

# Development of fire protection measures for vessels containing reactive chemicals

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Luc Véchot, Laurence Cusco & John Hare  
Health and Safety Laboratory  
Harpur Hill  
Buxton  
Derbyshire  
SK17 9JN

The objective of this work is to have a better understanding of the phenomena that occur when a vessel containing reactive chemicals is exposed to an external fire and so assess possible preventive and mitigation measures. The following approach has been adopted:

- an experimental calorimetric system for the simulating the effects on chemicals in vessels under fire loading was developed;
- the validity of theoretical models for the correction of adiabatic data were tested experimentally;
- dynamic simulations of large-scale vessels containing reactive chemicals exposed to a pool fire were carried out in order to study the effect of the presence of an insulation layer.

This work will form a useful basis for HSE to assess the adequacy of the 'fire case' for relief systems provided on a range of process reactors containing reactive chemicals and on storage vessels for reactive monomers. These installations vary in size from small reactors common in the pharmaceutical and fine chemical industries to the large, several hundred tonne capacity storage vessels used in the petrochemical industry.

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# CONTENTS

<b>1</b>	<b>INTRODUCTION.....</b>	<b>1</b>
<b>2</b>	<b>EXPERIMENTAL STUDY OF REACTIVE SYSTEMS SUBJECT TO EXTERNAL HEAT INPUT .....</b>	<b>2</b>
2.1	Experimental setup for the simulation of external heat input .....	2
2.2	Tests with reactive systems.....	10
2.3	Main outputs of the experimental investigations.....	16
<b>3</b>	<b>ASSESSMENT OF ADIABATIC DATA CORRECTION METHODS.....</b>	<b>18</b>
3.1	Description of the correction methods .....	18
3.2	Validation tests of the correction methods.....	20
3.3	Comparison and limits of the correction methods.....	24
<b>4</b>	<b>SIMULATION OF INSULATED VESSEL EXPOSED TO FIRE .....</b>	<b>25</b>
4.1	Heat input calculation methods .....	25
4.2	Dynamic simulation of a 2 m <sup>3</sup> vessel subject to fire.....	28
4.3	Vent sizing considerations.....	34
4.4	Suitability of vessel insulation.....	36
<b>5</b>	<b>CONCLUSION.....</b>	<b>37</b>
	<b>REFERENCES.....</b>	<b>39</b>
	<b>NOMENCLATURE.....</b>	<b>40</b>
	<b>APPENDIX 1: SCHEMATIC OF THE CUSTOM TEST CELLS.....</b>	<b>41</b>
	<b>APPENDIX 2: CHARACTERISATION TESTS WITH WATER.....</b>	<b>42</b>
	<b>APPENDIX 3: CALCULATION OF THE HEAT CAPACITY OF A CHEMICAL MIXTURE WITH SETUPS C AND D.....</b>	<b>46</b>
	<b>APPENDIX 4: LITERATURE AND EXPERIMENTAL DATA ON METHANOL/ACETIC ANHYDRIDE CHEMICAL MIXTURE .....</b>	<b>47</b>
	<b>APPENDIX 5: HARE <i>ET AL.</i> FIRE PROTECTION MEASURE FOR VESSELS CONTAINING REACTIVE CHEMICALS, ICHME SYMPOSIUM SERIES N°153, PAGES 1-6, 2007.....</b>	<b>49</b>



# EXECUTIVE SUMMARY

## Objectives

The objective of this work is to have a better understanding of the phenomena that occur when a vessel containing reactive chemicals is exposed to an external fire and so assess possible preventive and mitigation measures. The following approach has been adopted:

- An experimental calorimetric system for the simulating the effects on chemicals in vessels under fire loading was developed;
- The validity of theoretical models for the correction of adiabatic data were tested experimentally;
- Dynamic simulations of large-scale vessels containing reactive chemicals exposed to a pool fire were carried out in order to study the effect of the presence of an insulation layer.

## Main Findings

- 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.
- Some problems of reproducibility were experienced with the hydrolysis of acetic anhydride reaction, probably due the degradation of the cartridge heater by highly corrosive liquid (acetic anhydride and acetic acid).
- The validity of two theoretical correction methods of adiabatic data were tested experimentally using the data obtained with the methanol + acetic anhydride reaction:
  - *Huff's method* 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.
  - The *dynamic model taking into account the effect of external heating* is likely to give better results, however its implementation requires a detailed knowledge of the kinetics of the chemical system, which is not often available.
- When the chemical system is too complex to be simulated by a dynamic model, the kinetics 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.

- Some inconsistencies in API 521 and the UN methods for fire scenario design were noticed. It appeared that they could predict incorrect values in the following cases:
  - Large values of the thermal conductivity of the insulation layer;
  - Low values of the insulation thickness.
- Dynamic simulations of a 2 m<sup>3</sup> insulated vessel with passive fire protection (PFP) containing a reactive mixture (methanol and acetic anhydride) showed that an insulation layer could be a suitable passive protection method in case of external fire. It would lead to:
  - A decrease of the maximum temperature and pressure;
  - A decrease of the maximum temperature and pressure rise rates;
  - An increase of the reaction completion time;
  - A reduction of the required vent area.

## Recommendations

- Special care of the heat losses compensation calibration is required when using the calorimeter with a custom test cell (of smaller volume than the standard ones).
- The user of a heating system such as a cartridge heater (immersion heater) must ensure that:
  - The use of the chosen heating device does not interfere with the results;
  - The power input does not lead to a significant overheating of the vapour phase in the test cell.
- The suitability of passive fire protection seems case-dependent. A proper determination of the worst case would help to determine the suitability of the vessel insulation. It must be taken into account that:
  - In the case where the runaway reaction is initiated inside the vessel without any external heating, an insulation layer could limit the heat exchanges to the surroundings and lead to a more violent reaction than expected for a non-insulated vessel;
  - The insulation effect of PFP would reduce the effectiveness of any water deluge of fire-fighting water.

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# 1 INTRODUCTION

In the chemical industry, several incidents involving the exposure of reactor or storage vessels to fire have been reported [HID Semi Permanent Circular SPC/Tech/Gen/34 (December, 2004)]. The consequences of such incidents are related to the nature of the vessels or reactor contents. For vessels containing non-reactive liquid chemicals, fire exposure will cause the pressure to increase due to vapourisation of liquid and by thermal expansion of the vapour. For a vessel containing a self-reactive chemical, an exothermic runaway is initiated at a much earlier point in the conversion of reactants to products than would be the case with a process-induced runaway. The temperature is raised without a corresponding consumption of reactant, and the resulting higher concentration produces a much higher reaction rate. This would therefore lead to different venting characteristics and vent requirements.

To adopt suitable protection measures against fire, a better understanding of the phenomena involved in the runaway reaction of chemical systems with external heat input is necessary. Indeed, discussion of the limits of existing knowledge is available in open literature concerning:

- *The measurement of the temperature and pressure rise rates resulting from a runaway reaction with external heat input.* Some current standard commercially available adiabatic calorimeters propose an external heat input simulation mode. A certain number of uncertainties remain concerning the amount of heat entering the test cell. In parallel, Huff [1982] proposed a simple method to correct adiabatic data to take into account the external heat input. Even if this approach is accepted in the Design Institute for Emergency Relief System (DIERS) users group, this method has not been experimentally validated as far as we know.
- *The calculation of the amount of heat entering the vessel exposed to fire.* Current practice is typically to follow the standards (e.g. API 521) developed to protect liquefied petroleum gas (LPG) storage vessels against hydrocarbon pool fires. Roberts *et al.* [2003] showed that this might not be safe. Indeed, for chemicals undergoing decomposition or self-reaction (e.g. polymerisation) at elevated temperatures, there is insufficient knowledge of the amount of heating to which they may be safely exposed when held in pressure vessels. The adequacy in such circumstances of pressure relief, sized using current standards, is uncertain.

The main aim of this report is to obtain a better understanding of fire protection requirements for reactive chemical storage vessels. The following approach has been adopted:

- An experimental calorimetric system for simulating the effects on chemicals in vessels under fire loading was developed. Different heat input devices were tested with non-reactive and reactive systems.
- The validity of Huff's method for the correction of adiabatic data was tested experimentally. The results were compared to the ones obtained when using a dynamic model to take into account the effect of external heating.
- Dynamic simulations of large-scale vessels containing reactive chemicals undergoing a fire were carried out to observe the effect of the presence of a passive fire protection (PFP) insulation layer.

## 2 EXPERIMENTAL STUDY OF REACTIVE SYSTEMS SUBJECT TO EXTERNAL HEAT INPUT

The experimental work aimed to design a new heat input system for a modified adiabatic calorimeter. The concept was to adapt an existing adiabatic calorimeter (Phitec II) to 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. Experimental tests were also carried out with several reactive systems.

### 2.1 EXPERIMENTAL SETUP FOR THE SIMULATION OF EXTERNAL HEAT INPUT

The design of the experimental setup was intentionally kept simple and easily reproducible by any user of adiabatic calorimeters similar to the Phitec (e.g. VSP).

#### 2.1.1 Description of the experimental setup

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

- A Phitec II adiabatic calorimeter. The calorimeter is used without any modification of the original design or control software;
- A test cell containing the reactive substance;
- A simple standard independent external power supply;
- A heating element to heat the contents on the test cell.



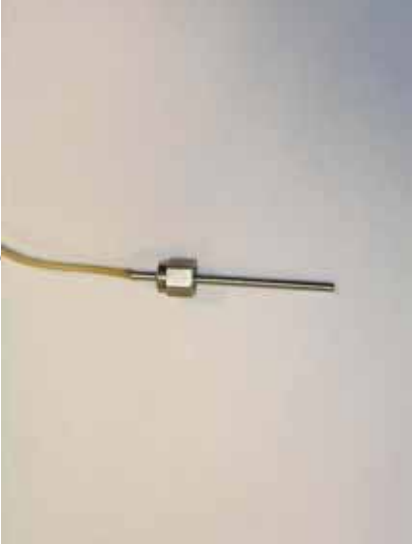

Four different heating elements, all commercially available, were tested (Table 1 and Figure 1):

- Two heating wires designed to be in contact with the external surface of a 110 ml standard test cell:
  - A 49 W wrapped around heater (side surface of a standard test cell);
  - A 50 W bottom heater (bottom surface of a standard test cell).
- Two cartridge heater aimed to be placed in a specially designed 82 ml test cell in order to heat directly the contents liquid:
  - A 30 W 1/4" cartridge heater;
  - A 30 W 1/8" cartridge heater.

The cartridge heaters were specifically designed, as far as technically possible, to have a minimum heating length located at the bottom end of the cartridge (Figure 2). The use of such cartridge heaters with the Phitec calorimeter required the design of custom test cells (Figure 1) equipped with a Swagelok male tube fitting on the top side to allow the insertion and the connection of the cartridge. The particular out centred position of the cartridge allows the heater to act as a baffle (improve agitation, prevent the formation of vortex). These tests cells (82 ml) are smaller than standard ones (110 ml) because of the limited space in the Phitec containment vessel. A schematic of the custom test cells is given in Table 2 and in Appendix 1. The tested heat input designs are (Figure 3):

- **Setup A:** 110 ml standard closed test cell + 49 W wrapped around heater
- **Setup B:** 110 ml standard closed test cell + 50 W bottom heater
- **Setup C:** 82 ml custom closed test cell + 30 W 1/4" cartridge heater
- **Setup D:** 82 ml custom closed test cell + 30 W 1/8" cartridge heater

The setup A and B required the use of insulation tapes between the heaters and the Phitec guard heaters. This was made to avoid any interference between the heating wire and the thermocouple of the guard heater (see Figure 3).

<p>49W wrapped around heater</p> 	<p>50W bottom heater</p> 
<p>1/8" cartridge heaters</p> 	<p>82 ml custom closed test cell for 1/4" cartridge heater</p> 

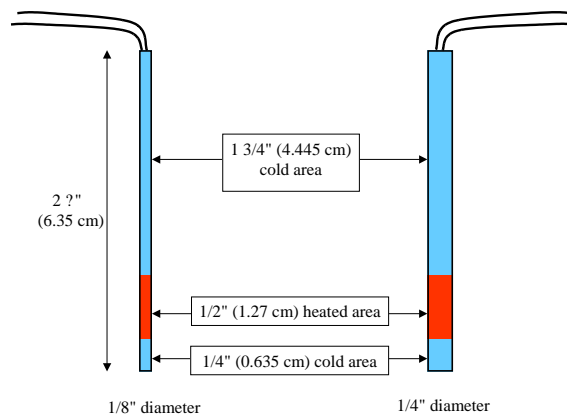
**Figure 1** Photograph of the custom test cell and the heating systems

**Table 1** Characteristics of the heating devices

	<i>Wrapped around heater</i>	<i>Bottom heater</i>	<i>Cartridge heater</i>	
			1/4"	1/8"
Voltage (V)	0-24	0-24	0-24	0-24
Resistance ( $\Omega$ )	12.5	11.2	19.8	17.95
Maximum Power (W)	49	50	30	30
Length (mm)	686	654	63.5	63.5
Diameter (mm)	1.57	1.57	6.35	3.17
Mass (g) (without wires and fittings)	11.615	10.812	6.125	3.45

**Table 2** Characteristics of the test cells

<i>Type of tests cell</i>	<i>Volume (ml)</i>	<i>Thermocouple</i>	<i>Fill line diameter (in.)</i>	<i>Heater connexion</i>	<i>Mass (g)</i>
Standard	110	1 type K	1/16	NA	38.2
Custom for 1/4" cartridge heater	82	1 type K	1/16	1/4" Swagelok fitting	42.3
Custom for 1/8" cartridge heater	82	1 type K	1/16	1/8" Swagelok fitting	40.0



24 VOLTS ; 30 WATTS

**Figure 2** Design of the cartridge heaters

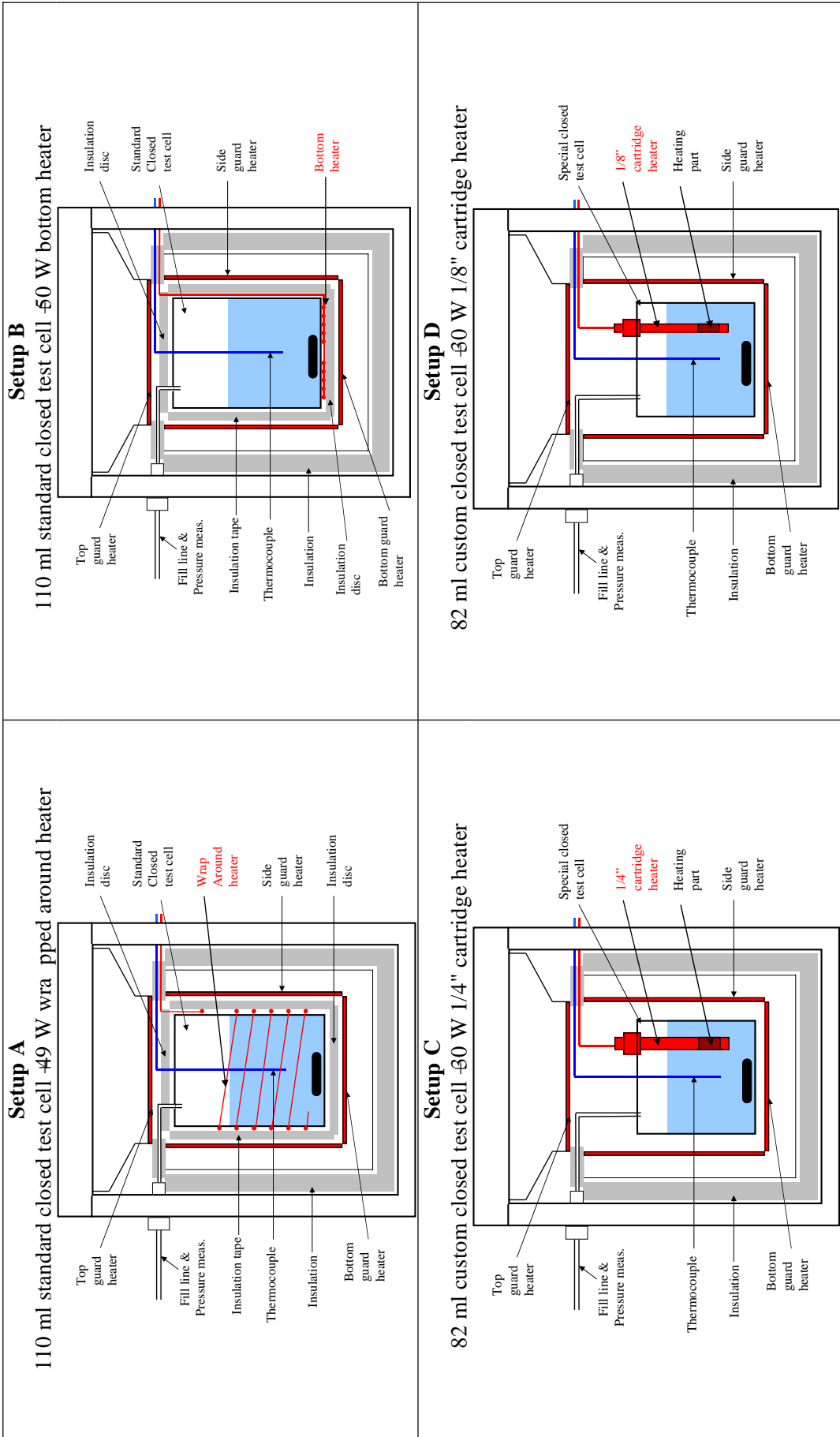


Figure 3 Experimental setup for external heat input

### 2.1.2 Heat loss compensation with the Phitec calorimeter

For each setup, a calibration of the Phitec calorimeter was made using test cells filled with Dimethyl Phtalate, to compensate for the heat losses. This consists of the calculation of the temperature difference between the liquid in the test cell and the Phitec guard heater (Figure 3) to compensate for the natural heat losses (maintain adiabaticity). The calibration aims to determine the parameters of an algorithm in the Phitec driving software that calculates the temperature difference to be applied as a function of the temperature of the liquid. This was easily achieved for the experimental setups involving standard test cells (setup A and B). However, the experimental setups involving the 82 ml custom test cell led to more important heat losses compared to standard test cells. The calculation of the parameters in these cases was not straightforward with the Phitec control software. A time-consuming investigation was necessary to obtain the correct parameters. This was one of the most significant technical problems of the experimental investigation.

### 2.1.3 Characterisation and comparison of the heat input devices

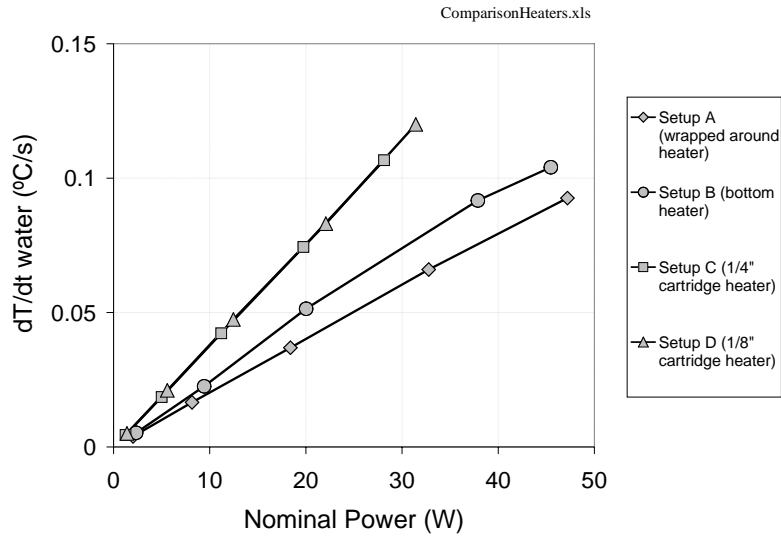
Each setup was used to heat a test cell filled at 70 % with water. The obtained water temperature rise rate ( $dT/dt$ ) is a function of:

- the nominal power ( $Q_{nom}$ ) delivered by the power supply;
- the power lost to the surroundings ( $Q_{lost}$ );
- the power absorbed by the test cell, the heater itself and the fittings. This is expressed as the thermal inertia ( $\phi$  or phi factor);
- the mass ( $m$ ) and the heat capacity of the liquid ( $Cp$ ).

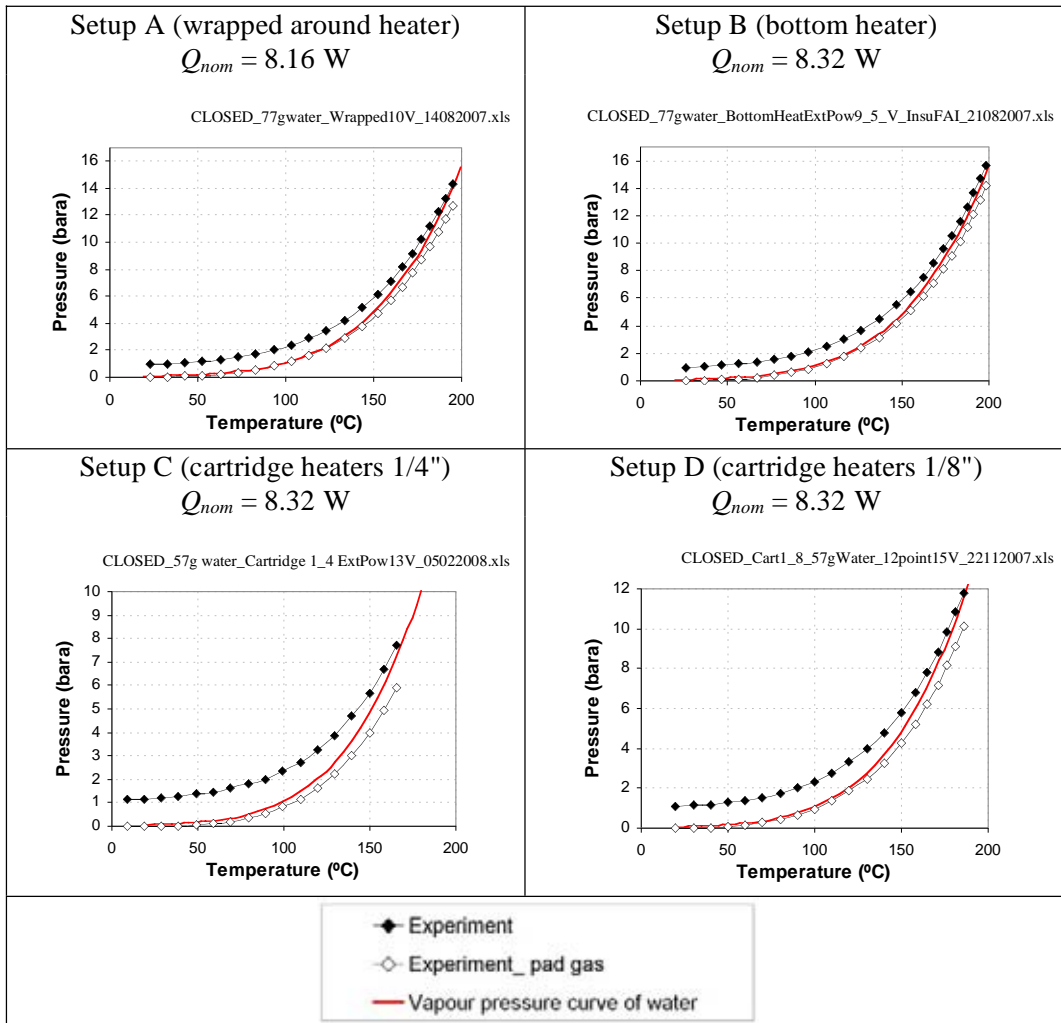
**Table 3** Experimental conditions of the characterisation tests with water

		<i>Setup A</i>	<i>Setup B</i>	<i>Setup C</i>	<i>Setup D</i>
Heater	Type	Wrapped around heater	Bottom heater	1/4" cartridge heater	1/8" cartridge heater
	Mass (kg)	0.011615	0.010812	0.006125	0.00345
	Cp (J.kg <sup>-1</sup> .K <sup>-1</sup> )	472	472	500	500
Test cell	Type	Standard (110 ml)	Standard (110 ml)	Custom (82 ml)	Custom (82 ml)
	Mass (kg)	0.0382	0.0382	0.0423	0.04
	Cp (J.kg <sup>-1</sup> .K <sup>-1</sup> )	472	472	472	472
Swagelok plugs	Mass (kg)	N/A	N/A	0.01066	0.00703
	Cp (J.kg <sup>-1</sup> .K <sup>-1</sup> )	N/A	N/A	472	472
Water	Mass (kg)	0.077	0.077	0.057	0.057
	Cp (J.kg <sup>-1</sup> .K <sup>-1</sup> )	4187	4187	4187	4187
Phi factor		1.073	1.072	1.12	1.1

Cp calculated at 30 °C



**Figure 4** Temperature rise rate of the water as a function of the nominal power



**Figure 5** Vapour pressure curves of water, comparison with literature data



Indeed the governing heat balance is:

$$\phi(mCp)_{liquid} \frac{dT}{dt} = Q_{nom} - Q_{lost} \quad \text{Equation 1}$$

With

$$Q_{nom} = RI^2 \quad \text{Equation 2}$$

$$\phi = \frac{(mCp)_{liquid} + (mCp)_{test\ cell} + (mCp)_{heater} + (mCp)_{fittings}}{(mCp)_{liquid}} \quad \text{Equation 3}$$

The efficiency of the heating device ( $\xi$ ) can be defined as the ratio of the power used to heat the liquid to the nominal power delivered by the power supply. This is given by:

$$\xi = \frac{Q_{nom} - Q_{lost}}{Q_{nom}} = \frac{\phi(mCp)_{liquid} \frac{dT}{dt}}{Q_{nom}} \quad \text{Equation 4}$$

All the graphs corresponding to the experiments are shown in Appendix 2. Figure 4 shows the measured temperature rise rate as a function of the nominal power delivered by the power supply. For the same nominal power, a higher temperature rise rate is obtained with the cartridge heaters.

Figure 5 shows the vapour pressure curves obtained with the different setups when a nominal power input of approximately 8 W is applied. To allow the comparison with water steam table data, the absolute pressure measured in the test cell was corrected to take into account the presence of pad gas. The vapour pressure curves obtained with the four setups show a reasonable agreement with the water steam table data. When more powerful cartridge heaters or heaters with a longer heating part are used, overheating 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.

The efficiency of the different setups, calculated with Equation 4, is shown in Figure 6:

- The wrapped around and the bottom heaters have an efficiency of 70 % and 80 % respectively. For these systems, a significant amount of heat (20 % to 30 % in this case) is lost to the surroundings. The heating wires represent the easiest way to simulate an external heat input, but large uncertainties remain regarding the exact amount of heat entering the test cell because of the heat losses to the surroundings. Indeed, the efficiency of such systems depends strongly on the quality of the insulation layer placed between the heaters and the Phitec guard heater (Figure 3). The type, the thickness, the age, the placement (which is operator-dependent) of the insulation layer can have an influence on the thermal properties and therefore the efficiency of the heating system. An experimental investigation of the efficiency of the entire setup is necessary beforehand.

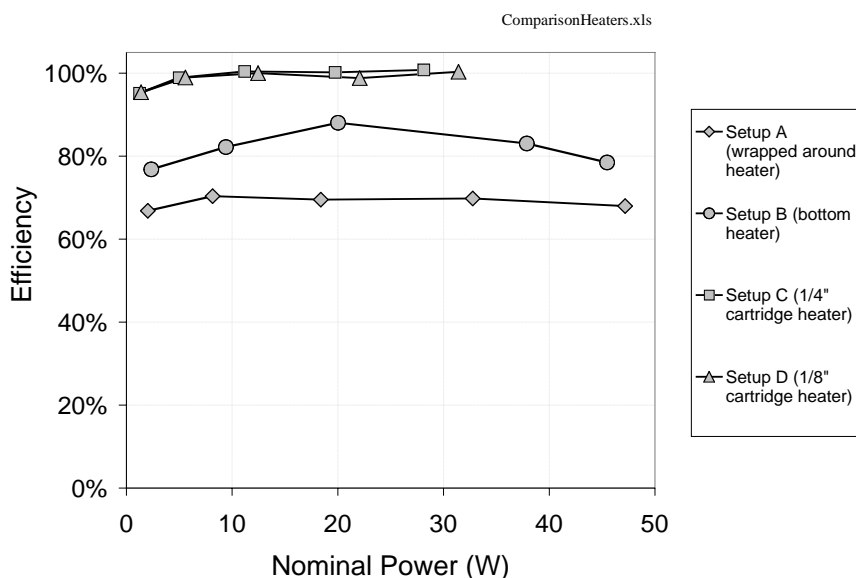
**Table 4** Comparison of the heating systems

	<i>Necessary equipment</i>	<i>Advantages</i>	<i>Disadvantages</i>
Heating wires	<ul style="list-style-type: none"> <li>Insulation tapes</li> <li>Power supply (integrated to calorimeter or external)</li> </ul>	<ul style="list-style-type: none"> <li>Standard test cell, low <math>\phi</math> factor</li> <li>Can be used without extra modification of the Phitec (or VSP2)</li> </ul>	<ul style="list-style-type: none"> <li>Power lost to surroundings (30 % for our experiments)</li> <li>Efficiency depends on insulation</li> <li>Need to calculate the efficiency</li> </ul>
Wrapped around heater	<ul style="list-style-type: none"> <li>Insulation tapes</li> <li>Power supply (integrated to calorimeter or external)</li> </ul>	<ul style="list-style-type: none"> <li>Standard test cell with low <math>\phi</math> factor<sup>1</sup></li> <li>No extra heating of the vapour phase</li> </ul>	<ul style="list-style-type: none"> <li>Power lost to surroundings (20 % for our experiments)</li> <li>Efficiency depends on insulation</li> <li>Need to calculate the efficiency</li> </ul>
Bottom heater	<ul style="list-style-type: none"> <li>Custom test cell equipped with extra fitting for the cartridge</li> <li>Power supply (integrated to calorimeter or external)</li> </ul>	<ul style="list-style-type: none"> <li>100 % efficiency</li> <li>Nominal power fully used to heat the system</li> <li>Exact amount of external heat is known</li> <li>Reproducible results</li> <li>Possibility to measure the Cp of a chemical mixture (see Appendix 3)</li> </ul>	<ul style="list-style-type: none"> <li>High <math>\phi</math> factor due to extra fittings and the lower volume of the test cell (Phitec)<sup>1</sup>.</li> <li>Special orders of custom test cells (time and money consuming)</li> <li>Difficult to limit the heat losses with the Phitec</li> <li>At high temperature, possible overheating of the vapour phase (not important for low wattage heaters)</li> </ul>
1/4"	<ul style="list-style-type: none"> <li>Custom test cell equipped with extra fitting for the cartridge</li> <li>Power supply (integrated to calorimeter or external)</li> </ul>	<ul style="list-style-type: none"> <li>100 % efficiency</li> <li>Nominal power fully used to heat the system,</li> <li>Exact amount of external heat is known</li> <li>Reproducible results</li> <li>Possibility to measure the Cp of a chemical mixture (see Appendix 3)</li> </ul>	<ul style="list-style-type: none"> <li>High <math>\phi</math> factor due to extra fittings and the lower volume of the test cell (Phitec)<sup>1</sup></li> <li>Special orders of custom test cells (time and money consuming)</li> <li>Difficult to limit the heat losses with the Phitec</li> <li>At high temperature, some heating of the vapour phase but less important than the 1/4" cartridge</li> </ul>
Cartridge heater	<ul style="list-style-type: none"> <li>Custom test cell equipped with extra fitting for the cartridge</li> <li>Power supply (integrated to calorimeter or external)</li> </ul>	<ul style="list-style-type: none"> <li>100 % efficiency</li> <li>Nominal power fully used to heat the system,</li> <li>Exact amount of external heat is known</li> <li>Reproducible results</li> <li>Possibility to measure the Cp of a chemical mixture (see Appendix 3)</li> </ul>	<ul style="list-style-type: none"> <li>High <math>\phi</math> factor due to extra fittings and the lower volume of the test cell (Phitec)<sup>1</sup></li> <li>Special orders of custom test cells (time and money consuming)</li> <li>Difficult to limit the heat losses with the Phitec</li> <li>At high temperature, some heating of the vapour phase but less important than the 1/4" cartridge</li> </ul>
1/8"	<ul style="list-style-type: none"> <li>Custom test cell equipped with extra fitting for the cartridge</li> <li>Power supply (integrated to calorimeter or external)</li> </ul>	<ul style="list-style-type: none"> <li>100 % efficiency</li> <li>Nominal power fully used to heat the system,</li> <li>Exact amount of external heat is known</li> <li>Reproducible results</li> <li>Possibility to measure the Cp of a chemical mixture (see Appendix 3)</li> </ul>	<ul style="list-style-type: none"> <li>High <math>\phi</math> factor due to extra fittings and the lower volume of the test cell (Phitec)<sup>1</sup></li> <li>Special orders of custom test cells (time and money consuming)</li> <li>Difficult to limit the heat losses with the Phitec</li> <li>At high temperature, some heating of the vapour phase but less important than the 1/4" cartridge</li> </ul>

<sup>1</sup> The configuration of the VSP2 calorimeter, supplied by FAI, would allow the use of standard volume test cells (110 ml) with extra fittings for the connexion of the cartridge. The resulting phi factor would then be lower than the 82 ml test cell used for this investigation.

- The 1/8" and 1/4" cartridge heaters are the *more efficient heating devices*. 100 % of the nominal power is used to heat the system (the heat losses therefore being negligible). This was as planned in this HSL design because the heater is immersed in the liquid. The cartridge heaters appeared to be the best setup to input external heat in a test cell, even if at high temperature possible heating of the vapour phase occurs, depending on the heating power.

Table 4 highlights the most important differences between the tested setups.



**Figure 6** Efficiency of the different heating devices

## 2.2 TESTS WITH REACTIVE SYSTEMS

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

- Two vapour pressure systems: methanol + acetic anhydride reaction and hydrolysis of acetic anhydride.
- One tempered hybrid system: the decomposition of 20 % di-tert-butyl peroxide (DTBP) in toluene.

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

### 2.2.1 Methanol + Acetic Anhydride

The reaction between methanol and acetic anhydride gives methyl acetate and acetic acid. This reaction is known as an autocatalytic [Balland *et al.*, 2002]. Seven tests were performed with setup A (wrap around heater) and setup D (1/8" cartridge heater) (Table 5). MAA\_1 and MAA\_4 are the adiabatic tests realised respectively with the setup A and D. The tests MAA\_5 and MAA\_6 were realised in the same condition at six month intervals, to check the reproducibility of the results.

Figure 7, Figure 8 and Figure 9 show the experimental 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 8 particularly shows that a good reproducibility was obtained with setup D (cartridge heater). Indeed, all the curves corresponding to the tests MAA\_5 and MAA\_6 are very well superposed.

Figure 10 plots the temperature rise rates from 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).

**Table 5** Test with methanol and acetic anhydride; experimental conditions

	<i>Wrapped around heater (Setup A)</i>			<i>Cartridge heater (Setup D)</i>			
	<i>MAA_1</i>	<i>MAA_2</i>	<i>MAA_3</i>	<i>MAA_4</i>	<i>MAA_5</i>	<i>MAA_6</i>	<i>MAA_7</i>
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

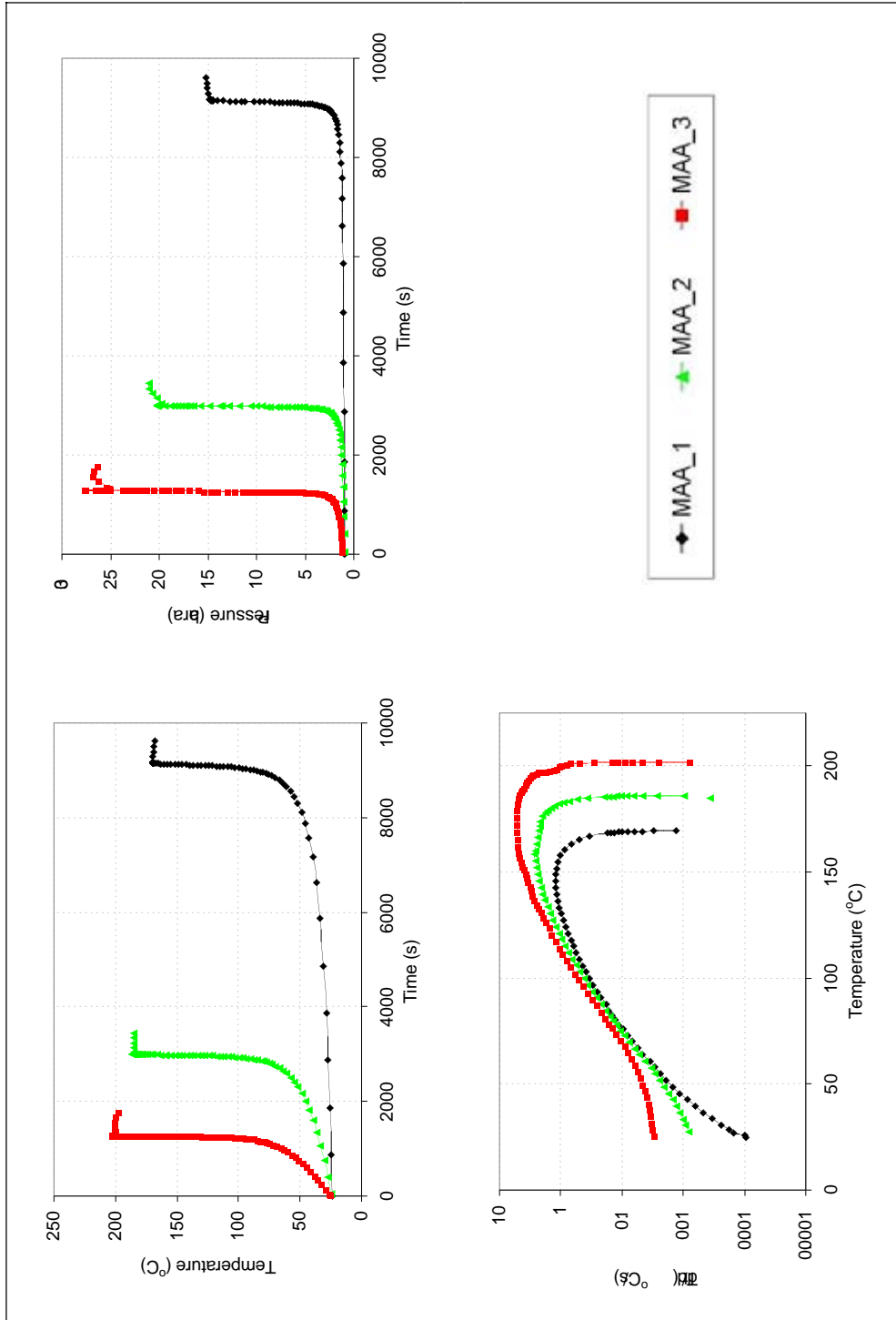


Figure 7 Runaway of methanol + acetic anhydride system with the setup A (wrapped around heater)

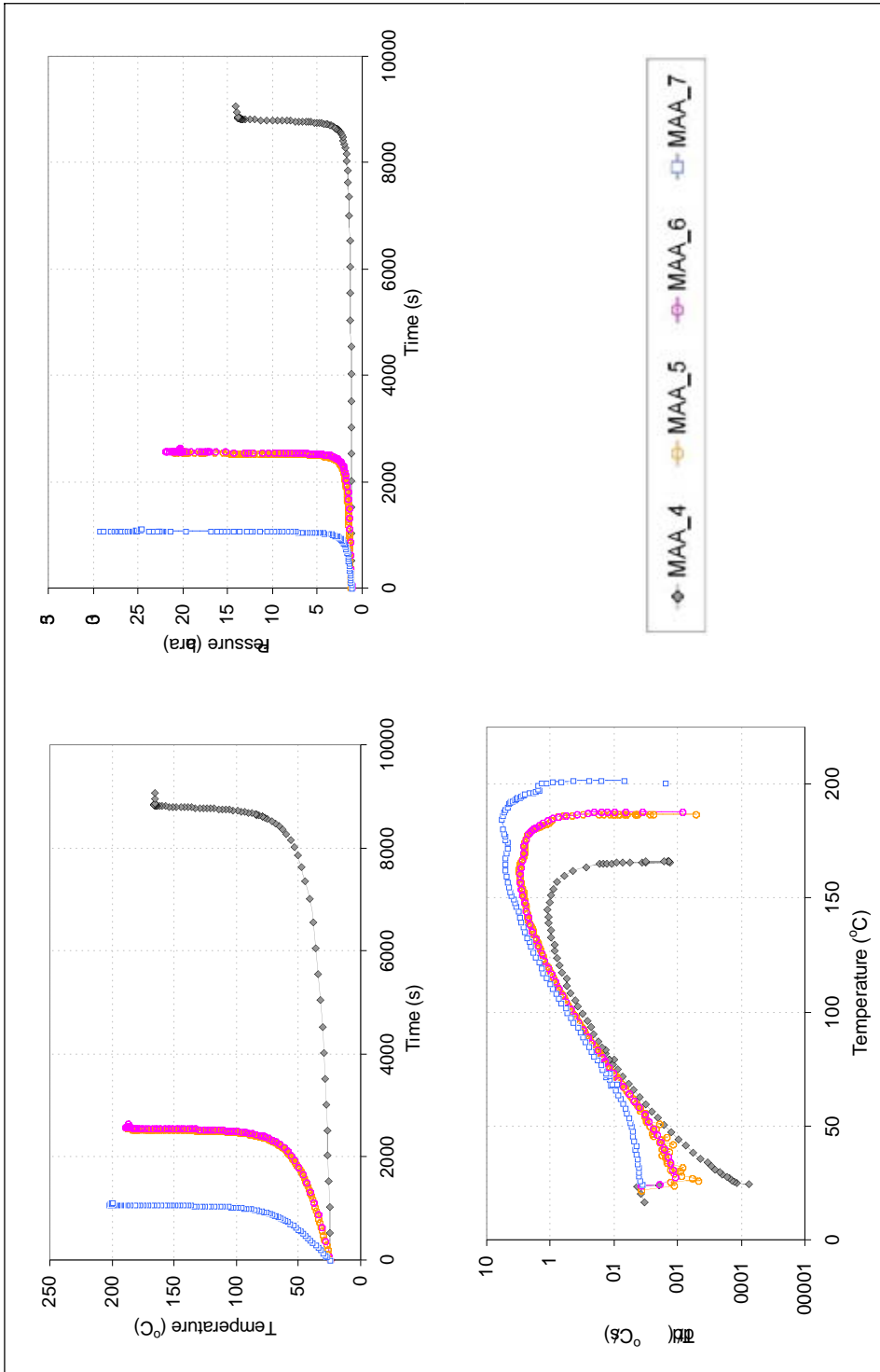
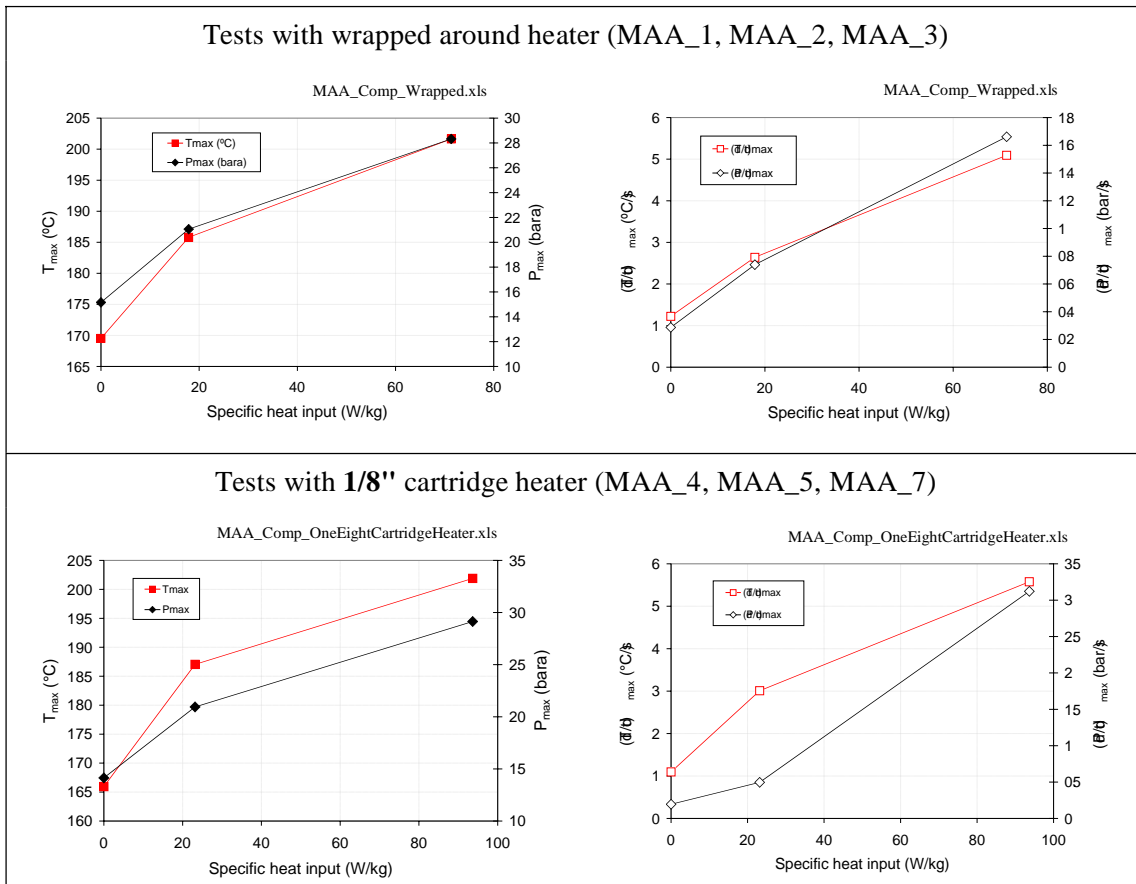
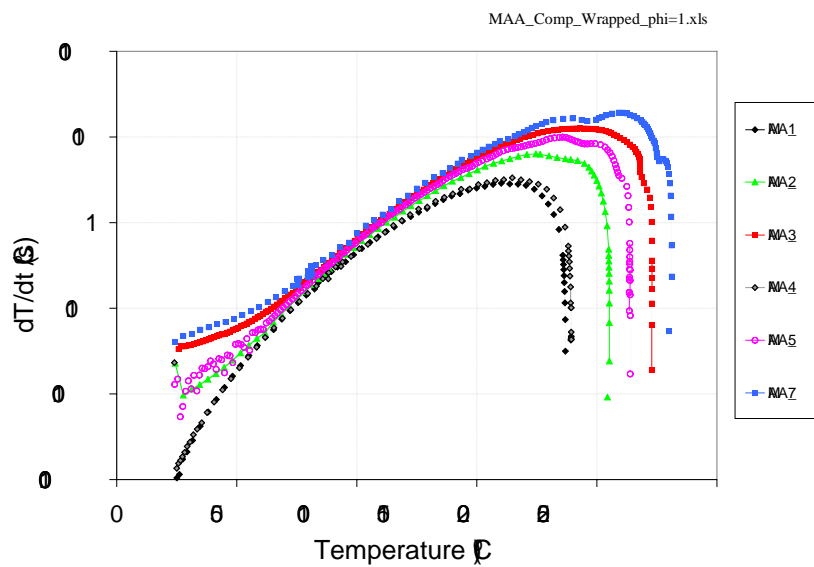


Figure 8 Runaway of methanol + acetic anhydride system with the setup D (cartridge heater)



**Figure 9** Runaway of methanol + acetic anhydride system  
Influence of the specific heat input



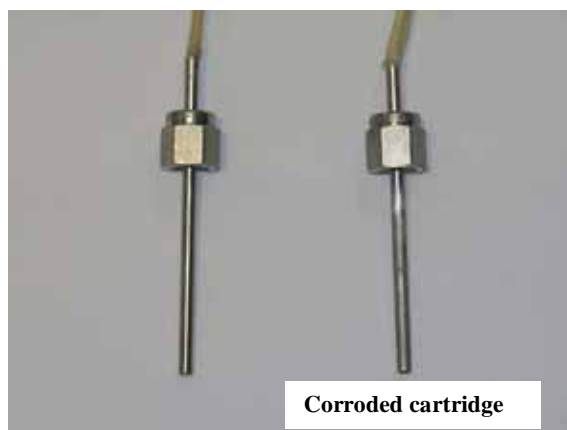
**Figure 10** Runaway of methanol + acetic anhydride system with setup A and D,  
comparison of dT/dt corrected by the phi factor

### 2.2.2 Hydrolysis of acetic anhydride

The reaction of acetic anhydride with water produces acetic acid. This reaction was tested only with the setup D (1/8" cartridge heater). The following difficulties were experienced:

- Some problems of reproducibility were observed when running several adiabatic tests.
- The cartridge heater was degraded by corrosion (see picture below), certainly because of the presence of a highly corrosive liquid (anhydride acetic and acetic acid).
- The formation of an unusual pink liquid product (acetic acid should be colourless), which may be due to the formation of metal complex, was observed. This could explain the problem of poor reproducibility.

This experiment showed the necessity to have a cartridge heater that does not influence the reproducibility of the results. In this case, this could have been achieved by using a different type of metal for the construction of the cartridge heater (perhaps hastelloy instead of stainless steel). Such reproducibility problems could occur when the metal of the test cell or the cartridge heater acts as a catalyst. One such example is the decomposition reaction of hydrogen peroxide in stainless steel test cells. In that particular case, a passivation of the test cell and the cartridge heater could solve the problem.



*Photograph of the test cell and the heating systems*

### 2.2.3 20 % DTBP in toluene

The decomposition of 20 % di-tert-butyl peroxide (DTBP) in toluene was investigated. This reaction is a tempered hybrid system. The pressure increase is due to the vaporisation of the contents and the production of non-condensable gas from the decomposition of the peroxide. Four experiments were performed with setup D (1/8" cartridge heater, Table 6). DTBP\_1 is the adiabatic tests. Tests DTBP\_2, DTBP\_3 and DTBP\_4 were realised with an external heat input of 8.26 and 22.9 W/kg. Tests DTBP\_3 and DTBP\_4 were realised in the same condition to check the reproducibility of the results. The specific heat inputs tested were quite low for safety reasons. Indeed, this reaction is quite violent and produces a large amount of gas. A specific heat input higher than 22.9 W/kg was tested but this led to the failure of the test cell.

Figure 11 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 (similar results obtained with DTBP\_3 and DTBP\_4). It is to be noted that very high pressures were obtained (up to 57 bara). In general good results were obtained with this system.



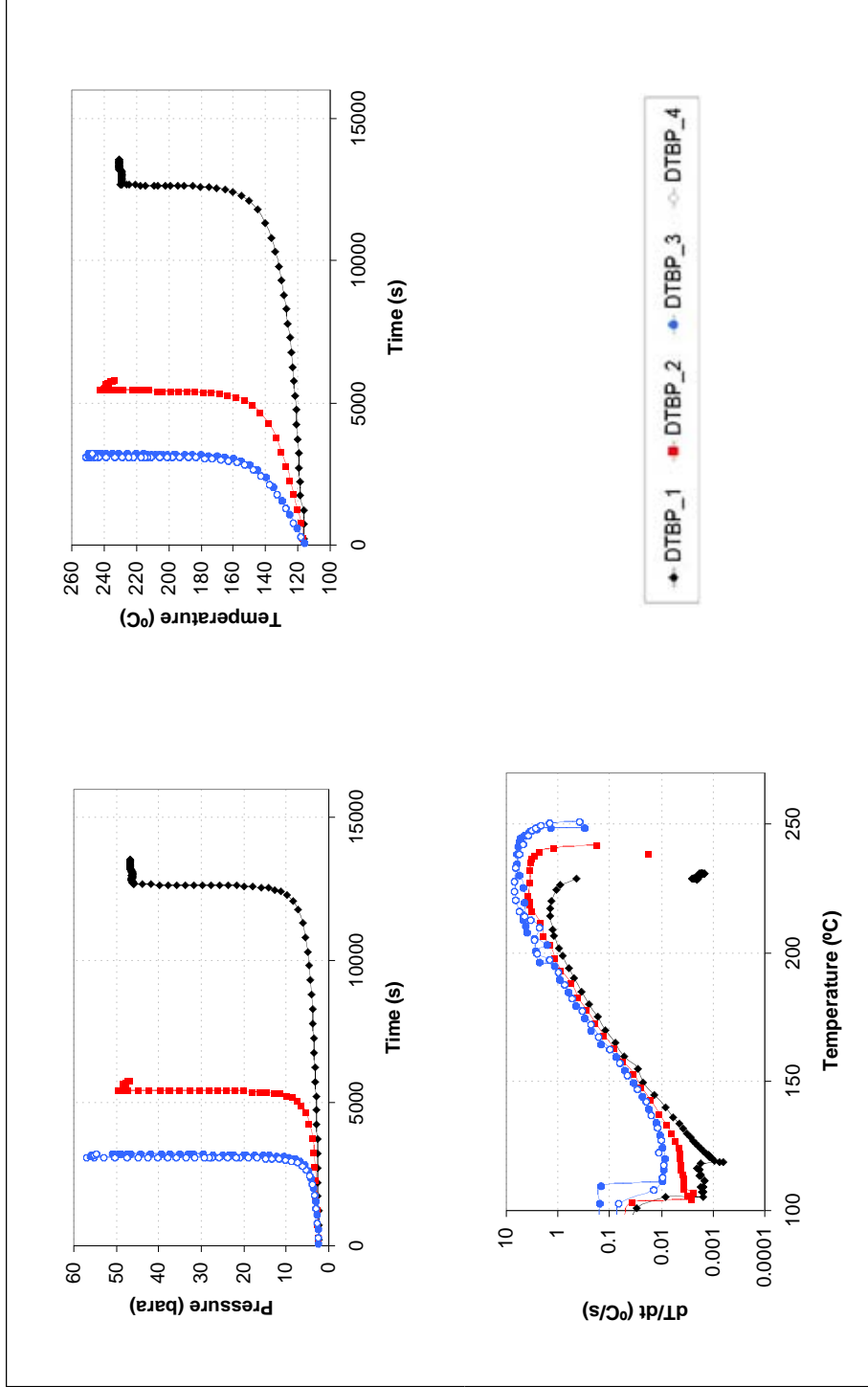
**Table 6** Decomposition of DTBP in toluene; experimental conditions

	<i>DTBP_1</i>	<i>DTBP_2</i>	<i>DTBP_3</i>	<i>DTBP_4</i>
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 (Watts)	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

### 2.3 MAIN OUTPUTS OF THE EXPERIMENTAL INVESTIGATIONS

The following findings were obtained from the experimental investigation:

- A Phitec calorimeter was successfully adapted to simulate the effect of external heat input on reactive chemicals.
- Four heat input designs were tested and compared:
  - *Setup A* (110 ml standard closed test cell + 49 W wrapped around heater) and *Setup B* (110 ml standard closed test cell + 50 W bottom heater):
    - They represent the simplest way to simulate an external heat input (use of standard test cells with standard values of phi factor).
    - Low extra heating of the vapour phase was observed.
    - The nominal power delivered by the power supply is partly used to heat the system (70 % to 80 %), a significant amount of heat being lost to the surroundings.
  - *Setup C* (82 ml custom closed test cell + 30 W 1/4" cartridge heater) and *Setup D* (82 ml custom closed test cell + 30 W 1/8" cartridge heater):
    - The design of the custom test cells and the calibration for the heat loss compensation may be time-consuming.
    - The phi factor is slightly higher than the phi factor of a standard test cell (approximately 5 % higher).
    - Overheating of the vapour phase can occur for high values of the heating power.
    - The nominal power is fully used to heat the system.
    - They appeared to be the best setup to input external heat in a test cell, the exact amount of heat input being known.
- Good results were obtained with the methanol + acetic anhydride reaction (vapour system) and the decomposition reaction of 20 % DTBP in toluene (tempered hybrid system) with setups A and D.
- 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.
- The hydrolysis of acetic anhydride reaction was tested with the setup D (1/8" cartridge heater). Some reproducibility problems were experienced, probably due the degradation of the cartridge heater by highly corrosive liquid (anhydride acetic and acetic acid).



**Fig 1** Decomposition of 20 % DTBP in toluene with setup D (1/8" cartridge heater)

### 3 ASSESSMENT OF ADIABATIC DATA CORRECTION METHODS

The experimental investigation described earlier allowed the development of an experimental setup to measure the temperature and pressure rise rates resulting from a runaway reaction with external heat input. 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.

#### 3.1 DESCRIPTION OF THE CORRECTION METHODS

##### 3.1.1 Huff's method

Huff [1982] proposed a simple method to correct adiabatic data. However, it has not been experimentally validated as far as we know. Huff's method is an iterative method that requires the adiabatic data and the value of the activation energy of the reaction to be implemented. It has the advantage that detailed kinetics are not required. It assumes that the reaction conversion is well defined by the fractional temperature rise for a given initial composition, independent of the temperature level. When a runaway reaction occurs with external heat input, the total temperature rise rate is due to both the external heat input and the reaction itself:

$$\left(\frac{dT}{dt}\right)_{total} = \left(\frac{dT}{dt}\right)_{reaction} + \left(\frac{dT}{dt}\right)_{fire} = \left(\frac{dT}{dt}\right)_{reaction} + \frac{q_{ext}}{Cp_{liquid}} \quad \text{Equation 5}$$

In this case, less reactant conversion is needed to reach a given temperature, the liquid being 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. Huff's idea is to calculate, from adiabatic data, adjusted values of temperatures and temperature rise rates corresponding to the same reaction conversion:

$$\left(\frac{dT}{dt}\right)_{adj} = \left(\frac{dT}{dt}\right)'_{reaction} + \left(\frac{dT}{dt}\right)_{fire} \quad \text{Equation 6}$$

Where

$\left(\frac{dT}{dt}\right)_{adj}$ : adjusted temperature rise rate

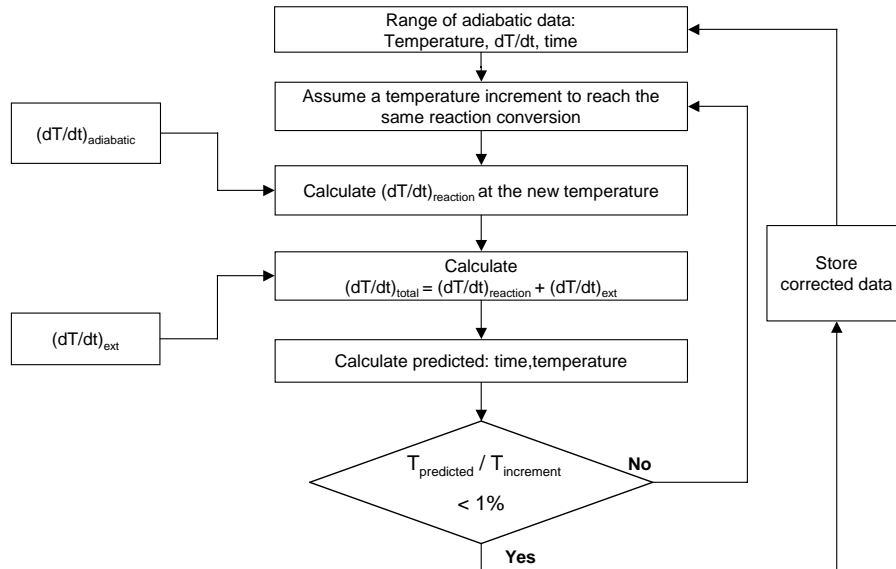
$\left(\frac{dT}{dt}\right)'_{reaction}$ : temperature rise rate due the reaction alone

$\left(\frac{dT}{dt}\right)_{fire}$ : temperature rise rate due to the external heating

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

$$\left(\frac{dT}{dt}\right)'_{reaction} = \left(\frac{dT}{dt}\right)_{Adiabatic} \exp\left[-\frac{Ea}{R}\left(\frac{1}{T'} - \frac{1}{T_{Adiabatic}}\right)\right] \quad \text{Equation 7}$$

The calculation of the adjusted values of the temperatures ( $T'$ ), temperature rise rates ( $\left(\frac{dT}{dt}\right)'_{reaction}$ ) in case of external heating requires an iterative calculation. This can be achieved by implementing macros on a spreadsheet. Figure 12 shows the implementation chart of Huff's method. Hare *et al* [2007] used Huff's methods to correct adiabatic data for two chemical reactions: decomposition of a peroxyester in isododecane and hydrolysis of acetic anhydride.



**5 2** Implementation chart of Huff's method

### 3.1.2 Dynamic simulation approach

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. The thermal balance corresponding to a closed vessel containing a reactive mixture and exposed to an external heat input is given by:

$$\phi C_p \frac{dT}{dt} = q_R + q_{ext} \quad \text{Equation 8}$$

$q_{ext}$  is the specific external heat input in  $(W.kg^{-1})$ . The reaction energy release rate ( $q_R$ ) is linked to the conversion rate ( $dX/dt$ ) by the following expressions:

$$q_R = \Delta H_r \frac{dX}{dt} \quad \text{Equation 9}$$

The heat of reaction ( $\Delta H_r$ ) can be measured from isothermal or adiabatic experiments. The reaction conversion rate is given by the following kinetic equation:

$$\frac{dX}{dt} = C \exp\left(\frac{-E_a}{RT}\right) (1-X)^n (B + X^r) \quad \text{Equation 10}$$

The determination of the kinetic parameters can be difficult. This requires special experimental investigations such as a series of isothermal tests. When the system investigated is a pure vapour system, the vessel pressure can be calculated using Antoine's equation:

$$\log_{10} P = K_1 - \frac{1000K_2}{T} \quad \text{Equation 11}$$



**Figure 13** Simulation tool developed under Visual Basic

An in-house simulation tool was developed under Visual Basic to numerically integrate the above differential equations using Euler's method (Figure 13).

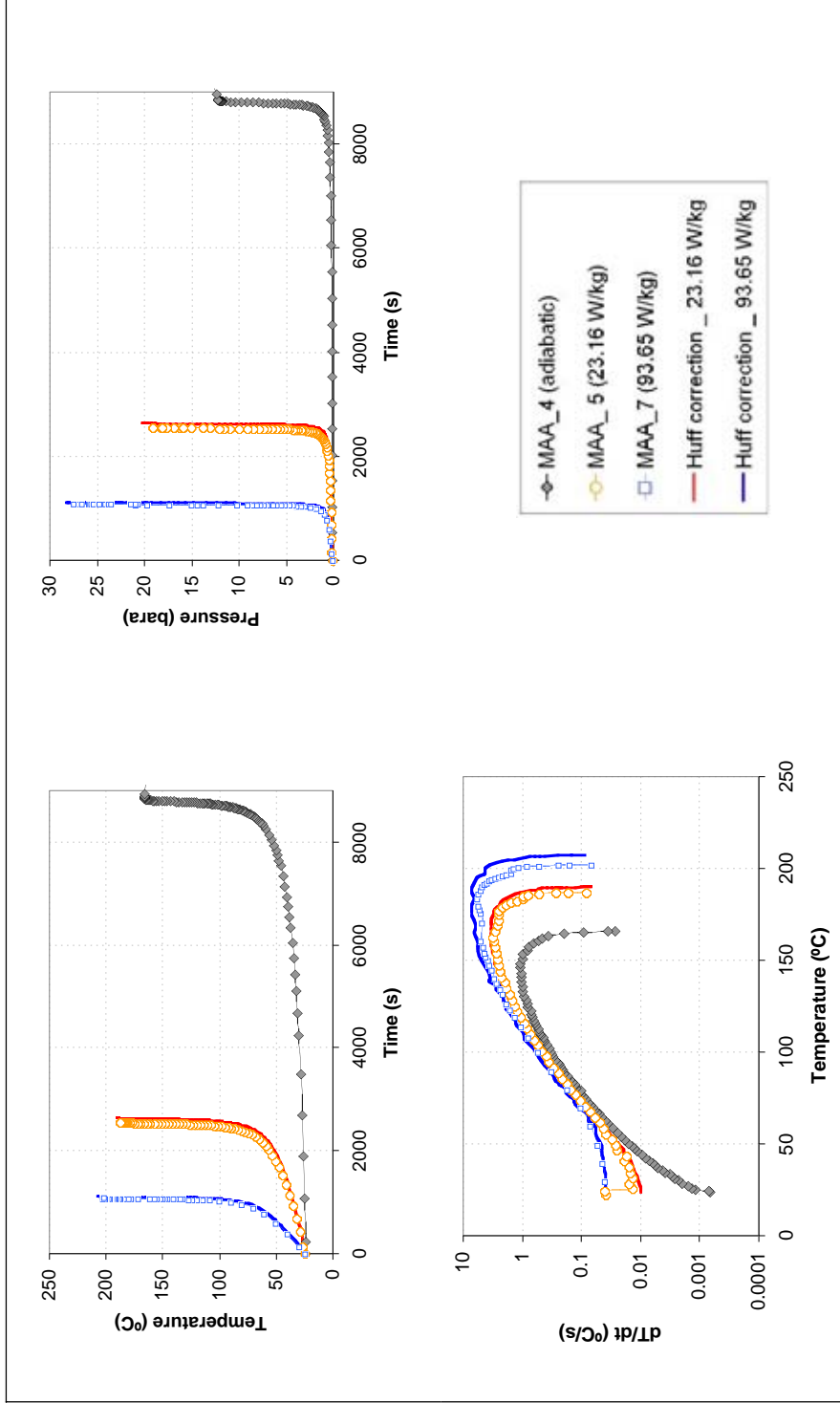
### 3.2 VALIDATION TESTS OF THE CORRECTION METHODS

The validity of the above correction methods were assessed using the experimental data obtained with the methanol + acetic anhydride system. The data obtained with using the setup D (1/8" cartridge heater, 2.2.1) were chosen because the exact amount of the specific heat input is known: MAA\_4 ( $q_{\text{ext}} = 0 \text{ W.kg}^{-1}$  (adiabatic test)), MAA\_5 ( $q_{\text{ext}} = 23.16 \text{ W.kg}^{-1}$ ) and MAA\_7 ( $q_{\text{ext}} = 93.16 \text{ W.kg}^{-1}$ ).

Table 7 summarises the physical and chemical properties of the investigated system. The experimental curves used to determine the activation energy and the vapour pressure curve of the chemical mixture are shown in Appendix 4. Average values of the density ( $946 \text{ kg.m}^{-3}$ ) and heat capacity ( $2500 \text{ J.kg}^{-1}.\text{K}^{-1}$ ; see the Cp of the pure components in Appendix 4) were chosen for the calculations. These values are in accordance with those proposed in the literature (Rogers, 1986). These parameters are assumed to be constant.

To implement Huff's method, only two parameters are necessary: the heat capacity of the solution and the reaction activation energy. Huff's correction was directly applied to experimental adiabatic data, without any correction for the phi factor. The effect of the phi factor is experimentally taken into account. Subsequent corrections for the phi factor would be necessary when using such data to scale up to larger vessels. Figure 14 shows that excellent predictions of the temperature and pressure profiles are obtained. Reasonable agreement between 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.

The implementation of the dynamic simulation approach was more time-consuming. It also required more experimental data (Table 7). A determination of the reaction kinetics was necessary. The methanol and acetic anhydride system is known as an autocatalytic system [Balland *et al*, 2002; Widel *et al*, 2006]. The chosen kinetic coefficients for Equation 10 are presented in Table 7. Figure 15 shows that these coefficients provided an acceptable fit of the adiabatic data. An experimental investigation using isothermal tests would allow a more accurate determination of these coefficients and then lead to a better fit of the experimental adiabatic data.



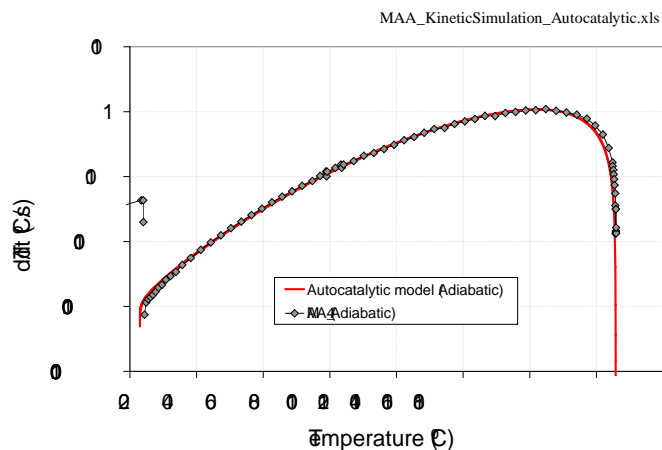
**Fig 4** Validation test of Huff's method with methanol and acetic anhydride

**Table 7** Chemical and physical properties and kinetics parameters of the system methanol + acetic anhydride in setup D

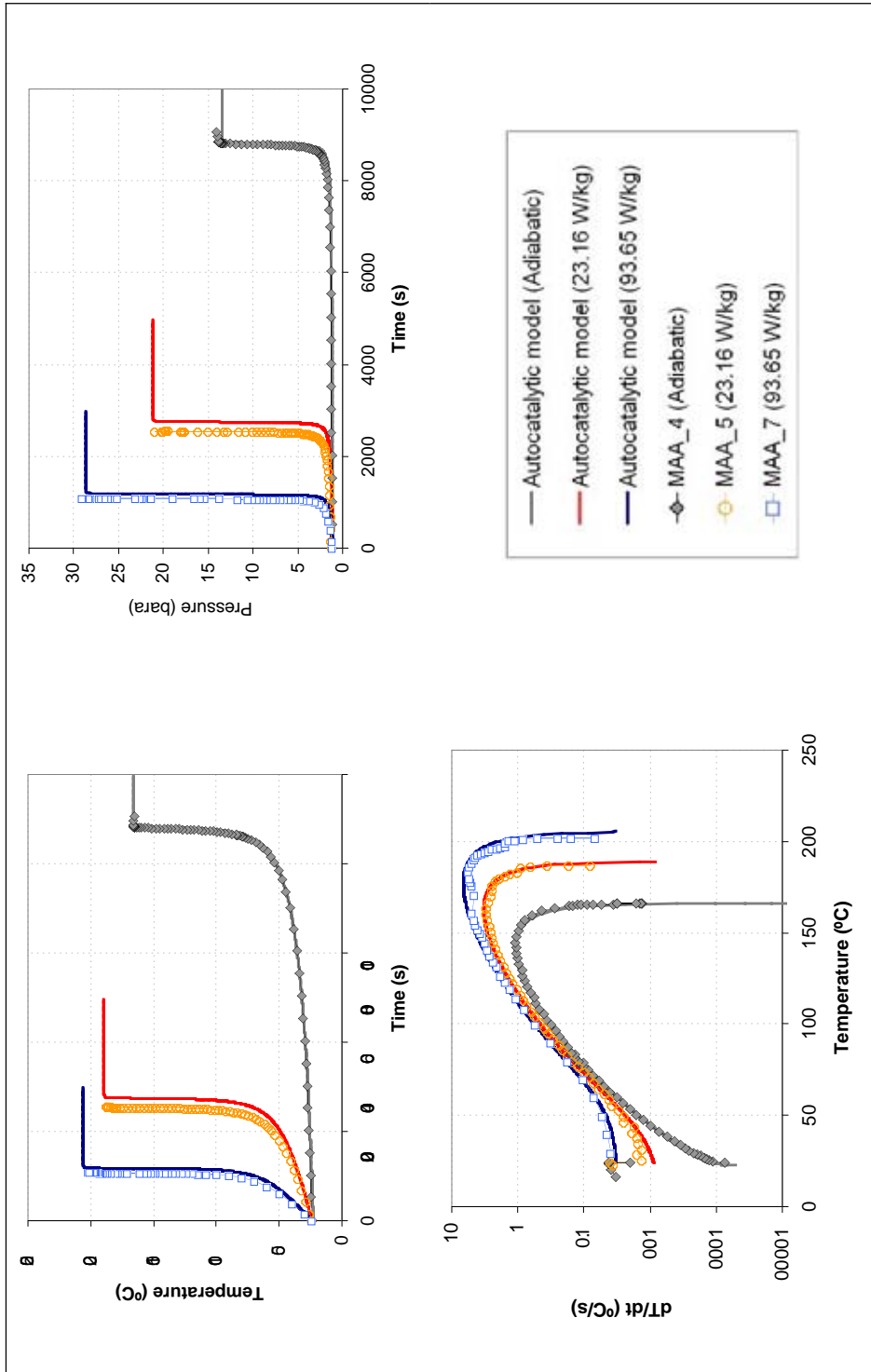
Methanol/Acetic Anhydride molar ratio	2:1
Density solution (kg.m <sup>-3</sup> )	946
Specific Heat (J.kg <sup>-1</sup> .K <sup>-1</sup> )	2500
Heat of reaction (J.kg <sup>-1</sup> )	416000
K <sub>1</sub> (bara)	5.2252
K <sub>2</sub> (bara.K)	1.812
Fill level (-)	76 %
Phi factor (-)	1.165
C (s <sup>-1</sup> )	1.13 x 10 <sup>8</sup>
Ea (J.mole <sup>-1</sup> )	73150
n (-)	1.23
q (-)	0.12
B (-)	0

Figure 16 shows the comparison between the dynamic simulation and the experimental data. With the chosen kinetic parameters, the predicted temperature and pressure 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 Huff's method. A better determination of the kinetics parameters could lead to a better 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.

This investigation also shows that the heat input setups developed in this work can be used to check the consistence of a kinetic model. For methanol and acetic anhydride reactive systems, some literature sources indicate that a first order equation could fit the adiabatic data (Rogers, 1986). A reasonable fit of the adiabatic data can indeed be obtained with such a kinetic expression. During this investigation it has been seen that the use of a first order model is not suitable to simulate the reaction when external heat input occurs.



**Figure 15** Adiabatic runaway reaction of methanol and acetic anhydride; comparison between experiment and autocatalytic model



**Fig 6** Validation of the dynamic simulation approach with methanol and acetic anhydride



### 3.3 COMPARISON AND LIMITS OF THE CORRECTION METHODS

The two investigated correction methods gave comparable results. They were both shown to be in reasonable agreement with the experimental data. Table 8 presents a practical comparison of the Huff's method and the dynamic simulation approach.

The main advantage of Huff's method is to provide conservative results with few input data. Indeed, this method requires only the adiabatic reaction data, the liquid heat capacity and the activation energy to be implemented. These data are commonly measured experimentally. No information on the reaction kinetics is required. Huff's method can give good results with systems for which the reaction conversion is well defined by the fractional temperature rise for a given initial composition, independent of the temperature level [Huff, 1982]. This would be the case in single reaction systems. However in the case of systems showing multiple overlapping reactions with different activation energies, Huff's approach would fail. A poor prediction of the temperature history in the region of overlap could be obtained. Deficiencies in the assessment of the liquid heat capacity would also be at the origin of the failure of Huff's method. The heat capacity of a chemical mixture can be a function of the conversion, the composition of the chemical mixture changing with time.

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 representatives governing kinetic equations are determined. The complexity of this approach can make it time-consuming. When the chemical system is too complex to be simulated by a model using the dynamic simulation approach or when it is outside the application range of Huff's method, the experimental measurement of the temperature and pressure rise rate using one the heat input setup developed in this work would be an easy, cheap and convenient alternative.

**Table 8** Comparison between Huff's method and the dynamic simulation approach

	<i>Huff's method</i>	<i>Dynamic simulation approach</i>
Experimental required investigation	<ul style="list-style-type: none"> <li>• Adiabatic test</li> </ul>	<ul style="list-style-type: none"> <li>• Adiabatic test</li> <li>• Isothermal tests</li> </ul>
Data needed	<ul style="list-style-type: none"> <li>• Activation Energy</li> <li>• Vapour pressure curve</li> </ul>	<ul style="list-style-type: none"> <li>• Activation Energy</li> <li>• Full kinetic equation</li> <li>• Heat of reaction</li> <li>• Phi factor</li> <li>• Cp liquid</li> </ul>
Calculation method	<ul style="list-style-type: none"> <li>• Simple iterative method</li> <li>• Excel can be used</li> </ul>	<ul style="list-style-type: none"> <li>• ODE Integration method</li> <li>• Excel can be used</li> </ul>
Comments	<ul style="list-style-type: none"> <li>• Simple (providing the method is carefully followed)</li> <li>• Conservative results (for vent sizing)</li> </ul>	<ul style="list-style-type: none"> <li>• Good results</li> <li>• Time consuming investigation ODE Integration method</li> <li>• Can be used to simulate dynamic behaviour of vessels undergoing runaway reactions</li> <li>• More powerful</li> <li>• Data required not often available</li> </ul>

## 4 SIMULATION OF INSULATED VESSEL EXPOSED TO FIRE

Dynamic simulations of a large-scale vessel containing reactive chemicals exposed to a pool fire were carried out in order to observe the effect of the presence of an insulation layer on the temperature and pressure in the vessel. This investigation required:

- The calculation of the amount of heat entering an insulated vessel exposed to fire. The current methods are presented and described.
- The use of the kinetic model developed in the last chapter for the chemical system methanol/acetic anhydride.
- The development of a dynamic simulation tool using Visual Basic.

### 4.1 HEAT INPUT CALCULATION METHODS

The calculation of the amount of external heat entering a vessel exposed to fire is necessary to correctly design an adequate fire protection system. The heat transfer phenomena occurring when a vessel is exposed to a pool fire are complex (Figure 17):

- The external surface of the vessel is heated by radiation and convection. The heat is absorbed however, mostly due to radiation phenomena. The resulting intensity of the heating would depend on the flame temperature, the vessel area that is exposed to the flames, the properties of the vessel's surroundings and the atmospheric conditions.
- The heat will be transferred by conduction through the insulation layers and the vessel's wall. This phenomenon will depend on the thermal conductivity of the construction material.
- The heat input can be limited by the convection phenomena in the vessel, depending on the physical properties of the vessel contents.

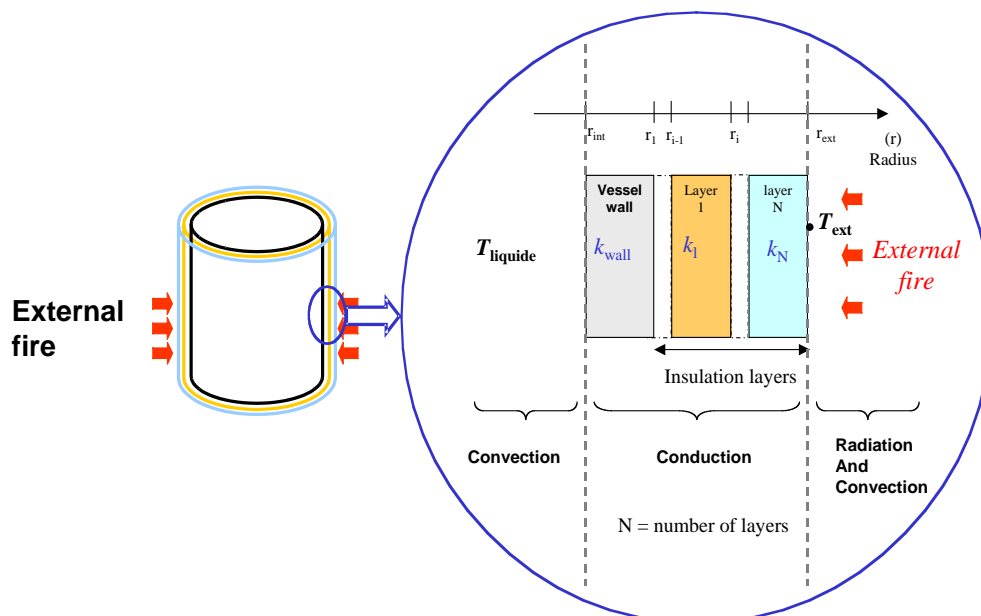


Figure 17 Overview of the heat transfer phenomena occurring when an insulated vessel is exposed to an external fire

The rigorous calculation method of the corresponding heat input in the case of a pool fire can be made using heat transfer models [Roberts, 2003]. Such models require a good knowledge of the fire properties, thermal properties of the vessel and its contents. Simpler calculation methods are available in the literature. Three of them are investigated:

- Method from API 521 international standard [Hare *et al*, 2007; Roberts *et al*, 2001];
- Method from the UN Recommendation on the Transport of Dangerous Goods, Manual of Test and Criteria [ST/SG/AC.10/11/Rev. 4];
- Method based on a rough evaluation of the vessel overall heat transfer coefficient.

#### 4.1.1 Method from API 521

The American Petroleum Institute proposed a calculation method in the API 521 standard. This method is based on experimental data obtained from different companies with large-scale vessels (between 0.14 m<sup>3</sup> to 800 m<sup>3</sup>) exposed to different types of open fires (pool fires). The use of this method is recommended in the British standard BS EN ISO 23251:2007.

The important factor in the calculation is the area exposed to the fire, the heat being mostly absorbed due to radiation phenomena. This exposed area depends on the geometry of the vessel. For instance, for storage vessels up to 7.6 m height the method recommends considering the wetted surface. Different rules are applied for higher vessels, spheres, spheroids, vessels having their base in contact with the ground, vessel partly protected with skirts, etc.

If there are prompt fire fighting efforts and drainage of flammable material away from the vessel, the following equation is used the total heat absorption ( $Q$  in watts) to the wetted surface ( $A_{ws}$  in m<sup>2</sup>):

$$Q_{AP\_Drainage} = 43000F_{AP}A_{ws}^{0.82} \quad \text{Equation 12}$$

The power 0.82 applied to the wetted surface tries to take into account the fact that large vessels are less likely to be exposed to the flame of an open fire.

If no adequate drainage and fire fighting equipment do not exist, the following equation is proposed:

$$Q_{API\_NoDrainage} = 70900F_{API}A_{ws}^{0.82} \quad \text{Equation 13}$$

Equation 13 and Equation 14 require an environment factor ( $F$ ) that takes into account the presence of an insulation layer. It is assumed that the outside temperature of the insulation layer has reached an equilibrium temperature of 904 °C. With this temperature and the temperature of the vessel's contents ( $T$  in °C), the thickness ( $\delta_{ins}$ ) and the thermal conductivity ( $k$ ) of the insulation layer, the environment factor is given by:

$$F_{API} = \frac{k(904 - T)}{66570\delta_{ins}} \quad \text{Equation 14}$$

The thermal conductivity of the insulation layer can increase with the temperature and has to be calculated at an average value of the temperature. For a bare vessel, the environment factor is 1.

#### 4.1.2 Method from the UN recommendation on the transport of dangerous goods

The UN recommendation on the transport of dangerous goods proposes a method in the Appendix 5 of the Manual of tests and criteria. For an insulated vessel, the methods require that the total heat input ( $Q_{UN}$ ) is equivalent to the heat input into the vessel *through the insulation* ( $Q_d$ ) plus the heat input *directly* to the vessel assuming 1 % of the insulation is missing ( $Q_i$ ):

$$Q_{UN} = Q_i + Q_d \quad \text{Equation 15}$$

With

$$Q_i = 70961 \times F_{UN} \times (1 - F_r) \times A_{ws}^{0.82} \quad \text{Equation 16}$$

$$Q_d = 70961 \times F_{UN} \times F_r \times A_{ws}^{0.82} \quad \text{Equation 17}$$

$F_r$  is the fraction of the tank that is directly heated ( $F_r = 1$  if non insulated,  $F_r = 0.01$  if insulated).

This method also includes a factor to take into account the presence of an insulation layer, called here the insulation factor ( $F_{UN}$ ):

$$F_{UN} = 2 \times \frac{k(923 - T)}{47032\delta_{ins}} \quad \text{Equation 18}$$

For a bare vessel  $F_{UN}$  equals to 1. In Equation 18, a multiplication factor of 2 is introduced to take into account a 50 % loss in insulation efficiency in the incident. No explanation is provided concerning the meaning of the coefficient 923. The temperature of the vessel contents ( $T$ ) is expressed in Kelvin.

#### 4.1.3 Simplified heat transfer method

An additional method could assume that the *heat transfer resistance of the vessel wall is negligible compared to the insulation layers*. The heat input ( $Q$ ) could be roughly evaluated with the following equation:

$$Q = UA_{ws}(T_{ext} - T) \quad \text{Equation 19}$$

For a vessel with several insulation layers, the overall heat transfer coefficient is given by (Figure 17):

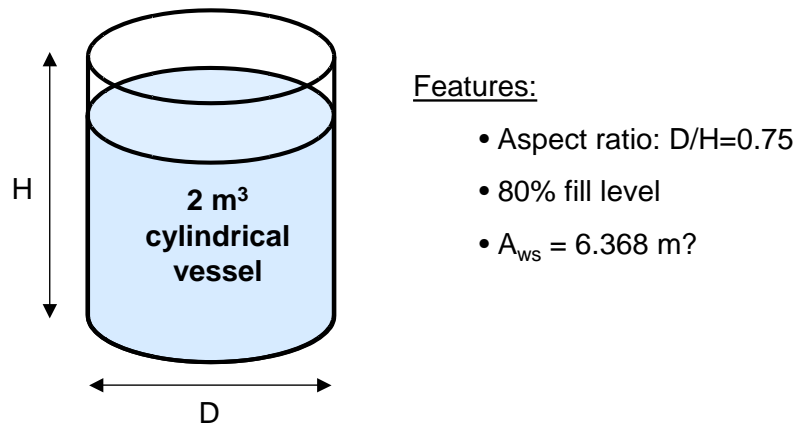
$$U = \left[ r_{int} \sum_i \frac{\ln\left(\frac{r_i}{r_{i-1}}\right)}{k_i} \right]^{-1} \quad \text{Equation 20}$$

The calculation of the heat input requires the values of the thermal conductivity of each insulation layer ( $k_i$ ), the internal diameter of the vessel ( $r_{int}$ ), and the temperature of the outside surface of the insulation layer directly in contact with the fire ( $T_{ext}$ ).

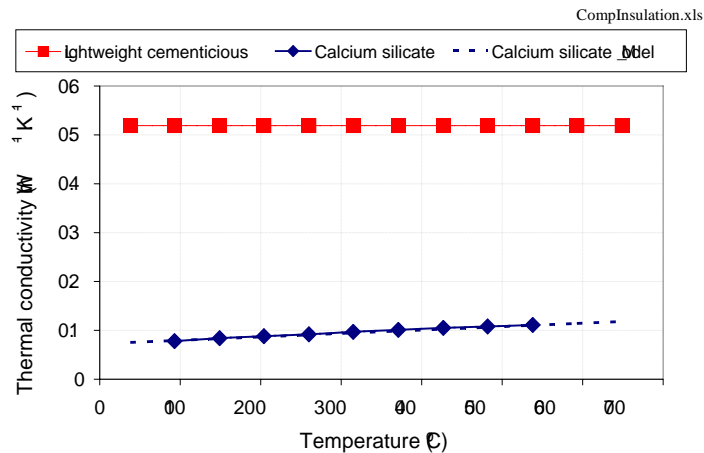
## 4.2 DYNAMIC SIMULATION OF A 2 M<sup>3</sup> VESSEL SUBJECT TO FIRE

The case of a 2 m<sup>3</sup> large-scale vessel containing reactive chemicals exposed to a pool fire was investigated (Figure 18). The effect of the heat input on the pressure and temperature rate were observed in the following cases:

- Bare vessel (no insulation layer);
- Vessel insulated with a single layer of lightweight cementitious;
- Vessel insulated with a single layer of calcium silicate (type II).



**Figure 18** Characteristics of the 2 m<sup>3</sup> cylindrical vessel



**Figure 19** Thermal conductivities of lightweight cementitious and calcium silicate

These types of insulation were chosen because data on thermal conductivity were proposed in API 521. Figure 19 shows that the thermal conductivity of the lightweight cementitious is significantly higher than the calcium silicate. The following assumptions are made:

- The vessel fill level is 80 %;
- The vessel wetted surface (6.368 m<sup>2</sup>) exposed to the fire includes the bottom surface (this could be the case of vessel located above the ground, on legs for instance).

### 4.2.1 Calculation of the specific heat input

The specific heat input was calculated using the methods described above. The temperature of the vessel contents is assumed to be 50 °C. As indicated in 4.1.1, the API 521 method assumes

that the temperature of the external surface of the insulation layer is 904 °C. This assumption is used with the simplified heat transfer method. The UN method was used with the assumption that 100 % of the wetted surface is exposed to the flame (instead of 99 % as recommended<sup>2</sup>).

Figure 20 shows that:

- An increase of the insulation thickness would lead to a decrease of the specific heat input, which was foreseeable;
- The values of the specific heat inputs are more important for the lightweight cementitious than the calcium silicate;
- The UN method gives some values of the specific heat input two or three times higher than the other methods. This is probably partly due to the factor of 2 introduced in the calculation of the insulation factor ( $F_{UN}$ ) to take into account a 50 % loss in insulation efficiency in the incident;
- The value of the specific heat input calculated with API 521 in cases where no drainage and fire fighting measures exist remains less important than the ones calculated with the UN method;
- The results obtained with API 521 in cases where adequate drainage and fire fighting measures exist are similar the ones obtained with the simplified heat transfer method.

The API 521 and UN Manual of test and criteria propose simple calculation methods to assess the external heat input in the case of a pool fire. Some inconsistencies in the use of these formulae have however been noticed. Figure 22 plots the specific heat input as a function of the thermal conductivity of the insulation layer in the case of 15 mm and 50 mm layers. It appears that these methods can predict values of specific heat input for insulated vessel higher than for bare vessel in the following cases:

- Large values of the thermal conductivity;
- Low values of the insulation thickness.

This is due to the fact that in these specific circumstances, the ratio of the thermal conductivity to the insulation thickness leads to environment factor, or insulation factor, larger than unity. Such results do not make sense. This means that such empirical formula must be used only within certain ranges. The determination of the range of applicability of these formulas and their improvement are worth investigating subsequently and disseminating.

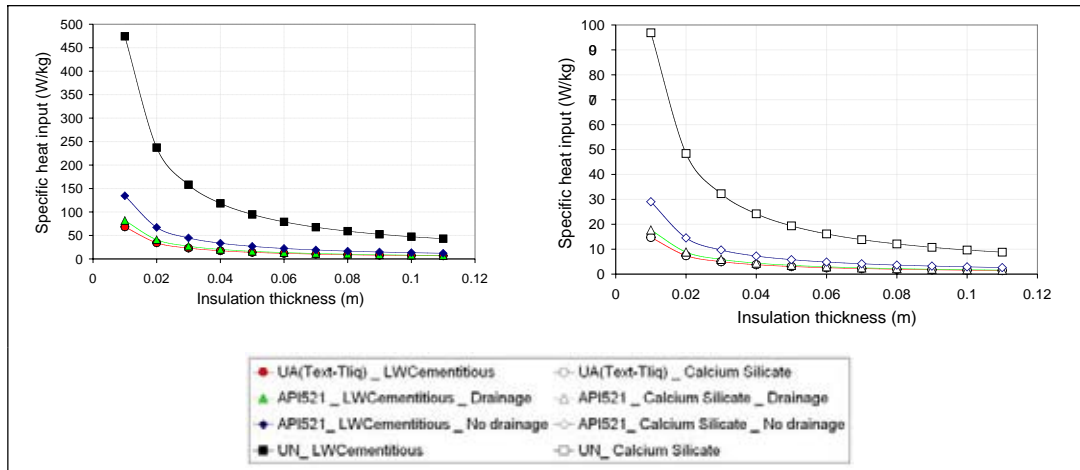
#### 4.2.2 Dynamic simulation

A simulation tool was developed under Visual Basic to calculate the temperature and pressure increase in a 2 m<sup>3</sup> vessel, filled at 80 % with a methanol + acetic anhydride mixture and exposed to a pool fire (Figure 21). The kinetic model described in 3.1.2 and 3.2 is used. The API 521 method was used to calculate the specific heat input (the outside temperature of the insulation layer is assumed to be 904 °C). The simulations were carried out in both cases where there are and there are not adequate drainage and fire fighting measures. The effects of the presence of different thicknesses (1, 2.5 and 5 cm) of lightweight cementitious or calcium silicate insulation were observed. The case of the bare vessel is also investigated. The vessels are assumed to stand any pressure increase (no simulation of the vessel venting). Figure 23 shows that a decrease of the specific heat input could significantly be achieved by increasing the insulation thickness, or taking the suitable adequate drainage and fire fighting measures. The lower the value of the thermal conductivity, the lower the specific heat input. The calcium silicate is in this case a better way to reduce the external heat input than the lightweight cementitious. Decreasing the external heat input by using insulation has a significant effect on (Figure 24):

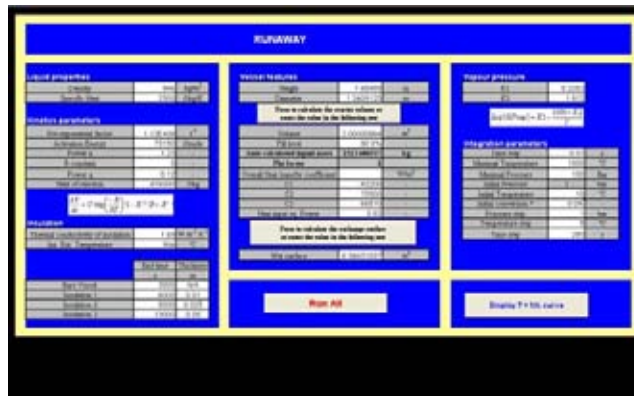
HeatInputCalc.xls

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<sup>2</sup> This does not affect significantly the results.



**Figure 20** Specific heat input into a 2 m<sup>3</sup> vessel filled at 80 %



**Figure 21** Simulation of a 2 m<sup>3</sup> vessel exposed to fire: dynamic simulation tool

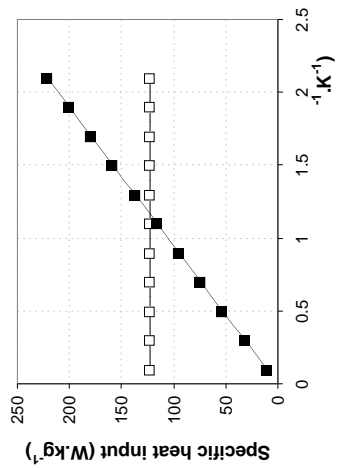
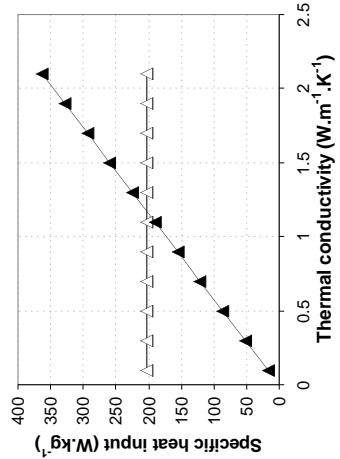
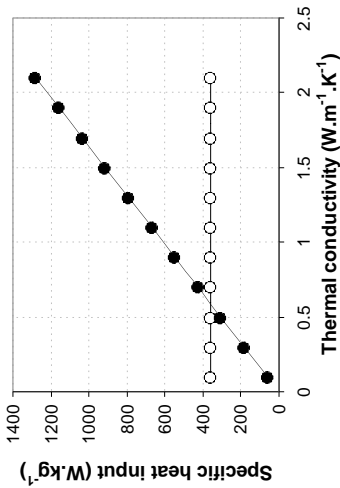
- The temperature and the pressure: the maximum temperature reached ( $T_{\max}$ ) and the maximum temperature rise rate  $(dT/dt)_{\max}$  are decreased. The pressure being temperature-dependent, the corresponding maximum pressure reached ( $P_{\max}$ ) and the pressure rise rate  $(dP/dt)_{\max}$  are decreased.
- The reaction completion time is significantly decreased.

Figure 25 shows the relative changes in  $P_{\max}$ ,  $T_{\max}$ ,  $(dT/dt)_{\max}$  and reaction completion time<sup>3</sup> when there is an insulation layer, compared to a bare vessel. The variations are calculated as followed:

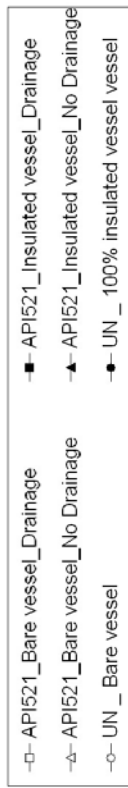
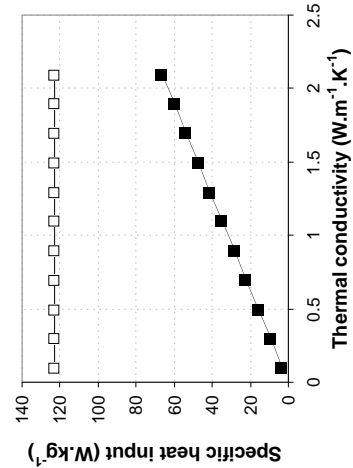
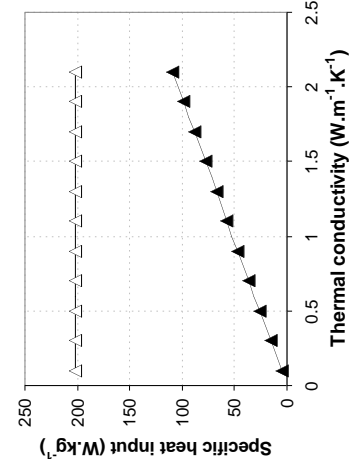
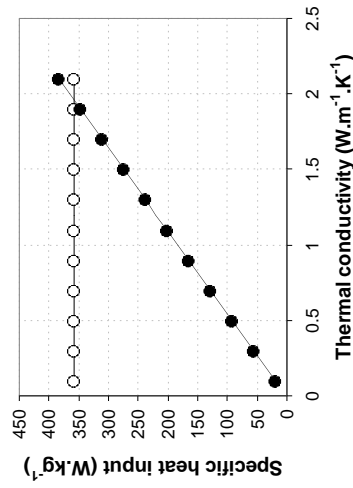
$$\text{Variation of the variable} = \frac{(\text{Variable})_{\text{with insulation}}}{(\text{Variable})_{\text{bare vessel}}} - 1 \quad \text{Equation 21}$$

<sup>3</sup> The variation of the reaction completion time being larger than the other variables, the actual value was divided by 10 to allow representation on the same graph.

**Insulation layer thickness = 15 mm**



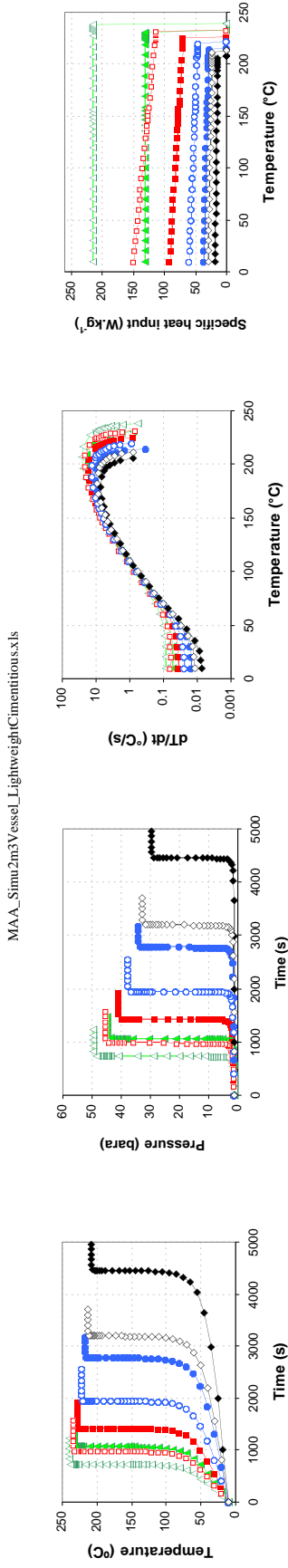
**Insulation layer thickness = 50 mm**



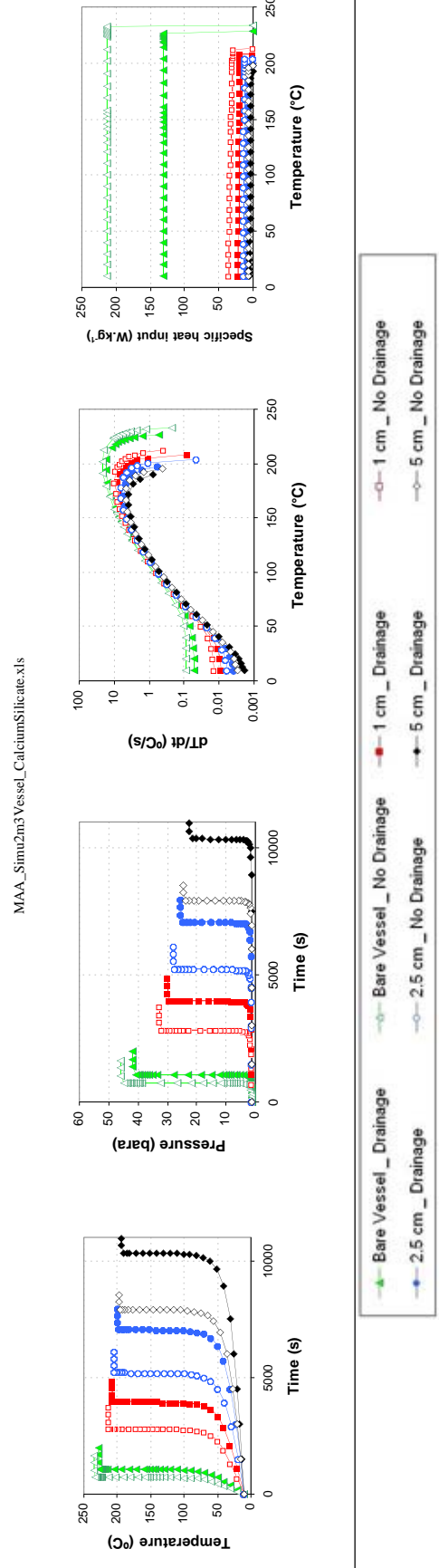
**Figure 2** Calculation of the specific heat input for a 2 m<sup>3</sup> vessel filled at 80 % with a liquid at 50 °C as a function of the thermal conductivity of the insulation layer



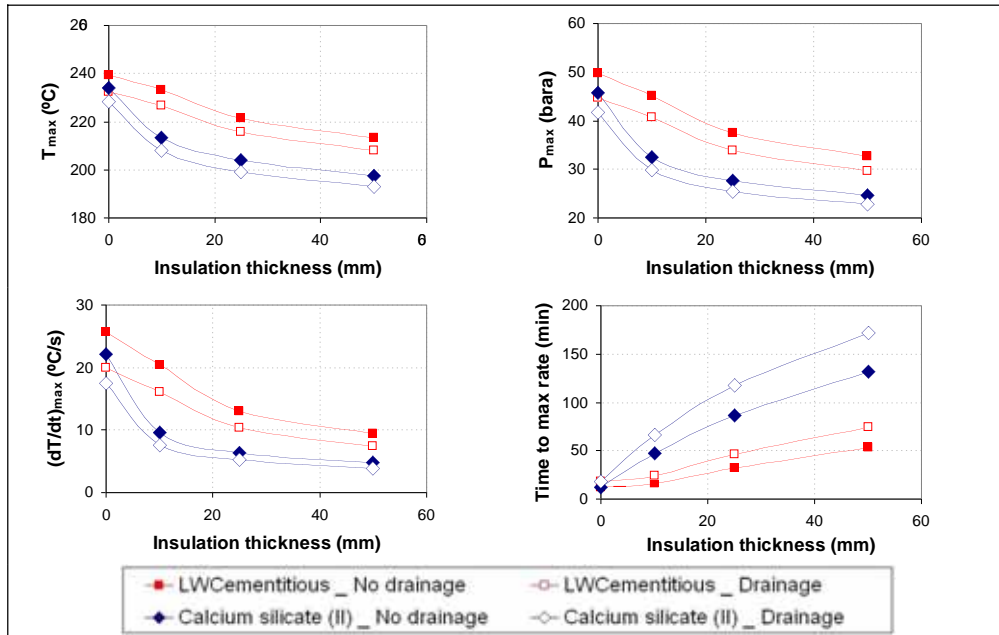
### Insulation layer: Lightweight cementitious



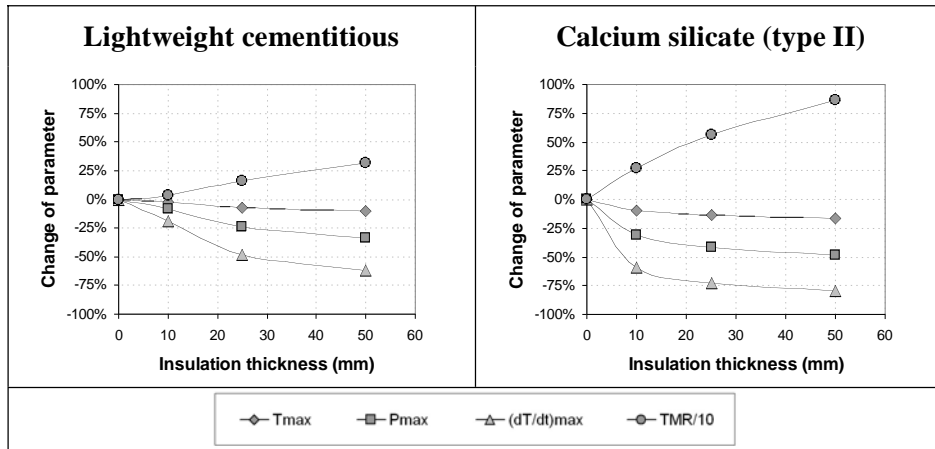
### Insulation layer: Calcium silicate (type II)



**Figure 2** Dynamic simulation of a 2 m<sup>3</sup> vessel filled at 80 % with a methanol + acetic anhydride acetic mixture and exposed to a pool fire!



**Figure 2** 2 m<sup>3</sup> vessel filled at 80 % with a methanol + acetic anhydride acetic mixture and exposed to a pool fire: effect of the insulation layer



**Figure 3** 2 m<sup>3</sup> vessel filled at 80 % with a methanol + acetic anhydride mixture with adequate drainage and fire fighting measures: Change of the variables compared to the case of the bare vessel

It appears that  $(dT/dt)_{max}$  can be decreased by 60 % and 75 % for a 50 mm insulation layer in the cases of the lightweight cementitious and the calcium silicate respectively. The extent of this decrease would be the same for  $(dP/dt)_{max}$ . The reaction completion time is the most sensitive variable. This shows that in case of fire, the time available for the application of safety measures (implementation of emergency plans, evacuation) would be longer when the vessel is adequately insulated.

### 4.3 VENT SIZING CONSIDERATIONS

The vent sizing calculation proposed by the DIERS for vapour systems (Leung's method [Leung, 1986]) require the calculation of the mass flow rate ( $W$  in kg/s) between the vent opening pressure and the maximum permitted pressure. Etchells *et al* [1998] propose to use a modified value ( $q_{mod}$ ) of the reaction heat release rate ( $q_R$ ) for the calculation of the mass flow rate. This conservative modification multiplies the external specific heating rate ( $q_{ext}$ ) per 2. This aims at taking into account any increase of the external specific heat input due the emptying of the vessel.

$$W = GA_{vent} = mq_{mod} \left[ \left( \frac{VT}{m} \frac{dP}{dT} \right)^{0.5} + (Cp\Delta T)^{0.5} \right]^{-2} \quad \text{Equation 22}$$

With:

$$q_{mod} = q_R + 2q_{ext} = 0.5Cp \left[ \left( \frac{dT}{dt} \right)_s + \left( \frac{dT}{dt} \right)_{max} \right] + 2q_{ext} \quad \text{Equation 23}$$

For a given vessel pressure, the reaction heat release rate would depend on the external heat input (Figure 26). This means that for the same vent opening pressure, different vent size would be required whether the vessel is insulated or not.

In the particular case of a vapour system, the heat release rate is linked to the vessel pressure by an Antoine type equation (see Equation 11).  $dP/dT$  is given by:

$$\frac{dP}{dT} = \frac{1000}{T^2} K_2 P \ln 10 \quad \text{Equation 24}$$

Assuming that friction can be neglected, the equilibrium rate model can be used to calculate the two-phase mass flow rate ( $G$ ) at inlet conditions (subscript 0) [Etchells *et al.*, 1998]:

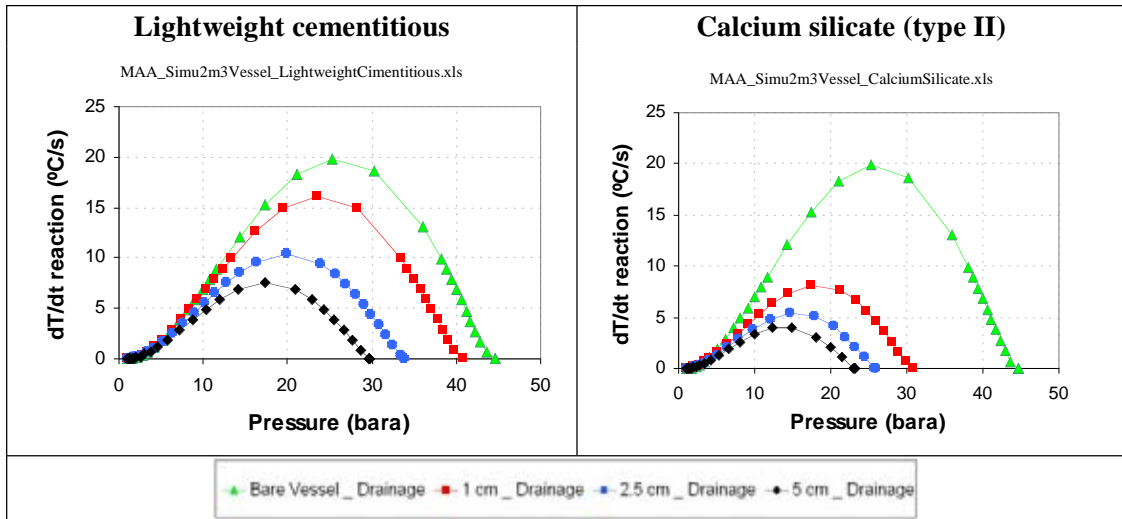
$$G = \left( \frac{dP}{dT} \right)_0 \sqrt{\frac{T_0}{Cp_0}} \quad \text{Equation 25}$$

Vent sizing calculations were carried out for a 2 m<sup>3</sup> vessel filled with a mixture of methanol and acetic anhydride. The maximum permitted pressure is assumed to be 20 % higher than the vent opening pressure. The influence of the insulation layer thickness (between 0 and 50 mm) and the vent opening pressure (4, 6, 8 and 10 bara) was investigated. Figure 27 shows that the higher the vent opening pressure, the larger the required vent size. It also shows that the presence of an insulation layer allows for a significant decrease of the required vent area. The reduction of the vent area due to the presence of the insulation layer is a function of:

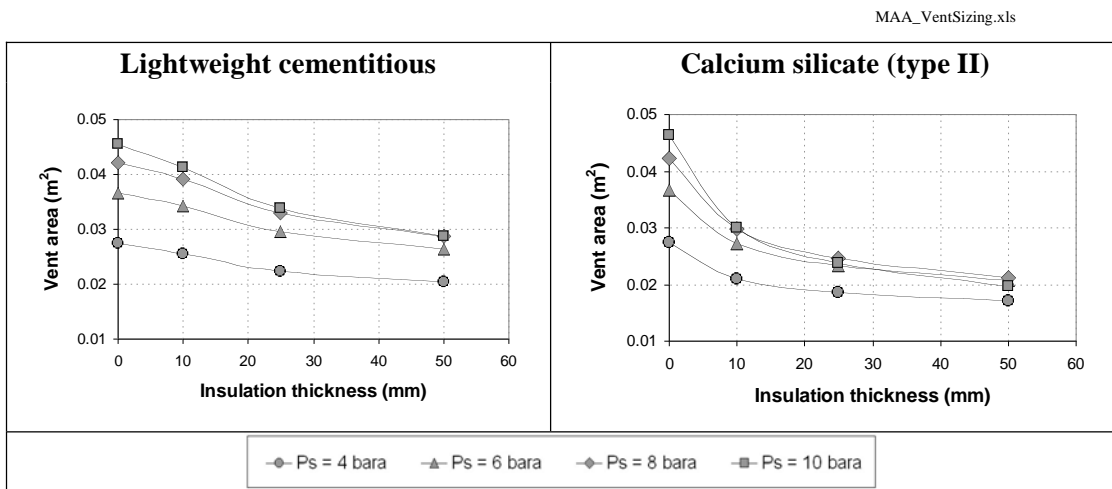
- The insulating properties of the insulation layer: the calcium silicate allowed is better than the lightweight cementitious in terms of reduction of the required vent size;
- The vent opening pressure: for high value of the vent opening pressure the effect of the insulation layer is relatively more important.

Figure 26 shows that the difference in reaction rate between a bare vessel and an insulated vessel is a function of the vent opening pressure. The lower the vent opening pressure, the smaller the difference in reaction rate between a bare and insulated vessels. For a vapour pressure system, according to the vent sizing formula (Equation 22), the lower the vent opening pressure, the smaller the difference in required vent area between bare and insulated vessels.

This would not necessarily be the case of a gassy system<sup>4</sup> (decomposition of certain peroxide compounds). Indeed, the vent sizing formula is based on the maximum pressure rise rate. At maximum rate, the difference between the gas production rate in a bare vessel and an insulated vessel could be important than during the early period of the runaway. So in the case of a pure gassy system the use of insulation could lead to a significant decrease of the required vent area.



**Figre 26** 2 m<sup>3</sup> vessel filled at 80 % with a methanol + acetic anhydride mixture with adequate drainage and fire fighting measures: dT/dt at different vessel pressure



**Figre 27** 2 m<sup>3</sup> vessel filled at 80 % with a methanol + acetic anhydride mixture with adequate drainage and fire fighting measures: required vent area at different vent opening pressures

<sup>4</sup> This does not mean that for a gassy system, the vent opening pressure does not have any influence on the required vent area. Such influence could be observed in particular cases [Véchet, 2008]

#### 4.4 SUITABILITY OF VESSEL INSULATION

The presence of an insulation layer on a vessel exposed to external heating containing reactive chemicals leads to:

- A decrease of the maximum pressure and temperature;
- A decrease of the temperature and pressure rise rates;
- An increase of the time to maximum rate (reaction completion time);
- A reduction of the required relief vent area.

The insulation layer is indeed a suitable possible passive protection method in case of external fire.

In the particular case where a storage tank containing a reactive chemical is heated by an external fire enough for the contents to start to self-react, and then the external fire is extinguished (for instance by water hydrants), the suitability of PFP is related to the exposure time to fire and the corresponding temperature reached in the vessel.

For very short exposure time:

- the temperature in a bare vessel would be higher than the insulated vessel, because of the higher heat input;
- the temperature in the bare vessel might be low enough so that:
  - the natural heat losses would be enough to "compensate" for the heat generation by the reaction which is relatively slow. This depends on the type of chemical (reaction kinetics, etc) and the vessel heat transfer characteristics. This is however more likely to happen with reactions that start to decompose or react at high temperature, and with relatively small vessels (large vessels being close to adiabaticity),
  - the decomposition starts but the time to maximum rate is long enough to take additional measures, like using water hydrants to cool the vessel (better if agitated);
- the time to maximum rate would be much more important for the insulated vessel. Additional measures could be taken to stop the reaction (inhibitors, etc). The use of water deluge to cool the insulated vessel would not be efficient.

For long exposure time:

- the temperature in the bare vessel would be higher than the insulated vessel, because of the higher heat input;
- the runaway would probably not be avoided. The natural heat losses would be significantly low compared to the heat generation rate when the fire stops;
- the time to maximum rate would be much more important for the insulated vessel and the maximum T, P, dT/dt and dP/dt would be less important.

In both cases, it seems that the insulated vessel would give more time to take further actions or decrease the violence of the reaction.

However, in the case where the runaway reaction is initiated inside the vessel without any external heating (loss of the agitation, incorrect reaction, contamination of the vessel contents, incorrect charging sequence etc), the insulation layer would limit the heat exchange to the surroundings. The temperature of the chemical mixture and therefore the reaction kinetics could be more important than for a bare vessel. Furthermore, the insulation effect of passive fire protection (PFP) would reduce the effectiveness of any water deluge or fire-fighting water. The suitability of passive fire protection seems therefore case dependent. A proper determination of the worst case would help to determine the suitability of the vessel insulation.

## 5 CONCLUSION

The aim of this report was to have a better understanding of fire protection requirements for reactive chemical storage vessels.

A Phitec calorimeter was adapted to simulate the effect of external heat input on reactive chemicals. Four heat input devices were designed and tested:

- 110 ml standard closed test cell + 49 W wrapped around heater (Setup A);
- 110 ml standard closed test cell + 50 W bottom heater (Setup B);
- 82 ml custom closed test cell + 30 W 1/4" cartridge heater (Setup C);
- 82 ml custom closed test cell + 30 W 1/8" cartridge heater (Setup D).

The use of setup A and B (heating wires) represents the simplest way to simulate an external heat input. The main advantages are that *standard test cells* can be used (standard values of phi factor) and low extra heating of the vapour phase occurs. However, the nominal power delivered by the power supply is partly used to heat the system (70 % to 80 %), a significant and inconsistent amount of heat being lost to the surroundings. With setup C and D (1/4" and 1/8" cartridge heaters), the nominal power is fully used to heat the system. They appeared to be the best setups to input external heat in a test cell, the exact amount of heat input being known. Setups C and D, however, showed a slightly higher value of the phi factor (approximately 5 % higher than the phi factor of a standard test cell) and the possibility of an overheating of the vapour phase for high values of the heating power. They also require the design of custom test cells.

The external heat input devices were tested with model reactive systems. Good results were obtained with the methanol + acetic anhydride reaction (vapour system) and the decomposition reaction of 20 % DTBP in toluene (tempered hybrid system). A good agreement between the results obtained with setup A and D was achieved. The results showed that increasing the amount of 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. The hydrolysis of acetic anhydride reaction was tested with setup D (1/8" cartridge heater). Some problems of reproducibility were experienced, probably due to the degradation of the cartridge heater by highly corrosive liquid (anhydride acetic and acetic acid). This showed the necessity of ensuring that the use of a cartridge heater does not influence the results.

The validity of two theoretical correction methods of adiabatic data were experimentally tested using the data obtained with the methanol and acetic anhydride reaction with setup D (1/8" cartridge heater):

- *Huff's method*: This theoretical correction gave 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.
- *Dynamic model taking into account the effect of external heating*: The predicted temperature and pressure are quite close to the experimental data. The dynamic simulation approach 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.

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.

It would be beneficial if some limited further experimental work was undertaken with reactive monomers of industrial interest (e.g. methacrylate).

Calculations of the heat input into a 2 m<sup>3</sup> insulated vessel (insulation type: lightweight cementitious or calcium silicate) exposed to pool fire were carried out using simple methods from the API 521 international standard and the UN recommendation on the transport of dangerous goods. Some inconsistencies in these methods were noticed. It appeared that they could (wrongly) predict values of specific heat input for insulated vessels higher than for bare vessels in the following cases:

- Large values of the thermal conductivity of the insulation layer;
- Low values of the insulation thickness.

Dynamic simulations and vent sizing calculations were carried out for a 2 m<sup>3</sup> vessel containing methanol and acetic anhydride mixture, and exposed to a pool fire. The heat input was assessed by the API 521 method. The simulations showed that the presence of a PFP insulation layer (insulation type: lightweight cementitious or calcium silicate) leads to:

- A decrease of the maximum temperature and pressure;
- A decrease of the maximum temperature and pressure rise rates;
- An increase of the reaction completion time;
- A reduction of the required vent area.

The insulation layer could be a suitable passive protection method in case of external fire. However, in the case where the runaway reaction is initiated inside the vessel without any external heating, an insulation layer could limit the heat exchanges to the surroundings. The temperature of the chemical mixture, and therefore the reaction kinetics, could be more important than for a bare vessel. The suitability of passive fire protection seems therefore case-dependent. A proper determination of the worst case would help to determine the suitability of the vessel insulation.

Furthermore, the insulation effect of passive fire protection (PFP) would reduce the effectiveness of any water deluge of fire-fighting water.

A matrix of possible combinations could be calculated and a look-up table prepared to aid decision making.

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- Wright T. K., Rogers R. L., *Adiabatic Dewar calorimeter*, Hazards in the process Industries: Hazards IX – Symposium series N°97, 121-134, 1986



## NOMENCLATURE

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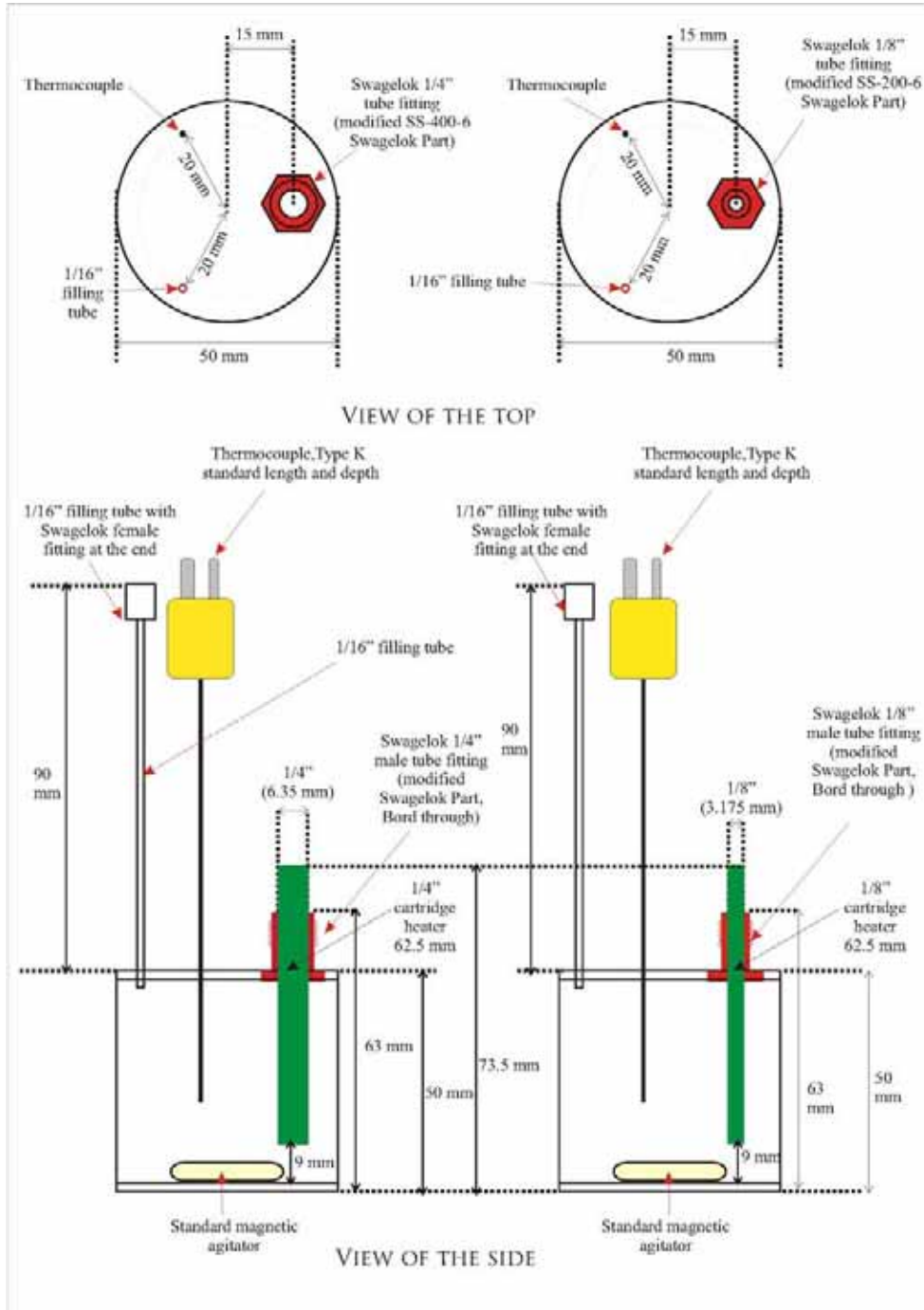
$A_{ws}$	Exchange surface (m <sup>2</sup> )
$A_{vent}$	Relief vent area (m <sup>2</sup> )
$B$	Kinetic equation coefficient (-)
$C$	Pre-exponential factor (-)
$C_p$	Specific heat capacity (J.kg <sup>-1</sup> .K <sup>-1</sup> )
$D$	Vessel diameter (m)
$(dT/dt)_s$	Temperature rise rate of the reacting mixture at vent opening (K.s <sup>-1</sup> )
$(dT/dt)_{max}$	Temperature rise rate of the reacting mixture at maximum permitted pressure (K.s <sup>-1</sup> )
$E_a$	Activation energy (J.mole <sup>-1</sup> )
$F$	Environment factor of insulation factor (-)
$H$	Vessel height (m)
$I$	Intensity (A)
$k$	Thermal conductivity (W.m <sup>-1</sup> .K <sup>-1</sup> )
$K_1$	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 (-)
$Q$	Heat input (W)
$Q_{nom}$	Nominal power delivered by the power supply (W)
$Q_{lost}$	Power lost to the surroundings (W)
$q_R$	Reaction specific energy release rate (W.kg <sup>-1</sup> )
$q_{ext}$	Specific external heat input (W.kg <sup>-1</sup> )
$R$	Resistance (Ω)
$r$	Vessel radius (m)
$t$	Time (s)
$T$	Temperature of the vessel contents (K)
$T_{ext}$	Temperature of the outside surface of the insulation layer directly in contact with the fire (K)
$U$	Vessel overall heat transfer coefficient (W/m <sup>2</sup> )
$V$	Vessel volume (m <sup>3</sup> )
$W$	Mass flow rate (kg.s <sup>-1</sup> )
$X$	Chemical reaction conversion (-)

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$\delta_{ins}$	Insulation layer thickness (m)
$\phi$	Adiabaticity factor, phi factor (-)
$\Delta H_r$	Reaction energy (J.kg <sup>-1</sup> )
$\Delta T$	Liquid temperature difference between the vent opening and liquid and the maximum permitted pressure (K)

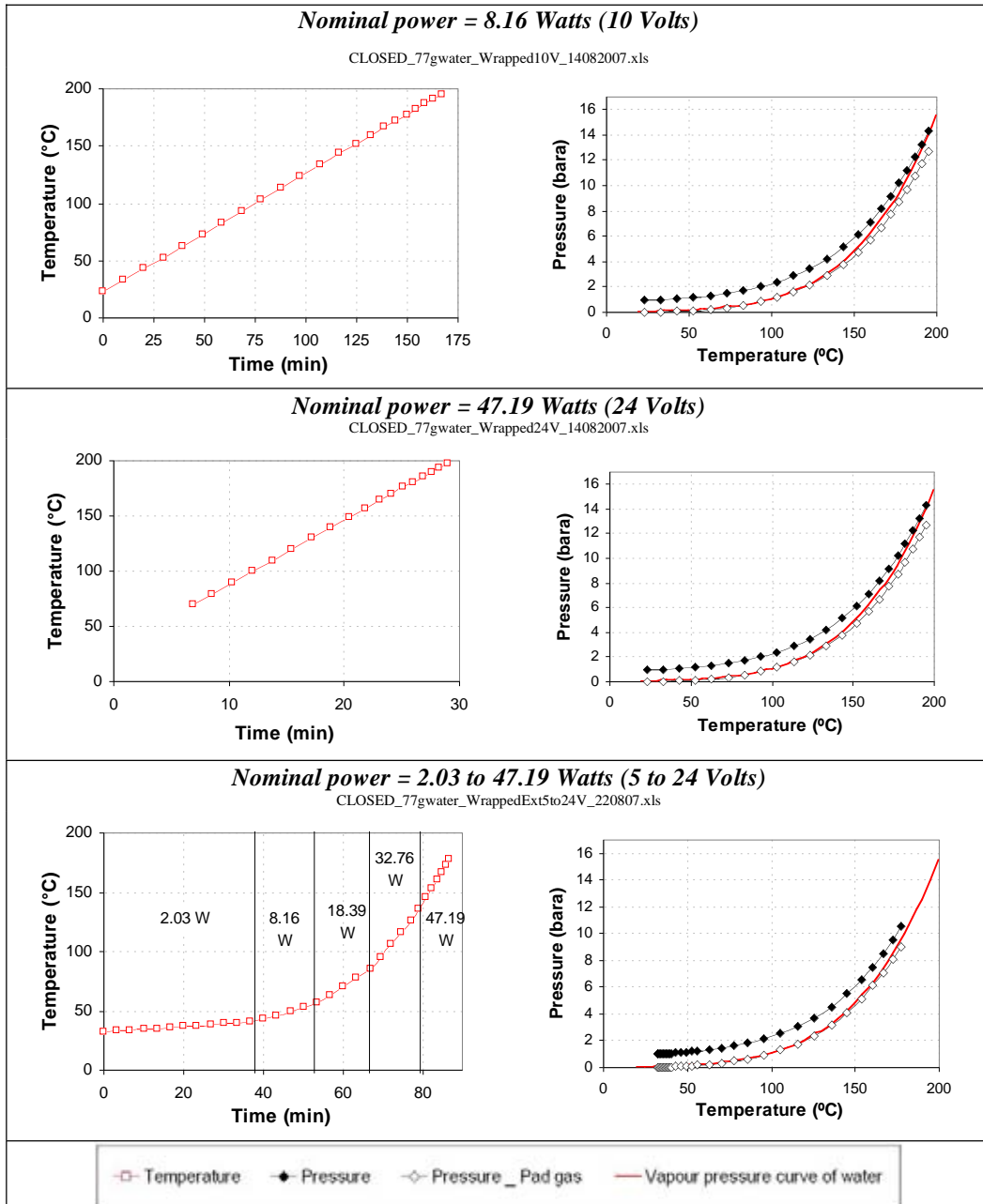
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# APPENDIX 1: SCHEMATIC OF THE CUSTOM TEST CELLS

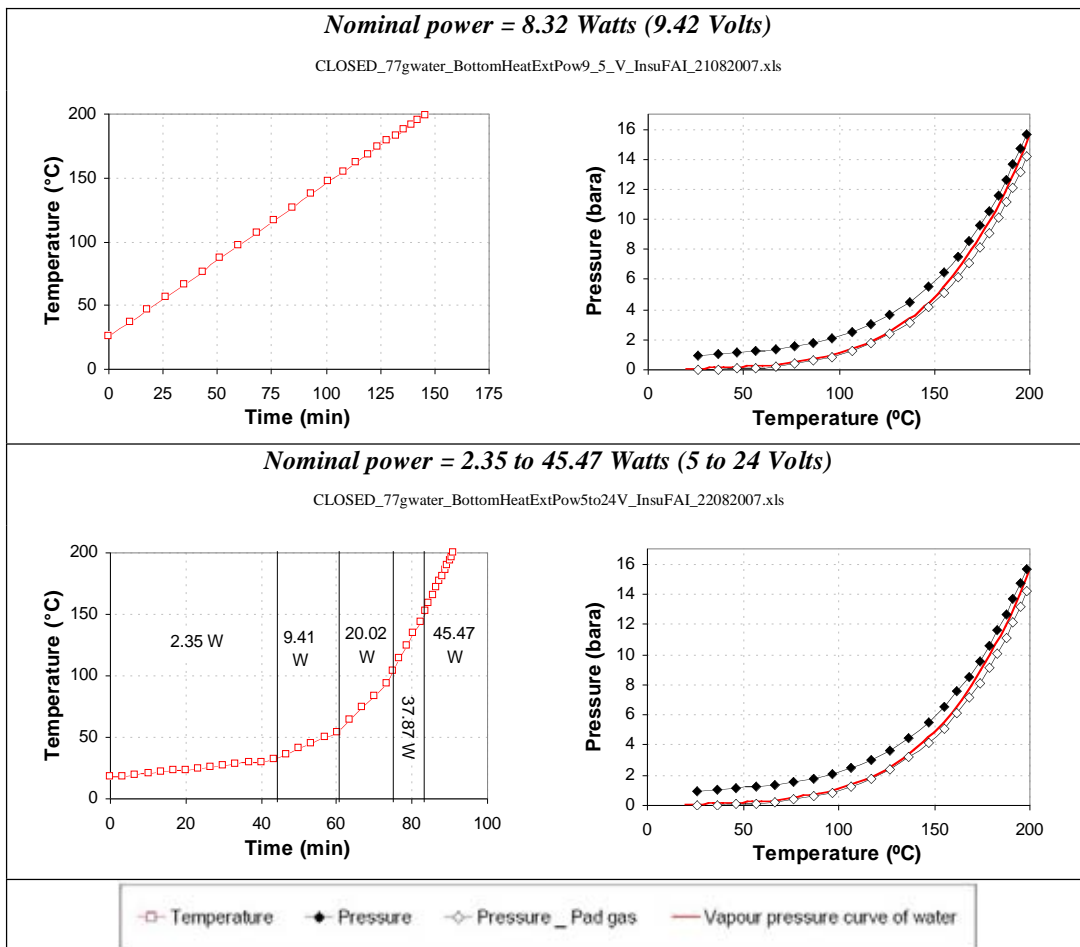


## APPENDIX 2: CHARACTERISATION TESTS WITH WATER

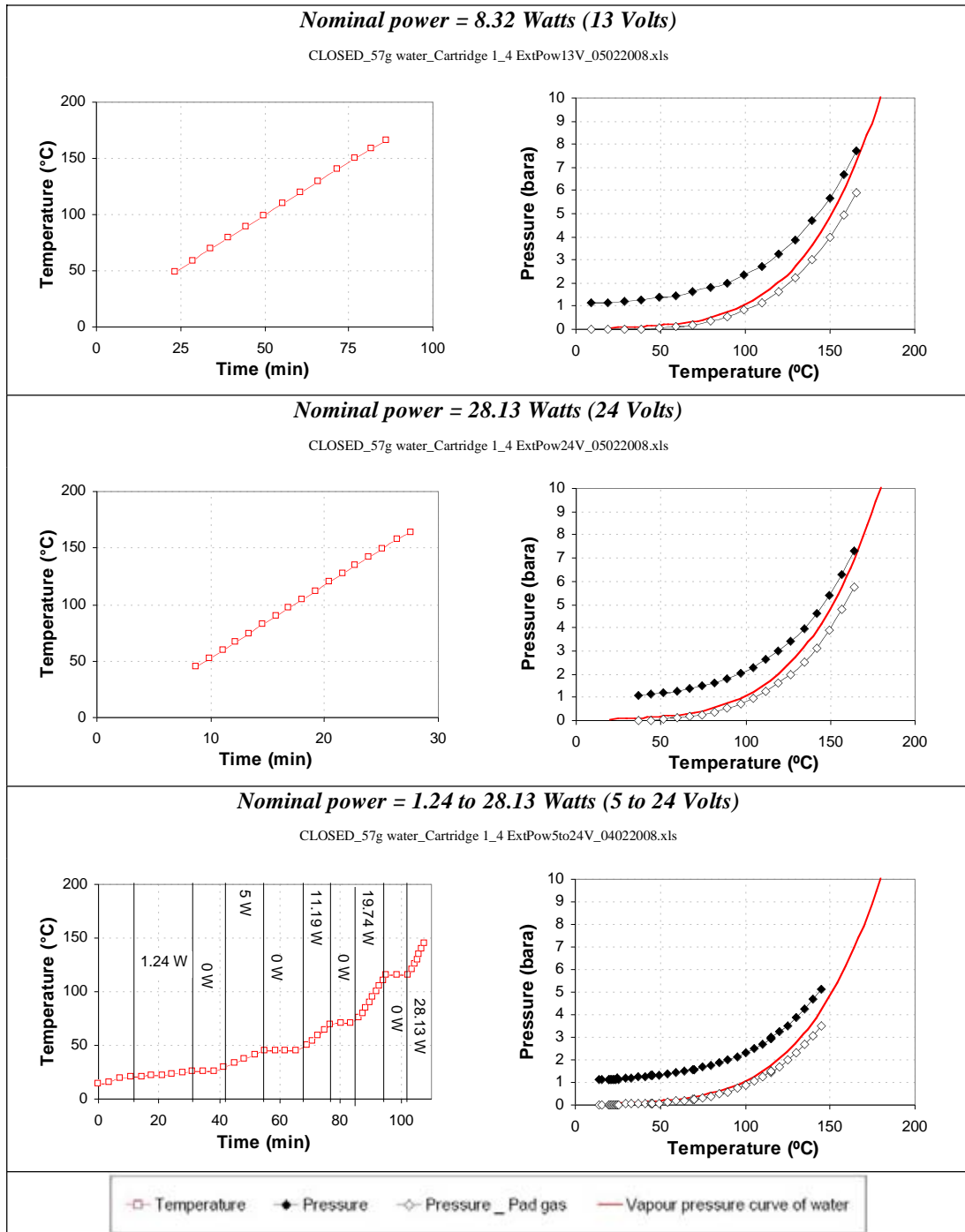
The characterisation tests of the different heat input setups were carried out by filling the test cells at 70 % with water and measuring the temperature increase resulting from different values of nominal powers delivered by the external power supply (see 2.1.3). The following graphs were used to calculate for the efficiency of each heating systems (see Equation 4).



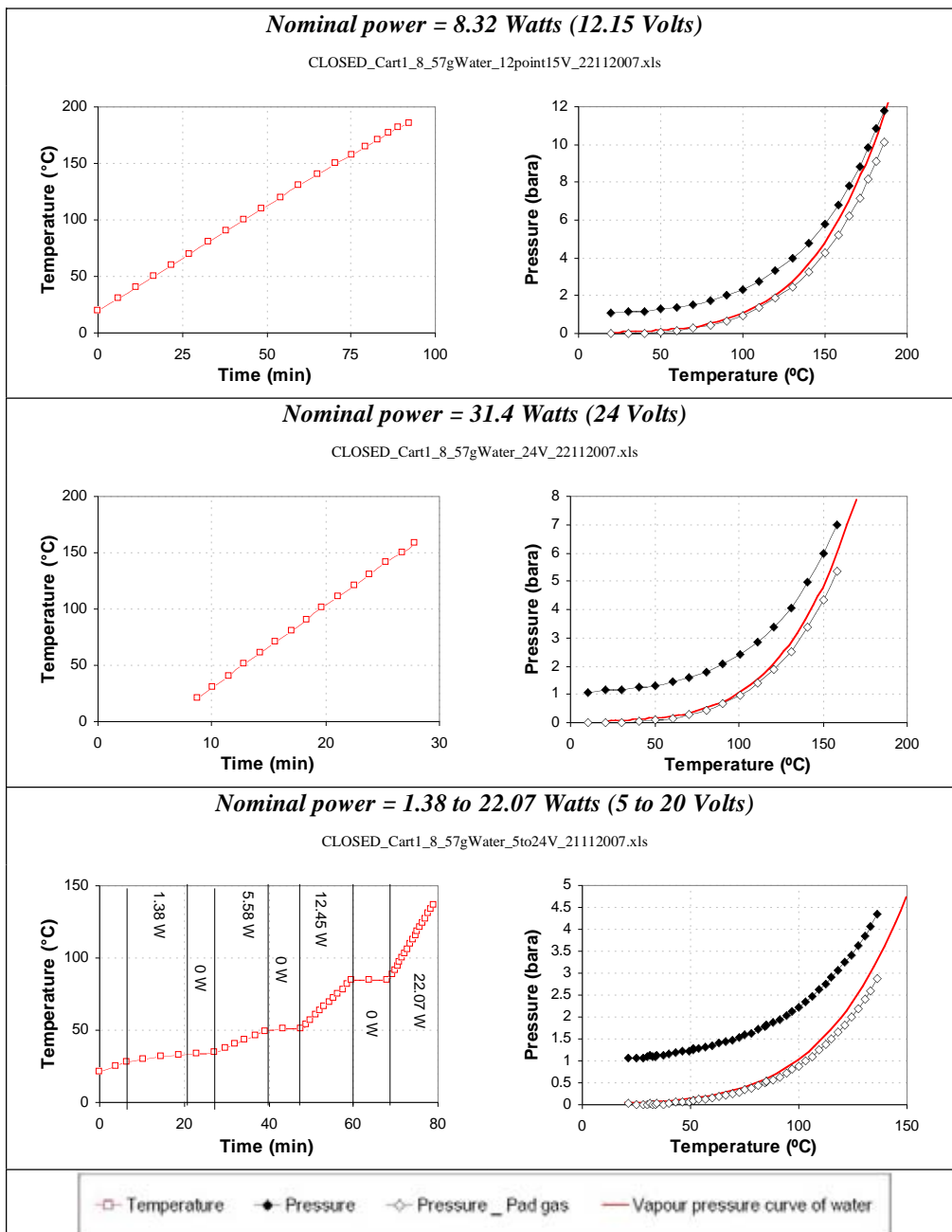
**Fig 2** Heating of water with setup A  
 (110 ml standard closed test cell + 49 W wrapped around heater)



**Figure 9** Heating of water with setup B  
(110 ml standard closed test cell + 50 W bottom heater)



**Figure 9** Heating of water with setup C  
(82 ml custom closed test cell + 30 W 1/4" cartridge heater)



**Figure 3** Heating of water with setup D  
(82 ml custom closed test cell + 30 W 1/8" cartridge heater)

### APPENDIX 3: CALCULATION OF THE HEAT CAPACITY OF A CHEMICAL MIXTURE WITH SETUPS C AND D

The heat input systems corresponding to the setups C (82 ml custom closed test cell + 30 W 1/4" cartridge heater) and D (82 ml custom closed test cell + 30 W 1/8" cartridge heater) could be used to measure experimentally the heat capacity of a liquid. This could be done by measuring the temperature increase resulting from a known value of the nominal power delivered by an external power supply, as long as no exothermic reaction occurs at the same time. The thermal balance in this case would be:

$$\phi(mCp)_{\text{liquide}} \frac{dT}{dt} = m_{\text{liquide}} \dot{q}_{\text{ext}} \quad \text{Equation 26}$$

with

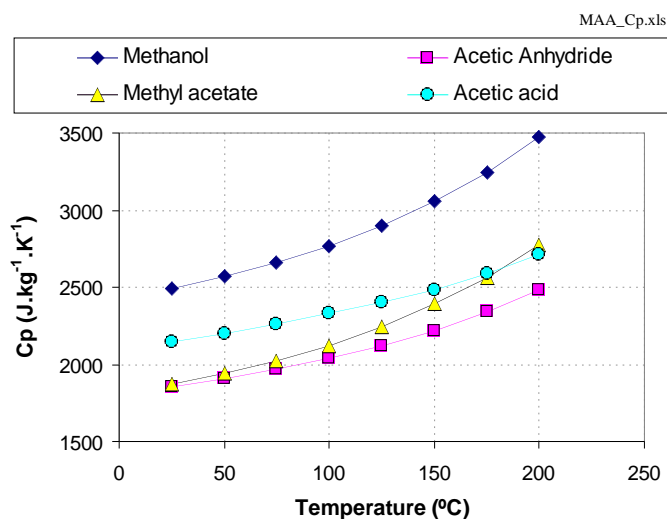
$$\phi = \frac{(mCp)_{\text{liquid}} + (mCp)_{\text{test cell}} + (mCp)_{\text{heater}} + (mCp)_{\text{fittings}}}{(mCp)_{\text{liquid}}} \quad \text{Equation 27}$$

The heat capacity is therefore given by:

$$CP_{\text{liquid}} = \frac{m_{\text{liquide}} \dot{q}_{\text{ext}} - [(mCp)_{\text{test cell}} + (mCp)_{\text{heater}} + (mCp)_{\text{fittings}}] \frac{dT}{dt}}{m_{\text{liquide}} \frac{dT}{dt}} \quad \text{Equation 28}$$

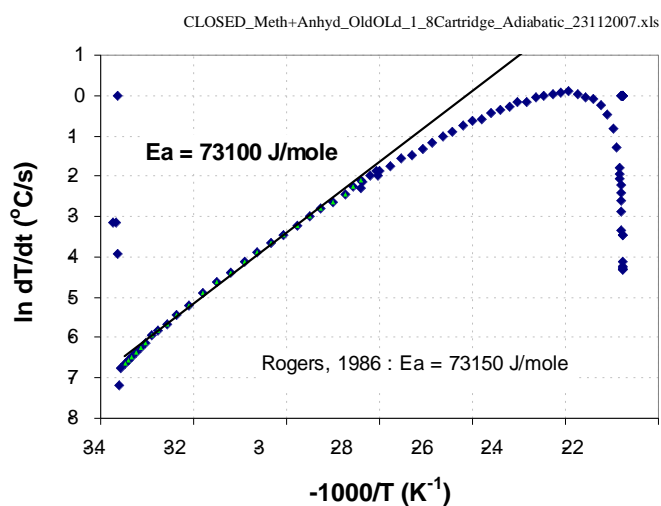
This measurement could be carried out with a reacting mixture before and after the chemical reaction. This would lead to a realistic assessment of the heat capacity instead of using the values from the pure components.

## APPENDIX 4: LITERATURE AND EXPERIMENTAL DATA ON METHANOL/ACETIC ANHYDRIDE CHEMICAL MIXTURE



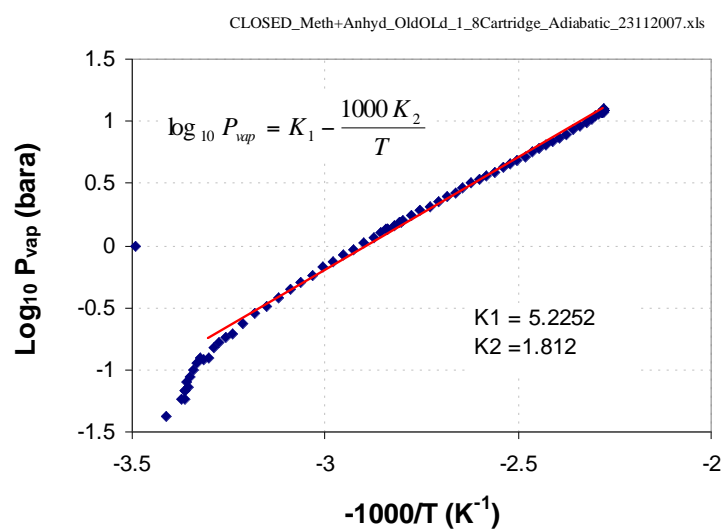
**Figure 32** Heat capacity of the pure component: methanol, acetic anhydride, methyl acetate and acetic acid

The activation energy of the methanol/acetic anhydride (molar ratio = 2:1) is calculated on Figure 33 from an adiabatic experiment. The slope of the early part of the curve  $\ln dT/dt = f(-1000/T)$  (corresponding to the low conversion of the reactants) equals to  $E_a/(1000 \times R)$ .



**Figure 33** Methanol/acetic anhydride (molar ratio = 2:1): determination of the activation energy from an adiabatic experiment





**Figure 34** Methanol/acetic anhydride reaction (molar ratio = 2:1): determination of Antoine's equation coefficient

# APPENDIX 5: HARE *ET AL.* FIRE PROTECTION MEASURE FOR VESSELS CONTAINING REACTIVE CHEMICALS, ICHME SYMPOSIUM SERIES N°153, PAGES 1-6, 2007

ICHEM SYMPOSIUM SERIES NO. 153

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## FIRE PROTECTION MEASURES FOR VESSELS CONTAINING REACTIVE CHEMICALS<sup>†</sup>

J A Hare<sup>1,3</sup>, L Cusco<sup>1</sup>, D C Kerr<sup>1</sup> and M D Bishop<sup>2</sup>

<sup>1</sup>Health and Safety Laboratory, Process Safety Section

<sup>2</sup>Health and Safety Executive, Hazardous Installations Directorate Chemical Industries

<sup>3</sup>Contact details: HSL, Harpur Hill, Buxton, Derbyshire, SK17 9JN, United Kingdom; Tel.: +44 (0)1298 218125, e-mail: john.hare@hsl.gov.uk

Several explosions have been reported at chemical plants handling and storing pressurised self-reacting chemicals. Some of these explosions resulted from of an external source heating up a reactor or storage vessel.

For vessels containing non-reactive liquid chemicals, fire exposure will cause the pressure to increase due to vaporisation of liquid and by thermal expansion of the vapour. However, if a vessel containing a self-reactive chemical is exposed to fire, an exothermic runaway is initiated at a much earlier point in the conversion of reactants to products than would be the case with a process induced runaway. The temperature is raised without a corresponding consumption of reactant and the resulting higher concentration produces a much higher reaction rate than would have been the case if the fire were not present. There is a highly, non-linear relationship between the amount of heat transmitted into a vessel and its contents and the time taken to reach the onset temperature.

Current practice for the protection of storage and transport pressure vessels containing reactive, flammable chemicals against external fires is typically to follow the standards (pressure relief and fire protection) developed to protect liquefied petroleum gas storage vessels against hydrocarbon pool fires. However, recent work has shown that this may not be safe. For chemicals undergoing decomposition or self-reaction (e.g. polymerisation) at elevated temperatures, there is insufficient knowledge of the amount of heating to which they may be safely exposed when held in pressure vessels. Such information is needed to correctly design an adequate fire protection system to be certain that a runaway reaction, which might be triggered by the heat from an external fire, may be prevented or mitigated. Notably, the adequacy in such circumstances of pressure relief, sized using current standards, is uncertain.

Furthermore, current industry trends include more use of temperature-controlled transport instead of using chemical inhibitors. There have also been recent changes in UN Transport of Dangerous Goods Model Regulations that remove the specific reference to 'inhibition' and replace it with the term 'stabilised'. Inhibitors can lose their effectiveness as the temperature is increased, as they are thermally unstable. The inhibitor will become ineffective at temperatures well below the critical failure temperature (circa 300 °C) used in the assessment of the passive fire protection for LPG.

This paper describes the development of an experimental calorimetric system for the simulating the effects on chemicals in vessels under fire loading, the evaluation of the validity of theoretical corrections to self-heat rates measured without external heating and the development of a procedure to calculate the required relief rate for such cases.

**KEYWORDS:** reactive chemicals, fire protection, vent sizing, simulation

### INTRODUCTION

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This paper describes the plans and initial work in an HSL research project on "Fire Protection Measures for Vessels Containing Reactive Chemicals", which has the following main work areas:

- Development of an improved experimental calorimetric system for simulating the effects on chemicals in vessels under fire loading.
- Evaluation of the validity of theoretical corrections to self-heat rates measured without external heating.
- Development of a procedure to calculate the required relief rate for such cases.

**SAFETY ISSUES**

Thermal runaway begins when the heat generated by a reaction (e.g. decomposition, polymerisation etc.) exceeds the heat that can be removed to the surroundings. The surplus heat increases the temperature of the reaction mass, which causes the reaction rate to increase and in turn accelerates the rate of heat production. Thermal runaway occurs because the rate of reaction (and hence rate of heat production) increases exponentially with temperature whereas the rate of heat removal only increases linearly. Hence thermal runaway can start slowly, but then accelerate, until eventually it may lead to an explosion. If there is fire engulfment, there are effectively no heat losses. Thermal runaway is particularly hazardous if the temperature can be raised to:

- a) the boiling point of the mixture at the maximum pressure permitted in the vessel; or
- b) to a temperature high enough to initiate a decomposition or polymerisation and the properties of the reaction products are more hazardous than those of the reactive chemical. Examples include reaction products that: include a permanent gas which will greatly raise the pressure; are more volatile than the reactants; cause auto-catalytic effects and increase the reaction rate; or are highly viscous or solid so that cooling of the reaction mixture becomes difficult and venting of the reaction mixture is difficult or impossible.

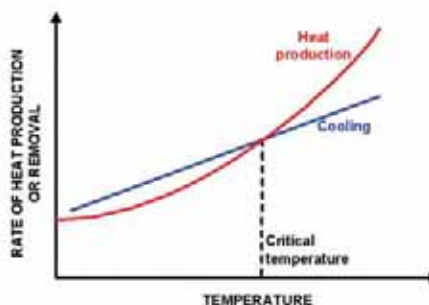


Figure 1. Critical temperature

For a runaway reaction, the critical temperature is defined as the temperature at which the rate of reaction just exceeds the rate of heat loss. This is illustrated graphically in Figure 1. Under normal circumstances (i.e. not in a fire), the rate of heat release depends on the volume of material but the rate of heat removal depends on the surface area. Hence, as the size of vessel increases, the critical temperature will reduce. In a fire, the surface will be heated and the additional heat input into the reactive chemical will depend upon the vessel surface area. If passive fire protection (PFP) is fitted to the vessel, this will lower the rate of transfer to the stored material in a fire but will also lower the heat losses during normal storage. In these circumstances, active cooling may be required to prevent a runaway reaction. This has been the case for the tank transport of some organic peroxides. If PFP is used, even a relatively small fire that is extinguished fairly rapidly, can result in a temperature rise, which, because of the insulating effect, can result in thermal runaway, particularly if local decomposition occurs resulting in an autocatalytic effect. Careful consideration is required, on a case-by-case basis, of the possible effects and the need to empty the vessel, inhibit the reaction or cool the contents.

In order to properly assess the requirements, for each reactive chemical, it is necessary to know the:

- rate and quantity of heat generation;
- rate of gas evolution;
- ideally, the kinetics of reaction;
- heat loss characteristics of the vessel; and
- thermal properties of the chemical and vessel walls.

Self-reactive chemicals are often stored with reaction inhibitors, which are only effective in preventing reactions at low temperatures. How they operate chemically also varies. Two examples of self-reactive chemicals, 1,3 butadiene and styrene, which are stored with inhibitors will be considered.

1,3 butadiene polymerization occurs in two ways: by peroxide initiation and temperature initiation. The usual inhibitor tert butyl catechol acts only to inhibit the peroxide

initiated reaction. It is also prudent to keep the system oxygen free. Thermal polymerization will start slowly at about 100 °C and full auto-polymerization will occur at about 150 °C. The critical temperature used in the assessment of passive fire protection is about 300 °C, but an insulated tank containing 1,3 butadiene will start to react at temperatures as low as 100 °C.

Styrene storage also uses tert butyl catechol (12–15 ppm) inhibitor. Here oxygen is required for the inhibitor to work effectively. The recommended storage temperature for styrene is below 32 °C; 18 °C should not be exceeded for long-term storage. At 28 °C, styrene can be stored in a vessel saturated with oxygen for 1 to 2 months; with less than 3 ppm oxygen, the styrene can only be stored for 4 to 5 days. Again in conditions of fire exposure, the inhibitor will cease to be effective.

### EXPERIMENTAL SIMULATION

Fire simulation calorimetry allows measurement of the rate of heat production and pressure rise due to both the exothermic reaction and applied heat load. The presence of a fire outside a vessel containing a reactive chemical will heat the system and cause the chemical to react at a higher rate than would be the case if the fire were absent. When there is external heating less reactant conversion is needed to reach a given temperature. The reaction rate at any temperature can therefore be higher than that measured at the same temperature under adiabatic conditions. This would lead to different venting characteristics and vent requirements. It is necessary to measure the rate of heat generation as a function of temperature conditions of external heating, which simulate the full-scale rate of external heating.

The method using a standard Phi Tec Calorimeter (Singh 1989) is to increase the temperature of guard heaters above that of the sample. This is similar to a heat loss compensation scheme. The software limits the maximum allowable temperature difference to 30 °C. Thus the effective maximum heat input is 1 W, which is equivalent to 0.8 K min<sup>-1</sup>. For a 2 tonne tank, this compares with about 2 K min<sup>-1</sup> using API 520, based upon pool fires and about 24 K min<sup>-1</sup> for exposure to a 2 kg s<sup>-1</sup> flashing liquid propane jet fire. The new heat input system will use an analogue heater power supply (up to ~70 W). The power input will be varied to enable the simulation of fire impingement on a range of storage vessel sizes. The calorimeter electronic rack will need upgrading. Software development and commissioning work will be needed and also the evaluation of heat losses with compensation if necessary.

It is planned to firstly undertake fire simulation calorimetry tests on a model vapour pressure system (acetic anhydride hydrolysis), using stainless steel test cells, with internal cartridge heaters. Secondly a similar series of calorimetric tests on (stabilized or temperature controlled) reactive monomer system or organic peroxide in a solvent will be performed.

### THEORETICAL SIMULATION

Adiabatic data, measured without external heating, can be corrected for the effects of any external fire. The proposed method of correction is based upon Huff (1982).

The temperature rate calculation is:

$$(dT/dt)_{adj} = (dT/dt)_{rxn} + (dT/dt)_{fire} \quad (1)$$

The temperature rate due to the reaction alone is scaled to a higher temperature T' (produced because of the fire) based on same extent of reaction.

$$(dT/dt)_{rxn}' = (dT/dt)_{rxn} \exp \{ (-E/R)[(1/T') - (1/T)] \} \quad (2)$$

To do the simulation, the temperature rise for the fire heating case must first be estimated, then the temperature rate due to the reaction alone is calculated using equation (2), the time taken for the temperature rise is calculated by dividing the temperature rise by the temperature rate for the reaction alone. The total temperature rate adjusted for the fire is then calculated using equation (1). The temperature rise for the fire heating case can now be checked: by multiplying the total temperature rate by the time taken for the temperature rise. The correct value for the temperature rate is achieved by iteration, easily done by implementing macros on a spreadsheet. The new temperature, with external heating, is obtained by adding the iterated temperature rise to the previous temperature, with external heating. Huff (1982) gave an equation to allow the pad gas corrected pressure to be calculated for fire case.

Theoretical simulations were undertaken for two example reactions. The first was the reaction between acetic anhydride and water giving acetic acid. This is a vapour pressure system, but is also autocatalytic. Figure 2 is the self-heat rate plot (log temperature rate versus reciprocal temperature) for the total temperature rate, with no external heating and with external heating rates of 3 °C min<sup>-1</sup> and 10 °C min<sup>-1</sup>. The total temperature rate is shown for the fire cases. It would be expected that the temperature rates would always be higher for the fire cases, but this is not the case. This is because the reaction is autocatalytic. With external heating the conversion will be lower for a given temperature. The rate of an autocatalytic reaction increases with increasing product concentration. As the conversion is lower for the external heating case, the reaction rate will also be lower. This will cause the temperature rate due to the reaction to be lower except at the maximum temperature rates see Figure 2.

The second was the decomposition of an organic peroxide in an organic solvent. The peroxide was a peroxy ester in isododecane. The reaction is a gassy system and can be treated as simple first order reaction. Figure 3 is self-heat rate plot for the total temperature rate, with no external heating and with external heating rates of 1 °C min<sup>-1</sup> and 3 °C min<sup>-1</sup>. Figure 3 shows how the total temperature rate increases significantly for the fire simulation cases. There is

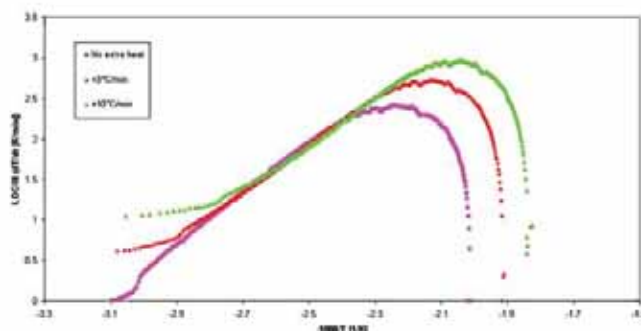


Figure 2. Acetic Anhydride – Water, PASS

no evidence of autocatalytic behaviour with this reaction system.

**VENT SIZING ISSUES**

There are three vent-sizing cases. For fire relief alone, using API (1997) to estimate the heat input and assuming vapour-only flow. For runaway reaction alone, assuming no heat comes from the fire engulfment, using two-phase flow methods. For a runaway reaction, allowing for the heat coming from the fire engulfment, using API methods to estimate the heat input and using two-phase flow methods. Echells (1998) deals with runaway reactions and both two-phase and vapour-only flow.

**FIRE RELIEF ALONE**

The heat input Q is calculated using equation (3) (where there is prompt fire fighting and good drainage) or equation

(4) (where there is no prompt fire fighting nor poor drainage).

$$Q = 43200 F S_u^{0.82} \tag{3}$$

$$Q = 70\,960 = F S_u^{0.82} \tag{4}$$

The required relief rate W is calculated using equation (5). The vent mass flux G (assuming vapour only flow) is calculated using equation (6). The vent area A is then calculated using equation (7).

$$W = Q/h_{fg} \tag{5}$$

$$G = C_d C_{cr} P(M_w/Z_w T)^{1/2} F_R \tag{6}$$

$$A = W/G \tag{7}$$

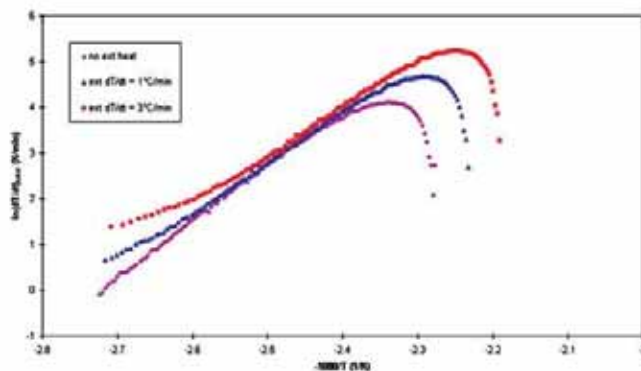


Figure 3. 20% Trigonox 21 in Shellsol T, PASS

**RUNAWAY REACTION ALONE**

The heat release rate per unit mass  $q$  is calculated as:

$$q = C_p(dT/dt)_{\text{ext}} \quad (8)$$

The mass flux  $G$  for a two-phase flow could be calculated using the Equilibrium Rate Model (equation 9). The vent area  $A$  is calculated using the Leung Equation (for vapour pressure runaway reactions) (equation 10).

$$G = (dP/dT)_m(T_m/C_{pm})^{1/2} \quad (9)$$

$$A = m_o q_m / \{G \{ (V/m_o)(h_{lgm}/V_{lgm}) \}^{1/2} + [C_{pm}\Delta T]^{1/2} \}^2 \quad (10)$$

**RUNAWAY REACTION AND FIRE RELIEF**

The extra temperature rate  $(dT/dt)_{\text{fire}}$  which is applied to the calorimeter throughout the experiment is calculated using equation (11). The rate of temperature rise due to the reaction alone  $(dT/dt)_{\text{rxn}}$  is obtained by subtracting the temperature rate which is simulating the fire from the total temperature rate  $(dT/dt)_{\text{adj}}$  (see equation 12). The heat release rate per unit mass ( $q$ ) is calculated using equation (8) with  $(dT/dt)_{\text{rxn}}$  being replaced by  $(dT/dt)_{\text{rxn}}$ . A modified heat release rate per unit mass (equation 13) is used in equation (10).

$$Q = m_{\text{sample}} C_p (dT/dt)_{\text{fire}} \quad (11)$$

$$(dT/dt)_{\text{rxn}} = (dT/dt)_{\text{adj}} - (dT/dt)_{\text{fire}} \quad (12)$$

$$q_{\text{modified}} = q + 2Q/m_o \quad (13)$$

**EXAMPLE**

Table 1 shows vent sizing results for the acetic anhydride – water system. The reactor was the AWARD 2 m<sup>3</sup> vessel (Snee 2006 and Hare 2006). The set pressure was 2 bara and the maximum pressure 3 bara. The fill levels were 50, 60 and 70%. Vent sizes shown are for nozzle flow so the effect of vent lines has been ignored. Vents were sized for runaway alone and for runaway reaction and fire relief (3 and 10 C/min external heating), see the self heat rate data in Figure 2. The vent sizes for the runaway plus external heating cases were similar and larger than the runaway alone case. However there is little difference between the 3 and 10 C/min cases. This is again due to autocatalysis

**Table 1.** Vent sizing calculations for Acetic Anhydride/Water (Award 2 m<sup>3</sup> reactor)

Case	Vent diameters (mm) for various fills		
	50 % fill	60% fill	70% fill
Runaway alone	285	317	347
Runaway + 3 C/min	319	355	388
Runaway + 10 C/min	319	354	387

for this reaction system. For a reaction system without autocatalysis the vent size for 10 C/min will be larger than that for 3 C/min external heating.

**DISCUSSION AND RECOMMENDATIONS**

- It is important to consider whether a fire will give rise to a runaway reaction. If so, two-phase venting will be expected and larger required vent sizes will result.
- Fire simulation calorimetry may be required to obtain data for vent sizing but may not be feasible in all cases. It is planned to develop an improved calorimeter.
- For reactive chemicals, the PFP needs to protect the wall of the vessel from reaching a temperature where weakening can occur, if possible, prevent a runaway reaction from being initiated and reduce the heat transfer to the vessel so that a relief device with a practical vent size can be used.
- The comparison and guidance work being done at HSL is designed to evaluate the suitability of the theoretical models by comparison with the experimental data, develop a procedure to calculate the required relief rate in such cases and give recommendations on the suitability of possible design methods.

**UNITS AND SYMBOLS**

$A$	vent area (m <sup>2</sup> )
$C_p$	reactant mixture specific heat (J kg <sup>-1</sup> K <sup>-1</sup> )
$C_d$	discharge coefficient
$C_{sv}$	flow correction factor, function of isentropic coefficient
$E/R$	activation temperature (K)
$F$	environmental factor
$F_b$	back pressure correction factor
$G$	mass flux (kg m <sup>-2</sup> s <sup>-1</sup> )
$h_{lg}$	latent heat of reactant mixture (J kg <sup>-1</sup> )
$m_o$	reactant mass (kg)
$m_{\text{sample}}$	sample mass used in calorimetric test (kg)
$M_w$	molecular weight
$P$	vessel pressure (Pa)
$dP/dT$	rate of change of pressure with temperature (Pa K <sup>-1</sup> )
$q$	heat release rate per unit mass of reactant (W kg <sup>-1</sup> )
$q_{\text{modified}}$	heat release from reactant plus external heat (W kg <sup>-1</sup> )
$Q$	heat input (W)
$S_w$	effective wetted surface area of vessel (m <sup>2</sup> )
$T$	reactant temperature, runaway reaction alone (K)
$T'$	reactant temperature, runaway and fire together (K)
$\Delta T$	temperature difference between temperatures at the relief set pressure and the maximum accumulated pressure (K)

$(dT/dt)_{rxn}$	rate of temperature rise due to reaction, runaway reaction alone ( $K s^{-1}$ )
$(dT/dt)'_{rxn}$	rate of temperature rise due to reaction, runaway and fire together ( $K s^{-1}$ )
$(dT/dt)_{fire}$	rate of temperature rise to simulate the fire, runaway and fire together ( $K s^{-1}$ )
$(dT/dt)_{adj}$	total rate of temperature rise, runaway and fire together ( $K s^{-1}$ )
$v_{lg}$	difference between vapour and liquid specific volume ( $m^3 kg^{-1}$ )
$V$	vessel volume ( $m^3$ )
$W$	required relief rate ( $kg s^{-1}$ )
$Z_c$	compressibility factor
<b>Subscripts</b>	
$m$	mean conditions between relief set pressure and maximum accumulated pressure

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# Development of fire protection measures for vessels containing reactive chemicals

The objective of this work is to have a better understanding of the phenomena that occur when a vessel containing reactive chemicals is exposed to an external fire and so assess possible preventive and mitigation measures. The following approach has been adopted:

- an experimental calorimetric system for the simulating the effects on chemicals in vessels under fire loading was developed;
- the validity of theoretical models for the correction of adiabatic data were tested experimentally;
- dynamic simulations of large-scale vessels containing reactive chemicals exposed to a pool fire were carried out in order to study the effect of the presence of an insulation layer.

This work will form a useful basis for HSE to assess the adequacy of the 'fire case' for relief systems provided on a range of process reactors containing reactive chemicals and on storage vessels for reactive monomers. These installations vary in size from small reactors common in the pharmaceutical and fine chemical industries to the large, several hundred tonne capacity storage vessels used in the petrochemical industry.

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