Kinetic Analysis Of TGA Measurements When Evaporation Is A Degradation Process In PCM

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Abstract

Phase change materials degradation kinetics determination is very important in order to assure their use in the long term. Thermo-gravimetric analysis is generally used for determining PCM degradation kinetics. However, the general approach used do not take into account parameters such as the potential evaporation of the PCM, mass and container geometry on the measurements due to the oven's particular operating conditions. The present work aims to develop a methodology that includes these parameters to obtain reliable PCM lifetime predictions.

Keywords: PCM Phase Change Materials, Degradation Kinetics, Thermo-Gravimetric Analysis

1. Introduction

Thermal energy storage (TES) has become increasingly important in engineering applications that involve intermittent energy sources, such as most renewable energy sources. Latent heat thermal energy storage (LHTES) relies on the use of Phase Change Materials (PCMs) to store thermal energy through the latent heat required for the melting/solidification process. It is necessary to take into account some characteristics that a PCM must meet in order to be considered competitive and suitable for its function, such as high thermal storage capacity, adequacy to application phase change temperature, low price, low toxicity, etc. The selected materials should however also fulfill another important requirement, which is the thermal stability upon operating time and cycling (Mehling and Cabeza 2007).

Therefore, the importance of developing methodologies that allow determining the PCMs lifespan is crucial in PCM selection for a determined application. One of the aspects involved in the stability of the PCM is the thermal degradation under working conditions (Quant et al. 2021). The thermal degradation implies the transformation of the original material into other compounds due to the exposure over time to the operation temperatures and, potentially, gaseous environment. This transformation is undesired as it may change in some extent the ability of the PCM to store and release energy, i.e the purpose of PCMs.

If a certain material (for example a PCM) undergoes mass loss due to gaseous evolution, the reaction kinetics can be determined by using Thermo-Gravimetric Analysis, TGA, which consists in monitoring the mass loss of a sample when it is heated at determined constant rate under a gas flow. The kinetics of the degradation reactions can be obtained by analyzing TGA data using different methods (Vyazovkin et al. 2011). The rate of PCM disappearance can be expressed as a function of its residual fraction:

$$r = \frac{d\alpha}{dt} = k(T) \cdot f(\alpha) = A . e^{-\frac{E}{R.T}} \cdot f(\alpha) \; [s^{-1}] \tag{eq. 1}$$

Where α is the degree of conversion or the fraction decomposed at time t, calculated as $\alpha = (m_{ini} - m)/m_{ini}$, k is the rate constant usually given by the Arrhenius law and depends on the temperature, $f(\alpha)$ is a function whose mathematical expression depends on the reaction mechanism.

Besides, estimations sometimes do not correspond to degradation occurring under real operation conditions. They

usually overestimate the degradation process. In previous works Bayón et al. (2020; 2021) studied the degradation kinetics of lauric acid as PCM by analyzing TGA measurements. However, results showed that the lifetime estimations obtained from TGA data analysis and isothermal tests in oven (i. e. experimental conditions being similar to operation conditions) did not match. In their study they concluded that evaporation was one of the degradation processes taking place, thus TGA measurements did not only report mass loss due to degradation processes. In the consulted PCM characterization literature, mass loss in TGA measurements is exclusively accounted to occur due to the thermal decomposition reactions: however, a different data treatment should be accounted when evaporation process is known to occur additionally to potential thermal degradation.

The general expression describing the free evaporation of a substance is the Knudsen-Langmuir equation. This equation describes the evaporation in vacuum. Nevertheless, the condition for a Kdnusen flow (low evaporation rates in high vacuum) is not satisfied in standard TGA equipments (Bassi 2011). Considering the specific experimental conditions of TG measurements, consisting in the diffusion of the evaporating liquid through a stagnant gaseous layer at atmospheric pressure in a cylindrical sample container, an alternative formulation (equation 2) of the evaporation rate has been proposed by Pieterse and Focke (2003). Equation 2 includes the influence of the experimental geometry, the temperature and pressure (the substance partial pressure is assumed to be 0 due to the gas flow). Several authors (Barontini and Cozzani 2007; Bassi 2011; Beverley, Clint, and Fletcher 1999; Pieterse and Focke 2003) have studied evaporation and developed expressions that describe the phenomenon using a TGA equipment with similar expressions.

Although equation 2 has been previously used for evaluating vapor pressures from mass loss measured during TGA analysis, this work proposes using it as well for evaluating the evaporation rate of a certain compound if vapor pressure is known (can be determined if Antoine equation coefficients are known).

$$r = -\frac{dn}{Sdt} = \frac{P_{eq}D}{zRT} \quad \left[\frac{mol}{m^2 s}\right] \qquad \text{(eq. 2)}$$
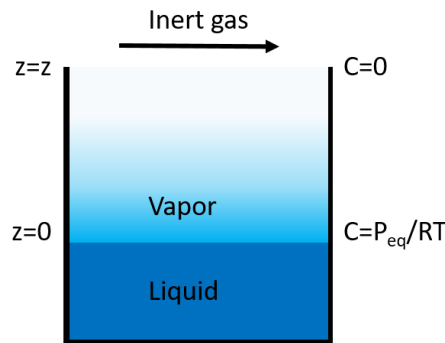

Fig. 1 Scheme of the TGA measurement spatial arrangement

As displayed in the scheme of Figure 1Fig. 1, z is de distance between the top of the container (where the concentration of evaporating molecules C=0) and the surface of the liquid (where C=P_{eq}/RT) and D is the diffusion coefficient of the substance in the stagnant inert gas (N_2 or air).

This diffusion coefficient depends on the temperature and can be estimated by using different models and group contributions (Poling et al., 2001). Taking into account a binary mixture of A and B, where A correspond to the PCM and B correspond to the gaseous environment, several proposed methods for estimating D_{AB} in low-pressure binary gas systems with empirical constants based on experimental data. These include Wilke and Lee (equation 3) and Fuller, et al. (equation 4) methods.

$$D_{AB\,Wilke-Lee} = \frac{\left[3,03 - \left(\frac{0,98}{M_{AB}^{1/2}}\right)\right] 10^{-3} T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^{1/2} \Omega_D} \qquad \text{(eq. 3)}$$

$$D_{AB\,Fuller} = \frac{0,00143 T^{1,75}}{P M_{AB}^{1/2} [\Sigma_A^{1/3} + \Sigma_B^{1/3}]^2} \qquad \text{(eq. 4)}$$

Where:

D_{AB} = binary diffusion coefficient [cm^2/s]

T = temperature [K]

M_A, M_B = molecular weights of A and B [g/mol]

$M_{AB} = 2 \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{-1}$

P = pressure [bar]

σ_{AB} = characteristic length [Å]

Ω_D = collision diffusion integral [dimensionless]

Σ_A, Σ_B = diffusion volumes summation

The σ, Ω_D, and Σ parameters can be obtained from (Poling et al. 2001).

Finally, the objective of this research work is to develop a methodology for kinetic analysis of TGA measurements when evaporation is one of the processes occurring, by including the expressions developed by Pieterse and Focke to the traditional reaction kinetics approach. For this purpose, water was used as reference material in the first instance (no chemical reactions occurrence in the experimental conditions). A similar study was performed using fatty acids: lauric, adipic and myristic acids as PCMs to determine their evaporation rates and potential thermal degradation kinetics.

2. Experimental

A series of dynamic experiments were performed by means of TGA technique. Two apparatus were used to perform the TG measurements and are described in Table 1. Open alumina crucibles were used as samples containers. Dry nitrogen (99.999% pure) was used as purge gas at 50 ml/min. The materials used and experimental conditions are described in Table 2.

Tab 1. TGA apparatus used in the experimental

Equipment	Crucible dimensions	
	Diameter (mm)	Height (mm)
Mettler-Toledo TGA/DSC1	4.8	4
Seiko TG-DTA 6300	5	2.25

Tab 2. Materials used and experimental conditions

Material	Heating rates [K/min]	Sample mass [mg]	TG apparatus
Distilled water	2, 5, 10, 15, 20	35	Mettler-Toledo
Lauric acid	2, 5, 10, 20	≈10	Mettler-Toledo, Seiko
Adipic acid	2, 5, 10, 20	≈10	Seiko
Myristic acid	2, 5, 10, 20	≈10	Seiko

3. Results and discussion

3.1 Evaporation rate determination

- Methodology set-up using water as reference material

Water was used as reference material taking into account that in the applied experimental conditions evaporation occurs, but no other chemical reactions are present. Evaporation rate was calculated by using the formulation

proposed by Pieterse and Focke (equation 2) for measurements performed in TGA equipment. Since diffusion coefficients could not be determined for the PCMs under study using theoretical formulations due to the lack of availability of molecular data, two empirical methods were used: Wilke and Lee (equation 3), and Fuller et al. (equation 4). The determined diffusion coefficients using both methods were very similar for water (Figure 2.a).

In order to validate the Antoine parameters taken from the literature (NIST Research Library Publications 2022), the experimental rate was introduced in equation 2 to obtain equilibrium pressure, which was compared with the equilibrium pressure calculated from those parameters. For that purpose, the evaporation rate was calculated from TG measurements which were done under the experimental conditions described in Tab 1 and Table 2 in terms of crucible dimensions and initial sample mass.

Finally, the pressure values obtained from the experimental measurements were similar to the literature values, which validates the use of Pieterse and Focke method. Figure 2.b shows the general evaporation rate curve of water versus temperature obtained using equation 2 and the experimental values for the heating rates studied. It is clearly seen that the calculated general evaporation rate matches the experimental rate curves for each heating rate studied.
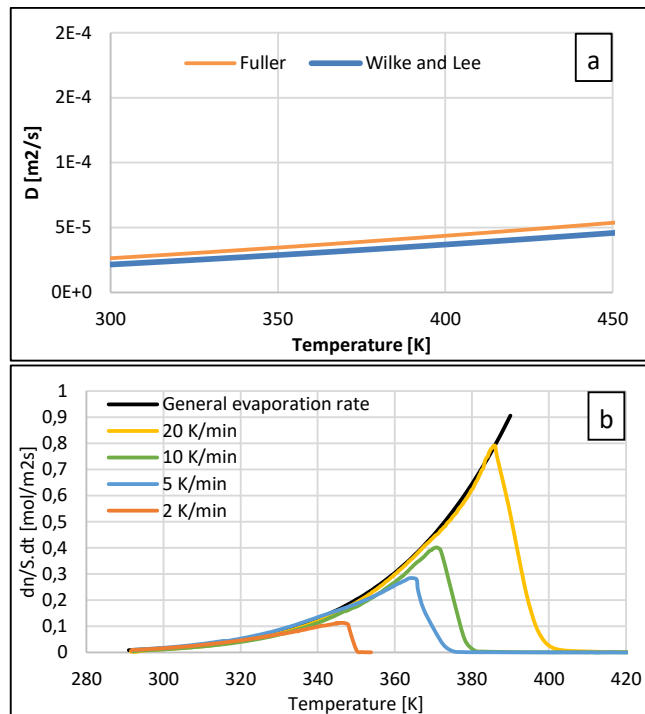

Fig. 2 a: Diffusion coefficient of water determined using Fuller and Wilke and Lee empirical methods. b: Evaporation rate of water per surface: general evaporation rate (determined using eq 2. and Wilke and Lee diffusion coefficient) and experimental curves for the tested heating rates

- Evaporation rate of fatty acids: lauric, adipic and myristic acid.

Lauric, adipic and myristic acid were submitted to TGA tests using the heating rates described in Table 2. In order to satisfy equation 2 Antoine parameters (Matricarde Falleiro et al. 2012) were used to determine the equilibrium pressures and the diffusion coefficients were determined using both Fuller and Wilke and Lee methods. As for the case of water both methods lead to similar values for these coefficients. The evaporation rates of the PCMs obtained using Wilke and Lee method are shown in Figure 3.
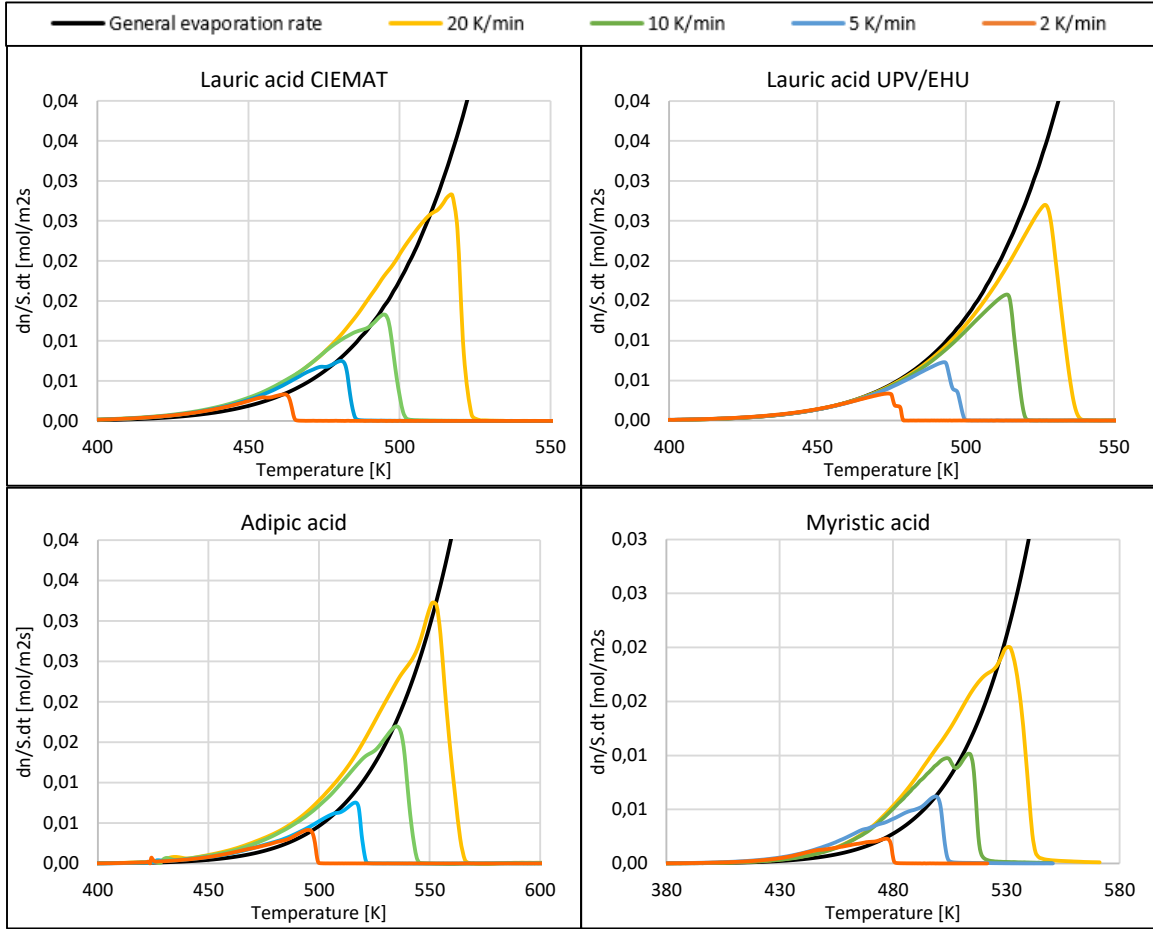
Fig. 3 Evaporation rate of lauric, adipic and myristic acids per surface: general evaporation rate (determined using eq 2. and Wilke and Lee diffusion coefficient) and experimental curves for the tested heating rates

3.2 Estimation of Arrhenius parameters

Once the evaporation rates per surface unity $\frac{dn}{Sdt}$ of the PCMs were obtained, they were fitted to the conventional rate equation (equation 1) adapted to the evaporation case by taking into account that it is a zero order process, so that $f(\alpha)=(1-\alpha)^0 = 1$. Therefore the energy of vaporization E_{vap} and the frequency factor $A_{n,S}$ was determined from equation 5 and the resulting values are shown in Table 3.

$$\frac{dn}{Sdt} = \frac{P_{eq}D}{zRT} \approx A_{n,S}e^{-E/RT}\ \left[\frac{mol}{m^2s}\right]$$ (eq. 5)

Tab 3. Estimation of E and A by fitting an F0 reaction mechanism ($f(\alpha)=1$) to the evaporation rates.

Material	Water	Lauric acid UPV/EHU	Lauric acid CIEMAT	Adipic acid	Myristic acid
E_{vap} [kJ/mol]	43.29	78.38	78.45	81.82	85.94
ΔH_{vap} [kJ/mol] NIST	40.6	81.3	81.3	92	88.9
$A_{n,S}$ [mol/m2s]	0.52 106	2.03 106	2.8 106	1.72 106	6.18 106

The activation energy of vaporization Evap of water obtained from the analysis of TGA measurements is 43.29

kJ/mol, which is very similar to the vaporization enthalpy ΔHvap= 40.6 kJ/mol. The value expected would be Evap = ΔHvap + Econ = 72.8 kJ/mol. On the other hand, the obtained Evap values for lauric, adipic and myristic acids were also very similar to ΔHvap reported in the literature (NIST Research Library Publications 2022) and shown in Table 3. This phenomenon has already been pointed out by Arias et al. (2009), who claim that the activation energy of vaporization is similar to the vaporization enthalpy in the case of caprylic acid. Besides, a plausible explanation is that the activation energy of vaporization decreases when low partial pressures are applied so that only the vaporization enthalpy is observed. This effect should be further studied and confirmed in the future.

Besides, lauric acid was measured in two different TGA equipments with different geometries available at CIEMAT and UPV/EHU. Differences in the experimental curves and in the determined general evaporation rate can be seen in Figure 3. It is believed that specific testing conditions have great influence on the mass variation at high temperature. Table 3 shows that the E_{vap} values obtained from both curves of lauric acid are very similar, however the An,S show greater variation due to the influence of the different experimental arrangements. It points out that the processes taking place are extremely sensitive to experimental conditions. It is important to point out that An,S is a function of the initial mass/moles and the particular geometry of the TGA equipment and should not be used straightforward for real condition rate estimations (Bayón et al. 2020).

3.3 Determination of potential chemical reactions: deconvolution of dTG curve

When evaporation and other chemical reaction are expected to takle place, each process will produce its own effect in the TG curve. Hence, if they are simultaneous processes, the TG curve will contain the addition of the individual contributions c_i, so that, $\sum_{i=1}^{n} c_i = 1$. The resulting dTG curve would be expressed as:

$$\frac{d\alpha}{dT} = \frac{d\alpha_1}{dT} + \frac{d\alpha_2}{dT} + \cdots + \frac{d\alpha_n}{dT} = \frac{c_1}{\beta} A_1 e^{\left(\frac{-E_1}{RT}\right)} f_1(\alpha) + \frac{c_2}{\beta} A_2 e^{\left(\frac{-E_2}{RT}\right)} f_2(\alpha) + \cdots + \frac{c_n}{\beta} A_n e^{\left(\frac{-E_n}{RT}\right)} f_n(\alpha) \qquad \text{(eq. 6)}$$

In such a case, experimental dTG curves should be deconvoluted in various peaks that would correspond to single step processes. Fraser-Suzuki FS functions (Cheng et al. 2015) are commonly used deconvoluting $\frac{d\alpha}{dT}$ vs. T curves into various peaks. The mathematical expression of the FS function is:

$$\frac{d\alpha}{dT} = h \, exp\left\{-\frac{ln2}{s^2}\left[\ln(1 + 2s\frac{T-p}{w})\right]^2\right\} \qquad \text{(eq. 7)}$$

The four parameters of the function are:

        h: amplitude (height)
        s: asymmetry factor
        p: position
        w: half height width

Some issues have to be taken into account when using this function for deconvoluting dTG curves. On the one hand, the FS curves used in the deconvolution should meet the requirement of the integral equal to 1 (=have a normalized area). Also, it is important to take into account that prior to any deconvolution it is worth having an estimation of values displayed by the FS parameters in relation to the different reaction mechanisms. This issues are will be analyzed and discussed in an out coming work.

If it is assumed that two processes occur in the TG measurement and one of them is evaporation, the curve of the unknown process can be determined taking into account the experimental curve and the evaporation curve determined above. As example, Figure 4 shows, the deconvolution for myristic acid tested at 5 K/min. The evaporation curve was built following the evaporation curve previously determined and a contribution of 55% and a F0 mechanism, and the curve potentially corresponding to other reactions was built to correspond to the 45% and an A3 (Avrami-Erofeev, n=3 (Vyazovkin et al. 2011)) mechanism. The addition of both curves render a curve very similar to the experimental curve. Once all experimental curves corresponding to several heating rates are deconvoluted, Kissinger method (Kissinger 1957) could be used to determine the kinetic triplet for the unkown reactions.
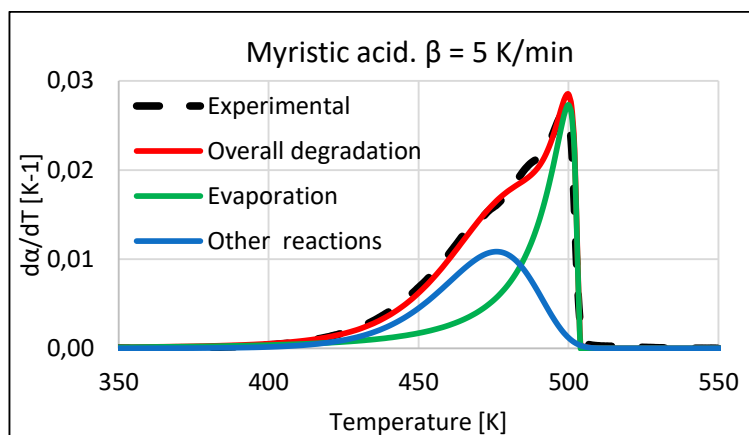
Fig. 4 Deconvolution of dα/dT curve of myristic acid at 5 K/min by means of Fraser-Suzuki functions

4. Conclusions

When used as PCM in latent storage systems, fatty acids are expected to suffer evaporation as one of their main degradation process under service conditions. Besides the potential evaporation, chemical degradation may also occur when heated above their melting temperature. TGA technique can evaluate both phenomena, however the resulting TG and dTG curves may be an addition of two or more process contributions: one potentially corresponding to evaporation and the others associated to chemical reactions taking place at high temperatures. Pieterse and Focke approach may serve as a tool to determine the evaporation rate and evaporation characteristics in the TGA specific conditions. With a known evaporation rate, deconvolution of dTG curves can be carried out by means of Fraser-Suzuki functions to determine the potential chemical reaction contribution to the TGA curve. The results of the present work point out that PCM degradation processes are extremely sensitive to experimental conditions: partial pressure, initial mass/moles and the particular geometry of the TGA equipment. Future work should include the extrapolation of the obtained kinetics to real operation condition kinetics.

5. Acknowledgments

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