Temperature-dependent thermal properties of solid/liquid phase change even-numbered \(n\)-alkanes: \(n\)-Hexadecane, \(n\)-Octadecane and \(n\)-Eicosane

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HIGHLIGHTS
- Thermal properties of \(n\)-hexadecane, \(n\)-octadecane and \(n\)-eicosane used as PCM are reported.
- Thermal conductivity and thermal diffusivity were measured by the hot wire technique at different temperatures.
- A discontinuity in thermal conductivity and diffusivity was detected near the melting temperature.
- No literature data were found for the thermal diffusivity of the three \(n\)-alkanes considered in this study.
- The cumulative heat stored increases with the number of carbon in the \(n\)-alkane hydrocarbon chain.

GRAPHICAL ABSTRACT
Variation of the cumulative heat stored in \(n\)-hexadecane (C16), \(n\)-heptadecane (C18) and \(n\)-eicosane (C20) as function of temperature.

Abstract
The thermal conductivity \((\lambda)\) and thermal diffusivity \((\alphaT)\) of the solid/liquid phase change linear \(n\)-alkanes were measured simultaneously by the transient multi-current hot wire technique at atmospheric pressure in the range 258–348 K. The same set-up was used to measure \(\lambda\) and \(\alphaT\) of the liquid and the solid states at different electrical currents. Three \(n\)-alkanes, \(n\)-hexadecane (C16H34), \(n\)-octadecane (C18H36) and \(n\)-eicosane (C20H42) were studied. Differential scanning calorimetry was applied at the temperature range 248–348 K to determine the melting/crystallization temperature, the heat of melting/crystallization and the specific heat of both the solid and liquid phases. Some results were compared with available literature data. The density of the \(n\)-alkanes at liquid state was also measured at different temperatures and their thermal diffusivity was estimated and compared to that obtained by the hot wire technique. The cumulative energy stored was estimated over a definite range of temperature for the three \(n\)-alkanes and this was found to be higher for eicosane.

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http://dx.doi.org/10.1016/j.apenergy.2015.01.054
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1. Introduction

Thermal energy can be stored as sensible heat, latent heat, thermo-chemical (i.e., heat involved in a reversible chemical reaction) or any combination between them. Among these methods, latent heat energy storage is particularly attractive due to its high-energy storage density (i.e., heat per unit volume) and to its ability to provide heat at a relatively constant temperature, which corresponds to the phase transition temperature of the used phase change material (PCM) [1–4].

In recent years, development of thermal energy storage systems using PCMs has gained a considerable importance in many applications such as in solar energy systems, in industrial waste heat and in energy-conserving buildings. PCMs can store from 5 to 14 times more heat per unit volume (i.e., storage density) than the sensible storage based materials such as water [2,5–8].

Among the four phase change possibilities (solid/gas, liquid/gas, solid/solid, and solid/liquid), solid/liquid transition is the most promising and economically attractive one for thermal energy storage systems. During melting cycle, energy is stored as latent heat of fusion, and then it is recovered during the solidification step. Compared to solid/gas and liquid/gas transitions, solid/liquid transition involves smaller change in volume (<10%) and therefore requires smaller space for storing although it involves, comparatively, smaller latent heat. On the other hand, in solid/solid transitions, heat is stored as a consequence of the crystalline change of the material and the involved latent heat as well as the volume change is less than those of solid/liquid transition. There are varieties of PCMs, both organic and inorganic, that melt and solidify at a wide range of temperatures and therefore are attractive in a number of applications [1,3,8–14]. A large number of solid/liquid PCMs have been studied for heating and cooling applications [7,9,15,16]. Therefore, for efficient heat recovery or energy storage design processes, it is necessary to have a good knowledge of the thermo-physical properties of these PCMs in a wide range of temperature intervals.

The PCM should have suitable thermo-physical and chemical characteristics such as a phase-transition temperature in the desired operating temperature range, a high latent heat of transition per unit volume to allow a small size of the energy storage container, a high specific heat to provide additional sensible heat storage, a high thermal conductivity of both solid and liquid phases, a high density, a small volume change on phase transition, non-toxic, non-corrosive, non-flammable and not expensive. Except for the melting point in the desirable operating range, the majority of the used PCMs do not satisfy all these cited properties for an adequate storage system.

The inorganic PCMs exhibit generally a volumetric latent thermal energy storage capacity higher than that of organic PCMs. However, the organic PCMs melt congruently, have self-nucleation and are non-corrosive of the materials of construction. Paraffin waxes and linear n-alkanes (with the chemical formula \( C_{n}H_{2n+2} \)) belong to the latter group of PCMs and have some attractive features for solar energy systems [17]. It must be clarified that linear n-alkanes with number of carbons between 12 and 40 are known as paraffins. The n-alkanes have a large range of latent heats, various melting points, densities and specific heats [17]. However, an undesirable characteristic of n-alkanes is their low \( \lambda \) values, which may diminish the rate of the charging and discharging of the energy storage during the melting and solidification cycles. In general, for PCMs the higher \( \lambda \) the more efficient is the rate of heat transfer. Different possibilities have been adopted in order to compensate for the low \( \lambda \) values such as the use of finned configurations, containers and heat exchangers with adequate and improved designs to ensure efficient extraction and storage of heat, PCM encapsulation in different geometries, formation of composite by dispersing high-conductivity particles of different sizes and shapes, embedding metal matrix structures into PCMs, etc. [1,6,11,12,14–18–21].

Specific heat of n-alkanes has been thoroughly investigated using differential scanning calorimetry (DSC) by different research groups [22–24]. Comparatively, few research studies have been carried out on \( \lambda \) measurements of liquid n-alkanes [25–36] and solid n-alkanes but most of them were carried out near the solid/liquid phase transition temperature [26,37–41]. The thermal diffusivity (\( \alpha_{r} \)) of n-alkanes including both solid and liquid phases has not yet been systematically studied by the hot wire technique. The reported data so far are for \( n \)-tricosanoic (\( C_{33}H_{68} \)), \( n \)-tetradecanoic (\( C_{24}H_{49} \)) and \( n \)-pentacosanoic (\( C_{52}H_{105} \)) measured by Fourier Transform Temperature Wave Analysis (FT-TWA) [42,43] and for liquid n-alkanes (\( C_{n}H_{2n+2} \), \( n = 5–10 \)) by the transient hot wire technique [36]. Additionally, \( \alpha_{r} \) was estimated for a commercial paraffin PCM from the measured thermal conductivity (\( \lambda \)), density (\( \rho \)) and specific heat (\( c_{p} \)) [5,44,45]. Moreover, it must be pointed out that most of the available \( \lambda \) values of n-alkanes are rather old and were performed either for the solid or for the liquid phases and not for both solid and liquid phases including the phase transition region.

The present paper is intended to discuss the thermal characteristics of the even-numbered n-alkanes, n-hexadecane, n-octadecane and n-eicosane for applications as low-temperature phase change energy storage medium. These n-alkanes are named hereafter \( C_{16}, C_{18} \), and \( C_{20} \), respectively. \( C_{16} \) is liquid at room temperature and atmospheric pressure, whereas \( C_{18} \) and \( C_{20} \) are waxy solids. The transient multi-current hot wire technique, accepted as the most precise and reliable method to measure \( \lambda \) of fluids over a wide range of temperatures and pressures [28–29], was used in this study for the first time for both \( \lambda \) and \( \alpha_{r} \) measurements of solid and liquid phases of PCMs. The melting/crystallization temperature, the heat of melting/crystallization and the specific heat of both the solid and liquid phases were determined by DSC.

2. Experimental

2.1. Materials

The used n-alkanes samples, n-hexadecane (\( C_{16}H_{34} \)), n-octadecane (\( C_{18}H_{36} \)) and n-eicosane (\( C_{20}H_{42} \)) having minimum purities of 99% by Sigma-Aldrich. The samples were used without any further purification or removal of dissolved water or air and no information was provided regarding the nature of the impurities. To check the adequate \( \lambda \) measurements of the wire, distilled water and dimethyl phthalate (90% purity, Sigma-Aldrich) with known \( \lambda \) values were used. Ethylene glycol (Fluka, 99.5%) was used as a thermostatic liquid. Methanol (99.8% purity, Sigma-Aldrich) and distilled water were used for calibration of the densimeter.

2.2. Measurements

The density of the n-alkane hydrocarbons was measured at different temperatures in liquid phase with a densimeter (Ludwig Schneider) having an accuracy of 1% and with an Anton Paar DMA 58 having a precision of ±0.05 kg/m³.

Temperature variation test of the samples with time was carried out using a glass tube placed inside a thermostatic bath (Lauda ECO RE630) with a graduated heating and cooling option. For these experiments the applied heating/cooling rate was set to 0.2 °C/min. The sample was first melted, if not liquid at room temperature, and
then it was introduced in the glass tube having an internal diameter of 4 cm and a height of 32 cm. The volume of the samples was maintained the same (350 ml). A calibrated platinum resistance thermometer (F250-MK2 Precision thermometer, Automatic Systems Laboratories LTD) was placed inside the glass tube containing the sample. The platinum thermometer was interfaced to a computer having a written code that permits to register the temperature each 4 min and control the experiment. These tests permit to localize the phase change temperatures and compare their corresponding time.

The melting ($T_m$) and crystallization ($T_c$) temperatures of the samples together with their corresponding latent heats ($\Delta H_m$ and $\Delta H_c$) were measured using differential scanning calorimetry (DSC1 instrument, Mettler Toledo) equipped with the software STARRe for thermal data analysis. Indium was used as standard reference for the calibration of the instrument and the samples (7–9 mg) were sealed in aluminum pans. The tests were carried out in the temperature range 248–348 K at a heating rate of 2 °C/min and under a constant nitrogen flow rate at atmospheric pressure. The specific heat ($c_p$) of both the solid and liquid samples was determined for each n-alkane by DSC performed under a heating/cooling rate of 5 °C/min using the following expression:

$$c_p = \frac{HF}{m \cdot v}$$

where $HF$ is the heat flow, $v$ is the used scanning speed and $m$ is the weight of the sample.

As it was indicated previously, $\lambda$ and $a_T$ were measured using the transient hot wire method. The experimental set-up shown in Fig. 1 and the method employed are essentially similar to the ones used in our laboratory for the measurement of $\lambda$ of several fluids [25–27]. Since the details of the experimental set-up and the principles of measurements have been described elsewhere [25–27], only some minor changes will be noted. A vertical straight platinum wire of 50 ± 0.001 μm diameter and 20.13 ± 0.01 cm length was used. The two wire ends were soldered to tabs in a chemically resistant flat frame cut from a circuit board. Two Teflon isolated leads were then soldered to the tabs, after which the connections were covered by a thermal resistant epoxy. To avoid electrical contact between the platinum wire and the samples, the wire and the frame supporting it were covered with a Teflon-based industrial coating with a thickness less than 1 μm. A Keithley 2400 source-meter, which can act simultaneously as current source and voltage meter, was employed for electrical measurements. This source-meter is interfaced to a personal computer and a software code was written to retrieve the measurement points, fit the data, and then calculate $\lambda$ and $a_T$. The electrical current is injected by two of the leads connected to the wire ends, while voltage measurements are acquired simultaneously using the other two leads. For each $\lambda$ and $a_T$ measurement, various current values, from 160 to 260 mA, were applied.

The n-alkane sample is first melted, if not liquid at room temperature, and poured in the inner volume of a double-wall cylindrical glass cell having an internal diameter of 4 cm, an external diameter of 6 cm and a height of 32 cm. Both the hot wire and the platinum resistance thermometer are inserted inside the cell containing the n-alkane sample. The platinum thermometer is also interfaced to the personal computer controlling the experiment, and the same computer code manages simultaneously the thermometer and the electrical source-meter. Ethylene glycol is circulated from a thermostated bath (Lauda ECO RE630) through the jacket of the measurement glass cell in order to control the temperature of the sample within ±0.05 K. The whole measurement cell is placed inside a controlled laboratory environmental chamber (Mytron) that is set at the same temperature of the thermostat. The humidity of the chamber was maintained around 40%.

To ensure the adequate measurements of the wire, series of experimental runs using distilled water and dimethyl phthalate at different temperatures were performed at the beginning and at the end of each experiment as well as when switching between the different n-alkanes. Comparisons with known values of $\lambda$ for distilled water and dimethyl phthalate were made.

At the first beginning of the experiment, the temperature is established. Once steady state is reached, by means of the developed software the electrical current was varied within the established range with a difference of 20 mA, which is applied to the wire every 4 min. The resistance of the wire ($R_0$) at the beginning of the heating step, the electric potential ($V$) and the temperature

![Fig. 1. Schematic representation of the experimental set-up for the measurement of the thermal conductivity ($\lambda$) and thermal diffusivity ($a_T$).](image-url)
$T$ versus time ($t$) are recorded. Each measurement 350 values of $V$ as a function of time are registered. Each temperature measurement is performed for at least 10–12 h depending on the set temperature and the state of the $n$-alkane hydrocarbon, solid or liquid, under study. A typical heating run lasts for approximately 1.6 s.

When the electrical current $I$ is circulated through the wire, because of Joule heating, the wire temperature increases. The rate of wire heating depends mainly on $\lambda$ and $a_T$ of the $n$-alkane surrounding the wire. As a consequence of the temperature increase, both the electrical resistance of the wire ($R$) and the voltage drop between the wire ends $\Delta V$ increase. For an infinite cylindrical straight wire, $\Delta V$ between two points, separated by a distance $L$, as a function of time $t$, can be approximated for large time, $t \gg \frac{L^2}{\alpha T}$, by Refs. [27,28,46]:

$$\Delta V(t) = V(t) - V_0 = \frac{I^2 R_0}{4\pi L} \left[ \ln \left( \frac{t}{t_0^2 \rho c_p} \right) - \gamma \right]$$  \hspace{1cm} (2)

where $R_0$ is the electrical resistance of the wire at the beginning of the heating ($t = 0$), $\gamma$ is Euler’s constant ($\gamma \approx 0.5772$), $\alpha$ is the temperature resistance coefficient of the wire material (Platinum) and $L$ is the wire length. This equation can be re-written as:

$$V(t) = m \frac{I^2 R_0}{4\pi L} \left[ \ln \left( \frac{t}{t_0^2 \rho c_p} \right) - \gamma \right] + V_0$$ \hspace{1cm} (3)

where ($m = \alpha R_0$) represents the slope of the [$R$, $T$] curve at the initial temperature of the heating run and the parameter $\beta$ (units of time) depends on $a_T$ of the sample and the wire radius ($r_0$) as follows:

$$\beta = \frac{r_0^2}{4\alpha_T}$$ \hspace{1cm} (4)

$\lambda$ of the sample is obtained by fitting, as required by Eq. (3), the data pairs [$V$, $\ln(t)$] acquired in each heating run to a straight line, from
which a slope \( \lambda \) and intercept \( B \) are derived. Since Eq. (3) is an asymptotic expansion for large \( t \), only the points acquired after \( \approx 412 \) ms were used in the fitting procedure. Finally, \( \lambda \) and \( a_1 \) can be determined from the following expressions:

\[
\lambda = \frac{m^3 R_0}{4 \pi T S^3} = A \frac{r_3^3 R_0}{S} \tag{5}
\]

\[
a_1 = \frac{r_3^2}{4} \exp \left( \frac{B - V_0}{S} + \gamma \right) \tag{6}
\]

where \( A \) is a constant of the wire that depends on its effective length.

### 3. Results and discussions

Fig. 2 shows the melting and crystallization temperatures variation curves with time of the three \( n \)-alkanes. The melting time was estimated from the temperature curves as the time corresponding to a constant temperature of the \( n \)-alkane. This is 24 min, 24 min and 22 min, for \( C_{16} \), \( C_{18} \) and \( C_{20} \), respectively. The detected melting temperature range is \((289.91–292.78 \text{ K})\), \((298.67–302.35 \text{ K})\) and \((307.68–310.45 \text{ K})\) for \( C_{16} \), \( C_{18} \) and \( C_{20} \) respectively. It must be pointed out that the reduction of the melting time corresponds to the higher \( \lambda \) value of the \( n \)-alkane or to the greater latent heat of melting and mass. Similar to the melting curve, from the solidification curve the corresponding temperature range and solidification time were determined for each \( n \)-alkane. The estimated crystallization time was 19 min for \( C_{16} \) and \( C_{18} \), whereas for \( C_{20} \) it was lower, 16 min and 13 min for liquid/solid transition and solid/solid transition, respectively. The crystallization temperature range was \((292.05–289.30 \text{ K})\) for \( C_{16} \), \( C_{18} \) and \( C_{20} \). The crystallization temperature range was \((292.05–289.30 \text{ K})\) for \( C_{16} \), \( C_{18} \) and \( C_{20} \). The minor peak represents the liquid/solid phase change (i.e., crystallization) while the large peak (called secondary peak) represents the solid/solid transition indicating the structural phase change in the solid [28]. It must be pointed out that the presence of two peaks for \( C_{20} \) is characteristic of odd-numbered \( n \)-alkanes and hydrocarbons with carbon number greater or equal to 19 (i.e., n-nonadecane, \( C_{19}H_{38} \)). Triclinic structure (i.e., crystalline I) has been confirmed by X-ray Diffraction (XRD) at lower temperatures than \( T_m \), while rotator crystal was reported for higher temperatures up to \( T_m \) [47,48].

### Table 1

<table>
<thead>
<tr>
<th>( n )-Alkane</th>
<th>Melting</th>
<th>Crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solid/liquid transition</td>
<td>Liquid/solid transition</td>
</tr>
<tr>
<td></td>
<td>( T_m ) (K)</td>
<td>( \Delta H_m ) (kJ/kg)</td>
</tr>
<tr>
<td>( C_{16} )</td>
<td>290.90 ± 0.006</td>
<td>235.13 ± 0.13</td>
</tr>
<tr>
<td>( C_{18} )</td>
<td>300.22 ± 0.095</td>
<td>243.68 ± 0.96</td>
</tr>
<tr>
<td>( C_{20} )</td>
<td>308.84 ± 0.15</td>
<td>247.05 ± 0.14</td>
</tr>
</tbody>
</table>

* For \( C_{20} \) the indicated latent heat is the total considering both solid/solid and solid/liquid phase changes.

### Table 2

<table>
<thead>
<tr>
<th>( n )-Alkane</th>
<th>( T_m ) (K)</th>
<th>( \Delta H_m ) (kJ/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{16} )</td>
<td>291.25</td>
<td>236</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>289.85</td>
<td>236</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>291.49</td>
<td>235.65</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>291.15</td>
<td>237</td>
<td>[50]</td>
</tr>
<tr>
<td>( C_{18} )</td>
<td>301.25</td>
<td>244</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>301.6</td>
<td>242.48</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>301.15</td>
<td>243</td>
<td>[50]</td>
</tr>
<tr>
<td>( C_{20} )</td>
<td>309.75</td>
<td>248</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>310.3 ± 0.1</td>
<td>247.6 ± 0.2</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>310.05</td>
<td>247.6</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>310.15</td>
<td>247</td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>312.3</td>
<td>237.1</td>
<td>[51]</td>
</tr>
</tbody>
</table>

* The data reported in [23,24] were obtained from DSC analysis while the other reported data in [17,49–51] no specific technique was mentioned. \( T_m \) and \( \Delta H_m \) values of \( C_{16} \) and \( C_{18} \) were not found. The only available \( T_m \) and \( \Delta H_m \) values are for \( C_{20} \) and these were reported by Genovese et al. [24] and indicated in the text of this study.
solid/solid phase change temperature of 306.23 K. This result is attributed to the heat evolved in the solid/solid conversion [24].

Some examples of heating curves \( [V, \ln t] \) used to determine \( \lambda \) of solid and liquid phases of the three \( n \)-alkanes are presented in Fig. 4. The solid lines represent the adjustment of the experimental points to Eq. (3) when the system reached asymptotic long times (i.e., \( >412 \) ms; The first 150 points have not been taken into account in the fitting). No deviations were observed between the registered data and the straight lines at long time asymptotic regime. This demonstrates that the measurements in liquid state are free of natural convection.

For each \( n \)-alkane sample, two series of measurements were performed, one from lower to higher temperature and the second from higher to lower temperature. \( R \) is registered for each sample both in solid or liquid phase, for each temperature and for each electrical current measurement. An average value is then determined and the dependence of \( R \) with temperature \( (T) \) is plotted in Fig. 5. The obtained \( m \) value is \( 0.04452 \) \( \Omega \) K. From the measured and reported \( \lambda \) values of water and dimethyl phthalate at different temperatures, \( A \) was determined (0.01783 \( \Omega \) K \(^{-1} \) m \(^{-1} \) and then the effective length of the wire \( (L_{\text{eff}}) \) was calculated from Eq. (5) \( (L_{\text{eff}} = m/(4\pi A)) \). The obtained value 19.87 cm is close to the used length of the wire 20.13 cm (1.3% deviation). This confirms that the measured \( \lambda \) and \( a_T \) data in this study are absolute values. It is worth quoting that the behavior of the electrical resistance with temperature permits to check the stability of the wire during the
measurements period. Most importantly, no differences were detected between tests performed with water and dimethyl phthalate at the beginning, at the end and when switching between tested alkane hydrocarbons.

Fig. 6 shows $\lambda$ of C16, C18 and C20 in both liquid and solid phases as a function of temperature together with the available literature data [26,29–35,39–41]. The reported standard deviations correspond to 100–445 measurements of each temperature. The uncertainty indicated for $\lambda$ values corresponds to random errors only and a systematic error contribution of ±2% should be added. This is considered in the supplementary Table summarizing $\lambda$ data. For clarity, horizontal lines were plotted to separate the measurements carried out in each phase. High dispersions of $\lambda$ were detected near the solid/liquid phase transition of the three n-alkanes. This is attributed to the latent heat of melting/crystallization that may affect the temperature of the wire. In any case, the error bars are between 0.6% and 2.2% for C16, 0.10% and 4.5% for C18 and 0.3% and 1.2% for C20. It can also be seen that the literature data [26,29–35,39–41] are within the margin of error in the liquid phase for C16 and C20, while for the solid phase it is impossible to make any comparison due to the insufficient available data in the literature. For C18, the obtained $\lambda$ values in liquid phase are quite similar to those reported by Yaws [31] but higher than those given by Mustafaev [34] and Rastorguev and Bogatov [35]. As it is reported previously, there is a lack of published data for the solid phases of the three n-alkanes and all published $\lambda$ values of the solid phase of n-alkane hydrocarbons correspond to temperatures very close to the transition temperature ($T_m$) without indication of the corresponding associated errors and these values are larger than $\lambda$ obtained in this study [26,29–35,39–41].

It can be observed in Fig. 6 that in the liquid phase $\lambda$ of the three n-alkanes tends to decrease with the increase of the temperature. However, for C16 and C20 in solid phase $\lambda$ is maintained nearly constant for temperatures much lower than $T_m$ and decreased gradually with temperatures near $T_m$. For C18 in solid phase, a more clear decrease of $\lambda$ was detected with the increase of the temperature (Fig. 6b). A discontinuity in $\lambda$ is detected near $T_m$ of each n-alkane being $\lambda$ of the same n-alkane in solid state higher than that of the liquid state and the jump of $\lambda$ at the liquid/solid phase transition is higher for the n-alkane having higher number of carbon atoms. This is attributed principally to the change of the density, typical of first order phase transition. The estimated ($\Delta \lambda = \lambda_{\text{solid}} - \lambda_{\text{liquid}}$) is 0.172, 0.182 and 0.263 W/m K for C16, C18 and C20, respectively. Moreover, in solid phase $\lambda$ is greater for the n-alkane having greater number of carbon in the molecular chain.
In liquid phase, \( \lambda \) is also higher for the hydrocarbon with more number of carbon atoms in the molecular linear chain. A gradual decrease of \( \lambda \) is observed for \( \text{C}_{16} \) and \( \text{C}_{20} \) in all studied temperature range and for \( \text{C}_{18} \) from its melting temperature to 333.15 K. A constant value of \( \lambda \) was measured for \( \text{C}_{18} \) from 333.15 K to 348.15 K. For \( \text{C}_{20} \) no \( \lambda \) variation could be detected for the two crystalline phases because of the close \( T_m \) and \( T_r \) values.

The reported \( \lambda \) values for \( \text{C}_{16} \) in liquid phase \([29,30]\) deviate only 2.5% from the values obtained in this study. For \( \text{C}_{18} \) and \( \text{C}_{20} \) in liquid phase the \( \lambda \) values obtained in this study are less than 2% and 2.9% higher than those reported by Yaws \([31]\) and Stryker and Sparrow \([39]\), respectively.

\( \alpha_T \) was also determined by the hot wire technique for both the solid and liquid phases of the three \( n \)-alkanes as it was explained previously (Eq. (6)). The results are plotted in Fig. 7 and summarized in Table 3. The uncertainty indicated for \( \alpha_T \) values in Fig. 7 corresponds to random errors only and a systematic error contribution of \( \pm 3.5 \% \) should be added. In Table 3, the total errors are indicated together with the obtained \( \alpha_T \) values. It can be seen that the uncertainty associated to \( \alpha_T \) obtained by the hot wire technique is greater than that of \( \lambda \). For both liquid \( \text{C}_{16} \) and \( \text{C}_{20} \), only very slight decrease was detected for \( \alpha_T \) with temperature (i.e., 18.0% for \( \text{C}_{16} \) and 8.5% for \( \text{C}_{20} \) when the temperature was reduced to 348 K) and \( \alpha_T \) of \( \text{C}_{20} \) is about 15% smaller than that of \( \text{C}_{16} \). By means of the transient hot wire technique, Wanatabe and Seong \([36]\) also observed a gradual decrease of \( \alpha_T \) with the increase of the temperature from 263 K to 343 K of \( n \)-alkanes \( \text{C}_n\text{H}_{2n+2} (n=5-10) \) and practically no difference was detected between \( \alpha_T \) values of these studied \( n \)-alkanes that were maintained in the range 7–8.9 \( \times 10^{-8} \text{ m}^2/\text{s} \). Wanatabe and Seong \([36]\) claimed that \( \alpha_T \) was maintained constant with the number of carbon atoms of these \( n \)-alkanes and within the studied temperature range 263–343 K. Providing that Morikawa and Hashimoto \([42]\) reported higher \( \alpha_T \) values for the \( n \)-alkanes \( (\text{n}-\text{tricosane} (\text{C}_{23}\text{H}_{48}), \text{n}-\text{tetrasane} (\text{C}_{24}\text{H}_{50}) \) and \( \text{n}-\text{pentasane} (\text{C}_{25}\text{H}_{52})) \), it seems that there may be an increase of \( \alpha_T \) with the number of carbon atoms \( n \) of linear alkanes.

It can be seen in Fig. 7, a slight enhancement of \( \alpha_T \) with temperature for \( \text{C}_{18} \) in liquid phase. This result is attributed partly to the insignificant variation of \( \lambda \) with temperature from 318 to 348 K. It is interesting to note that, similar to \( \lambda \) in liquid phase up to 330 K, \( \alpha_T \) with the number of carbon atoms of the \( n \)-alkanes was observed in the temperature range 310–325 K.

As it can be seen in Fig. 7, similar to \( \lambda \), \( \alpha_T \) of \( \text{C}_{16}, \text{C}_{18} \) and \( \text{C}_{20} \) in the solid phase is greater than that of the liquid phase and much dispersions were registered for \( \alpha_T \) near \( T_m \). Similar behaviors of \( \alpha_T \) were reported by Morikawa and Hashimoto \([42]\) for other \( n \)-alkanes \( (\text{n}-\text{tricosane} (\text{C}_{23}\text{H}_{48}), \text{n}-\text{tetrasane} (\text{C}_{24}\text{H}_{50}) \) and \( \text{n}-\text{pentasane} (\text{C}_{25}\text{H}_{52})) \) determined by means of Fourier Transform Temperature Wave Analysis (FT-TWA). It is worth quoting that no literature data were found for \( \alpha_T \) of the three \( n \)-alkanes considered in this study.

\( \alpha_T \) can be calculated using the obtained \( \lambda \) values in this study if \( c_p \) and \( \rho \) data are available. As it was mentioned previously, \( c_p \) of the three \( n \)-alkanes was determined from the DSC curves. The

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**Table 3**

Some \( \alpha_T \) data of \( \text{C}_{16}, \text{C}_{18} \) and \( \text{C}_{20} \) in liquid phase obtained by the hot wire technique and calculated \( (\alpha_T = \lambda/\rho c_p) \) from the measured \( \lambda, \rho \) and \( c_p \) in this study.

<table>
<thead>
<tr>
<th>( n )-Alkane</th>
<th>( T (K) )</th>
<th>( \alpha_T (\times 10^{-8} \text{ m}^2/\text{s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_{16} )</td>
<td>291.58</td>
<td>0.81 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>293.53</td>
<td>0.78 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>298.49</td>
<td>0.75 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>301.02</td>
<td>0.78 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>302.39</td>
<td>0.78 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>313.37</td>
<td>0.76 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>316.41</td>
<td>0.73 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>322.28</td>
<td>0.74 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>328.26</td>
<td>0.72 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>332.40</td>
<td>0.73 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>343.14</td>
<td>0.65 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>348.10</td>
<td>0.68 ± 0.22</td>
</tr>
<tr>
<td>( \text{C}_{18} )</td>
<td>303.36</td>
<td>0.60 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>308.318</td>
<td>0.62 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>313.24</td>
<td>0.67 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>318.05</td>
<td>0.68 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>323.019</td>
<td>0.73 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>327.96</td>
<td>0.83 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>332.91</td>
<td>0.86 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>337.92</td>
<td>0.88 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>342.90</td>
<td>1.01 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>347.81</td>
<td>1.07 ± 0.27</td>
</tr>
<tr>
<td>( \text{C}_{20} )</td>
<td>309.10</td>
<td>0.61 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>313.50</td>
<td>0.62 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>318.48</td>
<td>0.63 ± 0.09</td>
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<tr>
<td></td>
<td>323.48</td>
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<td>328.20</td>
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<td></td>
<td>333.69</td>
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<tr>
<td></td>
<td>338.04</td>
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<tr>
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<td>343.00</td>
<td>0.57 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>347.94</td>
<td>0.56 ± 0.09</td>
</tr>
</tbody>
</table>

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**Fig. 7.** Thermal diffusivity \( \lambda \) of solid and liquid phases as a function of temperature \( T \) of: (a) \( \text{C}_{16} \), (b) \( \text{C}_{18} \) and (c) \( \text{C}_{20} \). The measured \( \lambda \) data in solid phase near the transition temperature (presented as empty symbols) are affected by the latent heat.
results together with the reported data obtained from the literature [52–56] are presented in Fig. 8. There is an increase of \( c_p \) of the three \( n \)-alkanes with temperature in both solid and liquid phases. The deviation between the obtained \( c_p \) data in this study for the three \( n \)-alkane hydrocarbons in liquid phase are less than 1.61%, 0.91% and 0.36% for C16, C18, C20, respectively [53–56]. Greater deviation errors were found for the solid phase, which were 8.58%, 16.58% and 9.26% for C16, C18, C20, respectively [52,56]. This may be attributed to the different used measurement techniques. For C16 and C18 an aneroid calorimeter was used [52] whereas for C20 an adiabatic calorimeter was employed [56]. Table 4 summarizes the fitting coefficients of \( c_p \) values to the polynomial equation \( (c_p = aT^4 + bT^3 + cT^2 + dT + e) \).

\[ c_p \text{(kJ/kg K)} \text{ of the three } n \)-alkanes at liquid phase was measured at different temperatures. The results are plotted in Fig. 9 together with the data taken from the literature [57–59]. A gradual decrease of the density of the three \( n \)-alkanes is observed with the increase of the temperature and the density is higher for the \( n \)-alkane having a greater number of carbons. A good agreement was observed between the measured and literature data [57–59] (i.e., the maximum registered deviations were 0.20% for C16, 0.05% for C18 and 0.25% for C20).

Based on the measured values of \( \lambda \), \( c_p \) and \( \rho \) of the three \( n \)-alkanes in liquid phase, \( a_T \) was calculated and the results are given in Table 3 together with the \( a_T \) values determined from the hot wire technique and the corresponding deviations. These were found to be less than 17.1% for C16, 31.2% for C18 and 29.5% for C20. These high deviations are attributed to the greater uncertainty associated to the calculated \( a_T \) values that include both the random and systematic errors of \( \lambda \), \( c_p \) and \( \rho \). In any way, the obtained \( a_T \) values by the hot wire technique have less uncertainty and are more accurate.

An important thermal energy storage characteristic of an \( n \)-alkane is its cumulative thermal energy storage. This is defined as the thermal energy stored in an \( n \)-alkane by raising its temperature.
from a reference temperature to a higher temperature. In this study, the thermal energy stored per unit of mass of the hydrocarbon \( n \)-alkane (\( Q/m \)) was estimated for different heating temperatures up to 348.15 K with a reference temperature of 258.15 K using the following equation:

\[
Q/m = \int_{T_1}^{T_2} c_p dT + \Delta H_m + \int_{T_m}^{T_2} c_p dT
\]

(7)

where \( m \) is the mass of the \( n \)-alkane, \( \Delta H_m \) is its latent heat of melting, \( T_1 \) is the initial temperature, \( T_2 \) is the final temperature, \( c_{ps} \) and \( c_{pl} \) are the specific heats of solid and liquid \( n \)-alkane phases, respectively. The first term of the above equation represents the sensible heat of the solid \( n \)-alkane hydrocarbon phase, the second term is the latent heat of melting, and the third term is the sensible heat of the liquid \( n \)-alkane hydrocarbon phase.

Fig. 10 shows the cumulative heat stored by each \( n \)-alkane hydrocarbon as a function of the temperature. As an example, for a temperature of 348.15 K, this is found to be 425.9, 426.3 and 435.4 kJ/kg for \( C_{16} \), \( C_{18} \) and \( C_{20} \), respectively. The value of \( C_{18} \) is only slightly higher than that of \( C_{16} \) due to the lower \( c_{ps} \) values of \( C_{18} \) as presented in Fig. 8. It must be pointed out that the sensible heat contribution to the heat stored must be taken into account for any design calculation. For instance, it was observed that the contribution of the latent heat stored increased with the number of carbon in the \( n \)-alkane hydrocarbon chain (e.g., from 258.15 K to 442.3 K, this contribution is 60.8%, 63.4% and 64.7% for \( C_{16} \), \( C_{18} \) and \( C_{20} \), respectively).

4. Conclusions

The thermal properties of the even-numbered \( n \)-alkanes, \( n \)-hexadecane (\( C_{16} \)), \( n \)-octadecane (\( C_{18} \)) and \( n \)-eicosane (\( C_{20} \)) are measured at different temperatures including both liquid and solid phases and the results were compared with available literature data.

DSC thermograms of \( C_{16} \) and \( C_{18} \) have a single peak corresponding to melting/crystallization, whereas \( C_{20} \) exhibits two almost overlapping crystallization peaks, liquid/solid (i.e., crystallization) and solid/solid transitions (i.e., triclinic structure at lower temperatures than \( T_r \) and rotator crystal between \( T_r \) and \( T_m \)).

A gradual increase of \( \Delta H_m \), \( \Delta H_c \), \( T_m \), \( T_c \) and \( T_r \) with increasing the number of carbon atoms of the three \( n \)-alkanes was observed and the deviations respect to previously reported data were less than 0.8%.

The thermal conductivity (\( \lambda \)) and thermal diffusivity (\( \alpha_T \)) of the solid and liquid phases of \( C_{16} \), \( C_{18} \) and \( C_{20} \) were measured for the first time by the hot wire technique using the same set-up in the temperature range 258–348 K. The obtained values for the liquid phase cannot be in any reliable way extended to the solid phase. High deviations of \( \lambda \) and \( \alpha_T \) were detected near the solid/liquid phase transition of the three \( n \)-alkanes due to the latent heat of melting/crystallization that may affect the temperature of the wire. For the solid phase it is impossible to make any comparison due to the insufficient available data in the literature.

A discontinuity in \( \lambda \) was detected near \( T_m \) for each \( n \)-alkane being \( \lambda \) of the same \( n \)-alkane in solid state higher than that of the liquid state and the jump of \( \lambda \) near \( T_m \) was found to be higher for the \( n \)-alkane having higher number of carbon atoms. In liquid
phase, $\lambda$ was higher for the hydrocarbon with more number of carbon atoms and a gradual decrease of $\lambda$ was observed for C16 and C20 in all studied temperature range and for C18 from its $T_m$ to 333.15 K.

No literature data were found for $\alpha_2$ of the three n-alkanes considered in this study. For both liquid C16 and C20, very slight decrease was detected for $\alpha_2$ with temperature. However, a slight enhancement of $\alpha_1$ with temperature was observed for C18 in liquid phase attributed to the insignificant variation of $\lambda$ with temperature from 318 to 348 K. Similar to $\lambda$ in liquid phase up to 330 K, an increase of $\alpha_1$ with the number of carbon atoms of the n-alkanes was observed in the temperature range 310–325 K. Moreover, $\alpha_1$ of C16, C18 and C20 in the solid phase is greater than that of the liquid phase and much dispersions were registered for $\alpha_1$ near the solid/liquid transition temperature.

The cumulative heat stored by each n-alkane was estimated as a function of the temperature and it was found an increase of the contribution of the latent heat to the cumulative heat stored with function of the temperature and it was found an increase of the cumulative heat stored by C18 very slight and to C 19 and C20.

The cumulative heat stored by each n-alkane was estimated as a function of the temperature and it was found an increase of the contribution of the latent heat to the cumulative heat stored with function of the temperature.

The cumulative heat stored by each n-alkane was estimated as a function of the temperature and it was found an increase of the contribution of the latent heat to the cumulative heat stored with function of the temperature.

Acknowledgments

The authors gratefully acknowledge the financial support of the UCM-Banco Santander (GR3/14) and the I+D+I Project MAT2010-19249 (Spanish Ministry of Science and Innovation). Partial financial support from Abengoa Water, S.L.U. is also acknowledged.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2015.01.054.

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