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1 **Empirical equations for viscosity and specific heat capacity**
2 **determination of fatty acids**

3
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12
13 **Abstract**

14
15 Phase change materials (PCM) used in thermal energy storage (TES) systems have been
16 presented, over recent years, as one of the most effective options in energy storage. Saturated
17 fatty acids are one of the most used PCM in TES systems, as they have high phase change
18 enthalpy but in addition they do not present subcooling nor hysteresis and have proper cycling
19 stability. The simulations and design of a TES system require the knowledge of the
20 thermophysical properties of materials. Thermal conductivity, viscosity, specific heat capacity
21 (C_p) can be experimentally determined, but these are material and time consuming tasks. To
22 avoid or to reduce them, and to have reliable data without the need of experimentation, thermal
23 properties can be determined by empirical equations. In this paper, three empirical equations are
24 given to calculate the viscosity, solid C_p , and liquid C_p of the whole fatty acid family of PCM.

25
26 **Keywords:** empirical equations; viscosity; specific heat capacity; fatty acids; PCM; TES.
27
28

1. Introduction

The increasing energy demand and the global warming are the two most important issues that researchers in the energy field have to face nowadays. The reduction of the fossil-fuel energy consumption, and therefore CO₂ emissions too, is the main trend in which researches are focusing their work [1-2]. As a result of the wide research lately done in the field, energy storage is presented as a potential solution to fulfil the exposed goals, as it allows overcoming the gap existing between energy demand and the supply sources [3-4]. From the different thermal energy storage (TES) systems, latent heat systems use the latent heat of phase change materials (PCM), between solid and liquid states, to store or release heat depending on the application needs, being one of the most effective and promising solutions so far. Domestic hot water (DHW) installations, building comfort and solar power plants are examples of applications in which TES systems are used. Paraffin, salts and fatty acids are the most implemented PCM [5-9] in these systems.

Fatty acids are carboxylic acids with a long aliphatic chain that have an unbranched chain of an even number of carbon atoms, from 4 to 28. They can be saturated (no double bonds between carbon atoms) or unsaturated (one or more double bonds between carbon atoms, cis and trans configurations). Saturated fatty acids have high energy density storage capacity due to the high values of latent heat of phase change, along with a mostly stable and well defined phase temperature range, which makes them one of the most suitable and used materials in TES systems [10-12]. However, their design requires knowing other material properties such as the viscosity and the specific heat capacity (C_p) to simulate and optimize their performance.

The estimation of properties with empirical equations is used in chemical engineering. These are material and time saving tool to know in advance the material behaviour with no need of experimental tests [13-15]. However, the TES community does not use this tool widely. As Table 1 shows, some researchers have worked in the development of empirical equations of some fatty acid properties, but results are for specific fatty acid mixtures and fatty acid by-products. Moreover, no general equation for fatty acid PCM can be found.

Table 1. State-of-the-art on empirical equations for fatty acid materials

Material	Property assessed	Highlights	Reference
Fatty acid alkyl esters	C _p and Viscosity	No specific conclusions on specific heat measurements and calculations	[16]
Ternary and quaternary polyunsaturated fatty acid compounds	Viscosity	The use of UNIMOD model often gives satisfactory viscosity predictions for fatty mixtures	[17]
Pure liquid organic and some inorganic compounds.	C _p	Review on heat capacity calorimetry methods. Classification of materials by recommended heat capacity values	[18]
Vegetable oils from fatty acid composition	Viscosity	Equation as a function of the amount of PUFA or monounsaturated FA	[19]
Hexadecanoic acid, octadecanoic acid, and cis9-octadecenoic acid.	C _p	A comparison between two methods applied was presented.	[20]
Fatty Acids, Triacylglycerols, and Vegetable oils.	C _p	Estimation for all types of vegetable oils provided the fatty acid composition.	[21]
High-chain fatty acid esters of 1-octadecanol.	C _p	Coefficients for polynomial equations for liquid and solid states are given.	[22]
Saturated and unsaturated fatty acid methyl ester.	C _p	The use of an ideal mixing rule may be of use to formulate a predictive equation	[23]

67

68 On the other hand, empirical equations for the determinations of viscosity, and solid and liquid
69 C_p can be found in more general literature not related to PCM. For viscosity, Lide and Kehiaian
70 [24] gave two different equations, one for gases (equation 1) and another for liquids (equation
71 2); Furbo [25] presented an equation for water to be used between 10 °C-100 °C (equation 3):

72

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

73

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

74

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

75 where μ is the viscosity, $A(n)$ are the equation constants, and T the temperature at which the
76 viscosity wants to be known.

77

78 Regarding the specific heat capacity for solids, Lide and Kehiaian [24] proposed equation 4,
79 while Smith and Van Ness [24] gave equations (5) and (6):

80

$$C_p = A(1) + A(2) \cdot T[K] + A(3) \cdot (T[K])^2 + A(4) \cdot (T[K])^3 + A(4) \cdot (T[K])^4 \quad (\text{eq. 4})$$

$$C_p = A(1) + A(2) \cdot T[K] + A(3) \cdot (T[K])^2 \quad (\text{eq. 5})$$

$$C_p = A(1) + A(2) \cdot T[K] + \frac{A(3)}{(T[K])^2} \quad (\text{eq. 6})$$

81 For liquids, equation (7) proposed by Kubaschewski [27] can be found:

82

$$C_p = A(1) + A(2) \cdot T[K] + \frac{A(3)}{(T[K])^2} + A(4) \cdot (T[K])^2 \quad (\text{eq. 7})$$

83

84 The equations presented above are not specific for PCM, and in most of the cases the equation
85 constants for fatty acids and other PCM are not provided. Consequently, disperse results are
86 obtained with them when used with TES materials, leading in many cases to important errors in
87 systems simulations and design.

88

89 Empirical equations play an important role in the improvement of the system design stage by
90 providing reliable low error data, saving time and resources and conducting to better
91 simulations and thereby, better designs. As fatty acids are one of the most used PCM families
92 and to fill the existing lack of empirical equation for TES materials, this study presents three
93 low error empirical equations that respectively describe the viscosity, solid C_p and liquid C_p of
94 the whole fatty acid PCM family as a function of temperature, for use in TES systems modelling
95 and simulation.

96

97

98

99

100

101 **2. Materials and methods**

102

103 **2.1. Materials**

104

105 This study has used capric (decanoic acid, 98.5 %, $C_{10}H_{20}O_2$), myristic (tetradecanoic acid, 98
106 %, $C_{14}H_{28}O_2$), and stearic (octadecanoic acid, 98 %, $C_{18}H_{36}O_2$) acids commercialized by
107 Panreac, with respective melting points of 32 °C, 54 °C, and 66 °C, to formulate the empirical
108 equations presented. In addition, palmitic acid (hexadecanoic acid, 98 %, $C_{16}H_{32}O_2$), with
109 melting point of 62 °C, was used to validate the equations. All of them are widely used PCM in
110 thermal energy storage.

111

112 **2.2. Viscosity analyses**

113

114 A Brookfield RST Controlled Stress rheometer was used to measure the viscosity of the
115 materials. The measurements consisted on consecutive 1 minute isothermal stages ~~with no~~
116 ~~heating segments between~~, increasing the temperature 1 °C with every isotherm. 1 ml samples
117 were used and the measurements were performed with the RCT-50-1 cone spindle under a
118 constant rotation speed of 1100 rpm.

119

120 The viscosities of the three fatty acids were measured in liquid state, starting the measurements
121 after the phase change was complete and the material was totally melted. Capric acid viscosity
122 was measured between 40 °C and 60 °C, while myristic acid measurements were conducted
123 between 60 °C and 80 °C and stearic acid viscosity was acquired in the 75 °C-95 °C temperature
124 range. Validation measurements with palmitic acid were done from 65 °C to 85 °C.

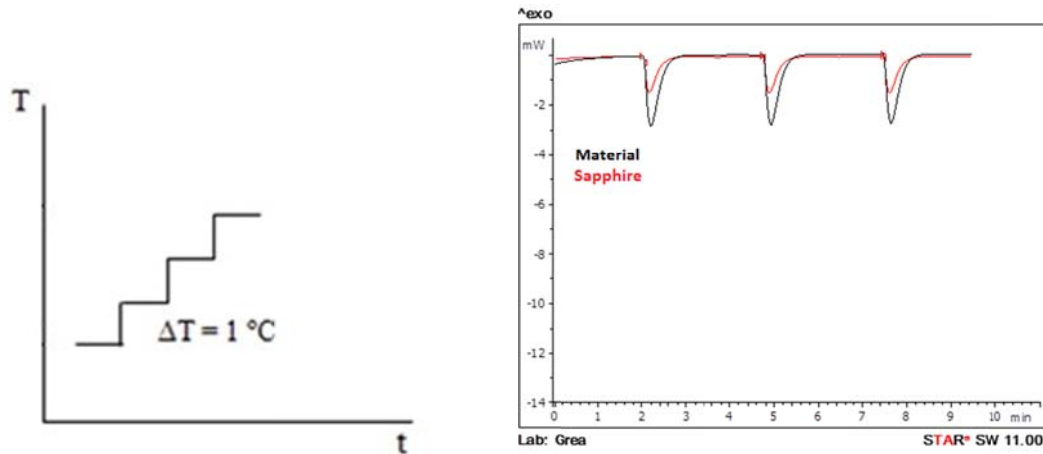
125

126 **2.3. Specific heat capacity analyses**

127

128 A Mettler Toledo DSC 822e was used to perform the C_p measurements. The experiments were
129 conducted under 200 ml/min constant N_2 flow, using 40 μ l aluminium crucibles and sample
130 mass around 10 mg weighed in a Mettler Toledo AG135 analytical balance with a precision of
131 0.01 mg. The DSC areas method described by the authors in [28-29] for C_p determination was
132 used to calculate the C_p of each material with 3 % of error. This method consists on consecutive
133 isothermal stages ~~with no heating segments amid~~, as Figure 1 shows.

134



a)

b)

136 Figure 1. a) DSC areas method. b) DSC signal obtained when using the areas method.

137

140 Each of the peaks of the DSC signal corresponds to every temperature step of the method. The
 141 temperature difference between isotherms is of 1 °C. Integrating the peak on the DSC curve for
 142 both sapphire and material and using equation (8), the C_p can be determined:

141

$$C_{p_m} = \frac{C_{p_s} \cdot A_m}{A_s} \quad (\text{eq. 8})$$

144 where A_s [J/g] is the integrated peak area for the sapphire DSC curve, A_m [J/g] is the integrated
 145 peak area for the material DSC curve, C_{p_s} [J/g·°C] is the specific heat capacity of sapphire, and
 146 C_{p_m} [J/g·°C] is the specific heat capacity of the material.

145

151 The C_p of the three fatty acids was measured in solid and liquid states by DSC using the
 152 procedure and testing conditions explained in former paragraphs. The measurements of the C_p
 153 values at solid state were carried out in the range of 10-25 °C for capric acid, 30-45 °C for
 154 myristic acid, 45-60 °C for palmitic acid and 40-55 °C for stearic acid. In liquid state, the C_p was
 155 measured in the range of 45-60 °C for capric acid, 60-75 °C for myristic acid, 70-85 °C for
 156 palmitic acid and 75-90 °C for stearic acid.

152

153 2.4. Empirical equations development and evaluation

154

157 The measured data have been numerically adjusted in order to find out empirical equations to
 158 calculate the viscosity and the C_p at both solid and liquid states. The palmitic acid measurements
 159 were carried out to validate the results. Thus, no adjustments of these data were needed.

158

160 The best fits were selected according to their R^2 , adjusted R^2 (values closer to 1 are the best),
 161 sum of squares due to error (SSE), and root mean standard error (RMSE) (values closer to 0

160 show better prediction uses of an equation) [30]. To complement the statistical analysis done
161 with the just mentioned parameters and select the best equation type, the relative errors between
162 each equation and the measured data have also been calculated according to equation (9):

163

$$relative\ error = \frac{x_m - x_c}{x_m} \cdot 100 \quad (eq. 9)$$

164 where x_c is the calculated property and x_m is the measured property.

165

166 For each fatty acid and for both viscosity and C_p properties, the equation with lower relative
167 error and deviation with respect to experimental values was selected.

168

169 **3. Results**

170

171 The measured viscosities and C_p in both solid and liquid state of capric acid, myristic acid and
172 stearic acid have been adjusted to find high significance fitting equations for the collected data
173 and to use them as empirical tools to calculate these properties. Just the equations with a fit
174 goodness (R^2 statistic) higher than 0.95 were considered in this study as potential predictive
175 equations suitable to formulate general equations for fatty acid PCM to respectively calculate
176 viscosity, solid C_p and liquid C_p .

177

178 The results were divided in three different sections, one for each property, and are presented
179 below. All the relative errors reported in this section correspond to the mean errors of the
180 respective data range.

181

182 **3.1. Viscosity**

183

184 The data measured was adjusted with different equations in Matlab. Besides equations (1) to
185 (7), rational, Gaussian and Fourier type equations were used to adjust the measured viscosity.
186 From all the equations used, the four equation types shown in Table 2 were found as the most
187 significant ones for the three fatty acids. All these equations have significances higher than 0.99
188 and really low values of the prediction parameters (SSE and $RMSE < 10^{-5}$), indicating their high
189 potential for empirical use.

190

191

192

193

194

Table 2. Suitable equations found for fatty acid viscosity empirical calculation

Equation	Formula
Polynomial 2	$\mu = p1 \cdot T^2 + p2 \cdot T + p3$
Polynomial 3	$\mu = p1 \cdot T^3 + p2 \cdot T^2 + p3 \cdot T + p4$
Exponential 2	$\mu = a \cdot e^{b \cdot T} + c \cdot e^{d \cdot T}$
Power 2	$\mu = a \cdot T^b + c$

195

196 The relative errors between the viscosities calculated with the just presented equations and the
 197 measured viscosities were calculated. Table 3 shows the results and allows appreciating how
 198 appropriate the adjustments are and which equations present better performances and more
 199 potential to formulate a general equation for fatty acid PCM.

200

201

Table 3. Relative error values of each equation type for viscosity prediction

Equation	Relative error [%]		
	Capric acid	Myristic acid	Stearic acid
Polynomial 2	0.009	0.274	-0.065
Polynomial 3	0.081	0.165	0.077
Exponential 2	-0.012	0.433	0.025
Power 2	-0.009	0.163	-0.151

202

203 As data show, the relative errors are lower than 0.5 % for all equations, and the mean
 204 percentages are around 0.1 % and really similar within the equations as well. As none of the
 205 presented equations outstands among the others, the formulation of a general equation for the
 206 whole fatty acid family was tried with each one of them. For this purpose, the mean values of
 207 each component were calculated for each equation type from the three respective fatty acid
 208 equations. To do so and for each equation type, the mean values of each component were
 209 calculated from the three respective fatty acid equations.

210

211 The polynomial 3 general equation next shown was the only one found to be worth to use for
 212 the prediction of viscosity values for fatty acids:

213

$$\mu[Pa \cdot s] = -3.42 \cdot 10^{-8} \cdot T^3 + 8.37 \cdot 10^{-6} \cdot T^2 - 7.80 \cdot 10^{-4} \cdot T + 2.95 \cdot 10^{-2} \quad (10)$$

214

215 In order to evaluate its performance, the relative errors obtained for each fatty acid were
216 calculated when using equation (10). The relative errors obtained are important, 65 % for stearic
217 acid and 138 % for myristic acid, reaching almost 600 % for capric acid.

218

219 Despite the errors being important, the error differences between materials suggest that the
220 different melting points of each fatty acid have some impact in the results.

221

222 The melting point is directly dependant of the intermolecular forces that need to be overcome to
223 melt the material. The carboxylic group present in the chemical structure forms hydrogen bonds
224 between molecules. These forces are temperature dependant and seem to have different effect
225 depending on the number of carbon atoms in the chain. Thus, considering the errors reported,
226 the effect of the acid group is more important in fatty acids with lower number of carbon atoms
227 in the chain.

228

229 In order to correct these high differences and to obtain better results, a correction parameter as a
230 function of the melting temperature was added to the general polynomial 3 equation, as shown
231 in equations (11) and (12):

232

$$\mu[Pa \cdot s] = (-3.42 \cdot 10^{-8} \cdot T^3 + 8.37 \cdot 10^{-6} \cdot T^2 - 7.80 \cdot 10^{-4} \cdot T + 2.95 \cdot 10^{-2}) \cdot c \quad (11)$$

$$c = 1.1 \cdot 10^{-3} \cdot T_m^2 - 0.3 \cdot T_m + 15.38 \quad (12)$$

233 where c is the correction parameter for each sample, T the temperature at which the viscosity
234 wants to be determined in [°C], and T_m the melting temperature of the material in [°C] given by
235 the manufacturer.

236

237 Better results were obtained with this correction and the errors decreased considerably, lowering
238 them to below 5 %. This correction factor cancels the acid group effect, being more effective for
239 low carbon fatty acids as capric acid, than for fatty acids with more carbons in their structure
240 such as stearic acid.

241

242 In addition, the good performance of the corrected equation was validated with the palmitic
243 acid. As palmitic acid has 16 carbon atoms, results between stearic and myristic acid values
244 were expected in order to confirm the acid group effect.

245

246 Table 4 shows the results that were obtained with equation (11). Results confirmed that the
247 effect of the acid group is cancelled with the correction factor added to equation 10. Moreover,
248 it is proved that the acid group effect is more important in low carbon chains, which explains

249 the lower errors obtained for capric and myristic acid compared to the stearic and palmitic acid
 250 errors.

251

252

Table 4. Relative errors obtained with equation 11

	Capric acid	Myristic acid	Stearic acid	Palmitic acid
Relative error [%]	0.05	0.48	4.79	4.36
Standard deviation	$2 \cdot 10^{-4}$	$4 \cdot 10^{-5}$	$4 \cdot 10^{-4}$	$2 \cdot 10^{-4}$

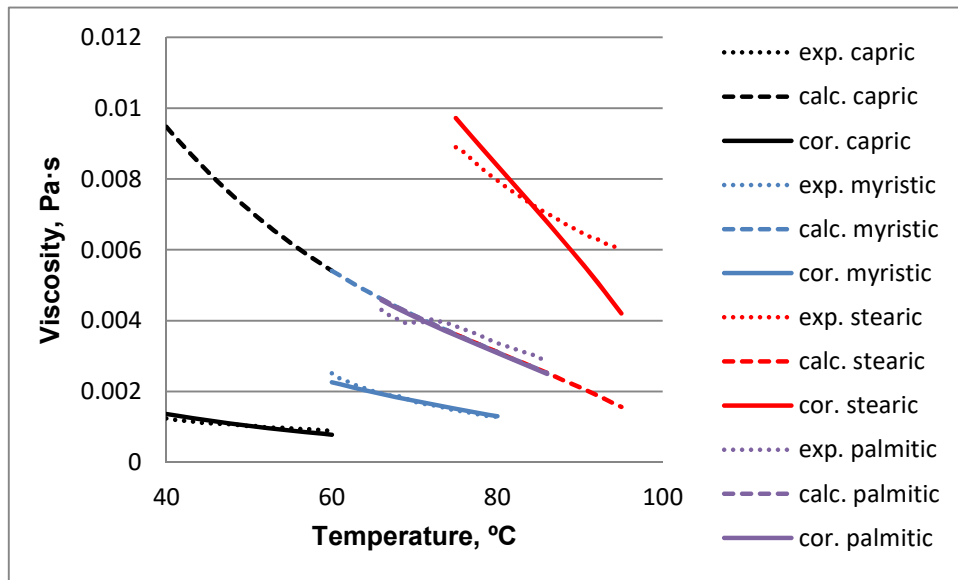
253

254 Figure 1 shows the results just presented. As seen, the corrected curves obtained with equation
 255 11 almost overlap with the experimental ones, while the values obtained with equation (10) are
 256 far from the real ones. Although being it small, deviation is observed with high temperature
 257 fatty acids, which matches with the almost 5 % of error reported before for stearic acid.

258

259 It is important to point out that PCM in TES systems are normally used in temperatures close to
 260 their melting ranges. Therefore, the relevance of the presented results relies on the low errors
 261 obtained at low temperatures, where the viscosities obtained with equation (11) almost overlap
 262 with the experimental measurements, and that match with the operational temperatures at which
 263 the PCM will be used.

264



265

266 Figure 1. Equation (10) (calc.) and equation (11) (cor.) curves vs. experimental viscosity for the four fatty acids used
 267 in the study

268

269 Finally, and to confirm that equation 11 is the best and most proper fitting for fatty acid PCM
 270 viscosity prediction purposes, the same procedure has been followed with the other candidate
 271 equations to formulate a general equation for the whole fatty acid family. General equations

272 were formulated with polynomial 2, exponential 2 and power 2 equations, and despite
273 correcting them with melting temperature depending factors such as it has been done with the
274 polynomial 3 equation, important errors are obtained and therefore, the three equation types
275 were discarded. Table 5 shows the errors obtained for the three equations once the correction
276 parameter has been applied.

277

278 Table 5. Relative errors for the general polynomial 2, exponential 2 and power 2 candidate equations

Equation	Relative error [%]		
	Capric acid	Myristic acid	Stearic acid
General Polynomial 2	3.7	66.9	119
General Exponential 2	10599	11.2	101
General Power 2	12.6	109	192

279

280 These high errors obtained confirm the polynomial 3 model presented as equation (11) as the
281 best option for empirical determination of fatty acid PCM viscosity.

282

283 In addition, these results are tied to an analogous study conducted by the authors [28], in which
284 a specific empirical equation to determine the viscosity of paraffin was presented. Paraffin are
285 linear hydrocarbon molecules, while fatty acids are linear hydrocarbon molecules as well, but
286 with a carboxylic group on the extreme of the chain. Therefore, it would be expected to predict
287 both materials viscosity with a similar equation, being the equations only differed by the action
288 of the carboxylic functional group present in fatty acids. Results show coincidence on the
289 equation model, as in both cases a polynomial 3 equation was found as the most suitable, and
290 small differences in the component values were found. They only differ on the action of the
291 corrective parameter, as the influence that the carboxylic group has in the melting temperature is
292 different and more important than the carbon atoms difference in paraffin chains. This
293 accordance to study [31] corroborates the suitability of the equation found in this study and
294 indicates that polynomial 3 models are useful equations to predict viscosity of organic PCM.

295

296 3.2. Specific heat capacity

297

298 As for viscosity, different equations such as rational, power and Gaussian, as well as the
299 equations found in the literature, were considered and used to adjust the measured C_p . From
300 within all the considered models, polynomial and exponential equations, along with equation (7)
301 suggested by Kubachewski, were found as the most significant to fit the measured C_p data of the
302 three fatty acids in both solid and liquid states. Polynomial 4 equation was only found
303 significant in solid state measurements. These equations, presented in the Table 6, were the ones

304 from which authors formulated two common equations, one for solid state and one for liquid
 305 state, that determine the respective solid and liquid C_p of all fatty acid PCM with low errors.

306

307

Table 6. Suitable equations found for fatty acid solid C_p empirical calculation

Equation	Formula
Polynomial 2	$C_p = p1 \cdot T^2 + p2 \cdot T + p3$
Polynomial 3	$C_p = p1 \cdot T^3 + p2 \cdot T^2 + p3 \cdot T + p4$
Polynomial 4	$C_p = p1 \cdot T^4 + p2 \cdot T^3 + p3 \cdot T^2 + p4 \cdot T + p5$
Exponential 2	$C_p = a \cdot e^{b \cdot T} + c \cdot e^{d \cdot T}$
Kubaschewski	$C_p = A1 + A2 \cdot T[K] + \frac{A3}{(T[K])^2} + A4 \cdot (T[K])^2$

308

309

310 It is important to point out that the utility of the equations given for both solid and liquid states
 311 relies on the use of the materials in TES systems. Fatty acids are normally used in TES as PCM,
 312 thus their temperature operational range is always around their melting point temperature.
 313 Therefore, the measurements in solid state were performed in a temperature range just 10 °C
 314 below the melting temperature range of each fatty acid to ensure that the material was solid,
 315 avoiding the possibility to undergo phase change. The same reasoning was applied to liquid C_p
 316 measurements, which were performed in a temperature range just 10 °C higher to the respective
 317 melting point of each fatty acid, ensuring the liquid state of the material by overcoming its
 318 phase change range.

319

320

3.2.1. Solid C_p

321

322 Polynomial 2 and 3 and exponential 2 fittings were found highly significant when adjusting the
 323 data of the three fatty acids, while polynomial 4 and Kubaschewski equation (7) only worked
 324 with capric acid, discarding them as potential candidates to formulate a common equation for all
 325 the fatty acid family. Good prediction parameters (SSE, RMSE) were again obtained for all the
 326 fittings, with values below 10^{-2} for all equations.

327

328 Relative errors between the C_p calculated with each equation and the measured ones were
 329 calculated in order to establish a more clear difference in the performance of the equations. As
 330 Table 7 shows, all errors were lower than 1 %. However, as the errors were so low, the three
 331 equations were considered for a general fatty acid solid C_p equation formulation.

332

333

Table 7. Relative errors of each equation type for solid C_p prediction

Equation	Relative error [%]		
	Capric acid	Myristic acid	Stearic acid
Polynomial 2	-0.082	0.171	-0.061
Polynomial 3	-0.047	0.139	-0.015
Exponential 2	-0.075	0.167	-0.067

334

335 As previously done to formulate the viscosity equation, the mean values of each component
 336 were calculated from the three respective fatty acid equations to formulate the different general
 337 fatty acid equations. From within the three formulated equations, just the general polynomial 2
 338 equation, next presented as equation (13), was found as useful for solid C_p prediction:

339

$$C_p [J / g \cdot ^\circ C] = 1.61 \cdot 10^{-3} \cdot T^2 - 5.38 \cdot 10^{-2} \cdot T + 2.89 \quad (13)$$

340 where T is the temperature at which the C_p wants to be determined in [$^\circ C$].

341

342 However, important errors were obtained for myristic acid (-53 %) and stearic acid (-71.5 %),
 343 while just 1 % of error is accounted for capric acid.

344

345 There might be a relation between the different melting points of each material, or what is the
 346 same, their chemical structure, and the errors obtained. As formerly mentioned, the carboxylic
 347 group present in the structure may have a different effect depending on the number of carbons
 348 of the chain. In order to establish this relation, correct these errors and obtain better results,
 349 equation (13) was corrected with a melting temperature depending factor, as shown in equation
 350 (14), determining the correction factor with equation (15):

351

$$C_p [J / g \cdot ^\circ C] = \frac{1.61 \cdot 10^{-3} \cdot T^2 - 5.38 \cdot 10^{-2} \cdot T + 2.89}{c} \quad (14)$$

$$c = 3 \cdot 10^{-3} \cdot T_m^2 - 4.94 \cdot 10^{-2} \cdot T_m - 0.2923 \quad (15)$$

352

353 where c is the correction parameter for each fatty acid and T_m the melting temperature of the
 354 material in [$^\circ C$].

355

356 The correction had the desired effect and, as Table 8 shows, results with errors lower than 4%
 357 were obtained with equation (14). Furthermore, the standard deviation was also low, around 0.1,

358 even lower for myristic and capric acids. In addition, the equation was validated with palmitic
 359 acid, obtaining low error results as well.

360

361 Contrary to what it was observed with viscosity, for solid state C_p determination the carboxylic
 362 group effect seems to be more important for high carbon structures.

363

364

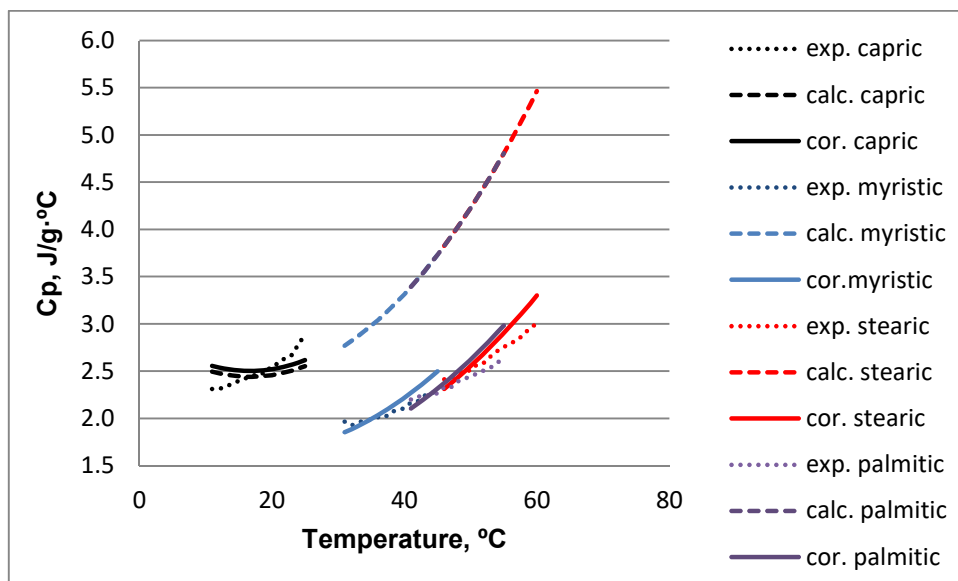
Table 8. Relative errors and standard deviations obtained with equation 14

	Capric acid	Myristic acid	Stearic acid	Palmitic acid
Relative error [%]	-1.39	-2.65	-3.60	-4.91
Standard deviation	0.088	0.062	0.094	0.106

365

366 Figure 2 compares the experimental measurements, equation (13) and equation (14) curves of
 367 the four fatty acids. The equation (13) calculated curves are far from the experimental values
 368 while equation (14) curves are quite approximated to the measured C_p , showing low deviation
 369 for all materials.

370



371

372 Figure 2. Equation (13) (calc.) and equation (14) (cor.) curves vs. experimental measurements for the four fatty acids
 373 used in the study

374

375 The exact same steps were followed with the general polynomial 3 and exponential 2
 376 formulated equations, and the results are presented in Table 9. High relative errors were
 377 obtained with the exponential 2 equation, while errors lower than 5 % were obtained with the
 378 formulated general polynomial 3 equation. This may suggest that this equation is as good as the
 379 formulated polynomial 2. However, despite being good, the deviation is 60 % higher with the

380 polynomial 3 equation, reason why it was discarded as a proper empirical equation and equation
 381 (14) was selected as the best option for fatty acid solid C_p prediction.

382

383 Table 9. Relative error and standard deviation for the general polynomial 3 and exponential 2 candidate equations

Equation		Material		
		Capric acid	Myristic acid	Stearic acid
General Polynomial 3	Relative error [%]	-3.21	-4.27	-3.59
	Standard deviation	0.10	0.22	0.28
General Exponential 2	Relative error [%]	5.80	99	100
	Standard deviation	1.56	1.46	1.89

384

385

386 Due to the operational temperatures at which fatty acids are used in TES systems, the accuracy
 387 of equation (14) is reliable for temperatures 5-20 °C lower to the melting point of each fatty acid
 388 PCM.

389

390 3.2.2. Liquid C_p

391

392 The measurements in liquid state were performed between 45 °C and 60 °C for capric acid, 60
 393 °C and 75 °C for myristic acid and 75 °C and 90 °C for stearic acid. Palmitic acid measurements,
 394 use for equation validation, were done in the 70 °C–85 °C temperature range.

395

396 The same equation types found as the most significant ones for solid state plus equation (7)
 397 were stated as the best fittings for liquid state. The predictive parameters SSE and RMSE are
 398 lower than 10^{-3} for all the fittings which, as Table 10 shows, calculate the liquid C_p with errors
 399 lower than 1 %.

400

401

402

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406

Table 10. Relative errors of each equation type for liquid C_p prediction

Equation	Relative error [%]		
	Capric acid	Myristic acid	Stearic acid
Polynomial 2	0.495	-0.038	-0.356
Polynomial 3	0.612	-0.186	-0.291
Exponential 2	0.475	-0.049	-0.351
Kubaschewski (eq. 7)	0.717	0.248	-0.499

407

408 Consequently, the four fittings were considered to formulate a general empirical equation by
 409 calculating the mean component values of each fatty acid equation. From the resulting general
 410 equations, the polynomial 2 fit, shown as equation 16, is the only one that adjusts the C_p with
 411 low errors and closer to the measured values for all fatty acids:

412

$$C_p [J / g \cdot ^\circ C] = 4.56 \cdot 10^{-5} \cdot T^2 - 4.47 \cdot 10^{-3} \cdot T + 2.739 \quad (16)$$

413

414 Oppositely from what happened with the viscosity and solid C_p general models, the first
 415 formulated general equation already gave good results, with relatively low errors, lower than 7
 416 % for all fatty acids. Notwithstanding, it seemed that as in viscosity results, there is a relation
 417 between the errors obtained and the effect of the carboxylic group, more important in liquid
 418 state for low carbon structures.

419

420 In order to see the effect that the carboxylic group has in liquid C_p , the equation was also
 421 corrected with a melting point dependant parameter, being equation (17) the result, and
 422 calculating the c factor with equation (18):

423

$$C_p [J / g \cdot ^\circ C] = \frac{4.56 \cdot 10^{-5} \cdot T^2 - 4.47 \cdot 10^{-3} \cdot T + 2.739}{c} \quad (17)$$

$$c = -3 \cdot 10^{-4} \cdot T_m^2 + 2.3 \cdot 10^{-2} \cdot T_m + 0.5903 \quad (18)$$

424 where c is the correction parameter for each fatty acid and T_m the melting temperature of the
 425 material in [$^\circ C$].

426

427 Results obtained with equation 18 are better and the errors are lowered down to 3 %, improving
 428 the adjustments and therefore, the predictive performance of the equation. It is also shown that
 429 the correction factor applied has more effect on the low carbon materials, thus, capric and

430 myristic acids, which is in accordance to what it has been reported in the viscosity section as
 431 well. This coincidence corroborates that, in liquid state, the carboxylic group effect is more
 432 important for structures with low number of carbons.

433

434 Table 11 presents these results, complemented with the standard deviation obtained for each
 435 fatty acid and including the results for the validation material palmitic acid.

436

437

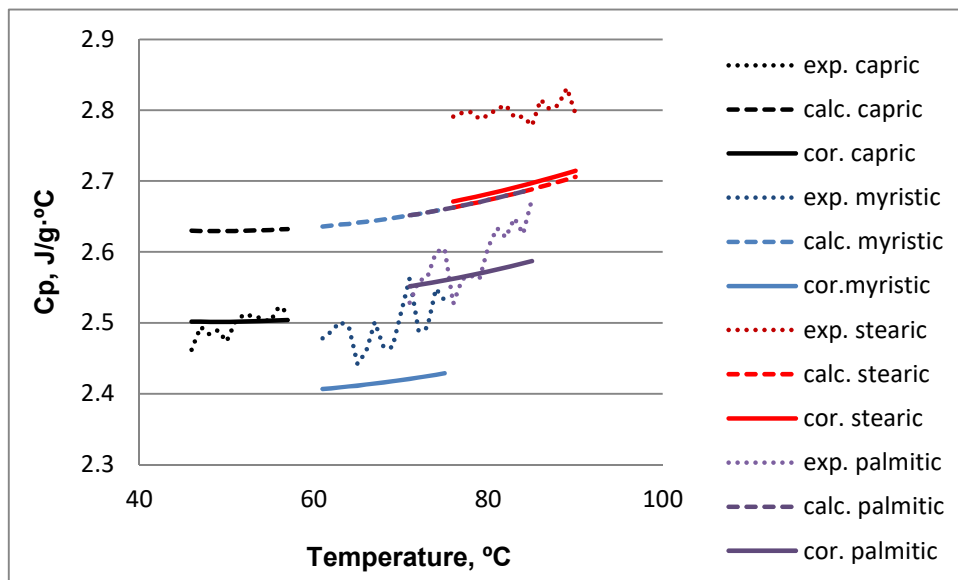
Table 11. Relative errors and standard deviations obtained with equation (17)

	Capric acid	Myristic acid	Stearic acid	Palmitic acid
Relative error [%]	-0.23	3.10	3.83	0.91
Standard deviation	0.01	0.06	0.08	0.02

438

439 The performance of equation 17 for fatty acid liquid C_p empirical calculation can be observed in
 440 Figure 3, where it is compared with the experimental and non-corrected polynomial 2 (eq. (16))
 441 curves. As shown, errors decreased with the correction parameter, and the differences with the
 442 experimental curves are really low, almost overlapping for capric and palmitic acids, slightly
 443 under the measured values for myristic and stearic acids, which matches with the respective 3 %
 444 and 4 % errors reported in former Table 10.

445



446

447 Figure 3. Equation (16) (calc.) and equation (17) (cor.) curves vs. experimental measurements for the four fatty acids
 448 used in the study

449

450 Again, and in order to corroborate equation (17) as the best one for empirical determination of
 451 fatty acid liquid C_p , the same steps were followed with the other candidate fittings, formulating
 452 by the same means general equations with the exponential 2, polynomial 3 and Kubaschewski

453 (eq. (7)) equations. Melting temperature correction parameters were used as well with these
 454 models, obtaining poor approximations and high deviations when compared to the measured C_p .
 455 The relative errors for the exponential 2 equation are higher than 50 %, already showing its poor
 456 performance and predictive usability, while the errors for polynomial 2 and Kubaschewski (eq.
 457 (7)) fittings are around 10 %. However, the key parameter to discard these last two equations
 458 was the standard deviation, shown in Table 12, 75 % higher than the deviation obtained with
 459 equation 18, which in addition presents lower relative errors on the calculations. Therefore, the
 460 use of these three equations was found totally unsuitable, confirming equation 18 as the best and
 461 most proper equation for fatty acid liquid C_p prediction.

462

463 Table 12. Relative error and standard deviation for the general polynomial 3, exponential 2 and Kubaschewski
 464 candidate equations

Equation		Material		
		Capric acid	Myristic acid	Stearic acid
General	Relative error [%]	-3.82	-9.44	-12.70
Polynomial 3	Standard deviation	0.11	0.17	0.26
General	Relative error [%]	102.0	44.8	45.2
Exponential 2	Standard deviation	1.81	0.79	0.89
General	Relative error [%]	-4.50	-9.42	-14.40
Kubaschewski (eq.7)	Standard deviation	0.29	0.17	0.29

465

466 As explained for solid C_p , the accuracy given by equation (17) is limited by the operational
 467 range in which fatty acid PCM are used in TES systems, and therefore its range of use is at
 468 temperatures between 5-20 °C higher to the melting point of each fatty acid PCM.

469

470 4. Conclusions

471

472 Empirical equations to calculate the viscosity, solid C_p , and liquid C_p of the whole fatty acid
 473 family for use in TES systems were formulated from capric, myristic and stearic acid
 474 measurements and are presented in this paper. All three equations have significances greater
 475 than 0.95 and have been selected among other tested equations. In addition, the performance of
 476 the three equations was validated with palmitic acid measurements.

477

478 Equation (11) was found as the best option for fatty acid viscosity prediction. The equation
 479 includes a melting temperature dependant correction parameter that adjusts the viscosity for
 480 each fatty acid depending on its melting point, obtaining results with less than 5 % of error and

481 deviations lower than $2 \cdot 10^{-4}$. In addition, and comparing equation (11) to an empirical equation
482 that authors presented in [28] for paraffin viscosity determination, polynomial 3 graded models
483 have been found as the most suitable for organic PCM viscosity prediction.

484 Solid C_p was found to be better predicted with equation (14), corrected with a melting
485 temperature dependant factor as well. The performance of this equation was demonstrated with
486 the low error results obtained, below 5 %, and the low deviations obtained, below 0.1. The other
487 high significant equations considered for solid C_p empirical calculation, polynomial 3 and
488 exponential 2 show worse performances, with higher errors and deviations in the results that
489 discarded them as the most proper tool.

490

491 Equation (17) was found to be the best option for liquid C_p empirical calculation. The equation
492 is also corrected with a melting temperature dependant factor, giving results with less than 4 %
493 of error and standard deviations lower than 0.1. The other high significant equations considered
494 present worse results, with errors higher than 10 % in all cases, and were therefore discarded.

495

496 The empirical equations given in this study are suitable for the temperature range in which fatty
497 acid PCM are implemented. Additionally, these equations represent an important advance for
498 simulation and system design purposes in the thermal energy storage field. These are reliable
499 tools that provide the viscosity, solid C_p and liquid C_p of the materials in advance without the
500 need of experimental runs, saving time and filling a gap that has limited researchers in process
501 simulations and system design for long time.

502

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504

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