DEVELOPMENT AND EVALUATION OF EXPERIMENTAL CALORIMETRIC SYSTEMS FOR THE SIMULATION OF AN EXTERNAL HEAT INPUT ON REACTIVE CHEMICALS AND MONOMERS†

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In the chemical industry, several incidents involving the exposure of storage, transport and reactor vessels to fire have been reported. The main aim of this paper is to identify methods to improve safety measures for vessels containing reactive chemicals (e.g. monomers) that could be exposed to fire. This is done by developing and assessing experimental and theoretical methods for the measurement of the temperature and pressure rise rates resulting from a runaway reaction with external heat input.

A commercially available adiabatic calorimeter was adapted for simulating the effect of an external heat input on reactive chemicals. Four heat input designs were tested. A new method of using an immersion cartridge heater with a custom test cell was shown to be the best heat input setup, the input power from the power supply being fully used to heat the system. Good experimental results were obtained with the methanol + acetic anhydride reaction (vapour system) and the decomposition reaction of 20% di-tert-butyl-peroxide in toluene (tempered hybrid system). It was measured experimentally that increasing the external heat input leads to a decrease of the reaction completion time, an increase of the maximum temperature and pressure, and an increase of the maximum temperature and pressure rise rates. This would have severe implications if it occurred in an industrial accident.

The validity of two theoretical correction methods of adiabatic data were tested experimentally using the data obtained with the methanol + acetic anhydride reaction. The correction method proposed by Huff[1] gave conservative results, with the significant advantage of only requiring limited input data. However, in the case of systems showing multiple overlapping reactions with different activation energies, Huff's approach would fail. A dynamic model taking into account the effect of external heating is likely to give better results, however its implementation would require a detailed knowledge of the kinetics of the chemical system, which is not often available.

Especially when the chemical system is too complex to be simulated by a dynamic model, the kinetic data is not available, or when it is outside the application range of Huff's method, the experimental technique developed in this work would be a reliable, cost-effective and convenient alternative.

KEYWORDS: runaway reaction, fire exposure, adiabatic calorimetry, reaction kinetics, methanol, acetic anhydride, di-tert-butyl peroxide, Huff's method

INTRODUCTION

Reactive chemicals and monomers are routinely used in the chemicals and plastics industries. They may be stored in bulk tanks or pressure vessels possibly containing hundreds of tonnes or in smaller transportable containers of up to 20 tonnes capacity. Process vessels typically contain volumes of one cubic metre or more. Sites using such materials need to understand and control the risks from their process, and many will be subject to Major Accident legislation such as the Control of Major Accident Hazards (COMAH) regulations (implementing the Seveso II Directive). The COMAH regulations require that dutyholders not only understand the risks from their process, including an appreciation of the worst case scenario, but also that they have reduced those risks as far as reasonably practicable. This demonstration will require the site operators to show they have used the most appropriate information when carrying out their risk assessment.

The potential consequences from the catastrophic failure due to fire engulfment (Figure 1) of a major storage vessel can be very severe and will require a rigorous demonstration that the risks have been reduced to as low as reasonably practicable (ALARP). Similarly the Regulator has to decide when the operator has carried out a sufficiently rigorous assessment and if the ALARP argument is acceptable.

Currently some occupiers have based their assessments on existing standards or guidance for non-reactive

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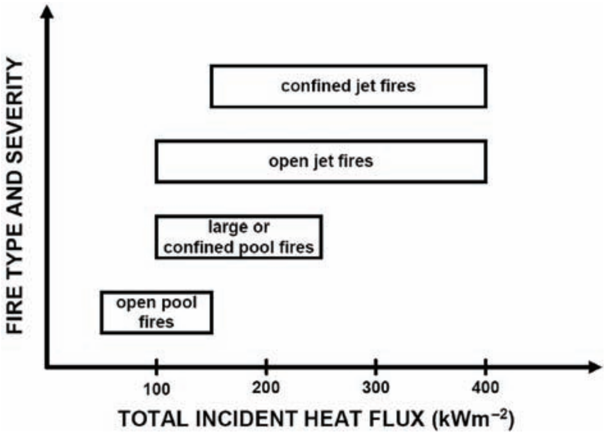

Figure 1. Illustrative heat fluxes for pool and jet fires[3]

liquid chemicals like flammable liquids or LPG on the basis that this is the best available information. For such vessels, the temperature increase resulting from fire exposure will raise the vapour pressure of the liquid and thus the pressure within the vessel. Thermal expansion of the vapour phase will also occur. For this case, the approach to sizing pressure relief systems is well-understood.

However, for a vessel containing a self-reactive chemical, the vent sizing approach is more challenging. Such chemicals are often stored with reaction inhibitors, which are only effective in preventing reactions at low temperatures. For example, 1, 3 butadiene and styrene are self-reactive monomers that contain tert-butyl-catechol as an inhibitor. For these monomers, polymerisation can occur in two ways: by peroxide initiation and by temperature initiation. In conditions of fire exposure, the inhibitor will cease to be effective and the monomer will start to self-react.[2] For a vessel containing a self-reactive chemical, less reactant conversion is needed to reach a given temperature, the liquid being also heated by the external heat input. The reaction rate at any temperature is therefore higher than that measured at the same temperature under adiabatic conditions. This would lead to different venting characteristics and vent requirements.

The experimental work presented in this paper aimed to design a new heat input system for a modified adiabatic calorimeter, to allow the measurement of the temperature and pressure rise rates resulting from a runaway reaction with external heat input. Four heat input designs were tested and compared with non-reactive and reactive chemicals. The experimental data were also used to test the validity of two theoretical methods for the correction of adiabatic data that take into account the effect of an external heat input: Huff's method[1] and a dynamic simulation model.

SETUP OF DIFFERENT HEAT INPUT SYSTEMS

DESCRIPTION

The experimental setup to simulate an external heat input is composed of:

- A Phitec II adiabatic calorimeter;
- A test cell containing the reactive substance (either standard or custom);
- An independent external power supply;
- A heating element to heat the test cell contents (either cartridge or immersion heaters).

Table 1 and Figure 2 present the four tested heat input designs. Setups A and B use external heating wires, a spiral wrapped around heater and a bottom heater respectively, in direct contact with the test cell walls. Insulation tapes were used to avoid any interference between the heating wire and the thermocouple controlling the temperature of the calorimeter guard heater (Figure 2).

Setups C and D use immersion heaters (respectively 1/4″ and 1/8″ cartridge heaters). They were specifically designed to have a minimum heating length located at the bottom end of the cartridge (Figure 3). The use of such cartridge heaters with the particular adiabatic calorimeter

Table 1. Characteristics of the heat input designs

		Setup A	Setup B	Setup C	Setup D
Test cell	Type	Standard	Standard	Custom	Custom
	Volume	110 ml	110 ml	82 ml	82 ml
	Thermocouple	1 type K	1 type K	1 type K	1 type K
	Fill line diameter	1/16″	1/16″	1/16″	1/16″
	Heater connexion	N/A	N/A	1/4″ Swagelok fitting	1/8″ Swagelok fitting
Heater	Type	Heating wire	Heating wire	1/4″cartridge	1/8″cartridge
	Location	Spiral wrapped around (test cell external surface)	Bottom (test cell external surface)	In the liquid (immersion heater)	In the liquid (immersion heater)
	Diameter	1.57 mm	1.57 mm	6.35 mm	3.17 mm
	Voltage	0–24 V	0–24 V	0–24 V	0–24 V
	Resistance	12.5 Ω	11.2 Ω	19.8 Ω	17.95 Ω
	Maximum power	50 W	50 W	30 W	30 W
	Length	686 mm	654 mm	63.5 mm	63.5 mm

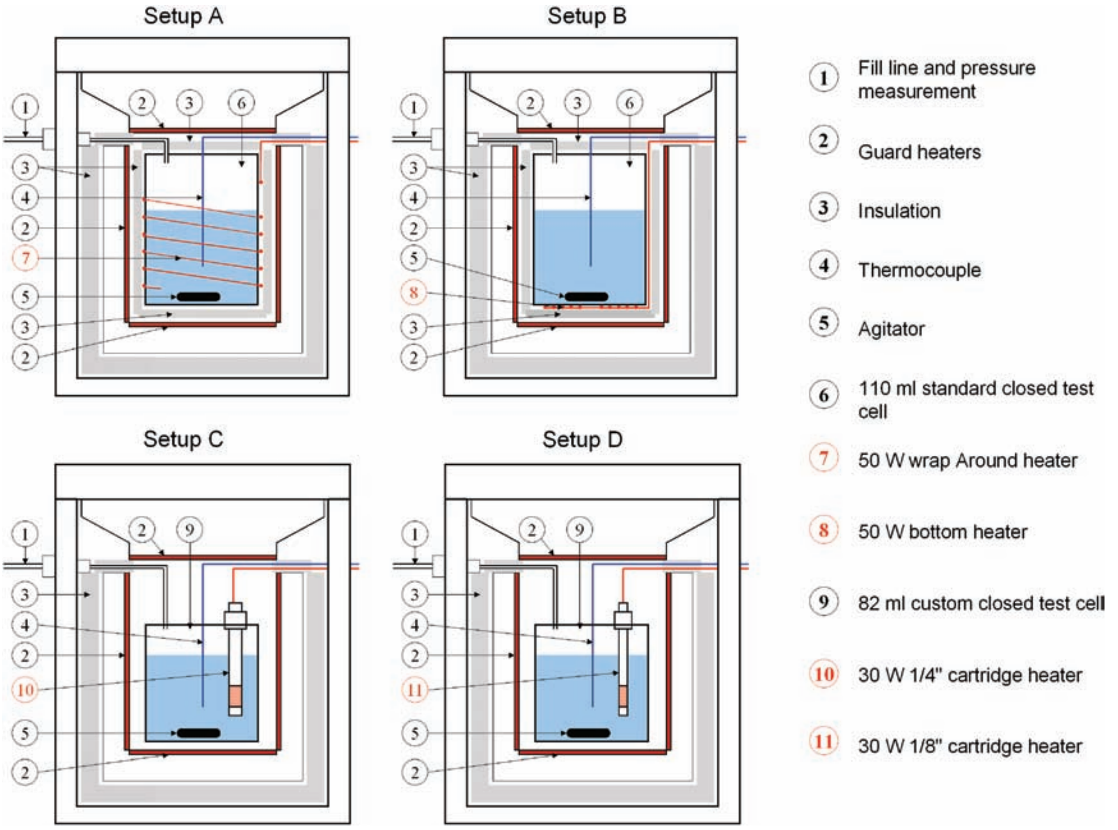

Figure 2. Experimental setup for external heat input options tested

required the design of custom test cells of smaller volume (82 ml) than the standard ones (110 ml) because of the limited space in the containment vessel. They are equipped with a male tube compression fitting on the top side to allow the insertion and the connection of the cartridge. The cartridges have an off-centred position, which allows the heater to also act as a baffle (improving agitation and preventing the formation of vortex).

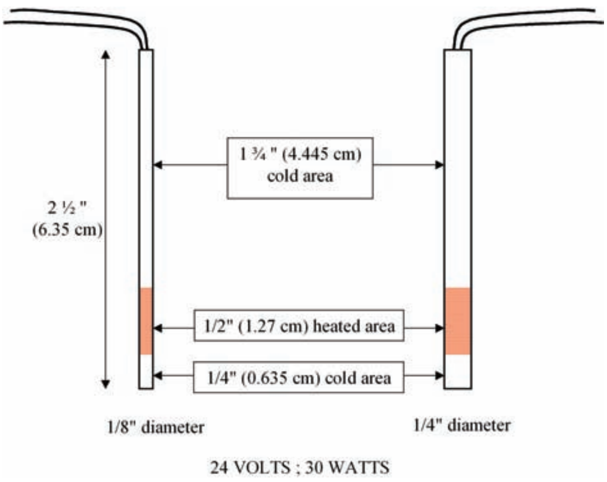

Figure 3. Design of the cartridge heaters

COMPARISON OF THE HEAT INPUT DEVICES

Each setup was used to heat a test cell filled to 70% with water. The obtained water temperature rise rate (dT/dt) was used to calculate the efficiency (ξ) of each of the heating devices. The efficiciency is defined as the ratio of the power used to heat the liquid to the nominal power delivered by the power supply (Q_{nom}):

$$\xi = \frac{\phi(mCp)_{liquid}\frac{dT}{dt}}{Q_{nom}} \tag{1}$$

Figure 5 shows the efficiency as a function of the nominal power, Q_{nom}. It appeared that the wrapped around and bottom heaters have an efficiency of 70% and 80% respectively, a significant amount of heat being lost to the surroundings. The heating wires represent the easiest way to simulate an external heat input, but large uncertainties remain regarding the heat losses. Indeed, the efficiency of such systems depends strongly on the quality, the type, the thickness, the age, the placement (which is operator-dependent) of the insulation layer between the heaters and

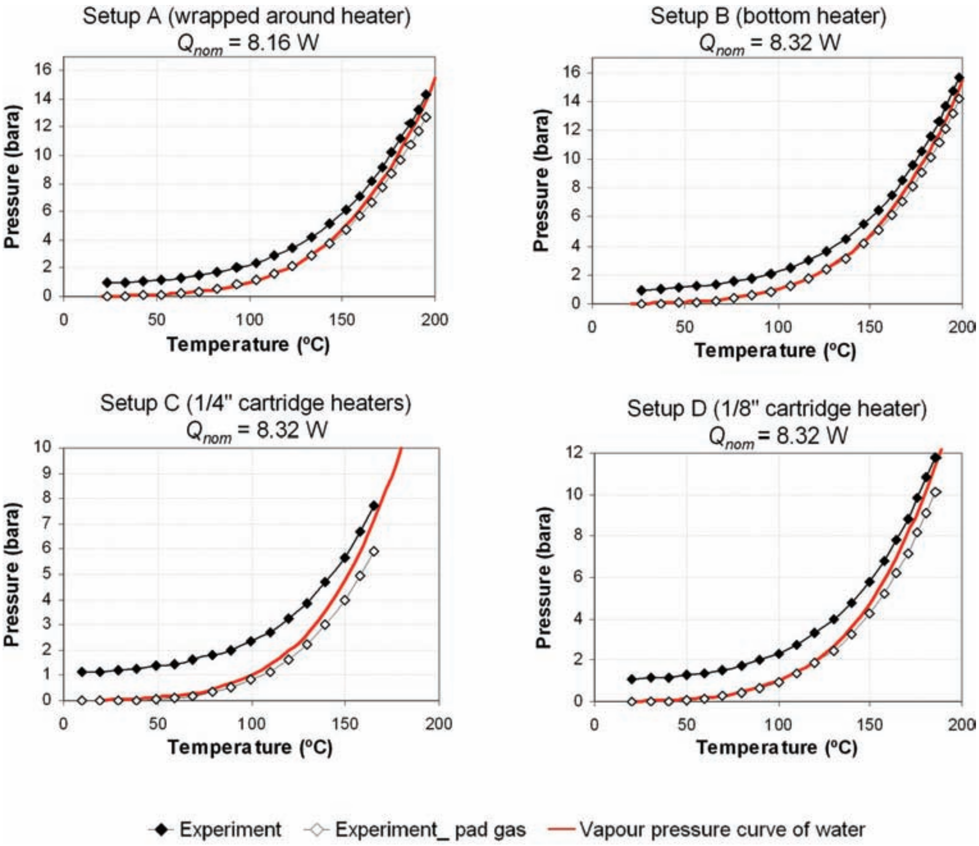

Figure 4. Vapour pressure curves of water, comparison with literature data

the Phitec guard heater (Figure 3). An experimental investigation of the efficiency of the entire setup is necessary beforehand. The 1/8″ and 1/4″ cartridge heaters are clearly the more efficient heating devices. As the heater is immersed in the liquid, the nominal power is fully used to heat the system.

Figure 4 shows the vapour pressure curves, corrected with the gas pad, obtained with the different setups when a nominal power input of approximately 8 W is applied. A reasonable agreement with the water steam table data was obtained. When more powerful cartridge heaters or heaters with a longer heating part are used, overheating

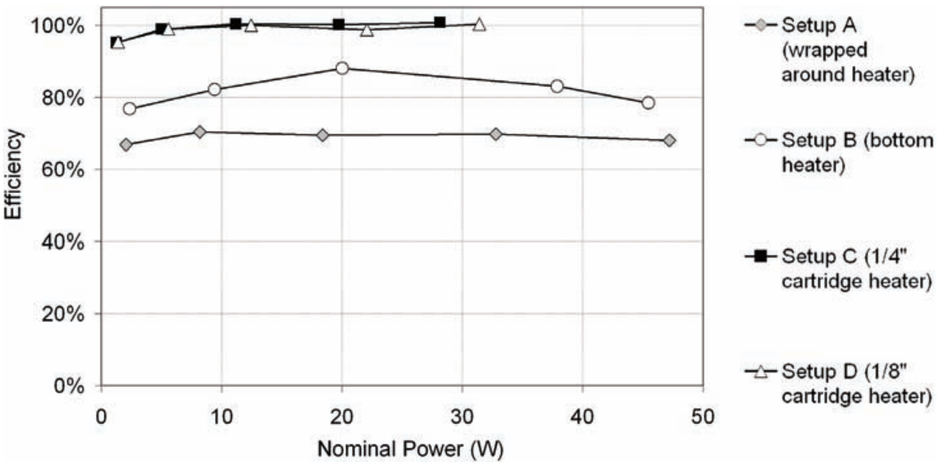

Figure 5. Efficiency of the different heating devices

Table 2. Experimental conditions of the characterisation tests with water

		Setup A	Setup B	Setup C	Setup D
Heater	Type	Wrapped around heater	Bottom heater	1/4″ cartridge heater	1/8″ cartridge heater
Test cell	Type	Standard (110 ml)	Standard (110 ml)	Custom (82 ml)	Custom (82 ml)
Water	Mass (kg)	0.077	0.077	0.057	0.057
Phi factor		1.073	1.072	1.12	1.1

Cp calculated at 30°C.

of the vapour phase by the upper part of the cartridge heater can occur. The measured pressure is therefore not only related to a thermodynamic equilibrium liquid/vapour, but also by the resulting thermal expansion of the vapour phase.

As a conclusion, the cartridge heaters appeared to be the best setups to input external heat in a test cell, providing the heating power does not lead to an unreasonable overheating of the gas phase.

TEST WITH REACTIVE SYSTEMS

Calorimetric tests in both adiabatic and external heat input mode were undertaken on two chemical systems:

- methanol + acetic anhydride reaction;
- decomposition of 20% di-tert-butyl peroxide (DTBP) in toluene.

These systems were chosen because they are well-known and often used as model systems for which reliable kinetic and physical properties are available in the literature.

METHANOL + ACETIC ANHYDRIDE

The reaction between methanol and acetic anhydride is a vapour pressure system. The reaction products are: methyl acetate and acetic acid. This reaction is autocatalytic. Seven tests were performed with setup A and setup D (Table 3). MAA_1 and MAA_4 are the adiabatic tests run respectively with the setups A and D. The tests MAA_5 and MAA_6 were run in the same condition at six-month intervals, to check the reproducibility of the results.

Figure 6 shows the results obtained. It clearly appears that increasing the external heat input leads to a decrease of the reaction completion time, an increase of the maximum temperature and pressure, and an increase of the maximum temperature and pressure rise rates. Figure 6 particularly shows that a good reproducibility was obtained with setup D. Indeed, all the curves corresponding to the tests MAA_5 and MAA_6 are very well superposed.

Figure 7 plots the temperature rise rates from both the setup A and D corrected by the phi factor. Good agreement between the two heating systems was obtained. It is also to be noted that similar results were obtained in adiabatic mode for the two setups (MAA_1 and MAA_4).

DECOMPOSITION OF 20% DTBP IN TOLUENE

This decomposition reaction is a tempered hybrid system, the pressure increase being due to the vaporisation of the contents and the production of non-condensable gas. Four experiments were performed with setup D (Table 4). DTBP_1 is the adiabatic test. DTBP_2 was run with an external heat input of 8.26 W/kg. DTBP_3 and DTBP_4 were both run with an external heat input of 22.9 W/kg in order to check the reproducibility of the results. The

Table 3. Tests with methanol and acetic anhydride; experimental conditions

	Wrapped around heater (Setup A)			Cartridge heater (Setup D)			
	MAA_1	MAA_2	MAA_3	MAA_4	MAA_5	MAA_6	MAA_7
External heat input	No	Yes	Yes	No	Yes	Yes	Yes
Nominal Power (W)	0	2.03	8.16	0	1.38	1.38	5.78
Power input (W)	0	1.42	5.71	0	1.38	1.38	5.78
Specific heat input (W/kg)	0	17.87	71.35	0	23.16	23.16	93.65
Mass methanol (g)	30.85	30.85	30.85	23.02	23.02	23.02	23.02
Mass acetic anhydride (g)	49.15	49.15	49.15	36.56	36.56	36.56	36.56
Total mass (g)	80.00	80.00	80.00	59.58	59.58	59.58	59.58
Methanol/Acetic Anhydride molar ratio	2:1	2:1	2:1	2:1	2:1	2:1	2:1
Fill level	76%	76%	76%	76%	76%	76%	76%
Phi factor	1.12	1.12	1.12	1.165	1.165	1.165	1.165
Initial temperature (°C)	24	24	24	24	24	24	24

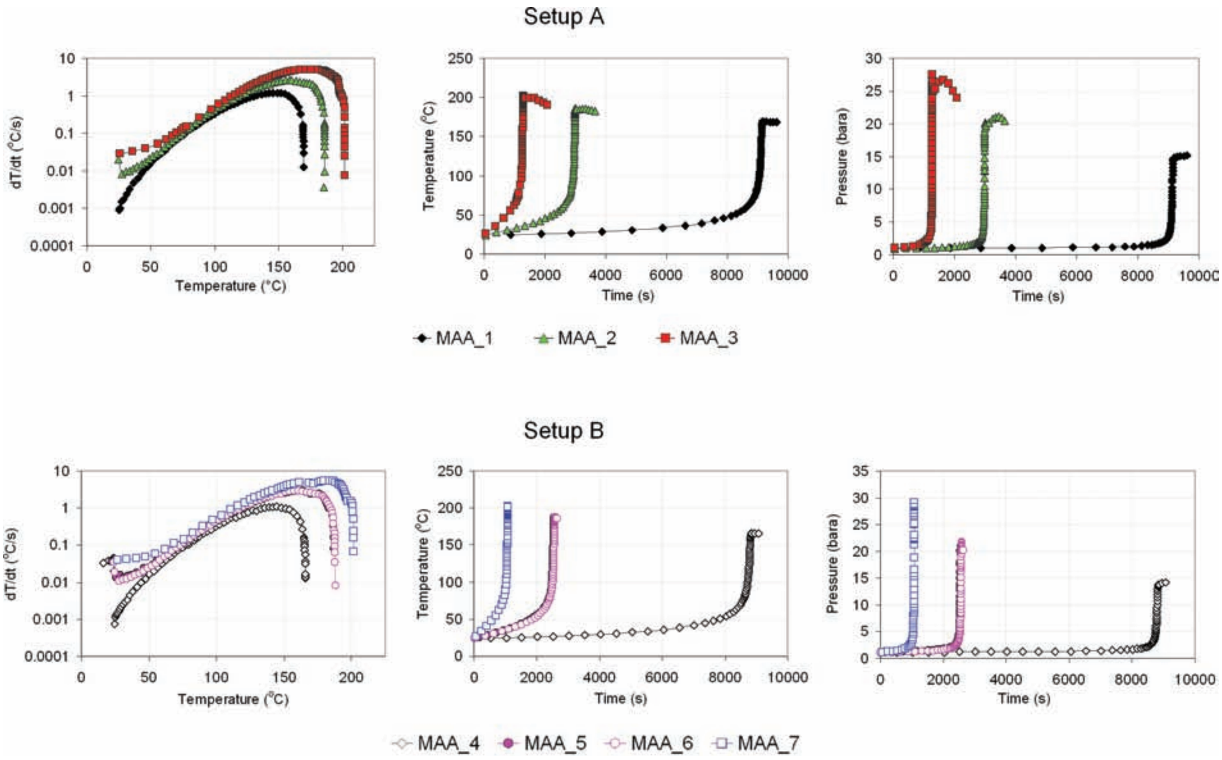

Figure 6. Runaway of methanol + acetic anhydride system

specific heat inputs tested were quite low for safety reasons. Indeed, this reaction is quite violent and produces a large amount of gas.

Figure 8 shows the results obtained. Like the methanol + acetic anhydride system, the results showed that increasing the external heat input leads to a decrease of the reaction completion time, an increase of the maximum temperature and pressure, and an increase of the maximum temperature and pressure rise rates. Good reproducibility was obtained for this system (DTBP_3 and DTBP_4).

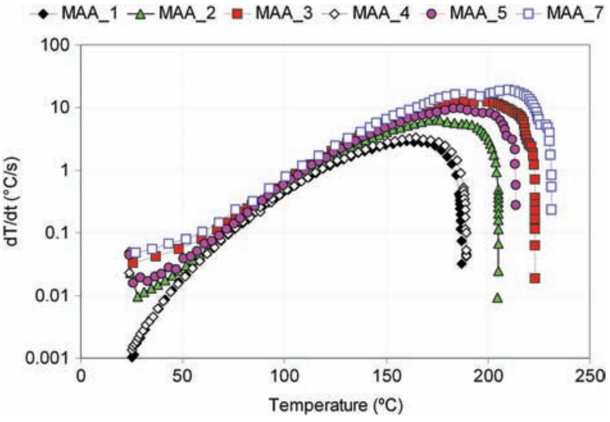

Figure 7. Runaway of methanol + acetic anhydride system with setup A and D, comparison of dT/dt corrected by the phi factor

TEST OF THE ADIABATIC DATA CORRECTION METHODS

The data obtained with methanol and acetic anhydride were used to evaluate the accuracy of two theoretical methods for the correction of adiabatic data to take into account the external heat input: Huff's method and a dynamic simulation approach.

4.1 HUFF'S METHOD

Huff[1] proposed a simple method to calculate, from adiabatic data, adjusted values of temperatures and temperature rise rates corresponding to the same reaction conversion, that take into account an external heat input:

$$\left(\frac{dT}{dt}\right)_{adj} = \left(\frac{dT}{dt}\right)^{/}_{reaction} + \left(\frac{dT}{dt}\right)_{fire} \tag{2}$$

Where

$(dT/dt)_{adj}$:	adjusted temperature rise rate
$(dT/dt)^{/}_{reaction}$:	temperature rise rate due the reaction alone
$(dT/dt)_{fire}$:	temperature rise rate due to the external heating

Table 4. Decomposition of 20% DTBP in toluene; experimental conditions

	DTBP_1	DTBP_2	DTBP_3	DTBP_4
Mass DTBP (g)	8.55	8.55	8.55	8.55
Mass toluene (g)	33.35	33.35	33.35	33.35
Total mass (g)	41.9	41.9	41.9	41.9
Fill level	60%	60%	60%	60%
Initial temperature (°C)	115	115	115	115
phi	1.34	1.34	1.34	1.34
Nominal Power (W)	0	0.346	0.959	0.959
Heat input (W)	0	0.346	0.959	0.959
Specific heat input (W/kg)	0	8.26	22.9	22.9

This assumes that the reaction conversion is well-defined by the fractional temperature rise for a given initial composition, independent of the temperature level.

The temperature rise rate of the reaction alone at a higher temperature for the same conversion rate is calculated from adiabatic data by:

$$\left(\frac{dT}{dt}\right)^{/}_{reaction} = \left(\frac{dT}{dt}\right)_{\text{Adiabatic}} \exp\left[-\frac{Ea}{R}\left(\frac{1}{T'}-\frac{1}{T_{\text{Adiabatic}}}\right)\right] \quad (3)$$

The calculation of the adjusted values of the temperatures (T'), temperature rise rates ($(dT/dt)^{/}_{reaction}$) in case of external heating requires an iterative calculation.

DYNAMIC SIMULATION MODEL

An alternative calculation method of the temperature and pressure rise rates resulting from a runaway reaction with external heat input consists of realising a dynamic simulation of the runaway. This requires the integration a set of differential equations describing the system:

$$\phi C_p \frac{dT}{dt} = q_R + q_{ext} \quad (4)$$

$$q_R = \Delta H_r \frac{dX}{dt} \quad (5)$$

$$\frac{dX}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(1-X)^n(B+X^r) \quad (6)$$

The heat of reaction (ΔH_r) can be measured from isothermal or adiabatic experiments. The determination of the kinetic parameters in equation (6) can be difficult. This requires special experimental investigations such as series of isothermal tests.

When the system investigated is a pure vapour system, the vessel pressure can be calculated using

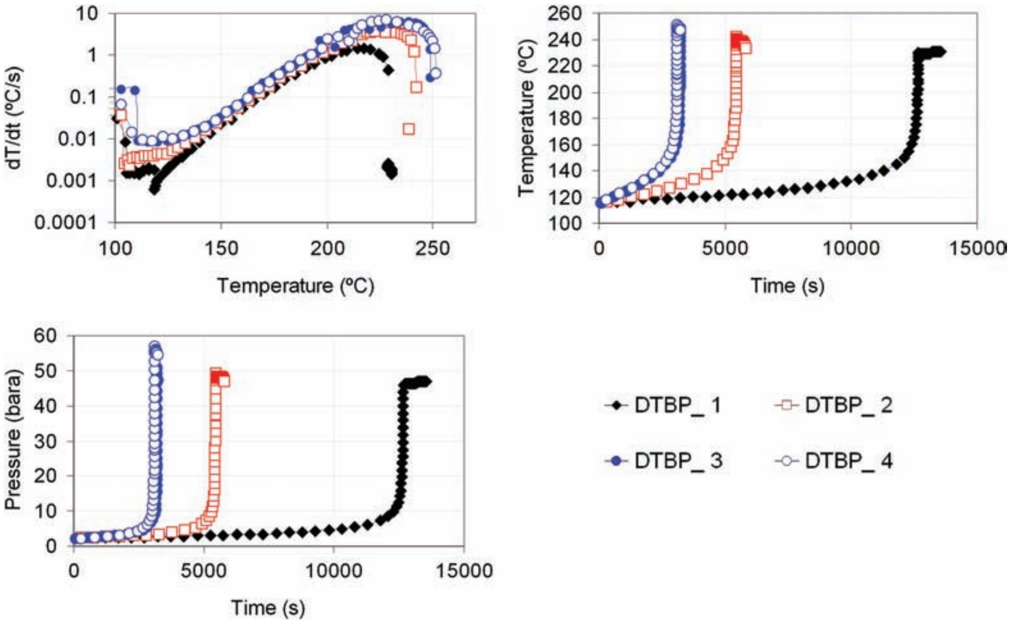

Figure 8. Decomposition of 20% DTBP in toluene with setup D (1/8″ cartridge heater)

Table 5. Chemical and physical properties and kinetics parameters of the system methanol + acetic anhydride in setup D

Methanol/Acetic Anhydride molar ratio	2:1	Phi factor (−)	1.165
Density solution ($kg.m^{-3}$)	946	C(s^{-1})	1.13×10^8
Specific Heat ($J.kg^{-1}K^{-1}$)	2500	Ea($J.mole^{-1}$)	73150
Heat of reaction ($J.kg^{-1}$)	416000	n(−)	1.23
K_1 (bara)	5.2252	q(−)	0.12
K_2 (bara.K)	1.812	B(−)	0
Fill level (−)	76%		

Antoine's equation:

$$\log_{10} P = K_1 - \frac{1000K_2}{T} \tag{7}$$

COMPARISON WITH EXPERIMENTAL DATA

Table 5 summarises the physical and chemical properties of the investigated system. These values are in accordance with those proposed in the literature.[4] These parameters are assumed to be constant.

Figure 9 shows the comparison between the correction methods and the experimental data. It appears that the two investigated correction methods gave comparable results.

Reasonable agreement between the theoretical Huff's method and the experimental data (MAA_5 and MAA_7) is obtained in terms of temperature rise rate. This theoretical correction gives conservative results. Indeed, the predicted temperature rise rates and the maximum temperature are higher than the experimental data.

With the chosen kinetic parameters, the temperature rise rates predicted by the dynamic model are quite close to the experimental data. A slight difference between the model and test MAA_5 is to be noted in terms of reaction completion time. This difference does not appear with

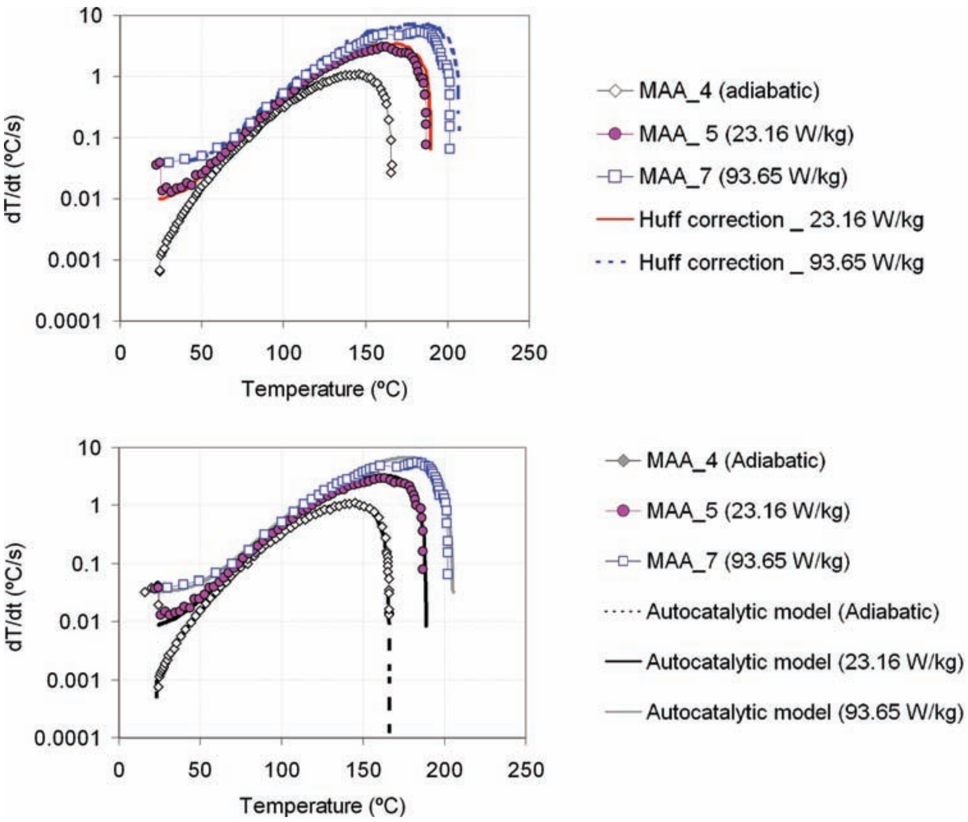

Figure 9. Validation test of Huff's method[1] and dynamic simulation method with methanol and acetic anhydride

Huff's method. A better determination of the kinetics parameters could lead to a improved prediction. The temperature rise rates predicted with the dynamic model are closer to the experimental data than those predicted by Huff's method. The predicted values of the maximum temperature and the maximum temperature rise rate are also better with the dynamic approach.

ADVANTAGES AND LIMITATIONS OF THE CORRECTION METHODS

The main advantage of Huff's method is to provide conservative results with few input data required (only adiabatic reaction data, liquid heat capacity and activation energy). These data are relatively commonly measured experimentally. No information on the reaction kinetics is required. Huff's method can give good results with single reaction systems. However, in the case of systems showing multiple overlapping reactions with different activation energies, Huff's approach would fail. Deficiencies in the assessment of the liquid heat capacity (which can be a function of the conversion) would also be at the origin of the failure of Huff's method.

The dynamic simulation is likely to give better results. But its implementation requires a good knowledge of the chemical system (thermodynamics, kinetics, physical and chemical properties), which is not often available. This more powerful approach can be used to simulate the dynamic behaviour of vessels exposed to fire, providing the parameters of the governing kinetic equations are determined. The complexity of this approach can make it time-consuming.

CONCLUSIONS

A commercially available adiabatic calorimeter was adapted for simulating the effect of an external heat input on reactive chemicals. Four heat input designs were tested.

A new method of using an immersion cartridge heater with a custom test cell appeared to be the best heat input setup, the input power from the power supply being fully used to heat the system.

Good experimental results were obtained with the methanol + acetic anhydride reaction (vapour system) and the decomposition reaction of 20% di-tert-butyl-peroxide in toluene (tempered hybrid system). It was experimentally shown that increasing the external heat input leads to a decrease of the reaction completion time, an increase of the maximum temperature and pressure, and an increase of the maximum temperature and pressure rise rates. This would have severe implications if it occurred in an industrial accident.

The experimental data allowed the experimental testing of the validity of two theoretical correction methods of adiabatic data. Huff's correction method was shown to give conservative results, with the significant advantage of only requiring few input data (adiabatic temperature rise rate and activation energy). However, in the case of systems showing multiple overlapping reactions with different activation energies, Huff's approach would fail. The use of a dynamic model taking into account the effect of external heating is likely to give better results. But its implementation requires a good knowledge of the chemical system, which is not often available.

When the chemical system is too complex to be simulated by a dynamic model, data is not available, or when it is outside the application range of Huff's method, the experimental measurement of the temperature and pressure rise rate using the heat input setup developed in this work would be a reliable, cost-effective and convenient alternative. This could provide a better set of calorimetric data for a safer and less over-conservative pressure relief system sizing. This could also be helpful in determining the choice of the best safety measures to be taken (prevention, passive fire protection, pressure relief system, water deluge, etc.).

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NOMENCLATURE

A	Pre-exponential factor (−)
B	Kinetic equation coefficient (−)
C_p	Specific heat capacity (J.kg^{-1} . K^{-1})
dT/dt	Temperature rise rate (K/s)
E_a	Activation energy (J.mole^{-1})
K_1	Coefficient of Antoine's equation (bara)
K_2	Coefficient of Antoine's equation (bara.K)
m	Mass of liquid (kg)
n	Kinetic equation coefficient (−)
P	Pressure (bara)
q	Kinetic equation coefficient (−)
r	Kinetic equation coefficient (−)
R	Gas constant (J.mol^{-1} . K^{-1})
Q_{nom}	Nominal power delivered by the power supply (W)
q_R	Reaction specific energy release rate (W . kg^{-1})
q_{ext}	Specific external heat input (W . kg^{-1})
T	Temperature of the liquid (K)
X	Chemical reaction conversion (−)
ϕ	Adiabaticity factor, phi factor (−)
ΔH_r	Reaction energy (J.kg^{-1})

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