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Original Paper

Phase Change Materials for Low Temperature Solar Thermal Applications

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Abstract

Latent heat storage in a Phase Change Material (PCM) is very attractive because of its high storage density with small temperature swing. It has been demonstrated that, for the development of a latent heat storage system, the choice of the PCM plays an important role in addition to heat transfer mechanism in the PCM. The information on the latent heat storage materials and systems is enormous and published widely in the literatures. In this paper, we make an effort to gather the information from the previous works on PCMs and latent heat storage systems. The paper contains a list of about 250 PCMs and more than 220 references.

Key words: Phase change material, Solar energy, Latent heat storage system

1. Introduction

Scientists all over the world are in search of new and renewable energy sources. One of the options is to develop energy storage devices, which are as important as developing new sources of energy. Thermal energy storage is essential for many processes. Latent heat storage is one of the most attractive because large amounts of energy can be stored in a small volume with a small temperature change in the media. Latent heat storage is a relatively new area of study and pioneered by Dr. Telkes in the 1940s [1]. It did not receive much attention however until the energy crisis of late 1970s and early 1980s where it was extensively researched for use in solar heating systems [1, 2]. When the energy crisis subsided much less emphasis was put on latent heat storage. Although research into latent heat storage for solar heating systems continues [3, 4], it is increasingly being considered for waste heat recovery and load leveling for power generation [5]. Latent heat storage can be accomplished through solid-liquid, liquid-gas, solid-gas, and solid-solid phase transformations, but the only two of practical interest are the solid-liquid and solid-solid. The solid-gas and liquid-gas systems are of limited utility because of the large volumes required for such systems. Of the two practical systems, the solid-liquid system is the most studied and most commonly commercially available. Solid-solid systems shows much promise, but are only recently being studied [6]. Many phase change materials (PCMs) have been studied for practical use. This paper is a compilation of much of practical information on different PCMs and system developed based on latent heat storage technology.

2.0 Thermal Energy Storage

Thermal energy storage can be stored as a change in internal energy of a material as sensible heat, latent heat and thermo - chemical or combination of these.

In Sensible Heat Storage (SHS), thermal energy is stored by raising the temperature of a solid or liquid. SHS system utilizes the heat capacity and the change in temperature of the material during the process of charging and discharging. The amount of stored heat depends on the specific heat of medium, the temperature change and the amount of storage material.

$$Q = \int mC_p dT = mC_{ap}\left(T_f - T_i\right) \qquad [1]$$

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Latent Heat Storage (LHS) is based on the heat absorption or release when a storage material undergoes a phase change from solid to liquid or liquid to gas or vice – versa. The storage capacity of the LHS system with a PCM medium is given by

$$Q = ma_m \Delta h_m + \int_i^m mC_p dT + \int_m^f mC_p dT$$
$$= m\left[a_m \Delta h_m + C_{sp}(T_m - T_i) + C_{lp}(T_f - T_m)\right] \qquad [2]$$

LHS systems have certain benefits in comparison with SHS systems. The most important is the higher energy density per unit mass and per unit volume.

Thermo chemical systems rely on the energy absorbed and released in breaking and reforming molecular bonds in a completely reversible chemical reaction. In this case, the heat stored depends on the amount of storage material, the endothermic heat of reaction, and the extent of conversion.

$$Q = a_r m \Delta h_r \qquad [3]$$

Amongst above thermal heat storage techniques, latent heat thermal energy storage is particularly attractive due to its ability to provide high energy storage density and its characteristics to store heat at constant temperature corresponding to the phase transition temperature of phase change material (PCM). Phase change may be in the following form: solid – solid, solid – liquid, solid – gas, Liquid – gas.

In solid – solid transitions, heat is stored when the material is transformed from one crystalline to another. This transition generally has smaller latent heat and volume changes than solid – liquid transitions. Solid–solid PCMs offer the advantages of less stringent container requirements and greater design flexibility [9]. Most promising materials are organic solid solution of pentaerythritol, pentaglycerine, Li_2SO_4 and KHF_2 [10]. Trombe Wall with these materials could provide better performance than a plain concrete Trombe Wall.

Solid - gas and liquid – gas transition through have higher latent heat of phase transition but their large volume changes on phase transition are associated with the containment problems and rule out their potential utility in thermal storage systems. Large changes in volume make the system complex and impractical.

Solid – liquid transformations have comparatively smaller latent heat than liquid - gas. However, these transformations involve only a small change (of order of 10 percent or less) in volume. Solid- liquid transitions have proved to be economically attractive for use in thermal energy storage systems. PCMs themselves cannot be used as heat transfer medium. Heat transfer medium must me employed with heat exchanger in between to transfer energy from the source to the PCM and from PCM to the load. The heat exchanger to be used has to be designed specially, in view of the low thermal diffusivity of PCMs in general. The volume changes of the PCMs on melting would also necessitate special volume design of the containers to wholes PCM. It should be able to absorb these volume changes and should also be compatible with the PCM used. Any latent heat energy storage system must, therefore, posses at least following three properties: a suitable PCM with its melting point in the desired temperature range, a suitable heat exchange surface and a suitable container compatible with the PCM.

3.0 Latent Heat Storage Materials

Phase Change Materials (PCM) is latent heat storage material. As the source temperature rises, the chemical bonds within the PCM break up as the material changes phase from solid to liquid (as is the case for solid-liquid PCMs which are of particular interest here). The phase change is a heat-seeking (endothermic) process and therefore, the PCM absorbs heat. Upon storing heat in the storage material, the material begins to melt when the phase change temperature is reached. The temperature then stays constant until the melting process is finished. The heat stored during the phase change process (melting process) of the material is called latent heat. The effect of latent heat storage has two main advantages: 1. It is possible to store large amounts of heat with only small temperature changes and therefore to have a high storage density. 2. Because the change of phase at a constant temperature takes some time to complete, it becomes possible to smooth temperature variations. They store 5 to 14 times more heat per unit volume than sensible storage materials such as water, masonry, or rock [14]. A large number of PCMs are known to melt with a heat of fusion in any required range. The PCM to be used in the design of thermal storage systems should passes desirable thermo physical, kinetics and chemical properties [11, 12].

Thermo physical properties

(i) Melting temperature in the desired operating temperature range.
(ii) High latent heat of fusion per unit volume so that the required volume of the container to store a given amount of energy is less.
(iii) High specific heat to provide for additional significant sensible heat storage.
(iv) High thermal conductivity of both solid and liquid phases to assist the charging and discharging of energy of the storage systems.
(v) Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem.
(vi) Congruent melting of the phase change material for a constant storage capacity of the material with each freezing/melting cycle.

Kinetic properties

(i) High nucleation rate to avoid super cooling of the liquid phase.
(ii) High rate of crystal growth, so that the system can meet demands of heat recovery from the storage system.

Chemical properties

(i) Chemical stability.
(ii) Complete reversible freeze / melt cycle.
(iii) No degradation after a large number of freeze / melt cycle.
(iv) Non-corrosiveness to the construction materials.
(v) Non-toxic, non-flammable and non-explosive materials for safety.

Moreover, low cost and large-scale availability of the phase change materials is also very important.

3.1 Classification of PCMs

A large number of phase change materials (organic, inorganic and eutectic) are available in any required temperature range. A classification of PCMs is given in Fig. 1.

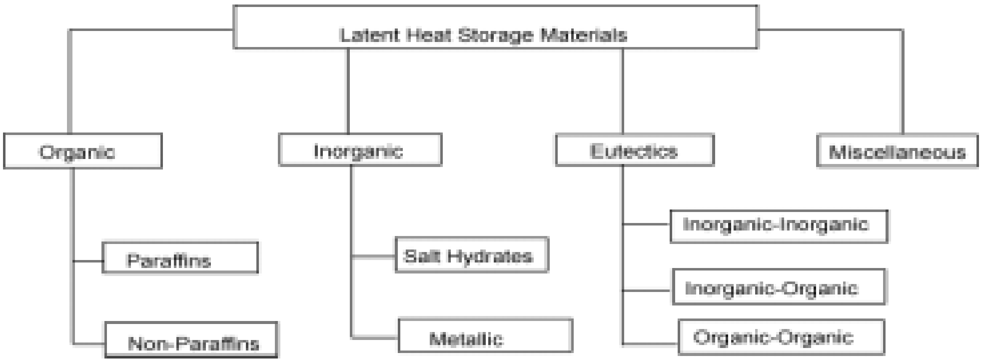


Fig.1: Classification of latent heat storage materials

There are a large number of organic and inorganic materials, which can be identified as PCM from the point of view melting temperature and latent heat of fusion. Organic and inorganic types of PCMs are given in Table 1 and 2 respectively. As no single material can have all the required properties for an ideal thermal storage media, one has to use the available materials and tries to make up for the poor physical property by an adequate system design. For example metallic fins can be used to increase the thermal conductivity of PCMs, super cooling may be suppressed by introducing a nucleating agent in the storage material and incongruent melting can be inhibited by use of suitable thickness. For their very different thermal and chemical behavior, the properties of each sub group, which affects the design of latent heat thermal energy storage systems using PCMs of that sub group, are discussed in detail below.

Table 1: List of organic PCMs [94 - 98]

Material	Melting point (^{O}C)	Latent heat of fusion (kJ/kg)	Material	Melting point (^{O}C)	Latent heat of fusion (kJ/kg)
N-Tetradeca	5.5	226	N-Penta Cosane	53.7	164
Formic Acid	7.8	247	Myristic Acid	54.0	199
N-Pentadeca	10.0	205	Oxolate	54.3	178
Acetic Acid	16.7	273	Tristearin	54.5	191
N-Hexadeca	16.7	237	O-Xylene	55.0	121
Caprilone	40.0	260	β-Chloroacetic	56.0	147
Docasyle	40.0	201	N-Hexacosane	56.3	255
N-Henicosan	40.5	161	Nitro Naphthalene	56.7	103
Phenol	41.0	120	α-Chloroacetic	61.2	130
N-Lauric	43.0	183	N-Octacosane	61.4	134
P-Joluidine	43.3	167	Palmitic Acid	61.8	164
Cynamide	44.0	209	Bees Wax	61.8	177
N-Docosane	44.5	157	Glyolic Acid	63.0	109
N-Tricosane	47.6	130	P-Bromophenol	63.5	86
Hydrocinna	48.0	118	Azobenzene	67.1	121
Cetyl	49.3	141	Acrylic Acid	68.0	115
O-Nitroanili	50.0	93	Dintro Toluene	70.0	111
Camphene	50.0	239	Phenylacetic Acid	76.7	102
Diphenyl	52.9	107	Thiosinamine	77.0	140

3.11 Paraffins

The normal paraffins of type $C_nH_{2n+}2$ are a family of saturated hydrocarbons with very similar properties. Paraffins between C_5 and C_{15} are liquids, and the rest are waxy solids. Paraffin wax is the mainly used commercial organic heat storage PCM [1,14]. It consists of mainly straight chain hydrocarbons that have melting temperatures from 23 to 67 °C [2]. Commercial grade paraffin wax is obtained from petroleum distillation and is not a pure substance, but a combination of different hydrocarbons. In general the longer the average length of hydrocarbon chain the higher the melting temperature and heat of fusion [13]. Properties of some paraffin are given in Table 3. Paraffins are easily available from many manufacturers and are usually more expensive than salt hydrates [1,14].

3.11.1 Advantages

Paraffin waxes show no tendency to segregate. They are also chemically stable although Lane [1] reports slow oxidation when exposed to oxygen requiring closed containers. Sharma [8, 145] reports stable properties after 1500 cycles in commercial grade paraffin wax. Paraffin waxes show high heats of fusion as shown in Table 3. They also have no tendencies to super cool, so nucleating agents are not necessary [1, 14]. Paraffin waxes are safe and non-reactive [14,15]. They are compatible with all metal containers and easily incorporated into heat storage systems [1]. Care however should be taken when using plastic containers as paraffin's have a tendency to infiltrate and soften some plastics [1].

3.11.2 Disadvantages

Paraffins have low thermal conductivity in their solid state as can be seen from Table 4. This presents a problem when high heat transfer rates are required during the freezing cycle. Velraj [16] reports that this problem can be decreased through the use of finned containers and metallic fillers or through combination latent/sensible storage systems. Aluminum honeycombs has been found to improve system performance [14]. Paraffins have a high volume change between the solid and liquid stages. This causes many problems in container design [15]. Paraffin's are flammable, this can be easily alleviated by a proper container [13 - 15]. Lane [1] also reports that paraffins can contract enough to pull away from the walls of the storage container greatly decreasing heat storage capacity. Unlike Salt Hydrates, commercial paraffins generally do not have sharp well-defined melting points.

Abhat [2] reports melting ranges of up to 43 °C. This is due to the fact that they are a mixture of materials and a solid-solid phase transformation in commercial grade parafffins immediately before melting that stores a great amount of the latent heat capacity of the material [2]. This decreases the efficiency of the heat storage system, as is no longer isothermal.

3.12 Non-paraffins

This is the largest category of candidate's materials for phase change storage. Lane et al [1, 18 - 19], Abhat [2] and Buddhi [12] have conducted an extensive survey of organic materials and identified a number of esters, fatty acids, alcohol's and glycol's suitable for energy storage. These materials are flammable and should not be exposed to excessively high temperature, flames or oxidizing agents. Non - paraffins are tabulated in Table 4.

3.13 Fatty acids

Fatty acids, characterized by the chemical formula $CH_3(CH_2)_{2n}COOH$, have much the same characteristics as paraffins. Their advantages of sharper phase transformations are offset by the disadvantage of about three times the cost of parffins [15]. They are also mild corrosive. Some fatty acids of interest to low temperature latent heat thermal energy storage applications are tabulated in Table 5. Sharma [8, 145] reports stable properties after 1500 cycles for stearic acid.

3.14 Salt hydrates

Salt hydrates are some of the oldest and most studied heat storage PCMs [1]. They consist of a salt and water, which combine in a crystalline matrix when the material solidifies. They can be used in alone or in eutectic mixtures [2]. Properties of some salt hydrates are given in Table 6. There are many different materials that have melting ranges from 15 to 117 °C [1]. Salt hydrates are the most important group of PCMs, which have been extensively studied for their use in latent heat thermal energy storage systems. Three types of the behavior of the melted salts can be identified: congruent, incongruent and semi congruent melting.

3.14.1 Advantages

Low cost and easy availability of salt hydrates makes commercial attractive for heat storage applications. Two of the least expensive and most available salt hydrates are $CaCl_2.6H_2O$ and $Na_2SO_4.10H_2O$ [1]. Many salt hydrates are sufficiently inexpensive for the use in storage [18]. Salt hydrates have a sharp melting point, this maximizes the efficiency of a heat storage system. They have a high thermal conductivity when compared with other heat storage PCMs. This can increase heat transfer in and out of the storage unit. They have a high heat of fusion to decrease the needed size of the storage system. Salt hydrates have a lower volume change than other PCMs.

3.14.2 Disadvantages

Segregation is formation of other hydrates or dehydrated salts that tend to settle out and reduce the active volume available for heat storage. Abhat [2] reports a decrease in heat of fusion of over 73% in $Na_2SO_4.10H_2O$ after 1000 melt/freeze cycles. This problem can be eliminated to a certain extent through the use of gelled or thickened mixtures [1] though this process negatively impacts the heat storage characteristics of the mixture and the mixture still degrades with time [2]. Salt hydrates shows supercooling because of not able to start crystallization at the freezing point of PCM. This can be avoiding using suitable nucleating materials to start crystal growth in the storage media. Lane [1] offers a comprehensive listing of nucleating materials for most common salt hydrates. Abhat [2] reports material degradation in $CaCl_2.6H_2O$ after only two cycles when the test sample was not hermetically sealed. Therefore it is necessary to design containers to contain the material without letting water out. Another problem of salt hydrates is their tendency to cause corrosion in metal containers that are commonly used in thermal storage systems [2]. Compatibility of PCM and container should always be checked before use.

3.15 Eutectics

A eutectic is a minimum melting composition of two or more components, each of which melts and freezes congruently [19]. Eutectic nearly always melts and freezes without segregation since they freeze to an intimate mixture of crystals, leaving little opportunity for the components to separate. On melting both components liquefy simultaneously. A list of eutectic is given in Table 7.

Table 2: List of inorganic PCMs [1, 2, 12, 94 - 98]

Name	Melting point (^{O}C)	Latent heat of fusion (kJ/kg)	Name	Melting point (^{O}C)	Latent heat of fusion (kJ/kg)
H_2O	0.0	333	BI_3	31.8	10
$POCl_3$	1.0	85	SO_3(β)	32.3	151
D_2O	3.7	318	$TiBr_4$	38.2	23
$SbCl_5$	4.0	33	$H_4P_2O_6$	55.0	213
H_2SO_4	10.4	100	SO_3 (γ)	62.1	331
IC l (β)	13.9	56	$SbCl_3$	73.4	25
MOF_6	17.0	50	$NaNO_3$	307	172 - 199
SO3(α)	17.0	108	KNO_3	333 - 380	116 - 266
IC l (α)	17.2	69	KOH	380	149
P_4O_6	23.7	64	$MgCl_2$	714 - 800	452 - 492
H_3PO_4	26.0	147	NaCl	800 - 802	466 - 492
Cs	28.3	15	Na_2CO_3	854	275
Ga	30.0	80	KF	857	452
$AsBr_3$	30.0	38	K_2CO_3	897	235

Table 3: Melting point and latent heat of fusion of paraffins [1, 2, 12, 94 - 99]

Name	No. of "C" Atoms	Melting point (^{O}C)	Density (kg/m^3)	Thermal Conductivity (W/mK)	Latent heat of fusion(kJ/kg)
n - Dodecane	12	-12	750	0.21^S	n.a.
n - Tridecane	13	-6	756		n.a.
n - Tetradecane	14	4.5 - 5.6	771		231
n - Pentadecane	15	10	768	0.17	207
n - Hexadecane	16	18.2	774	0.21^S	238
n - Heptadecane	17	22	778		215
n - Octadecane	18	28.2	814^S[14], 775^L	0.35^S [14], 0.149^L[14]	245
n - Nonadecane	19	31.9	912^S, 769^L	0.21^S	222
n - Eicosane	20	37			247
n - Heneicosane	21	41			215
n - Docosane	22	44			249
n - Tricosane	23	47			234
n - Tetracosane	24	51			255
n - Pentacosane	25	54			238
Paraffin Wax	n.a.	32	785^S[15],	0.514^S[15], 0.224^L[15]	251[15]
n - Hexacosane	26	56	770	0.21^S	257
n - Heptacosane	27	59	773		236
n - Octacosane	28	61	910^S, 765^L		255
n - Nonacosane	29	64			240
n - Triacontane	30	65			252
n - Hentriacontane	31	n.a.	930^S, 830^L		n.a.
n - Dotricontane	32	70			n.a.
n - Tritricontane	33	71			189

S: solid; L: liquid; n.a.: not available

Table 4: Melting point and latent heat of fusion of non - paraffins [1, 2, 12, 94 - 99]

Name	Melting point (^{O}C)	Density (kg/m^{3})	Latent heat of fusion (k J/ kg)
Formic Acid	7.8	1226.7^{15C}	247
Acetic Acid	16.7	1050^{20C}	187
Glycerin	17.9	1260^{20C}	198.7
Lithium Chloride Ethanolate	21	n.a.	188
Polyethylene Glycol 600	20-25	1100^{20C}	146
D – Lattic Acid	26	1249^{15C}	184
1-3 Methyl Pentacosane	29	n.a.	197
Camphenilone	39	n.a.	205
Docasyl Bromide	40	n.a.	201
Caprylone	40	n.a.	259
Heptadecanone	41	n.a.	201
1-Cyclohexylooctadecane	41	n.a.	218
4-Heptadacanone	41	n.a.	197
Cyanamide	44	1080^{20C}	209
Methyl Eicosanate	45	851^{79C}	230
3-Heptadecanone	48	n.a.	218
2-Heptadecanone	48	n.a.	218
Camphene	50	842^{54C}	238
9-Heptadecanone	51	n.a.	213
Methyl Behenate	52	n.a.	234
Pentadecanoic Acid	52.5	n.a.	178
Hypophosphoric Acid	55	n.a.	213
Chloroacetic Acid	56	1580^{20C}	130
Trimyristin	33-57	862^{20C}	201-213
Heptaudecanoic Acid	60.6	n.a.	189
Bee Wax	61.8	950	177
Glycolic Acid	63	n.a.	109
Oxazoline-Wax-TS 970	74	n.a.	
Arachic Acid	76.5	n.a.	227
Bromcamphor	77	1449^{81C}	174
Durene	79.3	838^{20C}	156
Acetamide	81	1159	241
Methyl Brombrenzoate	81	n.a.	126
Alpha Napthol	96	$1095^{98.7C}$	163
Glautaric Acid	97.5	1429	156
p-Xylene Dichloride	100	n.a.	138.7
Methyl Fumarate	102	1045	242
Catechol	104.3	1370^{15C}	207
Quinone	115	1318^{20C}	171
Acetanilide	115	1210^{4C}	142
Succinic Anhydride	119	1104	204
Benzoic Acid	121.7	1266^{15C}	142.8
Stibene	124	1164^{15C}	167
Benzamide	127.2	1341	169.4
Phenacetin	137	n.a.	136.7

Alpha Glucose	141	1544	174
Acetyl – p- Toluidene	146	n.a.	180
Phenylhdrazone Benzaldehy	155	n.a.	134.8
Salicylic Acid	159	1443^{20C}	199
Benzanilide	161	n.a.	162
O-Mannitol	166	1489^{20C}	294
Hydroquinone	172.4	1358^{20C}	258
p- Aminobenzoic Acid	187	n.a.	153

Table 5: Melting point and latent heat of fusion: Fatty acids [1, 2, 12, 94 - 99]

Name	Melting point (^{O}C)	Density (kg/m^3)	Thermal conductivity (W/mK)	Latent heat of fusion (kJ/kg)
Propyl Palmiate	10	n.a.	n.a.	186
Isopropyl Palmiate	11	n.a.	n.a.	100
Oleic Acid	13.5 - 16.3	863^{60C}	n.a.	n.a.
Isopropyl Stearate	14 - 19	n.a.	n.a.	140 - 142
Caprylic Acid	16	901^{30C}	0.149^{39C}	148
Butyl Stearate	19	n.a.	n.a.	140
Dimethyl Sabacate	21	n.a.	n.a.	120 - 135
Myristic Acid + Capric	24	888^{25C}, 1018^{1C}	0.164^{39C}, 0.154^{61C}	147.7
Vinyl Stearate	27 - 29	n.a.	n.a.	122
Methyl Palmitate	29	n.a.	n.a.	205
Capric Acid	32	878^{45C}	$0.153^{38.5C}$	152.7
Erucic Acid	33	853^{70C}	n.a.	n.a.
Lauric Acid	42 - 44	862^{60C}, 1007^{24C}	n.a.	178
Elaidic Acid	47	851^{79C}	n.a.	218
Pelargoinc Acid	48	n.a.	n.a.	n.a.
Myristic Acid	49 - 51	861^{55C}	n.a.	205
Palmitic Acid	64	850^{65C}	$0.162^{68.4C}$	185.4
Stearic Acid	69	848^{70C}	0.172^{70C}	202.5
Valporic Acid	120	n.a.	n.a.	n.a.

Table 6: Melting point and latent heat of fusion of salt hydrates [1, 2, 12, 94 - 99]

Name	Melting Point (^{O}C)	Density (kg/m^3)	Thermal Conductivity (W/m K)	Latent Heat (kJ/kg)	Melting Behavior^a [13]
$LiClO_3.3H_2O$	8	n.a.	n.a.	253	c
$NH_4Cl.Na_2SO_4.10H_2O$	11	n.a.	n.a.	163	n.a.
$K_2HO_4.6H_2O$	14	n.a.	n.a.	108	c
$NaCl.Na_2SO_4.10H_2O$	18	n.a.	n.a.	286	n.a.
$KF.4H_2O$	18	n.a.	n.a.	330	c
$K_2HO_4.4H_2O$	18.5	1447^{20C}, 1455^{18C},	n.a.	231	n.a.
$Mn(NO_3)_2.6H_2O$	25	1738^{20C}[12],	n.a.	148	n.a.
$LiBO_2.8H_2O$	25.7	n.a.	n.a.	289	n.a.
$FeBr_3.6H_2O$	27	n.a.	n.a.	105	n.a.
$CaCl_2.6H_2O$	29 - 30	1562^{32C}, 1802^{24C}	$0.561^{61.2C}$, 1.008^{23C}	170 - 192	ic
$LiNO_3.3H_2O$	30	n.a.	n.a.	189 - 296	c
$Na_2SO_4.10H_2O$	32	1485^{24C}	0.544	251 - 254	ic
$Na_2CO_3.10H_2O$	33 - 36	1442	n.a.	247	ic
$KFe(SO_4)_2.12H_2O$	33	n.a.	n.a.	173	ic

$CaBr_2.6H_2O$	34	1956^{35C}, 2194^{24C}	n.a.	115 - 138	n.a.
$LiBr.2H_2O$	34	n.a.	n.a.	124	ic
$Na_2HPO_4.12H_2O$	35	1522	n.a.	256 - 281	ic
$Zn(NO_3)_2.6H_2O$	36	1828^{36C}, 1937^{24C},	$0.464^{39.9C}$, $0.469^{61.2C}$	134 - 147	c
$Mn(NO_3)_2.4H_2O$	37	n.a.	n.a.	115	n.a.
$FeCl_3.6H_2O$	37	n.a.	n.a.	223	c
$CaCl_2.4H_2O$	39	n.a.	n.a.	158	ic
$CoSO_4.7H_2O$	40.7	n.a.	n.a.	170	n.a.
$CuSO_4.7H_2O$	40.7	n.a.	n.a.	171	n.a.
$KF.2H_2O$	42	n.a.	n.a.	162 - 266	c
$MgI_2.8H_2O$	42	n.a.	n.a.	133	n.a.
$CaI_2.6H_2O$	42	n.a.	n.a.	162	n.a.
$Ca(NO_3)_2.4H_2O$	43 - 47	n.a.	n.a.	106 - 140	c
$Zn(NO_3)_2.4H_2O$	45	n.a.	n.a.	110	n.a.
$K_3PO_4.7H_2O$	45	n.a.	n.a.	145	n.a.
$Fe(NO_3)_3.9H_2O$	47	n.a.	n.a.	155 - 190	ic
$Mg(NO_3)_3.4H_2O$	47	n.a.	n.a.	142	n.a.
$Na_2SiO_3.5H_2O$	48	n.a.	n.a.	168	n.a.
$Na_2HPO_4.7H_2O$	48	n.a.	n.a.	135 - 170	ic
$Na_2S_2O_3.5H_2O$	48	1600	n.a.	209	n.a.
$K_2HPO_4.3H_2O$	48	n.a.	n.a.	99	n.a.
$MgSO_4.7H_2O$	48.4	n.a.	n.a.	202	n.a.
$Ca(NO_3)_2.3H_2O$	51	n.a.	n.a.	104	n.a.
$Na(NO_3)_2.6H_2O$	53	n.a.	n.a.	158	n.a.
$Zn(NO_3)_2.2H_2O$	55	n.a.	n.a.	68	c
$FeCl_3.2H_2O$	56	n.a.	n.a.	90	n.a.
$CO(NO_3)_2.6H_2O$	57	n.a.	n.a.	115	n.a.
$Ni(NO_3)_2.6H_2O$	57	n.a.	n.a.	168	n.a.
$MnCl_2.4H_2O$	58	n.a.	n.a.	151	n.a.
$CH_3COONa.3H_2O$	58	n.a.	n.a.	270 - 290	ic
$LiC_2H_3O_2.2H_2O$	58	n.a.	n.a.	251-377	n.a.
$MgCl_2.4H_2O$	58.0	n.a.	n.a.	178	n.a.
$NaOH.H_2O$	58	n.a.	n.a.	272	n.a.
$Na(CH_3COO).3H_2O$	58	n.a.	n.a.	n.a.	n.a.
$Cd(NO_3)_2.4H_2O$	59	n.a.	n.a.	98	n.a.
$Cd(NO_3)_2.1H_2O$	59.5	n.a.	n.a.	107	n.a.
$Fe(NO_3)_2.6H_2O$	60	n.a.	n.a.	125	n.a.
$NaAl(SO_4)_2.12H_2O$	61	n.a.	n.a.	181	ic
$FeSO_4.7H_2O$	64	n.a.	n.a.	200	n.a.
$Na_3PO_4.12H_2O$	65	n.a.	n.a.	168	n.a.
$Na_2B_4O_7.10H_2O$	68	n.a.	n.a.	n.a.	n.a.
$Na_3PO_4.12H_20$	69	n.a.	n.a.	n.a.	n.a.
$LiCH_3COO.2H_2O$	70	n.a.	n.a.	150 - 251	c
$Na_2P_2O_7.10H_2O$	70	n.a.	n.a.	186 - 230	ic
$Al(NO_3)_2.9H_2O$	72	n.a.	n.a.	155 - 176	ic
$Ba(OH)_2.8H_2O$	78	1937^{84C}, 2070^{24C},	$0.653^{85.7C}$, $0.678^{98.2C}$,	265 - 280	c
$Al_2(SO_4)_3.18H_2O$	88	n.a.	n.a.	218	ic
$Sr(OH)_2.8H_2O$	89	n.a.	n.a.	370	ic
$Mg(NO_3)_2.6H_2O$	89 - 90	1550^{94C}, 1636^{25C}	0.490^{95C}, 0.502^{110C},	162 - 167	c

$KAl(SO_4)_2.12H_2O$	91	n.a.	n.a.	184	n.a.
$(NH_4)Al(SO_4).6H_2O$	95	n.a.	n.a.	269	n.a.
$Na_2S.51/2H_2O$	97.5	n.a.	n.a.	n.a.	n.a.
$LiCl.H_2O$	99	n.a.	n.a.	212	ic
$CaBr_2.4H_20$	110	n.a.	n.a.	n.a.	n.a.
$Al_2(SO_4)_2.16H_2O$	112	n.a.	n.a.	n.a.	n.a.
$MgCl_2.6H_2O$	115 - 117	1450^{120C}, 1442^{78C},	0.570^{120C}, 0.598^{140C},	165 - 169	n.a.
$NaC_2H_3O_2.3H_2O$	137	1450	n.a.	172	n.a.

n.a..: not available; c: congruent melting; ic : incongruent melting

3.16 Cross-linked polyethylene

Cross-linked Polyethylene is much like the polyethylene used in plastic bottles except for the fact that it is lightly cross-linked to prevent it from turning into a liquid when it melts. Like a liquid-solid PCM it stores energy in the forming and breaking of crystalline structure. Properties of two cross-linked polyethylene are shown in Table 8. Unlike a liquid-solid PCM, it has a stable form and can be used without encapsulation.

3.16.1 Advantages

Although higher cost than other PCMs, Therefore, low cost is required for entire heat storage system and more feasibilities than other PCMs [1]. Cross-linked polyethylene is nontoxic and mostly chemically inert.

3.16.2 Disadvantages

The operating temperatures of 110 to 140 °C are too high for some applications such as space and water heating. To the author’s knowledge no company has commercially developed cross-linked polyethylene for heat storage applications at this time.

3.17 Polyalcahols

There has also been research done in playschools [1]. Polyalcahols store energy in a structure change from a heterogeneous state at lower temperatures to a face centered cubic form at higher temperatures [6]. Polyalcahols have many advantages over solid-liquid PCMs such as small volume change, no leaking, and no degradation of the material [6]. These advantages come with the disadvantages of low latent heat, high phase change temperatures, and higher cost. Wang [6] reports a system of combining polyalcahols to adjust working temperatures. Some of his results are shown in Table 8 for Neopentyl Glycol (NPG)/ Penaerythritol (PE) and Neopentyl Glycol (NPG)/Trihydroxy Mthyl-Aminomethane (TAM) systems.

Table 7: List of organic and inorganic eutectics [1, 2, 10, 12, 94 - 99]

Name	Composition (wt %)	Melting point (^OC)	Latent Heat of fusion (k J/ kg)
$Na_2SO_4+NaCl+KCl+H_2O$	31+13+16+40	4	234
$Na_2SO_4+NaCl+NH_4Cl+H_2O$	32+14+12+42	11	n.a.
$C_5H_5C_6H_5+(C_6H_5)_2O$	26.5+73.5	12	97.9
$Na_2SO_4+NaCl+H_2O$	37+17+46	18	n.a.
$Na_2S_4+MgSO_4+H_2O$	25+21+54	21 - 24	n.a.
$C_{14}H_{28}O_2 + C_{10}H_{20}O_2$	34 + 66	24	147.7
$Ca(NO)_3.4H_2O + Mg(NO)_3.6H_2O$	47 + 53	30	136
$NH_2CONH_2 + NH_4NO_3$	-	46	95
$Mg(NO_3)_2.6H_2O + NH_4NO_3$	61.5 +38.4	52	125.5
$Mg(NO_3)_2.6H_2O + MgCl_2.6H_2O$	58.7 + 41.3	59	132.2
$Mg(NO_3)_2.6H_2O + Al(NO_3)_2.9H_2O$	53 +47	61	148
$Mg(NO_3)_2.6H_2O + MgBr_2.6H_2O$	59 + 41	66	168
Napthalene + Benzoic Acid	67.1 + 32.9	67	123.4
$AlCl_3+NaCl+ZrCl_2$	79+17+4	68	234

$AlCl_3+NaCl+KCl$	66+20+14	70	209
$NH_2CONH_2 + NH_4Br$	66.6 + 33.4	76	151
$LiNO_3 + NH_4 NO_3 + NaNO_3$	25 + 65 + 10	80.5	113
$AlCl_3+NaCl+KCl$	60+26+14	93	213
$AlCl_3+NaCl$	66+34	93	201
$NaNO_2+NaNO_3+KNO_3$	40+7+53	142	n.a.

Table 8: Melting point and latent heat of fusion of some selected solid - solid PCMs [1, 2, 10, 94- 99]

Name	Melting point (^{O}C)	Latent heat of fusion (kJ/kg)
38.2%NPG/61.8%PE	26 - 32	18 - 75
38.2%NPG/61.8%TAM	22 - 35	27 - 33
76.4%NPG/33.6%TAM	28 - 38	75 - 80
76.4%NPG/33.6%PE	31 - 37	35 - 46
91%NPG/9%PE	31 - 36	68
91%NPG/9%TAM	30 - 39	143 - 150
Neopentyl Glycol(NPG)	43	130
Diamnopentacrythritol	68	184
2-Amino - 2 - Methyl - 1, 3 - Propanediol	78	264
2 - Methyl - 2 - Mtro - 1, 3 - Propanediol	79	201
Trumethylolethane	81	192
Pentaglycerin	81	192
2-Hydroxymethyl-2-Methyl-1, 3 - Propanediol	81	192
Monoaminopentaerythritol	86	192
Cross-Linked Polyethylene	110 - 115	125 - 146
Tris(Hydroxymethyl)Acetic Acid	124	205
2-Amino-2-Hydroxymethyl-1, 3 - Propanediol	131	285
Cross-Linked HDPE	125 - 146	167 - 201
2,2-Bis(Hydroxymethyl) Propionic Acid	152	289
38.2%NPG/61.8%PE	170	147
Penterythritol(PE)	185	303

4.0 Latent Heat Storage Systems

The intermittent and dynamic nature of solar irradiance and the need to utilize solar energy systems in a continuous and static load, make the use of storage systems essential in most of the potential uses of solar energy. Amongst the various heat storage techniques of interest is latent heat storage in comparison to sensible heat storage. The use of phase change materials (PCMs) can be found in solar energy storage systems for water heating, green houses, heating and cooling of buildings, cooking and waste heat recovery systems.

4.1 Solar water heating

Solar water heater is getting popularity [21-23] since they are relatively inexpensive and simple to fabricate and maintain. Prakesh et al. [24] analyzed a built in storage type water heater containing a layer of PCM filled at the bottom (Fig. 2). During the sunshine hours, the water gets heated up which in turn transfers heat to the PCM below it. The PCM collects energy in the form of latent heat and melts. During off sunshine hours, the hot water is withdrawn and is substituted by cold water, which gains energy from the PCM. The energy is released by the PCM on changing its phases from liquid to solid. This type of system may not be effective due to the poor heat transfer between PCM and water.

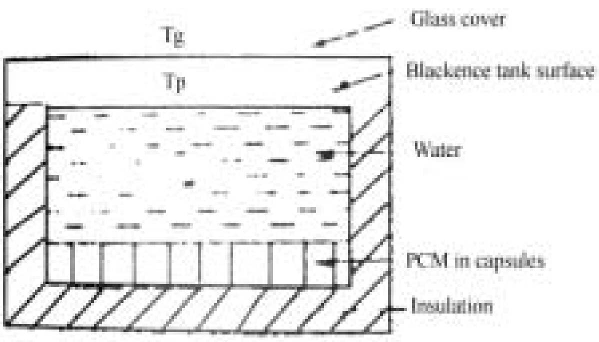


Fig.2: Built -in storage type heater with PCM layer

A cylindrical storage unit in the closed loop with a flat plate collector (Fig.3) has been theoretically studied by Bansal and Buddhi [25] for its charging and discharging mode. As a result, a theoretical model for cylindrical latent heat storage system was developed. The calculations for the interface moving boundary and fluid temperature were made by using paraffin wax (p-116) and stearic acid as phase change materials. Tiwari et al. [26] presented an analysis of a PCM storage for water heater by incorporating the effect of water flow through a parallel plate placed at the solid-liquid interface. In order to reduce the night heat losses from the exposed surface, movable insulation has been made. They concluded that the hot water (temperature 15 –20 °C > T_a) can obtain throughout the day and night, and the fluctuations in water temperature decrease with an increase in the melted region of the PCM water heater. Tayed et al. [27] developed a system for domestic hot water using $Na_2SO_4.10H_20$ as a PCM and compared with the simulation model which gives the optimum flow rate of the inlet water supply required to maintain the constant-temperature water at outlet. Font et al. [28] conducted a preliminary study for the design of a device for domestic water using solid - solid PCM. Numerical simulation has been made using unidirectional model and verified with the experimental results. The concordance between both experimentally and simulation results shows that this model is available to study the heat transfer phenomenon in the PCM in order to optimize the design of the device.

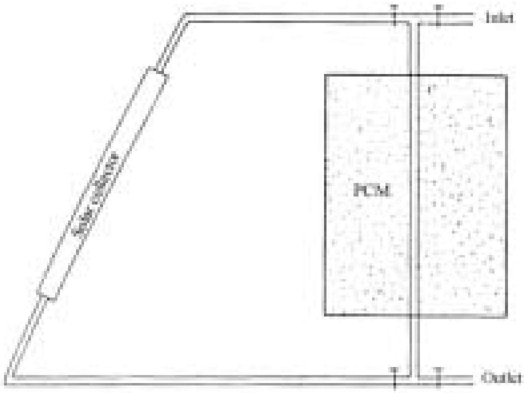


Fig.3: A domestic hot water system with separate PCM heat

Chauarsia [29] and Gu [32] reported that paraffin wax could be used as a storage system for solar water heating. Baran and Sari [30] reported the eutectic (melting point 52.3 ^{O}C, latent heat of fusion 182 kJ/kg) of palmitic acid (64.2wt%)+ stearic acid (35.8 wt%) is suitable for domestic water heating application. Bhargava [31] utilized the PCM in solar water heater and concluded that the efficiency of the system and the outlet water temperature during the evening hours increases with the increase in the thermal conductivity of the solid-liquid phases of the materials. Hasan et al. [33] has investigated some fatty acids as a phase change materials for domestic water heating. They recommended that myristic acid, palmitic acid and stearic acid, with melting temperature between 50 ^{O}C - 70 ^{O}C are the promising phase change materials for water heating. Thermophysical properties of identified PCMs were determined using differential scanning calorimeter (DSC). They concluded that the little reduction of the latent heat was found after 450 heating cycles (20–80°C), while a reduction of up to one-third of the latent heat was found after 21 heating cycles (20–150°C).

Kurklu et al. [34] developed a new type of water - PCM solar collector and its short-term thermal performance was investigated (Fig.4). The solar collector consisted of two adjoining sections one filled with water and the other with a PCM (Paraffin Wax, 45–50 ^{O}C). The results of the study indicated that the water temperature exceeded 55 ^{O}C during a typical day of high solar radiation and it was kept over 30 ^{O}C during the whole night. The present solar collector was much advantageous over the traditional solar hot water collectors in Turkey in terms of total system weight and the cost in particular. This type of collector might use of PCM–water solar panels on the south faces of buildings for energy storage applications.

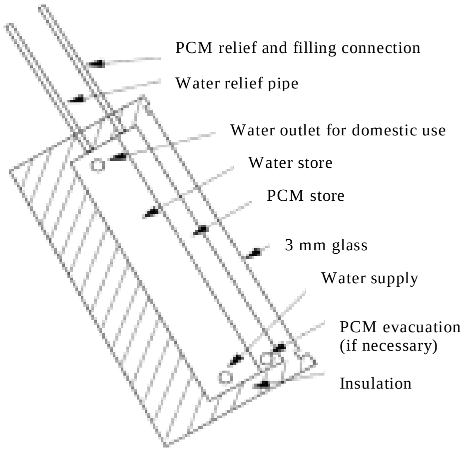


Fig.4: Water - PCM solar collector

4.2 Heating

Jurinak and Khalik [35, 36] have studied the effects of PCM on the performance of an air-based solar heating system. Their main conclusion was that the PCM should be selected based on its melting temperature, rather than its latent heat, i.e. melting temperature has a significant effect on system performance. They also reported that systems utilizing $Na_2SO_4.10H_20$ requires roughly the one-half storage volume of a conventional water tank system. An effective heat capacity for the latent heat storage unit was also obtained as a function of its mass, latent heat, specific heat, and melting temperature. Acquired effective heat capacity could used to estimate the thermal performance of the system utilizing PCM. Klein and Beckman [37] presented a simulation study for closed-loop solar thermal system, which could use for a variety of applications including space heating, absorption air conditioning, and certain types of process heating. This design method can be used to estimate the long-term performance of such type systems. Bulkin et al. [38] suggested a mathematical model for designing a solar heating and hot-water supply system on the basis of solar absorbers and a heat pump with two thermal-storage tanks, taking into account the system’s interaction with the outside climate and with the room being served. Ghoneim [39] has studied the effect of assumptions in the models of earlier studies on both the fraction of the load met by solar energy, and the required storage capacities.

Kaygusuz et al. [40] developed an experimental model to determine the dynamics of solar-assisted heat pump, collectors, dryer, and energy storage tank used for drying grains. Kaygusuz [41] investigated the performance of a dual-source heat pump system for residential heating (Fig.5). In the dual-source configuration, the evaporator is designed so that it can receive energy from either the atmosphere or from the solar-energy store. He concluded that the dual source system could save more energy than the parallel and series system. Kaygusuz [42] also conducted an experimental and a theoretical study to determine the performance of phase-change energy storage materials, and the variation of the outlet fluid temperature with different values of NTU (the number of transfer units of the storage unit) for water based solar heating systems (Fig.6). This system consists of the solar collector, energy storage tank, water-to-air heat exchanger, auxiliary electrical heater, water circulating pump and other measuring and control equipment.

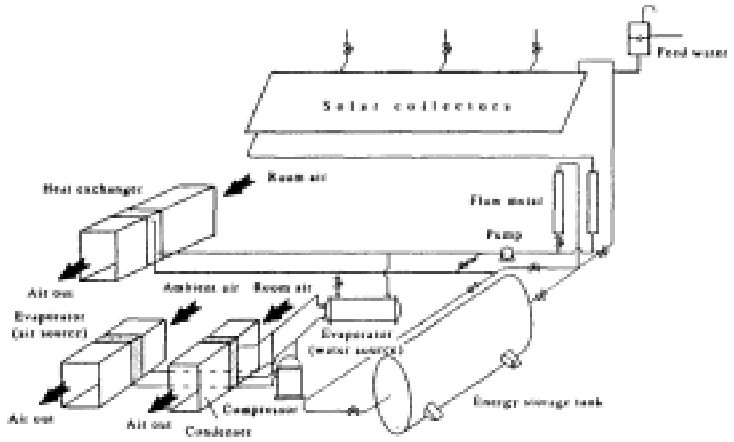


Fig.5: Solar -assisted heat pump system linked to energy storage tank

Whenever solar energy is available, it is collected and transferred to the energy storage tank that is filled by 1500 kg encapsulated phase change material (PCM) and the heat transfer fluid (water) flows parallel to them (Fig. 7). From the experimental and theoretical investigations, they concluded that heat storage is an important component in moderate climatic conditions (i.e. Trabzon, Turkey), and for this purpose, $CaCl_2.6H_20$ or $Na_2SO_4.10H_2O$ can be used as a PCM and would provide a desirable alternative to rock and water storage systems. PCM storage is more preferable as a heat source than the water and rock storage for a heat pump because the energy storage temperature of the PCM is around 25-35°C for either $CaCl_2.6H_20$ or $Na_2SO_4.10H_2O$. This temperature range is suitable for solar-assisted heat pump applications in Turkey. Mehmet [43] also investigated the thermal performance of a solar-aided latent heat storage used for space heating with heat pump using 1090 kg encapsulated PCM ($CaCl_2.6H_2O$). He concluded that the shorter and thinner pipe should be used for effective heating in the beginning of the experiments.

Fath et al. [44] developed a simple solar air heater integrated with thermal energy storage system shown in Fig. 8. Heat storage materials were filled in the tubes and set as an absorber of the collector. Paraffin Wax (melting point 50 ^{O}C, latent heat of fusion 190 kJ/kg) and $Na_2SO_4.10H_20$ (melting point 32 ^{O}C, latent heat of fusion 251 kJ/kg) are used as PCMs. These systems increase the heat transfer area; coefficient and reduce the radiation/convection losses. Based on a simple transient analysis, explicit expressions for the heater absorber and glass cover temperatures, effective heat gained, outlet air temperature, and the heater efficiency have been developed as a function of time. For the system with built-in PCM, the heat load could be provided for the 24 hrs/day, at almost constant temperature. The daily average efficiency, with paraffin wax, is about 63.35% as compared to 59% with sand as the storage material and 38.7% for the conventional flat plate heater system.

Strith et al. [45] used TIM (Transparent Insulation Material) and translucent PCM in the wall for heating the air for the ventilation of the house. Paraffin wax (melting point 25-30 ^{o}C, latent heat of fusion 150 kJ/kg) was used as a PCM and 60 kg was filled in a panel for space heating. The efficiency of solar energy absorbed into the PCM and transferred to the ventilation air was 45% on average. Manz et al. [46] also conducted same study with another PCM ($CaCl_2.6H_2O$). He developed a numerical simulation which agrees well with experimental results. He also reported that maximum time ratio parameter could be reached with a mean melting temperature of approximately 20 to 21^{O}C when building does not lose energy through the south facing TIM-PCM wall.

Arkar et al. [47] also designed a solar assisted ventilation system based on PCM storage. He recommended that paraffin - spherical encapsulations provide homogeneous porous effect in ventilation duct which can improve the thermal conductivity of paraffin. He reported that ambient air could be cooled for 3 to 4 K in a clear summer night.

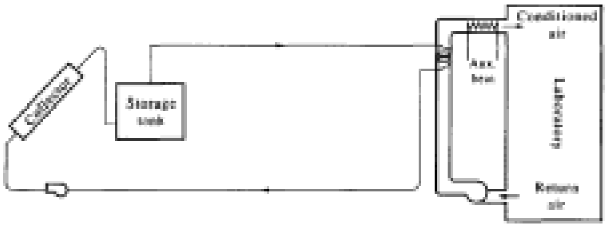


Fig.6: Schematic diagram of the base solar energy system

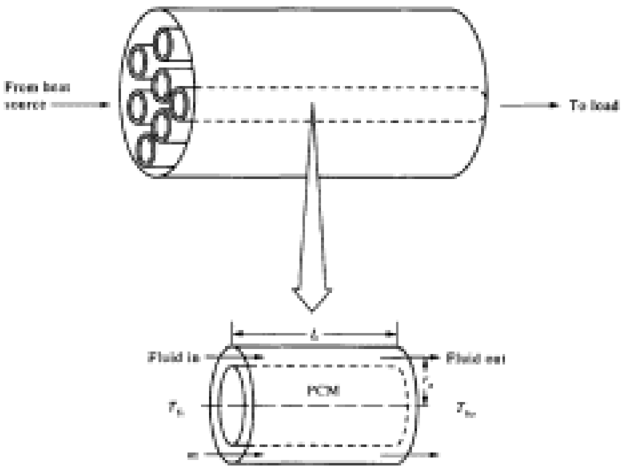


Fig.7: Schematic configuration of latent heat storage tank

A theoretical model of a shell-and-tube PCM storage unit was reported by Ismail and Alves [48]. Energy equation for the PCM is written in terms of the enthalpy. The numerical results show the effects of the Biot number, the relative diameters of the tubes, and the inlet fluid temperature on the thermal performance of the unit. Visser [49] developed a component model for numerical description of two different short term heat storage vessels. In both vessels, the energy is stored as the latent heat of PCMs. The transient simulation program was used to determine the performance of the cylindrical energy storage tank that can be used in the solar assisted domestic heating by heat pump system. Yimmer et al. [50] also developed a numerical model for optimizing a basic 1-D, shell-and-tube, thermal energy storage system. Again, an enthalpy approach was adopted for the PCM. A parametric study was then conducted to assess the effects of the inner tube and outer shell radii and of the liquid phase thermal conductivity of the PCM on the performance of the unit. Lacroix [51] developed a theoretical model to predict the transient behavior of a shell-and-tube storage unit with the PCM on the shell side and the HTF circulating inside the tubes. Then, parametric studies are performed to assess the effects of various thermal and geometric parameters on the heat transfer process and on the behavior of the system.

Sagara et al. [52] estimated the long term performance of an air based solar heating system using a PCM. Theoretical heat transfer models within a spherical capsules enclosed the PCM were studied. Effect on the overall COP was studied with respect to the capacity of the PCM storage tank, melting temperature, collector area and air flow rate. They reported that the simple uniform temperature model is useful for long term system simulations. Sari and Kaygusuz [53] developed a eutectic (lauric acid 75.5 wt% + stearic acid 24.5 wt%) for space heating. Developed eutectic melts at 37 ^{O}C with latent heat of 183 kJ/kg, thus, these properties make it an attractive PCM used for passive solar space heating applications such as building and greenhouse heating with respect to the climate conditions. Vakilaltojjar [54] developed computer models for the evaluation of thermal energy storage system for space heating and cooling applications. The effect of PCM slab thickness and fluid passage gap on the storage performance was investigated. He filled the PCMs ($CaCl_2.6H_2O$ and $KF.4H_2O$) in thin flat containers and air is passed through gaps between them. He concluded that the air velocity profile at the entrance does not affect the heat transfer characteristics and the outlet air temperature considerably. Using smaller air gaps and thinner PCM slabs can obtain better performance, however, this increases the number of PCM containers and the total volume of the storage system which will lead to higher-pressure drop across the storage system.

4.3 Cooling

The most common storage media for space cooling are water, ice and PCMs, commonly known as eutectic salts. PCMs have been used for various heat storage applications since the 1800s, but they have only recently been used as a storage media for space cooling. So far, most of the PCMs for cool storage are inorganic salt hydrates, organic paraffin waxes and mixtures of these. Literatures available on thermal storage at a temperature below the ambient, other than for ice are limited. A theoretical simulation of cool storage was reported by Solomar et al. [55]. BoHe et al. [56] investigated the potential for using cool storage systems using PCMs and static and dynamic cool storage process are discussed. They reported that the Rubitherm RT5 (melting point 7 ^{O}C, latent heat of fusion 158.3 kJ/kg) appears to be an excellent candidate as a PCM for cool storage because of its economical cost, congruently melting, self-nucleation property, no super cooling and stable during a number of cooling and heating cycles.

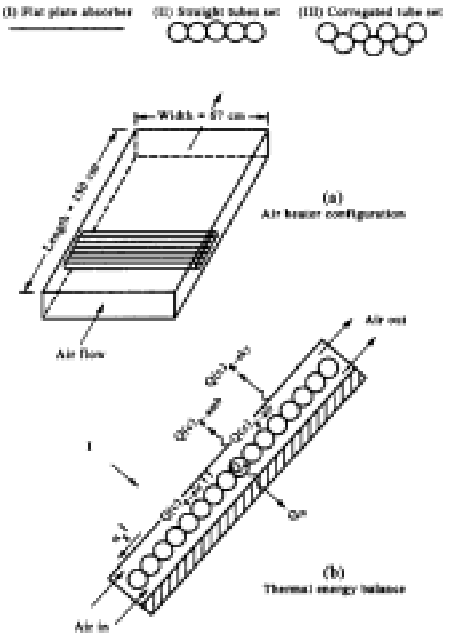


Fig.8: Solar air heater configuration with set of PCM tubes

A search for literature on commercial chemical products on PCMs for cool storage for the temperature range 15 - 23 ^{O}C was carried out [57]. Nagano et al. [58] investigated the thermal characteristics of manganese (II) nitrate hexahydrate (melting point 25.8 ^{O}C, latent heat of fusion 125.9 kJ/kg) as a PCM for cooling systems. They reported that almost all chlorides were effective in modulating the melting point of $Mn(NO_3)_2.6H_2O$. $MnCl_2$ $.4H_2O$ was an effective additive with respect to modulation of melting point, reduction of super cooling and quantity of the heat of fusion. The temperature differences required for melting and solidification from the melting point measured by DSC are about 6 ^{O}C for melting process and 4 ^{O}C for solidification process for the mixture of $Mn(NO_3)_2.6H_2O$ and 4.0 wt% of $MnCl_2$ $.4H_2O$ The indoor air at temperature of 28 ^{O}C in daytime and the outside cool air at night below 16 ^{O}C can be utilized to melt and solidify this mixture. Farid et al. [59] studied the feasibility of cool storage using dimethyl-sulfoxide (melting point 16.5 ^{O}C) as a PCM in rectangular container. Based on the experimental results and the model predictions, dimethyl-sulfoxide can be used as a PCM for cool storage. The results also show that, cooling extraction period depends on the amount of solidified PCM. The cool extraction period was completed when the outlet air temperature from the PCM section reached at 25 ^{O}C. This temperature is considered the highest temperature at which the human may feel comfortable.

Saitoh and Hirose [60] studied the thermal characteristics of an encapsulated thermal storage tank experimentally and theoretically. They used $Na_2HPO_4.12H_2O$ as PCM to fill cylindrical capsules with an inside diameter of 70.7 mm. They concluded that the main factors affecting the charging process were the capsule size, coolant flow rate, coolant temperature, and capsule material. Kondepudi et al. [61] discussed the effect of Biot number, Stefan number and Fourier number on the thermal performance of cold storage. Laybourn [62] utilized a concept of thermal resistance, which embraced the convective resistance, wall resistance, and ice layer resistance to calculate the cold storage of the tank with rectangular capsules. Arnold [63] analyzed the heat transfer during the freezing and melting process by performing a series of charging and discharging experiments. Chen [64 -66] developed a general lump model to predict the thermal performance of a cold storage system. The results showed that the lump model is a convenient and simple method to determine the thermal performance of cold storage system. Ryu et al. [67] used a rectangular storage tank with copper tube container and conducted a series of experiments using both vertical and horizontal tank to investigate the heat transfer characteristics. In the area of subcooling of water, Chen [68] conducted a series of experiments to investigate the subcooling phenomenon and the freezing probability of water with and without nucleation agents inside a cylinder. They verified that the addition of nucleation agents is one of the approaches to improve the subcooling phenomenon effectively. Chen et al. [69] experimentally investigated the pressure drop of an encapsulated thermal storage tank during the charging process. The cylindrical capsules inside the thermal storage tank utilize water added with nucleation agents as PCM, and the coolant is the aqueous solution of ethylene glycol. They concluded that high cold storage could obtain by using the lower inlet coolant temperature with high flow rate. The heat transfer coefficient increases as the coolant flow rate increases. The pressure drop flowing through tank is enlarged as the coolant flow rate increases during the charging process.

4.4 Green house heating

Solar agricultural greenhouses have been widely used in the past two decades in order to increase plant quality and productivity and to reduce consumption of fossil fuels for heating and cooling. The most effective greenhouses require control of temperature, humidity, solar irradiance and internal gas composition with rational consumption of energy. Research work in this area, involving studies of new materials, heat storage and heat exchange devices resulted in some interesting demonstration units followed by rapid commercial applications. The most frequently used PCM for these purposes is $CaC1_2.6H_2O$, $Na_2SO_4.10H_2O$, PEG, and paraffins.

Nishina and Takakura [75] conducted a research applying $Na_2SO_4.10H_20$ with some additives to prevent phase separation and degradation for heating a greenhouse in Japan. Fig. 9 shows the general view of the experimental set-up. This study concluded that although 8°C target inside was achieved, only 40-60% of the latent heat potential of the PCM was realized which indicated that almost half of the PCM was not used efficiently during the energy exchange processes. Takakura et al. [70] tested polyethylene glycol and $CaCl_2.6H_2O$ as a PCMs in greenhouse heating for 7.2 m^2 ground area. They compared conventional greenhouse with PCM storage type greenhouse. Efficiency of the greenhouse with PCM storage integrated with solar collector was 59 % and able to maintain 8°C inside the greenhouse at night, when the outside temperature dropped to - 0.6°C. A microcomputer control system has been developed in order to establish more accurate and more sophisticated control for solar greenhouse systems.

CNRE-France conducted a study using a glass-covered multi-span greenhouse with 500 m^2 ground area, dedicated to rose production, by utilizing 13.5 tons of $CaC1_2.6H_20$ (melting at 28°C) by Jaffrin and Cadier [66] and by Jaffrin [71, 72]. Thermal and crop performance of this greenhouse was compared with an air-bubble double plastic-covered and a conventional greenhouse. Figure 10 shows the arrangement of the PCM containers in underground. The containers were placed in concrete shelves with five layers in semi-circular tunnels and air was used to transfer heat. The outcome of this study was that with this system, propane gas savings of 80 and 60% in comparison with the conventional and double-covered greenhouses, respectively, was obtained. Electricity consumption of the fans was determined to be less than 10% of the heating load of the greenhouse.

Levav and Zamir [73] tested $CaC1_2.6H_20$ in greenhouse. They reported that required air temperature in the greenhouse was achieved without any increase in the relative humidity. It was stressed that the most important drawback of the system was the $1.1/kg cost of the PCM. Furthermore, they indicated that the 24°C melting temperature of the PCM could be high for some crops.

Kern et al. [74] used $CaC1_2.6H_20$ as a PCM in aerosol cans to investigate energy storage possibilities both inside and outside a 36 m^2-ground area greenhouse covered with fiberglass. Results of this study indicated that while the external unit released about 80-90% of the energy absorbed, this was 60-80% for the internal energy storage unit. Paraffin's have also been used for energy storage in greenhouses. A study performed by Bagetinelik et al. [78] was the only work in literature using paraffin (48 - 60 ^{O}C , Latent Heat of Fusion 190 kJ/kg) for greenhouse heating.

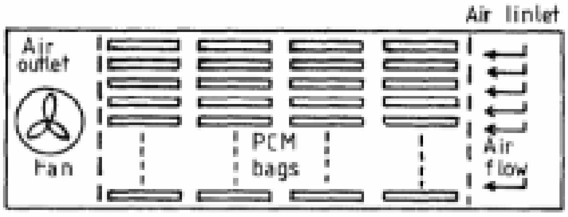


Fig.9: General view of phase change energy storage system

The latest studies on the $Na_2SO_4.10H_20$ based PCM applications in greenhouses were those of Ktirklti et al. [76, 77]. In their study, two types of a similar PCM, one with a melting range of 22 - 25°C and the other with about 8°C, were employed, the former for the reduction of peak temperatures towards summer and the latter for frost prevention in both greenhouses.

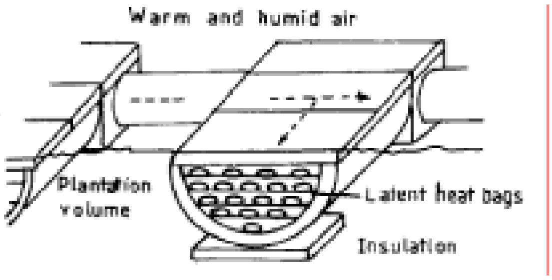


Fig.10: Underground tunnel: equipped with a PCM

Figure 11 shows the experimental set-up for both applications. Results revealed that about 2.5 - 3°C temperature difference existed between the PCM greenhouse and the control one throughout the experimental period, and that solar collection efficiency on an outside solar radiation basis was 29% for the experiments with the PCM with higher melting temperature. Similarly, the temperature difference and solar collection efficiency was found to be about 22°C and 30%, respectively during the frost prevention experiment, and frost occurrence was prevented on 7 out of 9 frosty occasions. Most applications were carried out in either double-covered greenhouses or greenhouses with one or more layers of thermal screens. The only study that barely defined the effect of the PCM store on the environmental parameters of a greenhouse seemed to be those of Kuruklu et al. [76, 77]. However, all studies imply that PCMs could be used for both energy storage and humidity control in greenhouses, in a way for energy management, effectively given the right choice and design of the whole system.

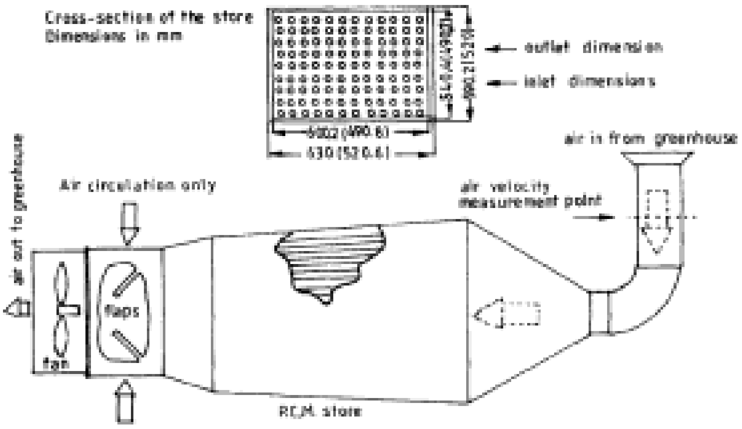


Fig.11: General view of the storage used for energy management in greenhouse

4.5 Solar cooking

Solar cookers are used to cook rice, vegetables, meat, bake cakes, etc. The detailed design, testing, theory and utility of box-type solar cookers are well developed [79 - 86]. The use of these cookers is limited because they do not have any storage, i.e. these cookers cannot be used on cloudy days or in late evening. The use of PCMs for storing the heat in the form of latent heat has been recognized as one of the areas to provide a compact and efficient storage system due to their high storage density and constant operating temperature [80, 81].

A box type solar cooker with latent heat storage has been designed and fabricated for the composite climatic conditions of India by Buddhi and Sahoo [87]. Commercial grade stearic acid (melting point 55 ^{O}C, latent heat of fusion 161 kJ/kg) used as a latent heat storage material. Fig. 12 shows the sketch of a box-type solar cooker for one vessel having a PCM to store the solar energy. The cooker consists of an aluminum-absorbing tray ‘A’. In the center of the absorbing plate, a cylindrical container of 0.165 m diameter and 0.02 m in depth has been welded (shown in Fig. 1by ‘C’), and the cooking pot is to be kept tightly in it. This container will provide a heat transfer from the absorbing plate and PCM. Moreover, aluminum fins were also provided at the inner side of the tray and cylindrical container. The outer tray ‘B’ is also made from the same aluminum sheet. The distance between tray ‘A’ and tray ‘B’ was kept at 0.025 m on the bottom side. Tray ‘B’ was filled with 3.5 kg of commercial grade Stearic Acid (PCM) and it was made sure that the PCM should be in good contact with the bottom side of tray ‘A’. The space between tray ‘B’ and the casing was filled with glass wool to provide thermal insulation to the bottom and sides of the solar cooker. A flat glass mirror was fixed in an aluminum cover to serve as a booster and as a cover for the glass lid when the cooker is not exposed to solar radiation. The aluminum tray ‘A’, cooking pot and its cover were painted with a dull black paint on the outside. The experimental results demonstrate the feasibility of using a phase change material as the storage medium in solar cookers, i.e. it is possible to cook the food even in the evening with a solar cooker having latent heat storage. It also provides a nearly constant plate temperature in the late evening.

Domanski et al. [88] investigated the possibility of cooking during off-sunshine hours using phase change materials (PCMs) as storage media. They designed the storage-cooking vessel for off sunshine hours (Fig. 13). For this purpose, two concentric cylindrical vessels (0.0015 m thick), made from aluminum, are connected together at their tops using four screws to form a double-wall vessel with a gap between the outer and inner walls. The outer and inner vessel has a diameter of 0.18 m and 0.14 m. The annular gap between the outer and inner vessels is 0.02 m. This gap is covered with a removable aluminum cover into which three circular holes were drilled to allow inserting of thermocouples and permit direct visualization during filling or removing of the PCMs. A circular aluminum cover is used as the lid for the inner vessel.

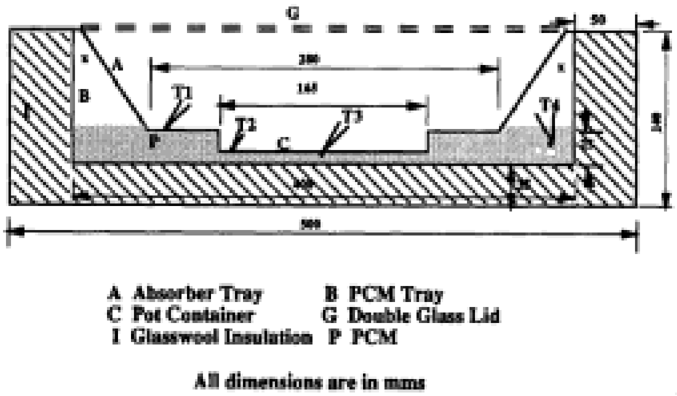


Fig.12: Schematic diagram of the box of a solar cooker with PCM storage

The outside surfaces of the outer vessel and the covers are painted using ordinary black paint for maximum absorption of available solar radiation. The gap between the outer and inner vessels is filled with 1.1 kg of stearic acid (69 ^{O}C, 95% pure), or 2 kg of magnesium nitrate hexahydrate (89 ^{O}C, 99% pure), which leaves sufficient space for expansion of the PCMs on melting. They concluded that the cooker performance evaluated in terms of charging and discharging times of the PCMs under different conditions. He reported that performance depends on the solar irradiance, mass of the cooking medium, and the thermo physical properties of the PCM. The overall efficiency of the cooker during discharging was found to be 3-4 times greater than that for steam and heat-pipe solar cookers, which can be used for indoor cooking. In such type of design, the rate of heat transfer from the PCM to the cooking pot during the discharging of the PCM is slow, and more time is required for cooking the evening meal.

Sharma et al. [89] designed and developed a cylindrical PCM storage unit for a box type solar cooker to cook the food in the late evening. Since this unit surrounds the cooking vessel, the rate of heat transfer between the PCM and the food is higher, and cooking can be faster. For this purpose, a PCM container to hold the cooking vessel was designed and fabricated as shown in Fig. 14. It has two hollow concentric aluminum cylinders of diameter 18 cm and 25 cm and 8 cm deep of 2 mm thickness. The space between the cylinders was filled with acetamide (melting point 82 ^{O}C, latent heat of fusion 263 kJ/kg) as a PCM. The dimensions of the vessel used for cooking were 17.5 cm and 10 cm in diameter and height, respectively, and it can be inserted inside the PCM container for cooking purposes. To enhance the rate of heat transfer between the PCM and the inner wall of the PCM container, 8 fins (1x3 cm) were welded at the inner wall of the PCM container. They reported that by using 2.0 kg of Acetamide as a latent heat storage material, the second batch of food could be cooked if it is loaded before 3:30 P.M. during the winter season. They recommended that the melting temperature of a PCM should be between 105 and 110 ^{o}C for evening cooking. Therefore, there was a need to identify a storage material with appropriate melting point and quantity, which can cook the food in the late evening. To store a larger quantity of heat in a PCM, more input solar radiation would be required. Hence, Buddhi and Sharma [90] used a latent heat storage unit for a box type solar cooker with three reflectors. They used acetanilide (melting point 118 ^{o}C, latent heat of fusion 222 kJ/kg) as a PCM for night cooking. To conduct the cooking experiments with the PCM storage unit, a double glazed (glass covers) box type solar cooker having 50 cm x 50 cm aperture area and 19 cm deep was used. In this solar cooker, three reflectors were provided, i.e. the middle reflector was mounted with a hinge and had rotation only about the horizontal axis. The other two reflectors were fixed by a ball and socket mechanism in the left and right sides of the reflector. This pair of reflectors has three degrees of freedom, i.e. they can have movement about the horizontal axis and vertical axis and can rotate about both the axes. By these mechanisms, efforts were made to keep the reflected solar irradiance on the absorber surface to enhance the incident solar radiation on the glass cover during the course of the sun exposure experiments.

Following Sharma et al. [90], a cooking vessel with latent heat storage was designed and fabricated to cook the food in night / late evening. The unit has two hollow concentric aluminum cylinders of diameter 20 and 30 cm and 12.5 cm deep of 2 mm thickness. The space between the cylinders was filled with 4.0 kg of PCM to conduct the cooking experiments with all three reflectors. The dimensions of the vessel used for cooking were 19 and 15 cm in diameter and height, respectively, and it can be inserted inside the PCM storage unit for cooking purposes. To enhance the rate of heat transfer between the PCM and the inner wall of the PCM container, 8 fins (1 cm x 3 cm) were welded at the inner wall of the PCM container. From the experimental results one can conclude that the cooking experiments were successfully conducted for the evening time cooking up to at 8 P.M. with 4.0 kg of PCM during winter season in India.

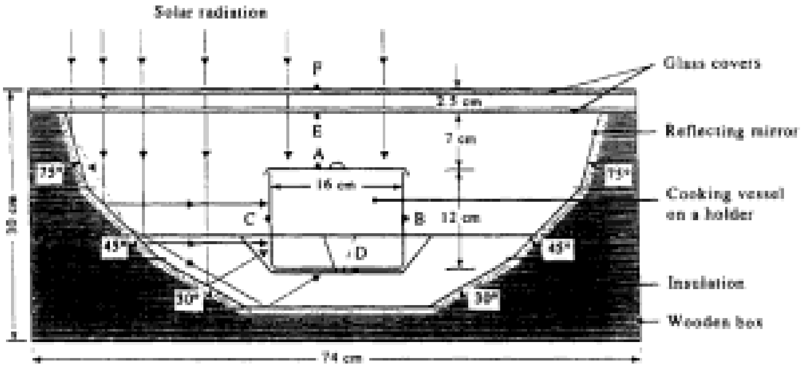


Fig.13: Solar Cooker with PCM Cooking Container

Sharma et al. [91] developed a solar cooker based on Evacuated Tube Solar Collector (ETSC) with PCM storage, as shown in Fig. 15. It consists of an ETSC, a closed loop pumping line-containing water as Heat Transfer Fluid (HTF), a PCM storage unit, cooking unit, pump, relief valve, flow meter and a stainless steel tubing heat exchanger. PCM storage unit has two hollow concentric aluminum cylinders, and its inner and outer diameters are 304 mm and 441 mm respectively and 420 mm deep with 9 mm thickness (Fig. 16). The space between the cylinders was filled with 45 kg erythritol (melting point 118 ^{O}C, latent heat of fusion 339.8 kJ/kg) used as the PCM. A pump circulates the heated water (HTF) from the ETSC through the insulated pipes to the PCM storage unit by using stainless steel tubing heat exchanger that wraps around the cooking unit by closed loop. During sunshine hours, heated water transfers its heat to the PCM and stored in the form of latent heat through stainless steel tube heat exchanger. This stored heat is utilized to cook the food in the evening time or when sun intensity is not sufficient to cook the food. They concluded that two-time cooking (noon and evening) was done in a day. Noon cooking did not affect the cooking in evening and evening cooking using PCM storage was found faster than noon cooking. Experiments and analysis indicated that the prototype solar cooker yielded satisfactory performance in spite of low heat transfer, the modified design of heat exchanger in the thermal storage unit will enhance the rate of heat transfer in the present set-up.

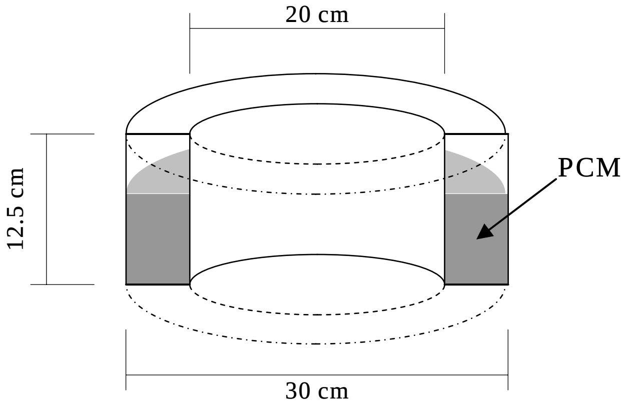


Fig.14: A schematic diagram of the latent heat storage unit

Ramadan et al. [92] designed a simple flat-plate solar cooker with focusing plane mirrors using energy storage materials. In his design, a jacket of sand (1/2 cm thick) around the cooking pot has improved the cooker performance tremendously. They concluded that six hour per day of cooking time has been recorded. Approximately three hours per day of indoor cooking has been achieved. An overall energy conversion efficiency up to 28.4% has been obtained. The possibility of using a PCM as a storage medium to obtain longer cooking periods was studied. A thin layer of the salt hydrate $Ba(OH)_2 \cdot 8H_2O$ as a jacket around the cooking pot was suggested. Bushnell [93] presented a prototype for solar ovens, which employs pentacrythritol as a solid-solid PCM. He described the performance from efficiency measurement and determination of figure of merit.

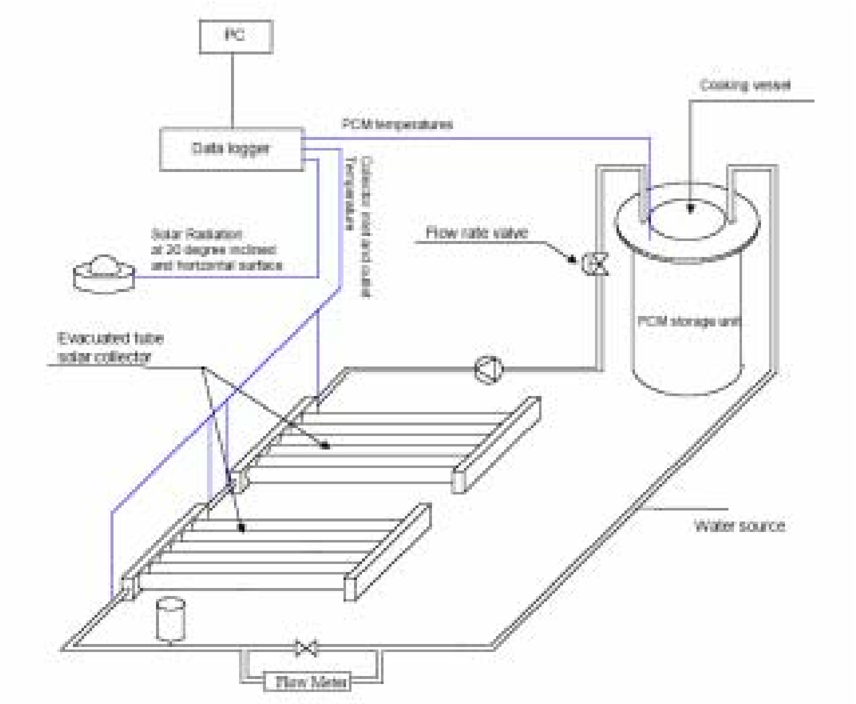
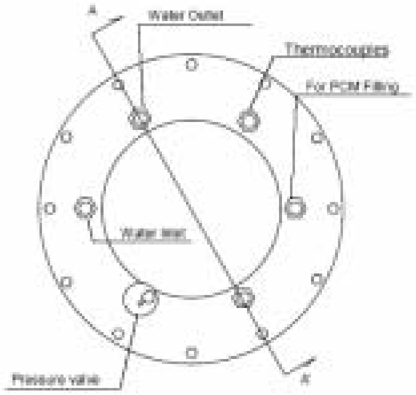


Fig.15: Outline of the prototype solar cooker based on evacuated tube solar collector with PCM storage unit



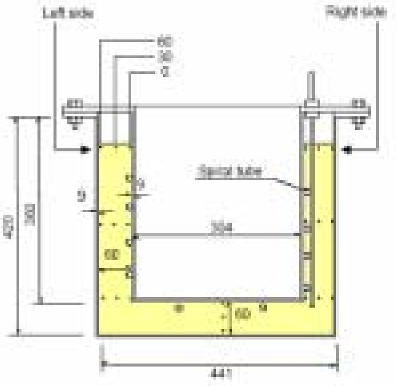


Fig. 16 (a): Sectional view of the PCM storage unit

Fig. 16(b): Vertical view of the PCM storage unit

4.6 Waste heat recovery systems

Air conditioning system ejects (sensible and latent) heat, in which sensible heat accounts for about 15 - 20% of the total exhausting heat [101]. The exhausting temperature of compressor is relatively high (< 65 ^{O}C) when using Freon as refrigerant. Therefore, it can be recovered using an accumulator and gets heat of higher temperature. Zu et al. [32] developed a heat recovery system using PCM to recover the ejected heat of air conditioning system and producing low temperature hot water for washing and bathing. They concluded that the heat recovery system decreases not only the consumption of primary energy for heating domestic hot water but also the calefaction to the surroundings due to the rejection of heat from air conditioning systems. It was observed that the efficiency ratio of the system is improved effectively when all the rejected (sensible and latent) heat from air conditioning systems is recovered. The technical grade paraffin wax and the mixtures with liquid paraffin and lauric acid qualify as PCM for heat recovery of air conditioning system.

An effective utilization of urban waste heat from co-generation systems, typically available at temperatures of 60 - 100 ^{O}C. Kakiuchi et al. have investigated erythritol (Melting point 118 ^{O}C; Latent heat of fusion 339.8 kJ/kg) [102, 103] that can be used for relatively high temperature industrial waste heat processes. Several studies have been done on stearic acid [104, 105]. This material has a melting point between 60 - 70 ^{O}C and is expensive. It has only found of limited use in waste heat systems. Nagano et al. [106] proposed a mixture of $Mg(NO_3)_2.6H_2O$ as a base material with $MgCl_2 \cdot 6H_2O$ as an additive to modulate the melting point. They reported that addition of 5 - 10 wt% of $MgCl_2 \cdot 6H_2O$ can set the $Mg(NO_3)_2.6H_2O$ (melting point 80 ^{O}C, latent heat of fusion 150 kJ/kg). Increasing the mix ratio had little effect on heat of fusion, but allowed the melting point to be reduced to about 60 ^{O}C. No degradation in the melting point and latent heat of fusion was observed after 1000 accelerated thermal cycles. Yagi et al [107] conducted fundamental studies on heat transfer for developing a heat storage process by latent heat for recovering the high temperature waste heat over 500 K. Heat transfer experiments were attempted for a single encapsulated phase change materials and for a packed bed. The metal PCMs were found to be excellent for heat storage because of uniform temperature in the capsule. Simulation results shows that the concurrent flow for heat storage and release showed better result for effective use of storage heat than counter-current flow.

Buddhi [108] designed and fabricated a shell and tube type heat exchanger for low temperature waste heat recovery using stearic acid (melting point 59 ^{O}C, latent heat of fusion 198 kJ/kg) was used as a PCM for this study. Thermal performance of this system was evaluated for charging and discharging process of PCM for different mass flow rates. Schematic diagram of the shell and tube heat exchanger is shown in Fig. 17. Used PCM has poor thermal conductivity, to enhance the effective thermal conductivity of the system, the radial distance between the tubes was kept 3 to 4 cm. Shell was filled with 50 Kg commercial grade stearic acid being used as latent heat storage media. Flowing hot water through HTF tubes started the energy-charging test, and the stored energy was extracted by passing cold water in the HTF tubes. Ambient temperature, flow rate and PCM temperatures of the heat exchanger were also measured simultaneously at an interval of 15 minutes. He concluded that the experimental results show the feasibility of using PCM as storage media in heat recovery systems. Due to poor thermal conductivity of the PCM the overall heat transfer coefficient is quite low and fins should be provided to increase the effectiveness of the heat exchanger. Distance between tubes, fins and mass flow rates should be selected carefully in order to optimize the performance of the heat exchanger. Paraffin wax (melting point 54 ^{O}C, latent heat of fusion 184 kJ/kg) was also used in shell and tube type heat exchanger for waste heat recovery [109]. Fins were also used for effective heat transfer.

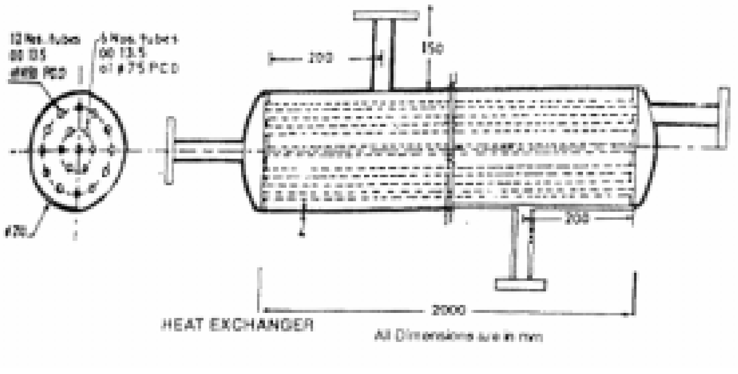


Fig. 17: Shell and tube type heat exchanger with latent heat storage material

5.0 Latent Heat Storage Exchanger

Latent heat storage systems mainly depends on heat storage material investigations and on the development of heat exchangers that assure a high effective heat transfer rate to allow rapid charging and discharging. Heat exchanger with high temperature PCM not only has a high capacity to store thermal energy, but also can make the stored energy to be highly applicable. It is always a problem to get a sufficient rate of heat transfer from the latent thermal energy storage systems due to the poor design of heat exchanger. So far, some different types of heat exchangers have been developed to overcome this shortage. Double pipe heat exchanger for latent thermal energy storage has been studied [110]. This research suggested that heat transfer rate can be enhanced by increasing the air inlet temperature, air mass flow rate and heat exchanger length. Single full-length heat exchanger exhibited better thermal effectiveness than two half-length and equal capacity parallel heat exchangers. A direct contact heat exchanger with an immiscible heat transfer fluid moving in the PCM has eliminated the permanent heat exchange surface and has been confirmed to prevent phase separation of the PCM [111 - 113].

Classical double-pipe or shell-and-tube heat exchangers have been applied in the storage energy systems and a relevant theoretical and experimental analysis of the phase-change phenomenon has been restricted to geometry of a cylindrical capsule [114], an annulus gap, spherical or rectangular enclosures [115]. Another novel configuration includes the use of three types of PCMs with different melting temperature [116]. This allows for maximum use of the HTF energy. Use of plate heat exchangers was thought to provide more efficient and compact heat exchange configuration [117]. Erk and Dudukovic [118] presented a novel energy storage system consisting of n-octadecane retained by capillary forces in a porous silica support. This configuration eliminates the expensive heat exchange surface, provides higher energy density, and gives higher rates of energy storage and release. Lecomte et al [119] presented a design method for sizing a shell-and -tube latent heat exchanger for a thermal system under thermodynamic conditions. They concluded that high flow rates could not deliver significant heat from PCM to the load. Discharging of heat from PCM to the load depends on the performance of the heat exchanger and thermophysical properties of the PCM. Bathelt [120] studied the heat transfer during melting from a horizontal cylindrical heat source with a uniform surface heat flux and a uniform surface temperature by circulating a fluid through a multipass heat exchanger embedded in n-heptadecane and n-octadecane. The instantaneous shape of the melt volume was recorded photographically and local heat transfer coefficients at the solid - liquid interface were determined. For quasi-steady melting, the local and average heat transfer is correlated in dimensionless form. Using the correlation, the solid-liquid interface position was calculated and found to be in good agreement with experimental data.

Saxena et al. [121] presented a preliminary model for estimating possible thermal energy storage in shell and tube heat exchanger. Effect of various parameters such as thermal and physical properties of PCM and convective fluid, heat exchanger dimensions and heat transfer fluid flow rates both in laminar and turbulent regime on energy storage times are discussed. El - Kassaby et al. [122] simulated the behavior of a low-temperature PCM in a heat exchanger for short-term storage. An excellent agreement was obtained for the outlet air temperature when compared with the experimental measurements, and differences did not exceed 0.5°C over the simulated period. This simulation approach can be used for any PCM with known thermophysical properties and able to predict the transient moving front for freezing or melting, mass fraction of either liquid or solid phase to the total PCM mass.

Kamimoto et al. [123] developed a latent heat thermal storage exchanger using form-stable high-density polyethylene. In their design, the hot fluid entered into the exchanger from the top end during the charging process, whilst cold fluid entered into the exchanger from the bottom end during the discharging process. No explanation was given as to why such an operation mode was adopted. Bellecci et al. [124] numerically simulated the cyclic thermal processes in a shell-and-tube latent heat thermal storage exchanger. In their design the hot and cold fluids were introduced from the same end of the storage exchanger for the successive charge and discharge processes. Gong et al. [125] tried to find, which operation mode is better in-between Kamimoto [123] and Bellecci et al. [124]. They developed a finite element model to simulate the cyclic thermal process occurring in a shell-and-tube latent heat thermal storage exchanger. This exchanger consists of a tube, which surrounds by an external coaxial cylinder made up of a PCM. A heat-transfer fluid flows through the tube to store or extract thermal energy from the PCM. Numerical experiments indicated that introducing the hot and cold fluid from the same end of the storage exchanger is more desirable than introducing the hot and cold fluid from different ends of the storage exchanger. Numerical results also provide the guidance for selection of the appropriate mode. The results are limited to only conduction-controlled melting/freezing heat transfer in the PCM.

Hasan[126] developed a simple tube-in-tube heat exchanger for thermal energy storage with stearic acid as a PCM. He found that the melting front moves in the radial direction inward as well as in the axial direction from the top toward the bottom of the PCM tube. Melting front speed was enhanced by a convection heat transfer mechanism in the melted PCM. Phase transition can also be fast by placing the heat exchanger in a horizontal position rather than a vertical one. He et al. [127] presented a theoretical analysis and experimental tests on a novel shell-and-tube latent heat exchanger which provides a basis for optimal design and operation of the heat exchanger. They reported that some parameters, such as the inlet temperature, the velocity of fluid, the thickness of the PCM and the length of the flow channel have visible effects on the heat transfer performance of the unit. Stable heat output can be obtained by increasing the entrance temperature of heat transfer fluid, PCM thickness, and flow channel length. Banaszek et al. [128] used a spiral heat exchanger in latent heat storage unit. Compactness, enhanced heat transfer due to centrifugal forces, easy sealing, large heat transfer surface, and a shorter undisturbed flow length are the most appealing features of this system. Qarnia et al. [129] presented a mathematical model for simulating the thermal behavior of a cross - flow heat exchanger with layers of PCM sandwiched between the hot and cold air streams to prevent frosting. Mathematical model was validated with experimental data. It was found that thermal resistance affects the exchanger performance by reducing the dimensionless outlet temperature of the cold air stream.

6.0 Measurement Techniques of Thermo-physical Properties

The different measurement techniques presently used for latent heat of fusion and melting temperature of PCMs may be classified as (i) Drop Calorimeter (DC) (ii) Differential Thermal Analysis (DTA) (iii) Differential Scanning Calorimeter (DSC). The DC method requires a long time and the accuracy of the results is also not good [21]. In DSC & DTA techniques sample and reference materials are heated at constant rate. The temperature difference between them is proportional to the difference in heat flow between the two materials and the record is called the DSC curve. The recommended reference material is Alumina (Al_2O_3). Latent heat of fusion is calculated using the area under the peak and melting temperature is estimated by the tangent at the point of greatest slope on the face portion of the peak. Lots of researchers have been used DSC for measuring the thermo physical properties of the PCMs (Flaherty, 1971; Giavarini et al., 1972;Cantor et al., 1978; Elder et al., 1980; Salyer et al, 1986; Bukovec N. et al., 1989; Dunn J.G. et al., 1989; Aboul-Enein et al., 1991; Takahashi Y. et al., 1991; Babich M.W. et al., 1992; Richardson M.J. et al, 1993, Gibbs et al, 1986; Feldman D. et al., 1996; Li W. et al., 1999; Sharma S.D. et al., 1999; Sharma, A. et al. 2002; Liu et al. 2001) [130 - 146].

The above methods are, in general, appreciated as an accurate means in measuring the heat of fusion. But the thermophysical properties of a very small amount (1-10 mg) of the sample PCM might be different from those of the bulk materials including heterogeneous additives. As another method for determining thermo physical properties of PCM, Zhang's proposed a T-history method [147] to be able to overcome the above limitation of DSC. Because this method does not take a small amount of sample, it is very convenient when a cycle test is carried out with sealed tubes containing newly developed PCMs. Nevertheless, the original T-history method has a restriction on accuracy of thermophysical properties owing to introduction of some invalid physical assumptions. Hong et al. [148] tried to improve the accuracy of T-history method for measuring heat of fusion of various materials. Marin et al. [149] also improved the Zhang et method to determine temperature dependent properties. They reported that using this method it is possible to obtain both properties and curves in a simple way which will be of great help in selecting heat storage material and in the subsequent design of a thermal energy storage system. The enthalpy–temperature curves represent an advance to obtain average properties of the materials since they enable an evaluation of the variation of the thermal properties against temperature.

7.0 Thermal Cycles

For latent heat storage, commercial-grade PCMs with a purity of about 95% is preferred due to their large-scale availability and low cost. In general, the thermo physical properties and behavior of commercial-grade materials are found to be very different from those quoted in the literature for laboratory-grade materials (purity more than 99%). Since limited data are available on the effect of thermal cycling on commercial grade PCMs, it is important to study the effects of thermal cycling on the melting temperature, latent heat of fusion and the specific heat of commercial grade PCMs. Sharma et al. [144, 145] conducted accelerated thermal cycle test for stearic acid, acetamide and paraffin wax. They concluded that commercial grade PCMs have shown no regular degradation in their melting points during repeated 1500 thermal cycles. Acetamide and paraffin wax have shown reasonably good stability for the cycling process and can be considered as promising PCMs. It is recommended that before employing a commercial grade material as PCM, its thermal cycle test should be conducted as the behavior may change. Ting et al. [150] conducted accelerated cycle tests on a PCM unit having (Na_2SO_4 .nH_2O) at different ratios by weight. They studied the effect of 1000 thermal cycles on the container tube, but did not analyze its effect on the thermophysical properties of the PCM. Fernanda [151] has also studied the thermal reliability of salt hydrate PCMs with melting temperatures between 15 and 32^{O}C by measuring latent heat of fusion and melting temperature after subjection to repeat cycles.

Sharma et al. [152] tested the effect of thermal cycling on urea and noticed that it did not melt after a several cycles. They suggested that urea should not be used as a PCM. Hadjieva [153] calculated the enthalpy of three paraffin mixtures and found the dependence on their oil content and the distribution of atoms defined by chemical and gas chromatographic analyses. Thermal cycle testing also carried out for the mixture of technical grade paraffins and found stable after repeating 900 heating/cooling cycles. Gibbs [141] reported that paraffin shows excellent thermal stability. Kimura and Kai [154] used NaCl to improve the stability of $CaCl_2.6H_2O$, containing slightly more water than the stoichiometric composition. The salt was found to be very stable after repeating more than 1000 heating/cooling cycles. Porisino [155] studied the thermal reliability of salt hydrate PCMs by measuring the latent heat of fusion and melting temperature after subjection to repeated cycles. Wada et al. [156] investigated the decreasing heat storage capacity of $CH_3COONa.3H_2O$ during thermal cycling and performed calorimetric measurements on three kinds of samples. Hasan and Sayigh [157] investigated the thermal properties of some saturated fatty acids using the DSC technique after a middle term period that includes heating - cooling cycles of 450 times. The thermal energy storage capacity of $Na_2SO_4.10H_2O$ was investigated with respect to thermal cycling by Marks [158]. Zhang et al. [159] studied the solid - liquid phase transitions in lauric, palmitic and stearic acids and their binary systems. They also investigated the stability of the thermal properties after many times of heating - cooling cycles, such as 30, 50, 80, and 100. Sari [160, 161] conducted 1200 accelerated thermal cycle tests to study the thermal reliability of lauric, myristic, palmitic, and stearic acid. Thermal cycling tests have also been conducted for 24 wt% PCM impregnated wallboards. The samples showed no tendency of the PCM (paraffin) to migrate within the wallboard, and there was no observable deterioration in the thermal energy storage capacity [162].

8.0 Corrosion of the PCMs

The corrosion of some salt hydrates and salt eutectics to different materials of container and their thermal stability were tested by Porosini [155] and Groll et al. [164]. Recently, Cabeza et al. [165 - 168] studied corrosion resistance of five common metals (aluminum, brass, copper, steel and stainless steel) in contact with molten salt hydrates (zinc nitrate hexahydrate, sodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate, sodium carbonate, potassium hydrogen carbonate, potassium chloride, water, sodium acetate trihydrate, and sodium thiosulphate pentahydrate) in an immersion corrosion test. Recently, Sari et al. [169] investigated the corrosion resistance of some construction materials to the fatty acids (stearic, palmitic, myristic and lauric acid) over a long period. The materials containers were stainless steel (SS 304 L), carbon steel (steel C20), aluminum (Al) and copper (Cu). It can concluded that stainless steel (SS304L) with chromium oxide (Cr_2O_3) surface layer and aluminum (Al) metals with aluminum oxide (Al_2O_3) layer surface are essentially compatible with the investigated fatty acids based on gravimetric and metallographic corrosion tests results. Carbon steel (Steel C20) and copper (Cu) metals, as storage container materials are preferentially compatible.

9.0 Heat Transfer Enhancement

In a latent heat storage system, the solid - liquid interface moves away from the heat transfer surface during phase change. During this process, the surface heat flux decreases due to the increasing thermal resistance of the growing layer thickness of the molten/solidified medium. In the case of solidification, conduction is the only transport mechanism, and in most cases it is very poor. In the case of melting, natural convection can occur in the molten layer and this generally increases the heat transfer rate compared to the solidification process (if the layer is thick enough to allow natural convection to occur). However, the generally low heat transfer rate can be increased considerably by using a suitable heat transfer enhancement technique. There are several methods to enhance the heat transfer in a LHTS system. The use of finned tubes with different configurations has been proposed by various researchers as an efficient means to improve the charge/discharge capacity of a LHTS system [170 - 179]. Other heat transfer enhancement techniques for LHTS systems are having the PCM inserted in a metal matrix [180 - 185], using PCM dispersed with high conducting particles [186], microencapsulation of PCM [187 - 188], embedded graphite matrix [189 - 190], carbon fiber brushes with a high thermal conductivity (190 W/mK) [191], exfoliated graphite (EG) for improving the thermal conductivity of the form-stable P/HDPE composite PCMs [192], copper plates inserted in spherical capsules for n- octadecane PCM [193], using metal screens/spheres placed inside the PCM [194]. Erik and Dudukovic [195] presented a novel energy storage system consisting of n-octadecane retained by capillary forces in a porous silica support. This configuration eliminates the expensive heat exchange surface, provides higher energy density, and gives higher rates of energy storage and release. Leoni and Amon [196] employed aluminum foam to enhance the heat transfer process in latent heat storage system.

10.0 New PCM Innovations

Ravankar [197] presented a new testing method for satellite power using latent heat storage. PCM becomes liquid under high temperature, which then freezes during hours of cold darkness and released its latent heat. The released heat can used to generate electricity by driving thermoelectric units. John et al. [198] designed a novel ventilation nighttime cooling system (a novel combination of PCM and heat pipes) as an alternative to air conditioning. The system offers substantial benefits in terms of reducing or eliminating the need for air conditioning. Microencapsulated PCMs can be included within textile fibers; composites and clothing to provide greatly enhanced thermal protection in both hot and cold environments [199]. Cabeza et al. [200] reported that the PCM can be used for transporting temperature sensitive medications and food because the PCMs capability to store heat and cold in a range of several degrees. Several companies are engaged in the research of transporting temperature sensitive PCMs for various applications [201 - 205].

Vasiliev et al. [206] developed the latent heat storage module for motor vehicle because the heat is stored when the engine stopped, and can be used to preheat the engine on a new start. It is possible to reach an optimized working temperature within the engine in a much shorter time using the heat storage than without heat storage. Pal and Joshi [207, 208] recommended the PCM to restrict the maximum temperature of electronic components. Tan et al. [209] conducted an experimental study on the cooling of mobile electronic devices, and computers, using a heat storage unit (HSU) filled with the phase change material (PCM) of n-eicosane inside the device. The high latent heat of n-eicosane in the HSU absorbs the heat dissipation from the chips and can maintain the chip temperature below the allowable service temperature of 50 ^{O}C for 2 h of transient operations of the PDA.

Climator [210] has developed a cooling vest for the athletes for reducing the body temperature. PCMs also proposed for cooling the newborn baby [211]. Koschenz et al. [212] developed a thermally activated ceiling panel for incorporation in lightweight and retrofitted buildings. It was demonstrated, by means of simulation calculations and laboratory tests, that a 5 cm layer of microencapsulated PCM (25% by weight) and gypsum surface to maintain a comfortable room temperature in standard office buildings. Heptadecance were tried as PCM in this prototype set-up. Naim et al. [213] constructed a novel continuous single-stage solar still with PCM. They reported that the productivity of a solar still can be greatly enhanced by the use of a PCM integrated to the still. Huang et al. [214] used PCMs for thermal regulation of building-integrated photovoltaic. Depending on ambient conditions, a PV/PCM system may enable the PV to operate near its characterizing temperature (25 ^{O}C). They developed PV/PCM simulation model and validated with experimental results. The improvement in the thermal performance achieved by using metal fins in the PCM container is significant. The fins enable a more uniform temperature distribution within the PV/PCM system to be maintained. An extensive experimental test has been undertaken on the thermal behavior of a phase change material, when used to moderate the temperature rise of PV in a PV/PCM system [215 - 217]. Use of PCM with photovoltaic (PV) panels and thermoelectric modules (TEMs) in the design of a portable vaccine refrigerator for remote villages with no grid electricity was proposed by Tavaranan et al. [218]. TEMs, which transfer heat from electrical energy via the Peltier effect, represent good alternatives for environmentally friendly cooling applications, especially for relatively low cooling loads and when size is a key factor. Thermoelectric refrigeration systems employing latent heat storage have been investigated experimentally by Omer et al. [219]. Duffy and Trelles [220] proposed a numerical simulation of a porous latent heat thermal energy storage device for thermoelectric cooling under different porosities of the aluminum matrix. They used a porous aluminum matrix as a way of improving the performance of the system, enhancing heat conduction without reducing significantly the stored energy.

Weinlader et al. [221] used PCM in double-glazing façade panel for day lighting and room heating. A facade panel with PCM shows about 30% less heat losses in south oriented facades. Solar heat gains are also reduced by about 50%. Facade panels with PCM improve thermal comfort considerably in winter, especially during evenings. In summer, such systems show low heat gains, which reduces peak cooling loads during the day. Additional heat gains in the evening can be drawn off by nighttime ventilation. If a PCM with a low melting temperature of up to 30 ^{O}C is used, thermal comfort in summer will also improve during the day, compared to double glazing without or with inner sun protection. Ying et al. [222] developed the test standards for PCM fabrics. Three indices have been proposed to characterize the thermal functional performance of PCM fabrics. The index of thermal regulating capability can described the thermal regulating performance of PCM fabrics, and is strongly dependent on amount of PCM. Khateeb et al. [223] designed a lithium-ion battery employing a novel phase change material (PCM) for thermal management system in electric scooter. Developed Li-ion battery was suggested in order to replace the existing lead–acid battery in the electric scooter with the Li-ion battery without introducing any mechanical changes in the battery compartment.

11.0 Conclusion

This review will help to find the suitable PCM for various applications, different techniques for the measurement of thermo physical properties of PCM, suitable heat exchanger with ways to enhance the heat transfer and provide the various designs to store the heat using PCM for different applications i.e. heating, cooling, cooking, greenhouse, water heating and waste heat recovery systems. Study on thermal cycles and corrosion of the materials for long term stability is discussed. Recent innovations on PCM applications are included for the awareness about new applications. More applications are yet to be discovered.

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Nomenclature

a_m	Fraction melted
a_r	Fraction reacted
Δh_m	Heat of fusion (kJ/kg)
Δh_r	Endothermic heat of reaction (kJ/kg)
m	Mass of heat storage medium (kg)
T_a	Ambient air temperature (^{O}C)
T_f	Final temperature (^{O}C)
T_i	Initial temperature (^{O}C)
T_m	Melting temperature (^{O}C)
C_p	Specific heat (kJ/kg K)
C_{ap}	Average specific heat between T_i and T_f (kJ/kg K)
C_{lp}	Average specific heat between T_m and T_f (kJ/kg K)
C_{sp}	Average specific heat between T_i and T_m (kJ/kg K)
Q	Quantity of heat stored (kJ)

Abbreviations

c	Congruent melting
CASE	Compressed air energy storage
EG	Exfoliated graphite
ETSC	Evacuated tube solar collector
HDPE	High density polyethylene
HTF	Heat transfer fluid
ic	Incongruent melting
LHS	Latent heat storage
L	Liquid state
n.a.	Not available
NPG	Neopentyle glycol
PCM	Phase change material
PE	Penaerythritol
PHPS	Pumped hydro power storage
PV	Photovoltaic
SHS	Sensible heat storage
S	Solid state
TAM	Trihydroxy methyl aminomenthane
TEM	Thermoelectric module

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