Phase change material: Optimizing the thermal properties and thermal conductivity of myristic acid/palmitic acid eutectic mixture with acid-based surfactants

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HIGHLIGHTS

- Myristic acid (MA) and palmitic acid (PA) are fatty acids component.
- The eutectic composition ratio of MA/PA obtained at 70/30, wt.%.
- 5% each acid-based surfactants were reduces the melting and undercooling temperature of MA/PA (70/30, wt.%).
- Thermal conductivity and $H_f$ of MA/PA (70/30, wt.%) were increased by adding 5% surfactants.
- MA/PA + 5% acid-based surfactants have a great potential to apply in LHTES applications.

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ABSTRACT

In this study the addition of surfactant to fatty acids as phase change materials (PCMs) for solar thermal applications is proposed. The incorporation of surfactant additives into a eutectic mixture of fatty acids can significantly increase the value of latent heat storage and can suppress undercooling. We report the preparation of myristic acid/palmitic acid (MA/PA) eutectic mixture as Phase Change Material (PCM) with addition of 0, 5, 10, 15, and 20% sodium myristate (SM), sodium palmitate (SP), and sodium stearate (SS), the influence of surfactant additives on thermal properties and thermal conductivity of eutectic mixtures. It was found that the addition of 5% SM, 5% SP, and 5% SS to MA/PA eutectic mixture is very effective in depressing the liquid/solid phase change temperature, reducing the undercooling and increasing the amount of latent heat of fusion as well as thermal conductivity of eutectic PCM compared to eutectic PCM without surfactants. Furthermore MA/PA + 5%SS has the highest latent heat of fusion of 191.85 J g$^{-1}$, while MA/PA + 5%SM showed the least undercooling of 0.34 $^\circ$C and the highest thermal conductivity of 0.242 W m$^{-1}$ K$^{-1}$.

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1. Introduction

Research and development on thermal energy storage (TES) have been conducted in order to obtain a heat storage system with a high heat capacity and good heat transfer mechanism. Determining the appropriate material to store the heat is the key in development of heat storage systems, particularly the investigation of solid–liquid phase change materials (PCMs) due to the following considerations: suitable range temperature, involves high latent heat PCMs, narrow phase transition temperature [1,2].

The selection of a suitable heat storage material is a very important factor in optimizing the thermal efficiency, economic feasibility, and durability of latent heat thermal energy storage (LHTES) systems.
[3]. In general, the disadvantages of materials in LHTES are the low thermal conductivity, density changes and thermal stability properties for long time utilization, and large undercooling [3].

Materials that have been developed for LHTES are organic or inorganic. In previous studies, the thermal properties and thermal stability of PCMs eutectic mixture such as Mg(NO$_3$)$_2$·6NH$_4$NO$_3$ + 6H$_2$O (61.5/38.5, wt.%), Mg(NO$_3$)$_2$·6H$_2$O + MgCl$_2$·6H$_2$O (58.7/41.3, wt.%), Mg(NO$_3$)$_2$·6H$_2$O + Al(NO$_3$)$_3$·9H$_2$O (53.47, wt.%), urea + acetamide (37.5/63.5, wt.%), naphthalene + benzoic acid (67.1/32.9, wt.%) were investigated, and it was concluded that those eutectics have potential as PCM for LHTES [4,9].

Fatty acids are selected for the development of heat storage material because they have thermodynamic and kinetic properties suitable for low temperature latent heat storage [4,9–12]. Fatty acids have a high latent heat of fusion and their volume changes during the phase transition are insignificant [11]. They also have a suitable melting temperature range for solar heating application [13]. These make them superior over other PCMs mostly due to congruent melting, good chemical stability and non-toxicity. Furthermore, fatty acids are more sustainable than other PCMs because they are derived from common vegetable and animal oils, which are renewable materials [14,15].

Sari et al. [1,7,16] prepared the myristic acid/palmitic acid (MA/PA) eutectic mixture and the result show that the melting temperature and latent heat of fusion of MA/PA eutectic mixture are 42.6 °C (58/42, wt.%) and 169.7 J g$^{-1}$, respectively [16]. Matsui et al. [17] improved the phase transition temperature and latent heat of fusion capric acid/lauric acid (70/30, wt.%) eutectic mixture by adding the acid based surfactant additives of 5, 10, 15, and 20%, respectively. In a recent study on MA and PA, the phase transition temperature and latent heat of fusion MA/PA eutectic mixture was improved by the addition of acid-based surfactants.

The objectives of this study to determine the suitable phase change transition temperature and the optimum latent heat of fusion of prepared MA/PA eutectic mixture and to observe the effect of adding surfactant additives such as sodium myristate (SM), sodium palmitate (SP), and sodium stearate (SS) as much as 5, 10, 15, and 20%, respectively. The thermal properties were determined using Differential Scanning Calorimetric (DSC) analysis techniques, and the thermal conductivity of eutectics PCM was evaluated using the hot wire method by KD2Pro thermal conductivity analysis.

2. Materials and methods

2.1. Preparation of MA/PA eutectic mixture

A eutectic mixture of myristic acid/palmitic acid (MA/PA) was formulated by blending the single components with mass fraction composition ratio of 0–100% in intervals of 10%. To obtain an accurate analysis, determination of thermal properties was repeated 3 times. Standard deviation of liquid/solid phase change temperature and latent heat of MA/PA eutectic mixture obtained were 0.064 °C and 2.7 J g$^{-1}$, respectively.

2.2. DSC thermal properties analysis

Thermal properties such as melting temperature ($T_m$), solidifying temperature ($T_s$), and the latent heat of fusion ($\Delta H_f$) of pure MA/PA and MA/PA with surfactant additives were identified using DSC thermal analysis (Mettler Toledo, DSC1 Star$^\text{®}$ system). The heating and cooling rate were set to 5 °C min$^{-1}$. To obtain an accurate analysis, determination of thermal properties was repeated 3 times. Standard deviation of liquid/solid phase change temperature and latent heat of MA/PA eutectic mixture obtained were 0.064 °C and 2.7 J g$^{-1}$, respectively.

2.3. Thermal conductivity analysis

Thermal conductivity of pure MA/PA and MA/PA with surfactant additives was determined using the hot wire method KD2Pro.
3. Results and discussion

3.1. Thermal properties of MA/PA eutectic mixture

The DSC curve analysis of single component fatty acids and fatty acid mixtures is shown in Fig. 2. The determination of melting/solidification temperature and latent heat of fusion of eutectic PCM was located from onset and normalized value in original graph of DSC analysis. It was shows that the melting temperature of MA and PA components was 54.7 °C and 63.08 °C, and that the latent heat of fusion (\( \Delta H_f \)) was 161.37 J g\(^{-1}\) and 173.69 J g\(^{-1}\), respectively. Thus, both of these components are selected as candidates to form MA/PA eutectic mixture with a large latent heat storage and suitable phase change temperature in LHTES applications. The prepared eutectic mixture of MA/PA in Fig. 3 shows that the lowest melting temperature occurs at the composition ratio 70/30 wt.%. Therefore this composition was used for further investigation. The same condition also reported by Karaipekli et al. [9,10] that obtained the melting temperature of CA/SA eutectic mixture (83/17, wt.%), CA/LA (64/36, wt.%), and CA/MA (73/27, wt.%) which were lower than the melting temperatures of their single components.

However, the phase transition temperature of MA/PA eutectic mixture (70/30, wt.%) indicated the occurrence of undercooling as there is a gap between the melting temperature and solidifying temperature of the eutectic mixture: the melting and solidifying temperatures of MA/PA were 46.73 °C and 44.76 °C, respectively. In this experiment, we expected the range of liquid/solid phase change temperature of eutectic PCM of 35–45 °C, and high latent heat. Therefore, the surfactant additives with acids base properties were added to MA/PA eutectic PCM to control the undercooling and depress the melting temperature as well as to increase the latent heat amount of the MA/PA eutectic mixture.

3.2. Effect of surfactant additives

Surfactants such as sodium myristate (SM), sodium palmitate (SP), and sodium stearate (SS) were added to the MA/PA (70/30,
heat of fusion value is 179.12 J g$^{-1}$, and the phase transition temperature with low subcooling and good latent heat of fusion, but it does not significantly lower the solid/liquid phase transition temperature of MA/PA eutectic mixture and it has large subcooling temperature. The same phenomenon is also

Table 1

<table>
<thead>
<tr>
<th>MA/PA (wt.%)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J g$^{-1}$)</th>
<th>$T_i$ (°C)</th>
<th>$\Delta H_i$ (J g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0–100.0</td>
<td>63.08</td>
<td>173.69</td>
<td>61.90</td>
<td>172.92</td>
</tr>
<tr>
<td>10.0–90.0</td>
<td>59.89</td>
<td>172.09</td>
<td>58.33</td>
<td>170.35</td>
</tr>
<tr>
<td>20.0–80.0</td>
<td>56.43</td>
<td>181.00</td>
<td>54.61</td>
<td>176.80</td>
</tr>
<tr>
<td>30.0–70.0</td>
<td>49.32</td>
<td>159.21</td>
<td>47.88</td>
<td>153.70</td>
</tr>
<tr>
<td>40.0–60.0</td>
<td>47.95</td>
<td>154.29</td>
<td>45.26</td>
<td>153.57</td>
</tr>
<tr>
<td>50.0–50.0</td>
<td>47.91</td>
<td>153.12</td>
<td>46.44</td>
<td>152.32</td>
</tr>
<tr>
<td>60.0–40.0</td>
<td>47.08</td>
<td>151.72</td>
<td>50.73</td>
<td>151.15</td>
</tr>
<tr>
<td>70.0–30.0</td>
<td>46.73</td>
<td>155.43</td>
<td>44.76</td>
<td>152.64</td>
</tr>
<tr>
<td>80.0–20.0</td>
<td>49.81</td>
<td>154.57</td>
<td>45.67</td>
<td>150.32</td>
</tr>
<tr>
<td>90.0–10.0</td>
<td>51.16</td>
<td>127.94</td>
<td>48.83</td>
<td>128.47</td>
</tr>
<tr>
<td>100.0–0.0</td>
<td>54.70</td>
<td>161.37</td>
<td>52.58</td>
<td>161.14</td>
</tr>
</tbody>
</table>
decreasing the undercooling of MA/PA binary mixture as compared to the binary mixture of MA/PA without surfactant addition.

Investigation of thermal properties of eutectic mixture MA/PA have observed by other researchers in the literature, Kauranen, P. et al. [20] obtained eutectic composition ratio of MA/PA (59/41, wt.%), \( T_m \) 39.8 °C and \( \Delta H_f \) 174.0 J g\(^{-1}\). Furthermore, San [1] conducted eutectic composition ratio of these binary mixture (58/42, wt.%), \( T_m \) 42.6 °C and \( \Delta H_f \) 169.7 J g\(^{-1}\). When comparing to thermal properties in the previous literature to our results, the present MA/PA eutectic mixtures as shows in Tables 2 and 3 indicated that they have a better thermal properties with the addition of 5% SM, SP, and SS. The composition ratio of MA/PA eutectics component in this study was difference to previous study caused by two factors: the content of impurities in the composition of eutectic mixture and the rate of heat flow in the DSC measurement [21].

The important novelty was found in determining the thermal properties of MA/PA eutectic mixture with addition of 5% SM, 5% SP, and 5% SS. It is potential to be applied as a heat storage material in thermal energy storage systems.

### 3.3. Thermal conductivity

Table 5 shows the thermal conductivity of MA/PA (70/30, wt.%) and MA/PA (70/30, wt.%) with addition of 5% SM, 5% SP, and 5% SS surfactants. The result indicated that adding surfactants increased the thermal conductivity of MA/PA eutectic mixture. Previous studies were determined the thermal conductivity of paraffin 0.21 W m\(^{-1}\) K\(^{-1}\) [22,22,23]. Lane [5], prepared the organic eutectic mixture of blended naphthalene and benzoic acid (67/32.9 wt.%), the thermal conductivity of this eutectic PCM is 0.136 W m\(^{-1}\) K\(^{-1}\). Thus, the thermal conductivity of eutectic PCM obtained in this study is better compared to other organic PCMs.

<table>
<thead>
<tr>
<th>Phase change materials (PCMs)</th>
<th>Thermal conductivity (W m(^{-1}) K(^{-1}))</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA/PA</td>
<td>0.225</td>
<td>30.19 (solid)</td>
</tr>
<tr>
<td>MA/PA + 5%SM</td>
<td>0.242</td>
<td>29.35 (solid)</td>
</tr>
<tr>
<td>MA/PA + 5%SP</td>
<td>0.236</td>
<td>29.85 (solid)</td>
</tr>
<tr>
<td>MA/PA + 5%SS</td>
<td>0.230</td>
<td>29.60 (solid)</td>
</tr>
</tbody>
</table>

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