Asian Journal of Chemistry Vol. 18, No. 2 (2006), 923–930

Thermal and Chemical Investigation of Some Fatty Acids Subjected to Accelerated Thermal Cycle

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Thermal and chemical investigations of the lauric, myristic, palmitic and stearic acids as latent heat storage materials subjected to accelerated thermal cycles (400, 700 and 1000 melt-freeze cycles) were carried out. The latent heats of fusion and melting temperatures of the fatty acids with industrial grade (90–97% purity) as functions of thermal stability after the repeated thermal (heating-cooling) cycles were measured by differential scanning calorimetry (DSC) technique. The DSC analyses showed that the decrease in the latent heats of fusion and the melting temperatures of the fatty acids are in the range of about 9–17.1% and 1.5–2.6°C, respectively during 1000 thermal cycles. The probable reasons for the decrease in these thermal properties were searched by Fourier transform infrared (FTIR) spectroscopic and potentiometric titration methods. The FTIR spectra and pK_a values with respect to the thermal cycle number indicated that the decrease in the thermal stability of the acids may be due to the amount of impurity in the acids.

Key Words: Fatty acids, Thermal cycle, Differential scanning calorimetry, Fourier transform infrared, Potentiometric titration method.

INTRODUCTION

Latent heat thermal energy storage (LHTES) by a phase change material (PCM) is considered as a developing energy technology and there has been an increasing interest in using this essential technique for thermal applications, such as heating, hot water, air conditioning and so on. The LHTES system offers the advantage of storing a large amount of energy in a small mass/volume. In an LHTES system, a PCM absorbs or reveals a quantity of heat as much as its latent heat of fusion when it melts or solidifies at the appropriate temperature[1].

A PCM which will be used for LHTES must have the following features: an appropriate phase change temperature, high latent heat of fusion, no or less volume change during the phase change process, no corrosion, no super cooling, no toxicity, no flammability, low cost and ready availability. Besides these features, it must have a long life in terms of thermal stability depending on the thermal cycle number. The decrease in the thermal properties (latent heat of fusion values and melting temperature) of a PCM after a large number of thermal cycles is to be at the minimum level. Therefore, a comprehensive knowledge of thermal stability of PCM with respect to repeated heating and cooling cycles is essential for an assurance of its long term energy storage performance. Moreover, the investigation of the chemical structure of the PCM before and after thermal cycle is also important in terms of determining the probable causes of the change in the thermal properties of the PCM.

A wide range of PCMs including salt hydrates and their mixtures as PCMs have been investigated for energy storage. The saturated fatty acids have the superior thermophysical properties as mentioned above[1]. The number of studies on their thermal stability or the reliability of thermal performance after many times of heating-cooling cycles is limited[2-4]. This study presents the decrease in the latent heat of fusion and melting temperatures of some fatty acids with respect to thermal cycle numbers (400, 700 and 1000). This investigation also deals with establishing the probable reasons of the decrease in the thermal properties of the fatty acids with respect to the repeated thermal cycles by using FTIR spectroscopy and potentiometric titration method.

EXPERIMENTAL

Fatty acids used as PCMs in this study are lauric acid ($C_{11}H_{23}COOH$, 90% purity), myristic acid ($C_{13}H_{27}COOH$, 95% purity), palmitic acid ($C_{15}H_{31}COOH$, 96% purity) and stearic acid ($C_{17}H_{35}COOH$, 97% purity). These acids were obtained from Aldrich and Fluka companies. Tetramethylammonium hydroxide ($(CH_3)_4NOH$, 25%) from Merck and tetramethylammonium chloride ($(CH_3)_4NCl$, 98%) from Fluka, HCl from Merck and potassium hydrogen phthalate (KHP) as buffer solution from Fluka were obtained.

To determine the effect of thermal cycle number on the melting temperatures and the latent heats of fusion of the acids, four cylindrical capsules were used. The capsules made of pyrex glass, which were airtight but containing a certain amount of air, were filled with 100 g of the selected acid sample and then they were set into a thermostatic chamber equipped with a temperature programmer in order to carry out controlled thermal cycles. The samples were first melted at 80°C, then solidified below the solidification temperature by shutting off the heating programmer. The above procedure was performed consecutively until the thermal cycle numbers were 400, 700 and 1000, respectively. The capsules were opened and the samples were taken for DSC thermal analysis; FTIR spectroscopy and potentiometric titration methods were performed on the fatty acids after the above number of thermal cycles.

DSC analysis technique was used to evaluate the melting temperatures and the latent heats of the fresh (uncycled) and cycled fatty acid samples. For this purpose, a DSC instrument (DuPont 2000) was used. All DSC samples were encapsulated in hermetically sealed aluminum pan with a mass of about 5.5 mg. Stearic acid of reagent grade (m.p. 73.2°C) was used as a reference for temperature calibration. The heating rate and the scanning temperature range for all runs were 5 deg/°C and 20–80°C, respectively. The melting temperature, which is referred to as onset temperature, corresponds to the point obtained by drawing a line at the point of maximum slope of the leading edge of the DSC peak and extrapolating baseline on the same side as the leading edge of the peak, as seen in Fig. 1. The latent heat of fusion was calculated by numerical integration of the area under the peak.

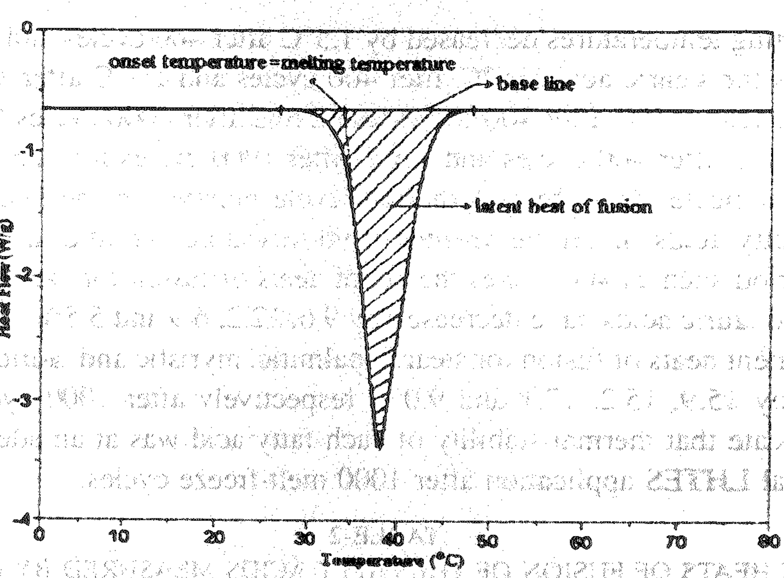


Fig. 1. A typical DSC output curve

Fourier transform infrared spectrophotometer (Jasco FTIR-430) was used to detect the probable changes occurring in the chemical structure of the cycled fatty acid samples. For the FTIR spectral analysis, samples were ground with KBr powder and then compressed to obtain transparent pellets.

All acids used were dissolved with ethyl alcohol (40%, v/v). 0.05 molal potassium hydrogen phthalate was prepared as buffer solution and used for the calibration of the combination pH electrode (a SenTix 20 pH combination electrode, WTW, Weilheim) according to the method of Molspin[5]. Carbonate-free standard $(CH_3)_4NOH$ solution (*ca.* 0.025 mol dm^{-3}) was used as titrant. HCl stock solution with pH 3.0 was prepared from concentrated HCl. The concentrations of the investigated acids were in the range of 1×10^{-4}–2×10^{-4} mol dm^{-3}. The pH measurements were carried out at an ionic strength of 0.100 mol dm^{-3} $(CH_3)_4NCl$. All titrations were carried out between pH 3.0–11.5. The pH data were used to calculate pK_a constants using the Superquad computer program[6].

RESULTS AND DISCUSSION

The melting temperatures of the cycled and uncycled fatty acids measured by DSC were given in Table-1.

TABLE-1
MELTING TEMPERATURES OF THE FATTY ACIDS MEASURED BY DSC (°C)

Fatty acid	Purity (%)	Number of cycles			
		0 (Fresh)	400	700	1000
Stearic acid	90	69.3	67.8	67.1	66.8
Palmitic acid	97	59.2	58.4	57.7	57.5
Myristic acid	95	51.4	50.9	49.4	48.8
Lauric acid	98	42.6	42.1	41.3	41.1

The melting temperatures decreased by 1.5°C after 400 cycles and 2.5°C after 1000 cycles for stearic acid, 0.6°C after 400 cycles and 1.7°C after 1000 cycles for palmitic acid, 0.5°C after 400 cycles and 2.6°C after 1000 cycles for myristic acid and 0.5°C after 400 cycles and 1.5°C after 1000 cycles for lauric acid.

Table-2 indicates the effect of thermal cycle number on the latent heats of fusion of fatty acids. It can be resulted from this table that after a middle-term thermal period such as 400 cycles the latent heats of fusion for stearic, palmitic, myristic and lauric acids have decreased by 9.6, 12.2, 6.9 and 5.5%, respectively; while the latent heats of fusion for stearic, palmitic, myristic and lauric acids have decreased by 15.9, 15.2, 17.1 and 9.0%, respectively after 1000 cycles. These results indicate that thermal stability of each fatty acid was at an adequate level for an actual LHTES application after 1000 melt-freeze cycles.

TABLE-2
LATENT HEATS OF FUSION OF THE FATTY ACIDS MEASURED BY DSC (°C)

No. of cycles	Stearic acid	Palmitic acid	Myristic acid	Lauric acid
0	174.6	197.9	189.8	211.6
400	157.7	173.7	178.6	199.8
700	146.7	169.5	171.4	194.3
1000	141.4	167.8	159.1	192.5

On the other hand, as seen in Figs. 2–5, the absorption of —OH stretching band in the wide range of 3200–2500 cm^{-1} indicates the existence of intermolecular hydrogen bonds in solid state. The unassociated —C=O stretching band is observed at 1760 cm^{-1} in FTIR spectra of saturated fatty acids, whereas the absorption of —C=O is normally centred at 1700–1720 cm^{-1} due to intermolecular hydrogen bonds which are established *via* the carbonyl group. Moreover, saturated fatty acids have a dimeric structure with an ionic resonance as follows:

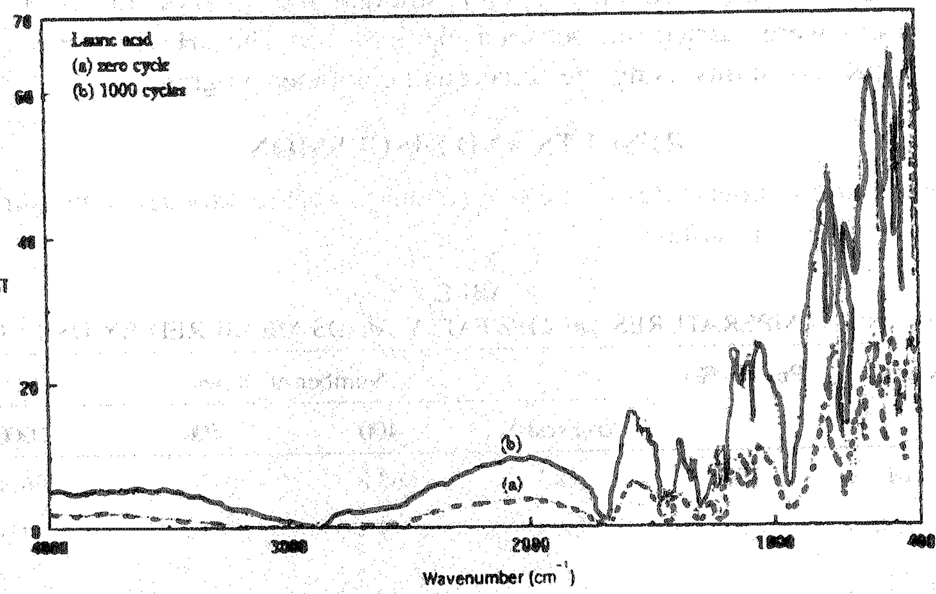


Fig. 2. FTIR spectra for (a) uncycled and (b) cycled lauric acid

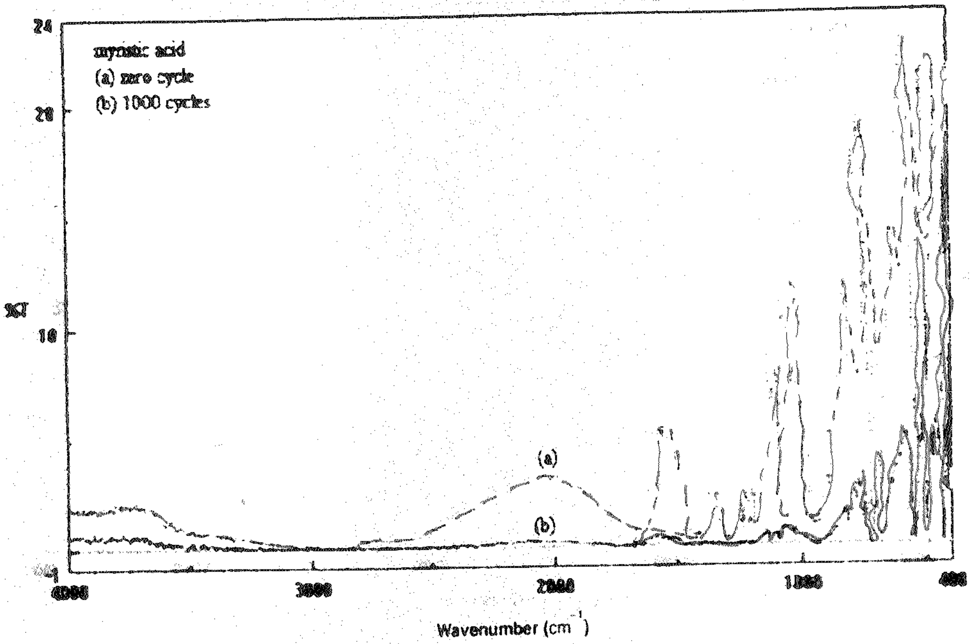


Fig. 3. FTIR spectra for (a) uncycled and (b) cycled myristic acid

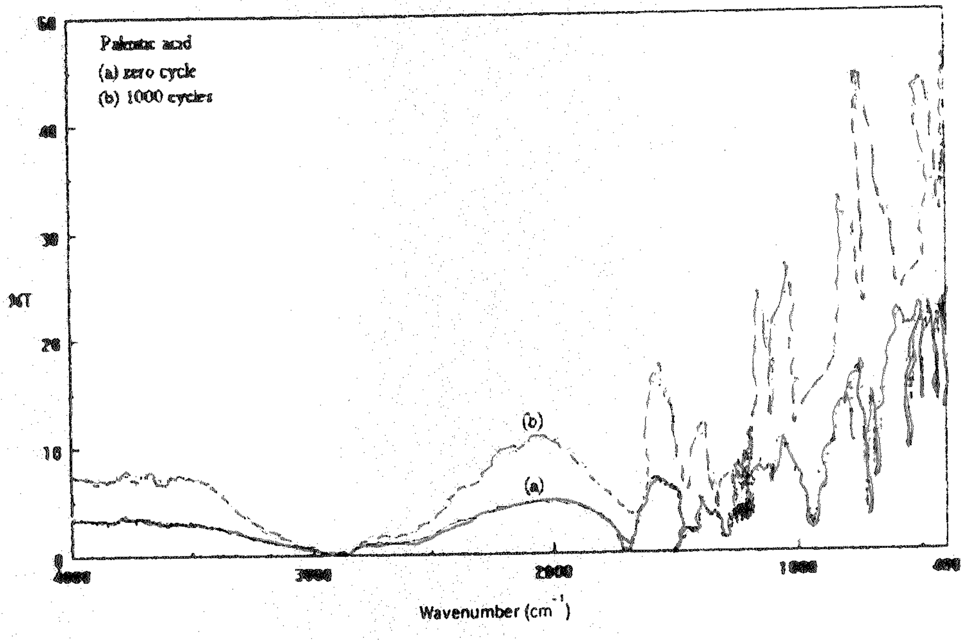


Fig. 4. FTIR spectra for (a) uncycled and (b) cycled palmitic acid

The exceptional strength of hydrogen bonding is explained on the basis of the large contribution of the ionic resonance structure[7]. However, broadened and weakened —OH and —C═O absorption bands with increase in the thermal cycle number may be due to the decrease of the ionic resonance contribution on the cycled fatty acid molecules in dimeric state owing to the amount of impurity in the acids.

There is no shift in the other absorption bands, especially in the finger region with respect to the accelerated thermal cycle except widening in the absorption bands of the —OH and —C═O groups. This means that there is no degradation in the chemical structures of the fatty acids subjected to the accelerated thermal cycles.

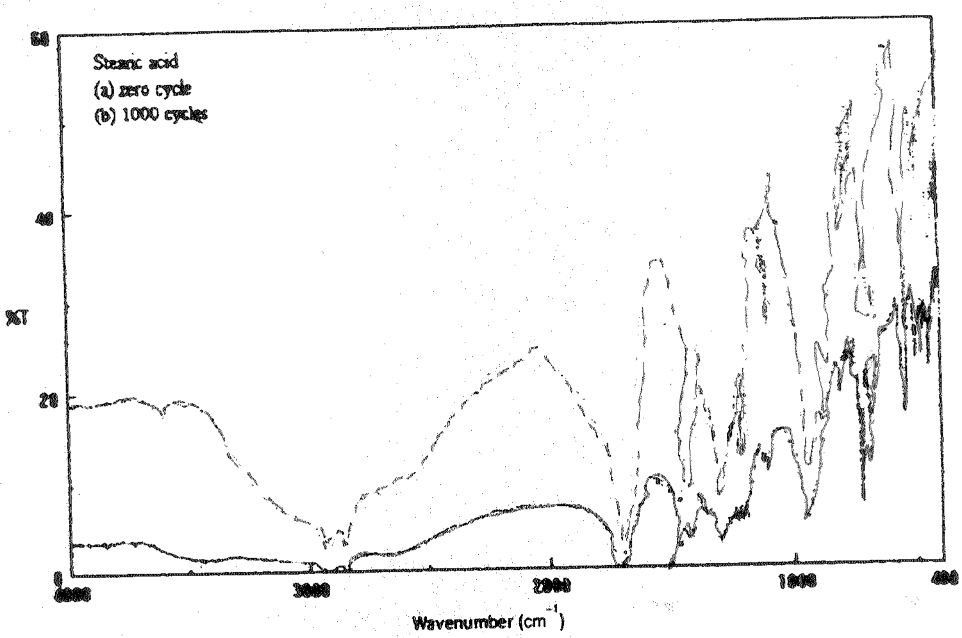
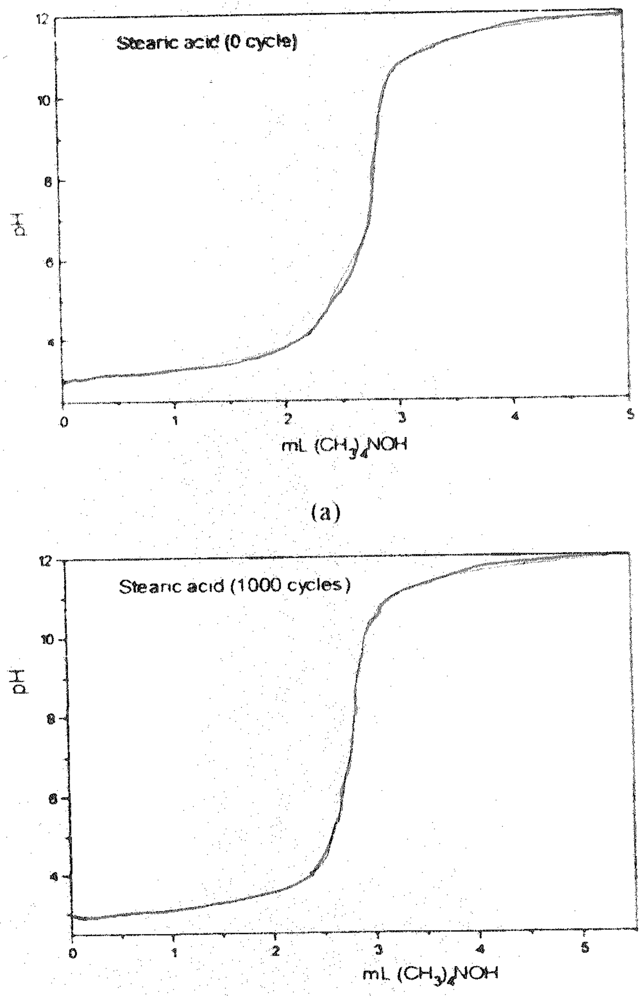


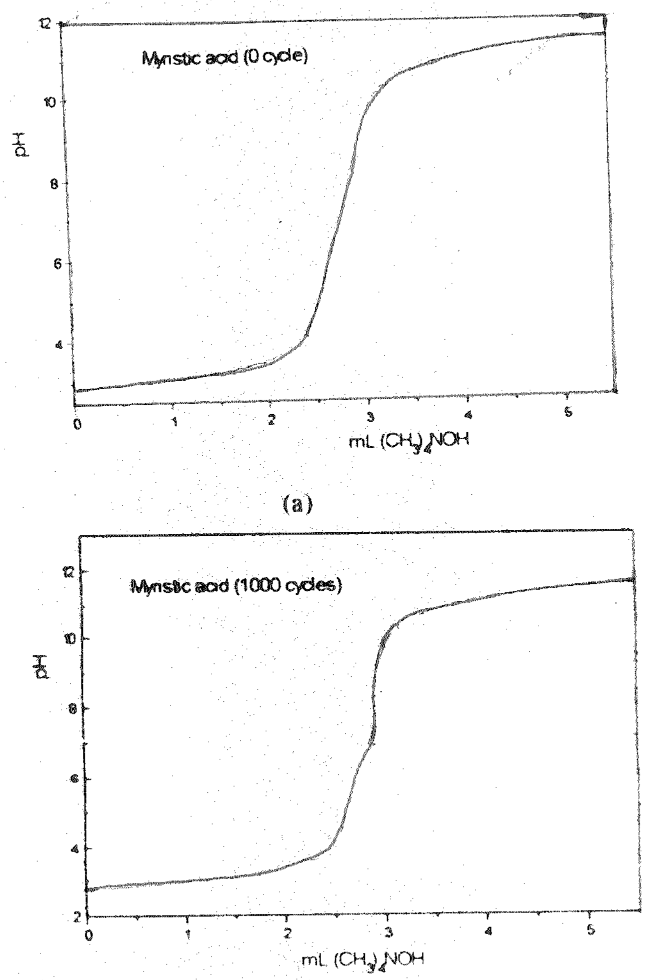
Fig. 5. FTIR spectra for (a) uncycled and (b) cycled stearic acid



(a)

(b)

Fig. 6. Potentiometric titration curves for stearic acid (a) uncycled (b) after 1000 cycles.



(a)

(b)

Fig. 7. Potentiometric titration curves for myristic acid (a) uncycled (b) after 1000 cycles

Furthermore, the pK_a constants for the acids obtained by potentiometric titration method and analyzed using Superquad are given in Table-3. Titration curves for stearic and myristic acids are given in Figs. 6 and 7. The titration curves of palmitic and lauric acids were similar. The pK_a values are getting higher with molecular weight except stearic acid. This is due to the fact that stearic acid contains > 40 wt. % palmitic acid and about 10 wt. % impurity. The pK_a values are also increased with thermal cycle number except lauric acid. This result means that the effect of thermal cycle on fatty acids with long-chain is higher. On the other hand, the pK_a values for stearic, palmitic and lauric acids in literature[8] have been determined as 7.45, 7.55 and 7.38 using the glass electrode method, respectively. As seen in Table-3, these values were found with respect to 6.15, 6.66 and 5.87, which are smaller than those of literature, because of using different experimental conditions ($I = 0.4$ mol dm^{-3} NaCl, 0.05 mol dm^{-3} sodium dodecyl sulfate). Based on the potentiometric results, it is worth that there is no significant difference between pK_a values with respect to increased number of thermal cycles. In addition, the potentiometric data are supported by DSC and FTIR findings.

TABLE-3
pK$_a$ CONSTANS FOR FATTY ACIDS
(I = 0.1 mol dm^{-3} at 25°C)

Fatty acids	0 cycle	after 400 cycles	after 1000 cycles
Stearic acid	6.15 ± 0.04	6.52 ± 0.04	6.71 ± 0.05
Palmitic acid	6.66 ± 0.06	6.70 ± 0.06	6.81 ± 0.04
Myristic acid	6.15 ± 0.07	6.22 ± 0.07	6.40 ± 0.04
Lauric acid	5.87 ± 0.08	5.64 ± 0.06	5.36 ± 0.04

Conclusions

The DSC analysis results reveal that the melting temperatures decreased 2.5°C for stearic acid, 1.7°C for palmitic acid, 2.6°C for myristic acid and 1.5°C for lauric acid during 0–1000 thermal cycles. The latent heat of fusions for stearic, palmitic, myristic and lauric acids have decreased by 15.9, 15.2, 17.1 and 9.0%, respectively after 1000 cycles. Furthermore, the spectroscopic analysis and potentiometric titration studies indicate that accelerated melt-freeze processes do not cause any degradation in the chemical structure of fatty acids. Therefore, the change in thermal properties with increasing thermal cycle is because of the presence of certain amount of impurities in the acids. Based on all the results, it can also be concluded that the investigated fatty acids as latent heat energy storage materials used for LHTES applications have shown reasonably good thermal reliability in terms of the change in latent heat fusion and melting temperature.

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(*Received*: 11 February 2005; *Accepted*: 12 December 2005) AJC-4509