<tr>
<td>5</td>
<td>Brij 52 0%, Tween 20 100%</td>
<td>16.7</td>
<td>≤5</td>
</tr>
</tbody>
</table>
2.2.2 Optimised blend of surfactants

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

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

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

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Surfactant types</th>
<th>%wt ratio</th>
<th>Calculated HLB</th>
<th>Separation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Brij 35/Brij 52</td>
<td>50:50</td>
<td>11.0</td>
<td>60%</td>
</tr>
<tr>
<td>7</td>
<td>HTAB/Brij 52</td>
<td>55:45</td>
<td>10.9</td>
<td>60%</td>
</tr>
<tr>
<td>8</td>
<td>Tween 60/Brij 52</td>
<td>60:45</td>
<td>10.9</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Tween 20/Brij 52</td>
<td>50:50</td>
<td>10.9</td>
<td>20%</td>
</tr>
<tr>
<td>10</td>
<td>Brij 58/Brij 52</td>
<td>50:50</td>
<td>10.5</td>
<td>50%</td>
</tr>
</tbody>
</table>

2.2.3 Concentration of Surfactant

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

In order to establish the appropriate level of concentration, 25% RT10 and water emulsions with different mass fractions of the blended surfactant (5-20% of oil phase) were prepared and tested for storage stability over a period of 72 hours. As summarised in Tab. 5,
sample No. 4 achieved the best stability result with no sign of chemical separation whereas samples No. 1-3 suffered from rapid chemical separation of various components before the end of testing period. Sample No. 5 (20% Surfactant/oil phase ratio) produced the worst result with large amount of bubbles during the emulsification process and was therefore considered unsuitable for testing.

Table 5: Evaluation test results for blended surfactants

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

2.3 Preparation of PCME

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

<table>
<thead>
<tr>
<th>Components</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT10</td>
<td>25.0</td>
</tr>
<tr>
<td>Tween 60</td>
<td>2.25</td>
</tr>
<tr>
<td>Brij 52</td>
<td>1.5</td>
</tr>
<tr>
<td>Water</td>
<td>71.25</td>
</tr>
</tbody>
</table>

3. Characterisation of developed emulsion (PCE-10)

3.1 Particle Sizing

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

Figure 2: Laser Particle sizing of PCE-10
3.2 Thermal Conductivity

The thermal conductivity of the sample was determined with a KD2 Pro Thermal Properties Analyser, which has the ability to test liquid samples with accuracy of ±5%. After repeated tests the average thermal conductivity of the PCE-10 was obtained as 0.4 W·m⁻¹·K⁻¹ at a temperature of 25°C as summarised in Tab. 7.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Temperature (°C)</th>
<th>Thermal Conductivity (W·m⁻¹·K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.94</td>
<td>0.409</td>
</tr>
<tr>
<td>2</td>
<td>25.00</td>
<td>0.406</td>
</tr>
<tr>
<td>3</td>
<td>25.22</td>
<td>0.400</td>
</tr>
<tr>
<td>Average</td>
<td>25.11</td>
<td>0.403</td>
</tr>
</tbody>
</table>

3.3 Phase Transition Temperature and Heat Capacity

The phase change temperature and the heat of fusion tests were conducted on 5mg sample of the PCE-10 with a Differential Scanning Calorimetry (DSC) apparatus type EXSTAR SII DSC6220 at a scanning rate of 1 °C·min⁻¹. DSC enables heat associated with flow in a sample to be evaluated as a function of temperature. This may be achieved by recording the difference in heat flow between a sample and a reference material as a function of temperature as expressed mathematically in Eq. 5 [24].

\[
\frac{dH}{dt} = \left(\frac{dH}{dt}\right)_\text{sample} - \left(\frac{dH}{dt}\right)_\text{reference}
\]  

(5)

As presented in Fig. 3, an average value for the heat of fusion was obtained as 30.5 kJ·kg⁻¹ (Δh_{f,p}) within a temperature range of 4 °C (T_e) and 11.94°C (T_c). Now by using Eq. (1), the heat storage capacity was calculated as 60.5 kJ·kg⁻¹ which is 1.8 times of water i.e. 33.4 kJ·kg⁻¹ within the same temperature range.
Sub-cooling lowers the crystallization temperature of a liquid or a gas, thus latent heat is released at a lower temperature or in a wider temperature range [25]. A large sub-cooling temperature is therefore not acceptable because it would enlarge the operating temperature range of a cooling system and thus affects its performance.

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

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

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

Kinexus Lab\textsuperscript{3} Rotational Rheometer was used to determine the viscosity of PCE-10. The plate diameter is 50mm, the cone diameter is 50mm, and the cone angle is 1°. Fig. 7 illustrates the relationship between viscosity and shear rate for the developed PCME at 25°C and 10°C. The emulsion is a pseudo-plastic fluid and shows a shear thinning behaviour. The viscosity of the emulsion reduced rapidly with increasing shear rate but stabilised at around 13mPas after 600s\textsuperscript{-1}. However, the viscosity appears quite high since it is about 13 times higher than that of water.
The non-Newtonian behaviour can be described using Ostwald Equation:

\[ \eta = K \times \gamma^{n-1} \] (5)

Where, \( \eta \) is the viscosity, \( \gamma \) 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

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>K</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1887</td>
<td>0.662</td>
</tr>
<tr>
<td>25</td>
<td>0.102</td>
<td>0.675</td>
</tr>
</tbody>
</table>
3.6 Stability Test

Non-cycling mode

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

Figure 8: Phase separation of emulsion
The stability of the sample was examined after being subjected to a number of thermal and mechanical loadings. The test rig as illustrated in Fig. 10, consists of a storage tank, a heat exchanger and a circulating pump. The sample was initially cooled down from 25°C to 5°C and then reheated to 15°C. After 500 cycles, a clear layer of oil was observed (i.e. oiling-off phenomena) as shown in Fig. 11 at the surface of the sample which was a sign of separation of the base material (RT10) from the emulsion.

The droplet size distribution, viscosity and thermal properties of the samples were then analysed and compared with the data before cycling. As shown in Fig. 12, there was a slight increase in viscosity from 13mPas to 16mPas at 500rpm. The droplet size also increased slightly from the original size of 3.14μm to 3.93μm (see Fig. 13). The latent heat of fusion was reduced from 30.5 to 29.9 kJ kg\(^{-1}\) as illustrated in Fig. 14. This was attributed to the fact that when the emulsion was heated above the melting point, the crystallized droplets melted and fused together thus leading to coalescence and oiling-off at the surface of the emulsion. Although some changes were observed in the properties, the emulsion remained in dispersion and maintained the heat capacity after the test.
Figure 10: Schematic diagram of the test rig

Figure 11: Oiling-off phenomena of PCE-10

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

In this paper, a novel paraffin-water emulsion (PCE-10) has been developed based on an organic paraffin material called RT10. In order to achieve good level of stability in the emulsion, the HLB method was used to obtain an optimum surfactant blend consisting of two selected surfactants (Tween 60 and Brij 52). Analysis of the thermophysical properties revealed the particle size of the PCE-10 sample to be 3µm with a storage heat capacity of almost twice as much as that of water and with a negligible level of sub-cooling. The PCE-10 also achieved a good level of storage stability for 9 months and was able to withstand over
500 freeze-thaw cycles in a pumping system without any significant sign of degradation to particle size and heat storage capacity.

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

Reference


