# Empirical equation to estimate viscosity of paraffin

Gerard Ferrer[1], Stefan Gschwander[2], Aran Solé[1], Camila Barreneche[1,3], A. Inés Fernández[3], Peter Schossig[2], Luisa F. Cabeza[1,*]

[1]

[1]GREA Innovació Concurrent, Universitat de Lleida, Lleida, Spain. Edifici CREA, Pere de Cabrera s/n, 25001-Lleida (Spain).

[2] Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, Freiburg, Germany

[3] Department of Materials Science & Physical Chemistry, Universitat de Barcelona, Barcelona, Spain. Martí i Franqués 1-11, 08028-Barcelona (Spain).

*Corresponding author e-mail: lcabeza@diei.udl.cat

**Abstract**

Thermal energy storage (TES) systems using phase change materials (PCM) are nowadays widely developed to be applied in solar power plants or cooling and domestic comfort services. The design of a TES system does not only rely on the energy density that a PCM can provide, but also on other important material properties such as its rheological behavior when the PCM is melted. Viscosity varies with temperature, but the lack of an empirical equation predicting its value has lead researchers to simulate the system performance taking constant viscosity values which, consequently, have led to errors on the designs. As paraffin are one of the most common PCM types used, the present paper evaluates the rheology of four commercial paraffin with different phase change temperatures in order to find out an empirical equation for the whole paraffin family. A polynomial 3 model type equation has been found as the best one to predict paraffin viscosity.

**Keywords**: empirical equation; viscosity; rheology; paraffin; thermal energy storage (TES); phase change materials (PCM).

## 1. Introduction

Thermal energy storage (TES) systems use has been widely increased over recent years as a response to the current energy demands focused on decreasing the use of fossil fuel and electricity consumption, and therefore reducing $CO_2$ emissions too. TES systems are used in a wide range of applications, as services like domestic hot water, [1] and building comfort, solar power plants, [2] or cold storage systems [3], and in all these applications phase change materials (PCM) are implemented to accomplish these goals. PCM can provide high energy densities due to the latent heat associated to their phase change, energy that when both stored and released can be profited depending on the needs [4] [5] [6].

Paraffin are linear hydrocarbon molecules (n-alkanes) with a general formula of $C_nH_{2n+2}$ that can contain from ten up to more than one hundred carbon atoms. Its use in heat storage systems has increased over the past years due to its high latent heat values that, along with their mostly stable and defined phase change temperatures, make them one of the most used PCM families [7] [8]. Thermal energy storage systems encapsulate the PCM in containers and take advantage of the melting and cooling latent heat of the materials for the installation purpose. However, the design of a TES system is more complex than just considering the latent heat of the PCM and other properties need to be known in order to optimize the design and simulate the installation performance. One of the parameters to consider is the viscosity of the PCM when it is melted.

The rheological behaviour of a PCM is important in the design and simulation of a TES system because it is not constant with temperature. Empirical equations are used in chemical engineering and other scientific and engineering fields [9][10][11] for the estimation of properties of chemicals and are applied in simulations and other design steps of a system [12]. Some predictive viscosity models can be found in the literature. Lide and Kehiaian [13] gave two different equations, one for gases (equation 1) and another for liquids (equation 2). Furbo [14] presented an equation for water in the 10 ºC – 100 ºC temperature range (equation 3),

$$\mu[Pa \cdot s] = A(1) + A(2) \cdot T[K] + A(3) \cdot (T[K])^2 + A(4) \cdot (T[K])^3 + A(5) \cdot (T[K])^4 \quad (1)$$

$$ln(\mu[Pa \cdot s]) = A(1) + \frac{A(2)}{A(3) - T[K]} + A(4) \cdot ln(T[K]) \quad (2)$$

$$\mu[m^2/s] = 1.477 \cdot 10^{-6} \cdot \exp(-1.747 \cdot 10^{-2} \cdot T) \quad (3)$$

where $\mu$ is the viscosity, *A(n)* the equation constants and *T* the temperature at which the viscosity wants to be known.

However, no specific equation for PCM has been found in the literature. This lack of an empirical model to calculate the viscosity for TES systems along with the disperse results obtained with the different literature models, has lead in many cases to consider viscosity as a constant property that does not suffer variations with temperature. This fact has led to important errors on the simulations and, consequently, on the system design as well. Therefore, it is of importance to know how the viscosity of PCM varies with temperature in order to have accurate simulations.

The present paper studies and evaluates the rheology of four paraffin with different phase change temperatures in order to find out an empirical equation that describes the viscosity behaviour of the whole paraffin family as a function of temperature for use in TES system modelling and simulation.

## 2. Materials and method

### 2.1. Materials

The paraffin used in the study are RT21, RT27, and RT55, commercialized by Rubitherm, as well as n-octadecane Parafol 18-97, produced by Sasol Chemicals.

### 2.2. Viscosity analysis

The viscosity measurements were done with the Anton Paar MCR 502 rheometer. A P-PTD-200 plate with the geometry PP60/Ti was used. The compliance of the geometry is 0.00165 rad/N·m. In the measurements the transducer was on the upper plate, so the samples were oscillated from above. The material was first kept at a constant temperature during 200 seconds and then heated up under constant rate of 0.1 K/min with a shear stress of 1 Pa and a frequency of 1 Hz. The measurements for RT21, RT27 and n-octadecane were done in the 10 ºC- 40 ºC temperature range, while the RT55 viscosity was measured between 40 ºC and 70 ºC. The normal force was kept at zero. The measurements have a standard deviation of ± 3%.

### 2.3. Empirical equations development and evaluation

The rheometry data obtained for paraffin RT21, RT27, and RT55 to measure its viscosity has been evaluated and numerically adjusted in order to find out empirical equations to calculate the viscosity of these PCM.

The best fits were selected according to their sum of squares due to error (SSE), $R^2$, adjusted $R^2$, and root mean standard error (RMSE) statistics [15] along with the calculated relative errors:

- The SSE is the sum of squares due to error. This statistic measures the total deviation of the response values from the fit to the response values. A value closer to 0 indicates that the model has a smaller random error component, and that the fit will be more useful for prediction.
- The R-square ($R^2$) measures how successful the fit is in explaining the variation of the data. R-square can take on any value between 0 and 1, with a value closer to 1 indicating that a greater proportion of variance is accounted for by the model.
- The adjusted R-square (adjusted $R^2$) is generally the best indicator of the fit quality when comparing two models that are nested, that is, a series of models each of which adds additional coefficients to the previous model. It can take on any value less than or equal to 1, with a value closer to 1 indicating a better fit.
- The RMSE is the root mean standard error, and it is an estimate of the standard deviation of the random component in the data. An RMSE value closer to 0 indicates a fit that is more useful for prediction.

To complement this statistical analysis the relative errors between the models have also been calculated according to equation 4:

$$relative\ error = \frac{\mu_m - \mu_c}{\mu_m} \cdot 100 \tag{4}$$

where $\mu_c$ is the calculated viscosity and $\mu_m$ is the measured viscosity.

The model with the best goodness and lower difference with respect to the measured viscosity values has been selected as the most representative for each paraffin.

## 3. Results

As reported in former paragraphs, the temperature ranges used in the measurements ensure the complete melting of all the paraffin. However, it is important to point out that during the melting range of each paraffin the values were inconclusive as part of the material was still at solid state and clear values could not be obtained until the materials had undergone its complete

melting. Therefore just the viscosity values at liquid state were taken to formulate the equation given in the paper.

The results are explained in the following paragraphs. First, the best models found for each paraffin are explained and compared, and later, a common equation for the whole paraffin family is presented.

### 3.1. Empirical equation for the different paraffin tested

The measured viscosities of RT21, RT27, and RT55 have been adjusted in order to find models that correlate to measured data, showing potential to empirically calculate the viscosity of each paraffin. From within all the models found, the ones with a fit goodness ($R^2$ statistic) higher than 0.99 have been chosen for this study in order to select the one with the best goodness and predictive conditions. Table 1 presents the eight models that accomplished this constraint and that are evaluated in the paper.

Table 1. Suitable mathematic models found for viscosity calculation.

| Model | Equation |
|---|---|
| Polynomial 1 | $f(x) = p1 \cdot x + p2$ |
| Polynomial 2 | $f(x) = p1 \cdot x^2 + p2 \cdot x + p3$ |
| Polynomial 3 | $f(x) = p1 \cdot x^3 + p2 \cdot x^2 + p3 \cdot x + p4$ |
| Exponential 1 | $f(x) = a \cdot \exp(b \cdot x)$ |
| Exponential 2 | $f(x) = a \cdot \exp(b \cdot x) + c \cdot \exp(d \cdot x)$ |
| Power 1 | $f(x) = a \cdot x^b$ |
| Power 2 | $f(x) = a \cdot x^b + c$ |
| Rational 21 | $f(x) = \frac{p1 \cdot x^2 + p2 \cdot x + p3}{x + q1}$ |

Model comparisons for each paraffin case are next presented. These comparisons are performed regarding different mathematical parameters. First, the regression statistics are compared in order to see the ones with best goodness and less deviation, and later a complementary analysis comparing the relative error of the models is also presented.

- RT21

The viscosity data for RT21 was obtained in the 20–30 ºC temperature range. Six models have been found as possible predictive equations for RT21 viscosity calculation. Table 2 presents its different statistic values in order to compare the models and select the best fit. As there are nested models for each different equation type, comparisons within the different equation types are first presented, followed by an overall model comparison.

Table 2. Models found for paraffin RT21 viscosity calculation

| **Model** | **SSE** | **$R^2$** | **Adjusted $R^2$** | **RMSE** |
|---|---|---|---|---|
| Polynomial 1 | 5.8e-09 | 0.9983 | 0.9983 | 1.135e-05 |
| Polynomial 2 | 1.145e-09 | 0.9997 | 0.9997 | 5.1e-06 |
| Polynomial 3 | 1.131e-09 | 0.9997 | 0.9997 | 5.128e-06 |
| Exponential 1 | 1.165e-09 | 0.9997 | 0.9997 | 5.088e-06 |
| Exponential 2 | 1.147e-09 | 0.9997 | 0.9996 | 5.166e-6 |
| Power 2 | 7.924e-09 | 0.9977 | 0.9976 | 1.342e-05 |

Focusing first on the three polynomial nested models, results clearly show that polynomial 2 and polynomial 3 fits have greater significance than polynomial 1 (higher $R^2$ value). The statistics that polynomial 2 and polynomial 3 fits present are almost equal and show low deviations (SSE and RMSE) and great significance. Both models present the same adjusted $R^2$ statistic, parameter used to compare the fit quality of two nested models, thus, both models fit excellent and with the same quality for the viscosity data obtained for RT21.

Regarding the two exponential models, they both present mostly equal statistics but, despite the difference being almost negligible, the exponential 2 fit has lower adjusted $R^2$ than the exponential 1, thus exponential 1 model fits better RT21 viscosity.

The power 2 model shows worse significance and statistics on its fit quality when compared both to the polynomial and exponential fits.

Summarizing, both polynomial and exponential models show great significance on the fit and low and mostly equal deviation parameters, thus, from this statistical outlook, the four models adjust the data perfectly and are likely models to be used for empirical viscosity calculation.

For a deeper analysis of the different models found and to complement the statistical evaluation, the relative errors between the models as well as the relative error of each model with respect to the experimental viscosity have also been calculated.

The relative error calculations are presented in Table 3. Column 3 shows the relative error calculated with respect to the polynomial 3 model, as it is the one with the lowest SSE statistic. For further comparison, the relative error of each model with respect to the measured value has also been calculated and is presented in column 4.

Table 3. Relative error values of each model for RT21 viscosity calculation

| **Model** | **μ (Pa · s) T=25 ºC** | **Relative error (%)** | |
|---|---|---|---|
| | | **Within models** | **With respect to measured μ** |
| Polynomial 1 | 3.62e-03 | -0.278 | -0.406 |
| Polynomial 2 | 3.62e-03 | -0.243 | -0.371 |
| Polynomial 3 | 3.61e-03 | - | -0.04 |
| Exponential 1 | 3.61e-03 | 0.020 | 0.009 |
| Exponential 2 | 3.61e-03 | 0.019 | -0.003 |
| Power 2 | 3.60e-03 | 0.421 | 0.294 |

Measured viscosity at 25 ºC: 3.61e-03 Pa · s

Low relative errors (< 0.3%) have been found within all the models, and from the six of them, polynomial 3, exponential 1 and exponential 2 show the most similar results. When comparing the viscosity value calculated by each model to the real measured one, the same three models have even lower relative errors (< 0.1%), thus they adjust excellently to the real value.

Within these three best models (polynomial 3, exponential 2 and exponential 1), the two exponential models have lower relative errors with respect to the measured viscosity than the polynomial 3, but this difference is mostly despicable, 0.03%. As seen in former paragraphs, exponential 1 has better adjusted $R^2$ statistic (higher adjusted $R^2$ value) , which means that it fits the data better than its nested model exponential 2, and, therefore, it would be the most proper model to empirically calculate RT21 viscosity. However, as the relative error differences are so small and the three models have great fit goodness, both exponential 2 and polynomial 3 models can also be considered as proper models for RT21 empirical viscosity calculation.

Figure 1 displays viscosity adjustment by the three best models found so far, exponential 2, exponential 3 and polynomial 3, along with the experimentally measured RT21 viscosity. As shown, due to the almost negligible differences between the calculated and measured viscosities already explained in former paragraphs, no differences can be appreciated between the fits.

Figure 1. Exponential 2, exponential 3 and polynomial 3 fittings compared to the experimental RT21 viscosity curve

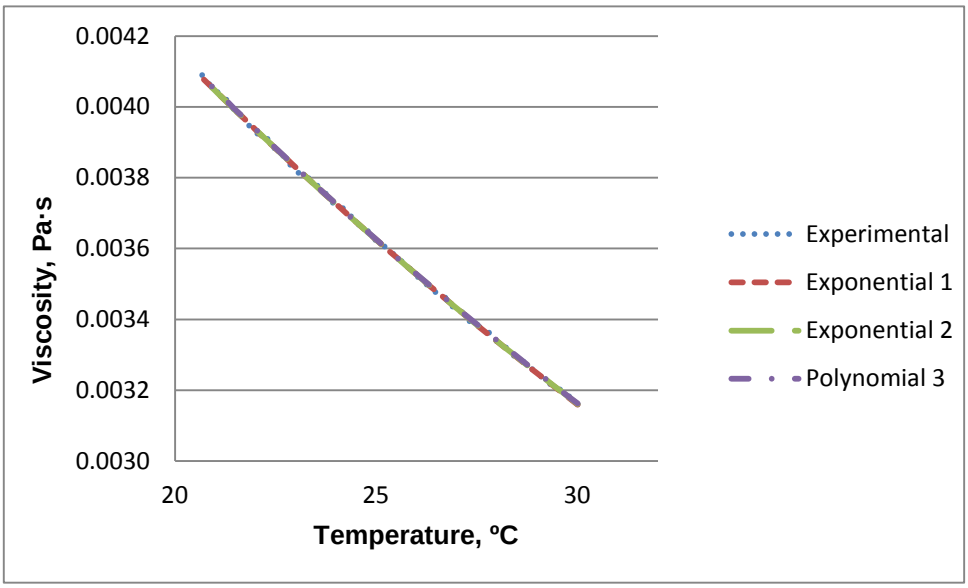



Table 4 presents the three models, exponential 1, exponential 2 and polynomial 3, along with their coefficients for RT21 empirical viscosity calculation.

Table 4. General models exponential 1, exponential 2 and polynomial 3 for RT21 viscosity calculation

| **Model** | General model Exponential 1 | General model Exponential 2 | General model Polynomial 3 |
|---|---|---|---|
| **Equation** | $f(x) = a \cdot \exp(b \cdot x)$ | $f(x) = a \cdot \exp(b \cdot x) + c \cdot \exp(d \cdot x)$ | $f(x) = p1 \cdot x^3 + p2 \cdot x^2 + p3 \cdot x + p4$ |
| **Coefficients (with 95% confidence bounds)** | a = 0.007198 (0.007171, 0.007225)<br>b = -0.02744 (-0.02759, -0.02728) | a = 0.007206 (0.00703, 0.007383)<br>b = -0.02749 (-0.02872, -0.02626)<br>c = 8.341e-11 (-1.551e-08, 1.568e-08)<br>d = 0.35 (-5.505, 6.206) | p1 = -3.292e-08 (-1.25e-07, 5.918e-08)<br>p2 = 3.971e-06 (-3.035e-06, 1.098e-05)<br>p3 = -0.000236 (-0.0004126, -5.948e-05)<br>p4 = 0.007558 (0.006084, 0.009032) |
| **Goodness of fit** | SSE: 1.165e-09<br>R-square: 0.9997<br>Adjusted R-square: 0.9997<br>RMSE: 5.088e-06 | SSE: 1.147e-09<br>R-square: 0.9997<br>Adjusted R-square: 0.9996<br>RMSE: 5.166e-06 | SSE: 1.131e-09<br>R-square: 0.9997<br>Adjusted R-square: 0.9997<br>RMSE: 5.128e-06 |

- RT27

The viscosity data for RT27 was acquired between 28 ºC and 40 ºC. Seven models have been found as possible empirical adjusts for RT27 viscosity determination. Table 5 shows the different statistical parameters of the models in order to compare the different fits and see the quality of each model adjustment. Further analyses are conducted in this paper in order to select the best predictive model for RT27 viscosity.

Table 5. Models found for paraffin RT27 viscosity calculation

| **Model** | **SSE** | **$R^2$** | **Adjusted $R^2$** | **RMSE** |
|---|---|---|---|---|
| Polynomial 1 | 1.645e-08 | 0.9977 | 0.9976 | 1.344e-05 |
| Polynomial 2 | 9.983e-10 | 0.9999 | 0.9999 | 3.331e-06 |
| Polynomial 3 | 9.052e-10 | 0.9999 | 0.9999 | 3.189e-06 |
| Exponential 1 | 1.937e-09 | 0.9997 | 0.9997 | 4.614e-06 |
| Exponential 2 | 9.033e-10 | 0.9999 | 0.9999 | 3.186e-06 |
| Power 2 | 7.384e-09 | 0.999 | 0.9989 | 9.058e-06 |
| Rational 21 | 2.496e-09 | 0.9996 | 0.9996 | 5.296e-06 |

Polynomial 1, despite being highly significant, is the model with the worst statistical values, thus, the model that would adjust worse RT27 viscosity. The power 2 model has better statistics and significance than polynomial 1 model but it is still worst to the other four models. Polynomial 2 and polynomial 3 models have similar values: great significance ($R^2$ = 0.9999) and low deviations, which make them valid candidates for this study purpose. The two exponential models show high significances and low deviations as well. The exponential 2 a more accurate model with respect to its nested exponential 1 model due to its adjusted $R^2$ value, closer to 1, and comparable to the two polynomial models just mentioned. Finally, the rational 21 model also presents great significance and low deviations, but its statistics are worse than those obtained by the polynomial and exponential models.

A step forward on this empirical model selection is the calculation of the relative error within the models as well as the relative error with respect to the measured data. These results, presented in

Table **6**, can complement perfectly the information already given by the different adjusts and the best model can be found.

Table 6. Relative error values of each model for RT27 viscosity calculation

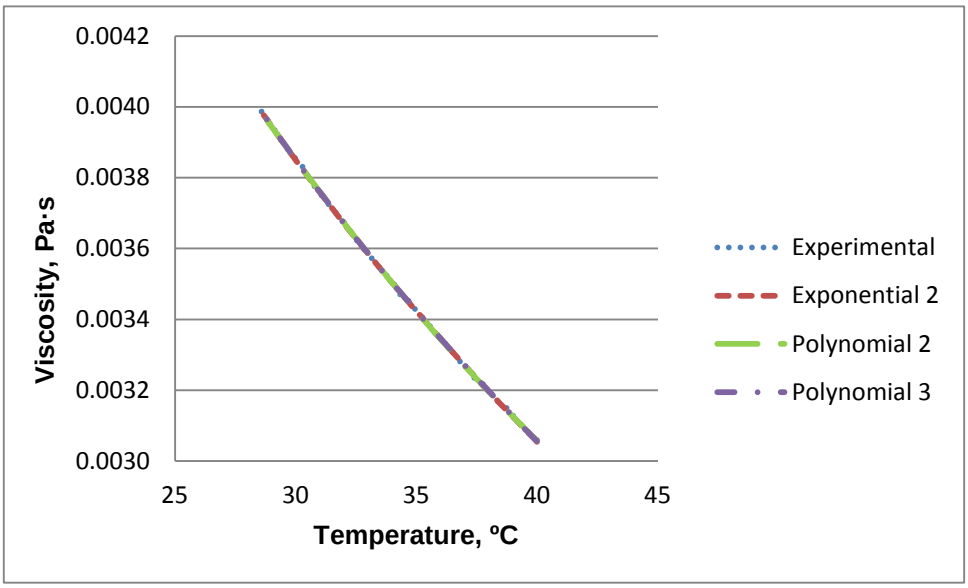
| **Model** | **μ (Pa · s) T=33 ºC** | **Relative error (%)** | |
|---|---|---|---|
| | | **Within models** | **With respect to measured μ** |
| Polynomial 1 | 3.60e-03 | -0.343 | -0.401 |
| Polynomial 2 | 3.59e-03 | - | 0.009 |
| Polynomial 3 | 3.59e-03 | 0.005 | -0.011 |
| Exponential 1 | 3.59e-03 | -0.080 | -0.137 |
| Exponential 2 | 3.59e-03 | 0.019 | 0.012 |
| Power 2 | 3.58e-03 | 0.247 | 0.190 |
| Rational 21 | 3.60e-03 | -0.092 | -0.149 |

Measured viscosity at 33 ºC: 3.59e-03 Pa · s

The relative errors between models are displayed in the first relative error column and in all cases are lower than 0.5%. When comparing the viscosity values obtained by each model with the measured ones (column 4), the differences are still small, but three models outstand among the others due to the low (< 0.1%) relative errors obtained: polynomial 2, polynomial 3 and exponential 2. According to the relative errors calculated, the exponential 2 model is the one that differs less from the measured viscosity.

Considering both analyses, the one regarding the goodness of the fit and the one considering the relative errors, three models show greater results: the polynomial 2, polynomial 3 and exponential 2 models. These three models present the same adjusted $R^2$ value, 0.9999, thus all models adjust the data with the same quality and significance level. The relative errors between the models are, in all cases, lower than 0.02%. Figure 2 shows these negligible differences between the models as well as with respect to the experimental viscosity points.

Figure 2. Exponential 2, polynomial 2 and polynomial 3 fittings compared to the experimental RT27 viscosity curve.




Thus, any of the three models can be used as a proper empirical equation for RT27 viscosity calculation, but according to the statistical model evaluation, exponential 2 and polynomial 3 models approximates the viscosity better to the real values measured (adjusted $R^2$), therefore, both are considered as the best predictive models to calculate RT27 viscosity. The three models are presented in Table 7.

Table 7. General models exponential 2, polynomial 2, and polynomial 3 for RT27 viscosity calculation

| **Model** | General model Exponential 2 | General model Polynomial 2 | General model Polynomial 3 |
|---|---|---|---|
| **Equation** | $f(x) = a \cdot \exp(b \cdot x) + c \cdot \exp(d \cdot x)$ | $f(x) = p1 \cdot x^2 + p2 \cdot x + p3$ | $f(x) = p1 \cdot x^3 + p2 \cdot x^2 + p3 \cdot x + p4$ |
| **Coefficients (with 95% confidence bounds)** | a = 0.0353 (-0.1494, 0.22)<br>b = -0.2332 (-0.4566, -0.009895)<br>c = 0.007478 (0.007181, 0.007775)<br>d = -0.02241 (-0.02332, -0.0215) | p1 = 1.262e-06 (1.195e-06, 1.329e-06)<br>p2 = -0.0001677 (-0.0001723, -0.0001631)<br>p3 = 0.007746 (0.007668, 0.007824) | p1 = -3.295e-08 (-5.46e-08, -1.131e-08)<br>p2 = 4.644e-06 (2.422e-06, 6.866e-06)<br>p3 = -0.0002827 (-0.0003584, -0.000207)<br>p4 = 0.009042 (0.008188, 0.009897) |
| **Goodness of fit** | SSE: 9.033e-10<br>R-square: 0.9999<br>Adjusted R-square: 0.9999<br>RMSE: 3.186e-06 | SSE: 9.983e-10<br>R-square: 0.9999<br>Adjusted R-square: 0.9999<br>RMSE: 3.331e-06 | SSE: 9.052e-10<br>R-square: 0.9999<br>Adjusted R-square: 0.9999<br>RMSE: 3.189e-06 |

- RT55

Viscosity data obtained in the 57-70 ºC temperature range was collected for RT55. Seven are the candidate models found to be used as equations for empirical RT55 viscosity calculation. Table 8 shows the different statistical parameters of the models in order to compare the quality of the fits and select the model that better adjusts RT55 viscosity.

Table 8. Models found for paraffin RT55 viscosity calculation

| **Model** | **SSE** | **$R^2$** | **Adjusted $R^2$** | **RMSE** |
|---|---|---|---|---|
| Polynomial 1 | 3.222e-08 | 0.9955 | 0.9955 | 1.795e-05 |
| Polynomial 2 | 1.475e-09 | 0.9998 | 0.9998 | 3.86e-06 |
| Polynomial 3 | 1.166e-09 | 0.9998 | 0.9998 | 3.45e-06 |
| Exponential 1 | 1.174e-08 | 0.9984 | 0.9983 | 1.084e-05 |
| Exponential 2 | 1.243e-09 | 0.9998 | 0.9998 | 3.562e-06 |
| Power 1 | 3.891e-09 | 0.9995 | 0.9995 | 6.238e-06 |
| Power 2 | 2.234e-09 | 0.9997 | 0.9997 | 4.75e-06 |

Results show three models with better statistics: polynomial 2, polynomial 3, and exponential 2. The three models have the same $R^2$ and adjusted $R^2$ values, which means that the three of them adjust the data with the same goodness. The deviation parameters, SSE and RMSE, are also the lowest ones and almost equal in these three cases, which means that their use for prediction is the most suitable of the seven models found.

Again, and as done for RT21 and RT27 with the aim to complement the model selection, further analyses have been conducted in order to see the quantitative differences between the models as well as the differences with respect to the measured viscosity. As Table 9 shows, the relative errors of the models have been calculated and compared.

Table 9. Relative error values of each model for RT55 viscosity calculation

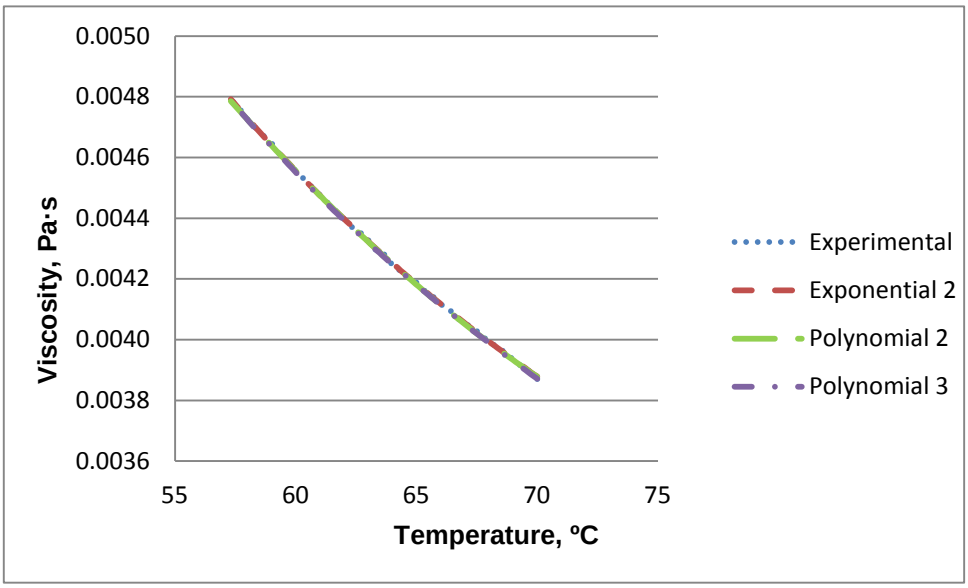
| **Model** | **μ (Pa · s) T=60 ºC** | **Relative error (%)** | |
|---|---|---|---|
| | | **Within models** | **With respect to measured μ** |
| Polynomial 1 | 4.55e-03 | -0.070 | -0.058 |
| Polynomial 2 | 4.55e-03 | - | 0.055 |
| Polynomial 3 | 4.55e-03 | 0.091 | 0.103 |
| Exponential 1 | 4.56e-03 | -0.016 | -0.113 |
| Exponential 2 | 4.55e-03 | -0.125 | 0.006 |
| Power 1 | 4.55e-03 | -0.005 | 0.007 |
| Power 2 | 4.55e-03 | 0.086 | 0.097 |

Measured viscosity at 60 ºC: 4.55e-03 Pa · s

The relative errors between models are in all cases lower than 0.2%, which means that differences are minimum between them. When comparing the viscosity values calculated by each model with the measured viscosity, the errors obtained are less than 0.2% as well. Thus, the significance and quality of all models is good. Nonetheless, exponential 2 is the model that obtained a viscosity value closer to the measured one, with just 0.006% of error. Polynomial 2 and power 1 models also present mostly equal values.

Summarizing, both analyses show that all models adjust with great significance RT55 viscosity. Exponential 2 and polynomial 2 and 3 are the models that show the best fit goodness, with greater significances (R2 = 0.9998) and lowest deviation parameters (SSE and RMSE) with negligible differences between models. That makes them the most proper models for prediction of the evaluated ones. In addition, all three models show mostly null differences with respect to the real values when calculations by each model and real data are compared, as Figure 3 shows. Thus, any of the three models can be used as empirical equation for RT55 viscosity calculation.

Figure 3. Exponential 2, polynomial 2, and polynomial 3 fittings compared to the experimental RT55 viscosity curve




The three models are presented in Table 10 .

Table 10. General models exponential 2, polynomial 2 and polynomial 3 for RT55 viscosity calculation

| **Model** | General model Exponential 2 | General model Polynomial 2 | General model Polynomial 3 |
|---|---|---|---|
| **Equation** | $f(x) = a \cdot \exp(b \cdot x) + c \cdot \exp(d \cdot x)$ | $f(x) = p1 \cdot x^2 + p2 \cdot x + p3$ | $f(x) = p1 \cdot x^3 + p2 \cdot x^2 + p3 \cdot x + p4$ |
| **Coefficients (with 95% confidence bounds)** | a = 0.03945 (-0.01832, 0.09721)<br>b = -0.06517 (-0.1174, -0.01298)<br>c = 0.006191 (0.0006708, 0.01171)<br>d = -0.008285 (-0.01731, 0.0007435) | p1 = 1.421e-06 (1.359e-06, 1.483e-06)<br>p2 = -0.0002525 (-0.0002604, -0.0002446)<br>p3 = 0.01459 (0.01434, 0.01484) | p1 = -4.388e-08 (-6.098e-08, -2.678e-08)<br>p2 = 9.801e-06 (6.536e-06, 1.307e-05)<br>p3 = -0.0007849 (-0.0009924, -0.0005773)<br>p4 = 0.02584 (0.02145, 0.03023) |
| **Goodness of fit** | SSE: 1.243e-09<br>R-square: 0.9998<br>Adjusted R-square: 0.9998<br>RMSE: 3.562e-06 | SSE: 1.475e-09<br>R-square: 0.9998<br>Adjusted R-square: 0.9998<br>RMSE: 3.86e-06 | SSE: 1.166e-09<br>R-square: 0.9998<br>Adjusted R-square: 0.9998<br>RMSE: 3.45e-06 |

### 3.2. Empirical equation for paraffin PCM

Results highlight two models that outstand among the others for all three paraffin: exponential 2 and polynomial 3 models. The differences between them are shown in Table 11, where the relative errors between both models are displayed for each paraffin case.

Table 11. Differences between the exponential 2 and polynomial 3 models for each paraffin

| Paraffin | Relative error (%) |
|---|---|
| RT21 | -0.036 |
| RT27 | -0.020 |
| RT55 | 0.055 |

To find out which model presents less error within all the paraffin family, the relative errors with respect to the measured viscosity have been calculated for each model/paraffin combination at three different temperatures, as shown in Table 12. The calculated error averages for both models show that the polynomial 3 model presents lower error than the exponential 2 model. Therefore, it would be the most suitable model for a whole paraffin empirical equation.

Table 12. Relative errors for each model/paraffin combination at three different temperatures and total error average

| Paraffin | | Relative error (%) | |
|---|---|---|---|
| | | **Exponential 2** | **Polynomial 3** |
| RT21 | T = 23 ºC | -0.206 | 0.086 |
| | T = 25 ºC | -0.108 | -0.128 |
| | T = 28 ºC | -0.077 | -0.127 |
| | **Average (%)** | **-0.131** | **-0.056** |
| RT27 | T = 29 ºC | -0.006 | -0.022 |
| | T = 32 ºC | -0.038 | -0.052 |
| | T = 37 ºC | -0.113 | -0.142 |
| | **Average (%)** | **-0.053** | **-0.072** |
| RT55 | T = 60 ºC | -0.004 | 0.149 |
| | T = 65 ºC | 0.064 | 0.149 |
| | T = 69 ºC | 0.117 | 0.258 |
| | **Average (%)** | **0.059** | **0.185** |
| **Total Average (%)** | | **-0.042** | **0.019** |

The former relative error comparison was done with each paraffin respective model components, being its respective p1, p2, p3 and p4 values the ones presented in former Table 4, Table 7 and Table 10, which are in the same order of magnitude for the three paraffin. The last step of the analysis is to find out the component values of the polynomial 3 model for the whole paraffin family. Therefore, the mean values of each component from the three paraffin equations have been calculated. Table 13 shows the general polynomial 3 model for paraffin with the mean component values.

Table 13. Polynomial 3 model with the mean component values for the whole paraffin family

| **Model** | General model Polynomial 3 |
|---|---|
| **Equation** | $f(x) = p1 \cdot x^3 + p2 \cdot x^2 + p3 \cdot x + p4$ |
| **Coefficients (with 95% confidence bounds)** | p1 = -3.66E-08<br>p2 = 6.14E-06<br>p3 = -4.35E-04<br>p4 = 1.41E-02 |

Table 14 shows the average relative errors obtained for each paraffin when the viscosity is calculated with the general paraffin model presented in former Table 13. As it can be seen, the error is higher than 40 % for all the paraffin.

Table 14. Relative errors obtained for RT21, RT27 and RT55 when the polynomial 3 model for paraffin is used

| | **RT21** | **RT27** | **RT55** |
|---|---|---|---|
| **Average relative error, %** | -80.59 | -43.43 | 55.84 |

The high errors obtained are probably related to the differences on paraffin structural chain, like the number of carbons, which is tied to the melting temperature of the materials and directly influences the viscosity.

Adding a correction parameter related to the melting temperature of each paraffin may reduce the relative errors and adjust much better the calculated viscosity to the measured one. The polynomial 3 model would then be as equation 5 shows:

$$\mu[Pa{\cdot}s] = (-3.66{\cdot}10^{-8}{\cdot}T^{3} + 6.14{\cdot}10^{-6}{\cdot}T^{2} - 4.35{\cdot}10^{-4}{\cdot}T + 1.41{\cdot}10^{-2}){\cdot}c \quad (5)$$

where $c$ is the correction parameter for each paraffin and T the temperature at which the viscosity wants to be determined in [ºC].

The correction parameter as a function of the melting temperature of the material is calculated with equation 6, which was obtained by adjusting the relation between the calculated viscosity and the measured viscosity for each paraffin:

$$c = 0.001{T_m}^{2} - 0.0215T_m + 0.5815 \quad (6)$$

where $T_m$ is the melting temperature of the material in [ºC].

Applying the respective correction parameters for each paraffin to the general paraffin polynomial 3 model better results are obtained. The relative errors obtained when comparing the calculated viscosity to the measured one are lower than 10%, as displayed in Table 15.

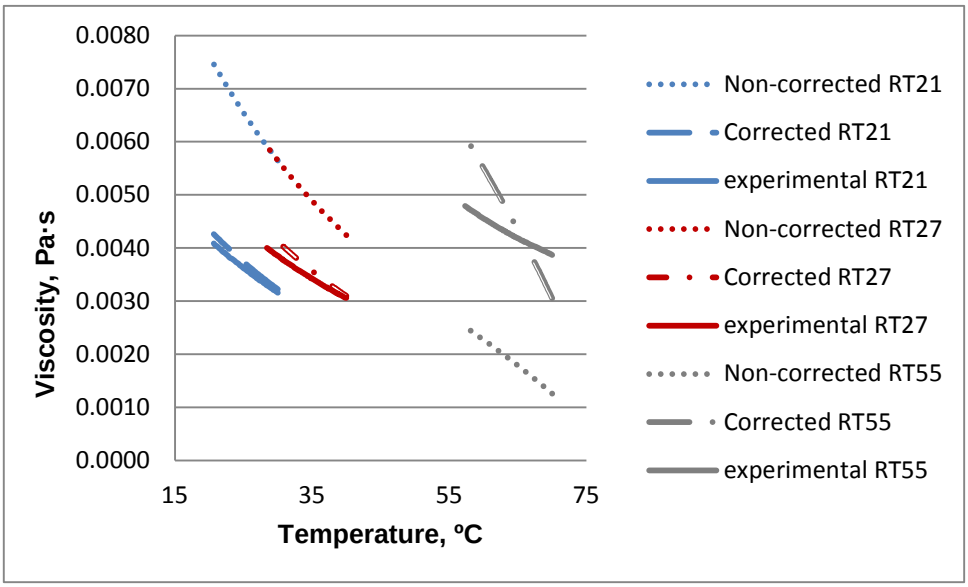
Table 15. Relative errors with and without the correction parameter for general paraffin model

| **Paraffin** | **Melting Temperature, ºC** | **Correction parameter** | **Average Relative error, %** | |
|---|---|---|---|---|
| | | | **Correction factor** | **No correction factor** |

| | | | | |
|---|---|---|---|---|
| RT21 | 21 | 0.57 | -3.12 | -80.59 |
| RT27 | 27 | 0.73 | -4.71 | -43.43 |
| RT55 | 55 | 2.42 | -7.04 | 55.84 |

These results are graphed in the following Figure 4. As it can be observed, the viscosities calculated with the non-corrected model are far from the experimental values for the three paraffin, while the corrected curves almost overlap with the experimental values. Hence, and as just shown in Table 15, the correction factor added to the polynomial 3 model has the corrective action desired and improved empirical results are then obtained.

Figure 4. Calculated vs experimental viscosity with correction factor added to the general paraffin model



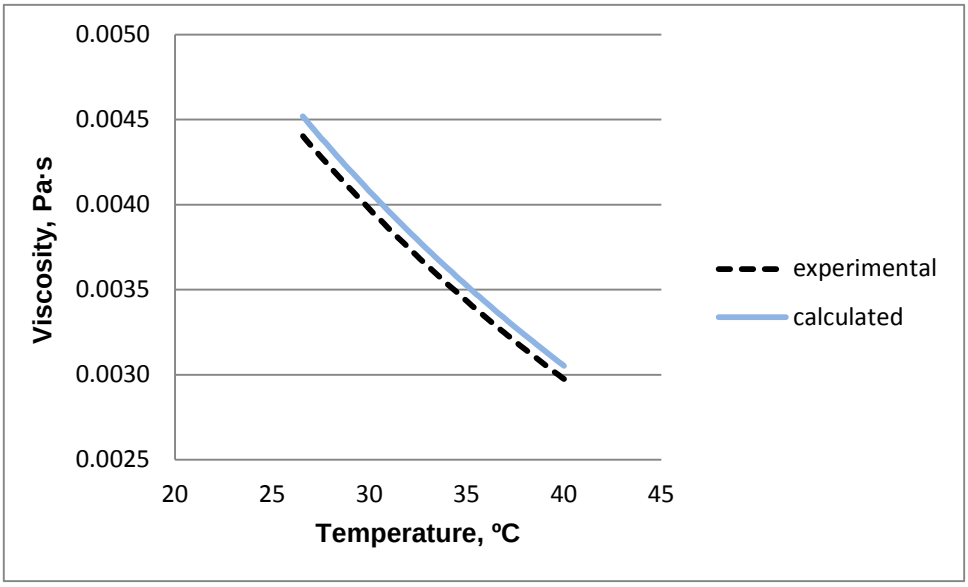

In addition, and in order to complement the results just exposed, equation 5 has been validated with another paraffin, n-octadecane Parafol 18-97, produced by Sasol Chemicals, with a purity of 97% and a melting temperature of 27 ºC. The results obtained with this material are presented in the following Table 16. Again, the relative error obtained is low and the correction parameter lowers down a 40 % the relative error of the equation.

Table 16. Validation results with n-octadecane Parafol 18-97

| **Paraffin** | **Melting Temperature, ºC** | **Correction parameter** | **Average Relative error, %** | |
|---|---|---|---|---|
| | | | **Correction factor** | **No correction factor** |
| n-octadecane, Parafol 18-97 | 27 | 0.73 | -4.59 | 43.27 |

To complement the validation results, Figure 5 is presented. As seen, the experimental and calculated curves almost overlap, confirming the low relative error the calculations have with the correction parameter included in the general paraffin model.

Figure 5. Calculated vs experimental curve for Parafol 18-97; general paraffin model validation




Therefore, the empirical model presented in equation 5 is found to be useful for the empirical determination of paraffin viscosities.

As the relative error differences between models showed in Table 12 were so small, and in order to see if the general polynomial 3 model presented in equation 5 is the best fitting, the same procedure was followed with the exponential 2 equation. A general model for the whole paraffin family was equally formulated, using the mean values of each component from the three paraffin equations. Errors higher than 1000 % were obtained, overcoming 100000 % for RT55, as shown in Table 17.

Table 17. Relative errors obtained for RT21, RT27 and RT55 when the exponential 2 model for paraffin is used

| | **RT21** | **RT27** | **RT55** |
|---|---|---|---|
| **Average relative error, %** | -1938 | -5302 | -100061 |

Hence, the exponential 2 equation use was discarded, confirming the general polynomial 3 model presented in equation 5 as the best and most useful equation to empirically calculate the viscosity of paraffin.

In addition, these results are tied to an analogous study conducted by the authors [16], in which a specific empirical equation to determine the viscosity of fatty acid PCM is presented. Paraffin are linear hydrocarbon molecules, while fatty acids are linear hydrocarbon molecules as well, but with a carboxylic group on the extreme of the chain. Therefore, it would be expected to predict both materials viscosity with a similar equation, being the equations only differed by the action of the carboxylic functional group present in fatty acids. Results show coincidence on the equation model, as in both cases a polynomial 3 graded equation is found as the most suitable, and small differences in the component values are found. They only differ on the action of the corrective parameter, as the influence that the carboxylic group has in the melting temperature is different and more important than the carbon atoms difference in paraffin chains. This accordance to study corroborates that the suitability of the equation found in this study and indicates that polynomial 3 graded models are useful equations to predict viscosity of organic PCM.

## 4. Discussion

The viscosity of three paraffin, RT21, RT27 and RT55 was measured. The data collected have been adjusted with different mathematical models in order to find good predictive equations for each paraffin viscosity calculation. Eight models of great goodness have been found and evaluated in this study as likely predictive models for RT21, RT27 and RT55. Exponential (1 and 2) and polynomial (2 and 3) models are the model types that better adjust the viscosity measured, and therefore, are here presented as the most proper ones to be used in viscosity empirical calculations of these three paraffin.

Three models, exponential 2, polynomial 2 and polynomial 3 have been found as the best predictive models for both RT27 and RT55. In addition, exponential 2 and polynomial 3 models have also been found as two out of the three best predictive models with RT21 rheometry data. Polynomial 3 model is the one that presents less relative error when compared to the real measured viscosity, therefore it is chosen as the best model for the three paraffin viscosity prediction. Moreover, a common model for the whole paraffin family has been found and proposed. However, high relative errors are obtained with this model alone, therefore a correction parameter that ties the material melting point with the viscosity value of the material has been added to the model and an equation to calculate this corrective factor for each paraffin is also given. This correction diminishes down the error and good predictive results are then obtained with the viscosity model proposed. The model has been validated with octadecane and good results have been obtained as well.

## 5. Conclusions

Exponential and polynomial models adjust with great goodness the rheometry data collected for paraffin RT21, RT27, and RT55. Three models with equal significances and mostly null relative errors between them have been found as excellent predictive models for each one of the paraffin tested. Exponential 1 model has been found as the best predictive model for RT21 viscosity determination. Exponential 2 and polynomial 3 have also been found as great predictive viscosity models for paraffin RT21. Exponential 2 model has been found as the best predictive model for both RT27 and RT55 viscosities calculation. Polynomial 2 and polynomial 3 models have also been found as excellent predictive models for both paraffin RT27 and RT55.

A comparison between exponential 2 and polynomial 3 models has been done in order to find out the best model for general paraffin viscosity prediction. Polynomial 3 is the model that shows less error when compared to the measured viscosity of each paraffin. Therefore, it is selected as the best model.

A common polynomial 3 equation for the whole paraffin family has been calculated. Results in its primary form are not proper enough, thus a correction parameter as a function of the melting temperature has been determined and added to the model in order to correct the deviation of the model for each paraffin and adjust better the calculated viscosity to the real one. Better results are obtained (relative errors 10 times lower) with this correction. In addition, the model has also been validated with another paraffin, n-octadecane, and results with just -4.59% of error have been obtained. Therefore, the general polynomial 3 model presented in equation 5 has been found as a useful model for the paraffin family viscosity prediction.

**Acknowledgements**

The work is partially funded by the Spanish government (ENE2015-64117-C5-1-R (MINECO/FEDER) and ENE2015-64117-C5-2-R (MINECO/FEDER)). The authors would like to thank the Catalan Government for the quality accreditation given to their research groups GREA (2014 SGR 123) and research group DIOPMA (2014 SGR 1543). The research leading to these results has received funding from RTC-2015-3583-5 (INPHASE) del Ministerio de Economía y Competitividad, dentro del Programa Estatal de Investigación, Desarrollo e Innovación Orientada a los Retos de la Sociedad, en el marco del Plan Estatal de Investigación Científica y Técnica y de Innovación 2013-2016, y ha sido cofinanciado con FONDOS FEDER, con el objetivo de promover el desarrollo tecnológico, la innovación y una investigación de

calidad, and from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° PIRSES-GA-2013-610692 (INNOSTORAGE) and from the European Union's Horizon 2020 research and innovation programme under grant agreement No 657466 (INPATH-TES). Dr. Camila Barreneche would like to thank Ministerio de Economia y Competitividad de España for Grant Juan de la Cierva, FJCI-2014-22886.

## References

1 Kousksou T, Bruel P, Cherreau G, Leoussoff V, El Rhafiki T. PCM storage for solar DHW: From an unfulfilled promise to a real benefit. Sol Energy 2011;85:2033–40. doi:10.1016/j.solener.2011.05.012.

2 Gil A, Medrano M, Martorell I, Lázaro A, Dolado P, Zalba B, et al. State of the art on high temperature thermal energy storage for power generation. Part 1—Concepts, materials and modellization. Renew Sustain Energy Rev 2010;14:31–55. doi:10.1016/j.rser.2009.07.035.

3 Oró E, Miró L, Farid MM, Cabeza LF. Improving thermal performance of freezers using phase change materials. Int J Refrig 2012;35:984–91. doi:10.1016/j.ijrefrig.2012.01.004.

4 Stritih U, Butala V. Energy saving in building with PCM cold storage. Int J Energy Res 2007;31:1532–44. doi:10.1002/er.1318.

5 Azzouz K, Leducq D, Gobin D. Performance enhancement of a household refrigerator by addition of latent heat storage. Int J Refrig 2008;31:892–901. doi:10.1016/j.ijrefrig.2007.09.007.

6 Zhao W, France DM, Yu W, Kim T, Singh D. Phase change material with graphite foam for applications in high-temperature latent heat storage systems of concentrated solar power plants. Renew Energy 2014;69:134–46. doi:10.1016/j.renene.2014.03.031.

7 Cabeza LF, Castell A, Barreneche C, de Gracia A, Fernández AI. Materials used as PCM in thermal energy storage in buildings: A review. Renew Sustain Energy Rev 2011;15:1675–95. doi:10.1016/j.rser.2010.11.018.

8 Medrano M, Gil A, Martorell I, Potau X, Cabeza LF. State of the art on high-temperature thermal energy storage for power generation. Part 2—Case studies. Renew Sustain Energy Rev 2010;14:56–72. doi:10.1016/j.rser.2009.07.036.

9 de Gracia A, Castell A, Fernández C, Cabeza LF. A simple model to predict the thermal performance of a ventilated facade with phase change materials. Energy Build 2015;93:137–42. doi:10.1016/j.enbuild.2015.01.069.

10 Chaudhari SK, Salavera D, Coronas A. Densities, Viscosities, Heat Capacities, and Vapor–Liquid Equilibria of Ammonia + Sodium Thiocyanate Solutions at Several Temperatures. J Chem Eng Data 2011;56:2861–9. doi:10.1021/je200038n.

11 Suresh A, Sreenivasulu B, Sivaraman N, Rao PRV. Empirical equations for the prediction of third phase formation limits in the extraction of thorium nitrate by tri-iso-amyl phosphate (TiAP). J Radioanal Nucl Chem 2015:1–7. doi:10.1007/s10967-015-4154-x.

12 Gómez E, Calvar N, Macedo EA, Domínguez Á. Effect of the temperature on the physical properties of pure 1-propyl 3-methylimidazolium bis(trifluoromethylsulfonyl)imide and characterization of its binary mixtures with alcohols. J Chem Thermodyn 2012;45:9–15. doi:10.1016/j.jct.2011.08.028.

13 Lide DR. CRC Handbook of Chemistry and Physics, 84th Edition. CRC Press; 2003.

14 Furbo S. Heat Storage for Solar Heating Systems. Department of Civil Engineering: Technical University of Denmark; 2005.

15 Sheskin DJ. Handbook of Parametric and Nonparametric Statistical Procedures: Third Edition. CRC Press; 2003.

16 Ferrer G, Barreneche C, Palacios A, Solé A, Fernández AI, Cabeza LF. Empirical equations for viscosity and specific heat capacity determination of fatty acids. Submited to Journal of Energy Storage, manuscript number: EST_2016_65.