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A Review of Phase Change Materials Utilized For Solar Cooking Applications

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ABSTRACT

Solar cooking presents a promising alternative to conventional cooking methods; however, its reliance on sunlight necessitates the integration of thermal energy storage for off-sun cooking. Phase Change Materials (PCMs) offer a viable solution to this problem. Despite their potential, many researchers have used PCMs in off-sun cooking tests without fully characterizing them to ensure they meet all storage requirements. For PCMs to be effectively utilized in commercial solar cookers, they must meet specific criteria. This review aims to address this gap by examining the PCMs employed in solar cooking, reviewing the thermal characterizations conducted on each, and highlighting any limitations reported in the literature. By comprehensively assessing the characteristics of these PCMs, this review serves as a valuable resource for evaluating their suitability and distinguishing between those that meet the necessary criteria and those that do not. Through this systematic analysis, researchers and practitioners can make informed decisions regarding the selection and utilization of PCMs in solar cooking applications.

KEYWORDS

Thermal Characterisation
Thermal Energy
Energy Storage
Solar Cookers
PCM Screening
Latent heat storage

1. INTRODUCTION

In both rural and some urban areas in the developing countries, non-commercial sources of energy such as firewood, charcoal, agricultural wastes, and kerosene are mostly used in the production of thermal energy for domestic purposes such as cooking and hot water needs (Sunil *et al.,* 2014). Over 90% of the rural population use these sources of energy for domestic purposes most of which is cooking (World Health Organisation (WHO), 2006). In the United States, cooking accounts for 37 to 53% of the total energy consumption (Aramesh *et al.* 2019). The World Health Organization (WHO) estimated that 4.3 million people die annually due to health issues arising from the inefficient utilization of these fossil fuels for cooking (Bhave *et al.*, 2018). To put it in perspective, a person cooking in an indoor location using solid fuels is exposed to CO concentrations 100% higher than the maximum recommended values and particulate matter emissions as high as 500- 2000 micrograms/m^3 depending on the type of cooking equipment (Sunil *et al.*, 2014). This is about 4 to 15 times the recommended value of air quality not to be exceeded for a 24-hour period in a year (WHO, 2021).

Using solar energy as a source of heat for cooking can eradicate these problems and have the advantage of little maintenance and operation cost, high nutritional value of food and high durability. Considerable research has been done in developing various solar cookers. The main problem hindering the competitiveness of using solar cookers is that cooking has to be done in the sun and during the sunshine hours. This thus restricts the potential of the cookers to serve as a mainstream thermal energy source.

Sensible and latent heat storage are the two options available for the storage of thermal energy in solar cooking devices (Mawire, 2015). The use of PCM (latent heat) has the advantage of high storage and power density meaning smaller and more compact storage integrated cookers. Since in latent heat storage systems, the material has an almost constant temperature, this means more efficient and better heat transfer characteristics. Despite these advantages, solar cookers with the required power density, and cost that can provide on-demand cooking any time of day or night of a wide range of foods are still not commercially available. To successfully develop a latent heat storage system the PCMs must satisfy various requirements for them to be suitable and cost effective.

Many researchers have selected and tested different PCMs arbitrarily in developing latent heat storage systems for Solar cooking applications. Aramesh *et al.* (2019) presented a review of the recent advances in solar cooking technology including the deployment of PCMs for heat storage in solar cookers. However, the review did not give details of the PCMs investigated and their degree of suitability for commercial solar cooker systems. Katlego *et al.* (2021) presented a review of parabolic solar cookers with storage and presented various designs of parabolic solar cookers integrated with latent heat storage systems but also there was no detail about the suitability of the PCMs or show that the PCMs used have been characterized to satisfy thermal storage requirements. Nazir *et al.* (2019) presented a review of the recent advances in the use of PCMs for different applications based on their thermophysical properties. This review did not focus on thermal storage in solar cooking applications. Other notable reviews on Solar cookers with latent heat storage system include Muley *et al.* (2020). There is no critical review on the PCMs suitable for solar cooking highlighting the characteristics that each material has satisfied regarding the characteristics required for suitable phase change materials for storage applications.

Therefore, there is a need for a comprehensive review to examine and document Phase Change Materials (PCMs) suitable for use in solar cooking applications. This review will identify materials that meet specific criteria and assess their suitability for solar cooking, while also highlighting areas requiring further investigation to enhance their suitability. By reviewing all materials reported in the literature for solar cooking, this study will provide insight into the tests conducted to evaluate their suitability, their current status, and the necessary analyses needed for further refinement. Through this systematic review, a clearer understanding of the suitability of PCMs for solar cooking can be achieved, informing future research and development efforts in this field.

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2. REQUIREMENTS FOR SUITABLE PCMs

The initial consideration in selecting a material for latent heat storage is its operating temperature range, which typically falls between 100°C and 300°C for solar cooking applications. Table 1 outlines the necessary properties for a material to be suitable for latent heat storage, along with the implications of each property. Key properties such as thermal cycling stability, reversible phase change, minimal supercooling and subcooling, and material compatibility are crucial factors that can impact the usability of a PCM for storage applications, even if it meets other criteria. These properties play a significant role in determining the effectiveness and reliability of the PCM in storing and releasing thermal energy in solar cooking systems.

3. PCMs TESTED IN SOLAR COOKERS FOR MEDIUM TEMPERATURE APPLICATIONS

Several studies have been conducted on the use of PCM in parabolic solar cookers, and most of these studies are for boiling type of cooking (temperature around 100°C) (Chaudhary, *et al.* (2013), Malik *et al.* (2020), Beekumar *et al.* (2017), Lecouna *et al.* (2013), Senthil and Cheralathan (2017) and Bhave and Thakare, (2018) and Saini *et al.* (1986)). These studies used PCMs with melting temperatures ranging from 90°C to 117°C. Table 2 presents a summary of the PCMs that have been employed in research in latent heat storage systems for boiling type of solar cooking applications with their reported thermophysical properties. In the sections that will follow each of these PCMs will be reviewed to ascertain all the works that has been done on their suitability as suitable PCMs for storage applications and thus highlighting their current suitability assessment status.

3.1. Acetanilide

Acetanilide (C_8H_9NO) having a reported melting temperature of 118.9°C and enthalpy of fusion of 222 kJ/kg was employed by Chaudhary *et al.* (2013), Saini *et al.* (2016) and Mussard and Nydal (2013) in solar cooking applications. Other researchers such as El-Sebaii found a melting temperature range of between 113.55 to 116.42 °C and an enthalpy of fusion of 169.41 kJ/kg. Its melting temperature being very close to the boiling point of water makes it a very suitable PCM for solar cookers for boiling type of cooking. El-Sebaii (2009) investigated the effect of thermal cycling on the melting temperature and enthalpy of fusion of commercial grade (purity > 98%) Acetanilide (C_8H_9NO) and compatibility with steel and aluminium containments. The melting point and the enthalpy of morphology (such as pits, crevice, etc.) using the SEM technique. In Table 2, the melting temperatures and enthalpy of fusion for different thermal cycles are presented. Notably, the properties of Acetanilide displayed irregular changes across the thermal cycles. After 500 cycles, a decrease of approximately

Table 1: Requirements of Suitable PCMs for Thermal Storage Application

Physical requirements	
High enthalpy heat of fusion	Requires less storage space for a specific capacity compared to sensible heat storage
High thermal conductivity	Enhances system dynamics by accelerating heat transfer rates.
Reversible Phase change	Facilitates cyclic operation
Negligible sub-cooling and super-cooling	Ensures freezing and melting occur at the same temperature.
High Density	Smaller storage capacity
Technical Requirements	
Minimal density change	Reduces unfilled space within the PCM container.
Low vapour pressure	Avoids the need for a pressurized container.
Chemical stability and compatibility with other materials of the system	Ensures long-term system durability.
Thermal Cyclic Stability	Maintains properties after repeated melting and freezing cycles.
Non-Flammable	To prevent fire hazard
Economic requirements	
Economical and widely available	To ensure it will be cost-effective.
Non-toxic and recyclable	To be environmentally friendly

Table 2: PCMs used by researchers for solar cooking (boiling type) applications.

S/N	Material	Chemical Formulae	Category	Tm (°C)	ΔH (kJ/kg)	ρ m^3/kg	$c_{p,solid}$ (kJ/kgK)	$c_{p,liquid}$ (kJ/kgK)	k_{solid} W/mK	k_{liquid} W/mK	Grade	Reference
1	Acetanilide	C8H9NO	Organic	118.9	222		2				Commercial	Chaudhary et al. (2013)
				116	142	1210					Commercial	Sharma and Sagara (2005)
2	Potassium Alum		Inorganic	90 – 95								Malik et al. (2020)
3	D-Sorbitol		Organic	91 – 101	187	1524	2.49					Beekumar et al. (2017)
4	Erythritol		Organic	118	340	1480, 1300	1.38	2.76	0.733	0.326		Lecouna et al. (2013)
5	Magnesium Chloride Hexa-hydrate	MgCl2.6H2O	Inorganic	117	167	1570, 1450	0.7	0.57	0.704	0.570		Senthil and Cheralathan(2017)
				118	167	1560	1.72	2.82	0.694	0.57		Bhave and Thakare (2018)
				116.7	168.8	1570; 1450	2.25	2.61	0.704	0.570		Choi and Kim (1995)
6	Magnesium Nitrate tetra chloride	Mg(NO3)2. 6H2O	Inorganic	89	163							Santhi and Sukchai (2018)
7	D-Mannitol	C6H8(OH)6	Organic	157 – 170	318	1490	2.5					Beekumar et al. (2017)
				166 – 176.9	279-308	1520						Aran Sole et al. (2014)
				162.15	326.8							Kumaresan et al. (2011)
				166 – 169	326.8	1490						Kumaresan et al. (2018)

6% and 2% was observed in the onset and peak temperatures, respectively, while the enthalpy of fusion decreased by 8%. The supplier specified a melting point of 116˚C and an enthalpy of fusion of 142 kJ/kg. However, DSC analysis revealed fluctuations in the enthalpy of fusion ranging from 146 to 180 kJ/kg over the cycles. This irregularity was attributed to improper crystallization of the material. It is worth noting that DSC measurements involve testing only a few milligrams of the sample, which may introduce limitations. To address this, it is suggested that multiple test samples be taken and analyzed during each measurement session to ensure accuracy and reliability.

Table 3: Impact of Thermal Cycling on the melting temperature and Enthalpy of fusion of Acetanilide (El-Sebaii, 2009)

S/N	No. of Cycles	Melting Range (°C)	Enthalpy of fusion (kJ/kg)
1	0	113.55 – 116.42	169.41
2	63	113.30 – 115.72	154.94
3	102	114.91 – 118.19	151.96
4	134	112.41 – 115.81	180.87
5	157	112.59 – 116.33	174.77
6	202	112.50 – 116.34	159.35
7	254	111.97 – 116.54	145.59
8	300	111.75 - 115.44	175.05
9	355	109.61 – 115.19	150.47
10	402	108.94 -114.79	155.49
11	425	105.89 – 114.50	154.2
12	500	106.00 – 114.40	154.00

The SEM photographs for aluminium and steel sample placed inside Acetinilide for the 0th and 500th cycles showed that the aluminium sample showed no sign of corrosion with only its contrast changing to a darker contrast than the original sample. Physical examination of the stainless-steel sample shows very strong corrosion and becomes golden colour. Thus, Aluminium containers can be used with Acetanilide but not stainless steel.

In summary, Acetinilide is a good PCM for solar cooking applications since there is no significant deviation in its melting temperature and enthalpy of fusion over 500 thermal cycles. Nonetheless, there is a need to determine the thermal endurance (stability) and the maximum temperature above which it will disintegrate.

3.2. Potassium Alum

Potassium Alum was employed by Malik *et al.* (2020) with a melting temperature between 90 to 95°C which is less than the boiling point of water, and discovered its suitability for low-temperature cooking applications. This material is not suitable for thermal storage applications in Solar cooking since the boiling point of water at atmospheric conditions is around 100°C.

3.3. Sugar Alcohols (SAs)

Three Sugar alcohols have been used by researchers in solar cooking applications. These are D-Sorbitol (Beekumar *et al.*, 2017), Erythritol (Lecouna *et al.* (2013), and D-Mannitol (Beekumar *et al.* (2017) and Aran Sole *et al.* (2014)). Sugar Alcohols happen to be a promising class of potential PCMs for storage applications, especially solar cookers since they have high heat of fusion, do not suffer phase segregation, compatible with traditional materials, non-toxic, non-flammable, safe, low environmental impact, are readily available and recyclable. Their main disadvantages are they have high supercooling, thermally unstable and degrade due to high temperatures.

3.3.1. D- Sorbitol

D-Sorbitol ($C_6H_{14}O_6$) also known as Glucitol with a reported melting temperature of 91 to 101°C was investigated in a solar cooker by Beekumar *et al.* (2017). Its melting temperature is very ideal for boiling type of cooking since it is just around the boiling point of water at atmospheric conditions. Tomassetti *et al.* (2022) presented a compilation of the melting temperature and enthalpy of fusion obtained by different authors using DSC technique (Table 4). The melting temperatures obtained from the literature vary from 93.2 to 101.1°C. while the enthalpy of fusion varies from 193 to 217 kJ/kg. The discrepancies in the figures can be attributed to the purity of the sample used and the heating rate used in the DSC. While some authors reported mean values, others reported peak values. Maximum thermal stable temperature of 307.1°C and a degradation temperature of 399.6˚C were found for D-Sorbitol in the nitrogen atmosphere (Tomassetti *et al.*, 2022). Tong *et al.* (2008) reported a maximum temperature of 256.4°C and a degradation temperature of 491.4°C. There are no reported works on cyclic stability of sorbitol and thus there is a need to conduct long-term cyclic stability tests in-order to determine the full suitability of D-Sorbitol for latent heat storage applications.

Table 4: Phase change temperature and enthalpy of fusion of D-Sorbitol determined using DSC (Tomassetti et al., 2022)

Melting Temperature °C (on set of melting)	Enthalpy of fusion (kJ/kg)	Heating Rate (°C/min)	Purity (%)
93.2	153.0	1	99.5
100.0	185.0	1	98
93.4± 0.3	166.0± 2.0	1	-
95.6± 0.3	167.3± 6.2	1	≥ 99.5
95.3± 0.5	172.2 ± 4.3	2.5	-
96.8	217.0	3.5	-
95.1	132.5	5	≥98
97.4 ± 0.2	164.0 ± 3.2	5	98
99.4 ± 0.2	184.4 ± 2.6	5	98
95.0 ± 1.2	165.0 ± 1.0	5	>97
97.0	110.0	5	>99
101.1 ± 0.1[a]	173 ± 5	10	>97
99.2[b]	168.3 ± 1.7	10	>99
98.0 ± 0.3	174.0 ±2	10	98.9
98.8	196.8	10	-
94.2	135.3	-	-
96.8± 2.3[c]	166.5 ± 24.7[c]	-	-

[a] Unspecified type of temperature

[b] Peak temperature

[c] Mean value ± Standard deviation

3.3.2. Erythritol

Erythritol (C_4H_6O) was used by Senthil and Cheralathan (2017) and Lecouna *et al.*, (2013) as PCM for thermal energy storage in a solar cooker. Erythritol is an organic material (Alcohol) with very high enthalpy of fusion of 340 kJ/kg and a melting temperature of 118°C, it is non-toxic and readily available. Shuckla *et al.* (2008) conducted a thermal cycling analysis for Erythritol by melting it at a constant temperature of 130°C in an oven. During each cycle, temperatures were recorded, and DSC curves illustrating the relationship between heat flow and temperature were generated for each sample. Table 5 shows the comparison between the melting temperatures and enthalpy of fusion at different thermal cycles. It was observed that Erythritol has a maximum supercooling temperature of 14°C and the enthalpy of fusion degradation started after 500 cycles with a maximum degradation of 35 to 40 kJ/kg at 1000th cycles. The maximum melting temperature change after 1000 cycles was found to be 9 -10°C. Pupponen *et al.* (2016) did not also observe significant degradation in melting temperature and enthalpy of fusion after many cycles. Other authors (Karthik *et al.* 2015; Agyenim *et al.*, 2011; Shobo *et al.* 2018; Shin *et al.* 2016 and Lee at al., 2014) conducted thermal cycling analysis of Erythritol for less than 100 cycles also reported a decrease in the melting temperature and enthalpy of fusion. Zeng at al. (2017) reported the high supercooling of erythritol.

Table 5: Melting and Solidification temperatures for thermal cycling of erythritol (Shuckla et al., 2008)

No. of Cycles	Measured by Data Logger		Measured by DSC	
	Melting Temperature (°C)	Freezing Temperature (°C)	Melting Temperature (°C)	Enthalpy of fusion (kJ/kg)
0	117	112	117	339
100	120	115	122	340
300	115	105	115	339
500	110	106	106	312
1000	107	105	119	305

The thermal endurance (stability for being kept at a constant temperature above its melting point) of erythritol was conducted by Alferez Luna *et al.* (2021) by keeping it at a constant temperature at 121°C, 131°C, and 141°C for 100 hours. Two mediums were used: ambient air and inert atmosphere. Erythritol in ambient air shows a decrease in the enthalpy of fusion and the use of antioxidants in Erythritol decreases the degradation of the enthalpy of fusion. In ambient air, there are signs of more oxidation/dehydration which is seen by the more browning of the sample. The use of inert atmosphere (argon) leads to lower degradation in the enthalpy of fusion and there was no observed oxidation/dehydration of Erythritol with antioxidants. In summary, these authors found out that erythritol is stable up to a temperature of 141°C under inert atmosphere (argon) for up to 935 hours.

Erythritol seems to be thermally stable and it is reported to have high supercooling. There is high discrepancy in what was reported in the literature regarding the cyclic stability of erythritol. Authors that have conducted thermal cycling analysis of less than 100 cycles reported high degradation in the melting temperature and enthalpy of fusion while some authors that conducted long-term thermal cycling analysis of up to 1000 reported an allowable degradation in the melting temperature and the latent heat. Also, most thermal cycling analyses showed erratic changes in the properties over different cycles. Although Erythritol seems to be a very good candidate PCM suitable for boiling type thermal energy storage solar cookers since it has high enthalpy of fusion and reasonable thermal stability characteristics, there is the need for further thermal cycling and materials compatibility analysis to ascertain its characteristics and development of strategies to reduce its supercooling problem.

Many techniques for addressing the supercooling problem of Erythritol have been investigated in the literature. These include Stirring (Ona *et al.*, 2001), ultrasonic irradiation (Ona *et al.*, 2002), electric current (Jankowski and McCluskey, 2010), bubbling (Yang *et al.*, 2020), microencapsulation (Wang *et al.*, 2017) and the use of nucleating agents (Zeng *et al.*, 2017). In summary to use Erythritol as a PCM in thermal storage applications one of these methods must be employed in addressing its supercooling problem.

3.3.3. D-Mannitol

D-mannitol ($C_6H_{14}O_6$) is an organic material that is found naturally in different trees and it is economically produced industrially mainly from the catalytic hydrogenation of glucose/fructose (1:1) mixture (Tomassetti *et al.*, 2022). In the medium temperature range for cooking Beekumar *et al.* (2017) and Kumaresan *et al.* (2018) used D-Mannitol as PCM and reported a melting temperature range of 157°C to 170°C and enthalpy of fusion of 166 kJ/kg to 169 kJ/kg respectively. It has a high enthalpy of fusion, cheap, readily available, and non-toxic which makes it attractive for storage in the medium temperature range. Its melting temperature is ideal for higher-temperature cooking even though it may not be suitable for baking and frying.

Kumaresan et. al. (2011) determined the enthalpy of fusion, melting temperature and the decomposition temperature of D-Mannitol with >99% purity using DSC. The temperature at the onset of melting was 162.15°C and the peak temperature of 167.8°C with the enthalpy of fusion of 326.8 kJ/kg. Thermal stability -decomposition temperature and mass change were determined using Thermogravimetry Differential Thermal Analysis, TG-DTA which showed that at temperatures up to 300.15 °C there is no mass loss. Beyond this temperature, the material begins to lose weight (starts to degrade). Thus, its maximum operating temperature is 300.15. Other authors such as Gil (2013) Investigated the melting and enthalpy of fusion of D-Mannitol using DSC and pilot scale experiments showed that D-Mannitol undergoes polymorphic structural changes, resulting in variable thermal properties. The melting temperatures of D-Mannitol differ depending on the specific polymorphic phase that is formed.

Soléa *et al.* (2014) investigated the thermal cyclic stability of D-Mannitol ($C_6H_{14}O_6$) by conducting 50 thermal cycles and measuring the melting temperatures and the enthalpy of fusion. It was found that after 50 cycles, the melting temperature was reduced by 12% and the enthalpy of fusion decreased by more than 50% (Table 6). The solidification temperature was also reduced by 51°C. This shows that D-mannitol is highly unstable over even small cycles and thus may not be suitable for thermal storage systems except if the thermal instability is addressed.

Table 6: Thermal Cycling Analysis of D-Mannitol during Melting and Solidification (Soléa et al., 2014)

No. of Cycles	Melting		Solidification	
	Melting Temperature (°C)	Enthalpy of fusion (kJ/kg)	Solidification Temperature (°C)	Enthalpy of fusion (kJ/kg)
0	150.96	234.35	114.08	224.55
20	138.25	152.60	89.04	156.2
50	131.92	99.48	62.53	109.5

Tomassetti *et al.* (2022) presented a review of all the studies that experimentally investigated the properties of D-mannitol and also conducted thermophysical, chemical, and thermal analyses on this material. Table 7 presents a summary of the results alongside others. This work reported a melting temperature of 165.6°C and solidification temperature of 120°C. From Table 7, it is observed that there are differences in the phase transition temperature during melting and solidification signifying a supercooling in the material.

Table 7: Phase change temperature and enthalpy of fusion of D-Mannitol determined using DSC by researchers (Tomassetti et al., 2022)

Melting Temperature (°C)	Latent heat during Melting (J/g)	Temperature (On set of crystallization) (°C)	Latent heat during crystallization (J/g)	Heating/ Cooling Rates	Purity (%)
166.2 ± 0.2	278.6 ± 0.9	118.5 ± 0.1	243.0 ± 0.6	0.5	98
151.0	234.4	114.1	224.6	1	
166.3 ± 0.2	278.7 ± 0.1	119.1 ± 0.1	242.8 ± 0.7	1	98
165.7	334.5	122.9	234.8	1	≥98
165.6 ± 0.1	284.3 ± 3.9	120.0 ± 0.2	238.6 ± 6.9	1	≥98
166.1	281.1 ± 1.3	111.1 ± 1.7	238.3 ± 5.9	5	≥98
166.0 ± 0.1	277.4 ± 1.1	114.1 ± 0.6	227.9 ± 0.9	5	99
166.6 ± 0.1	299.5 ± 0.4	110.9 ± 1	234.5 ± 0.7	10	98
166.4	281.9	120.2	219.5	10	99
165.3	282.0	123.0	241.3	10	98
166.2	288.1	115.0	228.0	10	-
165.0	295.2	109.4	213.0	10	98
168.8a	284.9	107.7a	214.4	10	99
170.2	293.1	118.0	238.2	-	99.5
165.4 ± 4.2b	285.3 ± 19.9b	116.0 ± 4.8b	231.4 ± 9.9b		

^{a}Peak temperature

^{b}Mean value ± standard deviation

The investigation of the thermal endurance of D-mannitol was done by Aran Sol'e *et al.* (2014), Burger *et al.* (2000), Bay´on and

Rojas (2017), and results showed that heating of D-Mannitol results into oxidation and the smaller the sample the higher the oxidation. The presence of oxidation is signified by the changing colour of the sample. FITR analysis showed that there are changes in the polymorphic phase of the sample. To reduce the effect of oxidation Sagara *et al.* (2014) impregnated D-Mannitol into nanosized pores of SiO_2 grains and the samples were maintained at a temperature above the melting point for several hours in an inert atmosphere. Results showed that D-Mannitol/SiO_2 composite increase the thermal degradation period by 13 times. Also, Rodrgues-Garcia *et al.* (2016) conducted a thermal endurance experiment on a 20g sample at 180°C in an inert atmosphere and found out that after 171hours, the dense brown material did not crystallize and samples investigated in Nitrogen had a smaller mass loss compared to those in an argon atmosphere. The authors concluded that thermal degradation is not caused by oxidation but rather by the caramelization process since regardless of the atmosphere large amounts of volatile species are produced and lead to the browning of the sample. The authors concluded that even though adding antioxidants and exposing D-mannitol to an inert atmosphere enhance its thermal stability, using D-mannitol as a PCM without any loss in enthalpy of fusion appears unfeasible. Consequently, the feasibility of employing D-mannitol as PCM in particular applications relies on the required number of storage cycles and the specific retention temperatures above its melting temperature.

In summary, D-mannitol is not a good PCM for latent heat storage systems especially for solar cookers since it suffers thermal degradation when it is heated beyond its melting point and also there is a decrease in the temperature and latent heat over many cycles. Also, when heated to 180°C and left for sometimes it suffers caramelization and will not recrystallize back.

3.4. Hydrates (Magnesium Chloride Hexahydrate and Magnesium Nitrate Tetrahydrate)

Hydrates i.e., Magnesium Chloride Hexahydrate ($MgCl_2$-$6H_2O$) (melting point of 117°C) and Magnesium Nitrate tetrahydrate (Melting Point of 89°C) are the most promising hydrates for boiling type of cooking. Magnesium Chloride Hexahydrate was used by Bhave and Thakare (2018) and Santhi and Sukchai (2018) in thermal energy storage systems for solar cooking. These hydrates have an enthalpy of fusion of 167 kJ/kg. Hydrated salts release their water of crystallization when heated and the solid salt will dissolve in the released water thus becoming liquid and storing the heat similar to melting. The release of heat from the dissolved solution leads to the solidification and absorption of the released water and the dissolved salt now becomes crystals of white solid. This process is utilized for thermal energy storage since it is similar to melting and solidification with storage and release of energy. Magnesium Nitrate hexa-hydrate has a reported melting temperature of 89°C and 117°C (Dinser and Rosen). This is a discrepancy that needs further investigation. These hydrates are very good PCMs for storage applications because of their material compatibility, low cost, and good thermophysical properties, and they are not toxic. There are two main problems in using hydrates: incongruent melting and supercooling.

3.4.1. Incongruent melting (phase separation)

This occurs during melting in which an anhydrous solid phase is formed, and it separates from the solution and settles at the bottom since the density of the solid is higher than that of the solution. During solidification, this anhydrous solid does not combine with the saturated solution to form the original salt and thus makes the process irreversible. This happens because during melting the released water is not sufficient to dissolve the salt. This problem can be solved by the addition of excess water to the salt so that enough water is available to dissolve the salt (Bhave and Thakare, 2018). El-Sebaii (2009), investigated the effect of thermal cycling on the enthalpy of fusion and melting temperature for $MgCl_2$. $6H_2O$ in an unsealed container for 500 cycles using the extra water principle, results showed that the excess water added to the material did not prevent the separation of the phases that occur during melting of the hydrate. Even with the added water, there were significant changes in the onset and peak temperatures and enthalpy of fusion and there was a decrease in the enthalpy of fusion by 45.2%. These researchers suggested that the decrease and the changes in the onset, peak temperatures and enthalpy of fusion is due to the dilution of the salt hydrate, phase segregation and the formation of lower salt hydrate with lower melting point due to the loss of water molecules due to heating. Thus, the amount of water added to the salt hydrate did not prevent the incongruent melting of the material. El-Sebaii *et al.* (2011) conducted 1000 thermal cycling on commercial grade Magnesium Chloride Hexa hydrate (purity >98%) in a sealed container (to prevent phase separation) to determine the effect of repeated cycling on the enthalpy of fusion and melting temperature of the PCM using the extra water principle. Although irregular changes in the properties were observed, results showed that after over 1000 cycles, the enthalpy of fusion only decreased by 5.1%, the onset and peak temperatures have a maximum deviation of +/- 8% and +/- 6% respectively. The decrease in enthalpy of fusion can be attributed to the dilution of the hydrate due to the extra added water. This thus showed that sealing the container during thermal cycling reduces the influence of phase segregation during repeated thermal cycles. Although Bhave and Thakare (2018) employed $MgCl_2.6H_2O$ as PCM in a sealed capsule using the excess water principle and tested it in a solar cooking system successfully, they did not determine the effect over several cycles. Thus, the use of excess water in sealed containers reduces the effect of incongruent melting but may lead to the reduction in the enthalpy of fusion of the PCM and thus there is a need to know how much excess water is just sufficient to dissolve the salt. Another way to solve the phase segregation issue is to use a thick or gelled mixture (Abhat, 1983).

3.4.2. Supercooling

Another problem with Hydrates is supercooling (Dincer and Rosen, 2011). El-Sabeii (2011) reported that supercooling was only observed in some cycles and the maximum supercooling was 3.5°C in Magnesium Hexahydrate for 1000 thermal cycles in a sealed container. Supercooling can be avoided by employing nucleating agents or the use of mechanical agitation methods to start the growth of the crystals. Lane (1978) has presented various materials that can aid crystal growth (Nucleation) in salt hydrates.

In summary, Magnesium Hexa-hydrate is a promising PCM and the problem of phase segregation can be solved by the addition of extra water and the sealing of the PCM container. Magnesium Chloride Hexahydrate was found to be highly corrosive to aluminium and stainless steel after 500 cycles (El-Sebaii, 2009).

4. PCMs TESTED FOR HIGH-TEMPERATURE COOKING APPLICATIONS.

For solar cookers to compete with conventional cooking systems, they must be able to perform off sunshine cooking and also must be able to operate at higher temperatures for cooking applications such as frying and baking. This means they must be able to reach temperatures above 200°C. The most widely employed PCM for high-temperature solar cooking is the eutectic mixture of Sodium and Potassium Nitrate.

4.1. Mixture of Sodium Nitrate and Potassium Nitrate

For solar cooking applications, researchers have employed eutectic mixture of Sodium and Potassium Nitrate in a 60:40 ratio for high-temperature cooking applications (Mussard *et al.* 2013; Tesfey *et al.* (2014); Senthil *et al.* (2017); Veramachi *et al.* (2016), Gabisa and Aman (2016) and Bhave and Kale (2020)). The main problem with eutectic mixtures is the determination of the eutectic composition ratio and the corresponding thermophysical properties. Many researchers have employed the use of DSC in the characterization of this PCM. Thirunavukkarasu (2020) prepared an eutectic mixture of Sodium and Potassium Nitrate in a 60:40 ratio using a method explained in Foong *et al.* (2011) and DSC was employed in determining the melting temperature and enthalpy of fusion of the PCM. Table 8 presents the thermophysical properties of the Eutectic Mixture of $NaNO_3$ and KNO_3 obtained.

Gabisa and Aman (2016) conducted the thermal characterization of this mixture and determined the thermophysical properties of different percentage mixture of $NaNO_3$ and KNO_3 using DSC, five prepared salt mixtures (30/70; 40/60; 50/50; 60/40; 70/30; percentage by mass) with different proportions of the individual salts were tested. The mixtures were analysed employing the standard ASTMD4419-90(2005) method using a DSC. It was found that a ratio of 60% $NaNO_3$ and 40% KNO_3 mixture was the promising one with a melting temperature of 225.38ºC and enthalpy of fusion of 120.91 kJ/kg.

Foong *et al.* (2011) presented the specific heat capacity of 60% $NaNO_3$/ 40% KNO_3 as a function of the different temperature ranges (Eq. (1). The enthalpy of fusion was presented as a form of enhanced specific heat over a phase change temperature range of 210 to 220ºC. This form is ideally suited for numerical studies. The enhanced specific heat corresponds to an enthalpy of fusion of 120 kJ/kg which seems to be consistence with other studies.

$$\boldsymbol{C}_p(kJ/kg) = \begin{cases} 0.75 & T < 110℃ \\ 4.2 & 110℃ < T < 120℃ \\ 1.4 & 120℃ < T < 210℃ \\ 12 & 210℃ \leq T \leq 220℃ \\ 1.6 & T > 220℃ \end{cases} \tag{1}$$

In Summary, a mixture of Sodium and Potassium Nitrate has an eutectic composition of 60% Sodium Nitrate and 40% Potassium Nitrate with a melting temperature of between 207ºC and 225ºC which is very good for high-temperature cooking applications. It seems to be the only PCM that has been investigated for high temperature solar cooking. We did not find any research in which the thermal cycling analysis and compatibility with different containment of this eutectic mixture in the operating range for solar cooking. There is the need to conducting the long-term thermal cycling analysis and thermal endurance (stability) analysis of this PCM to ascertain its suitability for long term use in solar cookers.

5. POTENTIAL PCMs WITH MELTING TEMPERATURE IN THE OPERATING RANGE OF SOLAR COOKERS THAT HAVE NOT BEEN INVESTIGATED.

Table 9 presents the list of inorganic materials with melting temperatures of between 100ºC and 300ºC that are within the operating temperature range for Solar cooking that have not been investigated for solar cooking applications. Most of the listed materials have also not been characterized to determine their suitability for latent heat thermal energy storage applications.

Among these organic materials, Myo-inositol has been investigated by researchers for suitability as a thermal storage material. Myo-inositol is abundant and is produced in the industry by the acid hydrolysis of phytate. Phytate is obtained from seeds and bran of plants (Li *et al.*, 2022). Tomassetti *et al.* (2022) conducted a thermal stability test on Myo-inositol and obtained a maximum thermal stable temperature of 323.1℃ and a degradation temperature of 456.5℃ using TGA at a heating rate of 10 ℃/min using Nitrogen as the purge gas. Alarcon *et al.* (2017) obtained a maximum thermal stable temperature of 271.6ºC and a degradation temperature of 526.7ºC using TGA at a heating rate of 10 ℃/min using air as a purge gas. The difference in the two results may be due to the purge gas used and also this shows that muo-inositol is stable and can be used in the operating temperature of solar cooking.

Thermal cycling stability for Myo-inositol was conducted by Soléa *et al.* (2014), Singh *et al.* (2017a) and Singh *et al.* (2017b) for 50 cycles. Their results showed a decrease in the melting temperature and enthalpy of fusion of the material after 50 cycles. This means there is a need for further thermal cycling tests with more thermal cycles to ascertain the suitability of Myo-inositol as a PCM for long-term storage applications even though Solea *et al.* (2014) reported up to 20% decrease in the enthalpy of fusion after 50 thermal cycles.

6. CONCLUSIONS

Various PCMs have been employed in the thermal energy storage of solar cookers. Most of the PCMs employed are organic compounds. It has been observed that many of these materials have been used by researchers in solar cookers for medium or low-temperature cooking without fully determining the suitability of the PCMs for long-term use especially long-term thermal stability and compatibility with the containment. From the review, it was found that organic materials such as sugar alcohols and hydrated salts have been extensively investigated and their long-term thermal stability established. In the medium temperature range (i.e. for boiling type of cooking) the following materials are very promising: Acetinilide, D-Sorbitol, Erithritol and Magnesium Chloride Hexa-hydrate ($MgCl_2$-$6H_2O$). Comparing their enthalpy of fusion, Erithritol has the highest with 340 kJ/kg compared to 169 – 222 kJ/kg for Acetinilide, 193-217 kJ/kg for D-Sorbitol and 167 kJ/kg for $MgCl_2$-$6H_2O$. Thus, these promising PCMs will result to smaller storage size compared to others. But erythritol is very expensive compared to the other PCMs. The final selection of a PCM has to also consider other factors such as cost, e.t.c. The review also found that, only the Eutectic Mixture of $NaNO_3/KNO_3$ was investigated for high-temperature solar cooking in a ratio of 60/40%. The literature search did not provide any long-term thermal cycling analysis of this mixture to determine its suitability for solar cooking applications. The paper finally presents suitable PCMs that have melting temperatures in the operating range of solar cooking that have not been investigated together with their thermal characteristics reported in the literature. This paper also forms a reference point for the different thermal properties of PCMs reported in the literature.

Table 8: Thermophysical Properties of Eutectic Mixture of $NaNO_3$ and KNO_3 reported in the literature

T_m (ºC)	$\Delta \boldsymbol{H}$ (kJ/kg)	$\boldsymbol{\rho}$ m^3/kg	$\boldsymbol{k_{solid}}$ W/mK	$\boldsymbol{k_{liquid}}$ W/mK	$NaNO_3$ - KNO_3 Ratio	Reference	Remarks
210 – 220	108.67				60:40	Mussard *et al.* (2013) Tesfey *et al.* (2014), Senthil *et al.* (2017), Bhave and Kale (2020),	Use
222					54:46	Abreha *et al.* (2019)	
207.5	107	1800 Solid and 1700 Liquid	0.5		60:40	Thirunavukkarasu *et al.* (2020)	Experiment
225.38	120.91					Greis *et al.* (1985)	Greis *et al.* (1985)

Table 9: Potential Inorganic Single and Eutectic PCMs with melting temperatures in the operating temperature range for solar cooking.

S/N	Materials	Melting Temperature (°C)	Enthalpy of fusion (kJ/kg)	Density (kg/m3)	References
Single-Component Materials (single compound)					
1	AlCl3	190	------	2.48	Nazir et al., 2018
2	LiNO2	222	----	1.615	ChemSpider
3	LiNO3	253	373	2.38	Kenisarin, 2010
4	NaNO2	270	180	1.81	Muhammad, 2018
5	ZnCl2	275	60	2.907	Nazir et al., 2018
6	Al(OH)3	300	-----	2.42	ChemSpider
7	NaNO3	300	200	1.9	Nazir et al., 2018
8	RbNO3	305	38	2.519	Muhammad, 2018
Two-Component Eutectic Mixture (bi-compound)					
15	KCl-LiNO3	165	200		Nazir et al., 2018
16	LiOH(30%)–NaOH (70%)	210–216	278–329		Kenisarin, 2010
17	NaNO3-KNO3	225	145		Nazir et al., 2018
18	KCl-ZnCl2	230	-----		Nazir et al., 2018
19	NaOH(20%)–NaNO2 (80%)	230–232	206–252		Abe et al., 1984
20	NaNO2(80)-NaOH (20%)	232	252		Kenisarin, 2010
21	NaNO2(27%)–NaOH (73%)	237	294		Kenisarin, 2010
22	NaOH(73%)–NaNO2 (27%)	237–238	249–295		Abe et al., 1984
23	LiCl-LiOH	265	-----		Nazir et al., 2018
Three-Component Eutectic Mixture					
32	NaCl(7.8)–6.4Na2CO3–85.5NaOH	282	316	2.13	Birchenall and Riechman, 1980
33	Na2CO3(6.4)–85.8NaOH –7.8NaCl	282	316		Kenisarin, 2010

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Table 10: Potential organic materials with melting temperatures in the operating temperature range for solar cooking.

S/N	PCMs	Melting Temperature (^{0}C)	Enthalpy of fusion (kJ/Kg)	Reference
1	HDPE	127	140	Gasia *et al.*, 2017
2	Adipic acid	151	230	Gasia *et al.*, 2017
3	Myo-Inositol	220	190	Maldonado *et al.*, 2018

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