The Influence of Moisture Content on the Evaluation of Latent Heat of Molten Salts Used for Thermal Energy Storage Applications

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Abstract

Precise measurements of the thermo-physical properties are essential for the process design of thermal energy storage systems. This paper is concerned with the measurement of heat of fusion of molten salts, which plays a key role in determining the storage capacity of latent heat based thermal energy storage units. The focus of the work is on the effect of moisture content of molten salts on latent heat measurements using a differential scanning calorimetry. The results reveal that, the change in the mass of the samples investigated is due to moisture content, and hence, this leads to a reduction in the value of the heat of fusion of the phase change material. For instance, the heat of fusion for one of the wet samples (containing moisture) was determined to be 314.29\textdegree\textit{J}/g. However, the calculated heat of fusion for the same sample without moisture is found to be 350.02\textdegree\textit{J}/g. This is associated with the methodology of the DSC analysis, which does not consider the mass of the moisture in the sample. It is found that, the deviation in the heat of fusion due to the effect of the moisture content in the investigated samples is proportional to the amount of moisture in the original sample. Therefore, it is imperative to consider the effect of the moisture content on the evaluation of the latent heat of molten salts. In order to obtain reliable findings, either the samples should be dried and then weighed promptly, or weighed after the test and then re-evaluate the latent heat using the new weight.

\textit{keywords}: Thermal energy storage systems; Phase change material; Differential; Scanning Calorimetry (DSC); Moisture content; Heat of fusion

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1. Introduction

One of the most important issues in the political agenda nowadays, is climate change and its impact on human life. There is a growing concern about the relationship between consumption of energy based on fossil fuel and climate change, it is strongly believed that consumption of fossil fuel is the major contributor to global warming phenomenon[1, 2]. In addition to that, according to the International Energy Agency (IEA) statistics, worldwide energy consumption will continue to increase by 2% per year; this means every 35 years [3], energy consumption will be doubled and this soar in energy consumption will lead to an enormous increase in global energy demand. As a result of this, it is expected there will be a shortage in current energy resources, moreover, in the seventies after the oil crisis in 1973-74, the politicians with responsibility for decision-making, realised that dependence on importing oil from unstable regions is a great threat to energy security [2, 4].

As a consequence to all that has been mentioned above, significant attention has been paid to the investigation of renewable and sustainable energy sources which are being seen as the lifeline for all future potential energy threats. Solar energy is one of the most important promising renewable, sustainable and environmentally friendly energy sources. However, as a result of its intermittent nature; this vital energy source is still expensive and not competitive with the energy produced from fossil fuels. Therefore, at the present time great interest is being paid in the development of thermal energy storage systems, which are considered to be a key component in managing solar energy in a cost effective way[5].

Thermal energy storage systems based on latent heat of PCM is an emerging technology and currently is receiving great attention as a consequence of its advantages, for example, high storage density in a relatively small volume in comparison with sensible heat storage, and thermal energy is stored almost isothermally or in small temperature variations[6-9]. However, in the process design of latent heat energy storage systems, it is a key issue to evaluate the thermo physical properties of the storage medium (PCM) precisely, the size and the storage capacity of a thermal energy storage system depend on the latent heat of the storage medium (PCM). The aim of this paper is to investigate the influence of the moisture content on the evaluation of latent heat of a binary mixture of Li$_2$CO$_3$-K$_2$CO$_3$ using differential scanning calorimetry (DSC).

2. Experimental set up

2.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is the most frequently used thermal analysis technique. DSC measures enthalpy changes in samples due to changes in their physical and chemical properties as a function of temperature or time. Mettler Toledo STAR® DSC 1 was employed in this study and is shown in Figure 1; the operation temperature range for this DSC is -150°C to 700°C. The heat flow and temperature can be detected in this instrument with accuracy of 0.04μW and ±0.2K, respectively, furthermore, it is supported by a sample robot which can process up to 34 samples, even if every sample requires a different method and a different crucible[10].

2.2 Materials

The phase change material PCM (storage medium) under investigation in this study is a binary mixture of 35% Li$_2$CO$_3$-65% K$_2$CO$_3$ based on weight fraction. Both Li$_2$CO$_3$ and K$_2$CO$_3$ were purchased from Fischer Scientific with a purity of 99 % [11].

2.3 Sample preparation

The sample was initially prepared using a mortar and pestle, in which 350μg of Li$_2$CO$_3$ and 650μg of K$_2$CO$_3$ were weighed and divided into 4 small portions, then 2 portions from each component (Li$_2$CO$_3$ and K$_2$CO$_3$) were mixed together, then the entire quantity was mixed together. This step was repeated 25 times in order to form, in total, 25g of this binary mixture, then the final step was mixing the whole quantity ( 25g) using a ball mill for 6 hours.
2.4 Effect of moisture content on the mass of the sample

To verify that the decrease in sample mass after performing a test in the DSC for the investigated samples is due to the moisture content, three samples underwent a thermal investigation test using the DSC, in the temperature range between 25°C, and 540°C (above the melting point), in which the sample was heated up to 25°C and kept at this temperature for 5 minutes in the first segment, then, the second segment was dynamic where the sample was heated up from 25°C to 540°C by heating rate 10°C/min, and the third segment was isothermal where the sample was kept at 540°C for 5 minutes. This test was conducted in 4 cycles for each sample.

2.5 Effect of moisture on evaluation of heat of fusion

In the analysis for the binary mixture of Li₂CO₃-K₂CO₃, the value of the latent heat of fusion was affected by the moisture content in the sample. Simply, this was revealed by comparing the sample weight before and after the analysis and revising the methodology which is employed by the DSC to evaluate the heat of fusion. In order to prove that, thermal analysis experiments have been carried out on 10 samples.

3. Results and discussion

3.1 Effect of moisture content on the mass of the sample

This test was conducted to ensure that the change in the sample mass after performing a thermal analysis test is due to the moisture content. As Figure (2) illustrates, three samples underwent a thermal analysis test according to the same method described in section 2.4 This test was repeated three more times for each sample, and the results obtained were very interesting. In the first run, there were two endothermic peaks: the first peak was around 100°C, which represented the heat of vaporization of water (moisture content) in the sample, whereas, the second peak was around 500°C where the process of formulation of the eutectic mixture took place and the sample underwent phase transition from solid to liquid. However, this was not the case in the subsequent three runs (second, third and fourth), where there was only one peak, and that was where the phase transition took place. It is worthwhile to indicate that the sample in the first run before the phase transition stage was a powder and each component (Li₂CO₃ and K₂CO₃) reserved its identity (non-eutectic), however, after the phase change took place in the first run, the eutectic form was formulated and therefore, the thermal analysis of the second, third and fourth runs (cycles) for the
same sample showed only one peak and that was where the phase transition took place. Moreover, the investigated samples were re-weighed after the test, and it was remarkable that, the sample’s mass had decreased. See Table (1). Furthermore, by evaluating ΔQ using the STAR© evaluation software for the first phase transition (first peak) and dividing the value obtained by the change in the sample’s mass, the result is almost equal to the amount of heat needed to vaporize one gram of water at atmospheric pressure (heat of vaporization of water), see Table (2) and Figure (2).

Table 1 The change in mass of the samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Pan mass(μg)</th>
<th>Before test</th>
<th>After test</th>
<th>Salt mass Difference (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Salt mass (μg)</td>
<td>Pan+Salt (μg)</td>
<td>Salt mass (μg)</td>
</tr>
<tr>
<td>1</td>
<td>49.888</td>
<td>20.275</td>
<td>70.163</td>
<td>18.647</td>
</tr>
<tr>
<td>2</td>
<td>50.232</td>
<td>21.360</td>
<td>71.592</td>
<td>19.761</td>
</tr>
<tr>
<td>3</td>
<td>50.074</td>
<td>22.347</td>
<td>72.421</td>
<td>20.843</td>
</tr>
</tbody>
</table>

Table 2 Relation between ΔQ and the change in sample mass

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Salt mass Difference (μg)</th>
<th>ΔQ (μ J)</th>
<th>Heat F calculated (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.628</td>
<td>-3676.75</td>
<td>-2358.45</td>
</tr>
<tr>
<td>2</td>
<td>1.599</td>
<td>-3619.8</td>
<td>-2263.79</td>
</tr>
<tr>
<td>3</td>
<td>1.504</td>
<td>-3408.46</td>
<td>-2266.26</td>
</tr>
</tbody>
</table>
3.2 Effect of moisture on heat of fusion evaluation

As mentioned in section 2.5 this test was conducted in order to evaluate the influence of moisture content on the evaluation of latent heat using DSC. Table 3 lists the details of the thermal investigations for 10 samples. Each sample was weighed before and after the test, and the samples’ mass after the test were detected by subtracting the mass of Pan+Salt (after test) from the Pan’ mass. The amount of moisture can be identified by either subtracting the mass of Pan+Salt (before test) from the mass of Pan+Salt (after test) or by subtracting the mass of samples before the test from the mass of samples after the test, $\Delta Q$ represents the quantity of heat in $\mu J$ which was supplied by the DSC to the samples investigated when the phase transition took place, in order to keep the sample pan and the reference pan at the same temperature. Heat F DSC is the evaluated heat of fusion using the DSC in J/g. Heat F calculated is the heat fusion calculated manually by dividing $\Delta Q$ upon the mass of sample after performing the test. It is worthwhile to note that the influence of moisture content on the evaluation of the heat of fusion using the DSC occurs due to the effect of the moisture content on the real sample weight, and to clarify this effect, the thermal analysis for sample (1) in Table 3 using the DSC is now explained in detail.

The first step is to weigh the sample, the mass of sample (1) when it was prepared was 10.450$\mu g$, (before test), see Table (3). The second step was putting the sample in the sample carrier in the DSC and carrying out the analysis method as described in section 2.4. In the third step, the experiment was named, the mass of sample (10.450 $\mu g$) and position were inserted. The fourth step was sample analysis.

After the analysis was finished, the sample was re-weighed and it was 9.383$\mu g$. The change in the mass of sample before and after the test was 1.067 $\mu g$ (moisture content). The fifth step was the final step and devoted to data evaluation; this step was conducted using STAR$e$ Software, and it can be divided into two aspects for the explanation.

The first aspect is visible in Figure (3), where there were two phase transition stages (two endothermic peaks); the first was in the temperature range 85$^\circ C$ to 160$^\circ C$ where the moisture content was vaporized and as a consequence of that, the sample’s mass fell to 9.383$\mu g$. (in accordance with the amount of moisture content in the sample). Furthermore, by dividing $\Delta Q$ for the first phase transition (first peak) (2423.77$\mu J$) upon the change in the sample’s mass (1.067$\mu g$), the result is 2271.57$\mu J/g$ which is again almost equal to the amount of heat needed to vaporize one gram of water at atmospheric pressure (heat of vaporization of water). However, the evaluated Heat F (using STAR$e$ evaluation software) for first phase transition is incorrect, because the total sample weight (10.450$\mu g$) was used in the evaluation process. The second phase transition stage was around (500$^\circ C$); where samples (1) underwent a phase transition process (solid to liquid).

The second aspect is invisible and represents data interpretation (evaluation of thermo physical properties) using STAR$e$ evaluation software, and was conducted based on the heat flow curve (Figure 3) and the data input (sample mass). $\Delta Q$ is evaluated by integrating the area under the heat flow curve, whereas, the latent heat H is evaluated by dividing $\Delta Q$ upon the sample’s mass which was inserted in the programming step. This is where the error in the evaluation of the latent heat using DSC occurs in the case of the wet samples, and in Table (3) $\Delta Q$ and H are 3284.33$\mu J$ and 314.29$\mu J/g$ respectively, and simply, the latter (H) as mentioned above resulted from dividing $\Delta Q$ (3284.33 $\mu J$) upon the sample’s mass 10.450$\mu g$ (containing 1.067$\mu g$ moisture). However, $\Delta Q$ (3284.33$\mu J$) was absorbed by 9.383$\mu g$ of sample (1) to establish the phase transition from solid to liquid, according to those quantities; the correct value of latent (H) heat should be 350.029$\mu J/g$. The DSC analysis was misguided by the 1.067 $\mu g$ of the moisture content. In other words, mathematically, the moisture content led to an increase in the denominator, which in turn led to a decrease in the result of the division process in the evaluation of latent heat. Nevertheless, the difference between the evaluated value of latent heat (using DSC) and the actual value (calculated based on the net mass without moisture) is -35.739$\mu J/g$. In general this difference or the deviation (the error %) is proportional to the amount of moisture content in the sample, which is subject to the percentage of humidity in the environment where the sample was prepared.
**Table 3** DSC analysis results for 10 samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Pan mass (μg)</th>
<th>Before test</th>
<th>After test</th>
<th>Mass Difference (μg)</th>
<th>ΔQ (μJ)</th>
<th>Heat F DSC (J/g)</th>
<th>Heat F calculated (J/g)</th>
<th>Heat F difference (J/g)</th>
<th>% Error in HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50.265</td>
<td>10.450</td>
<td>60.715</td>
<td>59.648</td>
<td>9.383</td>
<td>-3284.33</td>
<td>-314.29</td>
<td>-350.029</td>
<td>-35.739</td>
</tr>
<tr>
<td>2</td>
<td>50.211</td>
<td>10.931</td>
<td>61.142</td>
<td>60.087</td>
<td>9.876</td>
<td>-3471.7</td>
<td>-317.6</td>
<td>-351.529</td>
<td>-33.929</td>
</tr>
<tr>
<td>3</td>
<td>50.298</td>
<td>10.548</td>
<td>60.846</td>
<td>59.808</td>
<td>9.51</td>
<td>-3355.47</td>
<td>-318.11</td>
<td>-352.836</td>
<td>-34.726</td>
</tr>
<tr>
<td>4</td>
<td>50.316</td>
<td>10.345</td>
<td>60.661</td>
<td>59.651</td>
<td>9.335</td>
<td>-3302.06</td>
<td>-319.19</td>
<td>-353.729</td>
<td>-34.539</td>
</tr>
<tr>
<td>6</td>
<td>50.041</td>
<td>20.855</td>
<td>70.896</td>
<td>68.949</td>
<td>18.908</td>
<td>1.067</td>
<td>-3660.81</td>
<td>-316.56</td>
<td>-349.154</td>
</tr>
<tr>
<td>7</td>
<td>50.169</td>
<td>20.495</td>
<td>70.663</td>
<td>68.692</td>
<td>18.523</td>
<td>1.055</td>
<td>-3471.7</td>
<td>-317.6</td>
<td>-351.529</td>
</tr>
<tr>
<td>8</td>
<td>50.168</td>
<td>20.292</td>
<td>70.46</td>
<td>68.526</td>
<td>18.358</td>
<td>1.038</td>
<td>-3355.47</td>
<td>-318.11</td>
<td>-352.836</td>
</tr>
<tr>
<td>9</td>
<td>50.408</td>
<td>20.446</td>
<td>70.854</td>
<td>68.914</td>
<td>18.506</td>
<td>1.01</td>
<td>-3302.06</td>
<td>-319.19</td>
<td>-353.729</td>
</tr>
</tbody>
</table>

Fig. 3. DSC analysis for sample (1)
4. Conclusion

Thermal analysis of three wet samples revealed that, the change in samples’ mass before and after the test was due to moisture content, which was observed through the first peak in the first cycle which occurred in the temperature range 85°C to 160°C, where the moisture content was vaporized. In addition to that, a second peak was detected in the temperature range 470°C to 530°C where a phase transition took place and a eutectic form of the sample mixture was formed. However, in the last three cycles, only one peak was noticed in the temperature range 470°C to 530°C where phase transition occurred.

Thermal analysis of 10 wet samples for verifying deviations in latent heat due to moisture content concluded that, moisture content in the investigated samples misguided the DSC in evaluating the latent heat; this deviation (% error) is proportional to the amount of moisture content in the samples.

The final conclusion of this study is that, in the evaluation of latent heat using DSC, in order to obtain reliable results, the sample investigated should be dried and weighed promptly, or weighed after the test and re-evaluate the latent heat using the correct mass.

Acknowledgements

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References