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Thermal Stability of Paraffin Wax as Phase Change Material in Latent Heat Storage Unit

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Abstract

Successful utilization of the latent heat energy storage unit depends considerably on the thermal reliability and stability of the phase change materials (PCMs) used. Insufficiently long term use of PCMs is due to poor stability of the materi-al properties. Thus, thermal stability of paraffin wax (melting point 58-60oC) as a phase change material (PCM) in la-tent heat storage unit is established. Thermal stability of PCM is determined by measuring its latent heat storage capac-ity and phase transition temperature using differential scanning calorimeter (DSC). The changes in melting temperature and latent heat of fusion for paraffin wax are measured after every 50 cycles for a total of 600 thermal cycles. This is equivalent to two years of utility period of the PCM. Present experimental results illustrate small change in melting point and latent heat of fusion of paraffin wax even after 600 cycles of operations. This experimental study establishes the reliability of paraffin wax as phase change material in latent heat storage units for solar thermal systems.

Keywords: Phase Change Material; Paraffin Wax; Thermal Stability; Differential Scanning Calorimeter

1. Introduction

Successful application of intermittent sources of energy like solar energy depends to a large extent on the method of energy storage. Storage of energy in suitable form is a challenge to technologists. Energy storage not only provides bridge between energy supply and demand but also improves the performance and reliability of the system. The storage of thermal energy in the form of latent heat of phase change material (PCM) is an attractive option. This is because of higher storage density of such systems, small temperature variation between storage and retrieval and smaller storage requirement compared to that of sensible energy storage units [1-4].

Selection of suitable PCM plays an important role for the development of a latent heat storage unit. Number of PCMs has been developed in the last decade. These include paraffin wax, salt hydrates, fatty acid and eutectic mixtures [5-7]. The feasibility of using phase change material in any energy storage system depends on the desirable thermo-physical, kinetic, and chemical properties of the PCM in addition to its cost. Each class of PCM has its own characteristics, applications, advantages, and limitations [8]. The economic feasibility of employing a PCM in a system depends on the life and cost of the storage material. Hence in order to ensure long term performance and economic feasibility of latent heat storage systems, the stability of PCMs should be checked before using it to an actual application. The stability of a phase change material can be established by subjecting the PCM to a number of thermal cycles of operation and by measuring their thermal properties after these operations. A large degradation in terms of thermo-physical properties with time is not desirable for any PCM. The thermal properties measured in general include the latent heat storage capacity and phase transition temperature of the PCM.

A solar thermal system with latent heat storage undergoes at least one melt/freeze thermal cycle a day, and can be called as normal cycle. Thermal cycle tests can be carried out in the laboratory in a constant temperature oven or using electric hot plate with temperature controller. Such thermal cycle tests conducted in the laboratory under controlled conditions, are called the accelerated thermal cycle test [9].

2. Literature review on thermal stability of various PCMs

Thermal stability analysis of different groups of PCMs i.e. fatty acid, salt hydrate and paraffin wax has been reported in literature. Abhat and Malatidis [9] determined the latent heat for palmitic and lauric acid after a short-term thermal period of 120 thermal cycles. They observed small amount of supercooling during the freezing of fatty acids. Hasan and Sayigh [10] investigated myristic acid, palmitic acid and stearic acid for a domestic water heating system. They concluded that these PCMs lose up to 10% of storage capacity (heat of fusion) after 450 thermal cycles (i.e. approx. 1 year). Sari and Kaygusuz [11] studied thermal stabilities of industrial-grade (90–95 % purity) fatty acids like stearic acid, palmitic acid, myristic acid and lauric acid. They determined latent heat storage capacity and phase transition temperature of the PCMs after 910 repeated thermal cycles. They concluded that the palmitic acids and myristic acids may be considered as suitable PCMs in long-term solar thermal applications. Sarı et al. [12] carried out thermal stability test of lauric acid–stearic acid, myristic acid–palmitic acid and palmitic acid–stearic acid eutectic mixtures for 360 repeated melt/freeze cycles. Shilei et al. [13] conducted 360 accelerated thermal cycles to study the change in latent heat of fusion and melting temperature of phase change wallboards combined with the eutectic mixtures of capric acid–lauric acid. No regular degradation was found for 360 repeated thermal cycles.

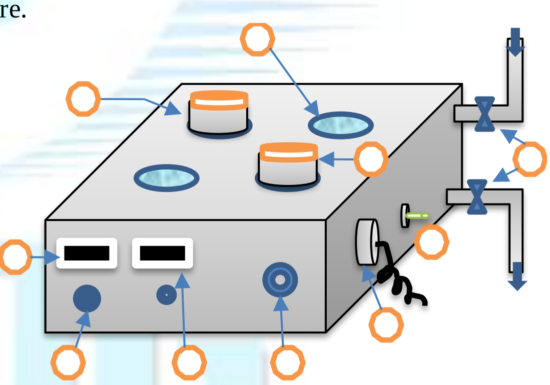
Wada et al. [14] investigated the decreasing heat storage capacity of sodium acetate trihydrate ($CH_3CO_2Na{\bullet}3H_2O$) for 500 thermal cycles. They concluded that heat storage capacity of technical grade sample decreases relatively slowly compared to that of guaranteed grade sample. Tyagi et al. [15] noticed that the $CaCl_2{\bullet}6H_2O$ melted between stable ranges of temperature and had shown small variations in the latent heat of fusion after 1000 accelerated thermal cycles.

Hadjieva et al. [16] considered three selected paraffins to study change in thermo-physical properties after 900 thermal cycles. They concluded that there was no noticeable degradation in the structure of paraffins tested on thermal cycling. Sharma et al. [17] analyzed the change in latent heat of fusion, melting temperature and specific heat of commercial-grade paraffin wax, stearic acid and acetamide by DSC techniques. The given paraffin wax was found to be more stable phase change materials (PCMs) after 300 repeated thermal cycles.

Phase change materials which can be used for low temperature solar thermal applications like water heating, baking and drying should have melting temperature in the range of 45ºC and 90ºC [9]. Paraffins can be used for such thermal energy storage because they are available at reasonable cost with moderate latent heat storage density and melting temperatures in this range. It also shows negligible supercooling, lower vapor pressure in melt. They are also chemically inert and stable [2, 7]. The objective of the present study is to determine the change in melting temperature and latent heat of fusion of paraffin wax after every 50 thermal cycle of operation for a total of 600 thermal cycles. The thermal properties are measured using differential scanning calorimeter (DSC).

3. Experimental setup

In order to carry out melt/freeze cycles of paraffin, a laboratory type constant temperature water bath is used as shown in figure 1. The PCM container is hermetically sealed and made of stainless steel of internal diameter 9 cm and height 8 cm. The container is filled with 200 g of PCM. When the system is 'ON', initially the heater heats the water to a prescribed temperature level. The PCM filled in the container melts completely due to hot water in the water bath. One can say that charging of the PCM is completed. The inside temperature of a bath is controlled by Selec make DTC 303NX temperature controller having PID control with auto tuning. The relay is 'ON' up to the set temperature and cuts 'OFF' above the set temperature.



(1) Main supply (2) Thermal cycle counter (3) Heater switch (4) Temperature indicator (5) PCM container (2 nos.) (6) Water (7) Solenoid valve (8) Thermocouple (9) Heater

Figure 1. Schematic of tailor made constant temperature water bath

Afterwards, with the use of hot water solenoid valve, the hot water is drained. When the water level reaches at a certain level, immediately hot water solenoid valve is closed and cold water solenoid valve is opened. The water bath is again filled with cold water up to a prescribed level. Heat is exchanged from PCM to cold water and water gets heated. A hot water solenoid valve is opened again to discharge the hot water. This process is continued till the water temperature in the bath reaches at ambient temperature. Meanwhile, the PCM temperature decreases and it starts to solidify. When the temperature of water reaches at ambient temperature, the PCM is also converted into solid. Thus, the discharging of the PCM is completed. Now, one thermal cycle is completed. Now, heater goes ON immediately and heats the water again for charging of the PCM. The cycle is now continued till PCM is discharged again. In this manner, number of thermal cycles is performed. About 1.5-2 h is required for one thermal cycle.

The container is filled with the 200 gm of paraffin wax which is procured from S.D. Fine Chemicals Ltd., India. The quoted melting temperature of paraffin wax was in the range of 58-60°C. About 2-3 g material sample is withdrawn after each 50th cycle for its DSC test.

4. Differential scanning calorimeter (DSC) analysis

Before starting the thermal cycle, a DSC analysis is carried out for the paraffin. DSC is used to obtain melting temperature and latent heat of fusion of paraffin wax. The DSC module, used here is Jade DSC manufactured by PerkinElmer Inc., USA. It is based on Perkin-Elmer's heat flux design. The Jade DSC is controlled by PyrisTM software. The DSC is tested using standard reference material, alumina (Al_2O_3), provided by the manufacturer of the DSC. In DSC, sample and reference materials are heated at a constant rate. The temperature difference between them is proportional to the difference in heat flow between the two materials. The variation of heat flow and temperature is drawn which is also called the DSC curve. Latent heat of fusion is calculated using the area under the peak. The phase transition temperature is taken as the onset obtained by line fitting of the rising part of the peak as shown in figures 2-5. The phase transition range is taken between onset temperature and the peak of the curve.

5. Results and Discussion

After every 50th thermal cycle, 2-3 grams of paraffin sample is taken out for DSC test. DSC curves indicate the phase transition temperature range and latent heat of fusion of paraffin wax. DSC curves for paraffin wax are shown in figures 2-5 for the 0th, 50th, 300th, and 600th thermal cycles respectively. In order to analyze the change in latent heat of fusion and phase transition temperature, a relative percentage difference is obtained after every 50th thermal cycles. The relative percentage difference (RPD) between any property i of the PCM at any number of cycles n and the 0th cycle may be defined as [18]:

$$RPD = \frac{X_{n,i} - X_{0,i}}{X_{0,i}} \times 100(\%) \qquad (1)$$

where $X_{n,i}$ denotes to the values of onset and peak temperatures and the latent heat of the PCM after n cycles and $X_{0,i}$ are the values of these quantities at 0th cycle.

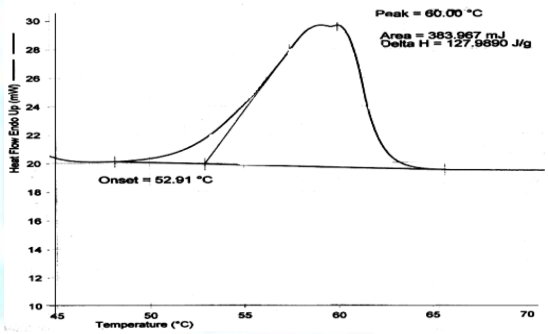


Figure 2. DSC measurement of the latent heat of fusion and the melting temperature of paraffin of the 0th cycle

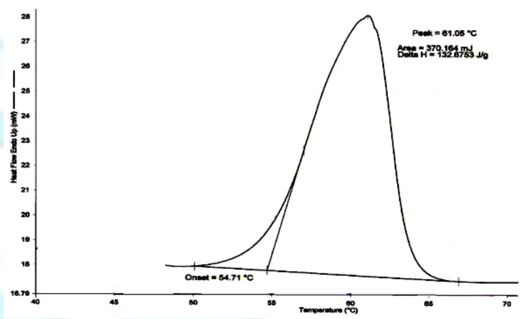


Figure 3. DSC measurement of the latent heat of fusion and the melting temperature of paraffin of the 50th cycle

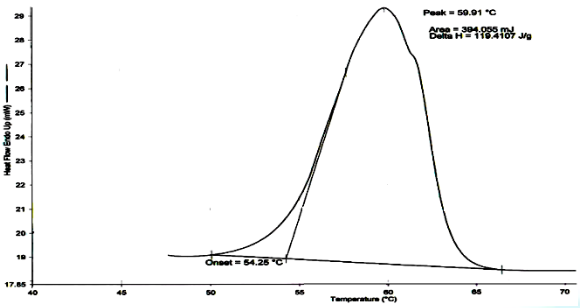


Figure 4. DSC measurement of the latent heat of fusion and the melting temperature of paraffin of the 300th cycle

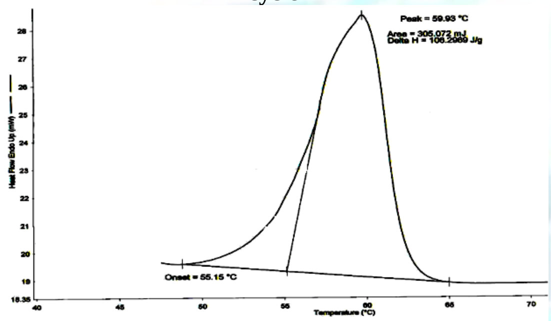


Figure 5. DSC measurement of the latent heat of fusion and the melting temperature of paraffin of the 600th cycle

Table 1 Changes in latent heat of paraffin as percentage after repeated thermal cycles

Sr. No.	No. of Thermal Cycles	Latent Heat (kJ/kg)	RPD (%)
1	0	127.98	--
2	50	132.67	+3.66
3	100	123.6	-3.42
4	150	120.32	-5.98
5	200	128.3	+0.25
6	250	124.29	-2.88
7	300	119.41	-6.69
8	350	123.93	-3.16
9	450	128.09	+0.17
10	500	118.42	-7.45
11	550	116.76	-8.76
12	600	106.29	-16.19

Table 2 Changes in phase transition temperature range of paraffin after repeated thermal cycles

Sr. No.	No. of Thermal Cycles	Onset Temperature (°C)		Peak Temperature (°C)		Phase Transition Temperature Range
			RPD (%)		RPD (%)	
1	0	52.91	-	60.00	-	52.91 – 60.00
2	50	54.71	3.40	61.05	1.75	54.71 – 61.05
3	100	54.69	3.36	60.60	1	54.69 – 60.60
4	150	54.55	3.09	59.71	-0.48	54.55 – 59.71
5	200	55.29	4.49	60.5	0.83	55.29 – 60.5
6	250	55.7	5.27	60.7	1.16	55.7 – 60.7
7	300	54.25	2.53	59.91	-0.15	54.25 – 59.91
8	350	54.06	2.17	60.39	0.65	54.06 – 60.39
9	400	52.72	-0.36	61.57	2.61	52.72 – 61.57
10	450	55.04	4.02	60.59	0.98	55.04 – 60.59
11	500	53.08	0.32	60.53	0.88	53.08 – 60.53
12	550	53.05	0.26	59.94	-0.10	53.05 – 59.94
13	600	55.15	4.23	59.93	-0.11	55.15 – 59.93

5.1 Change in Latent Heat of Fusion

From the figures 2-5, the changes in the latent heat of fusion of paraffin after various numbers of thermal cycles are observed. Values of RPD for the latent heat of fusion for paraffin for various numbers of cycles are shown in table 1. Table 1 shows the percentage change in latent heat of fusion of paraffin after every 50th cycles. The value of latent heat of paraffin at 0th thermal cycle is taken as the reference. It is also observed that the change in the latent heat of fusion is in the range of +3.66% to -16.19%. The positive and negative results show the higher and lower latent heat of fusion in comparison to the 0th thermal cycle test result

5.2 Change in Phase Transition Temperature Range

Table 2 summarizes the effect of a large number of thermal cycle on the phase transition temperature, RPD for the onset and peak temperatures of paraffin. The phase transition temperature of fresh paraffin is obtained through DSC curve as shown in figure 2 is 52.91-60.00°C. This shows paraffin starts to melt at temperature of 52.9°C (onset temperature) and complete at 60.00°C temperature (peak temperature). From the table 2, it is examined that melting temperature of paraffin is increased from 52.91°C to

55.15ºC after 600 thermal cycles. However, it is noticed that the increase in phase transition temperature of paraffin is not regular. It is also seen that the values of the RPD for onset and peak temperatures never exceed ±5.5% and ±3% (in many cases they are much less) respectively.

One of the reasons for the change in thermal stability may be due to changes in the chemical structure of the PCM with increase of number of thermal cycles. The PCM could not form the initial crystal structure (uncycled PCM) once it solidifies after complete melting. Hence it can be considered that a new as well as fresh compound may formed over a large number of melt/freeze cycles. A new compound will show different latent heat and melting temperature range than that of the fresh state. In addition, impurities and moisture present in the PCM may also cause of change in latent heat of fusion. It can be noted that the changes in the melting temperature and latent heat of fusion of the paraffin wax after 600 cycles of operation (approximately a 2 year utility period) is within an accepted level. Hence this paraffin wax can be considered a stable PCM which will be used in a latent heat storage system.

6. Conclusion

A thermal cycle test for paraffin wax is carried in order to check the thermal stability of the PCM. Experimental results show the variation in latent heat of in the range of +3.66% to -16.19% over a period of 600 thermal cycles. The variation in phase transition range is observed within ±6%. These variations may be due to impurities and improper crystallization of the PCM. This experimental study establishes paraffin wax as a promising PCM in latent heat energy storage system for solar applications.

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