Whitepaper

Link between Mixing Intensity and Reaction Kinetics

DEKRA Organisational and Process Safety

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The profound link between adiabatic calorimetry mixing intensity and reaction kinetics – don’t undersize your vent!

Abstract

There are a number of safety solutions available to protect reactors against over pressurisation from thermal runaway reactions; these include emergency cooling, quenching, physical containment and, most commonly, emergency (pressure) relief systems (ERS). When designed and operated robustly, such a system can be both cost effective and reliable. To ensure this robustness however, it is essential to understand the overall kinetics, thermochemistry, and physical property characteristics of each foreseeable runaway reaction scenario under relief conditions.

To satisfy the minimum dataset for ERS design calculations, failure scenarios representative of large-scale conditions are typically simulated using adiabatic calorimetry. It is well established that the thermal data generated in this manner should be corrected for thermal inertia to allow for scale-up, however the influence that mixing intensity also has on these results is perhaps often undervalued.

This report summarises an investigation of a standardised reaction to explore the ties between the thermal inertia and mixing intensity of an adiabatic calorimeter on the thermal data generated, and considers the implications of these findings on ERS design.

The design of an Emergency Relief System **must consider all credible failure conditions**

Emergency Relief Systems

Emergency pressure relief systems are the most commonly used basis of safety across the chemical, pharmaceutical and allied industries, used to offer protection to reactors, storage tanks, columns, dryers, and other process equipment alike.

The design of an ERS must consider all credible failure conditions, including runaway reactions, chemical decomposition, and fire engulfment, alongside physical overpressure events (e.g. blocked outlet, failure of control loops, utility failure, thermal expansion of liquids blocked in).

Calorimetry Data

Clearly any emergency relief system designed to accommodate an exothermic event will require a minimum data set to permit design calculations. This is achieved by conducting adiabatic calorimetry to simulate the failure condition and studying some, or all, the following parameters:

- The self-heat rate, pressure generation mode (vapour pressure, gassy, or hybrid), and rate of pressure increase during runaway reaction, decomposition, or fire-induced exotherm - an expression of the kinetics and thermochemistry
- The foaming characteristics
- The fluid viscosity
- The potential for hybrid behaviour and the measurement of vapour/gas proportions throughout the venting duration.

The **surface to volume ratio** in lab scale equipment is **many times larger** than that of a plant scale vessel

Adiabatic Dewar Calorimetry

Adiabatic Calorimetry has existed as a technique for characterising runaway reactions since the 1980's (Columbia Scientifics' Accelerating Rate Calorimeter being the first commercially available calorimeter of this type). DEKRA have developed a bespoke stirred pressure Dewar to perform chemical reactions under adiabatic conditions and quantify any ensuing energetic events, measuring thermal and pressure effects. The data from these tests can form the basis for vent sizing calculations, and may be used to define a basis of safety for large scale vessels including:

i. data relating to required relief area for process maloperation scenarios
ii. temperature / time data for calculation of required cooling capability
iii. upper safe working temperature to avoid secondary decomposition or side reaction events

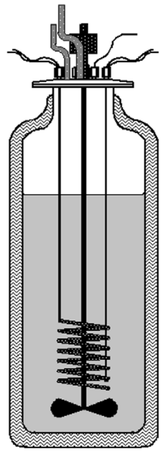


Figure 1. Adiabatic Dewar calorimeter diagram

Thermal Inertia

When using experimental data as a basis for vent sizing, it is important to correct for thermal inertia.

The thermal inertia, or phi-factor, of a vessel represents the amount of heat used by a reaction mixture to heat the vessel in which it is situated, and may be defined as the ratio between the heat capacities of the vessel and its contents:

$$\phi = 1 + \frac{m_v C_{p,v}}{m_s C_{p,s}}$$

For a full-scale reactor this value will approach ϕ = 1.

The surface to volume ratio in lab scale equipment is many times larger than that of a plant scale vessel, and the percentage of energy transferred to the vessel walls will be increased as a result. This discrepancy may lead to significant underestimation of the rate of reaction if left uncorrected, and by lowering the final temperature of the primary runaway, secondary events and decompositions which initiate at higher temperatures may be missed.

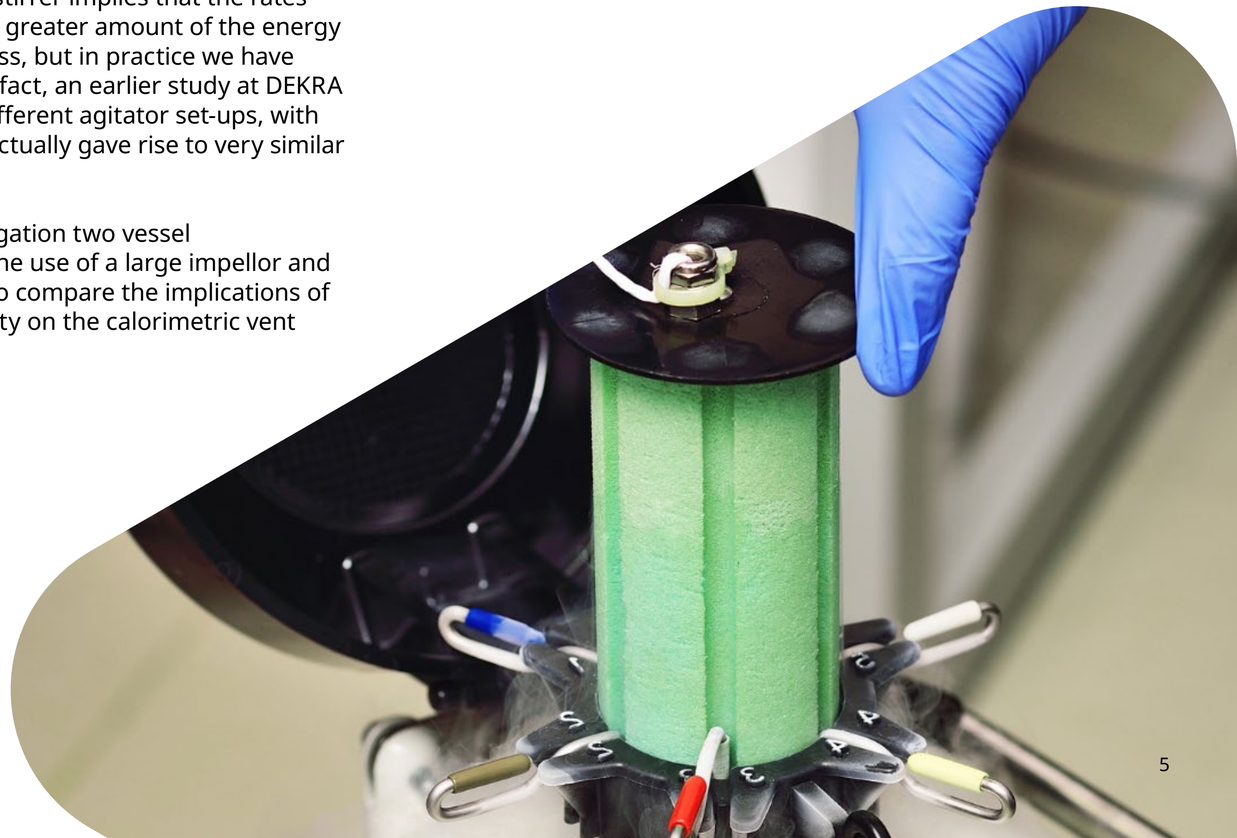
It is standard practice to use the **smaller impellor**, for mobile liquids, to achieve **the lowest phi possible** when performing tests

Stirring

In the case of the adiabatic Dewar, the heat capacity, and therefore phi, will depend on the different inserts and stirring configurations used. Larger agitators are therefore typically reserved for viscous mixtures or slurries where mixing is expected to be a challenge, as their greater masses will raise the heat capacity of the vessel. It is standard practice to use the smaller impellor, for mobile liquids, to achieve the lowest phi possible when performing tests.

The increased phi when using a larger stirrer implies that the rates during a reaction should decrease, as a greater amount of the energy will be consumed to heat the larger mass, but in practice we have seen this is not necessarily the case. In fact, an earlier study at DEKRA UK Ltd, inadvertently found that two different agitator set-ups, with correspondingly different phi factors, actually gave rise to very similar results.

For the purposes of this current investigation two vessel configurations have been considered: the use of a large impellor and that of a small impellor, in an attempt to compare the implications of both thermal inertia and mixing intensity on the calorimetric vent sizing data obtained.



Previous qualitative testing had shown **both stirrers to be proficient** at stirring mobile liquids across this range of stirring speeds

Methodology

To calculate and ultimately compare the phi factors of each configuration, it was first necessary to determine their respective heat capacities. Dewar vessels equipped with the two different stirrers were filled with 700 ml of toluene. With a constant stirrer speed of 300rpm, the reference material was heated in 10 K intervals at a fixed power of 30 W, allowing for periods of equilibration between each step, up to 70°C. From the resulting heat up rates it was possible to calculate the overall vessel heat capacity when using each stirrer, as displayed in Table 1.

Previous qualitative testing had shown both stirrers to be proficient at stirring mobile liquids across this range of stirring speeds, though the larger impellor demonstrated superior mixing at any given RPM due to its ability to displace greater volumes of liquid.

Friction between the stirring shaft and seal is a known source of additional heat input and was initially considered to be responsible for the rate increases seen using larger stirrers. Further investigations have demonstrated this to be of little consequence however, with frictional heat input very similar between setups and negligible at the speeds and viscosities involved in this study.

To investigate the effects of phi and stirrer speed on reaction behaviour (specifically kinetics), a standardised 2:1 molar esterification reaction between butanol (BuOH) and acetic anhydride (Ac2O) was performed using the two different stirrer configurations, repeated at stirrer speeds of 0, 150, 300 and 400 rpm.

Both reagents were charged to Dewar flasks which were then sealed and connected to all relevant logging and control systems. The internal heater was used to heat the mixture to 25°C, at which point the test was allowed to proceed adiabatically.

Dewar Configuration	Heat Capacity (J K-1)	Φ
Stainless-Steel Impellor	210	1.15
Titanium Large Impellor	240	1.17

Table 1. Experimentally determined Dewar heat capacities for different stirrer configurations, alongside the phi factor values for the standardised testing.

The trends for the small impellor at both 300 and 400 rpm **are also a close match**

Results

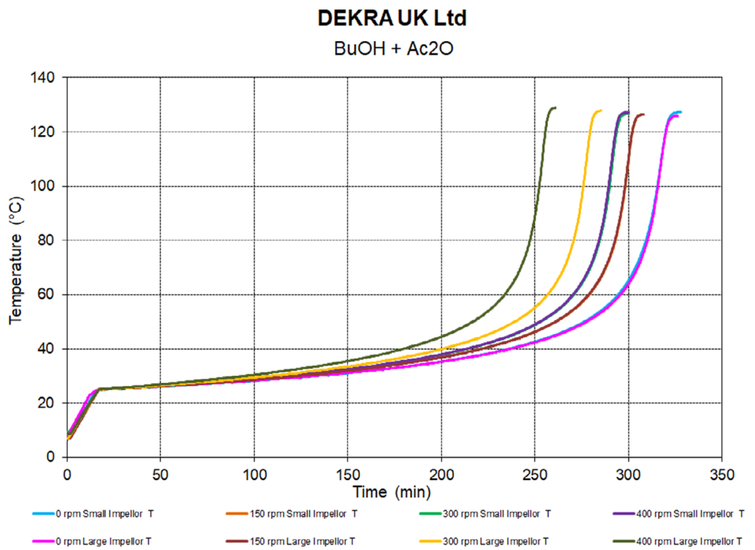


Figure 2. Temperature versus time for standardised testing using different stirrer set-ups and speeds.

Figure 2 demonstrates the relationship between temperature and time for the standardised test across the various stirrer set-ups. As stirring speed is increased the exotherm durations are generally shortened, with the shortest durations achieved using the larger impellor.

Interestingly, with no agitation the profiles for both impellors appear closely matched with the smaller stirrer peaking slightly higher (127.2 vs 126.0°C), presumably due to its marginally lower phi factor. The behaviour between the two agitators continues to match at 150 rpm; this appears to suggest that at this rate of mixing the increased agitation of the large impellor is balanced by the lower phi-factor of the small impellor.

The trends for the small impellor at both 300 and 400 rpm are also a close match. This may suggest that, for the small impellor, increasing the stirrer speed above 300 rpm will have a diminishing effect on the quality of mixing.

Conversely, when using the large impellor, peak temperatures continued to rise and exotherm durations consistently fell as the speed was increased, with the 400 rpm run maxing out at 128.9°C after 261 minutes.

The fact that the highest peak temperatures are observed while using the large impellor would appear to suggest that for this particular reaction system it is mixing, or the lack thereof, which is more influential than any difference in phi.

At the opposite end of the spectrum, **the tests without stirring** had TMRs exceeding 315 minutes [...]

Results

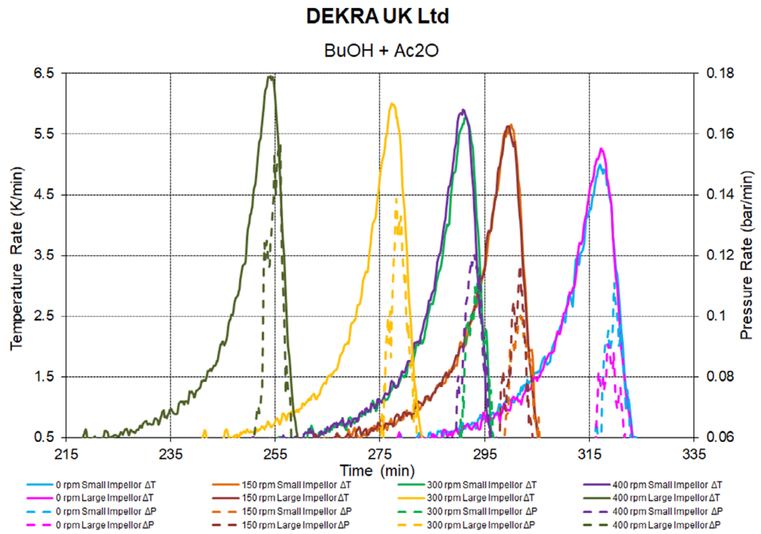


Figure 3. Temperature and Pressure rates versus time for standardised testing using different stirrer set-ups and speeds.

Figure 3 enables comparison between the rates of both temperature and pressure, and of the times taken for each configuration to achieve its maximum rate (TMR).

The rates attained using the larger stirrer generally peaked higher and earlier across the board than those of the small agitator at a given RPM, in spite of its larger Phi.

Not only did the large impellor operating at 400 rpm give rise to the highest temperature rate at 6.4 K min-1, but it did so after the shortest duration of time, hitting the peak rate after only 254 minutes.

At the opposite end of the spectrum, the tests without stirring had TMRs exceeding 315 minutes, with the small impellor reaching a test-low maximum temperature rate of just 5.0 K min 1.

Emergency relief systems for protection against runaway reactions **are sized based on the kinetics of the prevailing runaway**

Conclusion

The range of maximum temperatures, rates, and TMRs observed across the different levels of agitation underline its importance as a consideration when performing vent sizing calorimetry. Both the speed and geometry of a stirrer are seen to significantly influence calorimetry data, so these factors should be carefully selected to ensure the resulting data is representative. The general conclusion of the study is the reaction rates correlate with mixing intensity – suggesting that conservative adiabatic calorimetry results must use – wherever possible – high intensity mixing systems.

Emergency relief systems for protection against runaway reactions are sized based on the kinetics of the prevailing runaway. To avoid underestimating calorimetric rate data, and subsequently the area of relief vents, it may be preferable to sacrifice phi factor in favour of better agitation. Any deviations in the data obtained may significantly influence the results of the vent sizing calculations, and so to be conservative it is better to have estimated these values too high as an undersized vent may have catastrophic implications.

The reaction system studied here involved two mobile, miscible liquids in BuOH and Ac2O. In applications where the quality of mixing is of particular importance (e.g. surface-area controlled (Grignard, micelles, etc) or multiple immiscible liquid phases) then the need to ensure thorough mixing will only become even more pronounced.

DEKRA Organisational & Process Safety **Contact**

DEKRA Organisational and Process Safety are a behavioural change and process safety consultancy company. Working in collaboration with our clients, our approach is to assess the process safety and influence the safety culture with the aim of making a difference.
In terms of behavioural change, we deliver the skills, methods, and motivation to change leadership attitudes, behaviours, and decision-making among employees. Supporting our clients in creating a culture of care and measurable sustainable improvement of safety outcomes is our goal.
The breadth and depth of expertise in process safety makes us globally recognised specialists and trusted advisors. We help our clients understand and evaluate their risks, and we work together to develop pragmatic solutions. Our value-adding and practical approach integrate specialist process safety management, engineering, and testing. We seek to educate and grow client competence in order to provide sustainable performance improvement. Partnering with our clients, we combine technical expertise with a passion for life preservation, harm reduction and asset protection.
We are a service unit of DEKRA SE, a global leader in safety since 1925 with over 48,000 employees in 60 countries and five continents. As a part of the world's leading expert organisation DEKRA, we are the global partner for a safe world. We have offices throughout North America, Europe, and Asia.

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