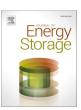
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Research papers



Accelerated testing methods to analyse long term stability of a Phase Change Material under the combined effect of shear stress and thermal cycling

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ABSTRACT

The long-term stability of a Phase Change Material (PCM) is a key point for its selection in energy storage devices. This work studies the suitability of a commercial paraffin wax in an active scraped surface heat exchanger for solar energy storage purposes. In these devices, the continuous scraping of inner walls during solidification removes PCM and increases the released heat. Hence, the PCM is affected by a high level of shear stress. In order to study a potential degradation of the paraffin, a novel accelerated procedure has been designed for obtaining samples with a different number of thermal and scraping cycles. The procedure allows to evaluate the effect of shear stresses, thermal cycles and their combined effects separately. Up to 3000 cycles have been generated, which accounts for around 8 years of continuous daily work in the heat exchanger. The measurements through Differential Scanning Calorimetry, rheometry and thermal conductivity analysis have shown that neither the thermal nor the scraping cycling have a significant impact on the paraffin thermo-physical properties. According to the findings reported in this work, paraffin wax RT44HC can be successfully used in scraped surface heat exchangers. It is expected that other commercial paraffins would be also suitable since most of them share the fact of being blends of alkanes and other hydrocarbons.

1. Introduction

In recent years, there is a strong uptrend in the use of renewable energies. The recent framework programme Horizon Europe [1], the EU's key funding programme for research and innovation, promotes for the period 2021–2027 an important reduction in the use of fossil fuels. Furthermore, it supports an increased weight of renewable energies in the total energy generation. According to the International Energy Agency's (IEA) World Energy Outlook 2020 [2], the average growth of renewable electricity is expected to be about 5 % per year from 2019 to 2030. With respect to the use of renewables for heat, they are expected to account for 14 % of total energy consumed by 2030.

Solar energy plays a central role among the renewable energy sources. The use of Phase Change Materials (PCMs) is an emerging technology to increase the energy storage capacity of conventional solar thermal systems. It allows to solve the decoupling between energy production and consumption, a typical problem that arises in the domestic hot water generation by solar energy [3–5].

Organic PCMs are materials that consist of a hydrocarbon chain. They can be classified into Non-Paraffins and Paraffins [6]. On one side, fatty acids, a non-paraffin type of PCM, are commonly used in building applications [7,8] due to their excellent thermal reliability [9,10]. On the other side, paraffins are thermically stable up to $500\,^{\circ}$ C, they are non-toxic and non-corrosive, relatively economical and present small changes in volume during phase transition. Those characteristics make paraffins especially suitable for residential use, as many related studies confirm [11–13]. Both, pure straight chain alkanes and commercial blends of alkanes and other hydrocarbons can be used. The latter are more widely used for enhancing solar thermal systems capability [14–16], due to their lower cost and because their temperatures of transition can be adapted to the system needs.

However, the integration of PCM energy storage modules in commercially available solar thermal systems is far from being a common practice. As Kahwaji et al. [17] pointed out, a possible reason is the lack of knowledge about the thermal properties of paraffins, especially in the melting/solidification temperatures (MT/ST) and the latent heat fluxes of melting and solidification (LHF_M/LHF_S). In particular, there is a

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Nomenclature

DSC Differential Scanning Calorimetry k Thermal conductivity (W/m·K) LHF_M Melting Latent Heat Flux LHF_S Solidification Latent Heat Flux Latent Thermal Energy Storage

MT Melting Temperature

MTPS Modified Transient Plane Source

n number of iterations in accelerated procedure

PCM Phase Change Material ST solidification temperature T temperature (K)

T temperature (K)

TES Thermal Energy Storage μ dynamic viscosity (Pa·s) U level of confidence (%) x number of scraping cycles y number of thermal cycles

need for further studies on how the successive cycles of phase change affect their physical properties. Although those materials are considered to have long term thermal stability, most research studies overlook the issue of paraffins' cyclability. As Dutil et al. [18,19] pointed out, the high level of uncertainty about the thermal properties of paraffins undermine the credibility of numerical simulations with those PCMs.

Regarding the experimental results reported for phase change enthalpies and temperatures in paraffins, they are usually obtained through Differential Scanning Calorimetry (DSC). There are important discrepancies among authors for a given compound. As an example, in the thorough review from Acree and Chickos [20], for a pure alkane such as eicosane the reported melting point and enthalpy of transition range from (308.8 to 311.6) K and (211.99 to 247.38) J/g, respectively. If octadecane is considered, the reported ranges are (300.2 to 303.6) K and (223.18 to 256.58) J/g. Moreover, the discrepancies are higher for commercial blends of paraffin waxes, where their properties are often quoted within a range of values [21,22].

On the other hand, if the studies on the thermal cyclability of PCMs are considered, there are authors that report great variations in MT and LHF_M with respect to the original values, whereas others do not find any significant changes. Anand et al. [23] recently published an extended review on the issue. Hadjieva et al. [24] studied the effect of thermal cycling in several commercial technical grade paraffin waxes. They did not inform about great differences in MT and LHF_M (around 1 % and 1.8 %, respectively). Sharma et al. [25] generated 20 to 300 thermal cycles in a paraffin wax and reported a small change of ± 1.8 for MT, but considerable higher changes (-12 to +2 %) for LHT. There was not a clear link between the degradation of properties and the number of cycles. In another study [26], the authors also reported an important variation in the thermal properties for a paraffin wax after thermal cycling. Up to 1500 cycles were applied, with a deviation range (-7.54-0%) for MT and (-27.71-0%) for LHF. Again, they observed an irregular degradation with the number of cycles.

Shukla et al. [21] tested the thermal stability of three different paraffin waxes and noted important variations in MT and LHF in a range of 600 thermal cycles, up to -10.34~% for MT and -38.46~% for LHF. They did not find a direct relationship between number of cycles and thermal degradation. Kahwaji et al. [22] studied the long term thermal stability of three pure alkanes (Nonadecane, Eicosane and Docosane) and three commercial mixtures from supplier Sigma-Aldrich (PW48, PW52, and PW58). They measured MT, LHF, solid density and the temperature dependences of the heat capacity and thermal conductivity in both liquid and solid phases. The authors concluded that both the pure paraffins and the blends were thermally stable, with no noticeable

changes to MT and LHF after 3000 melt-freeze cycles, which remained into the limits of the uncertainty analysis. They also showed that MT of commercial blends differed significantly from the supplier-specified values. Finally, they warned about a possible overestimation of LHF value due to the contribution of the solid-solid transition to the DSC endothermic peak.

In a recent work, Kahwaji et al. [17] stated that in the accelerated thermal cycle testing, many authors report percentages of degradation in MT or LHF that are in fact a result of a misinterpretation of measurements taken by Differential Scanning Calorimetry (DSC). Furthermore, in many cases the deviations reported are within the limits of experimental uncertainty, whose analysis is often missed in the literature. For DSC measurements in PCM materials, the authors recommend performing calibration tests prior to measurements, and to estimate de reproducibility and uncertainty of phase change temperatures and enthalpies of transition.

One of the main concerns about the use of paraffins in latent thermal energy storage systems (LTES) is that they have typically low values of thermal conductivity. This fact slows down the releasing and storing of energy. To overcome this issue, many authors have studied the effect of conventional passive heat transfer enhancement techniques, such as the use of extended heat transfer surfaces or the addition of high conductive materials/particles to increase the thermal conductivity of the PCM [27,28]. Zondag et al. [29] designed a shell and tube heat exchanger at laboratory scale and evaluated its performance both experimentally and numerically. They found that natural convection plays a central role in the melting process. Khan and Khan [30] incorporated longitudinal fins to a LTES system coupled to a conventional solar thermal collector. They found that the use of extended surfaces enhanced the melting process. They used commercial paraffin wax RT44HC by Rubitherm as PCM.

Most of the research studies about the implementation of paraffins as phase change materials in LTES focus on the melting stage and do not study solidification in detail. Therefore, the authors that aim to enhance those heat transfer processes tend to use enhancement techniques that are optimized for melting and not for solidification. Castell et al. [31] observed that the use of extended surfaces increased heat transfer in melting but to a much lesser extent in solidification. The problem that arises in the solidification was pointed out by Stritih [32], who stated that at that stage, conduction is the dominant form of heat transfer and thus passive techniques are not an optimal solution to enhance the process [33]. As Fadl, et al. [34] pointed out, discharging times are much longer than charging times due to the low thermal conductivity of the solid PCM layer which forms on the surface of the heat exchanger.

Some researchers have introduced active heat transfer enhancement techniques to overcome the above-mentioned issue. Scraping the heat transfer surface in PCM side to remove the solid layer created in the solidification process is a promising technology. Maruoka et al. [35] tested a rotative heat exchanger and demonstrated the relation between rotation velocity and heat release. The experiments showed an increase of six times in the heat release rate compared to no rotation mode. Tombrink et al. studied numerical [36] and experimentally [37] a rotating drum heat exchanger for LTES where the heat transfer walls were continuously scraped in order to minimize the layer thickness of the solidified PCM and maximize heat transfer. In that way, the authors were also able to easily manage the thermal power output.

The authors of present work are currently working on a prototype of scraped LTES system [38]. Both the processes of energy release and energy storage of a commercial paraffin wax (Rubitherm RT44HC) are studied. During the solidification tests, several rotating blades continuously scrape the paraffin in order to remove it from the heat transfer walls. Therefore, the PCM is subjected to a high level of shear stresses. This fact, in addition to the successive thermal cycling, could result in a degradation of the PCMs. In that way, there is the need to study the impact of a high level of shear stresses on the PCM specimen.

The main aim of this research work is to study the long-term reliability of commercial paraffin waxes for its use in scraped LTES systems.

Table 1Physical properties of RT44HC as given by Rubitherm GmbH.

Melting area Solidification area Heat storage capacity \pm 7.5 %, (temperature range $=$ 35 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$)	41–44 44–40 250	[°C] [°C] [kJ/kg]
Specific heat capacity	2	[kJ/kg·K]
Density solid ($T = 25$ °C)	0.8	[kg/l]
Density liquid ($T = 80$ °C)	0.7	[kg/l]
Heat conductivity	0.2	[W/
		(m·K)]
Volume expansion	12.5	[%]
Max. operation temperature	70	[°C]

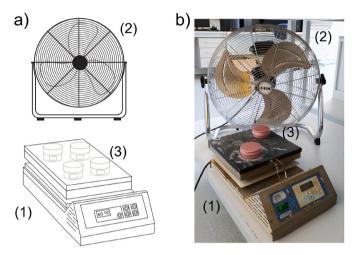


Fig. 1. Accelerated thermal cycling facility. (1) Electric hot plate (2) Fan (3) PCM samples.

The proposed methodology allows to study separately the effect of thermal cycles, scraping cycles and combined thermal/scraping cycles on the thermo-physical properties of the paraffin wax. The proposed methodology allows to study separately the effect of thermal cycles, scraping cycles and combined thermal/scraping cycles. The potential changes in the latent heats of fusion and solidification, melting and solidification temperatures, thermal conductivity and dynamic viscosity have been evaluated through experimental measurements in selected samples. To the knowledge of authors, this is the first study concerning the degradation in thermal performance of a phase change material after mechanical work.

2. Preparation of samples

The PCM used in this study is the commercial paraffin wax RT44HC supplied by Rubitherm GmbH. Their physical properties prior to cycling are listed in Table 1 [39].

2.1. Accelerated thermal cycling procedure

As is widely reported in the bibliography [17,21–25], in order to estimate the long-term durability of a given PCM for solar energy storage purposes, it is necessary to measure its physical properties at different numbers of melting and solidification cycles.

In this work, the facility for accelerated thermal cycling (Fig. 1a, b) consists of an electric hot plate to melt the samples (1) and a fan to accelerate the solidification process (2). Both devices are alternatively switched on and off by means of a set of programmable electrical relays by Denkovi Assembly Electronics LTD.

A volume of 25 ml of the sample to be cycled was placed at an aluminium cylindrical container (3), 70 mm diameter, 30 mm height.

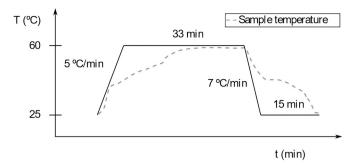


Fig. 2. Dynamic mode used for thermal cycling.

Aluminium does not present corrosion problems with Paraffin kind PCMs [22,23]. In order to ensure the complete melting and solidification of the sample, the dynamic procedure was developed according to the amount of sample used (Fig. 2). In the electric hot plate, the samples were heated from room temperature (25 °C) to 60 °C with a heating rate of 5 °C/min. Later, a 33 min isothermal step was applied in order to ensure the complete melting of the sample. After that, the plate was switched off and the fan was activated to cool down the sample to room temperature with a temperature step of 7 °C/min. Finally, an isothermal step of 15 min was applied to finish the cycle. The process was repeated until the desired number of thermal cycles was achieved. The PCM temperature was measured by means of a T-Type thermocouple. Its evolution over a complete thermal cycle is shown in Fig. 2. A maximum of 3000 melting/solidification cycles were performed, this value is equivalent to 3000 days of working in the scraper surface LTES system.

2.2. Accelerated scraping cycling procedure

The authors have recently developed a prototype of PCM heat exchanger to accelerate the energy release through the scraping of inner walls [38]. In order to study the effect of shear stresses in the PCM properties, the experimental set-up given in Fig. 3a, b has been built up. It consists of a scale model of the prototype (1) coupled to a variable-speed drill (2) and a voltage regulator (3) to control the drill speed. Its value is measured by means of a digital tachometer (4). The scaled model and the original prototype have the same ratio of scraped surface to volume of PCM, $15~\text{m}^2/\text{m}^3$. Hence, it can be assumed that the potential degradation in physical properties of paraffin at the scaled model can be extrapolated to that in the original prototype.

The prototype of PCM heat exchanger carries out a single cycle of storage/release of energy per day. The blades rotate only during the release of energy (solidification) at a nominal speed of 5 rpm. It has been experimentally measured that the solidification process takes place over 36 min. In the reduced scale model (Fig. 3a, b), the scraping process is accelerated by increasing the rotation speed of blades to 90 rpm. Therefore, every 2 min of scraping at the model accounts for 1 cycle (day) at the real prototype.

On the other hand, a specific procedure was developed in order to apply extreme shear stress conditions to the paraffin. In this way, the PCM was pulverized by means of a hand blender (Fig. 3c) at $10,000 \, \text{rpm}$ for 1 h. The obtained sample was a paraffin powder accounting for more than $3000 \, \text{cycles}$ or days of work at the prototype.

2.3. Sample generation procedure

The procedure for sample preparation is given in Fig. 4. It allows for obtaining either paraffin with scraping cycles, thermally cycled or with combined (scraping and thermal) cycles. If a sample with only a processing mode is to be generated, it is directly sent to the corresponding facility and cycled to the desired number. In order to obtain a combined sample, the uncycled sample is firstly processed to a number x of

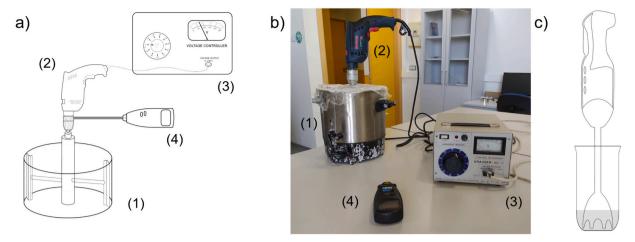


Fig. 3. Accelerated scraping cycling facility (a, b). (1) scraper, (2) drill, (3) voltage regulator, (4) tachometer. (c) Hand blender (used when a high number of scraping cycles is needed).

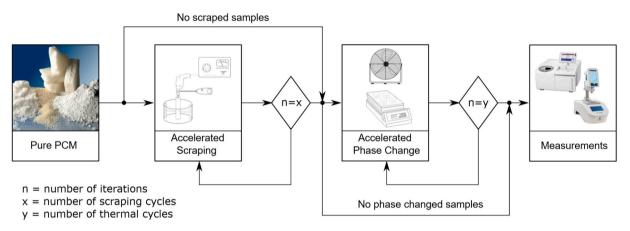


Fig. 4. Sample generation procedure.

Table 2
Measurement samples: scraped, thermally cycled and with combined effects.

Scraped samples	Thermally cycled samples	Combined cycled samples
150/0	0/150	150/150
300/0	0/300	300/300
3000/0	0/3000	3000/3000

scraping cycles, and secondly to the corresponding number of thermal cycles, $\mathbf{y} = \mathbf{x}$.

The samples obtained through the above-mentioned method are listed in Table 2. In this study the number of cycles has been set to 0, 150, 300 and 3000. The nomenclature used for a given sample is x/y (number of scraping cycles/number of thermal cycles).

3. Determination of thermophysical properties

In order to determine the potential variation in the thermophysical properties of cycled paraffin, measurements of melting and solidification temperature and latent heat flux through DSC (MT, ST, LHF $_{\rm S}$ LHF $_{\rm M}$), thermal conductivity and dynamic viscosity over temperature for liquid phase have been made.

The cycled samples generated through the procedure described in Fig. 4 have been used for the viscosity and thermal conductivity measurements. However, for convenience, in the DSC measurements only the scraped samples (Column 1, Table 2) have been used, and the

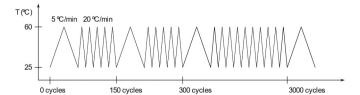


Fig. 5. Pyramidal programming for accelerated cycling at DSC measurements.

3.1. Differential Scanning Calorimetry

melting/solidification cycles have been done in situ.

The instrument DSC822 from Mettler Toledo was used to determine latent heat fluxes and phase change temperatures. A mass of 4.5 mg of PCM was sealed in a standard aluminium sample holder. During the DSC measurement a constant stream of nitrogen (50 ml/min) was applied as flushing gas during the measurement. The instrument was calibrated with indium standard prior to the test (LHF $_{\rm M}=28.45$ J/g and MT $=156.6~^{\circ}{\rm C}$).

A test with eicosane (CH3(CH2)18CH3, (CAS Number 112–95-8, Sigma-Aldrich, stated purity 99 %)) was performed in order to analyse the uncertainty from DSC measurements. This PCM was chosen because their properties are well defined in bibliography [20,22]. The results from the test indicated an expanded uncertainty (U, 95 % level of

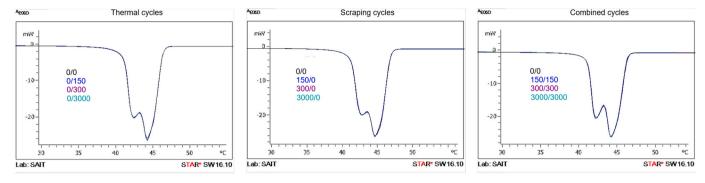


Fig. 6. Melting DSC curves. Left: Thermal cycled samples. Center: Scraping cycled samples. Right: Combined cycled samples.

confidence) of 10 % for LHF and ± 0.8 °C for MT and ST.

A pyramidal programming (Fig. 5) was carried out to perform the thermal cycles of melting and solidification. This programming was chosen in order to optimize the nitrogen flow for the maximum number of cycles with the same load. The measurements were conducted at the initial cycle (0 thermal cycles), 150, 300 and 3000 thermal cycles. In

these cycles the heating and cooling rates were 5 °C/min, a value in the range recommended by other authors [17,40–44]. Once the measurement at a target cycle was completed, a set of accelerated thermal cycles was programmed at heating and cooling rates of 20 °C/min.

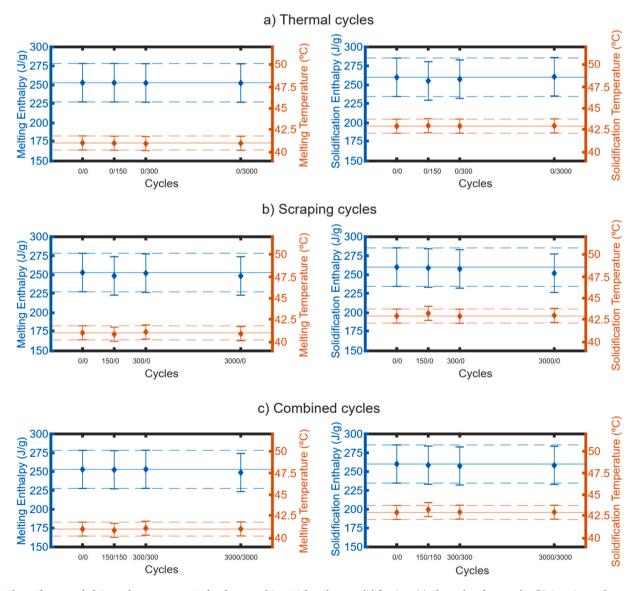


Fig. 7. Phase Change enthalpies and temperatures. Left column: melting. Right column: solidification. (a) Thermal cycles samples (b) Scraping cycles samples (c) Combined cycles samples. The solid lines correspond to the uncycled sample results (LHF_M = 252.96 J/g, LHF_S = 260.09 J/g, MT = 41.06 °C, ST = 42.97 °C).

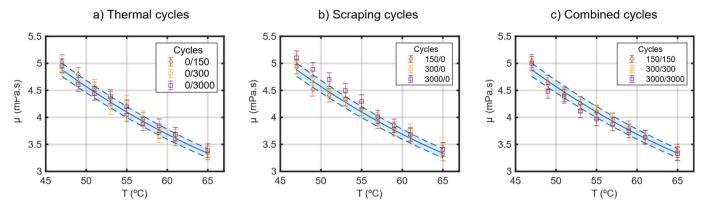


Fig. 8. Viscosity results as a function of temperature: (a) Thermal cycled samples (b) Scraping cycled samples (c) Combined cycled samples. The solid lines correspond to the uncycled sample results.

3.2. Viscosity measurements

It is unusual to find viscosity measurements in the studies on the long-term reliability of PCMs. This property plays a key role in the melting process, where the dominant mode of heat transfer is natural convection [34,45,46]. It has been considered of interest to study the impact of thermal and scraping cycles on the dynamic viscosity of the working paraffin.

Rheometer AR-G2 from TA Instruments was used to measure the dynamic viscosity of the PCM samples. The concentric cylinder configuration was used. The samples were melted through a pre-heating at 45 $^{\circ}$ C in a hot plate and poured into the outer cylinder. They were measured in the temperature range of 45–65 $^{\circ}$ C, every 2 $^{\circ}$ C, at 5 $^{\circ}$ C/min. Due to the low thermal conductivity of the paraffin, every target temperature of the samples was maintained for 120 s prior to measuring its viscosity through a Peak Hold test at constant shear speed (10 s $^{-1}$) during 300 s. The rheometer was calibrated using a silicone viscosity standard (RT5, supplied by Cannon) at 25 $^{\circ}$ C. The expanded uncertainty in the viscosity measurements was found to be 2.5 %.

3.3. Thermal conductivity measurements

Thermal conductivity stability along cycling is a key parameter to evaluate the possible degradation of PCM. The measurements were carried out with a TCi thermal conductivity analyser from C-Therm with the MTPS (Modified Transient Plane Source) method. The measurements for each sample were carried out at a constant temperature ($T=50~{\rm ^{\circ}C}$).

The samples and the sensor were introduced in a heater to reach the measurement temperature. Once the sample was ready, it was placed over the sensor and when the thermal equilibrium was achieved, the measurements started. For measuring, a heat pulse is given to the sample and the dissipation of that pulse is measured. Each measurement is the average of 10 consecutives pulses. The uncertainties in the measurement values were estimated in 12 % through testing of water.

4. Results and discussion

In the present work, the paraffin of study has been analysed based on its life cycle performance. The results of thermophysical properties obtained for each sample are compared to the corresponding value in the uncycled sample.

4.1. Phase change temperatures and enthalpies

Fig. 6 shows the melting DSC measurements for each sample group. There are apparently no differences between each sample and the 0/0 one. A same behaviour was observed for the solidification DSC

measurements. All the DSC results were analysed according to [47], where the latent heat was calculated as the area under the DSC curve, and the transition temperatures were obtained from the interception of tangent at the point corresponding to the largest slope on the face portion of the peak of the DSC curve with the pre-melting baseline.

The results for LHF $_{\rm M}$, LHF $_{\rm S}$, MT y ST before and after cycling for each sample group are presented in Fig. 7. The results for 0/0 sample (solid line) are in accordance with those reported by the supplier (Table 1). It has not been observed a significant change in the variables for any group with respect to the uncycled sample, even for a large number of cycles.

Regarding the evolution of thermal properties of paraffin with thermal cycling, the results are in accordance with those authors that have stated that paraffins do not suffer thermal degradation [22,24]. In addition, at present work the added shear stress effect does not seem to affect the phase change latent heat or temperatures of paraffin wax. The maximum observed deviations with respect to sample 0/0 have been +0.26~% and -3~% for LHFs (samples 0/3000 & 3000/0), +0.07~% and -1.7~% for LHFM (samples 300/300 & 150/0), $+0.33~^\circ\text{C}$ and $-0.02~^\circ\text{C}$ for ST (samples 150/150 & 300/0) and $+0.1~^\circ\text{C}$ and $-0.16~^\circ\text{C}$ for MT (samples 300/300 & 150/0).

From the DSC results, a direct relation between increasing the number of thermal cycles and degradation of thermal properties was not found. Those values are in every case inside the uncertainty limits (± 10 % for LHF and ± 0.8 °C for phase change temperatures).

4.2. Viscosity results

The evolution of the measured dynamic viscosity with temperature is shown for every group at Fig. 8. The results for the 0/0 sample are plotted as a continuous line; the dashed lines represent the limits of uncertainty (2.5 %, 95 % confidence level).

There is not a clear trend in the variation of viscosity with the number of thermal cycles (Fig. 8a). This fact is in disagreement with Vasu et al. [48] who, up to the author's knowledge, have been the only researchers who have studied the degradation of viscosity after thermal cycling of a paraffin. They found that the viscosity of a commercial wax with melting point 58–62 °C rose with the number of thermal cycles. However, there was not a clear trend, up to the point that the value for the sample with a higher number of cycles (200) was very close to that of the untreated sample. The viscosity for that sample was 5 % higher than the virgin sample, in contrast with a 25 % increase for the sample with 30 cycles. The authors assigned the variations in viscosity to the grades of void formation during solidification of samples. They did not report neither about the rheometer configuration nor the measurement uncertainties. Their conclusions are far from those obtained at present work.

The influence of the number of scraping cycles is not clear (Fig. 8b), and a direct correlation between the number of cycles and the change in

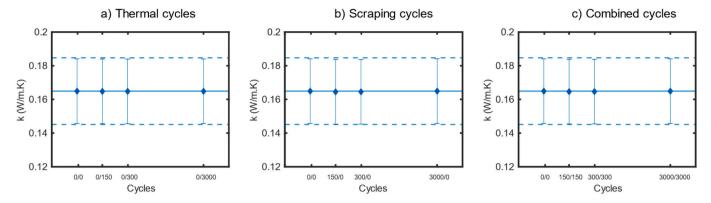


Fig. 9. Thermal conductivity results at T = 50 °C. (a) Thermal cycled samples (b) Scraping cycled samples (c) Combined cycled samples. The solid lines correspond to the uncycled sample results. (k = 0.165 W/m·K).

viscosity is not observed. The variations of viscosity remain within the uncertainty levels in all cases.

If the combined effect of shear stress and thermal cycling is considered (Fig. 8c), it seems that globally the values of viscosity for that group decrease with respect to the samples only scraped. This trend strengths as the number of cycles increases: there are not changes between samples 150/0 and 150/150, around 1.5 % between samples 300/0 and 300/300 and roughly a 3.8 % between 3000/0 and 3000/3000. However, it cannot be affirmed taxatively since all results for both groups fall between the limits of measurement uncertainty.

4.3. Thermal conductivity results

Fig. 9 shows the thermal conductivity results vs. number cycles for each group at $T=50\,^{\circ}$ C. The values for the uncycled sample (solid line) are not comparable to the one given by the supplier, a mean value between solid and liquid phases. The observed variations with respect to the uncycled sample are minimal (below 3 % for all groups). The results for the thermal cycling effect are in accordance with the variations reported by Vasu et al. [48], who gave a 3.2 % variation for 200 thermal cycles. It is clear that neither the thermal cycling nor the scraping cycling affect the thermal conductivity of the paraffin wax of study.

5. Conclusions

This work has studied the long-term suitability of a commercial paraffin wax as phase change material in an active scraped surface heat exchanger for solar energy storage. The measurements through Differential Scanning Calorimetry have shown that neither the thermal nor the scraping cycling have a significant impact on the phase change latent heat fluxes and temperatures. All the reported variations of the cycled paraffin samples have remained within the limits of experimental uncertainty.

A similar behaviour has been observed for the thermal conductivity, with minimal variations from the uncycled sample (below 3 % for all groups). Regarding dynamic viscosity measurements, there is not a clear influence of the thermal cycles. If the combined effect of shear stress and thermal cycling is considered, a global decrease of viscosity with respect to the uncycled sample is observed. However, it cannot be affirmed taxatively, since all the results for both groups fall between the limits of measurement uncertainty.

According to the findings reported in this work, paraffin wax RT44HC can be successfully used in scraped surface heat exchangers. It is expected that other commercial paraffins would be also suitable since most of them share the fact of being blends of alkanes and other hydrocarbons.

CRediT authorship contribution statement

A. Egea: Investigation, Software, Data curation. A. García: Methodology, Conceptualization, Formal analysis, Resources. R. Herrero-Martín: Supervision, Project administration, Funding acquisition. J. Pérez-García: Conceptualization, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] REN21.2021 Renewables 2021 Global Status Report, Paris: REN21 Secretariat, n.d. https://www.ren21.net/.
- [2] IEA, World Energy Outlook 2021, Paris, 2021. https://www.iea.org/reports/world-energy-outlook-2021
- [3] Y.B. Tao, Y.L. He, A review of phase change material and performance enhancement method for latent heat storage system, Renew. Sust. Energ. Rev. 93 (2018) 245–259, https://doi.org/10.1016/j.rser.2018.05.028.
- [4] L. Miró, C. Barreneche, G. Ferrer, A. Solé, I. Martorell, L.F. Cabeza, Health hazard, cycling and thermal stability as key parameters when selecting a suitable phase change material (PCM), Thermochim. Acta 627–629 (2016) 39–47, https://doi.org/10.1016/j.tca.2016.01.014.
- [5] A. Sharma, A. Shukla, C.R. Chen, T.-N. Wu, Development of phase change materials (PCMs) for low temperature energy storage applications, Sustain. Energy Technol. Assess. 7 (2014) 17–21, https://doi.org/10.1016/j.seta.2014.02.009.
- [6] A. Sharma, V.V. Tyagi, C.R. Chen, D. Buddhi, Review on thermal energy storage with phase change materials and applications, Renew. Sust. Energ. Rev. 13 (2009) 318–345, https://doi.org/10.1016/j.rser.2007.10.005.
- [7] B. Yang, J. Dong, L. Zhang, M. Song, Y. Jiang, S. Deng, Heating and energy storage characteristics of multi-split air source heat pump based on energy storage defrosting, Appl. Energy 238 (2019) 303–310, https://doi.org/10.1016/j. apenergy.2019.01.079.
- [8] M. Song, F. Niu, N. Mao, Y. Hu, S. Deng, Review on building energy performance improvement using phase change materials, Energy Build. 158 (2018) 776–793, https://doi.org/10.1016/j.enbuild.2017.10.066.
- [9] V.V. Tyagi, K. Chopra, R.K. Sharma, A.K. Pandey, S.K. Tyagi, M.S. Ahmad, A. Sarı, R. Kothari, A comprehensive review on phase change materials for heat storage applications: development, characterization, thermal and chemical stability, Sol. Energy Mater. Sol. Cells 234 (2022), 111392, https://doi.org/10.1016/j. solmat.2021.111392.
- [10] S. Mengjie, L. Liyuan, N. Fuxin, M. Ning, L. Shengchun, H. Yanxin, Thermal stability experimental study on three types of organic binary phase change materials applied in thermal energy storage system, J. Therm. Sci. Eng. Appl. 10 (2018), https://doi.org/10.1115/1.4039702.

- [11] A. Shahcheraghian, R. Ahmadi, A. Malekpour, Utilising latent thermal energy storage in building envelopes to minimise thermal loads and enhance comfort, J. Energy Storage 33 (2021), 102119, https://doi.org/10.1016/j.est.2020.102119.
- [12] J.H. Park, U. Berardi, S.J. Chang, S. Wi, Y. Kang, S. Kim, Energy retrofit of PCM-applied apartment buildings considering building orientation and height, Energy 222 (2021), 119877, https://doi.org/10.1016/j.energy.2021.119877.
- [13] Q. Al-Yasiri, M. Szabó, Thermal performance of concrete bricks based phase change material encapsulated by various aluminium containers: an experimental study under Iraqi hot climate conditions, J. Energy Storage 40 (2021), 102710, https:// doi.org/10.1016/i.est.2021.102710.
- [14] M. Kenisarin, K. Mahkamov, Solar energy storage using phase change materials, Renew. Sust. Energ. Rev. 11 (2007) 1913–1965, https://doi.org/10.1016/j. regr 2006.05.005
- [15] A.K. Pandey, M.S. Hossain, V.V. Tyagi, N. Abd Rahim, J.A.L. Selvaraj, A. Sari, Novel approaches and recent developments on potential applications of phase change materials in solar energy, Renew. Sust. Energ. Rev. 82 (2018) 281–323, https://doi.org/10.1016/j.rser.2017.09.043.
- [16] B. Kalidasan, A.K. Pandey, S. Shahabuddin, M. Samykano, M. Thirugnanasambandam, R. Saidur, Phase change materials integrated solar thermal energy systems: global trends and current practices in experimental approaches, J. Energy Storage 27 (2020), 101118, https://doi.org/10.1016/j. est 2019 101118
- [17] S. Kahwaji, M.B. Johnson, M.A. White, Thermal property determination for phase change materials, J. Chem. Thermodyn. 160 (2021), 106439, https://doi.org/ 10.1016/j.ict.2021.106439.
- [18] Y. Dutil, D.R. Rousse, N. Ben Salah, S. Lassue, L. Zalewski, A review on phase-change materials: mathematical modeling and simulations, Renew. Sust. Energ. Rev. 15 (2011) 112–130, https://doi.org/10.1016/j.rser.2010.06.011.
- [19] Y. Dutil, D. Rousse, S. Lassue, L. Zalewski, A. Joulin, J. Virgone, F. Kuznik, K. Johannes, J.-P. Dumas, J.-P. Bédécarrats, A. Castell, L.F. Cabeza, Modeling phase change materials behavior in building applications: comments on material characterization and model validation, Renew. Energy 61 (2014) 132–135, https://doi.org/10.1016/j.renene.2012.10.027.
- [20] W. Acree, J.S. Chickos, Phase transition enthalpy measurements of organic and organometallic compounds and ionic liquids. Sublimation, vaporization, and fusion enthalpies from 1880 to 2015. Part 2. C11–C192, J. Phys. Chem. Ref. Data 46 (2017) 13104, https://doi.org/10.1063/1.4970519.
- [21] A. Shukla, D. Buddhi, R.L. Sawhney, Thermal cycling test of few selected inorganic and organic phase change materials, Renew. Energy 33 (2008) 2606–2614, https://doi.org/10.1016/j.renene.2008.02.026.
- [22] S. Kahwaji, M.B. Johnson, A.C. Kheirabadi, D. Groulx, M.A. White, A comprehensive study of properties of paraffin phase change materials for solar thermal energy storage and thermal management applications, Energy 162 (2018) 1169–1182. https://doi.org/10.1016/j.energy.2018.08.068.
- [23] A. Anand, A. Shukla, A. Kumar, D. Buddhi, A. Sharma, Cycle test stability and corrosion evaluation of phase change materials used in thermal energy storage systems, J. Energy Storage 39 (2021), 102664, https://doi.org/10.1016/j. est 2021 102664
- [24] M. Hadjieva, S. Kanev, J. Argirov, Thermophysical properties of some paraffins applicable to thermal energy storage, Sol. Energy Mater. Sol. Cells 27 (1992) 181–187, https://doi.org/10.1016/0927-0248(92)90119-A.
- [25] S.D. Sharma, D. Buddhi, R.L. Sawhney, Accelerated thermal cycle test of latent heat-storage materials, Sol. Energy 66 (1999) 483–490, https://doi.org/10.1016/ S0038-092X(99)00045-6.
- [26] A. Sharma, S.D. Sharma, D. Buddhi, Accelerated thermal cycle test of acetamide, stearic acid and paraffin wax for solar thermal latent heat storage applications, Energy Convers. Manag. 43 (2002) 1923–1930, https://doi.org/10.1016/S0196-8904(01)00131-5.
- [27] N.I. Ibrahim, F.A. Al-Sulaiman, S. Rahman, B.S. Yilbas, A.Z. Sahin, Heat transfer enhancement of phase change materials for thermal energy storage applications: a critical review, Renew. Sust. Energ. Rev. 74 (2017) 26–50, https://doi.org/ 10.1016/j.rser.2017.01.169.
- [28] M. Al-Maghalseh, K. Mahkamov, Methods of heat transfer intensification in PCM thermal storage systems: review paper, Renew. Sust. Energ. Rev. 92 (2018) 62–94, https://doi.org/10.1016/j.rser.2018.04.064.

- [29] H.A. Zondag, R. De Boer, S.F. Smeding, J. Van Der Kamp, Performance analysis of industrial PCM heat storage lab prototype, J. Energy Storage 18 (2018) 402–413, https://doi.org/10.1016/j.est.2018.05.007.
- [30] Z. Khan, Z.A. Khan, Experimental investigations of charging/melting cycles of paraffin in a novel shell and tube with longitudinal fins based heat storage design solution for domestic and industrial applications, Appl. Energy 206 (2017) 1158–1168, https://doi.org/10.1016/j.apenergy.2017.10.043.
- [31] A. Castell, C. Solé, M. Medrano, J. Roca, L.F. Cabeza, D. García, Natural convection heat transfer coefficients in phase change material (PCM) modules with external vertical fins, Appl. Therm. Eng. 28 (2008) 1676–1686, https://doi.org/10.1016/j. applthermaleng. 2007.11.004
- [32] U. Stritih, An experimental study of enhanced heat transfer in rectangular PCM thermal storage, Int. J. Heat Mass Transf. 47 (2004) 2841–2847, https://doi.org/ 10.1016/j.ijheatmasstransfer.2004.02.001.
- [33] R. Velraj, R.V. Seeniraj, B. Hafner, C. Faber, K. Schwarzer, Heat transfer enhancement in a latent heat storage SYSTEM1, Sol. Energy 65 (1999) 171–180, https://doi.org/10.1016/S0038-092X(98)00128-5.
- [34] M. Fadl, D. Mahon, P.C. Eames, Thermal performance analysis of compact thermal energy storage unit-an experimental study, Int. J. Heat Mass Transf. 173 (2021), 121262, https://doi.org/10.1016/j.ijheatmasstransfer.2021.121262.
- [35] N. Maruoka, T. Tsutsumi, A. Ito, M. Hayasaka, H. Nogami, Heat release characteristics of a latent heat storage heat exchanger by scraping the solidified phase change material layer, Energy 205 (2020), 118055, https://doi.org/ 10.1016/j.energy.2020.118055.
- [36] J. Tombrink, D. Bauer, Simulation of a rotating drum heat exchanger for latent heat storage using a quasistationary analytical approach and a numerical transient finite difference scheme, Appl. Therm. Eng. 194 (2021), 117029, https://doi.org/ 10.1016/j.applthermaleng.2021.117029.
- [37] J. Tombrink, H. Jockenhöfer, D. Bauer, Experimental investigation of a rotating drum heat exchanger for latent heat storage, Appl. Therm. Eng. 183 (2021), https://doi.org/10.1016/j.applthermaleng.2020.116221.
- [38] Proceedings of the 15th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics (HEFAT2021), HEFAT, 2021.
- [39] Rubitherm GmbH. https://www.rubitherm.eu/, 2014.
- [40] A.A. Aydn, Fatty acid ester-based commercial products as potential new phase change materials (PCMs) for thermal energy storage, Sol. Energy Mater. Sol. Cells 108 (2013) 98–104, https://doi.org/10.1016/j.solmat.2012.08.015.
- [41] L. Yang, X. Cao, N. Zhang, B. Xiang, Z. Zhang, B. Qian, Thermal reliability of typical fatty acids as phase change materials based on 10,000 accelerated thermal cycles, Sustain. Cities Soc. 46 (2019), 101380, https://doi.org/10.1016/j. scs.2018.12.008.
- [42] M. Qu, C. Guo, L. Li, Preparation, characterization and thermal properties of dodecanol, palmitic acid and hydroxylpropyl methyl cellulose as novel form-stable phase change materials, J. Therm. Anal. Calorim. (2021), https://doi.org/ 10.1007/s10973-021-10915-v.
- [43] H. Fauzi, H. Metselaar, T.M.I. Mahlia, M. Silakhori, H.C. Ong, Thermal characteristic reliability of fatty acid binary mixtures as phase change materials (PCMs) for thermal energy storage applications, Appl. Therm. Eng. 80 (2015), https://doi.org/10.1016/j.applthermaleng.2015.01.047.
- [44] A. Sari, A. Karaipekli, Preparation and thermal properties of capric acid/palmitic acid eutectic mixture as a phase change energy storage material, Mater. Lett. 62 (2008) 903–906, https://doi.org/10.1016/j.matlet.2007.07.025.
- [45] A. Egea, J.P. Solano, J. Pérez-García, A. García, Solar-driven melting dynamics in a shell and tube thermal energy store: an experimental analysis, Renew. Energy 154 (2020) 1044–1052, https://doi.org/10.1016/j.renene.2020.03.078.
- [46] S. Jevnikar, K. Siddiqui, Investigation of the influence of heat source orientation on the transient flow behavior during PCM melting using particle image velocimetry, J. Energy Storage 25 (2019), 100825, https://doi.org/10.1016/j.est.2019.100825.
- [47] M. Wagner, 7 differential scanning calorimetry, in: Therm. Anal. Pract, Hanser, 2018, pp. 66–143, https://doi.org/10.3139/9781569906446.007.
- [48] A. Vasu, F.Y. Hagos, R. Mamat, J. Kaur, M.M. Noor, The effect of thermal cyclic variation on the thermophysical property degradation of paraffin as a phase changing energy storage material, Appl. Therm. Eng. 149 (2019) 22–33, https:// doi.org/10.1016/j.applthermaleng.2018.12.033.