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Empirical equation to estimate viscosity of paraffin

Gerard Ferrer[a], Stefan Gschwander[b], Aran Solé[a], Camila Barreneche[a,c,d], A. Inés Fernández[c,d], Peter Schossig[b], Luisa F. Cabeza[a,*]

[a] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001, Lleida, Spain
[b] Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, Freiburg, Germany
[c] Department of Materials Science & Physical Chemistry, Universitat de Barcelona, Martí i Franqués 1-11, 08028, Barcelona, Spain
[d] Martí i Franqués 1-11, 08028, Barcelona, Spain

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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.

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 [4–6].

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 [9–11] 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 (Eq. (1)) and another for liquids (Eq. (2)). Furbo [14] presented an equation for water in the 10 °C–100 °C temperature range (Eq. (3)),

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

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

* Corresponding author at: GREA Innovació Concurrent, Universitat de Lleida, Lleida, Spain.
E-mail address: lcabeza@diei.udl.cat (L.F. Cabeza).

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$$\mu[m^2/s] = 1.477\cdot10^{-6}\cdot\exp(-1.747\cdot10^{-2}\cdot T) \quad (3)$$

where μ 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 s 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 °C–40 °C temperature range, while the RT55 viscosity was measured between 40 °C and 70 °C. 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 Eq. (4):

$$relative\ error = \frac{\mu_m - \mu_c}{\mu_m}\cdot100 \quad (4)$$

where μ_c is the calculated viscosity and μ_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.

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.

3.1.1. RT21

The viscosity data for RT21 was obtained in the 20–30 °C temperature range. Six models have been found as possible

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	$f(x) = \frac{p1\cdot x^2 + p2\cdot x + p3}{x + q1}$