Fatty Acids used as Phase Change Materials (PCMs) for Thermal Energy Storage in Building Material Applications

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INTRODUCTION

Rapid development has lead to huge demand on energy. In an attempt to conserve energy and reduce dependency on fossil fuels and also to reduce the greenhouse gas emission, it is essential to seek effective means of reducing peaks in power consumption and to shift portions of the load from periods of maximum demand. Storage of thermal energy, hence, becomes an important aspect in engineering application, especially in energy conservation in buildings. For example, heat collected during periods of bright sunshine can be stored, preserved and later released for utilisation during the night in solar energy systems. Heat storage can also be applied in buildings where heating needs are significant and electricity rates allow heat storage to be competitive with other forms of heating.

The search for suitable heat storage materials has recently been directed towards the use of low melting organic materials in an effort to avoid some of the problems inherent in inorganic phase change materials, for example supercooling and segregation. An overview of the literatures on the characterisation, application and limitations of fatty acids as phase change material (PCMs) energy storage is presented as follows.

FATTY ACIDS AS PCMS

Fatty acids are one of the organic phase change materials. They possess some superior properties over other PCMs such as melting congruency, good chemical stability, non-toxicity and suitable melting temperature range for solar passive heating applications. These materials, in their liquid phase, have a surface tension in the order of 2-3 x10^{-4} N/cm that is high enough to be retained in the structure of the host material. These materials possess elevated latent heat of transition and high specific heat (in the range 1.9-2.1 J/g °C). It also exhibits only small volume changes during melting or solidification (example: melting dilatation is around 0.1-0.2 ml/g). In addition, little or no supercooling occurs during the phase transition with these materials, which is an important advantage over many other PCMs. Because of the protected carboxyl group, fatty acid base PCMs are chemically, heat and colour stable, low corrosion activity and non-toxic. The raw materials of fatty acids are derived from renewable vegetable and animal sources. This assures a continuing non-pollutant source of supply [1].

Fatty-acid based PCM can be produced in the following categories:

1. Naturally occurring triglycerides.
2. Hydrates of acids of triglycerides and their mixtures.
3. Esters of the fatty acids of naturally occurring triglycerides.
4. Refined/synthesised triglyceride products produced by a combination of fractionation and transesterification processes.
5. Synthesised triglyceride products using hydrogenation (or dehydrogenation) and fractionation.
6. Synthesised triglyceride products using cis-trans isomerisation and fractionation.
7. Synthesised fatty acid derivatives that have the desired freezing point temperatures.
8. Refined fatty acid hydrates that have the desired freezing point temperatures.
9. Prepared mixtures produced by essentially any of the previous processing approaches with other chemicals (preferable cheap and non-toxic) to produce eutectic compositions with the desired freezing point temperature range.

Tables 1-4 show the potential oleochemical use as PCMs and their physical and thermal properties [2-15].

FATTY ACIDS AS PCMS IN BUILDING MATERIALS APPLICATION

The characteristics of PCMs have made them inherently suitable for use in buildings for energy conservation purposes without the complications brought about by other thermal storage devices requiring separate plant and space. Solid/liquid transitions within the pores do not cause any leaking of materials in wallboard. Concepts of wallboard with PCMs thermal energy storage have been receiving increasing attention, particularly in countries with fluctuating climate conditions [1].

Several works have been carried out in order to study the thermal properties of the binary mixtures of fatty acid and its compatibility with the building materials. Study that carried out by Feldman *et al.* [1] found gypsum wallboard to be compatible with a broad range of PCMs, including fatty acids and esters. The compatibility of concrete blocks is basically dependent on the presence of calcium hydroxide ($Ca(OH)_2$) in the block, since certain organic PCMs will react with it. Feldman *et al.* [1] also demonstrated that a mixture of 20% methyl palmitate and 80% methyl stearate provided a sharp solid-liquid phase transition at ambient temperature with a latent enthalpy similar to that of paraffins--this mixture is one of many possible derivatives of fats and oils. Unfortunately, the highly refined methyl palmitate and methyl stearate are too costly to compete with paraffins.

Energy storage composite with an organic PCM were studied by Feldman *at al* [16]. Composite specimens were

Table 1: Oleochemical with potential use as PCM. [2, 3-7]

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m^3)
Propyl palmiate	10[a]	186[a]	n.a	n.a
Isopropyl palmiate	11[a]	95-100[a]	n.a	n.a
Capric-lauric acids + pentadecane (90:10)	13.3[a]	142.2[a]	n.a	n.a
Isopropyl stearate	14-18[a]	140-142[a]	n.a	n.a
Caprylic acid	16[a] 16.3[a] 16.7[c]	148.5[a] 149[a]	0.149 (liquid,38.6°C)[a] 0.145 (liquid,67.7°C)[a] 0.148 (liquid,20°C)[a]	901 (liquid, 30°C)[a] 862 (liquid, 80°C)[b] 866 (liquid, 75°C)[b] 981 (solid, 13°C)[a] 1033 (solid, 10°C)[a]
Capric-lauric acids (65mol%-35mol%)	18.0[a]	148[a]	n.a	n.a
Butyl stearate	19[a]	140[a] 123-200[a]	n.a	n.a
Capric-lauric acids (45-55%)	21[a]	143[a]	n.a	n.a
Dimethyl sabacate	21[a]	120-135[a]	n.a	n.a
34% Miristic acid + 66% Capric acid	24[a]	147.7[a]	0.164(liquid,39.1°C)[a] 0.154(liquid,61.2°C)[a]	888(liquid, 25°C)[a] 1018 (solid, 1°C)[a]
Vinyl stearate	27-29[a]	122[a]	n.a	n.a
Capric acid	32[a] 31.5[a] 31.6[c]	152.7[a] 153[a]	0.153(liquid,38.5°C)[a] 0.152(liquid,55.5°C)[a] 0.149(liquid,40°C)[a]	878(liquid,45°C)[a] 886(liquid,40°C)[a] 858(liquid, 75°C)[b] 853(liquid, 80°C)[b] 1004(solid, 24°C)[a]
Methyl-12 hydroxy-stearate	42-43[a]	120-126	n.a	n.a
Lauric acid	42-44[a] 44[a] 44.2[c]	178[a] 177.4[a]	0.147 (liquid, 50°C)[a]	862 (liquid, 60°C)[a] 870 (liquid, 50°C)[a] 852 (liquid, 75°C)[b] 848 (liquid,80°C)[b] 1007 (solid, 24°C)[a]
Myristic acid	49-51[a] 54[a] 58[a] 54.4[c]	204.5[a] 187[a] 186.6[a]	n.a	861 (liquid, 55°C)[a] 849 (liquid, 75°C)[b] 844 (liquid, 80°C)[b] 990 (solid, 24°C)[b]
Palmitic acid	64[a] 61[a] 63[a] 62.9[c]	185.4[a] 203.4[a] 187[a]	0.162 (liquid,68.4°C)[a] 0.159(liquid, 80.1°C)[a] 0.165 (liquid, 80°C)[a]	850 (liquid, 65°C)[a] 845 (liquid, 75°C)[b] 847 (liquid, 80°C)[b] 989 (solid, 24°C)[a]
Stearic acid	69[a] 60-61[a] 70[a] 69.6[c]	202.5[a] 186.5[a] 203[a]	0.172 (liquid, 70^{0}C)[a]	848 (liquid, 70°C)[a] 843 (liquid, 75°C)[b] 839 (liquid, 80kC)[b] 965 (solid, 24°C)[a]

% in weight; n.a. : not available.
[a] : [3]
[b] : [4]
[c] : [2, 5-7]

Table 2: Thermal and physical properties of some fatty acids [8-14]

Acid	Latent heat of fusion (kJ/kg)	Specific heat (kJ/kg °C) Solid	Liquid	Heat of vaporization (kJ/kg)	Refractive Indexes (_D)
Caproic	130.60	1.8815 (-33 to –10)	2.1369(0-23)	-	1.3972(70°C) 1.3944(75°C)
Caprylic	148.18	2.1139(18-46)	1.9464(0-12)	406.02[a]	1.4089(70°C) 1.4069(75°C)
Capric	162.83	2.0967(0-24)	2.0883(35-65)	355.79[a]	1.4169(70°C) 1.4149(75°C)
Lauric	182.92	2.1416(19-39)	2.1540(48-78)	288.82[a]	1.4230(70°C) 1.4208(75°C)
Myristic	197.15	2.1804(24-43)	2.1586(to84)	372.54[a] 380.91[b]	1.4273(70°C) 1.4251(75°C)
Palmitic	211.80	2.0594(22-53)	2.2670(to68)	246.96[a] 359.98[b]	1.4209(70°C) 1.4288(75°C)
Stearic	-	-	-	234.10[a] 334.86[b]	1.4337(70°C) 1.4318(75°C)

[a] Calculated for atmospheric pressure
[b] Calculated for 1-20mm Hg

Table 3: Thermal conductivities of commercial fatty acids [4]

Fatty acids	Temperature (°C)	Thermal Conductivity (W/m °C)
Lauric	72.5	0.1921
	90	0.1852
	106	0.1748
	148	0.1390
Oleic	72.5	0.1886
	90	0.1783
	106	0.1560
	148	0.1158
Palmitic	72.5	0.1719
	90	0.1573
	106	0.1384
	148	0.1026
Stearic	72.5	0.1603
	90	0.1468
	106	0.1321
	148	0.0966

prepared using coarse aggregates, gypsum, cement, sawdust and vermiculite and sand with water. The absorption capacities of PCM in the specimens and compressive strength tests show that the composite was capable of storing up to 30% wt of PCM. The composite can be produced in the form of floor, wall or ceiling tiles capable of storing energy up to 766 kJ/m^2.

Hawes and Feldman [17] also examined the mechanisms of absorption and established a means of developing and using absorption constants for PCM concrete to achieve diffusion of the desired amount of organic PCM and hence the required thermal storage capacity. The effects of temperature, PCM viscosity, concrete density and hydrogen bonding on PCM penetration was studied in order to optimise the effective use of PCM concrete.

Feldman and Shapiro[18] have analysed the properties of fatty acids (capric, lauric, palmitic and stearic acids) and their binary structures. The melting range of these fatty acids was observed to vary from 30 to 65°C and having the latent heat of transition vary from 153 to182 kJ/kg. These properties have made these fatty acids be the potential candidates in TES applications.

Nikolic *et al*. [19] measured specific heat of these composites materials in the temperature range –10–60°C, which are:

a. Gypsum:
   before impregnation, c_p = 1.8 kJ/kg °C;
   after impregnation, c_p= 2.0 kJ/kg °C.
b. Brick:
   before impregnation, c_p = 1.6 kJ/kg °C;
   after impregnation, c_p = 1.7 kJ/kg °C.

Their findings indicate that the latent heat of fusion has contributed to the overall heat storage capacity in a wallboard impregnated with the esters and their mixtures. Unlike the pure methyl stearate system, the thermal storage capacity of a gypsum wallboard impregnated with eutectic mixture of methyl stearate and methyl palmitate, as well as the value of the melting point of the eutectic, makes this combination promising for possible use in passive solar building. The eutectic mixture has shown the most sharp phase transition at the lowest temperature, 23.9°C, which has been almost an ideal value for passive solar applications (Figure 1).

Table 4: Boiling point of some fatty acids [15]

Pressure (mm Hg)	Boiling Point (°C)						
	Caproic	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic
1	61.7	87.5	110.3	130.2	149.2	167.4	183.6
2	71.9	97.9	121.1	141.8	161.1	179.0	195.9
4	82.8	109.1	132.7	154.1	173.9	192.2	209.2
8	94.6	121.3	145.5	167.4	187.6	206.1	224.1
16	107.3	134.6	159.4	181.8	202.4	221.5	240.0
32	120.8	149.2	174.6	197.4	218.3	238.4	257.1
64	136.0	165.3	191.3	214.6	236.3	257.1	276.8
128	152.5	183.3	209.8	234.3	257.3	278.7	299.7
256	171.5	203.0	230.6	256.6	281.5	303.6	324.8
512	192.5	225.6	254.9	282.5	309.0	332.6	355.2
760	205.8	239.7	270.0	298.9	326.2	351.5	376.1

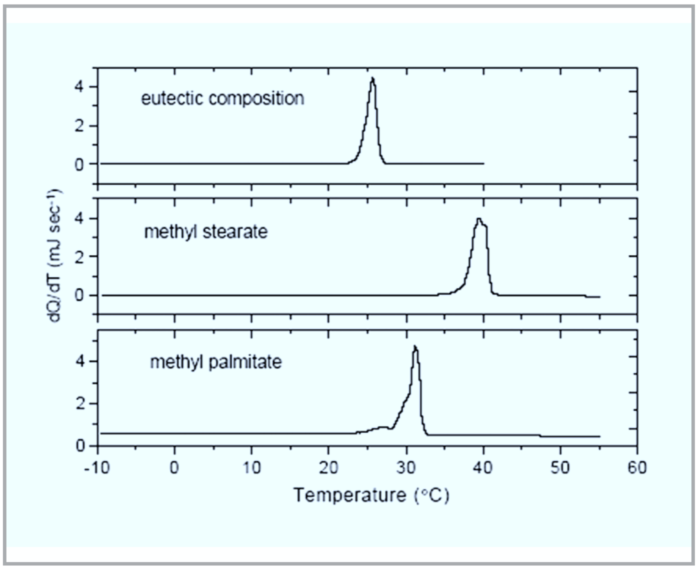

Figure 1: The endothermic DSC thermograms of: (a) methyl palmitate (b) methyl stearate and (c) their eutectic mixture [19].

Shapiro [20, 21] has shown several phase-change materials mixtures (methyl-esters, methyl palmitate and methyl stearate, and mixtures of short-chain acids, capric and lauric acid) to be suitable for introduction into gypsum wallboard with possible thermal storage application for the Florida climate. Although these materials had relatively high latent heat capacity, the temperature ranges required to achieve that thermal storage did not fall sufficiently within the range of comfort for buildings in hot climates.

Neeper [22, 23] has studied the thermal dynamics of gypsum wallboards impregnated by fatty acids and paraffin waxes as PCMs that are subjected to diurnal variation of room temperature. His findings had shown that the PCM-wallboard thermal storage would be sufficient enough to capture large solar heating fractions.

CONCLUSION

Latent heat storage is a developing technology that has been found to be very promising in recent times due to the several operational advantages it offers. Research is underway to develop many kinds of phase change materials (PCMs) as thermal energy storage. Fatty acids have good potential thermal characteristic as PCM since they have desired thermodynamic and kinetic criteria for low temperature latent heat storage. An added advantage is that fatty acids are derived from the common vegetable and animals oil that provides an assurance of continuous supply. This article has summarised the studies that have been carried out by many other workers on fatty acid as PCM in thermal energy storage.

However, in the present market situation, an investment in fatty acids as PCM storage in the building materials may not be economically justified if only energy savings were accounted for. Therefore, the effect of improved thermal comfort should also be taken into consideration. In order that more interest would be shown in the use of PCM building elements, it is obvious that more work should be done on enhancing and improving the economic viability of such an investment. ■

REFERENCES

[1] Feldman D., Banu D. and Hawes D. Low chain esters of stearic acids as phase change materials for thermal energy storage in building Solar Energy Materials and Solar Cells 1995; 36, 311-322.

[2] Zelba B., Marin J., Cabeza L. F., Mehling H. Review on thermal energy storage with phase change; materials, heat transfer analysis and application. Applied Thermal Engineering 2003; 23:, 251-183.

[3] Lutton E. S. Fatty acids: their chemistry, properties, production and uses, K. S. Markley (ed.), 2nd ed., Part 4. New York: Interscience, 1967.

[4] Formo M. W., Jungermann E., Norris F. A. and Sonntag N. O. V., Bailey's Industrial Oil and Fat Products: John Wiley & Sons; 1979.

[5] Bailey A. E., Melting and Solidification of Fats and Fatty Acids. New York: Interscience, 1950.

[6] Malkin T. Progress in the chemistry of fats and other lipids, vol.1. New York: Pergamon Press; 1952.

[7] Ferguson R. H .and Lutton E.S. Chem. Rev. 1941; 29, 355.

[8] Garner W. E. and Randall F. C. J. Chem. Soc.; 1924, 881.

[9] Garner W. E., Madden F. C. and Rushbrook J. E. J. Chem. Soc.; 1926, 2491.

[10] Garner W. E. and King A. M. J.Chem. Soc.; 1949, 1929.

[11] Kern D. Q. and. Van Nostrand W. Ind. Eng. Chem.1949; 41, 2209.

[12] Perry E. S., Weber W. H and Daubert B. F. J. Am. Chem. Soc. 1949; 71, 3720.

[13] Laderrer E. L. Seinfenseider-Ztg. 1930; 57, 67.

[14] Cramer J. S. N. Rec. Trav. Chim.1943; 62,606.

[15] Pool W. O. and Raalston A. W. Ind. Eng. Chem. 1942; 34, 1104.

[16] Feldman D., Khan M. A. and Bahu D., Energy storage composite with an organic PCM. Solar Energy Materials 1989; 18(6), 333-341.

[17] Hawes D. W. and Feldman D. Absorption of phase change materials in concrete. Solar Energy Materials and Solar Cells 1992; 27(2), 91-101.

[18] Feldman D., Shapiro M. M., Banu D. and Fuks C. J. Fatty Acids and their mixtures as phase-change materials for thermal energy storage. Solar Energy Matererials 1989; 18 (6), 201-216.

[19] Nikolic R., Marinovi_-Cincovi_ M., Gadzuri_ S.and Zsigrai I. J. New materials for solar thermal storage-solid/liquid transitions in fatty acid ester. Solar Energy Materials and Solar Cells 2003; 79, 285–292.

[20] Rudd A. F. Phase Change Material wallboard for distributed thermal storage in buildings. ASHRAE Transactions Research 1993; 99 Part 2, 3724.

[21] Shapiro M.M., Feldman D., Hawes D. and Banu D. PCM thermal storage in drywall using organic phase-change material. Passive Solar Journal 1987; 4(4), 419-438.

[22] Neeper DA. Potential benefits of distributed PCM storage. In: Coleman MJ,, editor. Proceedings of 14th National Passive Solar Conference. Denver, Colorado, USA: American Solar Energy Society; 1989. p. 283-289.

[23] Neeper DA. Thermal dynamics of wallboard with latent heat storage. Solar Energy 2000; 68, 393-403.