Application T-History method on measurement of thermal properties of phase change material as latent heat storage in solar water heating system

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Abstract. The advantages of latent heat storage systems are heat storage materials capable of providing large energy storage densities and are capable of storing heat at almost constant temperature according to the transition temperature at each phase change. The thermophysical properties of phase change material (PCM) materials are important to know before they are applied in a variety of uses. The thermophysical properties of PCM materials are very important to note i.e. melting point, super cooling temperature, latent heat, heat type and thermal conductivity of the PCM material. Methods of determining the thermophysical properties of PCM materials that have been widely used are differential thermal analysis (DTA), differential scanning calorimetry (DSC), and calorimetry. These three methods have weaknesses. DTA and DSC methods that have very small test samples (110 mg) cause the materials thermophysical properties to be different when used in larger quantities. Another disadvantage is that DTA and DSC measurement equipment is complex and expensive, and cannot measure latent heat, specific heat and thermal conductivity of multiple PCM samples simultaneously. The weakness of the calorimetry method is the process of changing the two phases of PCM that is difficult to observe. T-history method that uses simple equipment has been widely used at this time. In this research, we will use T-History method to measure the thermophysical properties of phase change materials that will be used as heat storage material in solar water heating system. The material is: paraffin, beeswax, cow fat, and mixture of the material with a certain ratio. From the test, results can be concluded that the use of T-History method gives good results with a difference of 7% with the measurement results using DSC.

1. Introduction
The use of heating water with solar energy significantly reduces the use of non-renewable energy sources and reduces air pollution increases; these results have obvious environmental and economic benefits.

However, traditional solar water heating systems present several problems, including intermittent surgery, weather instability, and low energy density, significant temperature fluctuations [1]. Adding
latent heat storage material to a heat storage unit can not only reduce volume but also allow heat to be stored and released at almost constant temperature, avoiding the shortage of traditional water tanks [2].

Latent heat storage utilizes latent heat contained in materials to store heat energy. Latent heat is the amount of heat absorbed during the phase change in the material from one phase to another. Latent heat smelting is the amount of heat absorbed when the phase material changes from solid phase to liquid phase or vice versa.

Many studies of potential utilization of PCM on solar water heating systems [3–6]. In addition, much research aimed at getting the kind of cheap and easy PCM handlers to use on solar water heating systems.

Differential Scanning Calorymetry Equipment (DSC) is commonly used for the characterization of PCM. The limitation of DSC is the accuracy of determining the thermophysical properties of PCM, the use of a sample mass of only 10 mg that does not represent the mass in the kilogram range often used in practical applications [7]. On the other hand, super cooling-sub cooling and melting properties that depend on the amount of PCM can vary substantially with changes in PCM sample mass from milligrams to kilograms.

With a mass of 10 mg a large heating rate can cause hysteresis between heating and cooling curves, while lower heating rates can increase errors in the calculated enthalpy changes due to decreased signal-to-noise ratios [8]. The small sample size increases the probability of sub-cooling and amplifies it, which deforms the cooling curve [9]. This deficiency led to the development of other techniques to characterize larger PCM samples using standard laboratory equipment.

The T-History Method was first developed by Yinping et al. in 1999 [10]. This method allows obtaining melting point, latent heat, subcooling rate, thermal conductivity and specific heat of several PCM samples simultaneously.

T-history is another method often used in practice and endorsed by Gütezeichen [11], but some authors have made a critical assessment of the data processing methodology. Lázaro et al. [12] verified the results of T-History testing, by comparing the resulting enthalpy temperature curve with DSC results. The experimental and set-up procedures used provide consistent results over several tests but no details about the variation of data processing from the T-history method used [13].

Marin et al. [14] proposes to analyze the T-history curve during very small temperature intervals, without changes to the applied method whether the interval is in a period of solid, liquid or phase change. This formulation produces a complete enthalpy temperature curve over the entire tested temperature range and, as evidenced by [15], this method can be directly applied to the cooling and heating process, which permits the assessment of hysteresis, or lack thereof.

Sandnes dan Rekstad [16] proposes to test references and PCM samples in separate experiments and to express heat transfer as a function of the temperature difference between the environment and the sample. The enthalpy change in PCM is then determined as a temperature function, producing an enthalpy temperature curve which may include subcooling.

Kravvaritis [17] choose to compare the delay time between PCM and reference samples during specified time intervals. The so-called "thermal delay method" introduces effective, specific thermal concepts that vary with PCM temperature and provides all the information necessary to create an enthalpy temperature curve for PCM testing.

In this research will be tested the properties of thermophysical material changing phase that is paraffin, beeswax, beef fat, and beeswax-fat mixture of cow. The objective of the study was to obtain cheap PCM and easy handling to apply to solar water heating system.

2. Material and methods
Phas change materials used in this study are paraffin, beeswax, cow fat, and beeswax-cow fat mixture. Paraffin used is paraffin available on the market, while beeswax used in batik making process, while cow fat, obtained from purification of cow's fat by heating and filtering. The equipment for the T-History test is as shown in Figure 1. The main equipment is a glass tube to hold PCM and water. Thermocouples are used to measure PCM, water and air temperature. Data logger for recording and storing data of thermocouple measurement results.
The test begins by heating the PCM and the water reaches the PCM temperature completely melting. Then PCM-liquid and water are fed into prepared glass tubes. Changes in PCM and water temperature during cooling in the room air are recorded with data logger. The calculation of the fusion enthalpy, specific heat and thermal conductivity of PCM uses the following equation:

\[ C_{p,n} = \frac{m_w C_{p,w} + m_t C_{p,t}}{m_p} \frac{A_2}{A_2} \frac{m_t}{m_p} C_{p,t} \]  

(1)

\[ C_{p,l} = \frac{m_w C_{p,w} + m_t C_{p,t}}{m_p} \frac{A_1}{A_1'} \frac{m_t}{m_p} C_{p,t} \]  

(2)

\[ H_m = \frac{m_w C_{p,w} + m_t C_{p,t}}{m_p} \frac{A_2}{A_1'} \left(T_0 - T_s\right) \]  

(3)

Where \( m_w \) and \( C_{p,w} \) are mass and specific heat of water. \( m_t \) and \( C_{p,t} \) are the mass and specific heat of the glass tube. \( A_1 \) and \( A_2 \) are the area under the PCM temperature change curve (figure 2) and the area under the water temperature change curve (figure 3).

The PCM temperature measurement results during cooling form a temperature curve over time called the T-History curve as seen in Figure 3, where \( \Delta T_m = (T_m - T_s) \) is the super cooling degree. \( T_m = \) melting temperature of PCM.

**Figure 1.** PCM thermophysical testing equipment.

**Figure 2.** The T-history curve of PCM during the cooling process (with super cooling).
Figure 3. T-history curve during the water cooling process.

Figure 4 shows a PCM curve which is cooled without super cooling (where the temperature range of the phase change process is between $T_{m,1}$ and $T_{m,2}$), the calculations for $C_p,l$ and $C_p,s$ are equal to the above equations, the melt enthalpy can be determined from:

$$H_m = \frac{m_w}{m_p} (T_0 - T_{m,1}) - \frac{m_t}{m_p} (T_{m,1} - T_{m,2})$$

3. Result and discussion
The test results are shown in the form of temperature-time curves for PCM paraffin, beeswax, and cow fat, each shown in Fig. 5-7.

Figure 4. The T-history curve of PCM during the cooling process.

Figure 5. The temperature-time curve for PCM beeswax.
From the above figure it is clear that the determination of the starting point of freezing and freezing end point can be determined based on ΔT which is close to zero or very small change. It can be stated, that the phase change occurs where ΔT is almost constant or equal to zero. Based on the above analysis it can be concluded that at the melting temperature the beeswax is at 57.40 °C - 61.79 °C. From the calculation of the melting enthalpy, the specific heat and thermal conductivity of all PCM is given in Table 1.

Table 1. Test results of PCM characteristics.

| No | Material                  | Tm  | Cp    | k     | Hm   | DSC Hm |
|----|---------------------------|-----|-------|-------|------|--------|
|    |                           | °C  | (Kj.kg/K) | (W/Mk) | (kJ/kg) | (kJ/kg) |
| 1  | Parafin                   | 51.72-53.90 | 4.77-6.60 | 0.21   | 151.65 | 141.08  |
| 2  | Beeswax                   | 57.40-61.79 | 4.86-8.45 | 1.23   | 148.71 | 138.18  |
| 3  | Cow fat                   | 38.0-41.0   | 3.19-4.16 | 0.18   | 112    | -       |
| 4  | 30% Cow fat, 70% Beeswax  | 51.72-54.90 | 3.89-2.88 | 0.13   | 135.05 | -       |
| 5  | 30% Cow fat, 70% Beeswax  | 44.40-47.14 | 2.55-7.64 | 0.58   | 136.15 | -       |
From the test results obtained enthalpy paraffin melt diffraction of about 7% with the results of DSC testing. This shows the T-History method can be used for testing the thermo physical properties of PCM. From the test results also obtained a mixture of cow fat with beeswax will be able to lower the melting temperature despite the decrease in melting enthalpy. From these results, it can be proposed that the cow fat-beeswax mixture can be considered as one of the energy storage materials in the solar water heater application.

4. Conclusion
From the results of testing the characteristics of PCM using T-History method, it can be concluded, T-history method can be used to test the thermo physical properties of phase change materials. From the results of this test, the beeswax obtained has the greatest melting enthalpy compared to paraffin and cow fat. However, higher melting temperatures, when applied to solar water heating systems will be difficult to reach these temperatures so that the heat storage process is difficult to occur. The cow fat-beeswax mixture can be considered as one of the energy storage materials in the application of solar water heating system because its melting temperature is in the temperature range of the collector.

References
[1] Zhao J, Ji Y, Yuan Y, Zhang Z and Lu J 2018 energy-saving analysis of solar heating system with pcm storage tank Energies
[2] Wang Z, Qiu F, Yang W and Zhao X 2015 Applications of solar water heating system with phase change material. renewable and sustainable Energy Reviews 52, 645–652
[3] Thaib R, Hamdani and Irwansyah 2014 Investigation performance of solar water heater system using paraffin wax ARPN Journal of Engineering and Applied Sciences, 9 (10)
[4] Xie L, Tian L, Yang L, Lv Y and Li Q 2017 Review on application of phase change material in water tanks Advances in Mechanical Engineering, 9(7), 1–13
[5] Mahfuz M H, Anisur M R, Kibria M A, Saidur R and Metselaar I H S C 2014 Performance investigation of thermal energy storage system with phase change material ( pcm ) for solar water heating application International Communications in Heat and Mass Transfer 57, 132–139
[6] Bouadila S, Fteïti M, Mehdi M, Guizani A, and Farhat A 2013 Enhancement of latent heat storage in a rectangular cavity : solar water heater case study Energy conversion and management
[7] Sarwar J and Mansoor B 2016 Characterization of thermophysical properties of phase change materials for non-membrane based indirect solar desalination application Energy conversion and management, 120, 247–256
[8] Günther E, Hiebler S, Mehling H and Redlich R 2009 Enthalpy of phase change materials as a function of temperature : required accuracy and suitable measurement methods Int J Thermophys, 30, 1257–1258
[9] Pereira J and Eames P 2016 Thermal energy storage for low and medium temperature applications using phase change materials - a review Applied Energy, 177, 227–238
[10] Yinping Z and Yi J 1999 a simple method , the t-history method , of determining the heat of fusion , specific heat and thermal conductivity of phase-change materials Measurement Science and Technology, 10(3), 201–205
[11] Gütesicherung R 2013 Quality and Testing Specifications for Phase Change Materials – PCM (Germany)
[12] Lázaro A, Günther E, Mehling H, Hiebler S, Marin J M and Zalba B 2006 Verification of a t-history installation to measure enthalpy versus temperature curves of phase change materials Measurement Science and Technology, 17(8), 2168–2174
[13] Solé A, Miró L, Barreneche C, Martorell I and Cabeza L F 2013 Review of the t-history method to determine thermophysical properties of Phase Change Materials (PCM) Renewable and Sustainable Energy Reviews 26, 425–436
[14] Marin J M, Zalba B, Cabeza L F and Mehling H 2003 Determination of enthalpy temperature curves of phase change materials with the temperature-history method: improvement to temperature dependent properties Measurement Science and Technology 14(2), 184–189

[15] Lazaro A, Peñalosa C, Solé A, Diarce G, Haussmann T, Fois M, Zalba B, Gshwander S and Cabeza L F 2013 Intercomparative tests on phase change materials characterisation with differential scanning calorimeter Applied Energy 109, 415–420

[16] Sandnes B and Rekstad J 2006 Supercooling salt hydrates: stored enthalpy as a function of temperature 80, 616–625

[17] Kravvaritis E D, Antonopoulos K A and Tzivanidis C 2011 Experimental determination of the effective thermal capacity function and other thermal properties for various phase change materials using the thermal delay method Applied Energy, 88(12), 4459–4469