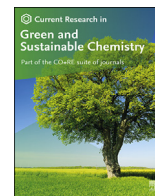




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Guidelines for a correct evaluation of Deep Eutectic Solvents thermal stability



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ARTICLE INFO

Keywords:

Deep eutectic solvents
Thermal degradation
Thermogravimetry
Choline chloride
Isothermal stability

ABSTRACT

Deep eutectic solvents (DESs) are a class of versatile and green emerging materials. Despite the huge amounts of applications proposed in the last years, studies on their thermal stability are often missing. In this short review, we propose a guide for a correct evaluation of DES thermal stability, conducted mainly by dynamical thermogravimetry (TGA). We collected all the data reported in the literature on choline chloride (ChCl)-based DESs, as proof of concept to show the potentialities of the technique, highlighting all the parameters that need to be considered for a correct analysis, with particular attention to the possible sources of misleading interpretations (e.g. the adsorbed water, or the formation of undesired products during DES preparation). In many cases, the additional use of isothermal TGA, or TGA coupled with online techniques such as Fourier Infra-Red Spectroscopy or Mass Spectrometry, may help for the data interpretation. Besides, we summarize in a graph the degradation temperatures of many DESs and their precursors, intended as an operative guide to choosing the correct DES for different applications. The findings reported to date, highlight the potentialities of thermal analysis on DESs, as a powerful tool to obtain essential information on their applicability, and to implement the knowledge of their nanostructure from a molecular point of view.

1. Introduction

Deep eutectic solvents (DESs) are a class of emerging materials commonly formed by a hydrogen (or halogen) bond acceptor (HBA), and a hydrogen (or halogen) bond donor (HBD) which form a eutectic mixture whose melting point is lower than what would be expected if the mixture behaved ideally in the liquid phase, giving rise to the definition of “Deep Eutectic” [1]. Their preparation simplicity (no purification is required), high yield, low-cost, low vapour pressure, and low toxicity make them appealing in many fields, ranging from the organic synthesis (e.g. (bio)catalysis), to industrial or biotechnological applications (e.g. biomasses dissolution and modification, metal processing) [2,3]. Despite the impressive amounts of studies reported in the recent literature on their applications, studies on their thermal stability are often missing. Nonetheless, these studies are fundamental to determine their temperature range of applicability and the safety conditions for their use, which include the identification and the toxicity study on the degradation

compounds. Moreover, thermal degradation studies could furnish interesting information on the DES nanostructures, in some cases still unclear.

In this frame, we report here a comprehensive review on the thermal stability of DESs made with choline chloride (ChCl), one of the most common HBA due to its inexpensiveness, biodegradability and low toxicity. We collected all the data reported to date on ChCl-based DESs thermal stability (Fig. 1), and we propose an applicative plot which can help to choose the correct DES for different applications, based on their degradation temperature. We also proposed a guide for the correct usage of the instruments for thermal analysis, in particular for dynamical thermogravimetry (TGA).

2. Thermal degradation studied by dynamical TGA

Craveiro et al. reported the degradation temperature of a set of natural DESs (NADESs) performed by Differential Scanning Calorimetry (DSC) [7]. Beyond this paper, dynamical TGA (a powerful technique

Abbreviations: ChCl, Choline Chloride; DESs, Deep Eutectic Solvents; DSC, Differential Scanning Calorimetry; FTIR, Fourier Transformed Infra-Red; HBA, hydrogen bond acceptor; HBD, hydrogen bond donor; ILs, Ionic Liquids; MS, Mass Spectrometry; NADESs, natural DESs; TGA, Thermogravimetric Analysis.

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<https://doi.org/10.1016/j.crgsc.2022.100333>

Received 26 May 2022; Received in revised form 20 July 2022; Accepted 24 July 2022

Available online 1 August 2022

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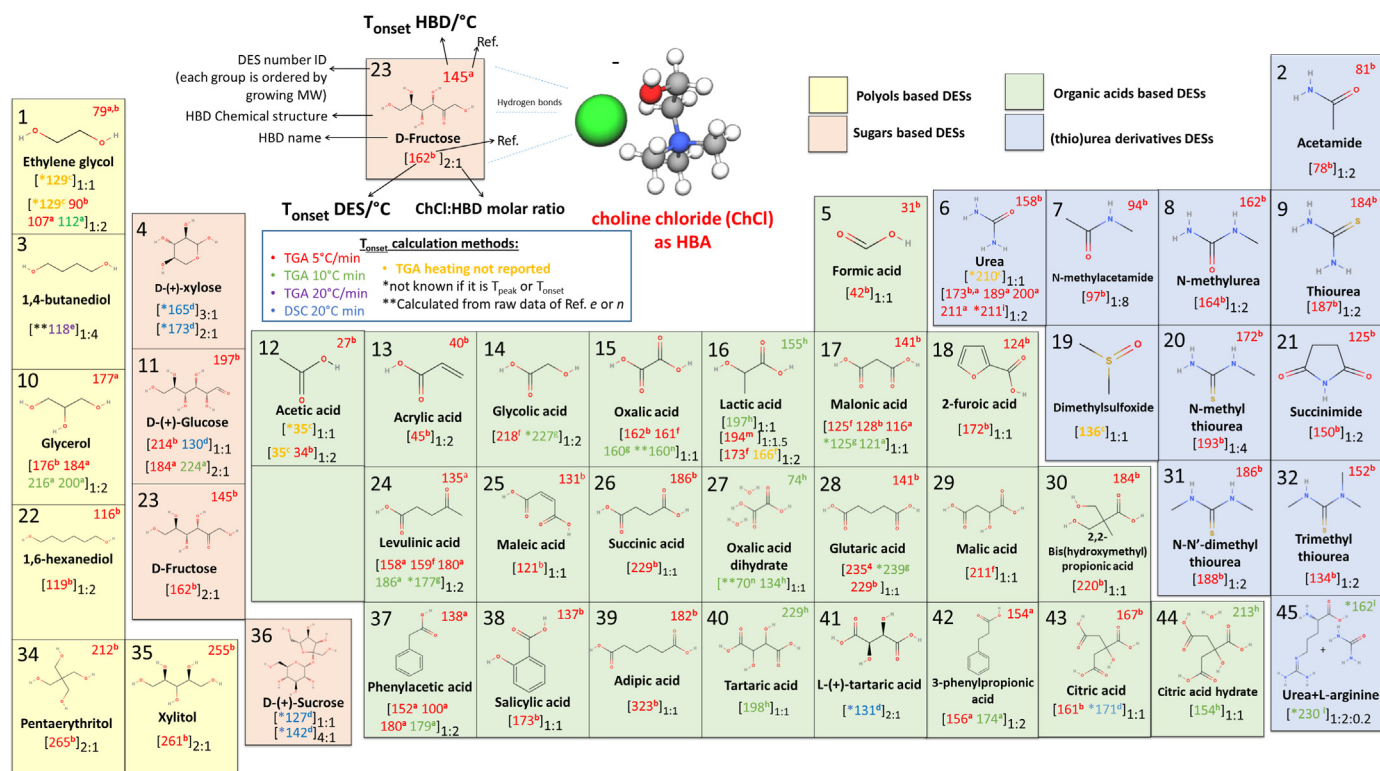


Fig. 1. Chemical structures of DESs discussed in this review, with the onset temperature of the DES degradation and the related HBD reported in the literature. The samples, identified by DES ID number, are ordered in each family group by the growing molar mass of HBD. The T_{onset} data were taken from the references: a: [4]; b: [5]; c: [6]; d: [7]; e: [8]; f: [9]; g: [10]; h: [11]; i: [12]; m: [13] n: [14].

already used to assess the thermal stability of ionic liquids [15,16] is the main technique proposed by the authors to assess the DES thermal stability. Representative thermal profiles obtained for a DES and its precursors (HBD and ChCl) are reported in Fig. 2a.

Fig. 2a highlights that the pure components usually have a sharp mass loss in a narrow temperature range, while many DESs degrade in a larger interval, with the presence of more loss steps in TGA, due to the degradation (or evaporation) of HBD and ChCl in the DES network. The mass

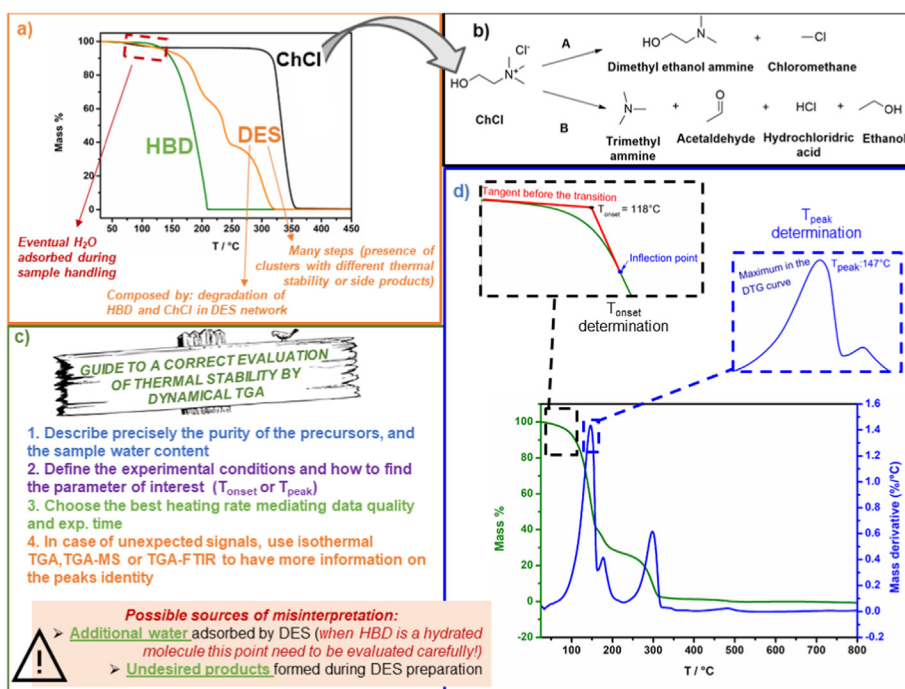


Fig. 2. a) Representative thermogram of a DES and its precursors obtained by dynamical TGA; b) two possible degradation mechanisms of ChCl, proposed by Gonzalez et al. [8] with the first one preferred; c) practical guide for a correct evaluation of DES thermal stability; d) graphical determination of T_{onset} and T_{peak} on a dynamical TGA performed on DES 3 (DES number ID reported in Fig. 1) at 20 °C/min.

loss below 100 °C, visible in many DESs and ChCl, is generally due only to the evaporation of water adsorbed during the DES preparation or handling, due to the strong hygroscopicity of ChCl, unless one of the precursors is also a low-boiling compound. Besides this step, HBDs are usually less thermally stable than ChCl, and DESs display an intermediate behaviour [8]. The thermal profile of DESs could show more steps than the ones shown by the precursors; this behaviour can be explained by the formation of side products during the DES preparation, or by the presence of clusters with slightly different thermal stability, highlighting the complex nature of these compounds.

One of the most relevant parameters obtained by TGA is the onset temperature of sample thermal degradation (T_{onset}), usually calculated in the mass loss curve as the intersection between the baseline and the line passing by the first inflexion point (Fig. 2d) [17]. This temperature determines the operative temperature range in which the samples can be used without decomposing. Alternatively, the T_{peak} (temperature of maximum degradation rate, identified as the temperature corresponding to the peak maximum in the derivative curve, DTG) can be reported.

An extensive collection of the onset temperatures for the thermal degradation of different ChCl-based DESs (and their HBDs) reported to date is shown in Fig. 1. Similar data are reported in the literature for other types of DESs, e.g. phosphonium-based DESs [18], PEGylates DESs [19], or hydrophobic natural DESs [20].

In general, the data reported in the literature for the DES thermal stability may be difficult to compare. First of all, it is important to remember that they depend on the experimental conditions used, e.g., the heating rate, the purity of the starting chemicals, or the water content; these elements are not always controlled during the formation of a new DESs (in particular the water content in the starting chemicals), and sometimes the experimental procedure for the DES preparation and the thermal analysis conditions are not described precisely in the papers. In some cases, authors discuss the samples' thermal stability without defining whether they are considering T_{onset} or the T_{peak} , in other cases, they discuss the T_{onset} , but they calculate it with non-standard procedures.

Another factor that makes the comparison among different literature data difficult is the use of dynamical TGA with various heating rates (5,

10 or 20 °C/min). In principle, it is not wrong to use one rate or another, remembering that different data can be correctly compared when acquired at the same heating rate. However, it is also useful to remember that, since the data are recorded dynamically during the thermal heating scan, a higher heating rate could lead to an over-estimation of the real data (especially for sharp mass losses), thus, the choice of the right speed must be a compromise between a good data quality and a feasible analysis time. We suggest the use of a heating rate of 10 °C/min as a reasonable compromise, aware that the general rule could be changed in specific cases.

Two additional points could lead to a misinterpretation of TGA data: i) as mentioned before, ChCl is highly hygroscopic; thus the samples can absorb water during the handling and the storage, responsible for a mass loss below 100 °C, which could be misinterpreted as the onset of DES thermal degradation; this error can be avoided by the application of an isothermal step at 80 or 100 °C before the thermal scan, when possible, to get rid of the adsorbed water; ii) the occurrence of undesired reactions during the DES preparation could lead to the presence of side products which give unexpected peaks in the DTG curve. In the latter case, to avoid misinterpretations, dynamical TGA can be implemented with the combined use of other techniques, as described in detail in paragraphs 3 and 4. In summary, all these issues need to be evaluated to perform a correct thermal analysis of DESs, as reported in Fig. 2c.

Finally, we collected some data on DES thermal stability in a scatter plot (Fig. 3), useful to compare the operative range of different DESs. More in detail, we reported the T_{onset} of DES and HBD thermal degradation respectively on the ordinate and abscissa axes. We added in the graph the bisector (represented by two lines, accounting for experimental error ± 1 °C), useful to determine at first glance if the DES is more thermally stable than the respective precursor, or vice versa. The plot can also be intended as an application guide, which helps to choose the most suitable DES based on the desired thermal stability.

We noticed that the onset temperature of DES thermal degradation (apart from DES 43, 25, 17, 32, 11 DES 2:1) is comparable to that of the corresponding HBD precursor, and in some cases even higher. In accordance with Wenjun et al. [5], we hypothesize that the presence in the DES nanostructures of a uniform and well-spatially distributed H-bond

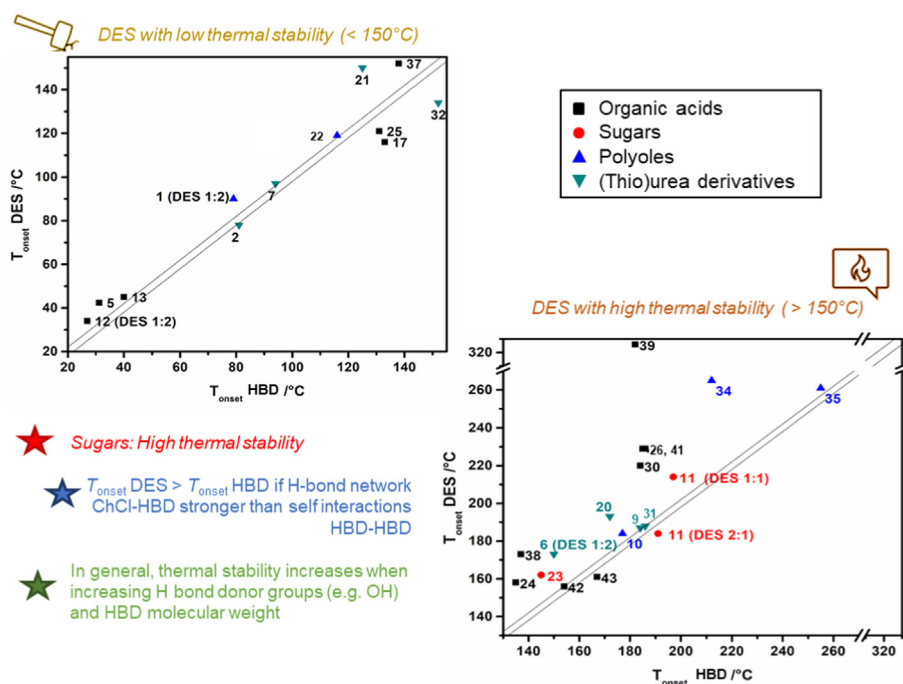


Fig. 3. Application plot for the usage of ChCl-based DESs, based on their thermal stability. DESs are identified with the ID number written in Fig. 1. The onset temperature for thermal degradation of DESs and the precursor HBDs are taken from Fig. 1, choosing the data acquired by dynamical TGA at 5 °C/min.

network (when stronger than that of like-like interactions HBD-HBD), could induce an increase in DES thermal stability.

3. Studies of evolved gas by TGA-FTIR or TGA-MS

The analysis of gases evolved during the DES thermal degradation is important both from a structural point of view, as it furnishes indirect details on DES structure, and from an applicative point of view, to evaluate the emission of harmful substances. Despite the importance of the topic, nowadays only a few studies with this focus have been published. The techniques commonly used to analyze the gases evolved during a thermal scan are FTIR spectroscopy and mass spectrometry (MS), coupled with the TGA unit through a heated transfer line to avoid condensation of gases outside the FTIR or MS device. In this chapter, we briefly summarize the results obtained by TGA-FTIR and TGA-MS analysis on some ChCl-based DESs.

Abbass et al. [6] and Pontillo et al. [13] demonstrated by TGA-MS (i.e. by the identification of the thermal degradation products) that the first part of the thermograms could be attributed to the HBD degradation, while the second part to ChCl degradation. Gonzalez et al. [8] published in 2020 a study on the thermal degradation of some DESs, consisting of choline as HBA and organic acids or polyols as HBD, performed by TGA-FTIR, including the analysis of evolved gases. Firstly, they studied the thermal degradation of pure ChCl, proposing two possible degradation pathways (Fig. 2b), with the first one preferred. They also compared the thermal degradation of the other pure components with that of the corresponding DES. They found out that, generally, pure polyols exhibit evaporation of the entire molecule during the degradation, while they decompose into smaller molecules in DES. This behaviour could indicate a strong bond between ChCl and the polyols in DESs.

4. DES thermal stability studied by isothermal thermogravimetry

Some recent studies [9] showed that dynamical TGA, even at a low heating rate (as 5 °C/min), often leads to an overestimation of the thermal stability, thus isothermal TGA is preferred to obtain more reliable information on the DES maximum operating temperature, useful for industrial applications [5,21,22]. More in detail, isothermal TGA allows

to monitor the percentage of mass loss over time at a chosen temperature, as shown in some examples reported in Fig. 4. This kind of study should be always performed before the use of the DES in new processes, testing its stability at the desired temperature and for the time required. Despite the importance of the topic, only a few studies on the mass loss in isothermal conditions of various DES at different temperatures have been reported to date [4,5,21,23,24].

Isothermal TGA was also applied to obtain additional information on the DES structure and physical-chemical properties. Shahbaz et al. used isothermal TGA to calculate the vapour pressure of five selected DESs, made by three different quaternary salts with either glycerol or urea [25]. They observed the mass loss over time at a fixed temperature and calculated the corresponding vapour pressure through the Langmuir equation. They demonstrated by this method that the DES vapour pressure was effectively lower than those of pure components but higher than the values reported for some common ionic liquids (ILs). Isothermal TGA was also used by Rodriguez et al. as a key technique to demonstrate the occurrence of a partial esterification reaction during the preparation of DES consisting of ChCl and organic acids [9]. This assumption, which explains some incongruences previously found in dynamical TGA measurements on these samples, is nowadays commonly accepted by the scientific community. Overall, we summarize in Fig. 4 the differences between dynamical and isothermal TGA to study the DES thermal degradation and stability, highlighting their potentialities.

5. Conclusions

This short review aims to bring clarity on the correct usage of thermogravimetric techniques in the determination of DES thermal stability. As proof of concepts, we collected the data reported to date on ChCl-based DESs thermal stability, discussing their operative temperature range. The consideration reported could be intended, more in general, as universal guidelines for a correct evaluation of the thermal stability of all the DESs. In particular, we reported that for correct usage of dynamical TGA in evaluating DESs thermal stability is important to: i) describe precisely the purity of the precursors, the sample preparation procedures and their water content; ii) define the TGA experimental conditions and the procedure to calculate the parameter of interest (T_{onset} or T_{peak}); iii)

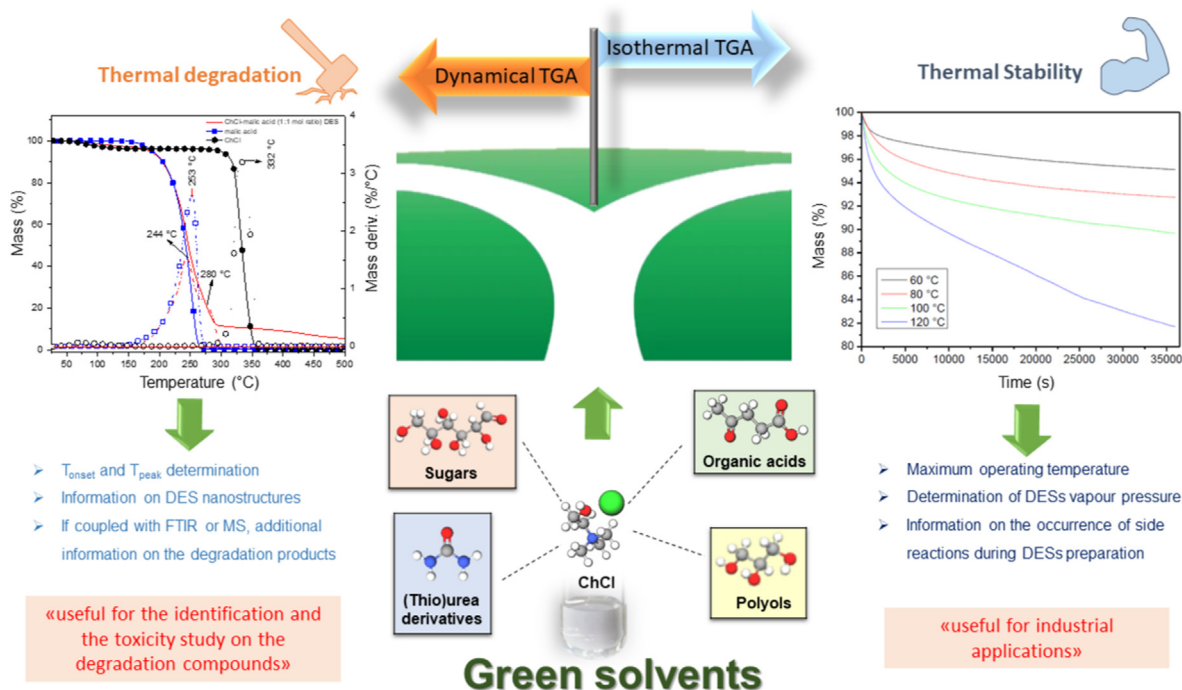


Fig. 4. Summary of the potentialities of dynamical and isothermal TGA in the study of DES thermal degradation and stability.

choose the best heating rate to ensure the best quality of the data obtained in a reasonable experimental time. We also demonstrated that iv) some misinterpretation of dynamical TGA can be avoided by the addition of complementary analysis, such as isothermal TGA, TGA-FTIR or TGA-MS. Overall, we highlight the importance of correct studies on DES thermal stability, which could give information on their range of operating temperature, essential to define their possible applications, and offer insight on their structure from a molecular point of view.

CRedit authorship contribution statement

José González-Rivera: Conceptualization, Methodology, Writing – original draft, Writing – review & editing. **Chiara Pelosi:** Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing. **Elena Pulidori:** Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Celia Duce:** Supervision, Funding acquisition. **Maria Rosaria Tinè:** Supervision. **Gianluca Ciancaleoni:** Supervision, Funding acquisition. **Luca Bernazzani:** Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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