

THE SOLIDIFICATION BEHAVIOR OF PHASE CHANGE MATERIALS FOR LOW-TEMPERATURE ENERGY STORAGE

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Discharge experiments on the 65 mol% of capric acid and 35 mol% of lauric acid (C-L acid) as the main phase change medium (PCM) in a vertical tube yielded results both for the heat transfer and the time-wise evolution of the solidification front. Numerical solutions based on the pure conduction model were performed for comparison purposes. The two-dimensional heat transfer was represented by a one-dimensional model. The model accounted for the effective thermal conductivity that considered both its natural convection and the two-dimensional effects. It was found that the rate of solidification and the heat transfer were insignificantly affected by the fluid motion in the solid phase during transition.

The mixture has a fairly sufficient heat storage capacity. However, its melting temperature is high to consider it for cooling application. Pentadecane has characteristics similar to the C-L acid. The extent of the homogeneity and effective solidification of the PCM mixture in equal volume proportions of C-L acid and pentadecane was initially investigated by conducting HPLC analysis during its solidification. Data analysis was based on the possibilities of uniform concentration all through the solidification process as well as of the concentration difference in different radii at fixed height locations. Both assumptions established negligible heat transfer effect and negligible difference in the heat transfer coefficients at different radii.

Keywords: phase change materials, C-L acid, low-temperature energy, energy storage

INTRODUCTION

The purpose of this paper is to propose a convenient method to cover on the evaluation of the heat transfer characteristics of the C-L acid during its solidification based on numerical analysis. This work was motivated not only because of the need for quantitative heat transfer data applicable to a

vertical tube configuration but also because of the employment of the C-L acid for practical thermal energy storage for cooling application. Such data are functional to the development and possible application to C-L acid as heat sink in the cooling of an electronic system, as a PCM in the recovery

of waste heat in an industrial plant, or more ambitiously, in the cooling of an industrial or residential unit. It is necessary for the scientifically based design of thermal energy, its cost-effective operation and control.

The problem of phase transition in a vertical tube is a moving boundary problem in a rather convoluted geometry. A simpler analysis of the problem would involve the solution of a 1-D energy equation coupled with the consideration of the effective thermal conductivity in the liquid layer in order to account for its 2-D effect as well as the natural convection mechanism during its phase transition. This is a demanding work that is agreeable to a numerical solution.

The quantitative nature of the heat transfer processes involved in solidification has been previously investigated (Hall *et al.*, 2001; Farid *et al.*, 1989; Kalhori and Ramadhyani, 1985; Sparrow *et al.*, 1981). A good number of numerical solutions of the rate of liquid to solid phase transition during a unidirectional heat transfer involving finite geometries has been presented. One effective method is numerical integration of which the finite difference method is particularly useful (Murray and Landis, 1959; Jaluria and Torrance, 1986). Attempts have been carried out as solved by Neumann (Carlslaw and Jaeger, 1959) employing the Fourier equation in both solid and liquid phases with the established initial and boundary conditions. Previous solutions have involved heat flow with conduction as the sole transport mechanism in both solid and liquid phases disregarding the presence of convection. The inward solidification of a PCM contained in a vertical tube is significantly affected by fluid motion in the liquid melt. In order to provide a better understanding of the phase change process in the C-L acid and its mixtures, computational studies are conducted for comparison with the experimental data.

Although the C-L acid possesses sufficient capacity for thermal energy storage, the assurance that it is a potential phase change material is being held in reservation specifically for the cooling application. Its melting point of 18°C is

considered high for cooling a space unit (Dimaano and Watanabe, 2002). A melting temperature of about 7 to 10°C is required to achieve dehumidification for cool thermal storage. The addition of pentadecane, that has a melting point of 9.9°C and a latent heat of 168 kJ·kg⁻¹, has been proposed (Dimaano and Watanabe, 2002). Discharge experiments showed that supercooling seems evident on the initial phase of the solidification of the 50 vol% C-L acid as demonstrated by the noticeable damp within its melting band. Such activities are caused by the increased non-homogeneity in the solution affected by the impurity contributed by pentadecane in the eutectic mixture of the PCM. More complications are experienced during solidification with higher concentration of pentadecane in the PCM mixture. The lower temperature the mixture gets, the solid C-L becomes richer in composition from which it tends to separate from pentadecane. Pentadecane has the actual higher concentration that is still in the liquid phase while C-L acid proceeds to complete solidification. Pentadecane obviously monopolizes on the behavior yielding a heterogeneous system characteristic to a ternary blend.

The melting of the PCM mixture is a lot simpler compared to solidification since the compound is fairly stable at its melting point and the solid and liquid of the same composition can coexist indicating a congruent mixture. But during solidification, the separation of the components becomes more pronounced. For all mixtures of C-L acid and pentadecane, there is a range of solidification the melting band of which increases with increasing concentration of pentadecane in the mixture. The behavior of the C-L acid and pentadecane mixture upon cooling depends upon the initial composition.

NUMERICAL ANALYSIS

The PCM is placed inside a vertically cylindrical tube with cold water flowing through the annulus. The radial

temperature and density distribution in the PCM tube are assumed to be axisymmetric representing the two-dimensional heat transfer by a one-dimensional model. The analysis takes into account the conduction-based treatment of the solid and liquid phases as well as the natural convection induced by temperature difference in the liquid phase. The following assumptions are made:

- The radial temperature and density distribution in the PCM tube are assumed to be axisymmetric representing the two-dimensional heat transfer by a one-dimensional heat conduction model.
- The direction of heat transfer is only radial.
- The phase change of the PCM is assumed to undergo isothermal phase change.
- There exists at all times a sharply defined line of division indicative of the solidification front between the solid and the liquid.
- The thermophysical properties in terms of the thermal conductivities and densities are different for the solid and liquid phases but remain constant in their corresponding solid and liquid phase domains.
- During phase transition, their values are taken on the average of the solid and liquid phases.
- C-L acid behaves ideally without supercooling and property degradation.

The system involves a non-linear transient heat conduction governed by a time-dependent, one dimensional energy equation inside the cylindrical storage capsule expressed in terms of enthalpy, H , as

$$\rho \cdot \frac{\partial H}{\partial t} = \frac{1}{r} \cdot \left[\frac{\partial}{\partial r} \cdot \left(k \cdot \frac{r}{c_p} \cdot \frac{\partial H}{\partial r} \right) \right] \quad (1)$$

where r is the interface location. The thermophysical properties are based on the prevailing liquid phase, phase transition, and liquid phase of the PCM. Corresponding to

the thermophysical properties in their respective domains, the following simplifications are applied accordingly to a one-dimensional heat conduction approach.

For the liquid phase:

$$\partial H = c_{p-L} \times \partial T \quad (2)$$

For the solid phase:

$$\partial H = c_{p-S} \times \partial T \quad (3)$$

A different treatment is made when phase transition occurs when the sharpest variation in the thermal properties occurs. The effect of natural convection is considered during phase transition using the effective thermal conductivity, k_e , in the liquid layer during phase transition that also includes the downward liquid layer effect over the whole axial length of the vertical PCM containment.

During phase transition, the governing equation is

$$\partial H = L_f \times \partial \alpha \quad (4)$$

The solid layer fraction (α) represents the latent heat (L_f) released during solidification. Phase transition is achieved as soon as the total latent heat of fusion is completed with the solid layer fraction equivalent to 1.0. All the heat rejected by the control volume that experiences phase transition is used for changing the amount of latent heat content of that control volume. Solid fractions are updated from the temperature field.

Geometry and Boundary Conditions

The initial temperature of the PCM is assumed to be uniform throughout the radial positions from the center to the wall. For the solidification process, the initial condition of the radial temperature distribution is

$$T(r,0) = 2.0^\circ\text{C} \quad 0 \leq r \leq R$$

Implicitly, the PCM tube wall does not go through a step change in its temperature. That is

$$T = T_w + (T_w + T_i) \exp(at) \text{ at } r = r_{wall}. \quad (5)$$

The exponential change is considered with the value of “ a ” evaluated from the experimental measurements.

For the center PCM temperature,

$$\frac{\partial T}{\partial r} = 0 \quad \text{at } r = 0.$$

Thermal Physical and Transport Properties

The thermophysical properties of the liquid and solid phases of the PCM are different but are independent of temperature. The viscosity of the liquid mixture of the C-L acid is estimated employing the Grunberg and Nissan method (Reid, *et al.*, 1987). Considering an isothermal wall surface applied to vertical cylinders, the empirical correlation between the *Nusselt* number and the *Rayleigh* number (Farid and Mohammed, 1987; Farid *et al.*, 1989) based on the PCM height and the temperature difference between the PCM surface and its melting point provides a relation to compute for the effective thermal conductivity per unit of cell as

$$k_e = k_L \times 0.28 \times Ra^{0.25} \times \left(\frac{\delta}{L} \right) \quad (6)$$

Numerical Model Discretization

The two dimensional grid regions for the first and second derivatives employing the Taylor Series approach provides the working equation employing the forward time central space (FTCS) explicit method as follows

$$T_{i,j+1} = T_{i-1,j} \times \gamma + T_{i,j} \times \left[1 - \frac{\gamma}{r} \times (\Delta r + 2r) \right] + T_{i+1,j} \times \left[\frac{\gamma}{r} \times (\Delta r + r) \right] \quad (7)$$

where γ is the grid Fourier number obtained from

$$\gamma = \frac{\alpha_e \times \Delta t}{\Delta r^2} \quad (8)$$

The γ is set lesser than 0.1 in order to minimize truncation error and thus maintain convergence and stability (Carnahan, *et al.*, 1969). The time required for the PCM to solidify completely inward was considered. A program employing the Digital Visual Fortran version 6.0 was used to compute for

the radial temperature distribution in the PCM.

HPLC ANALYSIS

In order to obtain information on the extent of homogeneity and effective solidification of the 50:50 C-L: pentadecane (PCM) mixture, HPLC analysis has been conducted during its solidification. Sampling of representative 30 μL of the mixture was made during its consequent solidification on designated points. Sampling points were taken at radial positions of 0, 7.5, and 13.5 mms in different height positions of 25, 100, 200 and 300 mm from the base of the copper tube.

RESULTS AND DISCUSSION

Temperature Distribution in the Solidification Process

The radial temperature distribution during solidification validates the applicability of the numerical model. The concurrency at different height positions between the simulated and the actual temperature profile as depicted in Fig. 1 is still within the agreeable range. The inconsistency in the temperature distribution during phase transition at the outermost radius indicates the normal and actual end effects abruptly experienced by the C-L acid due to its proximity to the heat source. The innermost radius manifests the best agreement in both numerical and experimental solidification results since the conditions governing in this position is considered ideally behaving due to the strength of the governing conduction heat transfer mechanism.

The heat transfer shift from convection to conduction proceeds fast. This is seen in Fig. 2 that signifies the stability controlled by the conduction mode of heat transport over natural convection.

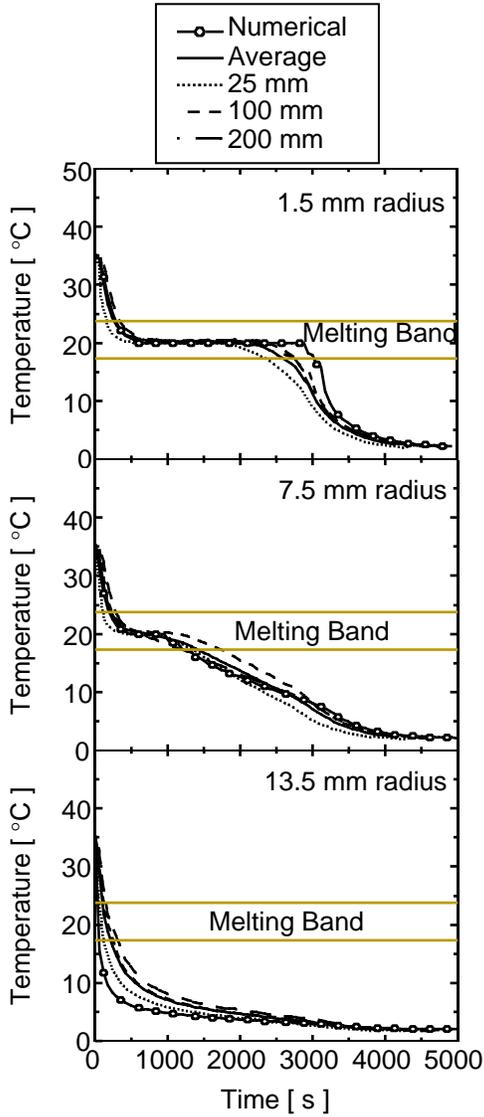


Fig. 1 Comparison of numerical with the experimental temperature history in three radial positions at different heights during melting of the C-L acid with 2.0°C of water temperature.

Consistency in the radial temperature profile at the lowest layer is shown during solidification. An apparent divergence in the numerical and experimental radial temperature distribution as the height is increased during solidification is seen in Fig. 3. The temperature distribution agreement in the 25 mm height position shows an ideal behavior since the lowest layer in reality solidifies faster than the higher layers. The concurrence of the experimental and

numerical results in different radial positions at varying times infers the stable heat transfer controlled by conduction.

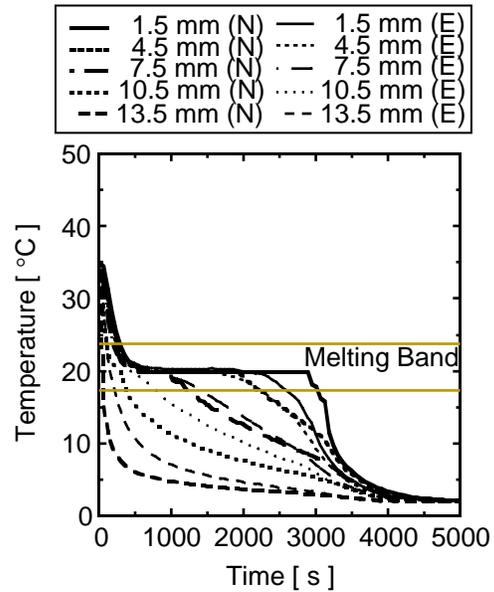


Fig. 2 Comparison of numerical (N) and averaged experimental (E) solidification temperature history of C-L acid at 2°C wall temperature.

Discharge Energy

The numerically estimated discharge energy of C-L acid is likewise in good agreement with the experimental results as presented in Fig. 4. The experiment is also based on the averaged temperature history in all height positions. The amount of heat discharged by the C-L acid obtained from the numerical analysis indicates a favorable energy with lower wall temperature. The greater temperature difference between the PCM melt and the wall temperature corresponds to a more effective conductive mechanism yielding higher discharge energy in the C-L acid.

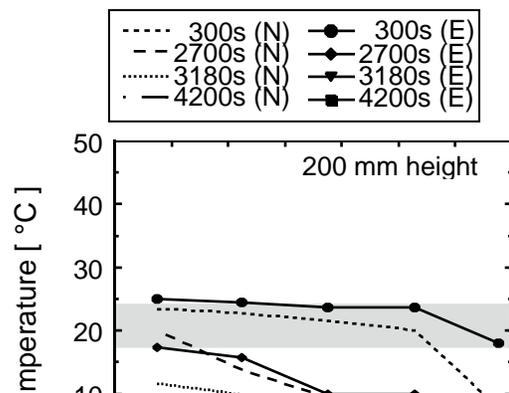


Fig. 3 The radial solidification temperature comparison between numerical (N) and experimental (E) profile of pure C-L acid at different probe height positions with water at 2.0°C.

Solidification Time

Different wall temperatures are assigned to ascertain the effect of temperature to solidification time. Figure 5 shows the increase in solidification time with higher wall temperatures. With smaller temperature difference between the C-L acid solidification and wall temperatures, the heat transfer mechanism becomes unstable and heat conduction weakens. Nevertheless, the numerical and experimental solidification times are still in good agreement further substantiating the applicability of the model.

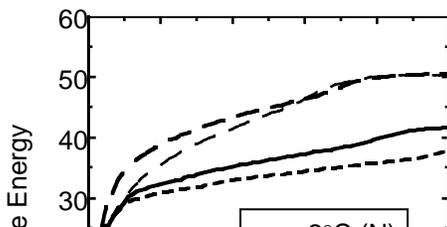


Fig. 4 Discharge energy with different wall temperatures.

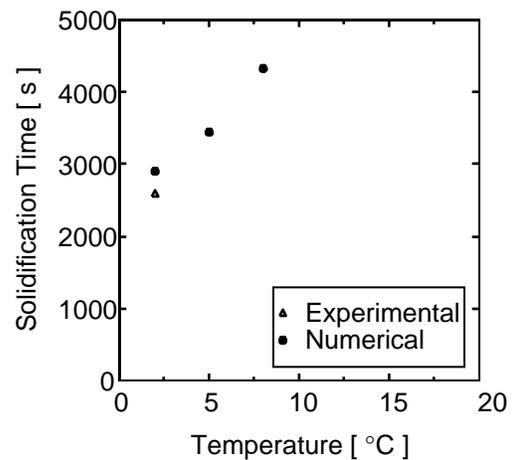


Fig. 5 Effect of temperature on solidification time with different wall temperatures.

Heat Transfer Characteristics

During solidification, the melting temperature difference with the wall has an insignificant effect on the liquid remaining width. It also has a small effect on the effective thermal conductivity. Small difference in the liquid layer at different low wall temperatures indicates the small time for convection to take place prior to solidification. This big difference between melting and solidification distinctly reveals the dominance of natural convection during

melting and the control of conduction during solidification.

The transition from natural convection to conduction of a PCM during phase change experienced in solidification involves a complicated analysis. One way of interpreting the heat transfer mechanism considering temperature distribution in the C-L acid is by means of its Grashof number and Nusselt number. The Grashof number

$$Gr = \frac{g \times \beta \times (T_w - T_{PCM\ melt}) \times L^3}{\nu^2} \quad (9)$$

accounts for the natural convection being developed in the melt layer, with an upflow adjacent to the tube wall and a downflow adjacent to the solidification front. A recirculation pattern normal for natural convection is accelerated by the rates of radial inward and downward melting of the PCM. Since melting proceeds in an unsteady state, a more vivid convection behavior in the PCM is depicted by applying the correlations applicable during the phase transition.

In the solid phase, the main heat transfer mechanism governing is conduction. In a conduction regime, $Ra < 10^3$. Following the natural convection heat transfer correlation for heat transfer from heated vertical plates, the log of Ra equated to 1000 provides a Nu of 3.98 (Holman, 1997). Furthermore, considering that the material is in the solid phase, the maximum boundary layer thickness is taken as one half the radius of the PCM in the capsule. Thus, it may also be expressed as (Kikuchi, *et al.*, 1990)

$$Nu = \frac{D}{\delta_{BL}} = 4 \quad (10)$$

This assumes the condition that the boundary layer thickness is not large compared to the diameter of the PCM capsule. Thus the vertical cylinder, in this case, may be treated as a vertical plate.

During solidification, convection mechanism is analyzed in terms of the equivalent radius (D_{eq}) of the PCM in cylinder treating it as a solid tube as

$$D_{eq} = r_{o,\alpha} \quad (11)$$

and applied in

$$Nu = 0.28 \times (Gr \cdot Pr)^{0.25} \quad (12)$$

The semilog plot of the Gr and Nu during the solid to liquid phase transition of C-L acid with different wall temperatures is presented in Fig. 6. Gr at the start is very large indicating the dominance of natural convection. Nu demonstrates a high value at the start and proceeds to decrease linearly until conduction heat transfer governs.

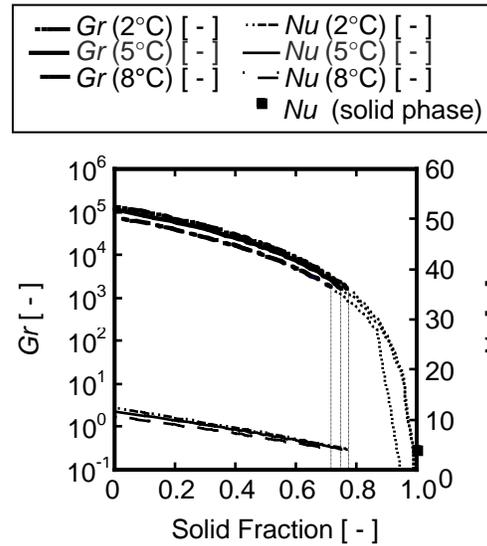


Fig.6 Convective behavior in the solidification phase transition of C-L acid with different wall temperatures.

HPLC Analysis

The results presented in Fig. 7 shows that uniform solidification exists at the lowest layer of the PCM. Since C-L acid has higher temperature in the lower limit of the melting band, it commences to separate out from the mixture and solidifies ahead of pentadecane. As solidification develops, the concentration of the C-L acid increases axially upward. The concentration difference is influenced by the conductive mode of heat transfer in C-L acid.

As C-L acid solid accumulates at the bottom, the pentadecane is left rich in its

liquid form. It is shown in the figure that pentadecane solidifies from the outer region inward at the higher fixed height location while more of C-L acid in the upper layer solidifies first in the inner region. Such concentration difference is strongly influenced by the natural convection governing in each component during phase transition. Natural convection in the remaining liquid-rich phase moves its way up in outward motion.

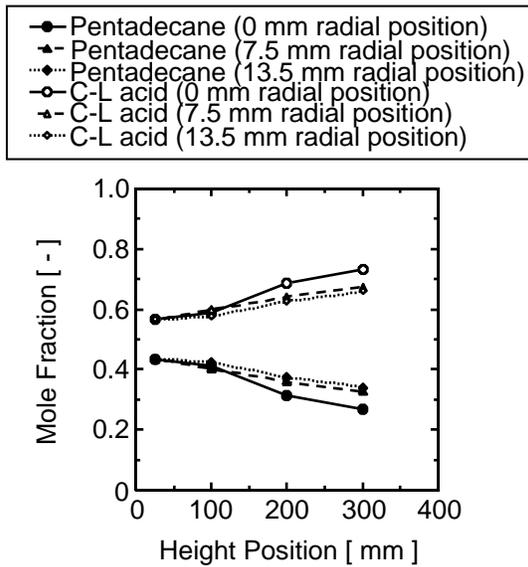


Fig. 7 Composition of component that has solidified in the 50 vol % C-L acid taken during solidification at the designated positions.

CONCLUSION

The experimental results are in good agreement with the numerically simulated solidification of C-L acid. The effect of considering the effective thermal conductivity to account for the natural convection in the heat conduction-based phase change model is validated for the C-L acid mixture on its solidification process.

The 50 vol% of C-L acid in the C-L acid and pentadecane mixture exhibited obvious heterogeneity that is not suitable for thermal energy storage.

NOTATION

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