Thermophysical Parameters of Organic PCM Coconut Oil from T-History Method and Its Potential as Thermal Energy Storage in Indonesia

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Abstract. The thermophysical parameters of organic phase change material (PCM) of coconut oil (co_oil) have been studied by analyzing the temperature vs time data during liquid-solid phase transition (solidification process) based on T-history method, adopting the original version and its modified form to extract the values of mean specific heats of the solid and liquid co_oil and the heat of fusion related to phase transition of co_oil. We found that the liquid-solid phase transition occurs rather gradually, which might be due to the fact that co_oil consists of many kinds of fatty acids with the largest amount of lauric acid (about 50%), with relatively small supercooling degree. For this reason, the end of phase transition region become smeared out, although the inflection point in the temperature derivative is clearly observed signifying the drastic temperature variation between the phase transition and solid phase periods. The data have led to the values of mean specific heat of the solid and liquid co_oil that are comparable to the pure lauric acid, while the value for heat of fusion is resemble to those of the DSC result, both from references data. The advantage of co_oil as the potential sensible and latent TES for room-temperature conditioning application in Indonesia is discussed in terms of its rather broad working temperature range due to its mixture composition characteristic.

Keywords: Phase Change Material (PCM), coconut oil, T-history method, thermophysical parameters.

1. Introduction

Thermal energy storage (TES) is a technology that saves thermal energy by heating or cooling a storage medium so that the stored energy can be used at a later time for heating and cooling applications [1-2]. For passive system, TES are used particularly in buildings to keep the thermal comfort of occupants [3-4]. For this application, TES system can help balance energy demand and supply on a daily, weekly and even seasonal basis. They can also reduce electrical energy consumption and its peak demand, as well as to reduce CO₂ emissions as the side effect of the use of airconditioning (AC) system. It will also increase overall efficiency of energy systems.
There are two kinds of physical TES systems, namely: 1) sensible heat storage that is based on storing thermal energy by heating or cooling a liquid or solid storage medium (e.g. water, bricks, rocks, etc.); 2) latent heat storage using phase change materials or PCMs (e.g. it involved the material that undergoes solid to liquid phase transition, or vice versa). Sensible heat storage is relatively inexpensive compared to PCM material and is applicable to domestic and district systems. However, in general sensible heat storage requires large volumes because of its low energy density and proper design to discharge thermal energy at constant temperatures. Thus, thermal energy storage system based on phase change material (PCM) is one of the feasible ways for energy conservation in the future because it can store relatively large heat at temperature around its phase transition (solid-liquid) region, and releasing the absorbed heat back to the environment when the ambient temperature is lower than the temperature of the material.

Mettawee et.al. in 2012 and 2013 have shown that coconut oil (co_oil) can be used as the medium of active and passive air conditioning system, namely as the agent that influence the initial temperature of the heat transfer fluid in air conditioning machine [5] and as the medium of heat exchanger in ceiling system [6]. These applications also in agreement with the result of DSC study that shown a big storing capacity of co_oil in the temperature range of 12 to 35°C [7]. Hence, co_oil as one of organic PCM have a capability to stores the latent heat and also sensible heat when the environment temperature is higher than its temperature and release the stored heats later to keep the room temperature relatively constant or conditioned. To get a reliable information for the application of co_oil, we present in this paper the thermophysical parameters of co_oil by means of T-history method proposed by Yinping et al. [8] and its modification by Hong et al. [9] to get the values of mean specific heat of the liquid and solid co_oil ($c_p,l$ and $c_p,s$) as well as the heat of fusion ($h_m$) for the solid-liquid transition of co_oil [1-3]. In order to get a reasonable value of solid specific heat, we proposed to adopt a combination of Yinping and Hong method, in particular for the determination of phase transition region, which might be related with the gradual nature for the phase transition of co_oil.

2. Methods
The coconut oil (co_oil) as PCM was purchased from local supermarket in Bandung. The setup of measurement adopting the T-history method is represented schematically in Figure 1 that shows the test tube in cooling bath. Each tube is equipped with the temperature sensors (T-type thermocouple with diameter about 1mm) that integrated to the data logger (Applent AT4508A from Applent Instruments Inc.) and computer. To characterize co_oil by this method, about 20gr reference sample (water) and 20g co_oil sample were placed in 150mm long glass test tube with 14mm internal diameter and 1mm wall thickness. These tube dimensions were selected to ensure that the heat transfer is occur one-dimension along the length of the tube, as measured by the Biot number defined by $Bi = hR/2\kappa \leq 0.1$, where $h$ is the natural convective heat-transfer coefficient, $R$ is radius of the tube and $\kappa$ is the thermal conductivity of the tube material [8]. In this case the temperature distribution in the sample can be regarded as uniform and the lumped capacitance method can be used [10].
Figure 1. Schematic diagram of T-history method: co_oil sample and water as reference in two different tubes were heated at temperature $T_0$. The tubes were then suddenly exposed into cool air environment (temperature $T_a$), and the temperature-time data were recorded automatically by using data logger and computer during the decrease of temperature by time.

Prior to the measurement, water and liquid co_oil contained in two different tubes were heated to a high temperature ($T_0$) above the melting point ($T_m$) and stabilized for a few minutes to ensure the temperature homogeneity in all part of the sample. The tubes were then subsequently exposed to a cooler environment ($T_a$) provided by a cooling bath (with diameter 100 × 50 × 45cm). During the cooling process, the temperature of the water and co_oil were recorded and plotted against time until the co_oil solidified. The experiments were repeated several times to ensure the accuracy and reproducibility of the data.

3. Results and Discussion

When the temperature of PCM (co_oil) and water in the tube are suddenly exposed to cool air atmosphere whose temperature is $T_a$ (which might be time dependent), the temperature vs time curve, i.e. the T-history curves are shown in Fig. 1. From this figure, while water in this temperature region experience only the temperature change without phase transition, co_oil material experience the temperature change and liquid to solid phase transition, with supercooling temperature and solidification temperature are each denoted by $T_s$ and $T_m$. The values of $T_s$ and $T_m$ as well as the difference between them as defined as the supercooling degree ($\Delta T_m = T_s - T_m$) for 5 set of data are shown in Table 1. From this table one can see that the variation of solidification temperature for different set of experiment is about 18–21°C, while the supercooling degree is about 2-3°C. We note that the resulted solidification temperature (heat release) is lower than the reported values [7] of melting temperature (heat absorption) based on exothermic mode of DSC measurement, which commonly occur in other kinds of material.
Figure 2. The temperature-time curves of PCM (co_oil) and water during the cooling process in cool air environment ($T_a$).

Table 1. Supercooling Temperature ($T_s$), solidification temperature ($T_m$), and supercooling degree ($\Delta T_m$) of PCM (co_oil) for 5 set of data experiment.

| No. of measurement | $T_s$(°C) | $T_m$(°C) | $\Delta T_m = T_m - T_s$(°C) |
|--------------------|-----------|-----------|-----------------------------|
| 1                  | 15.69     | 18.37     | 2.68                        |
| 2                  | 16.09     | 18.48     | 2.39                        |
| 3                  | 18.48     | 20.65     | 2.17                        |
| 4                  | 16.37     | 19.13     | 2.76                        |
| 5                  | 15.06     | 18.28     | 3.22                        |
| Average values     | 16.34     | 18.98     | 2.64                        |

Following the original T-history method by Yinping [8] and its modification by Hong [9], the energy equations are described in Eqs. (1)-(3) for PCM, each of them for liquid state, phase change, and solid state periods.

\[
\left(m_{t,p} c_{p,t} + m_p c_{p,t}\right)(T_0 - T_s) = hA_1A_t
\]  

(1)

\[
\left(m_{t,p} c_{p,t} + m_p \frac{c_{p,t} + c_{p,s}}{2}\right)(T_m - T_f) + m_p h_m = hA_2A_t
\]

(2)

\[
\left(m_{t,p} c_{p,t} + m_p c_{p,t}\right)(T_f - T_s) = hA_3A_t
\]

(3)

We note that the energy equations for water as the reference material with the similar periods are described in Eqs. (4)-(6),

\[
\left(m_{t,w} c_{p,t} + m_w c_{p,w}\right)(T_0 - T_s) = hA_1A_t'
\]

(4)
\[
\left( m_{t, w} c_{p, t} + m_{w} c_{p, w} \right) (T_m - T_i) = h A' c
\]

\[
\left( m_{t, w} c_{p, t} + m_{w} c_{p, w} \right) (T_i - T_f) = h A' c
\]

In those above equations, \( m_p, m_w \) and \( m_{t,p}, m_{t,w} \) are the masses of the PCM, water and tube used for PCM and water; \( c_{p,l} \) and \( c_{p,s} \) are the mean specific heats of liquid and solid PCM; \( c_{p,w} \) is the mean specific heat of water; \( c_{p,t} \) is the mean specific heat of tube material and \( h_m \) is the heat of fusion of PCM, while \( A_c \) is the convective heat-transfer area of the tube. In addition, set values of \( \{ A_1, A_2, A_3 \} \) correspond to the area below the curve of PCM’ temperature towards air environment, each of them for liquid, liquid-solid and solid periods, while the corresponding set values for water are \( \{ A'_1, A'_2, A'_3 \} \), each of them for the area below the curve of water’ temperature towards air environment, with the boundaries follow those of the PCM’s temperature [9], see Table 2. We note, however, that in the modified T-history method [9], the equation (2) that describe the liquid to solid phase transition has been corrected by the terms related to temperature change belongs to the tube and PCM, the later to take into account the possible release of sensible heat in the liquid and solid phases from the original formulation [8]. Besides that Hong et al. also proposed the end of phase transition process to be determined from the inflection point, where the first derivative of T-history curve for PCM becomes minimum [9]. This is rely on the fact that the temperature keeps constant in the latent heat release, but decreases exponentially in cooling process accompanying sensible heat alone [8].

### Table 2. Area of each period used for analysis of T-history curves of PCM and water as reference material (\( T_p \) and \( T_a \) are temperature of co_oil and water, respectively)

| Period         | Temperature Range | Range of time | Area                |
|----------------|-------------------|---------------|---------------------|
| co_oil liquid  | \( T_0-T_s \)     | \( t_0-t_1 \) | \( A_1 = \int_{t_0}^{t_1} (T_p - T_a) dt \) |
| phase change   | \( T_s - T_m - T'_s \) | \( t_1-t_2 \) | \( A_2 = \int_{t_1}^{t_2} (T_p - T_a) dt \) |
| solid          | \( T'_s - T_f \)   | \( t_2-t_3 \) | \( A_3 = \int_{t_2}^{t_3} (T_p - T_a) dt \) |
| Water liquid   | \( T_0-T_s \)     | \( t_0'-t_2' \) | \( A'_1 = \int_{t_0}^{t_2'} (T_p - T_a) dt \) |
| liquid         | \( T_m-T_i \)     | \( t_1'-t_3' \) | \( A'_2 = \int_{t_1}^{t_3'} (T_p - T_a) dt \) |
| liquid         | \( T_i-T_f \)     | \( t_3'-t_4' \) | \( A'_3 = \int_{t_3}^{t_4'} (T_p - T_a) dt \) |

The result for analysis the T-history curves for one set of experiment data of co_oil and water are shown graphically in Fig. 3.
Figure 3 (a) Illustration for the analysis of temperature-time curve for PCM (co_oil) and its derivative; $T_0$ is initialization temperature, $T_m$ is melting temperature, $T_s$ is supercooling temperature, $T_f$ is final temperature, $T_a$ is cool air temperature and $T_i$ is inflection point at the first derivative of co_oil’s temperature. (b) Illustration for the analysis of the corresponding temperature-time curve of water.

From this figure (Fig. 3(a)) one can see a clear inflection point in the first derivative of co_oil’s temperature. We found, however, that for the co_oil as the organic PCM that is investigated in this paper, the liquid to solid phase transition occurs rather gradually in the temperature regime of $T_m$ and $T_s$, and therefore the meaning of inflection to the phase transition of co_oil has become smeared out. We note that the gradual nature for the phase transition of co_oil might be related to the fact that it consists of many kinds of saturated and unsaturated fatty acids with the largest amount of lauric acid (about 50%) [7]. However, the inflection point is still needed to measure the corresponding area of the water as the reference material, in order to obtain a reliable value of solid specific heat as discussed in the following paragraph.

Finally, the thermophysical parameters of PCM consist of the mean specific heats of the liquid and solid co_oil ($c_{p,l}$ and $c_{p,s}$) and the heat of fusion ($h_m$) derived from this method are expressed as,

$$c_{p,l} = \frac{m_{l,w}c_{p,l} + m_{w}c_{p,w} A_1}{\Delta m} - m_{l,p} c_{p,l}$$

$$c_{p,s} = \frac{m_{l,w}c_{p,s} + m_{w}c_{p,w} A_2}{\Delta m} - m_{l,p} c_{p,s}$$

$$h_m = \frac{m_{l,w}c_{p,l} + m_{w}c_{p,w} A_1}{\Delta m} (T_m - T_i) - \frac{m_{l,p} c_{p,l} + c_{p,s}}{2} (T_m - T_i)$$

The results of analysis for 5 set data of co_oil are shown in Table 3, together with the average and standard deviation values for each parameters, to be compared with the same or similar materials from references using various experiment methods (Table 4).
Table 3. The values of liquid and solid specific heats of co_oil and heat of fusion related to phase transition of co_oil taken from the analysis of 5 set of data and their average values.

| Sampel | $c_{pl}$ [kJ/kg.K] | $c_{ps}$ [kJ/kg.K] | $h_m$ [kJ/kg] |
|--------|-------------------|-------------------|---------------|
| 1      | 2.83              | 3.26              | 88            |
| 2      | 2.25              | 3.29              | 72            |
| 3      | 2.20              | 3.14              | 78            |
| 4      | 2.31              | 3.24              | 83            |
| 5      | 2.14              | 3.13              | 90            |
| Average values | 2.35 | 3.23 | 82 |
| Standard deviation values | 0.28 | 0.07 | 7 |

Table 4. The thermophysical parameter values of co_oil, pure lauric acid, or mixture between lauric and capric acids derived from DSC and T-history measurements from references.

| Ref. | Material          | Method | $c_{pl}$ [kJ/kg.K] | $c_{ps}$ [kJ/kg.K] | $h_m$ [kJ/kg] |
|------|-------------------|--------|-------------------|-------------------|---------------|
| [7]  | Coconut oil       | DCS    | -                 | -                 | 103           |
| [8]  | Lauric acid       | T-history | 1.60-1.75    | -                 | 160-179       |
| [9]  | Lauric acid       | T-history | 2.14          | 2.81              | 186           |
| [11] | Capric-lauric acids | T-history | 2.12          | 1.80              | 179           |

From these two tables one can see that the mean values of liquid and solid specific heats of co_oil close to the corresponding values of pure lauric acid ($T_m \approx 45.9-50.3^\circ C$ [12]), while the heat of fusion resemble the value obtained from DSC [7]. We note hence, that the potential usage of co_oil as TES for room-temperature conditioning application in tropical climate area was supported by its composition that consists of many kinds of fatty acids where each kind of fatty acid have their own melting temperature, in which case it is commonly occur that the longer fatty acid chain imply the higher its melting temperature, which in turn give an implication to its rather broad working temperature range.

4. Conclusion
We have described in this paper the thermophysical parameters of coconut oil (co_oil) as one of organic PCM, based on the temperature vs data during solidification (T-history method) with water as the reference material. The data show that liquid to solid phase transition occur rather gradually with relatively small supercooling degree. The data have been further analyzed based on the lumped capacitance method to obtain the mean specific heat of the liquid and solid co_oil ($c_{pl}$ and $c_{ps}$) and the heat of fusion ($h_m$) related to the phase transition of co_oil. In different with the previous analyses, the period for latent heat release was determined based on the assumption that the process occur at temperature regime between the supercooling temperature ($T_s$) and solidification temperature ($T_m$). Although the first derivative of T-history curve of co_oil show a clear inflection point as the boundary between phase change and solid-state periods, its importance is to specify the related period of water in order to obtain the reliable value of mean specific heat of the solid co_oil. The obtained values of mean specific heats of the liquid and solid co_oil are $c_{pl} \approx 2.35$ kJ/kg.K and $c_{ps} \approx 3.23$ kJ/kg.K, i.e. they are close to the values belong to pure lauric acid, while the heat of fusion value ($h_m \approx 82$ kJ/kg) is close to the result from DSC. In addition, the co_oil that consists of many kinds of fatty acids has rather broad working temperature range so that it is potential as the sensible and latent TES in Indonesia.
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