





# Evaluating the thermal stability of chemicals and systems: A review

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## Abstract

In the realm of chemical processing, particularly at the industrial scale, safety is of utmost importance. A predominant factor causing accidents within the chemical industry is runaway phenomena, primarily initiated by uncontrolled exothermic reactions. This review critically examines the often-overlooked decomposition mechanisms as a significant contributor to thermal energy release, necessitating a comprehensive revision and understanding of both experimental and theoretical strategies for assessing thermal degradation. Key to this discourse is the explication of calorimetry as the principal experimental technique, alongside ab initio quantum chemistry simulations as a robust theoretical framework for quantifying the most relevant properties. However, more than mere cognisance of these methodologies is required for a meticulous thermal stability assessment. The review emphasizes identifying and quantifying fundamental parameters through experimental and theoretical investigations. Only upon acquiring these parameters, including kinetic, thermodynamic, onset, and peak characteristics of the exothermic decomposition reactions, can one effectively mitigate risks and hazards in designing and optimizing chemical processes and apparatus. Furthermore, this review delineates qualitative and quantitative methodologies for hazard assessment, proffering strategies for estimating safe operational conditions and sizing relief devices. The paper culminates in exploring future trajectories in thermal stability assessments, focusing on emerging applications in lithium-ion batteries, electrolyzers, electrified reactors, ionic liquids, artificial intelligence and machine learning approaches. Thus, the paper underlines the evolving landscape of thermal risk management in contemporary and future chemical industries.

## KEYWORDS

exothermic reactions, process safety, stability assessment, thermal phenomena

## 1 | INTRODUCTION

Introducing alternative industrial solutions and emerging technologies requires a proper hazard assessment to ensure the sustainability, safety, and social acceptability of the proposed strategies.<sup>[1]</sup> However, structured and

simplified assessments to study hazards and operability problems rely on information about the thermal stability of handled materials.<sup>[2]</sup> In safety science, the term thermal stability refers to the ability of a substance to resist undesirable side reactions when handled under operative conditions.<sup>[3]</sup> For this reason, the thermal stability

assessment is critical to ensuring safety in the process industry, where hazardous chemicals are present in large quantities, to prevent accidents and granting reliable operations.<sup>[4]</sup> For instance, runaway phenomena could arise if a compound can undergo an uncontrolled exothermic reaction.<sup>[5]</sup> Because of a thermal runaway, gaseous products can be generated, which, in turn, cause a pressurization of the system in which the phenomenon occurs, with the possibility of devastating explosions.

Thermal decomposition is an example of an unexpected exothermic side reaction during process or storage activities.<sup>[6]</sup> Being in all aspects a chemical reaction, the physicochemical nature of a particular decomposition reaction can be described from a thermodynamic and kinetic perspective. Reaction thermodynamics is related to quantifying the enthalpy variation associated with the transformation,<sup>[7]</sup> whereas reaction kinetic studies are related to the dynamic of the response itself.<sup>[8]</sup> From a general thermodynamic perspective, a thermal decomposition reaction is typically an exothermic unimolecular chemical transformation that determines a breakdown in the chemical structure of a molecule, with collateral production of heat and side-products, typically gaseous.<sup>[9]</sup> Kinetically speaking, a substance constantly undergoes thermal decomposition in all ranges of temperature, with a reaction rate that always depends on the temperature of the system and the concentration of the species involved in the reaction. It is expected to model the dependence on the temperature of the reaction with an Arrhenius-like expression.<sup>[10]</sup> In contrast, the dependence on the species' concentration is based on a power law relationship.<sup>[11]</sup> The possibility of observing decomposition mechanisms that exhibit a particular reliance on species' concentration is remarkable: the so-called autocatalytic reactions.<sup>[12]</sup> More specifically, the reaction rate typically depends only on the reactant concentration involved in the chemical reaction. On the other hand, in an autocatalytic transformation, the reaction rate depends also on the concentration of products.<sup>[13]</sup> This means that the reaction rate accelerates during its development; hence, the product acts like a catalyst, a promoter of the reaction.<sup>[14,15]</sup> Hence, the occurrence of an auto-catalytic mechanism must be carefully evaluated to avoid unsafe scenarios of a rapid generation of thermal energy that could trigger runaway conditions. Another specific feature in the framework of thermal degradations is the definition of an onset temperature ( $T_{\text{onset}}$ ). The concept of the  $T_{\text{onset}}$  has mainly a technical meaning. It is defined as the temperature at which the heat generated by a chemical reaction cannot be entirely withdrawn from the reactive system. This results in a detectable increase in temperature. The calculation of the  $T_{\text{onset}}$  depends on several factors, such as the size of the vessel, cooling, flow, and agitation characteristics,

the sensitivity of the instrument used for detection and reaction kinetics and thermodynamics.<sup>[16]</sup> For example, if a calorimetric experiment is carried out in an ideal adiabatic system, the onset temperature would be the initial temperature of the experiment. However, no onset temperature can be measured if the heat losses are too high due to geometric or operational factors. Despite this,  $T_{\text{onset}}$  is widely used as a reference value to prevent the decomposition rate from becoming too high and generating a large amount of heat, which could cause runaway scenarios.

Thus, since an exothermic decomposition reaction affects the safety of a chemical process and plant due to the risk of enabling runaway conditions, at least the thermodynamic, kinetic and onset characteristics must be assessed to support both the design and optimisation of processes, equipment, control, and safety systems.

Figure 1 reports a non-exhaustive list of the main functional groups prone to exothermic thermal degradations.

Different methodologies could be used to perform a thermal stability assessment. Traditionally, the most reliable procedure is based on empirical analysis, like calorimetry.<sup>[17]</sup> With calorimetric analysis, it is possible to determine the kinetic,<sup>[18]</sup> thermodynamic,<sup>[19]</sup> onset,<sup>[20]</sup> and peak<sup>[21]</sup> features of a reaction directly. Table 1 reports the main quantities useful for a thermal stability assessment and briefly describes their utility.

However, the apparent reaction pathway is studied during calorimetry, and the information linked to the detailed reaction mechanics is not achievable. Especially in the last 30 years, theoretical modelling has also gained more and more attention due to the possibility of obtaining in-depth information related to reaction mechanics and dynamics.<sup>[22]</sup> Theoretical thermal stability analysis is mainly based on ab initio quantum chemistry methods,<sup>[23]</sup> even if molecular dynamics<sup>[24]</sup> and statistical mechanics-based theories<sup>[25]</sup> could also be involved. Focusing on ab initio methodologies, they can provide detailed information related to the decomposition mechanism<sup>[26]</sup> and the single reaction's kinetic<sup>[27]</sup> and thermodynamic<sup>[28]</sup> data. Nevertheless, the intrinsic reaction information obtained with a theoretical approach is not applicable straightforwardly. Thus, theoretical modelling strategies are practically non-used for safety purposes unless combined with apparent experimental data.<sup>[29]</sup> On the one hand, data acquired via a calorimetric analysis can be quickly involved in hazard assessment and risk analysis. Meanwhile, intrinsic reaction information can give the safety analyst an in-depth knowledge of the reaction mechanics and a form of validation of the experimental data.<sup>[30,31]</sup>

Once an experimental or theoretical analysis has been performed, the thermal stability assessment still needs to

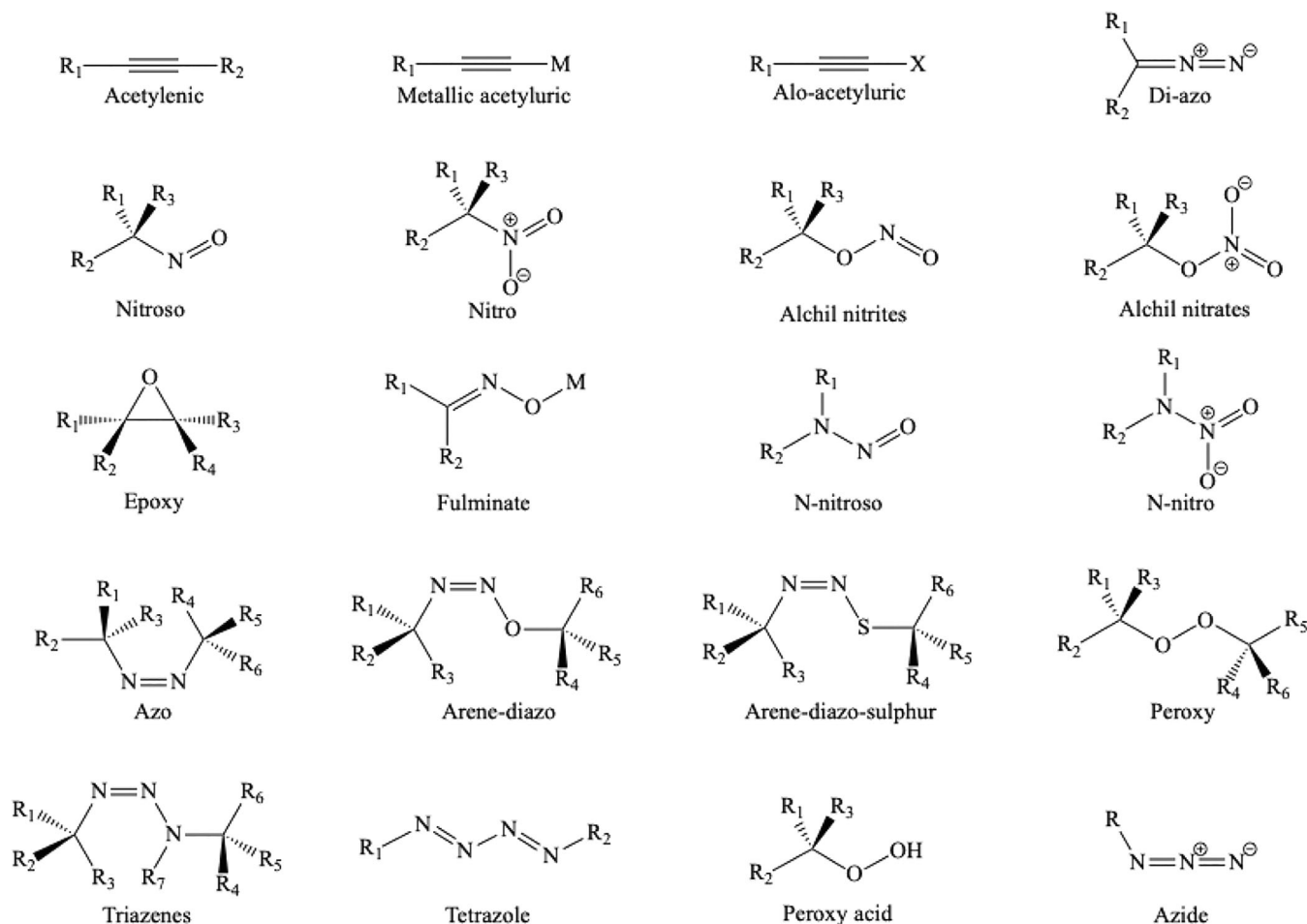


FIGURE 1 Functional groups prone to violent thermal decompositions.

be finished, elaborating the retrieved information to find safe operative conditions for process optimization and design, decision-making, and equipment and relief systems design. For instance, starting from the onset temperature of the decomposition reaction determined through calorimetry, it is possible to define a plausible process temperature.<sup>[32]</sup> Again, using a risk matrix or indexes,<sup>[33]</sup> it is possible to rank processes depending on their inherent risk of runaway induced by exothermic reactions, orienting decision-making and process design toward the safer and most reliable solution. Using the Design Institute for Emergency Relief Systems (DIERS) methodology,<sup>[34]</sup> it is possible to adopt experimental data to design relief systems to avoid explosions induced by uncontrolled exothermic reactions. Regarding process optimization and equipment design, the physicochemical information retrieved with experimental or modelled could be implemented in constructing a sensitivity-based stability diagram.<sup>[35]</sup>

Under these premises, this mini review aims to summarize the main experimental and theoretical techniques applicable in the thermal stability assessment

of hazardous chemicals prone to exothermic reactions. A particular focus on calorimetric and quantum chemistry methods will be given to the reader. Then, the main quantities obtainable through the experiments or modelling techniques will be presented. Specifically, kinetic, thermodynamic, onset, and peak features will be the quantities of interest when assessing materials' thermal stability. In addition, how to involve the retrieved quantities for a process safety-oriented thermal stability assessment will be elucidated. Eventually, emerging applications in the chemical industry will be examined, analyzing the need for detailed thermal evaluations to enhance process safety. The present work is not intended to provide a detailed picture of only experimental and theoretical techniques for thermal stability assessment, nor to address the topic of gaseous phases calorimetry extensively, but rather to structure and discuss a systematic approach to present, retrieve and use experimental or theoretical data to assess the stability of systems. The term system is not only limited to chemical reactors but also refers to new processes, emerging technologies, and innovative materials in the broadest sense. This perspective differentiates the present work from

**TABLE 1** Primary quantities of interest in the thermal stability assessment. Onset variables/parameters can be multiple in a system and related to a specific exothermic reaction.

Class of variables/parameters	Name	Application
Kinetic	Activation energy	Kinetic simulation, stability diagrams, evaluation of hazard and risk indexes.
	Arrhenius pre-exponential factor	
	Reaction order	
Thermodynamic	Heat of reaction	
Onset	Onset temperature(s)	Stability diagram, identification of inherent safe operating windows.
	Onset time(s)	
	Onset pressure(s)	
Peak	Maximum temperature	Design of equipment and safety devices.
	Maximum temperature rise rate	
	Maximum pressure rise rate	

others, which can be more oriented toward detailed specific stability-related features or systems. For instance, Yang et al.<sup>[36]</sup> and Kummer and Varga<sup>[37]</sup> particularly emphasized a discussion related to the review of the reactor runaway detection criteria. Other works of Yang et al.<sup>[38–40]</sup> specifically focused only on polymerization process safety. Huang et al.<sup>[41]</sup> and Archer and Schultz<sup>[42]</sup> discussed non-canonical calorimetric approaches like cone calorimetry and titration calorimetry, respectively, or again Liu,<sup>[43]</sup> Xu et al.,<sup>[44]</sup> and Hou et al.<sup>[45]</sup> have particularly investigated energetic materials and lithium-ion batteries (LIB). It is important to address the complexities of assessing the thermal stability of chemicals and systems. Therefore, it is necessary to adopt a broader framework instead of having a singular discussion on the topic. To ensure safety in laboratory and industrial frameworks, it is essential to have proficiency in specific skills and follow established protocols. A cohesive understanding of all aspects involved, including experimental and theoretical modelling, is necessary, as well as an awareness of available tools for data application. This is crucial for preventing potential risk scenarios. Therefore, a holistic approach is crucial to enhance safety measures and effectively validate research findings.

Figure 2 shows a map reporting the main keywords linked to thermal stability. 7345 articles related to the

chemical engineering category of Web of Science<sup>[46]</sup> have been used as a data set elaborated by the VOS viewer software.<sup>[47]</sup> The same colour has been assigned to keywords in the articles in five main thematic clusters. The obtained bibliometric network can be considered as a tool for a topic-oriented literature analysis, focusing on the primary research trends of a specific argument, avoiding leaving unreviewed characteristic aspects of a particular topic.

## 2 | EXPERIMENTAL STUDIES

Calorimetry is the most used and developed experimental strategy to assess the thermal stability of materials.<sup>[48]</sup> Indeed, a calorimetric study involves the measurement of heat exchanges between a sample and its surroundings associated with chemical or physical processes. In this way, valuable insights can be gained into the investigated substances' thermodynamic, kinetic, and safety properties.<sup>[49]</sup> More specifically, calorimetry is part of a broader family of methodologies named thermal analysis, aimed at measuring the behaviour of the physicochemical properties of a substance as a function of time or temperature, subjecting samples to a controlled thermal treatment.<sup>[50]</sup> Figure 3 reports the word cloud representation of the various calorimetric approaches developed over the years, classifiable based on how the heat is exchanged with the sample, considering the thermodynamical behaviour of the system itself or depending on the measured variation of a sample's particular properties.

Considering how heat is exchanged with the sample, calorimetric techniques can be categorized as isothermal (IC) and accelerated temperature rate (ARC) calorimetry.<sup>[51]</sup> Regarding the thermodynamic behaviour of the system, it is possible to distinguish reaction (RC) and adiabatic calorimetry (AC). Depending on the variation in the measured sample's properties, it is possible to classify the calorimetric experiments with canonical names. If the variation of heat flow ( $Q$ ) versus temperature ( $T$ ) or time ( $t$ ) is measured, a differential scanning calorimetry (DSC) is performed.<sup>[52,53]</sup> If, instead, the variation of temperature and pressure ( $P$ ) related to time ( $t$ ) has been measured, an ARC has been accomplished. Whereas if the sample's weight ( $m$ ) concerning  $T$  or  $t$  is recorded, a thermogravimetric analysis (TGA) is executed.<sup>[54,55]</sup> For clarity, the principal attributes of each different calorimetric approach are briefly summarized in Table 2, whereas further details will be given in the following subsections. On the contrary, Table 3 reports the strengths and weaknesses of each considered calorimetric technique. It should be noted that in this work, the terms IC, ARC, AC, DSC, and TGA refer to types of instruments and not to specific instrument brands.

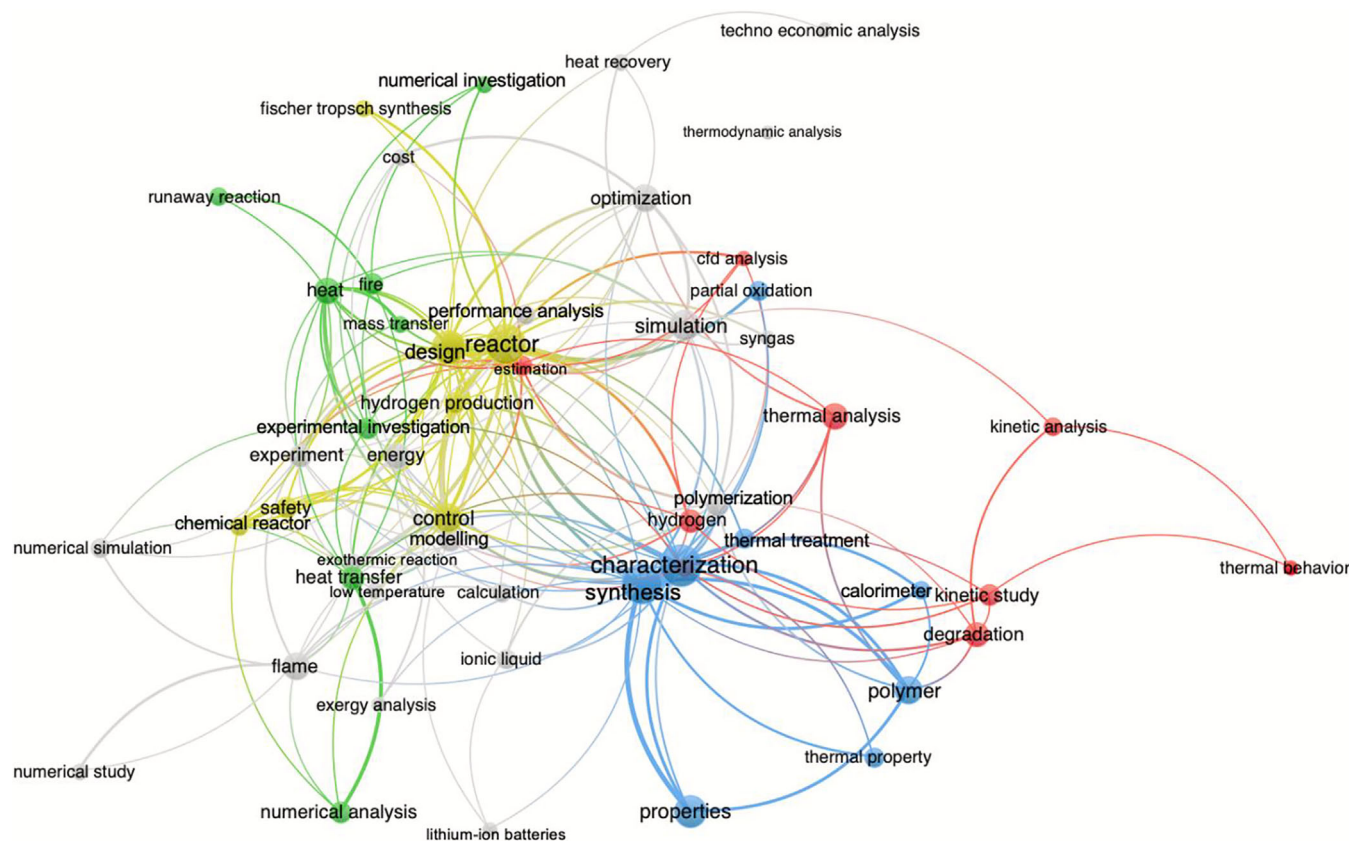


FIGURE 2 The bibliometric network of the main topics related to thermal stability assessment (VOS viewer). cfd, computational fluid dynamics.

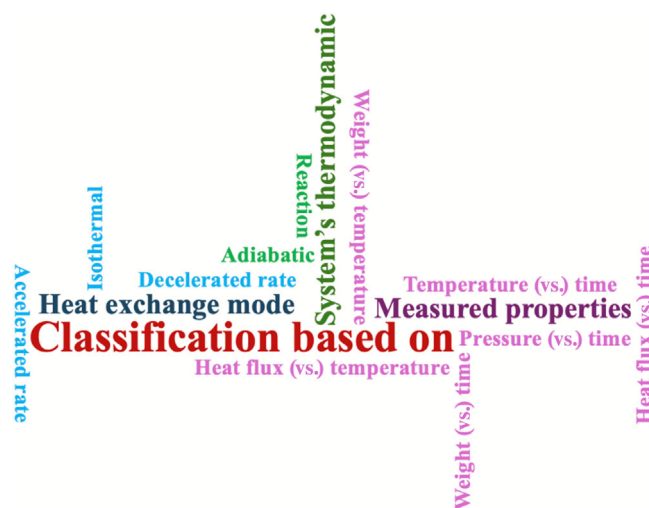


FIGURE 3 Word cloud representation of the various calorimetric approaches.

## 2.1 | Isothermal (IC) and accelerating rate calorimetry (ARC)

During an IC, the sample is kept at a constant temperature for a defined amount of time, defined as waiting time ( $wt$ ), and during which the behaviour of the sample is recorded.

The temperature is further increased or decreased once the  $wt$  has elapsed. Once the desired temperature is reached, the instrument switches to isothermal mode, keeping the sample's temperature constant again and always recording the system behaviour. Since isothermal analysis avoids the dynamic effect of continuous temperature variation over time, the sample is as close as possible to the thermodynamic equilibrium. However, a substantial limitation of the IC is the length of the experimental procedures since several runs are required to retrieve a sufficiently complete information set. Despite its limitations, the IC can still be used to determine thermodynamic and kinetic parameters for an autocatalytic decomposition reaction.<sup>[56]</sup> Eventually, regarding the sample volume used during an analysis, the reference value can vary depending on the type of equipment used, ranging from the reference value of an adiabatic calorimeter to the one of a reaction calorimeter.

Regarding ARC as an instrument typology, the sample is constantly heated by an oven,<sup>[57]</sup> continuously recording data.<sup>[58]</sup> The typical volume of an ARC cell test is around 10 mL, whereas a sample volume of 1 mL is commonly analyzed.<sup>[59]</sup> Even if ARC is, in principle, less precise and accurate than IC, it is also true that with data analysis, the data acquired can be corrected to reproduce

TABLE 2 Principle of operation and main applications of different calorimetric strategies.

Calorimetric strategy	Working principle	Common applications
Isothermal calorimetry (IC)	Measures the heat released or absorbed by a sample at a constant temperature. The reaction or process occurs isothermally, and the heat flow is monitored over time.	Detailed evaluations of reaction kinetics and thermodynamics under conditions close to the thermodynamic equilibrium.
Accelerated temperature rate calorimetry (ARC)	Temperature and pressure profiles are measured over time. During experiments, a heating or cooling rate is imposed on the sample. Results can be corrected to reproduce adiabatic conditions.	Primary tool for assessing kinetic, thermodynamic, and safety characteristics of hazardous substances.
Reaction calorimetry (RC)	Monitors the heat flow associated with chemical reactions. It can be conducted under isothermal or non-isothermal conditions. Experiments are performed in bench- or pilot-scale reactors to reproduce industrial conditions closely.	Widely used in the chemical and pharmaceutical industries to understand reaction kinetics, scaling up processes, and safety analysis.
Adiabatic calorimetry (AC)	Measures the heat exchange within a system thermally isolated from its surroundings. In alternative, temperature and pressure profiles over time can be quantified. It simulates worst-case scenarios in process safety, where no heat is lost to the environment.	Hazard evaluation, particularly in the chemical industry, investigation of exothermic decompositions, runaway reactions, and other safety-related phenomena.
Differential scanning calorimetry (DSC)	Measures the heat flow into or out of a sample compared to a reference under controlled heating or cooling. This allows for detecting transitions such as melting, crystallization, and glass transitions.	Material characterization in polymers, pharmaceuticals, food, and other materials science applications. It is used to study thermal transitions, oxidation stability, and purity.
Thermogravimetric analysis (TGA)	Monitors the change in weight of a sample as a function of temperature or time under a controlled atmosphere. Weight loss is due to chemical reactions, like decomposition or oxidation, that form volatiles.	Material characterization, particularly for determining composition, thermal stability, and moisture content. Common in polymers, pharmaceuticals, and inorganic materials.

isothermal conditions as closely as possible. In addition, some of the most advanced instruments able to perform ARC can also do IC to verify the experimental outcomes further. The strength of ARC is related to the possibility of expressing the experimental results in the form of temperature and pressure profiles as a function of time or temperature.<sup>[60]</sup> Thermodynamic and reaction kinetic parameters, onset and maximum temperature and pressure, and temperature and pressure rates can be assessed during test runs. Onset, maximum and rates data sets can be considered paramount safety parameters fundamental to assessing safety operative conditions and relief system design procedures. For these reasons, ARC is regarded as the most complete calorimetric analysis of data obtained during a single test run. The only limitations of the ARC are related to data analysis since kinetic and thermodynamic information can be obtained with a non-trivial methodological interpretation of the experimental temperature profiles. Eventually, with the ARC, it is also possible to assess the main characteristics of an autocatalytic decomposition reaction.<sup>[14,61]</sup>

## 2.2 | Reaction calorimetry (RC) and adiabatic calorimetry (AC)

It is possible to refer to RC when the analysis aims to simulate the behaviour of actual industrial equipment closely.<sup>[62]</sup> For this reason, experiments are performed in a scale-down system on a bench or pilot scale, focusing on quantifying the heat evolved and the rate of heat evolution under desired reaction conditions.<sup>[63]</sup> The RC is essential for the synthesis hazard analysis. It evaluates the safety limitations of chemical processes using a technical setup that closely resembles the full-scale application. This analysis is crucial in ensuring the safety of the chemical processes involved. Depending on the reactor size involved during the analysis, the order of magnitude of the samples' volume could vary from 0.01 to 100 L.<sup>[64]</sup> This information can be retrieved by elaborating experimental data sets, typically expressed as temperature and pressure as a function of time. Under this perspective, it is possible to classify RC further depending on the imposed reaction conditions, generally isothermal

TABLE 3 Strengths and weaknesses of different calorimetric strategies.

		CALORIMETRIC STRATEGY					
		IC	ARC	RC	AC	DSC	TGA
Strengths	Instrument's response close to the thermodynamic equilibrium	X					
	Possibility to perform also IC test		X	X			
	Experimental outcomes correction to remove the effect of instrument heat capacity		X		X	X	X
	Complete safety data set retrievable with a reduced number of test runs		X	X	X		
	Ability to reproduce industrial conditions closely			X			
	Analysis performed in instruments aimed to reproduce real reactors			X			
	Large amount of sample analyzed			X			
	Direct quantification of heat effects					X	
	Direct quantification of sample mass evolution for kinetic analysis						X
	Possibility to detect autocatalytic reactions	X	X	X	X	X	X
Possibility to stir the sample			X	X			
Weaknesses	Long duration of an experimental campaign	X		X			
	Large number of runs required to obtain a complete safety data set	X					
	No stirring of the sample	X	X			X	X
	Limited amount of sample analyzed	X	X			X	X
	Strong dependency on data analysis		X	X			
	High waste of sample per analysis run			X			
	High hazards linked to large-scale runaway scenarios			X			
	Necessity to perform preliminary tests before the intended analysis			X			
	High costs of instrumentation			X			
	Low versatility of a single apparatus			X			
Complete set of safety information not determinable					X	X	

Abbreviations: AC, adiabatic calorimetry; ARC, accelerated temperature rate calorimetry; DSC, differential scanning calorimetry; IC, isothermal calorimetry; RC, reaction calorimetry; TGA, thermogravimetric analysis.

(constant reaction temperature), isoperibolic (constant coiling or heating side temperature),<sup>[65]</sup> or general (variable reaction and service side temperature). Of course, RC can be performed in different types of equipment, depending on the kind of fluid dynamic condition that is wanted to be emulated, like stirred vessels,<sup>[66]</sup> tubular reactors,<sup>[67,68]</sup> and jet-stirred reactors.<sup>[69,70]</sup> Stirred vessels are involved when the heat generated by the reaction must be well dispersed from the reacting systems when mass transfer limitations are present or to examine a low potentiality system (i.e., for batch processes). Tubular reactors are usually involved in gas/gas reacting mixtures or when a fixed catalyst bed is

involved. Eventually, jet-stirred reactors are adopted for gas-phase reactions, especially in the case of oxygenations.

In AC, the goal is to measure the temperature, pressure, and rate of temperature and pressure variations during time as a direct consequence of the observed thermal phenomena without any effect induced by heat transports.<sup>[71]</sup> Depending on the experimental setup involved in the campaign, adiabatic calorimeters can be provided by a stirring system to limit the impact of heat and mass transport phenomena on the experimental outcomes. Specifically, the stirrer is typically needed for samples with a volume greater than 50 mL to avoid misleading conclusions,<sup>[49]</sup> and the order of magnitude of

the samples' volume could vary from approximately 1 to 100 mL.<sup>[72–74]</sup> It is possible to use AC to evaluate the decomposition features of autocatalytic decompositions.<sup>[13]</sup> Eventually, to refine the experimental outcomes, it is common practice to correct the data considering the amount of heat absorbed by the test cell and the effect of the presence of the instrument's cell on the experimental results.<sup>[75]</sup>

## 2.3 | Differential scanning calorimetry (DSC)

Heat fluxes are measured as a function of time or temperature during a DSC.<sup>[76]</sup> To perform these measurements, a reference is needed since heat fluxes are associated with energy variations and not with absolute energy values. Indeed, by thermally stressing the reference (typically the empty cell of the instrument) in the same way as the sample, it is possible to record both responses to the same external input to generate a differential measure. An advantage of the DSC is that it requires a reduced sample quantity for analysis.<sup>[77]</sup> Indeed, the typical sample volume analyzed during a DSC run is about 1 mL for liquids<sup>[78]</sup> or 1–2 mg for solids.<sup>[79]</sup> However, using a reduced sample size, weak-endothemic or exothermic peaks are challenging to determine. A limitation of the DSC is the liquid sample's analysis under unstirred conditions, limiting mass and heat transport phenomena.<sup>[80]</sup> There are other limitations to the DSC technique. One of them is that the reactions being assessed occur in a closed, non-ideal adiabatic environment.<sup>[81]</sup> Additionally, the calibration procedure used significantly impacts the results obtained.<sup>[82]</sup> Even with post-processing analysis, correcting for the influence of non-adiabaticity is possible, but if the system is not calibrated correctly, the experimental outcomes are dramatically altered.

By elaborating data acquired during a DSC analysis, it is possible to assess a phenomenon's thermodynamic, kinetic, and onset features. From a thermodynamic perspective, it is possible to quantify the enthalpy variation occurring during an observed phenomenon<sup>[83]</sup> and a sample's constant pressure heat capacity.<sup>[84]</sup> From a reaction kinetic perspective, it is possible to assess activation energies,<sup>[85]</sup> Arrhenius pre-exponential factor,<sup>[86]</sup> and reaction orders<sup>[87]</sup> once an expression for the reaction rate is provided.<sup>[88]</sup> In addition, the onset temperature can be determined based on the temperature at which a particular phenomenon occurs,<sup>[89]</sup> defining the onset temperature as the point of a generic plot obtained by calorimetric analysis at which the obtained data deviates from a reference baseline.<sup>[90]</sup> Different determination techniques can be used since this point could be hard to identify in practice.<sup>[91]</sup>

It is important to mention the process of autocatalytic decomposition. For this type of decomposition, information about the reaction kinetics is obtained through isothermal experiments,<sup>[92]</sup> fitting the general reaction rate expression of the autocatalytic decomposition.<sup>[93]</sup> Calorimeters performing isothermal measurements can be used to assess the kinetic and thermodynamic features of autocatalytic decomposition mechanisms.<sup>[94]</sup>

## 2.4 | Thermogravimetric analysis (TGA)

The TGA is one of the most popular calorimetric analyses with the DSC. The TGA is an experimental technique that records the sample's mass variation over time when subjected to a constant heating rate. As reported in the literature, the optimal range of samples' volume is 50–500  $\mu\text{L}$ .<sup>[95]</sup> Compared to the DSC analysis, TGA can provide a more limited amount of physicochemical information. If a decomposition reaction is considered, for instance, with a TGA, it is possible to determine reaction kinetics<sup>[96]</sup> and onset features<sup>[97]</sup> but not thermodynamics data related to the reaction enthalpy.<sup>[98]</sup> For this reason, in literature, DSC and TGA have often been coupled with each other.<sup>[99]</sup> On the one hand, with TGA, reaction kinetics data are obtained from the time profile of mass variation and the onset temperature. Then, with DSC, thermodynamic information can be retrieved, and reaction kinetics and the onset temperature can be further verified. With the TGA, it is possible to evaluate the information related to autocatalytic phenomena.<sup>[100]</sup>

## 2.5 | Coupled experiments for in-deep knowledge

The possibility of coupling different calorimetric approaches, like TGA and DSC<sup>[64]</sup> and different experimental and analytical techniques is remarkable. Indeed, during an experimental campaign aimed to analyze decomposition reaction features, it is common practice to couple calorimetric with analytical techniques to study the gaseous product or liquid residue produced during the reaction. Regarding the analysis of gaseous products, the involved methods are gas chromatography (GC),<sup>[101]</sup> Fourier-transform infrared (FTIR),<sup>[102]</sup> and mass spectrometry (MS).<sup>[103]</sup> Sometimes, the analysis of the decomposition products in the liquid phase is also performed with high-precision liquid chromatography (HPLC)<sup>[104]</sup> or with nuclear magnetic resonance (NMR).<sup>[105]</sup> In this way, it is possible to collect information related to reaction kinetics, thermodynamics, onset, and maximum features and determine an expression for the apparent decomposition reaction.



### 3 | THEORETICAL APPROACHES

Theoretical approaches can represent complementary tools to experiments.<sup>[106]</sup> While experimental studies focus on the model of apparent reaction features,<sup>[107]</sup> with theoretical modelling, it is possible to assess intrinsic reaction characteristics.<sup>[108]</sup> These theoretical studies are mainly based on ab initio quantum chemistry strategies. Moreover, molecular dynamics simulations<sup>[109]</sup> or statistical mechanics theories<sup>[110]</sup> can be considered alternatives. From a practical perspective, quantum chemistry methodologies must be preferred to molecular dynamics and statistical mechanics when modelling the decomposition reaction. Indeed, with ab initio methods, it is possible to directly retrieve each network reaction's reaction mechanism and kinetic and thermodynamic data.<sup>[111]</sup> In this way, ab initio methods can be seen as complementary to calorimetric experimental analysis, used to achieve a broader view of the reaction dynamic. In addition, with experimental procedures, the information obtained with a quantum chemistry simulation can be easily verified to prove the reliability of the modelling techniques.<sup>[112]</sup> Thus, in Section 3, the attention will be focused on ab initio-based strategies.

Ab initio quantum chemistry-based methods can model reaction mechanisms, kinetics, and thermodynamics using the first principles of quantum mechanics applied to chemistry.<sup>[113]</sup> Knowing reaction mechanisms makes it possible to understand the single chemical reactions that undergo an observed chemical phenomenon.<sup>[114]</sup> Typically, quantum chemistry calculations are based on the non-relativistic steady-state formulation of the Schrodinger equation.<sup>[115]</sup> The obtained outcomes are mainly limited, for example, by the extension of the basis set function involved in the simulation,<sup>[116]</sup> on the approximation of the Hamiltonian operator,<sup>[117]</sup> on the theory involved in the reaction rate calculations,<sup>[118]</sup> and on the strategies implemented for the solution of the Schrodinger equation.<sup>[116]</sup> However, the onset and peak features of the decomposition reaction can only be determined indirectly by simulating the system using the kinetic and thermodynamic data acquired theoretically or by dedicated calorimetric experiments. The advantage of the theoretical techniques is related to the detailed description of the intrinsic reaction mechanism and the ability to analyze decomposition phenomena at extremely high temperatures, which are unreachable by conventional calorimetric apparatus. Typically, calorimetric analysis can reach a maximum experimental temperature of 800°C.<sup>[119]</sup> When the theoretical campaign is performed to explore higher temperature ranges, shock tube experiments can be

performed to validate results.<sup>[120]</sup> Further details on the configuration of a shock tube can be retrieved in the literature.<sup>[121,122]</sup>

An example of the application of ab initio quantum chemical methodology to decomposition dynamics and mechanics can be retrieved in the work of Pio et al.<sup>[123]</sup> Here, a reaction network for the decomposition of hydroxylamine has been presented. For each chemical reaction involved in the mechanism, a detailed evaluation of the response kinetic in terms of activation energy, Arrhenius pre-exponential factor and reaction order was performed. Further information will be related to the reaction enthalpy, like in the work of Honorien et al.<sup>[124]</sup> By doing so, the system could be simulated numerically, determining the onset and peak features of the material and completing the set of safety quantities required for a thermal stability assessment. Other examples of quantum chemistry calculations applied to decomposition mechanisms are due to Wang et al.<sup>[125]</sup> and Huang et al.<sup>[126]</sup> On the contrary, Legg et al.,<sup>[127]</sup> Altarawneh et al.,<sup>[128]</sup> Wang et al.,<sup>[129]</sup> and Sundar et al.<sup>[130]</sup> focused both on mechanistic and kinetic modelling of decomposition reactions, whereas Notario et al.<sup>[131]</sup> have also given further insights on reaction thermodynamic. Finally, in Figure 4, the general workflow of the ab initio methodology applied to thermal stability assessment is presented.

Integrating ab initio quantum chemistry and machine learning (ML) is an innovative way of understanding and predicting thermal decomposition reactions.<sup>[132]</sup> Ab initio strategies offer a rigorous framework for simulating molecular structures and energetics, providing valuable insights into reaction mechanisms at the atomic level.<sup>[133]</sup> However, these simulations can be computationally intensive, which limits their use for complex systems. ML algorithms address this challenge by using the insights gained from ab initio calculations to develop predictive models that can rapidly and accurately estimate reaction pathways, kinetics, and thermodynamics.<sup>[134,135]</sup> ML models can capture the intricate relationships between molecular structures and reaction outcomes by training on vast datasets generated from quantum mechanical simulations.<sup>[136]</sup> This approach enables the exploration of reaction landscapes with unprecedented speed and accuracy, paving the way for designing more efficient catalysts, discovering novel materials, and optimizing chemical processes.<sup>[137,138]</sup> Nevertheless, integrating ab initio quantum chemistry with ML has limitations. One significant challenge is the availability and quality of training data.<sup>[139]</sup> Quantum calculations are computationally demanding, often restricting the size and diversity of the datasets used to train ML models. As a result, these models may need help to generalize to new chemical environments or reaction conditions beyond those represented in the training data.<sup>[140]</sup>

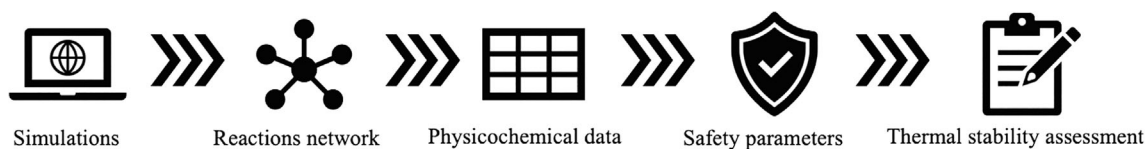


FIGURE 4 Workflow of the experimental analysis applied to the field of thermal stability assessment.

Additionally, the inherent complexity of chemical reactions, including transient intermediates and multiple competing pathways, poses challenges for accurate prediction by ML algorithms.<sup>[141]</sup> Moreover, the interpretability of ML models trained on quantum chemistry data remains a concern, as understanding the underlying physical principles driving the predictions is crucial for gaining insights into reaction mechanisms.<sup>[142]</sup> Overcoming these limitations requires innovative approaches to data generation, model development, validation, and continued collaboration between researchers in quantum chemistry and ML.

## 4 | CURRENT AND EMERGING APPLICATIONS

In the first part of this section, the link between safe and sustainable chemical processes and systems will be clarified (Section 4.1). Then, the purposes for which the acquired data can be used will be presented, ranging from process safety to process development and basic research.<sup>[143]</sup> More specifically, in Section 4.2, chemical stability assessment strategies will be presented, involving quantitative (Sections 4.2.1 and 4.2.2) and qualitative (Section 4.2.3) methods. Then, in Sections 4.3 and 4.4, the direct application for safe operative conditions determination and relief systems design purposes will be elucidated, respectively. Finally, in Section 4.5 the non-canonical application and future directions of the thermal stability assessment will be discussed.

### 4.1 | The role of inherent safety in sustainability

In 1987, sustainability was conceived as the integrated development around economics, environment, and society, which could offer substantial and maintainable benefits to the world.<sup>[144]</sup> Even if the role of safety does not appear immediately in the above-reported definition, by considering safety as ‘the prevention of accidents through the use of appropriate technologies to identify the hazards and eliminate them before they cause unintended damage to people, property or environment’<sup>[16]</sup>,

the interdependence of both the mentioned fields becomes immediately recognizable. Thus, by intensifying the safety culture with a constant reduction of risks and hazards related to industrial activities, it is possible to grant environmental and societal protection, always promising economic advances.

To understand where to act to optimize the sphere of process safety, as shown in Figure 5, safety barriers are reported in terms of layers of protection.<sup>[145]</sup> Referring to Figure 5, the first step toward safer industries is an intrinsically safer design of processes and equipment.<sup>[146]</sup> In this domain, the awareness of kinetic, thermodynamic, onset, and peak characteristics of attainable side reactions, like decompositions, are preminent.<sup>[147]</sup> Nonetheless, due to unpredictable events, inherent safety alone is insufficient to grant industrial plants reliability. Control systems, safety alarms, and relief devices can be vital tools for reducing and mitigating unforeseen risks.<sup>[148]</sup> Nevertheless, also in these cases, reference parameters for setpoint<sup>[149]</sup> and critical<sup>[150]</sup> temperature estimations, respectively, for control and emergency systems, and design parameters for orifice sizing of venting systems<sup>[150]</sup> must be retrieved experimentally or theoretically.

### 4.2 | Assessment of thermal stability

Chemical stability assessment aims to understand the hazard related to one or multiple exothermic chemical reactions. This safety evaluation can be performed quantitatively or qualitatively, as elucidated in Sections 4.2.1–4.2.3. The advantages, disadvantages, and applicability of these strategies for thermal stability assessment are discussed in Table 4.

#### 4.2.1 | System behaviour under adiabatic conditions

Adiabatic conditions are usually considered in process safety to simulate the worst-case scenario during an industrial or lab-scale accident.<sup>[9]</sup> The main quantities used for quantitative estimations of an adiabatic development of chemical reactions are the time to maximum rate under adiabatic conditions ( $TMR_{ad}$ ) and

**TABLE 4** Advantages, disadvantages, and applicability of the strategies for thermal stability assessment presented in Sections 4.2.1–4.2.3.

Strategy	Advantages	Disadvantages	Applicability
Adiabatic condition	1. Easy quantification of variables 2. Easy interpretation of results 3. Low time and computational effort	1. If multiple reactions are present, numerical simulations must be performed 2. Sometimes too conservative	Applicable to equipment and systems without any knowledge of constitutive models
Stability diagram	1. Specific methodology for equipment 2. Quantitative estimation of safety boundaries	1. High time and computational effort 2. Results depend on the theory involved in the construction of the diagram	Applicable to equipment and systems, knowing the constitutive models
Risk matrixes and indexes	1. Low time and computational effort 2. Easy interpretation of results	1. Quantitative estimation of risks and hazards 2. Strong dependence on the definitions of indexes 3. Strong dependence on the definitions of matrix	Applicable to equipment and systems without any knowledge of constitutive models

the adiabatic temperature rise ( $\Delta T_{ad}$ ).<sup>[151]</sup>  $TMR_{ad}$  can be considered an estimated time value during which runaway phenomena still need to be developed to take proper corrective actions. Meanwhile,  $\Delta T_{ad}$  can be involved as a rough index of the magnitude of an uncontrolled exothermic reaction development or to verify if plants and equipment could support the thermal stress induced by undesired heat sources. For a single exothermic chemical reaction, the quantities mentioned can be obtained using a simplified correlation retrieved in the literature, in their original<sup>[37,151]</sup> or improved formulation.<sup>[152]</sup> An alternative could be to simulate the system assuming adiabatic conditions, use theoretical modelling data, or consider multiple reactions.

The most direct application is during basic process design and development to provide a preliminary understanding of hazards for decision-making purposes.<sup>[153]</sup> Once the  $TMR_{ad}$  and  $\Delta T_{ad}$  have been estimated, the different processes can be classified into five classes, depending on their intrinsic criticality. As the numeric value related to the class of criticality increases, the inherent risk of runaway increases. Thus, operating conditions can be refined to reduce the related process's class. Different solvents could be involved to reduce the criticality level of a process, for instance. Having a solvent with a boiling point slightly higher than the maximum operating temperature helps to reduce the occurrence of runaway since the solvent's evaporation absorbs a high amount of thermal energy per unit mass of the solvent itself. Another strategy for risk reduction is to develop an innovative synthesis route that can reach low maximum operating temperatures. Indeed, the lower the process'

operating range temperature, the lower the possibility of triggering undesired side reactions, and the greater the freedom in solvent selection.

#### 4.2.2 | Stability diagrams

The stability diagram is a valuable tool applicable to equipment and process design.<sup>[154]</sup> This approach can be intended as a Westerterp-like map, reporting on the y-axis a dimensionless index of reactivity and on the x-axis a dimensionless index of reaction enthalpy.<sup>[155]</sup> Generally, a stability diagram can be produced only once a specific type of equipment is selected since it is based on the system's balance equations or experimental data sets. Sensitivity analysis is a theory that can produce model-based stability diagrams.<sup>[123]</sup> Due to the generality of the concept of sensitivity, based on the derivative of system-dependent variable (i.e., concentration or temperature) to the respect of a system dimensionless input (i.e., the dimensionless index of reaction enthalpy), it can be applied to storage vessels, ideal or non-ideal reactor configuration.<sup>[156]</sup> From this perspective, stability diagrams can be considered a valid and consistent tool that is valuable during equipment and process design or optimization. More specifically, during equipment design, the diagram can be used to verify if the geometry of a hypothetical reactor or storage vessel can prevent runaway conditions. Moreover, during process design and optimization, this type of parametric map can be involved in selecting safe operative windows to guarantee reliable operations while preserving the system's performance.

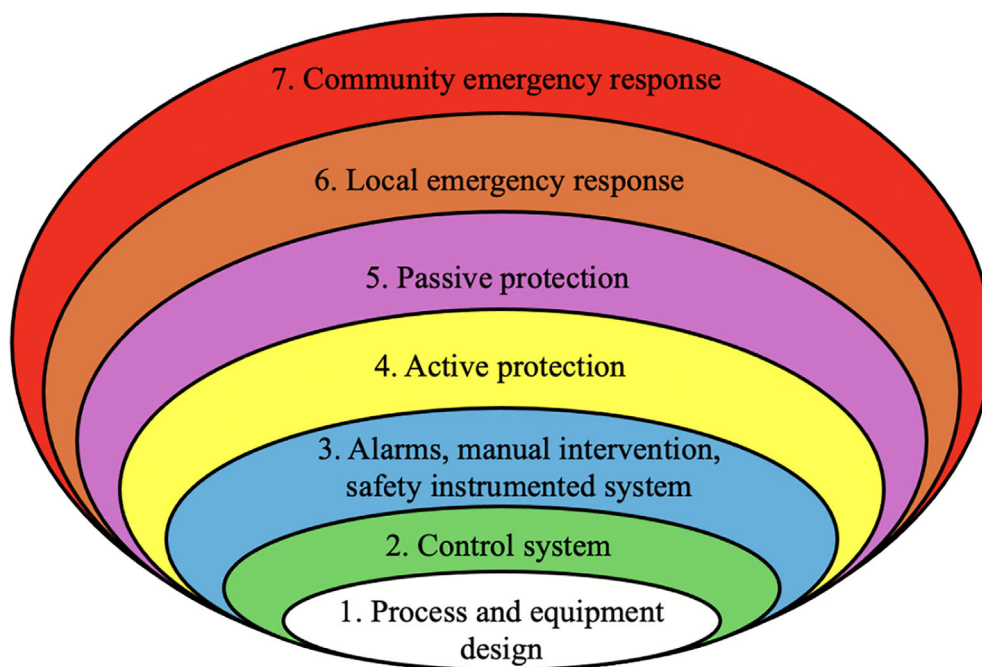


FIGURE 5 Layers of protection and safety barriers.

A schematic representation of a stability diagram is provided in Figure 6, and additional information can be found in the Data S1.

Something remarkable is the possibility of involving a stability diagram to analyze the occurrence of runaway phenomena during a general chemical process without knowing the equipment's details.<sup>[157]</sup> Indeed, involving the model of an adiabatic batch system, this kind of parametric map can be a valuable tool for risk assessment during process design. It could be involved in selecting a safe operating temperature to determine an intrinsically safe operating zone that can avoid the occurrence of a runaway and to quantify conservatively the time before a runaway occurs during accidents involving thermally unstable compounds. Eventually, additional information and a case study can be retrieved in Data S1.

#### 4.2.3 | Risk matrixes and indexes

Risk matrixes or indexes are simplified tools that can estimate process hazards qualitatively, and they can be based on quantities related to adiabatic conditions, such as the  $TMR_{ad}$  and  $\Delta T_{ad}$ . An example of a risk matrix-based approach for the qualitative hazard assessment of exothermic chemical reactions is the one proposed by Stoessel,<sup>[151]</sup> where the runaway's probability and severity depend on the  $TMR_{ad}$  and  $\Delta T_{ad}$ , respectively. More specifically, the higher the  $TMR_{ad}$ , the lower the frequency and the lower the probability, whereas the higher the  $T_{ad}$ , the higher the magnitude of the consequence. Using the two determined variables, it is

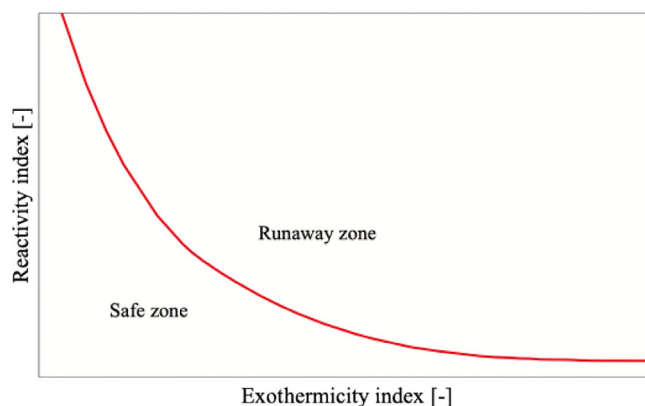


FIGURE 6 Schematic representation of a stability diagram. The diagram usually divides the space into different regions, each representing a state of the reaction. Safe zone: This area indicates conditions under which the reaction can be carried out safely. Runaway zone: The area where the reaction becomes uncontrollable. Once the reaction enters this region, it can accelerate rapidly with hazardous outcomes.

possible to enter a matrix that gives a qualitative idea of the hazard related to the chemical processes. For convenience, the mentioned risk matrix has been reported in Figure 7. An advantage of this method is the possibility of involving multiple chemical reactions, provided that the two indexes of adiabatic conditions are determined numerically. Alternatively, a simplified correlation can be retrieved in the literature.<sup>[158]</sup>

Regarding the index-based approach, an example could be the method proposed by Wang et al.,<sup>[159]</sup> where two indexes are determined: the thermal risk index (TRI)

Severity	High	$\Delta T_{ad} > 200$ K	Medium	High	High
	Medium	$50 \text{ K} < \Delta T_{ad} < 200$ K	Medium	Medium	High
	Low	$\Delta T_{ad} < 50$ K and no pressure	Low	Low	Low
			$\text{TMR}_{ad} \geq 24$ h	$8 \text{ h} \leq \text{TMR}_{ad} \leq 24$ h	$\text{TMR}_{ad} \leq 8$ h
			Low	Medium	High
			Probability		

FIGURE 7 Matrix for a qualitative assessment of the risk of runaway based on the maximum rate under adiabatic conditions ( $\text{TMR}_{ad}$ ) and the adiabatic temperature rise ( $\Delta T_{ad}$ ). Adapted from Bou-Diab and Fierz.<sup>[94]</sup>

and the reaction hazard index (RHI). As reported in Equation (1), the TRI can be the product of an index of probability that depends on the inverse of the  $\text{TMR}_{ad}$  and an index of magnitude that depends on the reaction enthalpy ( $\Delta \tilde{H}_r$ ). The RHI can be determined using Equation (2), which depends on the  $\Delta T_{ad}$  and the reaction activation energy ( $E_a$ ).<sup>[158]</sup> Both the achieved indexes allow the categorization of single chemical reactions in a class of criticality, expressed with a numerical value ranging from 1 to 4, which has the related thermal risk hazard increase, respectively. Table 5 reports the relationship between TRI, RHI, and the class of criticality. The major limitation of this method is that it allows for categorizing only single chemical reactions.

$$\begin{aligned} \text{TRI} &= \frac{\text{TMR}_{ad,reference}}{\text{TMR}_{ad}} \cdot \frac{\Delta \tilde{H}_r}{\Delta \tilde{H}_{r,reference}} \\ &= \frac{98(\text{min})}{\text{TMR}_{ad}} \cdot \frac{\Delta \tilde{H}_r}{556.47(\text{kJ/kg})} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{RHI} &= \frac{10 \cdot T_{\max}[\text{K}]}{T_{\max}[\text{K}] + 30 \cdot 4.184 \cdot E_a[\text{kJ/mol}]} \\ &= \frac{10(T_{\text{onset}}[\text{K}] + \Delta T_{ad}[\text{K}])}{T_{\text{onset}}[\text{K}] + \Delta T_{ad}[\text{K}] + 30 \cdot E_a[\text{kcal/mol}]} \end{aligned} \quad (2)$$

Illustrative examples are provided below to better understand how the risk matrix, the TRI, and RHI work. In particular, 14 different exothermic chemical reactions were examined. All the numerical values valid for the method implementation, retrieved in the literature,<sup>[33,159,160]</sup> have been reported in Table 6, together with the outcomes of the qualitative runaway risk and hazard assessment.

As seen from Table 6, the matrix and the risk-based approaches give different interpretations of the thermal criticality of an exothermic process. Still, they can be used as complementary tools. Indeed, for the last 12 reactions, the matrix approach estimates the highest level of severity and probability. In contrast, the risk index approach exhibits some sensitivity since the determined

TABLE 5 Criticality ranges based on the thermal risk index (TRI) and reaction hazard index (RHI).

Class of criticality	Indexes values	
1	$\text{TRI} \leq 1$	$\text{RHI} \leq 4$
2	$1 \leq \text{TRI} < 2$	$4 \leq \text{RHI} < 5$
3	$2 \leq \text{TRI} < 3$	$5 \leq \text{RHI} < 6$
4	$\text{TRI} \geq 3$	$\text{RHI} \geq 6$

criticality class varies from 1 to 4. This means that the matrix approach could be ideal for the categorization of less violent exothermic phenomena, as confirmed by the first two considered reactions in which the TRI's and RHI's criticality classes are the lowest possible (i.e., class 1) and the matrix approach classifies the risk of a runaway as in a high and medium range, respectively.

### 4.3 | Determination of safe operative conditions

Even if a stability diagram-based method can be involved for a more refined safe operative conditions assessment, it is also possible to use the onset temperature to determine a safe value of operative temperature during the prior stage of process development.

It is imperative to exercise caution when estimating the onset temperature of a material. The sensitivity of the instrument employed for experimental determination of the  $T_{\text{onset}}$  can impact the accuracy of calculations.<sup>[161]</sup> Additionally, other factors such as vessel size, cooling, flow, and agitation characteristics can also influence the outcome of the experiment. As noted in Section 1, these limitations imply that  $T_{\text{onset}}$  is a purely technical parameter that offers a preliminary indication of a material's stability. An example is represented by using the  $T_{\text{onset}}$  determined with a thermal screening unit ( $\text{TS}^U$ ) calorimeter.<sup>[32]</sup> To be more precise, by reducing the onset temperatures determined via  $\text{TS}^U$  analysis by  $75^\circ\text{C}$ , it is possible to quantify operative temperatures for industrial-scale applications.  $\text{TS}^U$  equipment has been developed as an alternative to DSC for primary thermal screening methods.<sup>[162]</sup> A detailed description can be found in McIntosh and Waldram.<sup>[163]</sup>

### 4.4 | Design of relief systems

The right choice of operative conditions and a reliable thermal hazard assessment can be considered inherent safety, which is fundamental for correctly designing processes and equipment.<sup>[164]</sup> However, due to unpredictable

TABLE 6 Risk assessment of the decomposition of some hazardous molecules.

Decomposition reaction	$\Delta T_{ad}$ (°C)	TMR <sub>ad</sub> (min)	$\Delta \tilde{H}_r$ (kJ/kg)	$T_{onset}$ (K)	Matrix risk level	TRI class	RHI class
Cyclohexanone (peroxydation)	54	1260	324	308	Medium	1	1
1,2-epoxypropane	130	100	16.0	433	High	1	1
2-amino-4-chlorophenol	217	100	11.5	437	High	1	1
Nitrobenzene	865	147	74.6	673	High	2	2
3-nitrotoluene	868	139	62.1	634	High	2	2
Trimethylamine N-oxide	680	105	50.9	475	High	3	2
2,3-epoxy-1-propanol	894	103	57.6	470	High	2	3
4-nitrotoluene	1241	139	88.9	639	High	2	3
Benzyl chloride	781	98	64.3	445	High	3	3
1,2-di formyl hydrazine	1130	111	72.7	507	High	3	3
Benzaldoxime	1650	110	98.0	509	High	3	4
Cyclohexanone oxime	1252	105	126.0	480	High	4	3
Cumene hydroperoxide	1689	100	107.1	460	High	4	4
Benzoyl peroxide	1818	83	104.7	381	High	4	4

scenarios like the failure of components and control system fluctuations, passive and active protective items can be used to keep hazards under control.<sup>[9]</sup> Relief devices can help avoid explosions and reduce undesired side effects of runaway reactions.<sup>[165]</sup> In the case of exothermic reactions, the sizing of relief devices is more complex than in the pressurization induced by fluids boiling, for example. DIERS provides a dedicated methodology for designing pressure relief systems based on data that can be acquired mainly with calorimetric experiments.<sup>[166]</sup> Indeed, the procedure is based on the knowledge of kinetic, thermodynamic, onset, and peak features of a particular exothermic reaction that trigger the runaway phenomena. The main limitation of this strategy is that it can handle only a single chemical reaction and on reliable experimental information. More specifically, following the DIERS methodology, three types of reactive systems are usually distinguished for venting character: vapour, gassy, and hybrid.<sup>[166]</sup> For the vapour system, in which the total pressure is equal to the vapour pressure, the principal parameter determining the vent size requirement is the rate of temperature rise, measured at the relief set pressure. Since the latent heat of vaporization entirely tempers the reaction for the vapour system, the lowest practical relief set pressure (always lower than the maximum allowable pressure) can be selected to obtain the smallest relief area requirement. For the gassy system, in which the total pressure is equal to the non-condensable gas pressure, in the absence of any tempering, the principal parameter determining the vent size requirement is the measured maximum rate of pressure rise. For the hybrid system, with gas production and vaporization occurring simultaneously,

the total pressure equals the sum of the gas partial pressure and the vapour pressure. In this case, both the rate of temperature rise and the rate of pressure rise are needed to determine the proper vent size for a specified venting pressure. Additional information related to the DIERS methodology can be retrieved in Data S1. Eventually, non-reactive mixtures can be further classified as foamy and non-foamy.<sup>[167]</sup> The main difference between these two systems is related to the occurrence or not of the formation of foam during venting. If the foam is formed during the release of uncondensed material, a larger orifice size is required since the foam itself is also dragged out during discharge, increasing the volumetric flow rate of the flowing material.

#### 4.5 | Emerging applications and future directions

An interesting recent development in thermal stability assessment is related to LIB. Indeed, several accidents are associated with LIB runaway mechanisms in industry and everyday life.<sup>[168]</sup> Thermal runaway is always triggered by mechanical, electrical, and thermal abuses,<sup>[169]</sup> which could lead to uncontrolled temperature increases in the battery.<sup>[170]</sup> The thermal runaway of LIB is induced by exothermic reactions related to the chemicals that form the electrolytes.<sup>[171]</sup> Then, gaseous products, which are responsible for increased internal pressure, can be generated.<sup>[172]</sup> At this point, two possible scenarios arise: the internal pressure accumulates until an explosion

occurs, or the generated gaseous mixture can be released through a device, potentially leading to fires in the presence of an ignition source due to the flammability of the generated gasses. Thus, calorimetric experiments have also recently been involved in assessing kinetic, thermodynamic, onset, and peak features of the apparent exothermic reactions responsible for the thermal runaway of the LIB.<sup>[173]</sup> Eventually, once the main feature of the response accountable for the runaway of the LIB has been determined, the Frank-Kamenetskii theory of self-heating can be employed for the determination of a safe size of the LIB, fixed the maximum temperature reachable during a particular application.<sup>[174]</sup>

Another technology central to the energy transaction is the electrolyzer,<sup>[175]</sup> in which hydrogen is produced from water using electrical current.<sup>[176]</sup> Nowadays, commercial solutions are polymer electrolyte membranes (PEM) and conventional liquid electrolyzers.<sup>[177]</sup> However, despite liquid electrolyzers typically containing electrolytes that are not prone to exothermic thermal degradations,<sup>[178]</sup> PEM electrolyzers are susceptible to thermal runaway.<sup>[179]</sup> Recent research shows that, as the volumetric flow rate of water decreases, the probability of runaway of a PEM electrolyzer increases due to heat accumulation inside the device.<sup>[180]</sup> As a runaway occurs, a peak in both the temperature and cell voltage is involved.<sup>[181]</sup> When water decreases in the device, the cell's voltage increases due to the lack of the component to be electrolyzed. This, in turn, also causes an increase in the device's internal temperature due to the conversion of electrical energy into heat. Then, the heat generated starts to accumulate in the system due to the absence of water, which also requires the removal of heat from the device due to evaporation. Heat accumulation, in turn, causes temperature increases and gas product generation, which could lead to explosions, and voltage increases could lead to sparks and electrical discharges. However, even if the literature frequently debates voltage runaway as the leading cause of loss of control of the system in PEM electrolyzers,<sup>[182,183]</sup> specific tools aimed at the prediction of the occurrence of voltage and related temperature runaway must be developed, together with an in-depth knowledge of the fundamental phenomena.<sup>[180]</sup> The primary reported cause of voltage runaway is the accumulation of electrical energy inside the device, which, in turn, induces temperature runaway. Nevertheless, the causes of this energy accumulation can be various, and they have not yet been clearly assessed. Another cause of thermal runaway, in the analogy to LIB's thermal runaway, is mechanical damage to the electrolyte membrane.<sup>[179]</sup> Still, a detailed description of the sequence of events that links the mechanical failure to the thermal runaway has not yet been reported in the

literature. This evidence of a lack of knowledge in thermal risk assessment of this emerging technology can be caused by the fact that safety studies on the thermal runaway of PEM electrolyzers are less developed than those of the LIB's thermal assessment. Thus, further efforts must be devoted to analyzing a detailed runaway dynamic for the PEM electrolyzer, aimed to evaluate kinetic, thermodynamic, onset, and peak features and describe the evolution of a canonical runaway scenario, the possibility of ignition of the gaseous products, and the severity of possible explosions.

Nonetheless, even if electrolyzers are a possible solution for large-scale molecular hydrogen production, nowadays hydrogen is mainly produced through steam methane reforming (SMR).<sup>[184]</sup> The major challenge of this technological solution is the heat requirement of the process since SMRs are based on endothermic chemical reactions.<sup>[185]</sup> To avoid supplying heat via combustion, a greener alternative is expected to be electrified reactors (ER).<sup>[186]</sup> Different strategies could be adopted to provide heat in the ER, such as Joule, induction, or microwave heating.<sup>[187]</sup> From a safety perspective, endothermic processes are intrinsically safe because they cannot undergo runaway reactions. However, other safety problems could arise with ER. For instance, sparks can occur due to the high electrical current supply in Joule heating. Since sparks are a localized energy source, they can ignite mixtures inside the flammability range, with devastating consequences for a hypothetical plant due to explosions. Other issues could be related to the interaction between safety and control systems with magnetic fields, causing malfunctioning. Eventually, like in the case of the PEM electrolyzer, further detailed investigations are required for proper safety assessment of electrified reacting systems.

Shifting the attention from innovative technologies to new materials, ionic liquids (ILs) must be mentioned. IL currently means a broad class of low-melting point salts, typically below 100°C,<sup>[188]</sup> that can be used as environmentally friendly solvents.<sup>[189]</sup> From the chemical industry perspective, ILs can be used either for synthesis or absorption separations.<sup>[190]</sup> The strength of ILs lies in their versatility in terms of the countless variety of chemical structures that can be given to the material, which governs the performance of IL in a chemical process.<sup>[191]</sup> Another essential feature of ILs regards thermal stability since these materials exhibit a very low tendency to decompose with exothermic effects.<sup>[192]</sup> However, even if the wide variety of chemical structures of ILs determines their high versatility, regarding the thermal degradations, detailed and specific calorimetric analysis is required to assess the thermal behaviour toward decomposition reactions.<sup>[193]</sup>

Thus, to reduce the environmental impact of chemical processes and to explore new technological solutions, it will be highly desirable to involve ILs as alternative substances at the industrial scale due to the high potential of these materials. Eventually, a detailed thermal assessment must be performed before implementing their large-scale applications because of their complex chemical nature and the absence of aprioristic predictive models of their stability toward thermal degradations.

Integrating ML and artificial intelligence (AI) in chemical engineering is bringing a new era of efficiency, innovation, and safety.<sup>[194]</sup> AI encompasses various programming techniques to mimic human intelligence,<sup>[195]</sup> like understanding natural language, recognizing patterns, making decisions, and solving problems.<sup>[196]</sup> ML focuses explicitly on developing statistical algorithms that enable computers to learn from data and make predictions or decisions.<sup>[197,198]</sup>

ML approaches are mainly applied nowadays to identify thermal hazards caused by unwanted chemical reactions, offering a data-driven strategy to recognize and predict potential risks.<sup>[199]</sup> By analyzing extensive datasets encompassing thermal signatures, battery compositions, usage patterns, and environmental factors, ML algorithms can discern subtle indicators of potential risks, such as overheating and thermal runaway events.<sup>[200–203]</sup>

Techniques like supervised learning, anomaly detection, and neural networks can detect known thermal hazards and uncover unforeseen risks, enhancing pre-emptive measures and ensuring safer operations in diverse sectors ranging from manufacturing and energy production to electronics and transportation.<sup>[204]</sup> These systems have produced significant results in thermal hazards caused by unwanted chemical reactions, mainly regarding LIBs.<sup>[205]</sup> Therefore, expanding the field of application of thermal hazard prevention to other fields of chemical engineering related to exothermic reactions would unlock new frontiers in process efficiency, sustainability, and safety, propelling the field toward greater heights of achievement and impact.

## 5 | CONCLUSIONS

On an industrial scale, hazardous materials prone to exothermic decomposition reactions are usually processed in large quantities. If not adequately managed, chemical phenomena that generate thermal energy could lead to runaway conditions, devastatingly affecting goods, people, and the company's reputation. For this reason, thermal analysis is paramount to enhance process safety and system reliability to assess the kinetic, thermodynamic, onset, and peak features of exothermic reactions.

Not surprisingly, the most recurrent terms reported in Figure 2 retrieved from a bibliographic analysis related to thermal stability are 'reactor', 'characterization', 'design', 'control', and 'safety'. Typically, the properties needed for a proper thermal stability assessment are quantified through experimental campaigns performed in calorimeters. However, several types of calorimetric equipment have been developed, and depending on the instrument's arrangement, different data analyses could be required to obtain the needed information for a complete thermal stability assessment. Theoretical analysis could be coupled to the calorimetric analysis to provide a broader framework of the decomposition mechanism and intrinsic features.

An example could be the coupling between experiments and ab initio methods to check and validate experimental results with theoretical values and have a more comprehensive framework of the decomposition mechanism determining the reaction network, contributing to the observed overall reaction. Alternatively, analytical techniques could also be helpful to assess the overall observed decomposition products and residues. Ab initio quantum chemical methods are the most encouraged and complete theoretical instruments for determining detailed reaction mechanisms and dynamics. On the other hand, the primary strategies for analyzing gaseous decomposition products obtained experimentally are GC, FTIR, and MS. In contrast, if liquid side-products are to be investigated, NMR and HPLC must be involved. Measured or modelled features concerning the decomposition reaction can be involved in stability assessment, determination of safe operative conditions, and relief device design. The stability assessment of hazardous chemicals can be performed both qualitatively and quantitatively. Qualitative estimation mainly relies on using risk matrixes and risk and hazard indexes.

Conversely, quantitative estimation could be performed to determine the reactive properties of the mixtures under adiabatic conditions or stability diagrams. Adiabatic conditions are usually considered during risk analysis and hazard assessment to simulate the worst-case scenario during a hypothetical industrial accident. Stability diagrams are robust equipment, process design, and optimization tools. Alternatively, onset temperature could also be involved in quantifying safe process conditions. Knowing the temperature value at which an exothermic side chemical reaction could occur, it is possible to define a safe margin and, therefore, a value of operative temperature to avoid thermal degradation of handled substances. In addition, a thermal stability assessment could enhance intrinsic safety and the design of active and passive measures like relief devices. Indeed, using the DIERS methodology, the data retrieved experimentally could be



used to properly size the orifice of bursting disks and pressure relief valves. With this kind of device, the overpressure generated by an uncontrolled exothermic phenomenon degenerated in a runaway reaction could be safely vented, avoiding explosions and catastrophic equipment failure. Finally, a brief review was given on the future application of the thermal stability assessment regarding LIB, electrolyzers, electrified reacting processes, and ILs.

Further research is necessary to analyze safety concerns surrounding new technologies and processes. Efficient integration of these technologies into current contexts requires assessing and mitigating potential risks to ensure the well-being of companies, workers, the environment, and the population while preserving the integrity of infrastructures. Engaging in open and transparent discussions about the safety implications of emerging industrial technologies can help stakeholders work together to develop strategies and solutions that prioritize safety while fostering innovation and progress. To achieve this, more detailed tools for thermal stability assessment need to be developed to consider emerging scenarios not contemplated by present analysis strategies. For example, AI and ML can be integrated into the safety framework of chemicals and systems. Advanced predictive models can be developed using system data to alert operators of potential loss of control due to the onset of runaway conditions, which can be retrieved through experimental or theoretical analysis.

## AUTHOR CONTRIBUTIONS

**Giuseppe Andriani:** Conceptualization; investigation; methodology; validation; software; writing – original draft; formal analysis. **Gianmaria Pio:** Writing – review and editing; validation; software; data curation. **Ernesto Salzano:** Writing – review and editing; project administration; supervision. **Chiara Vianello:** Writing – review and editing; project administration; supervision; resources. **Paolo Mocellin:** Funding acquisition; visualization; formal analysis; resources; writing – review and editing; project administration; supervision; conceptualization.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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