High density polyethylene spheres with PCM for domestic hot water applications: water tank and laboratory scale study

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Abstract

Renewable energy is a potential alternative energy provider with fewer CO₂ emissions. However, the mismatch between energy supply and demand is the main disadvantage. Therefore, thermal energy storage becomes an essential technology for enhancing renewable energy efficiency and providing energy supply to the end user. In solar thermal energy systems, hot water tanks are widely used as sensible heat storage technology. Moreover, water storage usually requires large volumes and their improvement has been studied in terms of shape and arrangement. Latent heat storage materials are a potential technology for implementation in water storage tanks in order to reduce their volume and to enhance their efficiency. In this paper, the incorporation of shape high density polyethylene spheres with PCM into domestic hot water tanks is studied. Undesired results obtained in the water tank set-up lead the authors to analyse the PCM leakage in the laboratory. Laboratory analysis pointed out that the PCM-spheres must be thermally cycled and cleaned before their implementation in real application of domestic hot water in order to stabilize the PCM content inside the PCM-spheres.

Keywords: thermal energy storage (TES), water tank, phase change materials (PCM), encapsulation, stabilization

1. Introduction

Renewable energy systems are characterized as providing energy with fewer CO₂ emissions than conventional systems (Garg et al. 1985). However, the main drawback
of renewable energy is the gap between supply and consumption (Gil et al. 2010). Therefore, energy storage technologies are an important part of the system to ensure the energy supply available to the end user. Thus, the energy storage system plays a very important role to define the energy efficiency of the system (Medrano et al 2010).

In the case of solar energy, the sun as an energy source can be guaranteed only for few hours a day and it has variable intensity during daytime (Garg et al. 1985). These facts require a storage system capable of providing heat during periods of reduced solar radiation (Kenisarin and Mahkamov 2007). Moreover, the use of thermal energy storage (TES) technologies has high potential to shift or smooth the peak power demand, as it is demonstrated by Nkwetta et al. 2014a. Nowadays, heat storage in a hot water tank is the most widely used system, where the sensible heat is stored in a liquid medium. Many studies have focused on improving these tanks in terms of shape (Altuntop et al. 2005), material (Esen and Ayhan 1996), envelope (Fazilati and Alemrajabi 2013) and the tank arrangement (Andersen et al. 2008).

A promising energy storage technology is the use and implementation of phase change materials (PCM) (Zalba et al. 2003). In this case, the latent heat absorbed and released during the phase change from solid to liquid is used. With these materials a larger amount of thermal energy can be stored compared to the sensible heat absorbed by the water (Shukla et al. 2009). In addition, the PCM works within a specific temperature range (phase change temperature), between 55 °C and 70 °C in the case of domestic hot water tanks, which allows the design of the system to be related to the desired application for obtaining the maximum amount of energy (Cabeza et al. 2011).

The inclusion of PCM to improve the performance of the TES systems have been studied by improving heat transfer through the application of fins, enhancing thermal conductivity, application of tube-in-shell TES, and using microencapsulation (Nkwetta and Haghhighat 2014). In a study done by Cabeza et al. (2006), the authors concluded that it is a very promising technology, because it provides hot water for a longer period of time. Moreover, Nkwetta et al. (2014b) used a numerical investigation to study the performance of a domestic hot water tank with integrated PCM. The impact of different PCM, its amount and location inside the water tank were the principal aspects analysed. The authors concluded that for practical application, the PCM should be placed at the
top of the tank to promote stratification and take advantage of it in order to achieve high energy storage performance. Moreover, Farid et al. (2004) in their review provided a vision on PCM encapsulation, concluding that macro-encapsulation offered more benefits in solar thermal energy storage applications.

In a domestic heating solar-aided system, Esen et al. (1998) studied two different designs for a latent heat storage tank. A tank with PCM encapsulated in cylinders, studied in detail by Esen (2000) in a later article, and a tank filled with PCM which contained pipes were the HTF flows through. Authors concluded that the PCM melting time depends not only on the thermo-physical properties of the PCM, but also on the geometric parameters.

The geometrical configuration of the PCM encapsulation is an issue that Barba and Spiga (2003) took into account. The performance of three different cases (slab, cylinder and sphere) was analysed during the discharging process of a domestic hot water tank. The authors concluded that the best configuration was represented by small spherical capsules if a rapid discharge mode was desired. The same conclusion drew Wei et al. (2005) where different geometric properties of the macro-encapsulation were also studied.

The encapsulation methods most used in domestic hot water systems or solar thermal energy storage applications are the macro-encapsulation (also called core-shell) and shape-stabilized PCM (Milián et al. 2017). Different materials have been used to contain the PCM such as acrylics, urea, formaldehyde and silica based polymers, metals and carbon based composites as graphene and graphite, among others (Milián et al. 2017). Shape stabilized PCM presents some interesting advantages such as high amount of PCM content can be integrated into the material matrix and thermal reliability over a long time period (Zhang et al. 2006). In this context authors found a commercial product, where the PCM is impregnated in a high-density polyethylene in spherical form. Therefore, the inclusion study of a new spherical product containing phase change materials in a domestic hot water tank solar-assisted is presented in this paper. Different amounts of PCM inclusion were studied in order to determine the most appropriate implementation according to their thermal behaviour. Moreover, a laboratory analysis of the spherical product was carried out to evaluate its thermal stability.
2. Pilot plant scale

2.1. Experimental set-up

An experimental set-up was prepared to analyse the effect of adding phase change materials (PCM) in the top part of a water tank. The experimental set-up consisted of a transparent acrylic plastic water tank of 600 x 400 x 500 mm supplied by an external power source that simulated a solar collector. The tank was instrumented with 15 thermocouples type-T prepared in the laboratory according to the EN-60584-1:2013, related to the applicable accuracy to this type of sensors, with a standard deviation of 0.16 °C. The sensors were placed inside a PVC pipe as shown in Figure 1 in order to measure the temperature of the water at different levels of the tank.

Figure 1. Left, water tank installation; right, thermocouples type T.

A commercial product (Ball-ICE® marketed by PCM Products) of polyethylene spheres impregnated with a paraffin mixture that has a melting point of 58 °C (Figure 2), were tested. The spheres were analysed with the differential scanning calorimetry (DSC) in order to obtain their thermal properties and the results are shown in Table 1 together with the ones provided by the manufacturer.
Table 1. PCM spheres physical properties.

<table>
<thead>
<tr>
<th>PCM spheres A58</th>
<th>Manufacturer</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase change temperature</td>
<td>58</td>
<td>T\textsubscript{m} 55 – T\textsubscript{s} 45 (ºC)</td>
</tr>
<tr>
<td>Density</td>
<td>910</td>
<td>-</td>
</tr>
<tr>
<td>Latent heat capacity</td>
<td>132</td>
<td>135 (kJ/kg)</td>
</tr>
<tr>
<td>Volumetric heat capacity</td>
<td>120</td>
<td>- (MJ/m\textsuperscript{3})</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>2.2</td>
<td>- (kJ/kg·K)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.22</td>
<td>- (W/m·K)</td>
</tr>
</tbody>
</table>

T\textsubscript{m}: melting temperature; T\textsubscript{s}: solidification temperature

2.2 Methodology

The experiments consisted of heating the water tank up to 62 ºC. Once the water reached the maximum temperature these conditions were maintained during 1 hour and afterwards the tank was cooled down naturally to 32 ºC. This experiment was carried out with the water tank without PCM and with different amounts of PCM spheres, thus increasing the energy storage capacity of the water tanks by 17% and 33%, respectively (Table 2). Each experiment was duplicated to have repeatability.

The storage density provided in Table 2 is calculated through the addition of the energy provided by the amount of PCM spheres (Q\textsubscript{pcm}) to the energy provided by the water in the tank (Q\textsubscript{water}). The following equations were used:
\[ Q_{pcm} = m_{pcm} \cdot L_{pcm} \]  
(1)

where, \( m_{pcm} \) is the total PCM spheres mass incorporated in the system and \( L_{pcm} \) is the latent heat of fusion.

\[ Q_{water} = m_{water} \cdot C_{water} \cdot \Delta T_{exp} \]  
(2)

where, \( m_{water} \) is total water mass, \( C_{water} \) is the water specific heat capacity, \( \Delta T_{exp} \) is the temperature difference performed in the water tank during the experiment (62 °C to 32 °C).

Table 2. PCM spheres mass added to the water tank.

<table>
<thead>
<tr>
<th>TES material</th>
<th>Theoretical increase [%]</th>
<th>Storage density [kJ] (( \Delta T=30 ^\circ C; \ V=100 \ L ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-</td>
<td>12544</td>
</tr>
<tr>
<td>10.5 kg PCM spheres + water</td>
<td>17</td>
<td>14623</td>
</tr>
<tr>
<td>21 kg PCM spheres + water</td>
<td>33</td>
<td>16702</td>
</tr>
</tbody>
</table>

2.3 Results

First of all, an experiment without PCM was performed in order to have a reference pattern, which will be used to discern the effects of PCM inclusion. The water blank experiments took 920 and 932 minutes, respectively, to cool down to 32 °C.

The next test increased 17% the storage capacity of the tank with the addition of 10.5 kg of PCM spheres. The discharge period was increased compared to the water blanks, lasting 1057 min. In the second replication of this experiment the authors found out that keeping the tank at 62 °C for a period of about 10 hours after this temperature was reached, the cooling down process lasted longer (1256 min). This fact could be occurring because in the first test the PCM was not completely melted due to the low thermal conductivity of the plastic material of the spheres.

The same effect was registered when the storage capacity of the tank was increased to 33% by using 21 kg of PCM spheres. When the charge period was longer the cooling rate lasted 1543 min while a shorter charge period corresponds to 1295 min to cool it down.
Figure 3 shows the average temperature of the water tank for the experiments described above with different amounts of PCM. The experiments with PCM addition do not show the expected flat line around the phase change temperature (58 °C) due to the phase change process. Nevertheless, different cooling rates were registered and a delay at the end of the discharging process were seen when PCM was added, most probably due to the storage effect. A summary of the data obtained in the experiments is shown in Table 3.

![Graph showing temperature change over time for different conditions (water blank, PCM 17%, PCM 33%)](image)

**Table 3. Summary of experimental results.**

<table>
<thead>
<tr>
<th>PCM</th>
<th>Discharge period (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water blank</td>
<td>932</td>
</tr>
<tr>
<td></td>
<td>920</td>
</tr>
<tr>
<td>PCM 17%</td>
<td>1057</td>
</tr>
<tr>
<td></td>
<td>1256</td>
</tr>
<tr>
<td>PCM 33%</td>
<td>1295</td>
</tr>
<tr>
<td></td>
<td>1543</td>
</tr>
</tbody>
</table>
During the experiments the authors observed that the PCM spheres were losing the paraffin wax mixture. The leakage was completely visible at the end of the experiments as Figure 4 shows, the spheres were encapsulated in solidified paraffin. This effect should be a problem affecting the storage performance of the PCM spheres, as it may lose storage capacity, and also the system (water pumps, pipes) where the PCM is implemented could be damaged. Furthermore, any direct storage system may lead to the PCM being discharged to taps. This phenomenon was also detected in McClenaghan et al. (2014) study where the wax leaked from the spheres and solidified in the exit pipe blocking the flow.

![Figure 4. PCM spheres (Ball-ICE®) after the tests in the experimental set-up](image)

Since the authors registered unexpected thermal behaviour in the water tank installation and phase change material leakage from the spheres, a laboratory methodology was defined in order to identify the phenomenon occurring with this type of material.

**3. Laboratory analysis**

**3.1. Methodology**

In order to analyse the PCM lost out of the spheres two laboratory scale methodologies were designed and evaluated. The aim of these methodologies were to detect the rate of the PCM leakage and if this loss affected the energy storage capacity of the PCM-spheres.
First of all the PCM-spheres were pre-treated based on the manufacturer recommendations in order to remove the excess of PCM and to have spheres that were materially stabilized. The pre-treatment consisted of cycling the samples five times by heating up and cooling down the spheres. The water was changed after each thermal cycle, thereby PCM excess is extracted.

Once the pre-treatment was done to all the samples, two different methodologies were followed. The first one is named as Cycling consisting of:

1. Submerge the PCM sphere into water the PCM sphere in a glass beaker of 150 mL (see Figure 5).
2. Heat up the beaker from 30 ºC to 70 ºC during 3h in a programmed muffle furnace.
3. The temperature inside the muffle furnace is maintained at 70 ºC for 5:40 h.
4. Cooling down naturally to 30 ºC.
5. Repeat again from step 1 for 25 thermal cycles.

The second methodology called Washing follows the same procedure as that for Cycling but after each thermal cycle the water is changed to perform the next cycle with clean water.

Initially, a sample of a PCM-sphere that was not treated with any of those methodologies (Cycling and Washing) was analysed as a starting point result. A further sample of a PCM-sphere, removed from the experimental water tank installation after the testing described in section 2, was also analysed.
Additionally, five PCM-spheres were tested for each methodology (Cycling and Washing) 5, 10, 15, 20, and 25 times, respectively. Three triplicates of each samples was performed. Samples of each sphere as well as the washing/cycling water were analysed. Thereby, after several cycles the amount of PCM that was remaining inside the spheres as well as the paraffin flowing out to the washing/cycling water could be analysed and compared to the initial quantity.

The quantity of PCM inside the spheres after washing/cycling tests was analysed using DSC. This is one of the most powerful techniques to analyse the thermophysical properties of substances as melting temperature and melting enthalpy. The melting enthalpy was characterized in order to understand the PCM quantity of the spheres. Thus, the PCM percentage in weight is calculated following Eq. (1):

\[
\%_{w}(\text{PCM}) = \frac{\Delta H_{\text{sample}}}{\Delta H_{\text{purePCM}}} \times 100
\]  

The DSC analyses were performed under 0.5 K/min heating rate between 30 - 75 °C under 50 mL/min H₂ flow within 40 ml aluminium crucible with a DSC822e from Mettler Toledo.

The paraffin content on the washing/cycling water was also quantified by using gas chromatography coupled with a mass spectrometer (GC-MS).

3.2. Results

DSC results are shown in Table 4. Several samples from several parts of each sphere were evaluated. Authors found out that the spheres provided by the manufacturer (PCM Products) do not have the same PCM content, hence PCM quantity should not be directly compared. For this reason, the PCM content of the sample was analysed in the centre and on the external surface of the sphere and a ratio of difference between these samples was calculated. Moreover, the initial samples (without any washing-cycling process) and a sample used in the experimental study at pilot plant scale have been analysed as well.
The results are compared in Table 4 where the percentage in weight of PCM is calculated based on the DSC results and Eq. (1). Results show that the sample under pilot plant conditions, the sample washed 25 cycles and the initial sample have almost the same PCM content difference between centre and surface, while the PCM content for the sample cycled 25 times presents a higher difference. This is due to the PCM migration from the middle of the PCM-spheres to the surface when it is thermally cycled.

Table 4. PCM content of sample (average of three triplicates) under study based on DSC results and calculated following Eq. (1)

<table>
<thead>
<tr>
<th>Centre (kJ/kg)</th>
<th>Surface (kJ/kg)</th>
<th>(% difference between centre-surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not treated</td>
<td>61.0</td>
<td>56.6</td>
</tr>
<tr>
<td>Washed</td>
<td>61.5</td>
<td>57.2</td>
</tr>
<tr>
<td>Cycled</td>
<td>78.5</td>
<td>59.4</td>
</tr>
<tr>
<td>Experimental water tank</td>
<td>64.7</td>
<td>59.3</td>
</tr>
</tbody>
</table>

On the other hand, the GC-MS results have been analysed and the paraffin content into the washing/cycling water was quantified. Table 5 lists the paraffin content into the water. When PCM spheres are used following the Washed methodology, which simulates a direct charge/discharge application, there is no significant PCM leakage; when the Cycled methodology is used, which simulates an indirect application, the PCM leakage can be substantial and would affect the system components. These results indicate that the PCM-spheres must not just be pre-treated but thermally cycled between 20 and 25 times before their use, in order to stabilized the PCM content and achieve proper results.

Table 5. PCM content into the water used to wash the PCM-spheres.

<table>
<thead>
<tr>
<th></th>
<th>5 cycles sphere (mg/kg)</th>
<th>10 cycles sphere (mg/kg)</th>
<th>15 cycles sphere (mg/kg)</th>
<th>20 cycles sphere (mg/kg)</th>
<th>25 cycles sphere (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washed</td>
<td>0.54</td>
<td>0.15</td>
<td>0.1</td>
<td>1.17</td>
<td>0.23</td>
</tr>
<tr>
<td>Cycled</td>
<td>120</td>
<td>170</td>
<td>330</td>
<td>230</td>
<td>255</td>
</tr>
</tbody>
</table>
Moreover, the chromatograms obtained of the sample washed 25 times and cycled 25 times are presented in Figure 6. Note that the PCM chemical composition of the washing/cycling water samples is very similar, therefore PCM was not degraded during testing.

Figure 6. Chromatogram of the paraffin wax PCM contained on cleaning water (Cycled samples on the top, and Washed samples at the bottom).

5. Conclusions

An experimental set-up consisting of a water tank supplied by a heat source was used to test the energy density improvement with the implementation of phase change materials. Polyethylene spheres in which PCM is embedded were located at the top of the water tank in order to enhance the stratification and hence to improve the energy density.

Results obtained in the experimental set-up of the water tank showed that the effect of PCM is beneficial to keep the water hot for longer. However, ICE-Balls with A58 PCM are made of polyethylene, which means that they have a low thermal conductivity. This
fact makes it difficult to melt the PCM inside the spheres and it takes long time to charge the PCM which is inside the tank.

Moreover, PCM leakage was observed during the tests undertaken in the water tank and a laboratory methodology was designed to analyse this phenomenon since it strongly affects the use of PCM in a real application.

The laboratory analysis indicates that the PCM-spheres must be thermally cycled and cleaned before their implementation in real application of domestic hot water in order for the PCM content to be stabilized inside the spheres. Moreover, the paraffin wax-PCM floating on the system water should be controlled; otherwise thermal performance efficiency could decrease affecting the charging/discharging system processes.

There are several recommendations/alternatives to enhance the way to proceed when PCM-spheres are implemented in domestic hot water system. First of all, at least 25 thermal-cycling process is recommended before the PCM-spheres are introduced. Some alternatives could be done to improve the thermal performance of the PCM-spheres: to use a coating on the external surface of the spheres in order to ensure the PCM stability inside the spheres and to change the material used as the matrix in order to enhance the thermal conductivity and reduce the PCM leakage.

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