

Study of Thermal Degradation of Adipic Acid as PCM Under Stress Conditions: A Kinetic Analysis

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Abstract

Adipic acid is a PCM with $T_m = 152$ °C, which makes it very interesting for being used as latent storage medium for mid-temperature applications. Hence, thermal degradation analyses on this PCM are crucial for ensuring its long-term performance under operating conditions. For this purpose, both TG measurements and isothermal tests under stress conditions in an oven were carried and the experimental data were kinetically analyzed not only from the classical approach but also from the evaporation point of view. From the results of this analysis we concluded that adipic acid mainly undergoes evaporation as soon as it melts and this prevents this PCM for being used for latent storage in not sealed systems. Moreover, the strong color change from white to brown after isothermal test proved that it also undergoes other degradation mechanisms that could lead to changes in the thermophysical properties (T_m and ΔH_m). In a further step, the degradation products will be analyzed and additional isothermal test will be carried out in closed containers to avoid evaporation.

Keywords: PCM, Adipic acid, Degradation kinetics, Evaporation, TGA, Isothermal tests

1. Introduction

The storage of thermal energy is a key component in some domestic and industrial processes as well as in power generation systems. It ensures system reliability, power dispatchability and also economic profitability. The latent heat technology based on phase change materials (PCM) is a method of thermal energy storage (TES) that has gained renewed attention in recent years owing to its high thermal storage capacity, operational simplicity and transformative industrial potential. Phase change materials (PCM) with melting temperatures (T_m) above 100 °C are of particular interest for solar thermal energy storage in the mid-temperature range. One of the most critical issues when choosing a PCM for a certain storage application is to be sure that it has a successful performance during its operation life-time. Usually melting/freezing cycles are carried out to assess the life-time performance, however, if a PCM undergoes some degradation after melting due to a chemical reaction or phase segregation, it will be hindered during the freezing period. This means that this kind of tests is not sufficient for validating a PCM. Another way to assess long-term performance of PCMs is to carry out kinetic studies of possible degradation processes (Bayón and Rojas, 2019). In principle, if a PCM undergoes degradation due to the occurrence of chemical reactions in liquid state, thermogravimetric (TG) measurements can be used for determining the kinetics of such reactions (Vyazovkin et al. 2011). However, care must be taken when the long-term behavior of a PCM is predicted only from the kinetic analysis of TG measurements, because the results may not be reliable, specially if evaporation is one of the main degradation processes. On the other hand, from previous studies of lauric acid, which undergoes evaporation under stress thermal conditions (Bayón et al. 2020 and 2021), it was concluded that isothermal experiments with larger amounts of sample are necessary for obtaining degradation curves that are more representative of the degradation processes occurring under real operation conditions.

In this work, hexane dioic acid ($\text{HOOC}(\text{CH}_2)_4\text{COOH}$), also known as adipic acid, with a melting temperature of 152 °C, was studied with the aim of being assessed as PCM for mid-temperature applications. Isothermal tests under stress conditions were carried out at various temperatures (160 °C-240 °C) and times (1h-6h) in open containers to evaluate the mass loss under these conditions. Alternatively, TG measurements were carried out under either N_2 or air atmosphere at various heating rates ($\beta = 2-20$ °C/min). Both kinds of experimental data were kinetically analyzed from the classical approach and also by considering evaporation as main degradation process. From the results of these studies, the long-term behavior of adipic acid in terms of evaporation has been predicted.

1.1 Theoretical background

If a PCM undergoes degradation due to the occurrence of chemical reactions in liquid state, TG measurements can be used for determining the kinetics of such reactions (Vyazovkin et al. 2011). The starting point for the kinetic analysis of TG measurements is the equation that represents the reaction rate:

$$\frac{d\alpha}{dt} = Ae^{\left(\frac{-E}{RT}\right)} f(\alpha) \quad (\text{eq. 1})$$

where α is the degree of conversion at a certain time, calculated as $\alpha = (m_{ini} - m)/m_{ini}$; A , E and R are the frequency factor, the activation energy and the molar gas constant, all present in the Arrhenius law for the reaction rate constant and $f(\alpha)$ is a function whose form depends on the mathematical model describing the reaction mechanism.

In a dynamic TG measurement performed at constant heating rate $\beta = \frac{dT}{dt}$, eq. 1 becomes:

$$\frac{d\alpha}{dT} = \frac{Af(\alpha)e^{-E/RT}}{\beta} \quad (\text{eq. 2})$$

For the case of isothermal tests, the kinetic analysis is based on the fact that $k(T) = Ae^{(-E/RT)} = cte$, so that the general equation of the reaction rate becomes a linear expression (Vyazovkin & Wight, 1999):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T)t \quad (\text{eq. 3})$$

Where α is the conversion calculated as and $g(\alpha)$ is a function associated to the reaction the mechanism through $f(\alpha)$. Hence, by using the experimental values of α , $g(\alpha)$ function can be calculated assuming different reaction mechanism (Vyazovkin & Wight, 1999) and plotted vs. time in order to check which one leads to the best linear plot. Then the rate constant at a certain temperature is obtained from the corresponding slope. If this procedure is done for each isothermal test (i), the Arrhenius parameters, A and E can be determined from the linear plot:

$$\ln k(T_i) = \ln A - \frac{E}{RT_i} \quad (\text{eq. 4})$$

However, if evaporation is one of the main degradation processes, the kinetic analysis has to be done from a different approach. The general expression describing the free evaporation of a substance in vacuum is the Knudsen-Langmuir equation:

$$r = -\frac{dn}{Sdt} = \frac{\alpha_{vap}P_{eq}}{\sqrt{2\pi MRT}} \left[\frac{mol}{m^2s} \right] \quad (\text{eq. 5})$$

Where dn/Sdt is the evaporation rate per unit area in mol/m^2s , being S the evaporating surface, P_{eq} is the equilibrium vapor pressure, M is the molecular weight of the evaporating substance, R is the gas constant, T is the temperature and α_{vap} is the vaporization constant whose value is 1 if the evaporation takes place in vacuum and condensation is neglected. However, this situation does not usually happen neither in TG measurements, where a gas carrier is used, nor in HDR oven tests, where the liquid evaporates from the sample surface due to a concentration gradient. 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 of the evaporation rate has been proposed by some authors (Pieterse and Focke, 2003; Bassi, 2011).

$$r = -\frac{dn}{Sdt} = \frac{P_{eq}D}{zRT} \left[\frac{mol}{m^2s} \right] \quad (\text{eq. 6})$$

As displayed in the scheme of Fig. 1, z is the distance between the top of the container (where the concentration of evaporating molecules is $C=0$) 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 based on functional group contributions (Poling et al. 2001). Although eq. 6 is normally used for evaluating vapor pressures from mass loss measured during TG analysis (Pieterse and Focke, 2003; Bassi, 2011), this equation could be used as well for evaluating the evaporation rate of a certain compound if vapor pressure is known, i. e. if the coefficients of Antoine equation are known.

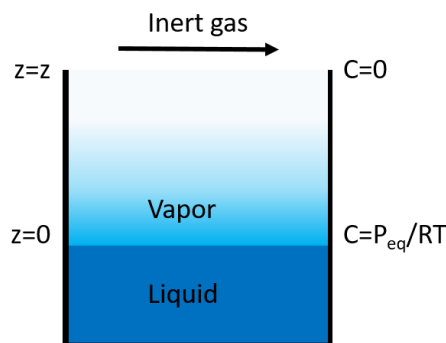


Fig. 1. Schematic of a TG measurement. The evaporating liquid diffuses from the surface through the gas region inside the pan and the purge gas swipes it as it emerges from top of the cup.

On the other hand, Vlasov (Vlasov, 2019) proposed another formulation of eq. 5 by applying the collision theory to the evaporation processes. The resulting equation for the evaporation rate is quite similar to eq. 5, but for the introduction of P as partial pressure near the liquid surface and the substitution of the vaporization constant, α_{vap} , by an exponential term depending on the activation energy of condensation, E_{con} .

$$r = -\frac{dn}{Sdt} = \frac{(P_{eq}-P)}{\sqrt{2\pi MRT}} e^{\frac{-E_{con}}{RT}} \left[\frac{mol}{m^2s} \right] \quad (\text{eq. 7})$$

As we can see, Eq. 7 does not include any geometric parameter associated to the experimental set-up apart from the sample surface. Also it does not consider an inert gas flowing so that evolved vapor molecules are not removed from the upper part of the container. However, it includes a classical kinetic term with an activation energy that meets the condition: $E_{con}=E_{ev}-\Delta H_{vap}$. In principle this equation cannot be applied to the case of TG experiments.

2. Experimental

Dynamic thermogravimetric (TG) analysis of adipic acid were performed in a Seiko TG-DTA 6300 apparatus and the measurements were carried out at heating rates, β , ranging from 2 °C/min to 20 °C/min under either N₂ or air atmosphere at 50 ml/min. Samples of 10-12 mg were contained in platinum crucibles of 4.5 mm diameter and 3 mm height. Isothermal tests were performed under air in the vertical oven (called HDR) displayed in Fig. 2, which has a cylindrical ceramic cavity where the sample can be allocated (left) and allows performing tests under controlled heating rate with stand-by periods at constant temperature. Its upper part can be covered with a double glass trap (Fig. 2. right), where most of the evolved gases can be condensed. The oven is installed inside an extraction hood for removing the non-condensed gases so that thermal degradation tests can be carried out in a secure way (Rathgeber et al., 2020).



Fig. 2: Pictures of HDR oven: experimental set-up for performing thermal degradation tests.

For isothermal tests, adipic acid samples of about 3,5 g were contained in open glass vials of 2 cm diameter and 5 cm height (see Fig. 2. left). The vial with the sample was located inside the ceramic cavity at room temperature and heated up to the test temperature. Tests were performed for periods of 1h to 6 h in the temperature range 160 °C to 240 °C and the heating rate to achieve the target temperature was 5 °C/min. After each test, the oven was open and the sample was taken out and allow cool down at room temperature. Samples were weighed before and

after the tests in a scale with 0.1 mg accuracy and, in each case, a new vial was used so that the degraded sample could be stored for further characterization.

3. Results and discussion

3.1 Classical approach

Since the aim of this work is to assess the long-term performance of adipic acid working as PCM for latent heat storage, the evaluation of its thermal degradation kinetics is mandatory. Therefore, in a first approach, both TG measurements and isothermal tests in HDR oven were analyzed from the classical kinetics point of view. In this sense, TG measurements were analyzed by using Friedman method, which belongs to the so-called model-free isoconversional methods that allow the activation energy to be estimated as a function of α without choosing any reaction model. Friedman method is based in the following equation, which is derived from eq. 2 (Vyazovkin et al., 2011):

$$\ln \left[\beta \left(\frac{d\alpha}{dT} \right)_{\alpha} \right] = \ln [f(\alpha)A_{\alpha}] - \frac{E}{RT_{\alpha}} \quad (\text{eq. 8})$$

The basic assumption of isoconversional methods is that the reaction rate at constant extent of conversion, α , depends only on temperature so that constant activation energy values should be expected for the whole conversion range. Comparing with other isoconversional methods, Friedman's is one of the most accurate because it does not make any assumption or simplification beyond the one already stated.

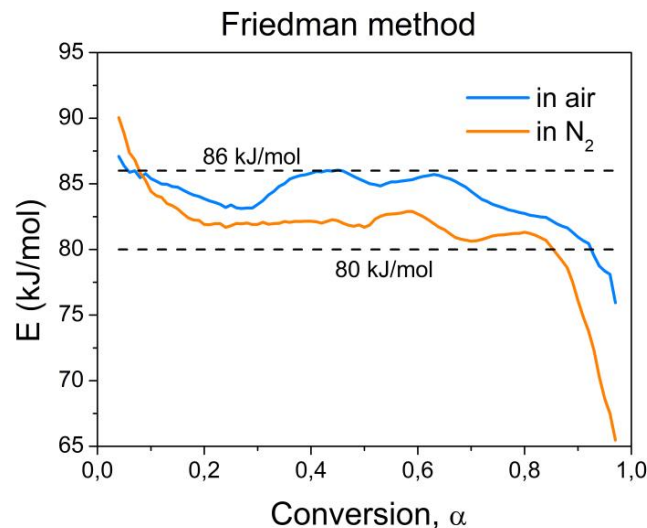


Fig. 3. Activation energy calculated by Friedman method for TG measurements of adipic acid carried out in N₂ and air.

As we can see, the values of activation energy, E , obtained for adipic acid samples are slightly below the value of vaporization enthalpy reported in de literature 89 ± 1 kJ/mol (Wright et al. 2004). Moreover, not much difference is observed between the values calculated from TG measurements under N₂ and air, although the energy values obtained in N₂ are lower. Isoconversional methods are not fully accurate, but still can be used for having a preliminary estimation of E (Budrugaec, 2018). However, the observed variation of E with α may be due to the occurrence of multi-step processes and their different relative contribution to the overall reaction rate.

For the samples tested under isothermal conditions in HDR oven, a mass decrease was observed in all cases and also an important amount of solid was deposited in the glass traps located at the top. In Fig. 4, the variation of conversion vs. time is displayed for the experiments performed at 4 different temperatures: 160 °C, 180 °C, 200 °C and 220 °C.

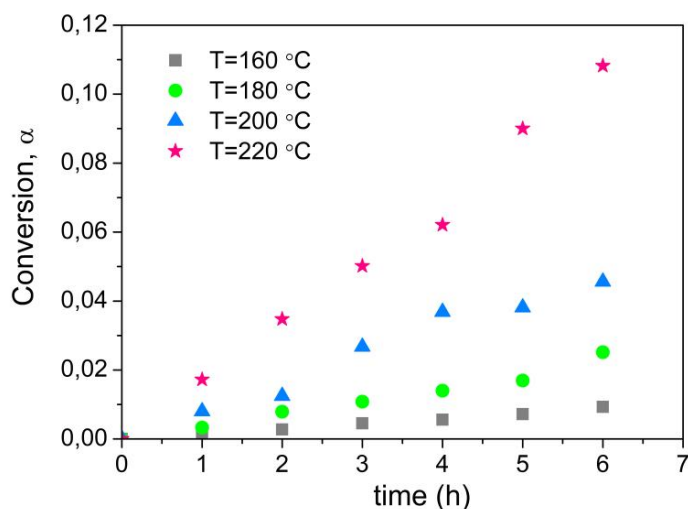


Fig. 4. Conversion vs. time for isothermal tests performed in HDR oven at different temperatures.

For evaluating the degradation of adipic acid, four different mechanisms were selected for applying eq. 3 (F0, F1, R2 and A2). Their corresponding $g(\alpha)$ expressions are recorded in Tab. 1. The mechanisms F0, F1 and R2 lead to quite good linear fits assuming that conversion is zero when reaction time is zero (see R^2 value recorded in Tab. 1). However, $g(\alpha)$ calculated for mechanism A2 did not show a linear behavior with time as evidenced by the low regression value obtained. In Tab. 1, the activation energies obtained from the linear plots of eq. 4 are recorded as well for reaction mechanism F0, F1 and R2. In all cases, a similar activation energy of about 72 kJ/mol is obtained. However, if we compare this activation energy with the ones obtained by applying Friedman's method to the TG measurements shown in Fig. 3, we can see that they are about 10-15 kJ/mol higher.

Tab. 1: Activation Energy obtained from isothermal tests assuming different reaction mechanism.

Mechanism	$g(\alpha)$	R^2 for eq. 3	E (kJ/mol)	$\ln A$ (s ⁻¹)
F0	α	0,965	72,45	5,43
F1	$-\ln(1 - \alpha)$	0,965	73,63	5,76
R2	$1 - (1 - \alpha)^{1/2}$	0,965	73,03	4,90
A2	$[-\ln(1 - \alpha)]^{1/2}$	0,879	-	-

The difference between the activation energies calculated from the isothermal experiments, compared to the TG measurements, could be due to the fact that not a single mechanism is occurring during the thermal degradation of adipic acid. Therefore, a deconvolution of DTG curves to separate the possible mechanisms and evaluate them independently could be a next step. The similarity of the activation energies of adipic acid under air and nitrogen obtained by Friedman's isoconversional method is also noted, so it can be deduced that the ambient atmosphere does not have much influence on the degradation mechanisms of this fatty acid.

3.2 Evaporation approach

During isothermal tests it was observed that an important amount of adipic acid was evaporated and hence collected as a white powder in the glass traps placed at the top of the HDR oven. This means that evaporation is the predominant degradation process for the adipic acid in open systems so that the occurrence of this process must be taken into account when analyzing both TG measurements and isothermal tests in oven. In this sense, another approach was done for both kinds of experiments.

For the case of TG measurements, the eq. 6 proposed by Pieterse and Focke (Pieterse and Focke, 2003) and Bassi (Bassi, 2011) was applied for calculating de evaporation rate of this fatty acid. A more detailed study of how to analyze TG measurements when evaporation is one of the main degradation processes is presented at this

conference in another work (Quant et al. 2022). In the case of adipic acid evaporation, the parameters S and z were calculated from crucible dimensions (4.5 mm diameter and 3 mm height), D was calculated by using the method of Wilke and Lee (Poling et al., 2001) and P_{eq} was calculated from Antoine equation with the coefficients found in the literature (Stephenson and Malanowski, 1987). In Fig. 5 the resulting evaporation rate in mol/m²s has been plotted together with the corresponding experimental curves for the TG measurements performed at different heating rates ($\beta=2$ °C/min, 5 °C/min, 10 °C/min and 20 °C/min). As we can see, the experimental curves fit quite well the theoretical curve predicted by eq. 6, although a slight difference in all the curves is observed, which could indicate that, apart from evaporation, and additional degradation process may be occurring.

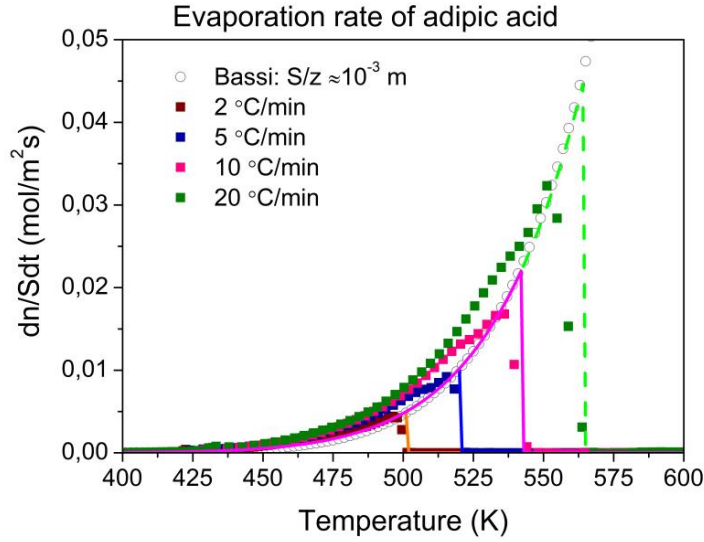


Fig. 5. Comparison of evaporation rate calculated from TG measurements at different heating rates with the predicted by eq. 6.

Alternatively, the conventional rate equation (eq. 1) can be 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, eq. 1 expressed in mol/m²s becomes:

$$-\frac{dn}{Sdt} = \frac{n_{ini}}{S} A e^{\left(\frac{-E}{RT}\right)} \quad (\text{eq. 9})$$

If eq. 9 is fitted to eq. 6, the resulting kinetic parameters for the case of adipic acid are: $E= 81.82$ kJ/mol and $n_{ini}/S=1.73$ E6 mol/m²s. It is interesting to note that the value obtained for the activation energy is in the range of the values calculated by Friedman method (see Fig. 3). However, in contrast to the classical approach, the pre-exponential factor in the evaporation approach not only depends on the initial amount of material, n_{ini} , but also on the sample surface, S .

From these results, it seems clear that adipic acid degradation must be approached from the evaporation point of view. In this sense, it must be taken into account that HDR tests are affected by the partial pressure of the vapor above the sample bottle, hence these measurements cannot be analyzed by eq. 6 because the experimental conditions do not meet the corresponding requirements (i. e. no purge gas removes the evaporated liquid from the sample top). Hence, for analyzing the isothermal tests in HDR oven, eq. 7 was used by assuming that temperature is constant. In such case eq. 7 becomes eq. 10 and is the evaporation rate, which is the term in brackets, is constant.

$$-\frac{dn}{S} = \left[\frac{(P_{eq}-P)}{\sqrt{2\pi MRT}} e^{\frac{-E_{con}}{RT}} \right] dt \quad (\text{eq. 10})$$

In Fig. 6, the amount of adipic acid lost in mol/m² has been plotted vs. time for each series of tests performed at the same temperature. The slope of each linear plot corresponds to the evaporation rate in mol/m²s.

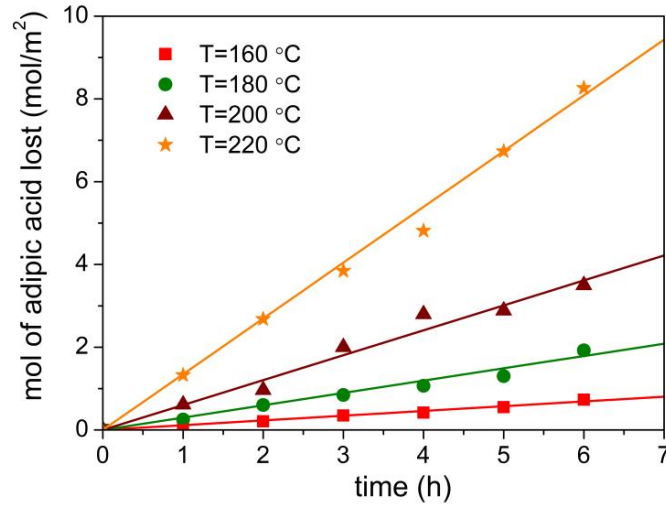


Fig. 6. Amount of adipic acid lost (in mol/m₂) vs. time for isothermal tests performed in HDR oven at different temperatures.

According to eq. 10, if the natural logarithm of evaporation rate is plotted vs. the inverse of its corresponding temperature, E_{con} could be obtained from the slope of the expected linear plot. However, it is very important to remark that the evaporation rate obtained for each temperature is expected to be affected by the partial pressure of adipic acid, P , which should depend on the temperature of the test. This means that, in principle, E_{con} cannot be obtained from the plot mentioned above. In order to evaluate the effect of partial pressure when evaporation tests are carried out in HDR oven, water was evaporated at different temperatures because its E_{con} value is known (32.3 kJ/mol) (Vlasov, 2019). For evaluating the effect of partial pressure in the HDR oven tests, eq. 6 was converted in eq. 11, the natural logarithm of evaporation rate for different partial pressures, P , was calculated and then plotted vs. the inverse temperature.

$$\ln r = \ln \left[\frac{(P_{eq} - P)}{\sqrt{2\pi MRT}} \right] - \frac{E_{con}}{RT} \quad (\text{eq. 11})$$

The resulting curves for the water are plotted in Fig. 7 (left) together with the logarithms of the evaporation rates obtained experimentally from HDR test. In this plot, the partial pressure values were selected so that evaporation rate curves could fit the experimental rate values (see graph legend) (Bayón et al. 2021). This graph also includes the evaporation rates reported by Borodacheva et al. (Borodacheva et al. 2011) who carried out experiments of steady-state water evaporation in an open system. As we can see, the rate values they obtained perfectly fit the evaporation rate curve of water when partial pressure is equal to zero. However, for the case of water evaporated in the HDR oven, partial pressures higher than zero had to be included in eq. 11 for the curves to fit the experimental rate values. As can be seen in the legend, the partial pressure of the vapor above the sample had to be increased with testing temperature and this decreased the evaporation rate.

A similar approach was done for analyzing the isothermal tests of adipic acid carried out in the HDR oven. In this case, since the activation energy of condensation that should be included in eq. 11 is not known, different E_{con} values were checked according to two criteria. If we assumed that the rate curve for $P=0$ crossed the evaporation rate obtained for the tests at 160 °C, maximum $E_{con} = 40$ kJ/mol had to be used. In contrast when the partial pressure, P , to be included in eq. 11 corresponded to an equilibrium temperature one degree below the test temperature, a minimum $E_{con} = 30$ kJ/mol had to be selected. Taking into account this, E_{con} value for adipic acid could be estimated as 35 ± 5 kJ/mol. In Fig. 7 (right), the rate curves with $E_{con} = 35$ kJ/mol have been plotted together with the evaporation rates obtained experimentally from HDR tests. In the legend, the partial pressure of adipic acid used in the construction of each curve has been recorded as well together with its corresponding equilibrium temperature. Additionally, the evaporation rates obtained from TG measurements have been included for comparison. As we can see, the rates obtained from HDR tests are about one order of magnitude ($\ln 10 = 2.3$) lower than the rates obtained from TG measurements. As discussed above, the evaporation in HDR oven is slowed down because the evaporated material is not removed from the sample surface so that the vapors just

move upwards by diffusion and hence partial pressure is quite close to the equilibrium pressure. However it is interesting to note that evaporation rates obtained from TG measurements are very close to the values predicted by eq. 11 when $P=0$ and hence there is no adipic acid on the liquid surface.

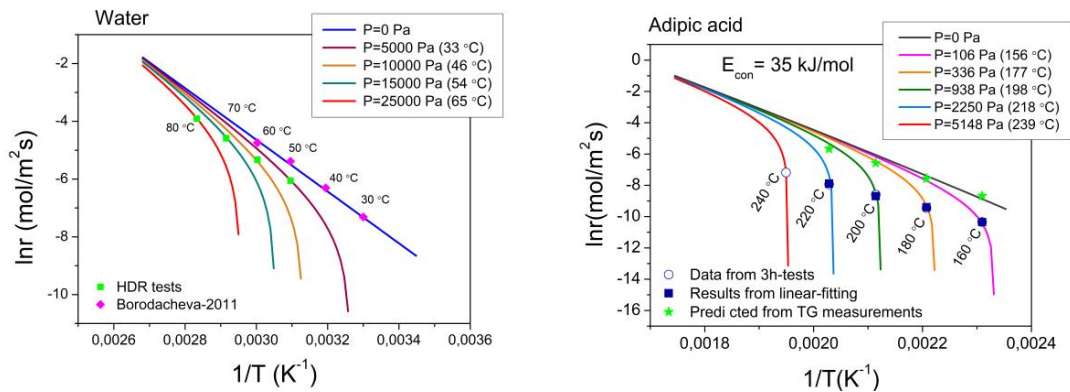


Fig. 7. Evaporation rates of water (left) and adipic acid (right) calculated with eq. 11 at different temperatures.

3.3 Prediction of evaporation under long-term working conditions

If we assume that the evaporation rate results obtained in previous section can be extrapolated to real working conditions, we could calculate the amount of adipic acid that would evaporate after a certain time if it is kept at constant temperature. Therefore for predicting the expected degradation of adipic acid due to the evaporation, the amount of this PCM lost over time at $T_m+8\text{ }^\circ\text{C}$ ($160\text{ }^\circ\text{C}$), $T_m+18\text{ }^\circ\text{C}$ ($170\text{ }^\circ\text{C}$) and $T_m+23\text{ }^\circ\text{C}$ ($175\text{ }^\circ\text{C}$) was simulated with the evaporation rates calculated from both TG measurements and isothermal tests in the HDR oven. For the case of rates from TG measurements, a S/z ratio of 10^{-3} m was used while for the case of rates from HDR tests, they were calculated assuming the best situation in which partial pressure of adipic acid is the equilibrium pressure at $4\text{ }^\circ\text{C}$ below the constant operation temperature. It must be pointed out that this situation might not be very realistic because in real working conditions partial pressure can be lower than in HDR tests and hence evaporation rate would be higher. On the other hand, the situation described by TG measurements might not be realistic as well because this would imply that all adipic acid evaporated is immediately removed from the liquid surface. The resulting curves that predict the amount of adipic lost in kg by square meter of surface are plotted in Fig. 8. As expected, the mass loss predicted from TG measurements (Fig. 8. left) is much higher than the predicted from HDR tests (Fig. 8. right). However, even in the most favorable case in which evaporation rate is slowed down by the presence of adipic acid vapors on the liquid surface (Fig. 8. right), the amount of PCM lost after 1 year would be about 100 kg/m^2 even if temperature is kept only $8\text{ }^\circ\text{C}$ above T_m . The main issue is that adipic acid evaporates as soon as it melts, which prevents this PCM for being used for latent storage at least if the storage container is not sealed.

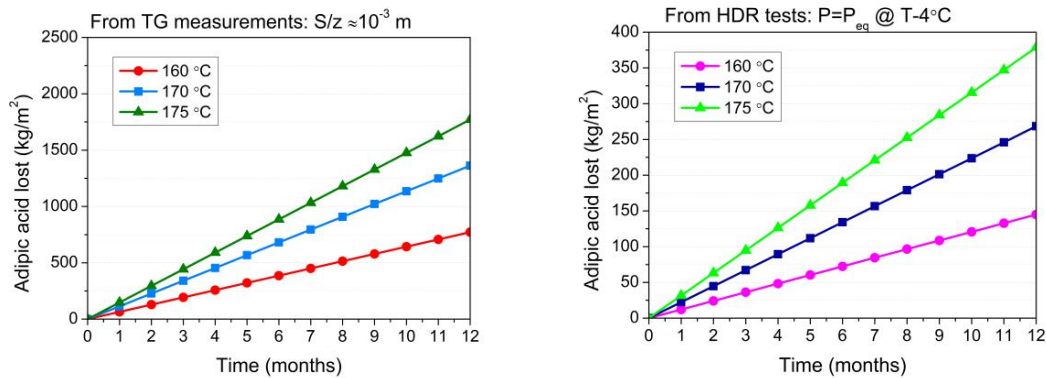


Fig. 8. Prediction of adipic acid mass loss over one year when kept melted at constant temperatures ($T_m+8\text{ }^\circ\text{C}$ + $18\text{ }^\circ\text{C}$ and + $23\text{ }^\circ\text{C}$), from the results of TG measurements (left) and HDR isothermal tests (right).

4. Conclusions and future work

In this work, the thermal degradation of adipic acid ($T_m = 152\text{ °C}$) has been studied in order to assess its feasibility as PCM for latent storage in intermediate temperature ranges by predicting its long-term performance under operating conditions. For that purpose, TG measurements and isothermal tests under stress conditions in an open air oven have been carried out. In a first approach, both kinds of experimental data have been analyzed by applying the traditional kinetic approach and the approach assuming that evaporation is one of the degradation mechanisms. Although there are some differences in the kinetic results obtained by both approaches, we can conclude that adipic acid undergoes fast evaporation as soon as it melts, which prevents this PCM for being used for latent storage at least in not sealed (or open) systems. Apart from evaporation, a strong color change of adipic acid (from white to brown) after isothermal tests was observed. This proves that this PCM also undergoes other degradation mechanisms that produce colored products, which could lead to changes in the thermophysical properties (T_m and ΔH_m). As future work, the formation of colored degradation products will be studied by Vis-UV spectroscopy and also by using other characterization techniques such as FTIR, DSC, chromatography, etc. Moreover, isothermal tests in closed containers will be performed as well to avoid evaporation and the possible effect of O_2 in adipic acid degradation.

Acknowledgments

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References

- Bassi, M., 2011. Estimation of the vapor pressure of PFPEs by TGA. *Thermochimica Acta* 521(1-2) 197-201. <https://doi.org/10.1016/j.tca.2011.04.024>.
- Borodacheva Y. V., Lotkhov, V. A., Dil'man, V. V., Kulov N. N. 2011. Kinetics of steady-state evaporation of single-component liquids into an inert gas. *Theoretical foundations of chemical engineering* 45 (6): 805-810. <https://doi.org/10.1134/S0040579511060030>.
- Bayón, R., Rojas, E., 2019. Development of a new methodology for validating thermal storage media: Application to phase change materials. *Int. J. Energy Res.* 43, 6521-6541. <https://doi.org/10.1002/er.4589>.
- Bayón R., Bonanos, A., Rojas. E. 2020. Assessing the long-term stability of fatty acids for latent heat storage by studying their thermal degradation kinetics. *Proceedings of Eurosun 2020*. Online conference. <https://doi.org/10.18086/eurosun.2020.07.10>.
- Bayón R., Gismera, V., Rojas. E. 2021. Validation of lauric acid as PCM: study of thermal degradation under quasi-real working conditions. *ENERSTOCK 2021*. Online Conference. Oral presentation.
- Budrugaec, P., 2018. A simple and precise differential incremental isoconversional method to kinetic analysis of heterogeneous processes under arbitrary temperature programs. *Thermochimica Acta*, 661, 116-123. <https://doi.org/10.1016/j.tca.2013.05.020>.
- Pieterse, N.; Focke W. W. 2003. Diffusion-controlled evaporation through a stagnant gas: Estimating low vapour pressures from thermogravimetric data. *Thermochimica Acta* 406, 191-198. [https://doi.org/10.1016/S0040-6031\(03\)00256-9](https://doi.org/10.1016/S0040-6031(03)00256-9).
- Quant, L. Bayón, R., García R. J., Rojas, E. 2022. Kinetic analysis of TGA measurements when evaporation is a degradation process in PCM. *Eurosun 2022*. Kassel.
- Rathgeber, C., Hiebler S., Bayón R., Cabeza L. F., Zsembinszki G., Englmaier G., Dannemand M., Diarce G., Fellmann O., Ravotti R., Groulx D., Kheirabadi A. C., Gschwander S., Höhle S., König-Haagen A., Beupere N., Zalewski L. 2020. Experimental Devices to Investigate the Long-Term Stability of Phase Change Materials

under Application Conditions. Applied Sciences, 10, 7968. <https://doi.org/10.3390/app10227968>.

Poling, B. E. Prausnitz, J. M., O'Connell, J. P. 2001. The properties of gases and liquids, fifth ed., McGraw-Hill, New York, Ch. 11. <https://doi.org/10.1021/ja0048634>

Shen, L., Alexander, K. S., 1999. A thermal analysis study of long chain fatty acids. Thermochemica Acta 340-341, 271-278. [https://doi.org/10.1016/S0040-6031\(99\)00272-5](https://doi.org/10.1016/S0040-6031(99)00272-5).

Stephenson, R.M., Malanowski, S. 1987. Handbook for Physicochemical Properties of Organic Compounds, Elsevier Science, New York. https://doi.org/10.1007/978-94-009-3173-2_1

Vlasov, V. A. 2019. Modeling of evaporation and condensation processes: a chemical kinetics approach. Heat and Mass Transfer 55, 1661-1669. <https://doi.org/10.1007/s00231-018-02549-y>.

Vyazovkin, S., Wight, C. A., 1999. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. 341, 53-68. [https://doi.org/10.1016/S0040-6031\(99\)00253-1](https://doi.org/10.1016/S0040-6031(99)00253-1)

Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C., & Sbirrazzuoli, N., 2011. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochemica Acta, 520(1-2), 1-19. <https://doi.org/10.1016/j.tca.2011.03.034>.

Wright, S.F., Dollimore, D., Dunn, J.G., Alexander, K., 2004. Determination of the vapor pressure curves of adipic acid and triethanolamine using thermogravimetric analysis. Thermochemica Acta 421, 25-30. <https://doi.org/10.1016/j.tca.2004.02.021>.