LATENT HEAT STORAGE SYSTEM FOR SOLAR THERMAL ENERGY APPLICATIONS

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Abstract

The progression of energy supply always possesses some difficulty as the supply does not commensurate with demand. The demand for energy remains higher than production which always leads to imprudent exploitation of precious natural resources, which is available in limited quantities on the mother earth. Energy from non-renewable resources leads to dwindling of natural sources and global warming, whereas energy from renewable resources is sporadic. Solar energy is the primary energy source in renewable energy. The intermittent nature of solar energy necessitates the use of a storage medium. The storage medium stores energy when it is available in excess quantities and delivers the stored energy when the supply is inadequate. Thermal energy storage system plays a major role to achieve high efficiency and uninterrupted operation for solar thermal energy applications such as space heating, solar drying, solar water heating, and industrial process heat and electricity generation. In this article, an attempt has been made to focus on the scope of thermal energy storage system and different techniques of storing solar thermal energy. Scientific investigation was carried out to determine the suitability of an organic phase change material in solar thermal energy storage. This article is expected to be an aid to the scientific society to explore current trends, opportunities and advancement in solar thermal energy storage systems.

Keywords: *Solar energy, Latent heat storage, Phase change materials, Thermal energy storage, Thermo-physical properties.*

Nomenclature

a_m	fraction melted
a_r	fraction reacted
C_p	specific heat (J/kg K)
C_{sp}	average specific heat between T_i and T_m (kJ/kg K)
C_{lp}	average specific heat between T_m and T_f (J/kg K)
dt	change in time
m	mass of heat storage medium (kg)
Q	quantity of heat stored (J)
T_f	final temperature (°C)
T_i	initial temperature (°C)
T_m	melting temperature (°C)
$Äh_m$	heat of fusion per unit mass (J/kg)
$Äh_r$	endothermic heat of reaction

The fossil fuel continues to be the primary energy source in industrial and agricultural sectors in the developing economy. The drastic increase in energy requirement tends to be the major cause for increase in fuel price and negative effects on earth's atmosphere such as CO_2 emission, global warming, pollution and exhaustion of natural resources. Many scientists and researchers are focused their attention to derive alternative sources of energy which are renewable and non- polluting in nature. Solar energy is the only energy source among renewable energy, found to be most suitable for numerous applications. But availability of solar energy is occasional, nonconsecutive and irregular therefore it has to be utilized whenever it is available; here comes the role of energy storage to solve the problem of mismatch between demand and supply.

Energy storage systems are also of equal importance as much as finding the new sources of energy. Energy storage system increases the performance and reliability of a device by delivering constant energy. Different types of energy storages are available such as chemical, electrical, mechanical, electrochemical and thermal energy.

Applications that require thermal energy for its operation can utilize solar thermal energy to conserve the natural resources and prevent global warming. Some of the applications that can make use of solar thermal energy are water heating, agriculture crops drying, green house heating, industrial process heating, space heating, cooking, electricity generation, refrigeration and air conditioning. Figure -1 shows the broad applications of solar thermal energy. A detailed study on solar thermal energy applications integrated with latent heat thermal energy storage system was done by Sharma and Sagara (2005) and Sharma, Kitano and Sagar (2004). This paper deals with the necessity of energy storage in solar thermal energy applications and also the role of PCMs as a thermal energy storage material. The chosen PCM material for PCM application should be able to resist any property degradation over large number of melt/freeze cycles. An extensive review of literature was carried out to analyze the suitability of various system developed so far towards this.

Need for storage for solar thermal applications

Thermal energy storage is mainly used to solve the problem of mismatch between supply and demand. Storage system 'stores' energy which can be used for later use. The storage system comes into picture whenever there is a sudden high energy demand or a fluctuating energy supply and also plays a role when there is no supply of energy for long term. These are few conditions which makes thermal energy storage system very important, either short term or long term storage based on solar thermal energy applications.

Thermal energy storage systems are designed based on the energy required for a particular application. Amount of energy (E) required to heat a volume (V) of substances to a particular temperature is given by

$$E = mC(T_2 - T_1)$$
$$= \rho VC(T_2 - T_1)$$

Where m is mass, r is the density and C specific heat capacity of the substance. T_1 is the initial temperature of the storage material and T_2 is the final temperature to which the material to be heated. Thermal energy storage proves to be more effective and efficient particularly for solar thermal energy applications.

Basic process involved in thermal storage includes charging, storing and discharging. Charging is the foremost step where the heat energy from the solar collector field is transferred to the thermal energy storage reservoir through the heat transfer fluid, followed by storing, that is heat energy gets accumulated in storage tank. Finally the stored heat is removed through heat transfer mechanism for different thermal energy application known as discharging. When all these process takes place concurrently it is called cycle. Figure -2 shows the schematic representation of thermal energy storage system used in solar thermal energy applications.

Some of the desired requirements of the thermal energy storage system are high heat storage efficiency, large storage capacity per unit mass and volume, no degradation in efficiency after many charging and discharging cycles, compact in design, very small heat losses, should be non-corrosive, non-hazardous, non-toxic, high speed of charging and discharging cycles and long life with low cost.

Thermal energy storage techniques

Based on the properties like specific heat capacity, latent heat of fusion, endothermic and exothermic reaction of the material, thermal energy can be stored as either sensible heat, or latent heat or by chemical storage. A detailed description of various thermal energy storage techniques has been presented by Zalba, Marýn, Cabeza and Mehling (2003), Abhat (1980) and Atul Sharma et al (2009). Figure -3 shows the different techniques used for thermal energy storage. A short overview on these techniques is described below.

Chemical heat storage

Thermal energy is stored and retrieved using the chemical reactions by breaking and reforming of molecular bonds. Chemical heat storage has more advantages such as high energy density, possibility of heat pumping and long distance energy transport. But this technique is still immature and efficiency has not yet been proved. Different types of thermal energy storage system using chemical reactions was presented by Garg, Mullick and Bhargava (1985), Garg and Prakash (2002). Thermal energy storage through chemical reaction is based on the amount of storage material, endothermic heat of reaction and the extent of conversion which is given by the formula:

$$Q = a_r m \Delta h_r$$

Three types of thermal energy storage is possible through chemical heat storage technique. It can be either reversible reaction (exothermic and endothermic reactions) or through thermo chemical pipeline energy transport where reversible reactions occurs over a long distance capable of transporting thermal energy or finally through chemical heat pump storage where a carrier gas is used to carry the heat evolved from the chemical reactions. Few examples are given in Table -1 for thermal energy storage thorough chemical reactions.

Sensible heat storage

Specific heat capacity of the material is utilized to store the thermal energy in sensible heat storage. Figure-4 illustrates the process of sensible heat storage system. Sensible heat storage occurs in both solid and liquid phase, where the material does not undergo any phase transformation during charging or discharging cycles and the temperature of the material will not remain constant. The amount of energy stored using sensible heat is given by:

$$Q = \int_{T_i}^{T_f} mC_p \, dt$$

$$= mC_p (T_f - T_i)$$

The amount of thermal energy stored depends upon the amount of the storage material, specific heat of the medium and difference between the change in temperature at initial and final stage. Water with heat capacity of 4190 (J/kg K) serves as the best liquid sensible heat storage medium upto 100°C and rock with heat capacity of 800-900 (J/kg K), as a solid sensible heat storage.

Latent heat storage

The process of storing and retrieving the thermal energy is based on the latent heat of fusion of the material, where storage medium undergoes a phase transformation which can be either solid to solid or solid to liquid. Figure -4 illustrates the principle involved in latent heat storage system. Temperature is almost constant and the energy stored in latent heat storage medium is given by:

$$Q = \int_{T_i}^{T_m} m\mathrm{C_p dt} + \mathrm{ma_m} \Delta h_m + \int_{T_m}^{T_f} mC_p \, dt$$

$$= m[C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{lp}(T_f - T_m)]$$

Latent heat storage materials can be of organic, or inorganic salts or eutectic compounds. Organic phase change materials proves to be more efficient than inorganic (salt hydrates) and eutectics (various composition of salt hydrates or organic compounds) due to its

high heat of fusion, no tendency of supercooling but it has got the demerits of poor thermal conductivity and high cost with low operating temperature of less than 500°C. Only disadvantage of inorganic salts is incongruent melting and supercooling but it can be used for nearly 1000°C. Few examples of latent heat storage materials are given below in Table -2. A detailed review on latent heat storage materials, properties and systems was reported by Sharma and Sagara (2005).

Research and development in the field of latent heat thermal energy storage

Various research activities are being carried out in developing the thermal energy storage system using latent heat storage technique. Figure -5 shows the possible research areas and development of thermal energy storage for solar thermal applications. Analysis of thermal and physical properties of phase change materials, design and development of heat exchangers, efficiency, energy and exergy analysis of thermal storage and development of standards for testing thermal energy storage are the major research areas in the field of thermal energy storage.

Identification, analysis and optimization of thermal and physical properties of phase change materials is the foremost step in developing the thermal energy storage system using latent heat storage materials. Melting point, latent heat, thermal stability, thermal conductivity, supercooling, and density are few of the thermo-physical properties to be analyzed. Differential scanning calorimetry and thermal conductivity analyzer are used to analyze these parameters.

Kenisarin (2010) has reviewed on the investigations and developments of various high temperature inorganic PCMs of salt hydrates and metal alloys that is capable of storing thermal energy from 120°C to 1000°C along with the thermo-physical properties and corrosion behavior of containers for repeated cycles. Feldman, Shapiro and Banu (1986) has reported the measurements of melting point, freezing point, and the latent heats of melting and fusion of 12 organic materials of fatty acid esters, ethoxylated alcohols, alkyl phenol and sulphur compounds with melting points in the range 10-43°C for space heating and cooling applications. Arndt, Dunn and Willix (1984) has reported the melting range, enthalpy of fusion, flash point and thermal stability of few organic PCM for thermal energy storage in the temperature range of 60-90°C. Aboul-Enein and Olofa (1991) analyzed the thermo-physical properties of hexadecane, decanol and caprilic acid PCM for solar energy application that can be used in the latent cold storage systems (0-20°C). Arndt, Dunn and Willix (1981) also experimentally studied the thermal cycling of organic PCM naphthalene for 220 cycles. It is found that the melting onset temperature was 81°C and solidification onset temperature was 67°C with latent heat of fusion 148J/g. Thermal cycle testing of calcium chloride hexahydrate as a possible PCM for latent heat storage has been performed by Tyagi and Buddhi (2008) for 1000 cycles. It is reported that calcium chloride hexahydrate as a good inorganic PCM for low temperature applications which has only small variations in the latent heat of fusion and melting in the stable range of temperature.

El-Sebaii et. al (2009,2011) has experimentally investigated, the influence of melting/solidification on melting point and latent heat of fusion by fast thermal cycling for one thousand cycle of magnesium chloride hexahydrate ($MgCl_2.6H_2O$). The study used extra water principle to avoid segregation of PCM during solidification. The author concluded that $MgCl_2.6H_2O$ solidifies with a slight degree of supercooling in the range of 0.1–3.5°C. El-Sebaii also investigated the thermal cycling of acetanilide (C_8H_9NO) and magnesium chloride hexahydrate ($MgCl_2.6H_2O$) for 500 cycles. Shukla, Buddhi and Sawhney (2008) investigated the thermal cycling tests to check the stability in thermal energy storage systems on some selected organic and inorganic phase change materials. Paraffin wax(A), Paraffin wax(B), Paraffin wax(C), Sodium hydroxide (NaOH), Di-Sodium borate decahydrate ($Na_2B_4O_7.10H_2O$), Ferric nitrate hexahydrate ($Fe(NO_3)_3.6H_2O$), Barium hydroxide octahydrate ($Ba(OH)_2.8H_2O$), Erythritol ($C_4H_6OH_4$) are few of the PCMs selected for studies. Thermal cycle tests were performed for 1000 cycles. It is stated that the selected inorganic PCMs are not suitable for latent heat thermal energy storage purposes due to large variation in thermo-physical properties. Paraffin waxes (A, B, and C) and erythritol has good thermal reliability in latent heat of fusion and melting temperature with respect to thermal cycling and hence can be used as a PCM for low temperature applications.

Once the material is identified then parameters such as heat exchanger geometry, corrosion analysis, energy and exergy balances, efficiency, charging and discharging period, temperature distribution, and thermodynamics for different heat transfer fluid flow rates has to be studied. Based on the results numerical modeling and simulations has to be performed by varying different parameters to achieve highly efficient system for various applications to implement in large scale.

Jesumathy, Udayakumar and Suresh (2012) reported the heat transfer characteristics of paraffin PCM based on three important issues like temperature distribution, heat transfer phenomenon during total melting and solidification, Reynolds number based on inlet of heat transfer fluid. Abduljalil, Sohif Bin Mat, Sopian, Sulaiman and Abdulrahman (2013) presented a review on numerical modeling of phase change materials (PCMs) through a commercial computational fluid dynamic (CFD) software and developed a program to study the heat transfer phenomena in PCMs which tends to be accurate and can be used to simulate for different applications, that reduces time and money with maximum efficiency. A detailed study with few case studies on the energy and exergy analysis, along with the numerical modeling and simulation has been explained by Dincer and Rosen (2011), Zalba, Marýn, Cabeza and Mehling (2003) and Sharma, Tyagi, Chen and Buddhi (2009) for thermal energy storage systems and applications.

The optimized parameters are used to design and develop the thermal energy storage system which can be integrated with the thermal energy applications powered by solar thermal energy. Performance of the overall system has to be examined and studied for further developments to achieve increased and better efficiency with low cost.

Methodology

Based on these literature review, a detailed thermo-physical investigation was carried out in Solar Thermal Energy Laboratory to explore the suitability of commercial grade acetamide for the usage of storage material in solar thermal energy applications. The study on the thermal stability of acetamide for 100 thermal cycles was performed by accelerated thermal charging (melting) and discharging (solidification) cycles. Acetamide of 99.9% purity was purchased from Spectrochem Pvt. Ltd., India. Initially 15gms of Acetamide was taken in a steel container and kept in an oil bath heated by hot plate for three different temperatures 60°C, 80°C and 100°C to optimize the time duration required to charge the PCM. Once the PCM completely melted out, it was taken from the oil bath and cooled to room temperature by natural cooling. The temperature of the PCM was recorded at an interval of one minute for charging and discharging and the graph was plotted (Figure -6). Finally it is optimized to have an oil bath at a constant temperature of 100°C for charging cycle. After each corresponding cycle 20mg of the acetamide was taken for DSC-TGA analysis.

Results & Discussion

Heat storage and retrieval duration for one complete charging and discharging cycles was plotted as time versus temperature graph and is shown in Figure 6. This study was carried out for three different heating temperatures of 60°C, 80°C and 100°C and the corresponding duration for one complete cycle was found to be 79mins, 48mins and 38mins. From the results it is optimized to perform the charging cycle at 100°C and discharging at natural cooling process at room temperature for accelerated 100 thermal cycles.

Thermo-physical properties such as onset temperature, melting temperature, latent heat of fusion and mass loss were measured for different number of charging and discharging cycles for upto 100 cycles. Figure-7 and Figure-8 shows the DSC and TGA curve of acetamide for 0^{th},1^{st},10^{th},50^{th},100^{th} thermal cycles and Table -3 shows the thermal stability of acetamide in terms of onset temperature, melting point, latent heat of fusion, relative percentage difference (RPD) and mass loss during phase change temperature for 0^{th}, 1^{st}, 10^{th},50^{th},100^{th} thermal cycles. From the results using the values of 0^{th}(zeroth) cycle as reference, relative percentage difference for melting temperature and latent heat of fusion was determined by using the formula suggested by El-Sebaii A.A. (2011),

$$RPD(\%) = \frac{X_n - X_0}{X_0} \times 100$$

Where X_n denotes the value of melting temperature and latent heat of fusion at n^{th}cycle and X_0 denotes the values of these quantities at 0^{th}cycle. The initial melting temperature and latent heat of fusion of acetamide was 82.76°C and 339.7 J/g, however the values after 100 cycles were 82.55°C and 307.6 J/g which is found to be decreased. After 100 cycles the relative percentage difference was only 0.25% for melting temperature and 9.44% for latent heat of fusion compared to initial sample. TGA curves show the percentage of mass loss with respect to increasing temperature. It is found that 1.70%, 0.40%, 2.48%, 4.66% and 6.81% mass loss was observed at phase change temperature of corresponding thermal cycles. The studies on thermal stability of acetamide corresponding to different thermal cycles suggest that, it can be used for the applications that require operating temperature from 40°C to 140°C. Therefore acetamide tends to be the most promising phase change material for solar space heating, water heating and solar drying applications.

Conclusion

An overview on solar thermal energy storage system using phase change materials, its necessity, techniques used and possible research areas in the field of solar thermal energy for thermal applications are outlined in this article. Commercially available Acetamide was chosen as PCM for the present study. The study revealed that there is only negligible variation in the latent heat of fusion and melting point over a number of melt-freeze cycles. The present study revealed that Acatamide is a promising material as PCM for solar thermal applications for temperature requirements upto 80°C. The major challenge is to design a sophisticated heat exchanger with adequate heat transfer facility that will help to have a constant energy delivery from the storage system. Study towards this direction is well progressing among our research group. This paper will help the researchers to explore the concepts and methodologies of solar thermal energy technology on new and novel techniques and create awareness among scientific society to exploit solar energy for thermal applications.

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TABLES

Table 1 - Examples for thermal energy storage using chemical reactions

Chemical Reaction	Heat of Reaction [ΔH°(kJ)]
$Mg(OH)_{2\ (S)} \leftrightarrows MgO_{\ (S)} + H_2O_{(g)}$	81.6
$SO_{3\ (g)} \leftrightarrows SO_{2\ (g)} + ½O_{2(g)}$	98.94
$NH_4F_{\ (S)} \leftrightarrows NH_{3\ (g)} + HF_{(g)}$	149.3
$C_6H_{12\ (g)} \leftrightarrows C_6H_{6(g)} + 3H_{2(g)}$	206.2
$CH_{4\ (g)} + CO_{2\ (g)} \leftrightarrows 2CO_{\ (g)} + 2H_{2(g)}$	247.4

Table 2 - Few phase change materials for latent thermal energy storage

Phase change material	Latent heat of fusion (kJ/kg)	Phase change material	Latent heat of fusion (kJ/kg)
Myristic Acid	199	$(NH_4).Al(SO_4).6H_20$	269
Acetamide	241	$Na_2SO_4.10H_2O$	251-254
Methyl Fumarate	242	$C_{14}H_{28}O_2+C_{10}H_{20}O_2$	147.7
$CaCl_2.12H_2O$	174	$AlCl_3+NaCl+ZrCl_2$	234
$Ba(OH)_2.8H_2O$	265-280	MgCl+NaCl	328

Table 3 - Thermal stability analysis of melting point, latent heat of fusion and mass loss of Acetamide at 0th, 1st, 10th, 50th, 100th thermal cycles

No. of cycles	Onset melting temperature (°C)	Melting Temperature (°C)	RPD (%)	Phase change temperature (°C)	Latent Heat of Fusion (J/g)	RPD (%)	Weight Loss at melting temperature (%)
0	80.28	82.76	-	80.28-82.76	339.7	-	1.71
1	77.55	82.17	0.71	77.55-82.17	305.9	9.94	0.94
10	79.34	82.63	0.15	79.34-82.63	310.2	8.68	2.48
50	77.08	82.68	0.09	77.08-82.68	312.8	7.91	4.66
100	77.71	82.55	0.25	77.71-82.55	307.6	9.44	6.81

FIGURES

Figure 1 - solar thermal energy applications.

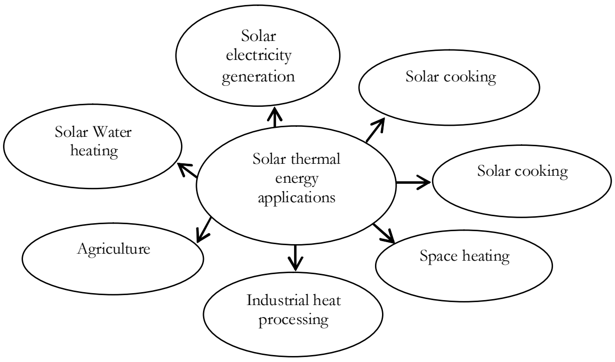


Figure 2 - Cyclic process in solar thermal energy storage system

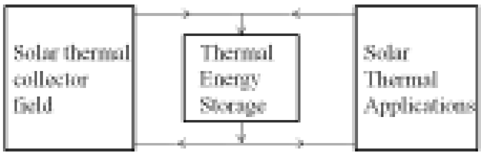


Figure 3 - Classification of Thermal energy storage.

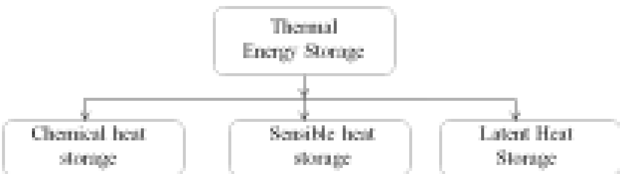


Figure 4 - principle of sensible and latent heat.

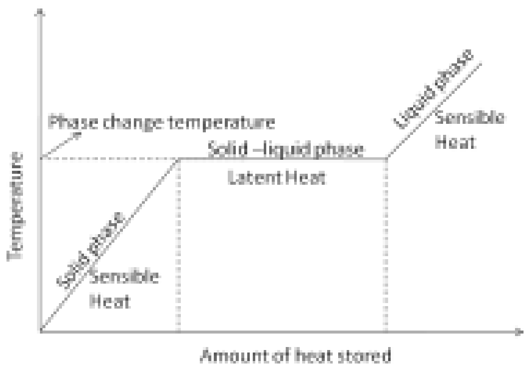


Figure 5 - Various research areas in the field of solar thermal energy storage.

Figure 6 - Heat storage and retrieval duration of acetamide

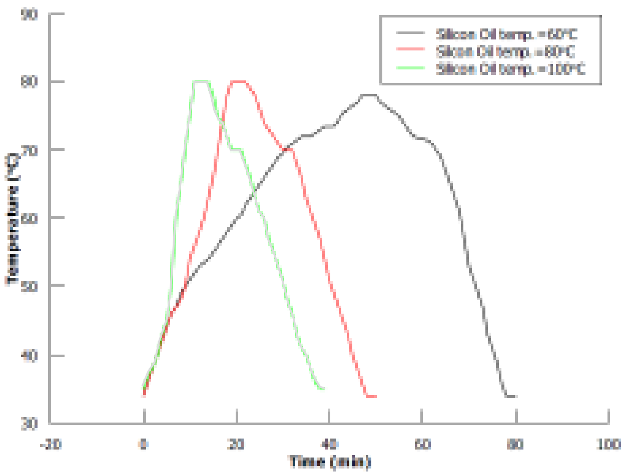
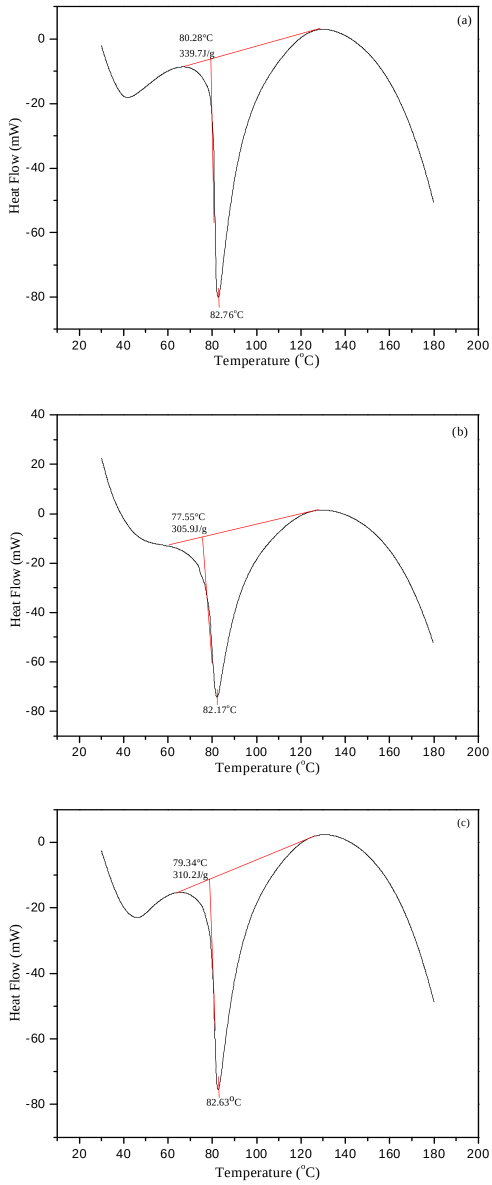
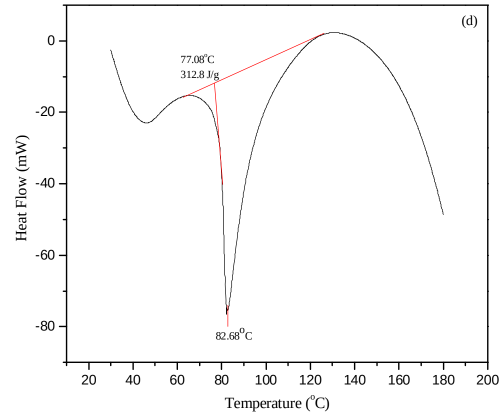


Figure 7 - DSC curve of Acetamide for (a) 0th cycle (fresh sample) (b) 1st cycle (c) 10th cycle (d) 50th cycle (e) 100th cycle





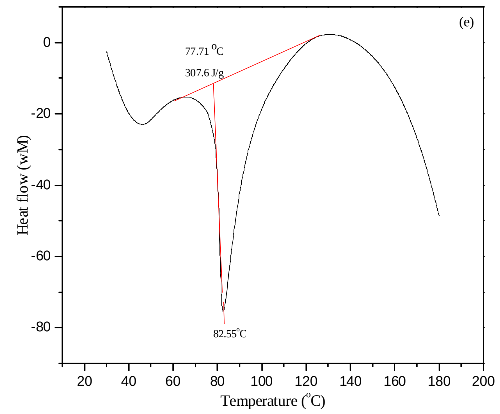


Figure 8 - TGA curve of Acetamide for (a1) 0th cycle (fresh sample) (b1) 1st cycle (c1) 10th cycle (d1) 50th cycle (e1) 100th cycle.