

Accuracy improvement of T-history method for measuring heat of fusion of various materials

Hiki Hong^{a,*}, Sun Kuk Kim^b, Yong-Shik Kim^c

^a*School of Mechanical and Industrial Systems Engineering, KyungHee University, Yong-in, Kyung-gi, 449-701, South Korea*

^b*School of Architecture and Civil Engineering, KyungHee University, Yong-in, Kyung-gi, 449-701, South Korea*

^c*Department of Architectural Engineering, University of Incheon, Incheon 402-749, South Korea*

Received 17 October 2003; received in revised form 20 November 2003; accepted 10 December 2003

Abstract

T-history method, developed for measuring heat-of-fusion of phase change material (PCM) in sealed tubes, has the advantages of a simple experimental device and convenience with no sampling process. However, some improper assumptions in the original method, such as using a degree of supercooling as the end of latent heat period and neglecting sensible heat during phase change, can cause significant errors in determining the heat of fusion. This problem has been improved in order to predict better results by us. The present study shows that the modified T-history method is successfully applied to a variety of PCMs such as paraffin and lauric acid having no or a low degree of supercooling. Also it turned out that selected periods for sensible and latent heat do not significantly affect the accuracy of heat-of-fusion. As a result, the method can provide an appropriate means to assess a newly developed PCM by a cycle test even if a very accurate value cannot be obtained.

© 2004 Published by Elsevier Ltd and IIR.

Keywords: Material; Phase change; Process; Calculation; Latent heat, Fusion

Amélioration de la précision de la méthode de l'historique des températures utilisée afin de mesurer la chaleur de fusion de plusieurs matériaux

Mots clés : Matériau ; Changement de phase ; Procédé ; Calcul ; Chaleur latente ; Fusion

1. Introduction

Latent heat storage has an important role for many applications such as solar thermal systems and midnight electric power storage devices. Suitable phase change materials (PCMs) for the thermal storage have been used in these fields and developed to stabilize thermo-

physical properties without thermal degeneration. In the process developing the superior PCM, measurement of the thermophysical properties is necessary and important for assessing its performance.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods are popular in means available for determining the heat of fusion and the specific heat. The properties of PCMs including various additives like thickening and nucleating agents should be carefully measured by using the DSC and DTA methods [1,2]. These methods are, in general, appreciated as an accurate means in measuring the heat

* Corresponding author.

E-mail addresses: hhong@khu.ac.kr (H. Hong); kimsuk@khu.ac.kr (S.K. Kim); newkim@cwunet.ac.kr (Y.-S. Kim).

Nomenclature

A_c	Convective heat transfer area of a tube [m ²]
Bi	Biot number [= hR/k]
C_p	Constant-pressure specific heat [kJ/(kg·K)]
H_m	Heat of fusion [kJ/kg]
h	Convection heat transfer coefficient [W/(m ² ·K)]
k	Thermal conductivity [W/(m·K)]
m	Mass [kg]
T	Temperature [°C]
t	Time [sec]

Subscript

'	Pure water
0	initial state
a	atmosphere
f	final
i	inflection point
l	liquid
m	melting point
p	PCM
s	solid
t	tube
w	water

of fusion. But the thermophysical properties of a very small amount of the sample PCM might be different from those of the bulk materials including heterogeneous additives.

As another method for determining thermophysical properties of PCM, Zhang et al. proposed a T-history method [3] to be able to overcome the above limitation of DSC. Because this method does not take a small amount of sample, it is very convenient when a cycle test is carried out with sealed tubes containing newly developed PCMs. Nevertheless, the original T-history method has a restriction on accuracy of thermophysical properties owing to introduction of some invalid physical assumptions.

In the previous study [4], we analyzed thoroughly the principles of the original T-history method and proposed a modified alternative to enhance the measurement accuracy through experiment taking sodium acetate as a representative specimen.

Paraffin and fat acid which can be used as latent heat storage materials have characteristics of no or a low degree of supercooling and great temperature drop in solidification differently to sodium acetate. The goal of the present work is to verify that the modified method can be applied to several PCMs having different freezing patterns with a good accuracy. Also, it will be found out how determined periods for sensible and latent heat influence the accuracy of result.

2. Method of measurement and analysis

It is important that experimental conditions in T-history method satisfy that Biot number is less than 0.1 so that the lumped capacity method is applicable. As shown in Fig. 1, test tubes are filled, respectively, with the PCM and reference material (pure water used generally) whose temperatures initially remain identical and greater than the freezing temperature of PCM. Experiment of the T-history method is very simple; the test tubes are first kept vertically in a constant temperature bath, and then suddenly exposed to the atmosphere. Temperatures in the test tubes and the atmosphere concurrently start to be measured. The two T-history curves that are timewise variation of temperature are obtained for the PCM and reference material as shown Fig. 2(a) and (b). Thermal properties such as heat of fusion and specific heats can be calculated from the measured data and curves. The original T-history method proposed by Zhang et al. has advantages such as its simplicity and convenience without expensive devices. In the previous paper, we however found that it has two fatal problems in the process of analysis, which lowers the accuracy of the result and makes it impossible to obtain the heat of fusion for some PCMs. Also it was presented the modified method which improves the accuracy and robustly finds the thermal properties with physical meanings for any PCM.

Fig. 2 represents the typical T-history curve for PCM with supercooling. The first crucial problem in the original method is to adopt the release point [a in Fig. 2(a)] of supercooling as the end of phase change period. A degree of supercooling is varied with conditions such as cooling speed, purity and vibration and is completely independent of the end of phase change. Instead of it, the modified method uses an inflection point (b in Fig. 2) as the boundary between phase change and solid-state periods, where the first derivative of T-history curve for PCM becomes minimum [4]. This can be justified by the fact that the temperature keeps constant or decreases gradually in the latent heat release, but decreases exponentially in cooling process accompanying sensible heat alone. The temperature difference between points a and b is only 3 °C in the sodium acetate, but reaches to 10 °C in lauric acid, which exerts great influence on the results

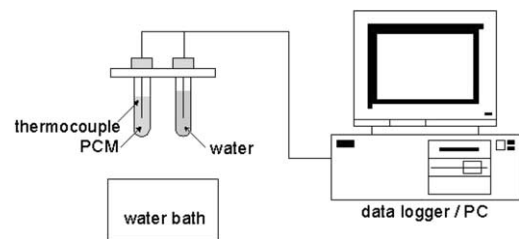


Fig. 1. Schematic diagram of experimental apparatus.

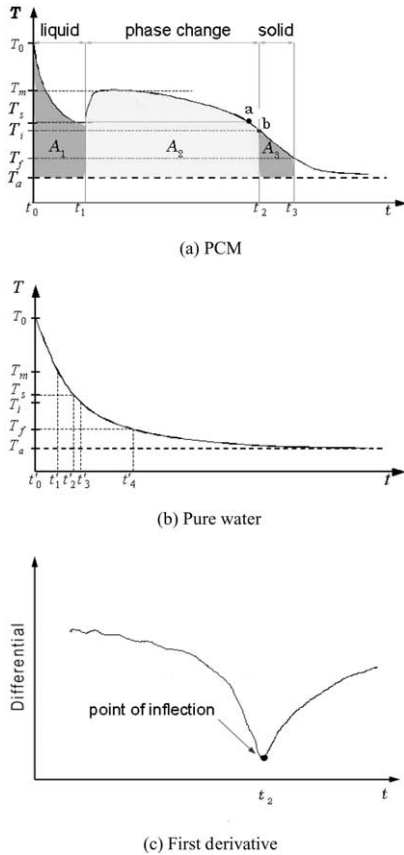


Fig. 2. A typical modified T-history curve.

in the view of accuracy. The second is not to include the sensible heat in the phase change period, where the temperature drop can be witnessed more or less in Fig. 2. This effect also can be considered in the analysis process of the new method.

Also, there was no detailed explanation for the heat transfer area of the tube contacting with PCM in the original method, but the area apparently varies in the process of solidification with volumetric change. The mean value for areas before and after phase change is applied in the modified method.

The energy equations including these factors are arranged in Eqs. (1)–(6); Eqs. (1)–(3) are for liquid-state, phase change, and solid-state periods on PCM respectively; Eqs. (4)–(6) are on reference material.

$$(m_{l,p}C_{p,l} + m_p C_{p,l})(T_0 - T_s) = hA_c A_1 \tag{1}$$

$$\left(m_{l,p}C_{p,l} + m_p \frac{C_{p,l} + C_{p,s}}{2}\right)(T_m - T_i) + m_p H_m = hA_c A_2 \tag{2}$$

$$(m_{l,p}C_{p,l} + m_p C_{p,s})(T_i - T_f) = hA_c A_3 \tag{3}$$

$$(m_{l,w}C_{p,l} + m_w C_{p,w})(T_0 - T_s) = hA'_c A'_1 \tag{4}$$

$$(m_{l,w}C_{p,l} + m_w C_{p,w})(T_m - T_i) = hA'_c A'_2 \tag{5}$$

$$(m_{l,w}C_{p,l} + m_w C_{p,w})(T_i - T_f) = hA'_c A'_3 \tag{6}$$

In the above equations, $A_1 = \int_{t_0}^{t_1} (T_p - T_a) dt$ which corresponds to the area below the curve in the period of liquid-state in Fig. 2(a), and the others are summarized in Table 1.

Finally, the modified T-history method provides specific heats and heat of fusion derived from the above equations as follows:

$$C_{p,l} = \frac{m_{l,w}C_{p,l} + m_w C_{p,w} A_c A_1}{m_p A'_c A'_1} - \frac{m_{l,p}}{m_p} C_{p,l} \tag{7}$$

$$C_{p,s} = \frac{m_{l,w}C_{p,l} + m_w C_{p,w} A_c A_3}{m_p A'_c A'_3} - \frac{m_{l,p}}{m_p} C_{p,l} \tag{8}$$

$$H_m = -\left(\frac{m_{l,p}}{m_p} C_{p,l} + \frac{C_{p,l} + C_{p,s}}{2}\right)(T_m - T_i) + \frac{m_{l,w}C_{p,l} + m_w C_{p,w} A_c A_2}{m_p A'_c A'_2} (T_m - T_i) \tag{9}$$

The temperatures are measured in the interval of 10–30 s according to freezing speed and then plotted against time. From these, the start and end of each period are determined. The series of calculation such as the areas in the graph are not complex but very tedious, so it is desirable to program the procedure.

3. Results

The experimental results for sodium acetate ($\text{CH}_3\text{COONaH}_2\text{O}$), a kind of inorganic hydrate, have been reported in detail in the previous paper [4] for validity of the modified T-history method. A representative T-history curve is shown in Fig. 3. As the inflection point appears apparently, each period shown in Fig. 2 can be easily determined. The temperature difference between the supercooling release and the inflection points is only 3 °C in the case of sodium acetate, so the effect adopting the inflection point rather than the

Table 1
Areas of each period used in equations

Period	Range of temperature	Area	Range of time	Area	Range of time
liquid	$T_0 - T_s$	A_1	$t_0 - t_1$	A'_1	$t'_0 - t'_1$
phase change	$T_m - T_i$	A_2	$t_1 - t_2$	A'_2	$t'_1 - t'_2$
solid	$T_i - T_f$	A_3	$t_2 - t_3$	A'_3	$t'_2 - t'_3$

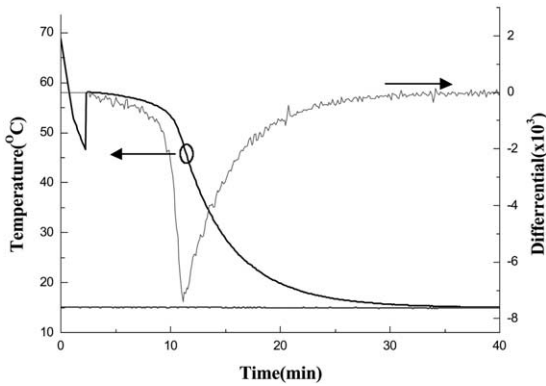


Fig. 3. T-history curve for sodium acetate.

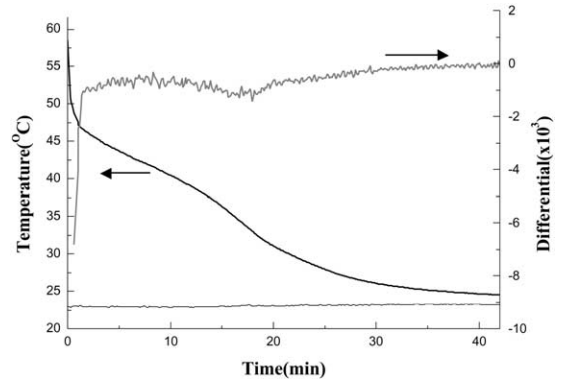


Fig. 4. T-history curve for paraffin.

supercooling release point as the ending boundary of the phase change was estimated to relatively small extent. The effect of sensible heat included in the period of phase change is dominant and shows the difference up to 1.7 times comparing to the original method in calculated heat of fusion. The results are summarized in Table 2 together with those by DSC.

As no supercooling phenomenon is observed in solidifying process of paraffin, the temperature tends to descend continuously in the period of phase change as shown in Fig. 4. The original method can be applied in obtaining heat of fusion only when the temperature keeps almost constant in phase change. In Fig. 4 the temperature drop occurs markedly during solidification and it is difficult to find the boundaries of each period. This induces the original method not to be applicable at all.

It was explained earlier that the modified method utilizes the inflection point as the end of phase change period. Moreover, since the paraffin has no supercooling that makes it difficult to select the solidification start

point, the alternative point where differential value abruptly changes was adopted as the beginning point of phase change period. Analysis process is the same to that of hydrates other than using T_m instead of T_s in Eqs. (1) and (4).

Experiment using six specimens of n-Docosane ($C_{22}H_{46}$) was executed and the results are revealed in Table 3. For the same specimen, the heat of fusion was measured by DSC, which coincides well with that by the modified T-history method.

The T-history curve for lauric acid, a kind of fatty acid having a small degree of supercooling, is shown in Fig. 5. The significant temperature drop in phase change period does not permit application of the original method similarly to the paraffin. If the release temperature of supercooling is chosen as the end of phase change, the period of latent heat becomes extremely short to make it meaningless to evaluate the heat of fusion. The proposed method solving these problems can give a considerably precise value 4% larger than that by DSC in heat of fusion as shown in Table 4.

Table 2
Heat of fusion and specific heats for sodium acetate

Sample	$C_{p,l}$ [kJ/kg·K]	$C_{p,s}$ [kJ/kg·K]	H_m [kJ/kg·K]
1	2.86	2.17	262
2	3.35	2.19	242
3	3.71	2.42	237
4	4.29	2.29	242
5	3.93	2.44	240
6	4.29	2.22	244
Average ± 95% confidence limit	3.74 ± 0.59	2.26 ± 0.13	245 ± 9
DSC	—	—	253
Reference value [1]	3.05	—	226
Reference value [6]	3.68	2.11	263

Table 3
Heat of fusion and specific heats for paraffin ($C_{22}H_{46}$)

Sample	$C_{p,l}$ [kJ/kg·K]	$C_{p,s}$ [kJ/kg·K]	H_m [kJ/kg·K]
1	1.89	5.50	141
2	2.83	5.09	127
3	1.79	5.96	126
4	2.35	4.75	143
5	2.50	4.88	138
6	1.75	4.49	132
Average ± 95% confidence limit	2.19 ± 0.19	5.11 ± 0.56	135 ± 8
DSC	—	—	130
Reference value [6]	—	—	156.8

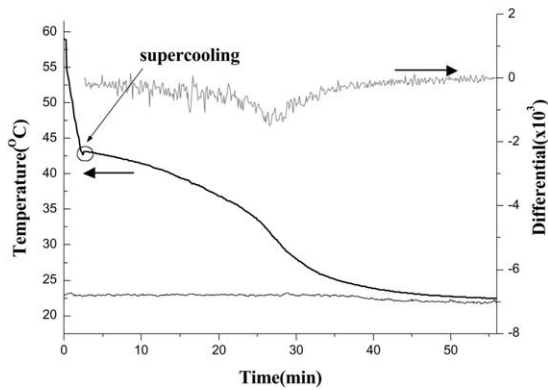


Fig. 5. T-history curve for lauric acid.

Table 4
Heat of fusion and specific heats for lauric acid

Sample	$C_{p,l}$ [kJ/kg·K]	$C_{p,s}$ [kJ/kg·K]	H_m [kJ/kg·K]
1	2.16	3.01	171
2	2.10	1.98	191
3	1.93	2.50	192
4	2.45	3.70	186
5	2.16	2.81	197
6	2.17	2.85	184
Average ± 95% confidence limit	2.14 ± 0.46	2.81 ± 0.60	186 ± 10
DSC			179
Reference value [1]			177
Reference value [6]	2.38	1.80	183

4. Discussion

Regardless to a degree of supercooling, the heat of fusion obtained by the modified T-history method is in good agreement with that by DSC in only 4% difference. The specific heats yielded additionally, however, displays larger discrepancy and severe scattering according to specimens. It is desirable to reply on the other methods when precise values are demanded. The specific heats $C_{p,l}$ and $C_{p,s}$ included in Eq. (9), however, does not greatly affect the heat of fusion H_m having a variation of H_m with $C_{p,l}$ 0.05%/1%.

In the present method, it is essential to measure precisely the latent heat of PCM filled in an encapsulated tube with keeping its reproduction. It is necessary to note the variation according to the samples. Tables 2–4 summarize the estimation of confidence interval where the real value is included with the probability of 95% [5]. It turns out that the interval is about ±5% for six times measurement, which is not so great to a practical extent. Hence, we recommend that the measurement should be performed five times in order to maintain this con-

fidence interval. As the factors affecting scattering, uncertainty of the period selection, variation of heat transfer coefficient and location of thermocouples can be considered.

The inflection point was used as the boundary between the periods of latent and solid-state sensible heat. It was sometimes encountered that the extreme value of the first derivative of the T-history curve are not so evident to choose easily. For instance, it is feasible to select it in Fig. 3 for the sodium acetate, but somewhat difficult to grasp the exact point in Figs. 4 and 5. A difference of 1 min. in time reading roughly leads to variation of 1 °C in temperature. To analyze this effect, the heat of fusion calculated using the temperature at the inflection point was compared with those using the temperatures 1 °C greater and lower than it. In the case of sodium acetate, it can be seen that the effect can be almost neglected in most specimens in spite of some variation according to specimens. The sensitivity is 3.1%/°C in maximum; it can be allowed to calculate it approximately even when the precise inflection point cannot be obtained (Table 5).

There is no particular difficulty in selecting the liquid-state period which is ranged from t_0 to t_1 in the time, correspondingly from T_0 to T_s in the temperature in Fig. 2. There is however a possibility that subjective judgment and uncertainties intervene in selecting the period of solid-state of t_2 – t_3 . The inflection point was used as a starting point of the interval, but the temperature below it can be also utilized in the meaning of perfect elimination of latent heat effect.

Fixing the ending point T_f of Fig. 2 as 20 °C, the effect of the starting temperature in the solid-state period was examined by varying 25, 30, 35, 40 and 45 °C that is an inflection point in the sodium acetate. The summary for $C_{p,s}$ and H_m is arranged in Table 6. This can change not only the specific heat $C_{p,s}$, but also the heat of fusion H_m which depends on $C_{p,s}$ itself like Eq. (9). As a result of analysis, there is almost no difference in heat of fusion though any temperature is selected below the inflection point, which means that the effect of latent heat diminishes in the vicinity of the point. Also, there is no problem to use the ending point of latent

Table 5
Variation according to selection of inflection point

Sample	$C_{p,s} \pm$ sensitivity [kJ/kg·K] (%/°C)	$H_m \pm$ sensitivity [kJ/kg] (%/°C)
1	2.15 ± 2.0	262 ± 3.1
2	2.22 ± 2.6	241 ± 2.5
3	2.33 ± 0.7	242 ± 0.5
4	2.45 ± 0.4	237 ± 0.6
5	2.48 ± 4.7	240 ± 0.4
6	2.16 ± 0.9	232 ± 1.5

Table 6
Variation according to selection of start point of liquid-state period

Sample	$C_{p,s} \pm 95\%$ confidence limit [kJ/kg·K]	$H_m \pm 95\%$ confidence limit [kJ/kg]
1	2.21 ± 0.03	261 ± 0.9
2	2.06 ± 0.12	242 ± 0.9
3	2.21 ± 0.08	237 ± 0.6
4	2.36 ± 0.07	243 ± 0.7
5	2.28 ± 0.12	241 ± 0.6
6	2.23 ± 0.10	232 ± 0.6

heat period as the starting point of solid-state sensible heat period.

Usually, the end of solid-state sensible heat period is determined arbitrarily between the atmosphere temperature T_a and the inflection point T_i . Similar analysis was performed that the end of solid-state period was changed fixing the starting temperature T_i . Its effect is estimated by far less than that of the starting temperature. It was found out that the most important thing in selecting the period is the inflection point which is a crucial value determining a precise heat-of-fusion.

It was assumed that the heat transfer coefficient on the outer surface of a test tube is constant during experiment. But the surface temperature varying with elapse of time induces the change of the coefficient dominated by the natural convection in the room. The surface temperature varies approximately from 30 °C to 60 °C, which actually makes the coefficient to change in the range of 3–5 W/m²·K. So it is not so suitable that the value is assumed to be kept completely constant through the entire range. As an alternative, it can be regarded as a partial constant in each period whose temperature change is not relatively great.

In Eqs. (1)–(6), to replace the heat transfer coefficient h by h_1 in a liquid-state range, h_2 in a latent heat and h_3 in a solid-state range results in the same Eqs. (7)–(9) fortunately. It is because these values are eliminated in processes arranging the equations. Therefore, though the coefficient varies in the entire range, the introduction of partial constant leads to better validity of Eqs. (7)–(9) and makes the effect of the varying heat transfer coefficient less serious.

The lumped capacity method induced by supposing $Bi < 0.1$ through experiment permits the assumption of a uniform temperature of PCM in a test tube. Such an assumption can be applied if only a sensible heat is accompanied other than a latent heat. In general, there exists temperature distribution inside the PCM during solidification. Hence, though the condition of $Bi = hL/k < 0.1$ is satisfied, it does not assure the uniformity of temperature inside the PCM. For an outer diameter 10

mm tube, the Biot number is in the range of 0.01–0.04 for inorganic hydrates with 0.5–2W/m·K in conductivity; 0.06–0.13 for organic substance with 0.15–0.35W/m·K in conductivity; these satisfy the condition of $Bi < 0.1$ in a whole. Enhancement of measurement accuracy for organic substance having much less thermal conductivity than inorganic hydrate needs a tube with smaller diameter in a feasible extent. Of course, such a satisfaction does not sufficiently guarantee the uniformity of temperature. Fig. 6 shows the results of temperatures measured by thermocouples whose junctions are located at several positions in a radial direction, i.e. 0, 3, 6 and 7 mm apart from the centerline. For the test, the sodium acetate was used as a specimen and filled into a test tube 16 mm in inner diameter. It was proved that no appreciable difference was observed in the heat of fusion calculated by using the measured temperatures between in the centerline and 3 mm apart from it. On the other hand, the values at 6 mm and 7 mm are 10% less than those near centerline.

The temperature keeps comparatively constant in the vicinity of the centerline. Since the solidification progresses ahead on the inner surface of the tube, the temperature decreases more steeply, which makes the area below the curve small. The reduced area consequently results in the decrease of heat of fusion from Eq. (9). The trend is almost the same in the test carried out in tube 10mm in diameter. As a result, the heat of fusion calculated by using the temperature measured in the centerline approaches to those of DSC and literatures [1,6]. It is however very difficult to explain the reason qualitatively by using only the results of the experiment, which is necessary to be clarified analytically and numerically. In addition, it was verified that there is no influence on the results wherever the position of temperature measurement is vertically.

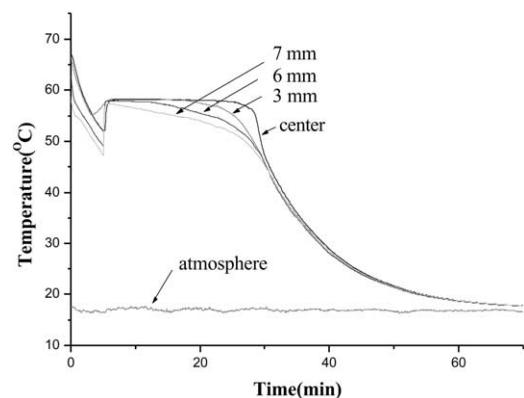


Fig. 6. Timewise temperature variation according to position of measurement.

5. Conclusion

The modified T-history method improving the original can be applied to several PCMs having different freezing patterns. The results can be summarized as follows.

1. Even for the PCM having no or a low degree of supercooling, the modified T-history method can yield the heat of fusion, which are in good agreement with that by DSC within 4%. There exists some scattering for evaluated values of heat-of-fusion and the confidence interval of 95% is about $\pm 5\%$ for six times measurement which is not serious from an engineering aspect.
2. In the process of selecting the end of the latent heat period, uncertainty of ± 1 min in time reading is anticipated. This, however, brings about almost no influence in the result.
3. It was validated that the start and end of the solid-state sensible heat period can be taken as arbitrary temperatures below the inflection point and over the atmosphere, respectively.
4. The specific heats obtained additionally display larger discrepancy and severe scattering according to specimens. So it is desirable to rely on the other methods when precise values are demanded.
5. The heat of fusion calculated by using the temperature measured in the vicinity of the

centerline of the tube approaches to that by DSC. Also, it was verified that there is no influence on the results wherever the position of temperature measurement is vertically.

Acknowledgements

The work was supported by KyungHee University's Research Funds.

References

- [1] Park WH. 1989. A system development of thermal energy storage at high temperatures, KIST.
- [2] Kim SD. 1992. Heat transfer characteristics in latent heat storage systems using salt hydrates, KIST.
- [3] Zhang Y, Jiang Y. A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Measurement and Science Technology* 1999;10:201–5.
- [4] Hong H, Park CH, Choi JH, Peck JH. Improvement of the T-history method to measure heat of fusion for phase change materials. *Int J of Air-Conditioning and Refrigeration* 2003;11(1):32–9.
- [5] Park SH. *Design of experiment*, 2nd ed. Seoul: Min-yongsa; 1995.
- [6] Perry RH, Green D. 1973, *Perry's Chemical Engineering Handbook*, 6th ed.