

Effect of Chemical Additives on the Capric-Lauric Acid Mixture as Phase Change Materials for Cooling Application

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Abstract. The mixture of 65 mol % capric acid and 35 mol % lauric acid (C-L acid) is a potential phase change material (PCM) for thermal energy storage system. However, its melting point of 18.0°C is considered high for cooling application. The effects of organic chemical additives on the properties of the C-L acid have been examined using the available organic chemical additives. The thermophysical and heat transfer characteristics of the C-L acid with some organic additives are investigated. Compatibility of C-L acid combinations with additives in different proportions and their melting characteristics are DSC analyzed. The heat transfer behavior and thermal storage performance of each combination are evaluated. The radial and axial temperature distribution during charging and discharging in each combination are experimentally determined in a vertical storage capsule that is mounted at the center an acrylic cylinder. The thermal performance based on the total amount of transferred energy reveals the effect of the chemical additives to the C-L acid. Methyl salicylate in 0.10 mol fraction in the C-L acid mixture provided the most effective chemical additive.

Keywords: C-L acid; phase change materials; thermal energy storage; chemical additives

Introduction

The cool thermal energy storage provides the cooling capacity by extracting heat from a phase change material (PCM). It can be utilized in various industrial and process applications to reduce operating cost, promote capital cost savings on premium fuels, and cost effectiveness due to energy wastage reduction. Several PCMs had been identified. Most commonly used are the eutectics of inorganic salt hydrates that are considered cheap. However, it still encounters the major drawbacks

on supercooling and incongruity in melting. A study on the mixture of capric acid and lauric acid (C-L acid) indicated its potential as a storage material for latent heat energy storage system. More significantly, they are both coconut oil derived fatty acids that is abundant in the Philippines. However, its melting point of 18°C is considered high for cooling application. A melting temperature of 7 to 10 °C is required for cool energy storage to sustain a comfortable room temperature of 22 to 25°C in an environment with an ambient temperature of 30 to 35°C.

Multiple PCMs and foreign substances added to form composite materials had been proposed (Himeno et al., 1988) to lower the melting temperature and improve the melting characteristics of PCMs. Other investigation (van der Leeden et al., 1993) conducted concerning the effect of additives on nucleation rate and crystal growth have induced the idea of adding organic chemicals to the C-L acid base PCM to obtain the desired melting range for cool energy storage. It is then the objective of this study to determine the compatible organic chemical additives that can lower the melting point of the C-L acid and at the same time maintain a substantial heat of fusion for an adequate cooling capacity.

Materials and Methods

Materials. The C-L acid is composed of 65 mol % capric acid and 35 mol % lauric acid. The chemical additives are chosen based on their thermophysical properties, their solubility in the C-L acid, their safety and economic features. The chemical additives have melting temperatures 8 to 11°C lower than the C-L acid with sufficient heat of fusion value. Carcinogens, flammable, toxic, volatile, hazardous vapor emitting and environmentally degrading additives are eliminated in the selection. Most of the additives with high heats of fusion are discarded due to their halogen contents that cause the ozone depletion. Although the heats of fusion of other organic chemicals are not available in literature, they are considered in the selection to provide information on the characteristic extent of the melting point lowering of the C-L acid. The readily obtained additives were caproic acid, cineole, ethyl benzoate, eugenol, oleic acid, pentadecane, pentanediol, benzaldehyde, methyl salicylate and diethylene glycol. Each PCM mixture individually consisted of the additives with C-L acid as the base system.

DSC analysis. Nine mole fractions (0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40, & 0.50) each of the chemical additives were individually prepared and made homogeneous in the C-L acid system. The thermophysical properties and the melting characteristics of each C-L acid with chemical additive combination were evaluated using a Mettler Toledo DSC821. Each sample weight of 8–15 mg was subjected to a heating rate of 2.5°C/min. A minimum of two thermal cyclic runs was conducted for each PCM sample.

Storage performance test facility. The schematic diagram of the experiment set-up used to evaluate the latent heat storage performance of the PCM mixtures is shown in Fig. 1. A PCM mass of 0.23 kg was placed inside the copper tube. Water served as the heat transfer fluid and flowed continuously from the bottom through the acrylic cylinder. Its temperature was controlled at 35°C during charge (melting)

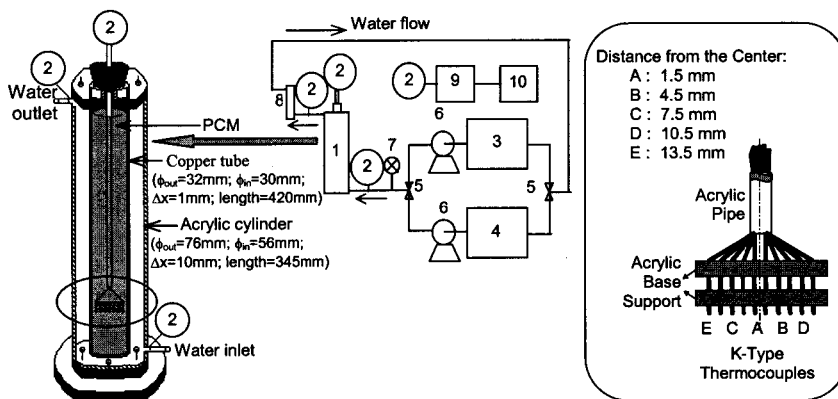


Fig. 1. A schematic diagram of the experimental set-up. Details of (1) storage capsule are indicated. Inset shows the PCM probe fixture. (2)-thermocouple/s; (3)-cooler; (4)-heater; (5)-gate valve; (6)-pump; (7)-water regulator; (8)-rotameter; (9)-datalogger; (10)-computer.

process and at 2.0°C during discharge (solidification) process at a flowrate of $2.51 \times 10^{-5} \text{ m}^3/\text{s}$. The cooler and heater provided the controlled temperature environment of the system. A probe set-up composed of 10 K-type thermocouples as shown in the inset of Fig. 1 was used to monitor the radial temperature distribution in the PCM for every 6 s of time interval. Its height position was varied at 25, 100, 200, and 300 mm from the base of the copper tube.

Results and Discussion

Thermal analysis. The melting behavior of each PCM mixture was characterized by the heat of fusion, the melting temperature, and the melting width of its thermogram obtained from the DSC analysis. The differences in melting behavior of duplicate PCM mixture samples yielded almost identical DSC results. A more consistent decreasing trend followed a linear correlation between the temperature depression and the concentration of the mixture, as shown in Fig. 2, demonstrating

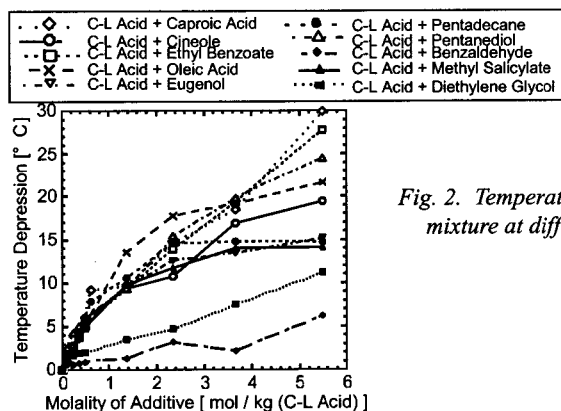


Fig. 2. Temperature depression of the C-L acid mixture at different molalities of chemical additives.

Table 1. Melting band temperature limits of C-L acid and its combination with 0.10 mol fraction of chemical additives obtained from DSC analysis.

Chemical Additive Added to C-L Acid	Melting Peak [°C]	Melting Band [°C]	
		Lower Limit	Upper Limit
—	22.4	17.5	24.0
Methyl Salicylate	18.9	7.6	21.3
Cineole	19.7	7.5	21.5
Eugenol	20.9	8.6	23.8

the colligative property of the PCM mixture in very dilute solutions, except with benzaldehyde and diethylene glycol. A non-linear behavior subsisted as the maximum limit of additive concentration was reached and manifested visibly at higher additive concentrations.

All PCM mixtures showed a consistent trend in their upper melting band temperatures at different concentrations. It manifested the distinctiveness of the C-L acid due to its dominance in the concentration. Fluctuations in the lower melting band temperature of C-L acid with benzaldehyde, diethylene glycol, and pentanediol were observed. Ethyl benzoate demonstrated an obviously low lower melting band temperature limit with a greater melting band width. For applicability in the present investigation, the lower melting band temperature limit of the PCM mixture must not be below 2.5°C. Among the chemical additives, the 0.10 mol fraction of methyl salicylate, cineole, and eugenol provided the least melting band width with higher heats of fusion. Supplementary DSC analysis of 0.10 mol fraction of methyl salicylate, cineole, and eugenol in the C-L acid system provided the relevant melting

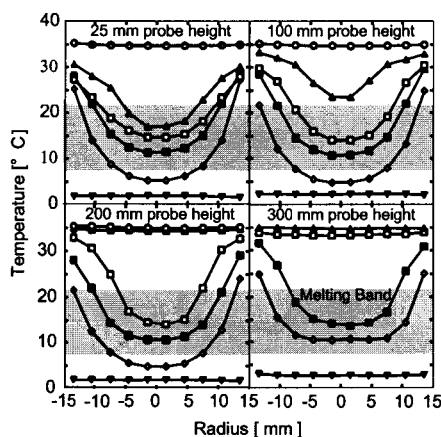


Fig. 3. Radial melting temperature profile at different probe height positions of 0.10 mol fraction of cineole in C-L acid.

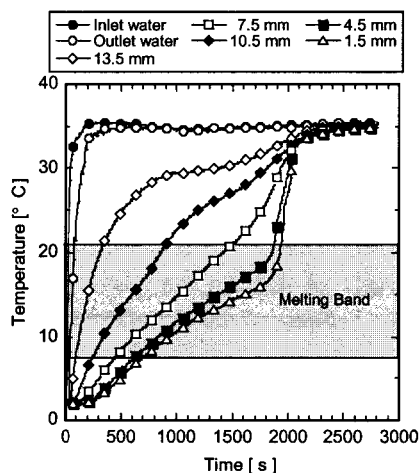


Fig. 4. Temperature history of 0.10 mol fraction of cineole in C-L acid during melting monitored at 100 mm probe height position.

characteristics and are presented in Table 1. A narrow melting band provides a more defined and constant melting temperature during phase transition in the PCM. The C-L acid with methyl salicylate presented the narrowest melting band width. Different lower concentrations of the methyl salicylate in the C-L acid mixture were then subjected to a series of charging and discharge processes. The best concentration of the methyl salicylate was substantiated as evaluated from their effectiveness in the thermal energy storage for cooling application.

Melting behavior of the PCM mixtures. The melting behavior at 0.10 mol fraction of methyl salicylate, cineole, and eugenol was evaluated subjecting each PCM mixture to a series of charge and discharge processes. Representative radial temperature profiles during charging are shown in Fig. 3. The melting band defines the phase transition region evaluated from the DSC analysis. Below the melting band is the solid phase and above the melting band is the liquid phase. Immediate melting is observed on the outermost radius while slow melting proceeded in the inner radii. Temperature gradients distinctly occurred during melting within the melting band. Complete melting is indicated by the radial temperature distribution finally levelling off on the liquid phase region. The flattening of the radial temperature distribution were relatively faster at higher height positions. The characteristic feature of the PCM blend is manifested in the melting temperature history as represented in Fig. 4. The phase transition in the PCM mixture does not occur isothermally but over a certain range of temperature within its melting band. On the other hand, solidification proceeds radially inward. The melting peak of the PCM mixture is clearly manifested during solidification as indicated by the flattening of the radial temperatures within the melting band.

Thermal storage performance of the PCM mixtures. The thermal energies of each PCM mixture were estimated from its radial temperature distribution at different height positions. The latent heat energy storage used some sensible heat

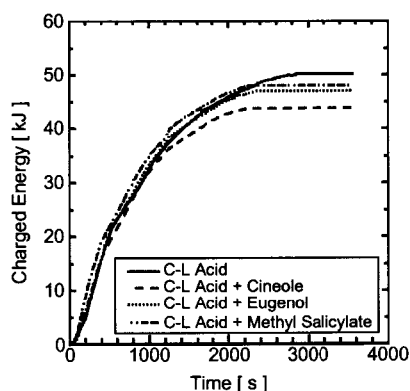


Fig. 5. Total heat charged during melting of the indicated 0.10 mol fraction of chemical additives in C-L acid.

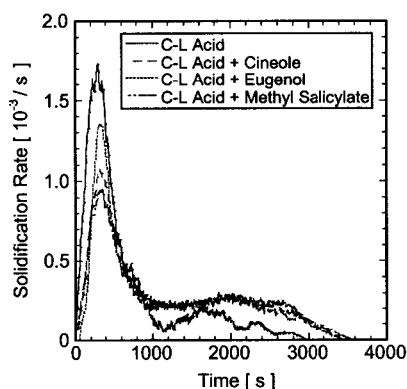


Fig. 6. Solidification rates of the indicated 0.10 mol fraction of chemical additives in the C-L acid.

storage below and above the PCM mixture melting temperatures, in addition to the sensible and latent heats drawn from its large melting band during phase transition. These were estimated from the relation,

$$dQ = 2\pi \rho_s c_{ps} l r dr \int_{T_s}^{T_m} dT + 2\pi \rho_{ave} c_{p_{ave}} l r dr \int_{T_m}^{T_h} dT + 2\pi \rho_{ave} L l \alpha r dr + 2\pi \rho_L c_{p_L} l r dr \int_{T_h}^{T_f} dT, \quad (1)$$

accounting the stepwise changes during the entire charging/discharging process and considering the melt/solid fraction (α) that developed as the PCM mixture gave up its heat of fusion. The total thermal energies were estimated throughout the process by integrating eqn (1) over the PCM radius as

$$Q = \int_0^R dQ \quad (2)$$

The thermal storage performance based on the total amount of heat stored during the PCM charging is shown in Fig. 5. The upper melting band temperature limit affected the liquid sensible heat yield of the PCM mixtures during melting. The lower melting band temperature affected the sensible heats generated from phase transition up to complete solidification. From these results, individual lower concentrations of methyl salicylate in the C-L acid were subjected to the same storage performance test. Their transferred energies showed negligible differences.

Melting and solidification rates. A thermal energy load that is accomplished fast and delivered at a longer time period gauges the efficiency of a storage system for industrial and residential applications. The melting rates determined for all PCM mixtures consistently exhibited multiple peaks indicating the complications that existed because of simultaneous convection and conduction during the entire melting process. On the other hand, the solidification rate was more stable as shown by the dominant single peaks in Fig. 6. It demonstrated the regular formation of solid layers over the whole length of the PCM tube due to a more defined heat transfer that started with natural convection and finally completed by conduction.

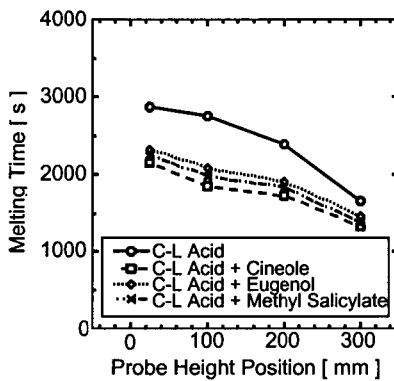


Fig. 7. Melting time of the PCM mixtures at different axial positions.

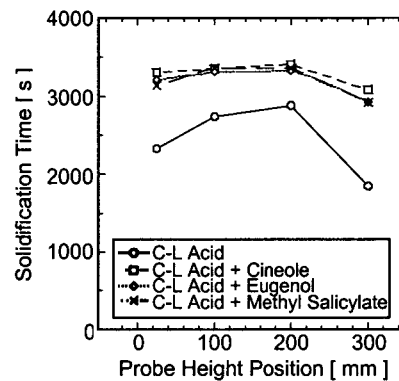


Fig. 8. Solidification time of the PCM mixtures at different axial positions.

The results depicted in Fig. 7 showed the improvement of the C-L acid in terms of higher latent heat with lower melting point and lesser melting time expended during the PCM charging. A shorter solidification time as shown in Fig. 8 was observed with just C-L acid compared with the three PCM mixtures. Such behavior emphasized the ternary blend composition of the PCM mixture.

Conclusion

The C-L acid with methyl salicylate manifested the favorable heat transfer characteristics based on the shorter charge and discharge rates corresponding to a narrower melting band width and a higher heat of fusion value. This ensures an improvement in the melting characteristic of the C-L acid system for the cooling application of thermal energy storage.

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