Thermal analysis of a Phase Change Material for a Solar Organic Rankine Cycle

M Iasiello*, K Braimakis**, A Andreozzi* and S Karellas**
* Dipartimento di Ingegneria Industriale - Università degli Studi di Napoli Federico II - Piazzale Tecchio, 80, 80125 Napoli, Italy
** Laboratory of Steam Boilers and Thermal Plants, School of Mechanical Engineering, National Technical University of Athens, Zografou, 15780 Athens, Greece
Email: marcello.iasiello@unina.it

Abstract. Organic Rankine Cycle (ORC) is a promising technology for low temperature power generation, for example for the utilization of medium temperature solar energy. Since heat generated from solar source is variable throughout the day, the implementation of Thermal Energy Storage (TES) systems to guarantee the continuous operation of solar ORCs is a critical task, and Phase Change Materials (PCM) rely on latent heat to store large amounts of energy. In the present study, a thermal analysis of a PCM for a solar ORC is carried out. Three different types of PCMs are analyzed. The energy equation for the PCM is modeled by using the heat capacity method, and it is solved by employing a 1D explicit finite difference scheme. The solar source is modeled with a time-variable temperature boundary condition, with experimental data taken from the literature for two different solar collectors. Results are presented in terms of temperature profiles and stored energy. It has been shown that the stored energy depends on the heat source temperature, on the employed PCM and on the boundary conditions. It has been demonstrated that the use of a metal foam can drastically enhance the stored energy due to the higher overall thermal conductivity.

1. Introduction
Organic Rankine Cycle (ORC) represents a promising technology with which it is possible to use low-temperature heat to generate electrical power. This low-temperature heat can be obtained from various sources, like a gas turbine or an internal combustion engine [1-7]. ORCs can also be coupled with environmentally friendly renewable energy sources (RES), such as solar. Especially regarding solar ORCs, they can play an important role in decentralized power generation, while they can be especially important in islanded microgrids. Additional applications include cogeneration for community or industrial use.

The intermittent nature of solar radiation can lead to discrepancies between demand and heat source availability. The addition of thermal energy storage (TES) systems makes it possible to redirect excess energy produced during daytime to nighttime or periods of unfavorable meteorological conditions, thus making the power system more efficient, flexible and reliable. A key advantage of solar ORCs over photovoltaic systems is the opportunity to integrate TES equipment to store excess heat energy in thermal rather than electrical form. TES, which is currently cheaper than commercial batteries and has a longer usable lifetime, comes in many varieties.

In the present study, thermal energy is stored in the latent heat of a phase-change material (PCM) [8]. Since latent energy of phase-change transitions is much higher than specific heat capacity, PCM
storage has the potential for much higher energy storage density than sensible TES. It has to be observed that PCMs can be used also for mechanical energy systems or for buildings [9, 10]. Another key advantage of latent storage is that the phase transition is a quasi-isothermal process, a feature that facilitates TES integration and control within the ORC plant. The tradeoff, however, is the low thermal conductivity of the storage media which results in an excessive charging and discharging time for thermal storage. Faster response times can be achieved by adding high-conductivity materials (e.g., metals or graphite) within the PCM. Media for latent storage include organic materials (e.g., paraffins and fatty acids), inorganic compounds (e.g., salt hydrates), and various eutectic mixtures. Despite its technical advantages compared to sensible technologies, latent heat storage is more expensive and still at the prototype phase.

The melting point of PCMs can be chosen in order to have the desired operation temperature for the ORC. Zalba et al. [11] provide a review of studies dealing with TES using phase change materials. The authors categorized different materials depending on the following criteria: 1) Phase change materials, 2) Heat transfer analysis, 3) Applications. Wang and Baldea [12] analyzed latent-heat storage using phase-change materials (PCM) as a mean for improving temperature control and energy management in cooling systems. They proposed a novel, systems-centric approach to PCM-based thermal management and established a connection between the quantity and geometric properties of the PCM, the dynamics of the integrated system, and potential energy savings. They focused on composite heat sinks consisting of PCM elements encapsulated in a conductive matrix material as a practical implementation of PCM-enhanced thermal management. Most PCMs present the common problem of low thermal conductivity that strongly limits the energy charging/discharging rates. Therefore, the introduction of highly conductive materials embedded with PCMs has been already proposed in literature in order to improve the heat exchange process [13].

In this paper, a thermal analysis of a PCM for a solar ORC is carried out. Three different types of PCM are herein analyzed. The energy equation for the PCM is modeled by using the heat capacity method, and it is solved by employing a 1D explicit finite difference scheme. The solar source is modeled with a time-variable temperature boundary condition, with experimental data taken from the literature and referred to two different solar collectors. At the PCM/ORC interface, a sensitivity analysis on the boundary conditions is carried out in order to analyze the different cases. Results are presented in terms of temperature profiles and stored energy.

2. Mathematical model
2.1. Description of the storage system
A diagram of the PCM-solar-assisted ORC is presented in Fig. 1. Since the ORC requires a relatively low-temperature heat source [14], a medium-temperature solar collector can be employed for this purpose. Having a constant temperature solar heat source is pretty challenging, thus an integrated system is required. The PCM has the role of storing solar energy and giving it to the ORC when the solar source cannot produce sufficiently high operation temperatures, while a high temperature heat pump can be employed to further integrate the process.

In this paper, it is assumed that the ORC fluid works at a maximum operation temperature of about 90 °C. Thus, the solar collector has to provide an outlet fluid temperature that is in the range between 100 and 160 °C. For this purpose, two different solar collectors, a parabolic trough solar collector (39 m² made up of three modules in series, with a 19.6 geometric concentration ratio) and an evacuated tubes solar collector (two panels with 6 collector tubes, with 2.76 and 1.82 m² gross and net absorber area, respectively) have been employed. The first is referred to an experimental study performed in Tunisia [15], while the second in Japan [16]. The collector fluid outlet temperature profiles are presented in Fig. 2, showing that these vary in the range from 120 to 160 °C, with maximum values achieved around midday, when the solar radiation is maximized. Sixth-order polynomial fits were performed on experimental data, in order to obtain analytical function that can be used as a boundary condition for the PCM. The collector gives heat to the PCM, for which the melting point must be in the range of about 110-130 °C, in order to exploit the energy gain due to the phase change. Among various PCMs, two of these were chosen due to their melting points: erythritol and magnesium
chloridehexahydrate MgCl$_2$ 6H$_2$O. Their thermophysical properties are resumed in Table 1 [17], together with melting characteristics that will be described in the following. For the sake of simplicity, the thermal conductivity and density variation with temperature are neglected in the present study (temperature variations through the space and time are less than about 50 °C), thus solid phase thermophysical properties are employed.

![Figure 1](image1.png)

**Figure 1.** A sketch of the thermal system with boundary conditions employed in the present paper.

**Table 1.** PCMs thermophysical properties.

| PCM               | $k$ (W/m K) | $\rho$ (kg/m$^3$) | $c_{p,s}$ (kJ/kg K) | $c_{p,l}$ (kJ/kg K) | $\lambda$ (kJ/kg) | $T_m$ (°C) | $\Delta T$ (°C) |
|-------------------|-------------|-------------------|---------------------|---------------------|------------------|------------|---------------|
| Erythritol (A)    | 0.733       | 1480              | 1350                | 2740                | 339              | 122.0      | 20            |
| MgCl$_2$ 6H$_2$O (B) | 0.704       | 1569              | 2250                | 2610                | 134              | 121.2      | 10            |

![Figure 2](image2.png)

**Figure 2.** Temperature profiles during the day for Tunisia [15] and Japan [16] heat sources.

### 2.2. Mathematical model

In order to analyze temperature fields and energy stored, the energy equation of the PCM is solved. Due to temperature gradients, natural convection occurs; but for lower temperature gradients through the domain, it is reasonable to neglect them. The PCM starts from an initial temperature that is below the melting point, and the melting front moves from the heated boundary to the opposite one with a certain velocity. Since this front is not known a priori, a fixed grid technique is used. With this
technique, the energy equation is characterized depending on the punctual temperature of the computational domain. This characterization happens by employing the apparent heat capacity method, with which the energy equation is described by assuming that the enthalpy is proportional to the temperature by means of the heat capacity, and the heat capacity is characterized depending on the PCM phase. For a 1D coordinate system, the transient energy equation is as follows:

\[ \rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \]  

(1)

The heat capacity curve is obtained starting from Direct Scanning Calorimetry (DSC) of the substance, taken from literature [18, 19]. By means of a graphical construction, it is possible to obtain from experiments the latent heat of fusion, the melting temperature, and a temperature difference \( \Delta T \) in which the melting occurs. Such curves are reported in Fig. 3, together with the graphical construction and the heat capacity vs. temperature curve obtained. The latent heat is taken from the aforementioned literature source, while melting temperature and range are herein derived (Fig. 3). From the heat capacity curve, it is shown that the erythritol has more storage capacities when compared to the magnesium chloride hexahydrate. The heat capacity is described with the following equation:

\[ c_p = c_{p,s} \left[ 1 - \alpha(T) \right] + c_{p,l} \alpha(T) + \lambda \frac{d\alpha}{dT} \]  

(2)

where \( \alpha \) is the alpha function. The function alpha is also known as the melting fraction, and it has the physical meaning of porosity, since it described how the PCM melts by determining the ratio between the two phases volume. It is equal to 0 for a pure solid and 1 for a pure liquid. In order to make the solid-liquid transition smoother, a sinusoidal function is employed:

\[ \alpha(T) = \frac{\sin \left( \frac{\pi}{2\Delta T} (T - T_m) \right) + 1}{2} \]  

(3)

valid for 0<\( \alpha < 1 \). This operation also avoids derivative discontinuities in the points \( T_m = T \pm \Delta T \).

Boundary conditions are presented in the following and resumed in Fig. 1. For \( t = 0 \), all the solid PCM is at a temperature of 100 °C. At the right boundary of the domain (\( x = L = 0.1 \) m), different boundary conditions are analyzed, making references to four cases. The first is a Dirichlet boundary condition (Fig. 1a), that can occur for example with very high heat transfer coefficients at the right boundary of the domain. The second and the third (Figs. 1b and 1c) are Neumann conditions, respectively fixed heat flux and adiabatic condition. The first simulates a heat storage system that guarantees the operation of the PCM, while the second simulates a case in which the PCM has the role of storing thermal energy. Finally, the last boundary condition is a Robin one (Fig. 1d), that simulates heat given to a fluid, that might be represent the environment, at a temperature just below the PCM operation point. All these boundary conditions are resumed in Table 2.

In order to solve Eq. 1, a finite-difference explicit scheme is herein employed. Grid convergence has been checked in terms of temperature profiles and stored energy and presented in Fig. 4a, for erythritol with \( T_m = 122 \) °C and \( \Delta T = 20 \)°C, with adiabatic boundary condition on the right side of the PCM and by using the heat source referred as Tunisia (Fig. 2). In calculating the energy stored, and as it will be done in the rest of the paper, it is assumed that the height of the PCM is equal to the length 0.1 m, obtaining a square PCM. The time step is chosen with references to the numerical stability of the problem. Finally, a comparison with a solution developed with a Galerkin-based finite element scheme by means of the commercial code COMSOL Multiphysics has been performed. It is observed
that the finite-element code models the phase change by means of a smoothed Heaviside function. Results in terms of temperature profiles are presented in Fig. 4b, showing an excellent agreement.

**Table 2. Investigated boundary conditions.**

| Boundary condition | Mathematical description |
|--------------------|--------------------------|
| BC$_1$ Dirichlet    | $T = T_\infty$, $T_\infty = 90 \degree C$ |
| BC$_2$ Neumann     | $-kdT/dx = Q/A$, $Q = 200$ W |
| BC$_3$ Neumann     | $-kdT/dx = Q/A$, $Q = 0$ W |
| BC$_4$ Robin       | $-kdT/dx = h(T-T_\infty)$, $T_\infty = 90 \degree C$ |

**Figure 3.** Derivation of the effective heat capacity curves.

**Figure 4.** a) Grid independence check and b) comparisons with results obtained with a finite-element scheme for temperature profiles for erythritol, adiabatic boundary condition and Tunisia.
3. Results

Results will be presented in terms of temperature profiles and cumulated energy. The total cumulated energy per unit length $U$, in (J/m), can be calculated from the following relationship:

$$\int_{t_{in}}^{t_{fin}} dU = \rho A \left( \int_{t_{in}}^{t_{fin}} C_{p,\alpha} dT + \lambda \int_{t_{in}}^{t_{fin}} C_{p,\beta} dT \right)$$  \hspace{1cm} (4)

where the subscript $in$ and $fin$ respectively refer to initial and ending conditions and $A$ is the PCM area. Since the apparent heat capacity method is herein applied, the energy $\Delta U$ cumulated between two time steps referred to $t$ and $t+1$ is herein derived from the following:

$$\Delta U = U(t + 1) - U(t) = \rho \Delta x^2 C_p(t) [T(t + 1) - T(t)]$$  \hspace{1cm} (5)

where $\Delta x$ is the grid size. It is important to observe that the heat capacity is calculated at a time step referred to $t$, since an explicit method is here used. The energy cumulated is obtained by making the sum of consecutive energy accumulations, starting from an initial state with zero-energy.

In Fig. 5, a comparison between two different PCMs (PCM_A denotes Erythritol, while PCM_B denotes MgCl$_2$ 6H$_2$O) is presented. Results are presented in terms of temperature profiles for different times, and energy cumulated. The Robin boundary condition is used (BC_4, see Table 2), for climate date referred to Tunisia (Fig. 2). With reference to the temperature profiles, it is shown that the temperature on the left increases in the first half of the simulations that follows what reported in Fig. 2, while a drop occurs for the other parts of the simulations, due to the fact that the sun provides lower energy. For the phase change, it is shown that the heat moves from the left to the right, causing a general increase of the temperature profile, that means phase change. With reference to the cumulated energy, it is shown that there is a high increase at the beginning of the simulations, while a maximum is reached just before the end. The reason of this is that the solar source doesn’t provide constant temperature, thus at the end of the transient the reduction of temperature could cause an inversion of heat flux, making energy in the PCM to become lower. By comparing the two PCMs, it is shown that the erythritol melts easier than the magnesium chloride hexahydrate, since the slightly lower heat capacity in the solid phase (Fig. 3) means less resistance to the heat that comes from the solar collector. On the other hand, the erythritol makes possible to accumulate more energy; this happens because the heat capacity is in general higher.

In Fig. 6, different boundary conditions (see Table 2) are compared in terms of temperature profiles and stored energy. The analysis is referred to erythritol (PCM_A) and for climate date referred to Tunisia (Fig. 2). It is shown that the adiabatic condition (BC_3) provides higher temperature values, since the heat comes from the solar collector without any exits, causing temperature increases higher than the other boundary conditions investigated. As obvious, this boundary condition also provides higher stored energy values. On the other hand, the Dirichlet boundary condition (BC_1) provides lower temperature profiles and stored energy. This happens because the locked temperature is a constraint in terms of temperature enhancing through the PCM. With references to the other two BCs, the Robin condition (BC_4) provides a slight increase with respect to the time for the temperature at the right end of the PCM ($x = 0.1$ m), since the heat that comes from the solar system is higher than the heat that goes to the environment. Similar conclusions can be made for the Neumann BC (BC_2).

In Fig. 7, different solar sources (see Fig. 2) are presented. Results are referred to erythritol (PCM_A) and for the Robin boundary condition (BC_4). The computations in which the solar source named Tunisia are the ones that have higher temperatures and energy stored, since the solar source temperatures are in general higher than that for Japan.
It is important to observe that at about midday the energy stored for Japan starts to decrease, since the solar source starts to become lower, as depicted in Fig. 2. It is widely known that the weakest point, from the thermodynamic point of view, is the relatively low thermal conductivity of the PCM. Indeed, this causes the PCM to have some problems in melting at all [20]. For this purpose, various techniques have been proposed during the years to increase the conductivity [21]. One of these consists into using a metal foam that has the ability of increasing the overall thermal conductivity of the foam, since a high conductivity material with high porosity is put in the PCM. In this paper, simulations for an aluminum foam with 90% of porosity are carried out. In order to take into account the foam in the computational domain, the thermophysical properties are averaged over the computational domain, as follows:

\[ \rho = \rho_{PCOM} + \rho_{foam} = \rho_{PCOM} + (1 - \varepsilon) \rho_{foam} \]  
\[ k = k_{PCOM} + k_{foam} = k_{PCOM} + \frac{(1 - \varepsilon)}{3} k_{Al} \]  
\[ c_p = c_{p,PCOM} + c_{p,foam} = \varepsilon \left( c_{p,foam} \left[ 1 - \alpha(T) \right] + c_{p,Al} \right) + \frac{\lambda \, d\varepsilon}{dT} + (1 - \varepsilon) c_{p,Al} \]  

**Figure 5.** Temperature profiles for different times and cumulated energy for different PCMs, for Robin BC (BC4) and Tunisia.

**Figure 6.** Temperature profiles for different times and cumulated energy for different BCs, for erythritol (PCMA) and Tunisia. Legend for temperature profiles is the same reported in the figure on the right.
The aluminum thermophysical properties, denoted with the subscript Al, are evaluated at 400 K. It should be noted that the thermal conductivity relationship for the foam is taken from [22, 23], since it has been demonstrated that a weighted average or a series model is not accurate enough [24, 25]. Density and heat capacity, respectively Eqs. 6 and 8, are taken as the weighted average with respect to the porosity, as usually done for porous media [26]. The porosity is here the ratio between the PCM volume and the total volume. The heat capacity (Eq. 8) is obtained by observing that the PCM heat capacity has been already presented in Eq. 2. Results in terms of temperature profiles and stored energy and referred to PCMₐ, BC₃ (adiabatic) and Tunisia, are presented in Fig. 8. It is shown that the metal foam drastically enhances both temperature values and stored energy. This because the higher thermal conductivity causes the melting front to proceed faster from the left side to the right one, obtaining more melting fraction through the foam. However, the overall heat capacity tends to reduce because the foam has lower heat capacity than the PCM, but this effect is overwhelmed by the higher melting fraction. It has to be observed that the foam cumulated energy reaches a maximum at the middle point of the curve. This occurs since the melting process becomes very fast with a foam, then from that peak the temperature heat source reduction (Fig. 2) is as prominent as to make the temperature reducing in the PCM, thus cumulated energy starts to reduce. This effect is also evident with references to the temperature profiles, since from 4.50 h to 9.00 h the profiles are almost uniform, and they tend to reduce following the temperature of the heat source on the left.

4. Conclusions
In this paper, various aspects of a solar-assisted PCM for ORC energy storage have been numerically investigated with the apparent heat capacity method. Since the PCM needs to operate close to 100-120 °C, two different PCMs are analyzed and compared: erythritol and magnesium chloride hexahydrate. Making reference to such temperature range, two solar heat sources from the literature have been chosen and compared. Various boundary conditions were analyzed, in order to investigate different configurations. Finally, a comparison with a PCM-metal foam system has been reported.

Results, presented in terms of temperature profiles and stored energy, show that the latent heat has a primary role in storing energy, since the PCM with an higher latent heat (Erythritol) can store higher amounts of energy when compared to the other investigated PCM (about less than 30%). As expected, higher solar source temperature increases the temperature and the stored energy of the system. Finally, it has been shown that using a metal foam can drastically enhance stored energy, since melting occurs easily due to the relatively high thermal conductivity of the foam. Finally, it is possible to conclude that ORC temperatures can be controlled when the solutions proposed in the paper are employed.
Figure 8. Temperature profiles for different times and cumulated energy with and without aluminum foam, for erythritol (PCMA), adiabatic BC (BC3) and Tunisia. Legend for temperature profiles is the same reported in the figure on the right.

5. Nomenclature

| Symbol | Description |
|--------|-------------|
| A      | Area (m²)   |
| c_p    | Heat capacity (J/kg K) |
| h      | Heat transfer coefficient (W/m²K) |
| k      | Thermal conductivity (W/m K) |
| L      | Length (m) |
| Q      | Heat rate (W) |
| t      | Time (s) |
| T      | Temperature (°C) |
| x      | Axial coordinate(m) |
| U      | Energy per unit length (J/m) |
| α      | Alpha function |

Greek symbols

| Symbol | Description |
|--------|-------------|
| PCM    | Phase Change Material |
| s      | Solid PCM |
| m      | Melting |
| l      | Liquid PCM |
| fin    | Final |
| foam   | Aluminum foam |
| ε      | Porosity |
| λ      | Latent heat of fusion (J/kg) |
| ρ      | Density (kg/m³) |
| ∞      | Environment |

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