

THERMAL PROPERTIES OF BEESWAX/CuO NANO PHASE-CHANGE MATERIAL USED FOR THERMAL ENERGY STORAGE

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ABSTRACT

Experimentation on and implementation of phase-change materials for thermal storage is attracting increasing attention by those seeking a potential resolution to energy issues. This study investigates beeswax as a high thermal-capacity phase-change material with the objective of analyzing the thermal properties and behaviors of beeswax/CuO nano-PCM. The study uses differential scanning calorimetry apparatus to measure the melting temperature and thermal capacity of nano-PCMs. The study found nano-PCM melting temperatures of 63.62°C, 63.59°C, 63.66°C, 63.19°C, and 62.45°C at 0.05, 0.1, 0.15, 0.2, and 0.25 wt%, respectively. FTIR testing found no chemical reaction between CuO and beeswax. The existence of CuO nanoparticles enhanced thermal conductivity of beeswax but reduced its heat capacity. However, the change in latent heat caused no significant effects in the performance of beeswax/CuO. Thus, the results showed that heat transfer of composite beeswax/CuO melts faster than base phase-change material.

Keywords: Beeswax/CuO; Nano particles; Thermal storage; Latent heat; Thermal conductivity

1. INTRODUCTION

The consumers of electricity are residential buildings (Busch, 1992), especially during peak load. Electricity consumption in buildings is very wasteful, necessitating innovations in energy reserves—thermal energy in the form of latent heat—to reduce electricity consumption. This thermal energy can be stored in particular materials, called heat storage materials or phase-change materials (PCMs), which have a certain mass and are subject to changing phases from solid to liquid or vice versa. The advantages of PCMs are that they are capable of storing large amounts of heat in small volumes, and the absorption and release of energy occurs at an almost constant temperature (Sharma et al., 2009).

Four groups of PCM materials are frequently used in PCM research: organics, inorganics, fatty acids, and commercial PCMs (Abhat, 1983; Sharma et al., 2009; Zalba et al., 2003). Organics are the most popular PCMs. Paraffin is an organic PCM that comes from many sources, including plants, animals, minerals, and petroleum. Paraffin derived from coconuts is called palm wax. An example of paraffin derived from animals is beeswax, which is manufactured in hives by bees. This study used beeswax as a core material.

Beeswax is in the category of organic PCMs and consists of esters of fatty acids and long-chain

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alcohols. The empirical formula for beeswax is $C_{15}H_{31}COOC_{30}H_{61}$, which consists of palmitate, palmit oleate, hydroxyl palmitate, and oleate esters of long-chain aliphatic alcohols. Beeswax comes in two types: yellow and white. Yellow beeswax may be light brown in addition to yellow. It has a solid phase but is rather brittle when cold and smells distinctly like honey. White beeswax has a solid phase, is a thin white layer or a yellowish, translucent layer, and smells slightly like honey. Beeswax is not soluble in water but is slightly soluble in alcohol and very soluble in chloroform, ether, or volatile oil. Beeswax has been shown to have melting points of 61.8°C (Ramnanan-Singh, 2012; Su et al., 2015), 64.4°C (Knuutinen & Norrman, 2000), $62\text{--}65^{\circ}\text{C}$ and $60\text{--}67^{\circ}\text{C}$ (Kuznesof, 2005), and $61\text{--}67^{\circ}\text{C}$ (Tulloch & Hoffman, 1972), as well as latent heat of 122 kJ/kg (Knuutinen & Norrman, 2000) and 177 kJ/kg (Su et al., 2015) and densities of 970 kg/m^3 (Ramnanan-Singh, 2012) and 950 kg/m^3 (Su et al., 2015).

The weakness of PCM material is that it has low thermal conductivity (Sari & Karaipekli, 2007). One way to improve the thermal conductivity of a PCM material is by adding nanoparticles, which have a high thermal conductivity (Harikrishnan & Kalaiselvam, 2012). When nanoparticles are distributed throughout a PCM, they increase its thermal conductivity, resulting in a decrease of latent heat. Adding and deleting nanoparticles can increase or decrease thermal conductivity (Harikrishnan et al., 2013; Yu et al., 2013). An important parameter for improving the heat transfer of PCMs is the size and shape of these added nanoparticles (Özerinç et al., 2010). CuO is a nanoparticle that has high thermal conductivity (Taufik et al., 2015).

Many nanoparticle studies have added CuO to PCM materials. Harikrishnan and Kalaiselvam (2012) added CuO to PCM materials, obtaining results showing that the more CuO that is added to oleic acid, the more its thermal conductivity is increased. Karunamurthy et al. (2012) added CuO nanoparticles to paraffin (N-docosane) in various concentrations, resulting in increased thermal conductivity of the paraffin. Wu et al. (2010) also added Cu nanoparticles to accelerate thermal conductivity of paraffin. PCM material has a stable thermal cycle during repeated heating and cooling up to 100 cycles. Kibria et al. (2015) conducted a review of the properties of PCM material during the addition of nanoparticles. Other researcher who have added CuO to PCM materials include Wu et al. (2010).

The present study analyzed the heat transfer performance of beeswax/CuO nano-PCM. CuO nanoparticle with various mass fractions were added to beeswax. The study tested material compability using FTIR test. In addition, the study analyzed thermal properties of sample including latent heat, thermal capacity, and thermal conductivity.

2. MATERIALS AND METHOD

2.1. Materials

This study used beeswax (see Figure 1) as its PCM material, along with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NaOH. Deionized water was used to make CuO by the sol-gel method (Hong et al., 2008; Taufik et al., 2015).

2.1.1. Preparation of nanoparticles

CuO nanoparticles were synthesized by the sol-gel method (Hong et al., 2008; Taufik et al., 2015). First, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 100 ml of deionizer water. The solution was stirred under constant speed by magnetic stirring. Then, 0.05 mol of NaOH in 150 ml of deionizer water was dropped into the solution until the pH value increased to 12. Then, the solution was maintained at 80°C under stirring for 3 hours to form a gel. Finally, the gel was dried at 80°C for 4 hours and annealed at 125°C for 8 hours. The outcome was powdered CuO with 14–100 nano meters.



Figure 1 Beeswax

2.1.2. Preparation of nano-PCM

Nano-PCM with 0.05, 0.1, 0.15, and 0.25 wt% was synthesized using the ultrasonic method. The careful mixing of nanoparticles into the PCM is important to enhancing the thermal characteristics of the PCM. An ultrasonic vibrator was used to minimize the possibility of agglomeration of the nano-PCM (Ibrahim & Sreekantan, 2011; Zeng et al., 2006).

Table 1 Mass ratio of beeswax and nanoparticles

Mass Ratio	Beeswax (g)	CuO (g)
0.05	30	0.0974
0.10	30	0.1950
0.15	30	0.2920
0.20	30	0.3900
0.25	30	0.4890

Solid beeswax was prepared by shaving it. The sample was melted at 66°C for 30 min. Then, nanoparticles were added to the melted sample based on the calculation of mass ratio presented in Table 1. The resulting solution of beeswax and CuO was mixed for 5 min before being put into a sonicator with 40 kHz frequency at 66°C to keep the sample a liquid. Vibration by sonicator was continued for 2 h, until the nanoparticles were completely dispersed throughout the beeswax. When this was accomplished, the beeswax turned black.

2.1.3. Preparation of nanoparticles

The characterization of the nano-PCM was investigated by transmission electron microscopy (TEM), x-ray diffraction analysis, and FT-IR spectrometer analysis. TEM was used to investigate the size of the synthesized CuO nanoparticles under 20, 40, 60, 80, 100, and 120 kV. X-ray diffraction analysis was performed to identify the crystal size of the CuO nanoparticles. The FT-IR spectrometer was used to characterize the chemical compatibility of the CuO and the base fluid beeswax.

The study performed differential scanning calorimetry (DSC) to determine the latent heat and the heat capacity of the samples. Nitrogen at a flow rate of 20 ml/min was used as a cooling medium. The samples were tested using a 10°C/min scan rate. Four grams of sample was kept under the aluminum DSC pan. DSC software was used to numerically integrate the peak to

determine the melting temperature and latent heat. The heat capacity was calculated based on a graphic created by the DSC software.

Figure 2 shows the measurement of the thermal conductivity of the beeswax/CuO nano-PCM with the OSK 4565-A thermal conductivity measuring apparatus. The measurement was repeated 3 times to ensure accuracy. The samples were formed into cylindrical shapes using a cylindrical mold. Then, the melted samples were poured into molds. After a sample had solidified completely, it was removed from the mold. There were 2 samples, each with a different thickness: 2 mm and 4 mm. Each sample was put into the sample holder of the thermal conductivity measuring apparatus. A polyurethane thermal insulation was used to prevent heat loss. The cooling medium was water at 28°C. The temperature data was recorded using the National Instrument Data Acquisition System, model 9111 to automatically capture data, which was then recorded using LabVIEW 8.5 software. Temperature measurements were made using chromel (Nickel-Chromium) and alumel (Nickel-Aluminum) K-type thermocouples with a diameter of 0.05 mm.

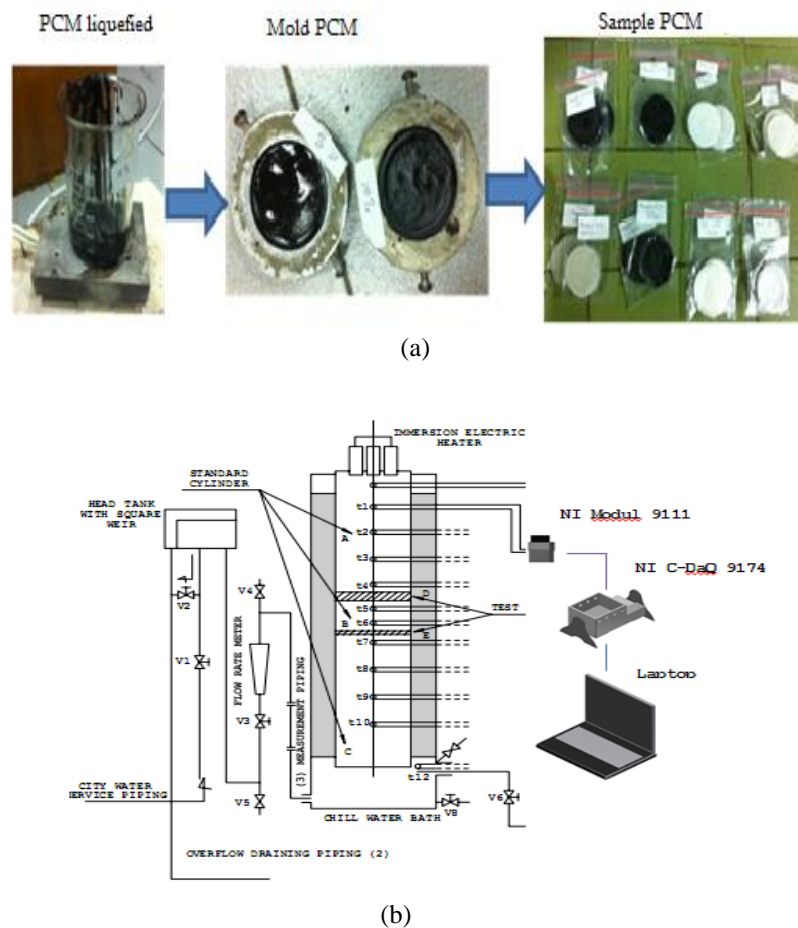


Figure 2 (a) Manufacture of PCM samples for thermal conductivity investigation; (b) Schematic of Ogawa Seiki Thermal Conductivity Measurement Apparatus

3. RESULTS AND DISCUSSION

3.1. Beeswax Properties

Figure 3 shows values of the properties of beeswax obtained from DSC measurements, which show that the beeswax had a melting point of 64.22°C and latent heat of 395.2945 kJ/kg.

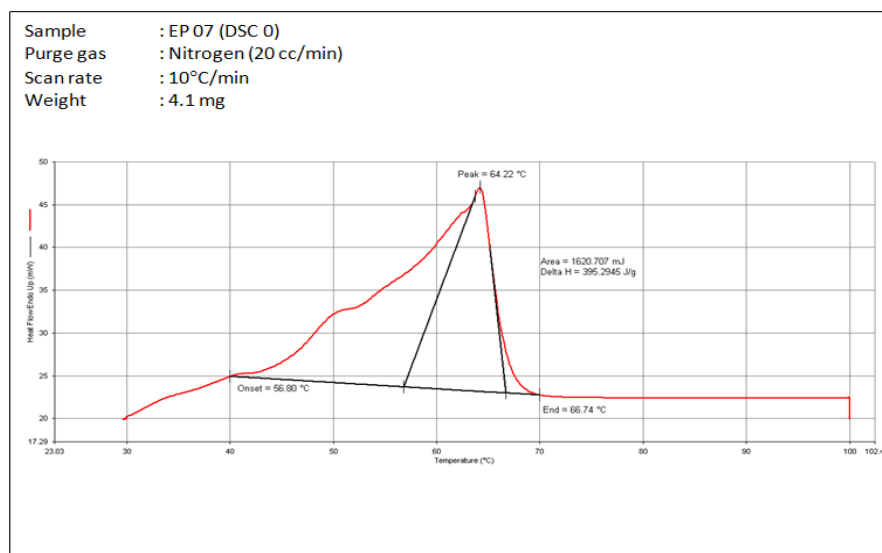


Figure 3 Results of beeswax measurement using DSC

Table 2 compares the properties of beeswax to those found by some other studies.

Table 2 Comparison of beeswax properties to those in other studies

Properties	Beeswax	References
Melting Temperature (°C)	64.22	61.8 (Ramnanan-Singh, 2012; Su et al., 2015), 64.4 (Knuutinen & Norrman, 2000), 62–65; 60–67 (Kuznesof, 2005), 61–67 (Tulloch & Hoffman, 1972)
Latent Heat (kJ kg ⁻¹)	395.29	122 (Knuutinen & Norrman, 2000), 177 (Su et al., 2015)
Density (kg m ⁻³)		
- Melting	789.47	970 (Ramnanan-Singh, 2012),
- Solidification	819.75	950 (Su et al., 2015)

3.2. Characterization of Nano Phase-change Material

The dispersion of nanoparticle throughout the PCM was uniform. As Figure 4 shows, based on the FT-IR spectrum graph, no new peak was found. The FT-IR spectrum graph indicated that there was no chemical reaction from the mixing of these materials. There was only a physical interaction between the beeswax and the CuO nanoparticles, as the graph shows.

3.3. Thermal Conductivity of Beeswax/CuO

The heat transfer occasioned by the melting and solidification of PCM depends on its thermal conductivity. Enhancement of thermal conductivity significantly changed the efficiency of the PCM. Adding CuO nanoparticles to the PCM reduced the release times in the material's phase-change process. Figure 5 shows the results of the thermal conductivity measurements with respect to the mass fraction of the nanoparticles. As the mass fraction increased, the thermal conductivity of the nano-PCM also increased, indicating that thermal conductivity enhancement was directly proportional to the mass fraction of the nano-PCM. However, if addition of nanoparticles increased enough, thermal conductivity enhancement could not be expected to be linear due to the agglomeration of the nanoparticles. Thermal conductivity enhancement of the beeswax/CuO was reached by 0.53, 1.55, 1.91, 1.97, and 2.07 W/mK for 0.05, 0.1, 0.15, 0.2, and 0.25 wt% of nano-PCM, respectively.

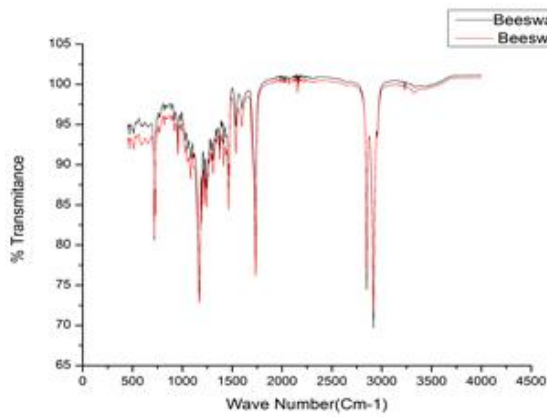


Figure 4 FT-IR spectra of beeswax/CuO and beeswax

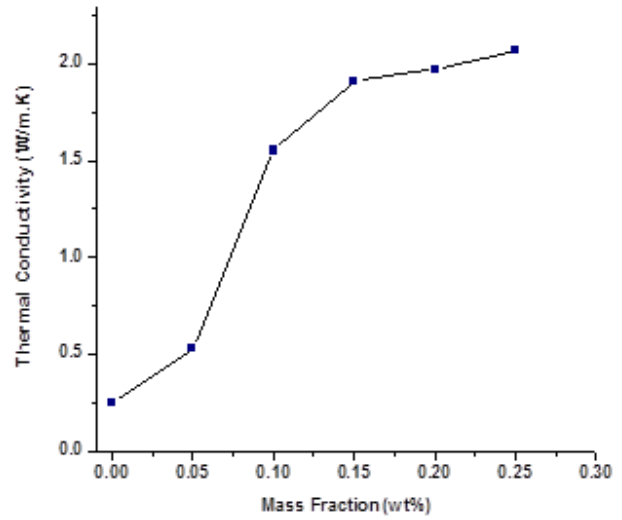


Figure 5 Effect of nanoparticles on thermal conductivity of nano-PCM

Enhancement of thermal conductivity was strongly related to the heat transfer rate and the melting rate of the nano-PCM. Figure 6 shows the effect of the nanoparticles on melting rates. As thermal conductivity increased, the melting point of the material decreased. The addition of CuO nanoparticles to a fluid can increase its thermal conductivity and enhancement its heat transfer (Arasu et al., 2012; Vanaki et al., 2016). As seen in Figure 6, the melting temperature of the nano-PCM slowly decreased. It can be said that enhancing the thermal conductivity decreases the melting time of nano-PCM.

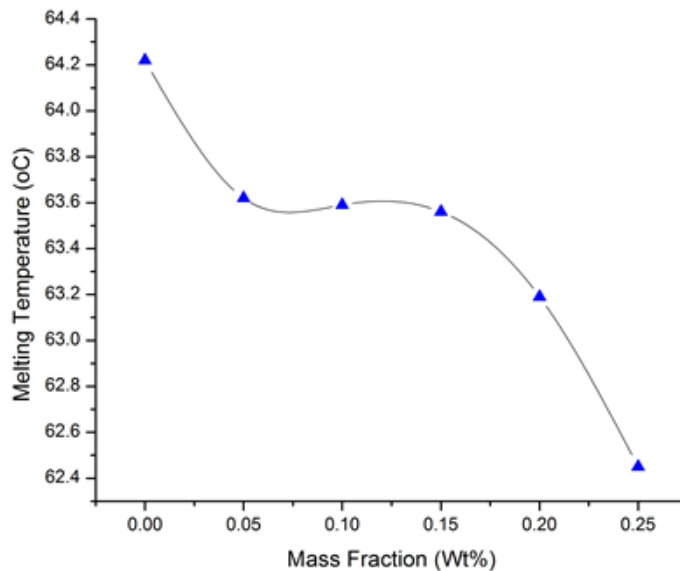


Figure 6 Effect of nanoparticles on melting temperature of nano-PCM

Table 3 shows the effect of additional CuO nanoparticles on thermal conductivity and melting temperature.

Table 3 The effect of additional CuO nanoparticles on thermal conductivity and melting temperature

Mass Ratio	CuO (g)	Thermal Conductivity (W/mK)	Melting Temperature (°C)
0	0	0.25	64.22
0.05	0.0974	0.53	63.62
0.10	0.1950	1.55	63.59
0.15	0.2920	1.91	63.66
0.20	0.3900	1.97	63.19
0.25	0.4890	2.07	62.45

3.4. Latent Heat of Beeswax/CuO

DSC measurement was used to investigate the latent heat and heat capacity of beeswax/CuO nanoparticle PCM with various mass fractions. Figure 7 shows the effect of additional CuO nanoparticles on latent heat reduction. It can be seen that adding CuO nanoparticles impaired the latent heat of beeswax. Accordingly, Arasu et al. (2012) investigated the reduction in latent heat caused by the friction factor between the nanoparticles and the fluid when PCM was melted. The addition of CuO nanoparticles also reduced the stability of nano-PCM due to agglomeration and sedimentation. Therefore, selecting the appropriate nanoparticle material and concentration is very important, with the aim being to enhance the heat transfer capability of the PCM during the process of either melting or solidification.

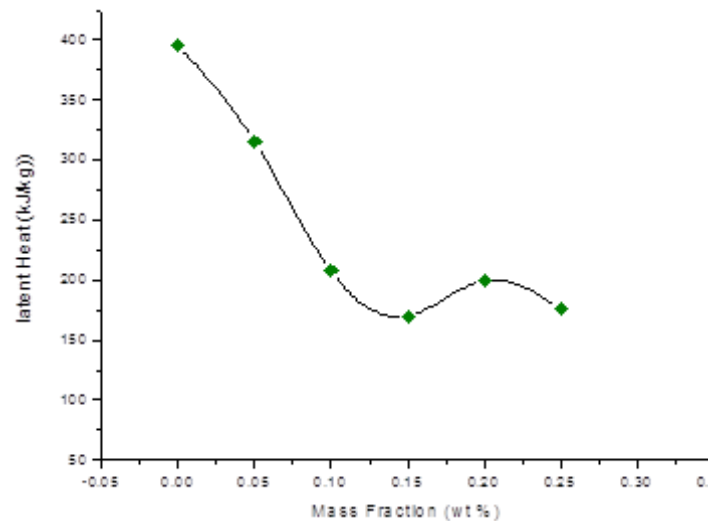


Figure 7 Effect of adding CuO nanoparticles on latent heat reduction of nano-PCM

As latent heat was reduced, the heat capacity of the nano-PCM also decreased, as seen in Figure 8. The heat capacity of the nano-PCM was calculated based on the DSC heat-flow curve. The heat capacity of the nano-PCM was reduced by 2.04, 1.69, 1.123, 1.12, 1.033, and 0.87 kJ/kg°C for 0, 0.05, 0.1, 0.15, 0.2, and 0.25 wt% of nanoparticles, respectively.

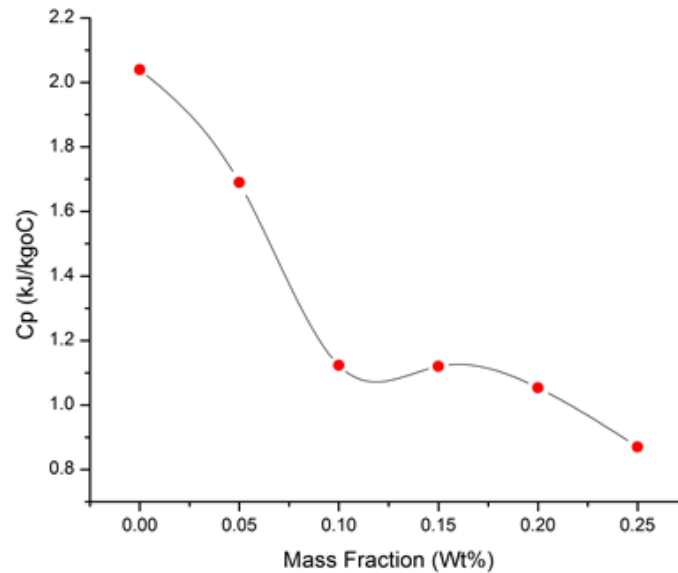


Figure 8 Effect of nano-PCM on heat capacity

Table 4 shows the effect of adding nanoparticle CuO on latent heat and heat capacity. Dispersing CuO nanoparticles throughout beeswax significantly changed the thermal properties of the nano-PCM. Adding nanoparticles to the nano-PCM increased its thermal conductivity but reduced its latent heat and heat capacity. Past research on paraffin has found similar result (Wu et al., 2010).

Table 4 The effect of adding nanoparticle CuO on latent heat and heat capacity

Mass Ratio	CuO (g)	Latent Heat (kJ/kg)	Heat Capacity (kJ/kg°C)
0	0	395.29	2.040
0.05	0.0974	315.12	1.690
0.10	0.1950	207.43	1.123
0.15	0.2920	170.07	1.120
0.20	0.3900	199.67	1.033
0.25	0.4890	176.49	0.870

4. CONCLUSION

This study analyzed beeswax/CuO with various mass fractions of nanoparticles to study the thermal properties of nano-PCM for low temperature application. The study found no chemical reaction of nano-PCM to prove the compatibility of CuO and beeswax. Adding nanoparticles increased the thermal conductivity of the nano-PCM but reduced its latent heat and heat capacity.

5. ACKNOWLEDGMENT

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