CHEMICAL ENGINEERING TRANSACTIONS
VOL. 90, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Aleš Bernatík, Bruno Fabiano

ISBN 978-88-95608-88-4; **ISSN** 2283-9216
DOI: 10.3303/CET2290102

Experience Report on Adiabatic Reaction Calorimetry in Safety Engineering

Ömer F. Delibalta, Lukas Engel, Martin Gosewinkel

Evonik Operations GmbH, Hanau-Wolfgang, Germany
Oemerfaruk.delibalta@evonik.com

This article is intended to provide a bridge between a conservative view of safety, an understanding of the interactions and a certain degree of pragmatism in the evaluation of chemical reactions. Based on different reaction systems (esterification, decomposition and organic peroxide), practical experiences, so-called rules of thumb, are to be presented in the next chapters, which are appropriately proven in Evonik in the evaluation of chemical reactions. The focus is on adiabatic reaction calorimetry as well as the characteristics of temperature rise rate and time-to-maximum rate. Likewise, this contribution should also serve as an inspiration for others to share their experiences to develop a common understanding of safety engineering among stakeholders in a project.

1. Introduction

Exothermic chemical reactions running in process plants contain eminent potential hazards accompanying the triggering of undesirable and non-controllable operating conditions. TRAS 410 provides a basis for the safety assessment of exothermic chemical reactions and gives advice on how to recognise and manage such operating conditions and to prevent them. Occurring hazards are systematically identified and evaluated, and the selection and scope of measures to prevent such incidents are derived. A series of characteristic physic-chemical parameters of the substances and equipment involved are used to identify the thermal hazard potential, e.g:

- Heat of reaction Q_R of the primary and secondary reactions
- Heat production rate (dQ_R/dt, reaction power)
- Heat release rate of the system (dQ_K/dt)
- Limit temperature T_{exo}...

These parameters can be determined with various calorimetric methods and equipment. Due to different detection limits of the equipment (e.g. DSC, VSP2, ARC....), varying measuring values and thus different characteristics are to be expected. The most important aspects for the derivation of the characteristics from these measuring values as well as for the evaluation and clarification of the scale-up from laboratory to industrial scale are as follows:

- Safety-conservative selection of boundary conditions (physical material values, process parameters...),
- Understanding of interactions between measuring data and characteristics and measures.

2. Experimental setup and procedure

In the adiabatic calorimeter, large-scale reactions can be simulated in a harmless manner in a small thin-walled reaction cell with little sample material (see *Figure 1*). Adiabatic means essentially that a thermodynamic process takes place in a pressure vessel without heat exchange with the atmosphere. This is ensured by a reaction cell, whose internal temperature is regulated by a trace heating system. Additionally, the pressure in the Vessel (P2) is regulated to the pressure in the test cell (P1), so that the test cell is preventing of bursting. An calorimeters of the type VSP2 (from Fauske) is used by the safety lab of Evonik.

Paper Received: 31 January 2022; Revised: 13 March 2022; Accepted: 29 April 2022
Please cite this article as: Delibalta Ö.F., Engel L., Gosewinkel M., 2022, Experience Report on Adiabatic Reaction Calorimetry in Safety Engineering, Chemical Engineering Transactions, 90, 607-612 DOI:10.3303/CET2290102

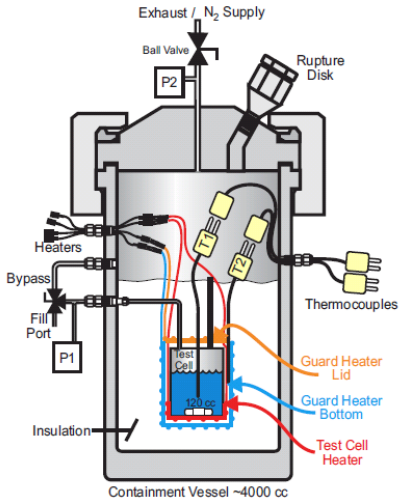

Figure 1: Measurement technique of the adiabatic VSP2 calorimeter

The mentioned questions can be answered by different experimental modes. On the one hand, chemical reactions in adiabatic mode are pursued. The reaction partners are mixed via the fill port, and the course of the exothermic reaction is observed (*Figure 3a*). On the other hand, the testing of the thermal stability of substances can be examined in the so-called "Heat-Wait-Search" test by gradually increasing the temperature (typically 5 K steps, 15 min holding time). After each heating step it is checked whether a thermal reaction starts. With both modes can also be carried out for the design of emergency relief devices.
Through these investigations of exothermic processes in the adiabatic calorimeter, different safety-related parameters can be calculated from the measured temperature-time and pressure-time curves. The temperature rise rate, the rate of pressure increase and - in case of decomposition gas formation - the rate of gas generation. Various theoretical models according to Semenov, Frank-Kamenetzkii or Thomas are applied to calculate other important parameters such as TD_{24} and T_{exo} on the basic of kinetic parameters (Activition Energy E_A and pre-exponential factor k_0/Q_0).
In certain cases it is necessary to protect a reactor or plant component with an emergency relief device (bursting disc, safety valve) for a worst-case scenario. The dimensioning of the emergency relief device is calculated on the basis of the rate of temperature and pressure increase.
With this measurment setting different reaction systems will be observed, and the influence of the different calculation ways for the temperature rise and kinetic parameters will be evaluated.
In the course of experimental investigations, the apparatus-specific temperature and pressure limits of the adiabatic calorimeter are often exhausted. In higher pressure ranges, especially in reaction systems with solvents with a high vapor pressure, obviously exothermic reactions can occur. These exotherms occur due to evaporation effects of the solvent, which cannot be compensated by the calorimeter itself.
For the VSP2, a so-called "temperature offset calibration" is usually carried out for a defined test cell setup. The procedure is to determine the temperature offset between sample and heater temperature required to eliminate drift at a specific temperature and pressure usually using a solvent like the reactive system to be subsequently tested. The disadvantage of this approach is the significant time and material effort because the test-rig test cell/insulation/heater set-up is "calibrated" as a system. In general, this procedure shall be carried out for every new reaction system.
In order to circumvent this obstacle, an optimized test rig was developed within the scope of several test series in which a newly developed insulation material (CALOSTAT®) with improved insulation properties (lower thermal conductivity, dosage form) was implemented. The procedure was tested with various substances with varying vapor and operating pressures for its suitability and reliability. As an example the test system of the vapor pressure test with water and different isolation materials (INSULFRAX λ= 0.05 W/m/K; Air λ= 0.026 W/m/K; CALOSTAT® λ= 0.019 W/m/K) is displayed in the following figure.

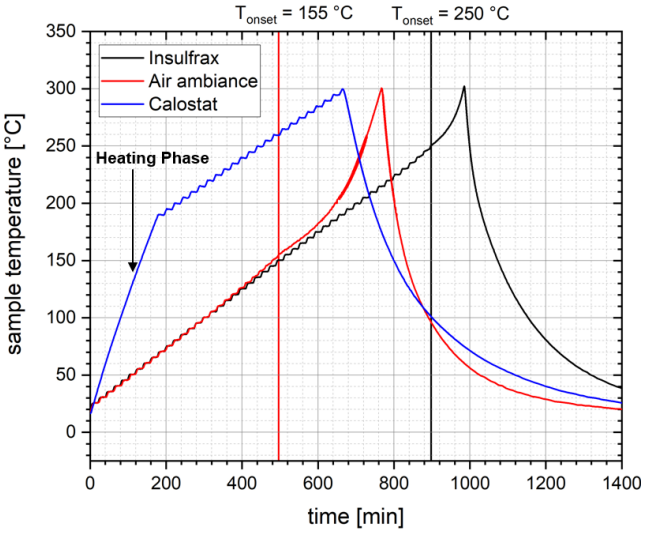

Figure 2: Effect of various insulation materials on heating behaviour of the calorimetric device

With the conventional insulation (INSULFRAX), water shows an apparent exothermic reaction with an onset temperature of 250 °C, with air as isolation the onset temperature lowers to 155 °C. By using the new insulation material, this effect completely disappeared.

3. Practical experiences regarding data analysis -rules of thumb-

3.1 Kinetic prediction

Experimental measurements of three different reaction systems (esterification, decomposition and organic peroxide) are carried out in adiabatic VSP2 calorimeter for kinetic evaluations. The pressure and temperature behavior of the chemical reaction are exemplarily illustrated for the esterification of methanol with acetic anhydride in *Figure 3a*. The heat loss due to the cooling of the system after injection of methanol is compensated by reheating, so the onset of exothermic esterification was observed at a temperature of 32 °C with a maximum temperature of 178 °C.

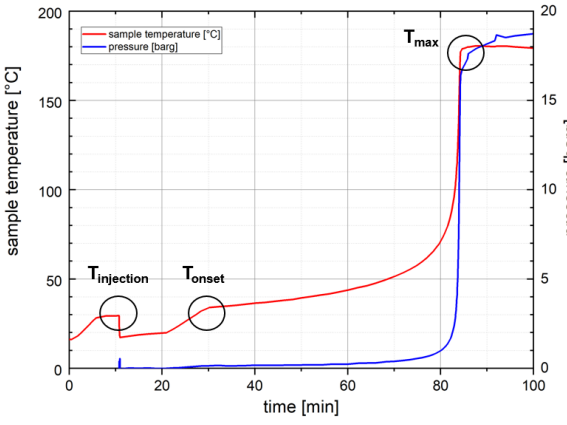

Figure 3a: Course of sample temperature and pressure as a function of time

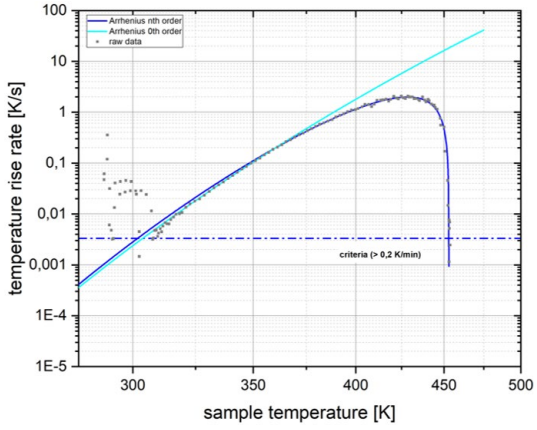

Figure 3b: Arrhenius approach for kinetic prediction

To estimate the kinetics of the chemical reaction, the rate of temperature rise is plotted against the sample temperature according to the Arrhenius approach. The kinetic parameters such as the activation energy EA and the pre-exponential factor k0 can be determined by a mathematical fit function to the measurement data. These are determined depending on the conversion α for a high-order reaction and compared with a conservative calculation assuming a 0th-order kinetic (Figure 3b). The equations used are listed below.

nth-order kinetic: $$\frac{dT}{dt} = k_0 \cdot e^{\left(\frac{-E}{RT}\right)} \cdot (1-\alpha)^n \quad (1)$$

0th-order kinetic: $$\frac{dT}{dt} = Q_0 \cdot e^{\left(\frac{-E}{RT}\right)};\ \text{where}\ Q_0 = \frac{k_0 H_0}{c_p} \quad (2)$$

While the nth-order function agrees closely with the experimental data, the fit function for the conservative case deviates due to the linear course with increasing sample temperature. However, the ascertained kinetic data are in a comparable range (*Table 1*). The deviation of the estimated activation energies is E_A about 4 %. Consequently, it can be concluded that a conservative assumption of a 0th order kinetics yields a sufficient result based on practical experience. This insight is to be considered as a rule of thumb and can be adopted for simplified calculations.

Table 1: Kinetic parameters based on Arrhenius approach

Kinetic	E_A [kJ/mol]	k_0/Q_0 [1/s]
nth order	69,39	$2{,}51 \cdot 10^9$
0th order	72,16	$6{,}69 \cdot 10^7$

3.2 ϕ-factor correction for adiabatic state

The VSP2 calorimeter is an adiabatic system with a high level of sensitivity. Nevertheless, particularly for slow chemical reactions, a completely adiabatic state is not achieved. Thermal heat loss due to insufficient insulation or condensation effects cannot be avoided and should be considered by a correction factor. Accordingly, the correction of measurement data by a ϕ-factor requires kinetic data. Referring to the DIERS methodology, the following correlations are applicable for nth-order kinetic.

$$\frac{1}{T_{A0}} = \frac{1}{T_{M0}} + \frac{R}{E} ln\ \phi \quad (3)$$

$$T_A = T_{A0} + \phi(T_M - T_{M0}) \quad (4)$$

$$\left(\frac{dT}{dt}\right)_{A(\phi=1)} = \phi \exp\left[\frac{E}{R}\left(\frac{1}{T_M} + \frac{1}{T_A}\right)\right] \left(\left(\frac{dT}{dt}\right)_{M(\phi>1)}\right. \quad (5)$$

Assuming a 0th order reaction, the measured parameter can be simply multiplied by the ϕ-factor to achieve adiabatic conditions. The resulting difference in the evaluation methods is shown in the following table based on the determined maximum temperature rise rate and adiabatic temperature rise for the esterification of methanol with acetic anhydride

Table 2: ϕ-factor correction depending on reaction kinetic

Kinetic	0th order	nth order
$(dT/dt)_{max}$ [K/min]	35,4	37,4
$T_{adiabatic}$ [K]	50	48

The deviation of the evaluated data is approx. 4% and is therefore negligibly small, so that the simple and conservative method can be used to correct the measurement data assuming 0th order kinetic.

3.3 Data evaluation for safety relief devices

For the design of a safety valve according to the ISO4126-10 standard, the specification of an experimentally measured temperature rise rate of the reaction is required. This is used to calculate the heat flux of reaction, which is subsequently applied to determine the discharged mass flow in application of the correlations specified in the standard. Based on this, the required narrowest cross-section of the safety device is estimated. The desired temperature rise rate can be assessed by three different methodologies:

- A linear function is fitted to the exothermic temperature increase of the target reaction over the temperature-time curve. The slope of the fit function corresponds to the average temperature rise rate utilized for valve sizing *$(dT/dt)_{average}$*).
- Using the maximum rate of temperature rise for valve sizing. This value is determined from the derivative of the temperature against time *$(dT/dt)_{max}$*).

- The required parameter is derived from the design criteria of the safety relief valve. For this purpose, the temperature (T_{psv}) corresponding to the specified valve opening pressure (p_{psv}) is determined experimentally. The temperature rise rates are precisely ascertained for this temperature and for a further temperature including a safety margin (T_{psv} + T_{over}). A mean value is derived from the respective values $(dT/dt)_{psv}$).

Using an example calculation following the standard ISO4126-10 for an organic peroxide system in an 8 m^3 reactor with a valve response pressure of 1.3 bar, the effect of the different evaluation methods for temperature rise rate on the essential relief cross-section is illustrated (*Table 3*). The calculated valve diameters using various measurement data are in a comparable order of magnitude. In conclusion, the evaluation method has no significant influence on the result of the valve design and can be individually selected depending on the design criteria.

Table 3: Safety valve design according to ISO4126-10 with various data evaluation

dT/dt in [K/min]	$(dT/dt)_{average}$	$(dT/dt)_{max}$	$(dT/dt)_{psv}$
valve diameter [cm]	37,7	38,9	35,0

3.4 Calculation of TD24 for secondary reactions

Organic reaction systems can exhibit thermal instabilities at excessive operating conditions and could devolve into uncontrolled decomposition reactions with catastrophic consequences. Correspondingly, for technical safety reasons, a limiting temperature T_{exo} should be specified. This designates the maximum permissible temperature at which a substance or reaction mixture can just still be handled without danger. The temperature for the adiabatic induction time (to maximum conversion) of 24 h is obtained from kinetic data as shown in the following equation.

$$TD_{24} = \frac{1}{Q_0} \cdot \frac{R}{E_A} \cdot T_0^2 \cdot e^{\left(\frac{E_A}{R}\frac{1}{T_0}\right)} \quad (6)$$

For various calorimetric methods (VSP2, DSC and Dewar-storage), the temperature T_{exo} is determined according to TRAS 410 by reducing the calculated TD24 by a defined factor (*Table 4*). Practical experience proves that the reaction order has no significant influence on the T_{exo} calculations. Conservatively, a 0^{th}-order reaction can be assumed. The T_{exo} calculation was carried out for a decomposition of di-tert-butyl peroxide in view of divergent sensitivities of the measurement systems (*Table 4*). According to TRAS 410, the DSC screening method results in a limiting temperature of 39 °C, considering a safety margin of 100 K. From the adiabatic calorimetry data (VSP2), a T_{exo} of 87 °C has been acquired. For this purpose, kinetic data are applied obtained by the Arrhenius approach (see *Figure 4*).

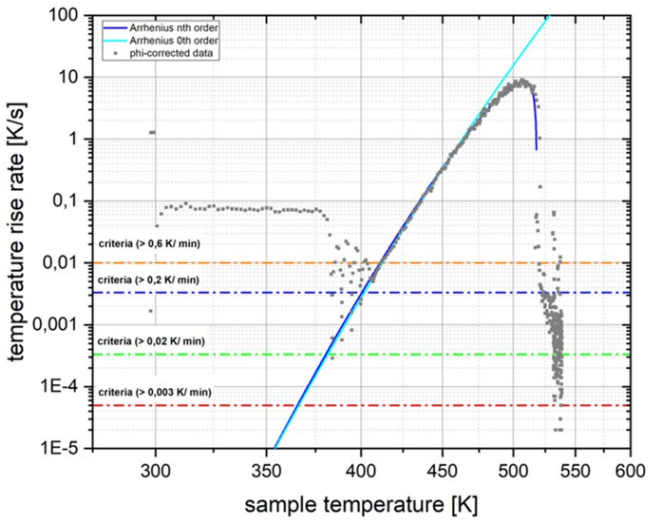

Figure 4: Kinetic estimation of decomposition reaction of di-tert-butyl peroxide by Arrhenius

For an adiabatic storage test in a Dewar vessel, an exothermic criterion of 0.003 K/min is expected corresponding to the high sensitivity of the method. Extrapolating the kinetic measurement data from the VSP2 experiment linearly to the specified criterion of a Dewar test, experiences show that the TD_{24} is assignable by

deducing the interception point. The derived T_{exo} agrees well with the calculated value based on kinetic data. Accordingly, the safety-related parameter can be estimated graphically without extensive calculation effort. This has been proven for a large quantity of studies of different reaction systems.

Table 4: T_{exo} calculation for various calorimetric devices

Device	Exothermic. Criteria [K/min]	Limiting temperature T_{exo} [°C]
DSC	0.6	$T_{exo} = T_{onset} - 100$ K 139°C -100 K = 39 °C
VSP2	0.2	$T_{exo} = TD_{24} - 10$ K 97°C -10 K = 87 °C
Dewar	0.003	$T_{exo} = T$ (0,1W/kg) – 10 K 95°C -10 K = 85 °C

4. Conclusions

Adiabatic reaction calorimeters like the VSP2 ("Vent Sizing Package 2") are the best and most reliable way for determining adiabatic rates of temperature and pressure rise for very fast exothermic reactions. These data are necessary for an effective design of chemical process emergency relief systems.
Although these devices seem simple to handle and evaluate at first glance, they already challenge the Although these devices seem simple to handle and evaluate at first glance, they already challenge the experimental realisation as well as the evaluation and assessment of the data.
Over the last 3 years, a broad range of reaction systems have been investigated and evaluated in the adiabatic reaction calorimeter. In the context of this, different methods and techniques for the implementation and evaluation were compared and benchmarked against each other.
In summary, the following rules of thumb were derived, with the help of which adiabatic investigations and results can be evaluated conservatively and simply in terms of safety.

1. 0^{th} order approach and simple Φ-correction applicable for conservative kinetical estimation
2. deviations in safety valve size due to analysis methods regarding temperature rise rates up to 5 %.
3. TD_{24} corresponds to the intersection temperature at a sensitivity of 0.1 W/kg

In summary it has to pointed out that an interpretation of an adiabatic experiment with the above-mentioned simplifications (0^{th} order kinetic approach) is to be assessed as conservative in terms of safety.
Additionally, an optimized test rig provided the opportunity to perform experiments in the high-pressure range reliably and in a time-saving manner, without usually reaction system specific time-consuming calibration procedures.

References

Barton, J.; Rogers, R.: Chemical Reaction Hazards, 2nd Edition Edited by J. Barton and R. Rogers. Institute of Chemical Engineers: Rugby, U.K. 1997

DIN ISO 4126-10: Sicherheitseinrichtungen gegen unzulässigen Überdruck - Teil 10: Auslegung von Sicherheitsventilen bei Zweiphasenströmung (flüssig/gas)

DGUV Information 213-067, „Thermische Sicherheit chemischer Prozesse“, 12/2015

Grewer, T, Thermal Hazards of Chemical Reactions, Industry Safety Series, No 4, 1994, Chapter 2.4 "Thermal Explosions"

Fisher, H.G. et al.: Emergency Relief System Design Using DIERS Technology: The Design Institute for Emergency Relief Systems (DIERS) Project Manual, American Institute of Chemical Engineers, 1992

Stoessel, F., „What´s your Thermal Risk ?“, Chem. Eng. Prog. 10 (1993) 68-75.

Stoessel, Francis: Thermal Safety of Chemical Processes: Risk Assessment and Process Design, Wiley VCH, 2020

TRAS 410, „Erkennen und Beherrschen exothermer chemischer Reaktionen“, 11/2019