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Vent sizing: Analysis of the blowdown of a hybrid non tempered system

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ABSTRACT

The runaway and blowdown of a non tempered hybrid chemical system (30% cumene hydroperoxide) exposed to an external heat input was investigated using a 0.1 l scale tool.

The maximum temperature and the maximum temperature rise rate were showed to be sensitive to the vent size. An Antoine type correlation between the maximum temperatures and pressures was observed. These resulted from the presence of vapour, mainly generated by the reaction products. Increasing the initial filling ratio resulted in an earlier vent opening but did not have a significant influence on the blowdown. Three types of mass venting behaviour were observed, when changing the vent area to volume ratio (A/V):

- for large A/V, two-phase venting occurred from the vent opening until the end of the second pressure peak;
- for medium A/V, two-phase venting occurred before and after the turnaround. The data seem to indicate that gas only venting occurred at turn-around;
- for low A/V, two-phase venting was observed only after the second pressure peak.

Two-phase venting after the second pressure peak probably results from the boiling of the hot reaction *products* at low pressure.

1. Introduction

DIERS[3] research work introduced a classification for runaway reactions according to which chemical systems are either tempered or non tempered (with vapour and gassy systems as limiting cases). According to Huff or Leung “the so-called tempering condition is achieved if the evaporative heat removal becomes equal to the reaction heat release” [1,2]. As a consequence, “the ERS[4] device is able to control T ($dT/dt = 0$) and P ($dP/dt = 0$) at the set pressure”. On the other hand, “the ERS device is not able to control T ($dT/dt \gg 0$) and P ($dP/dt \gg 0$) at the set pressure” for hybrid non tempered reactions [3]. A “tempering effect” is however sometimes mentioned when vaporization phenomena reduce the reacting mixture temperature and the severity of runaway reaction, without controlling the temperature [4].

DIERS vent sizing methodology was largely developed and used for tempered systems [3]. A method was also proposed for purely gassy systems [5], but very few investigations were published for hybrid non tempered systems. No vent sizing criterion that would take vapour influence into account is available although it was demonstrated that it greatly modifies the necessary vent size [6–10].

Few experiments involving the runaway and blowdown of non tempered systems were published [11–15]. These tests were performed with the objective of developing the UN 10 l method based on the similarity principle.

The present work was aimed to gain a better understanding of the blowdown of non tempered hybrid systems, and more precisely to observe the sensitivity of the temperature, pressure and vented mass to the vent area to vessel volume ratio (A/V). The experimental study uses a recently developed 0.1 l scale tool [6,16]. Adiabatic calorimetry tests with closed and open cells according to the DIERS methodology were also carried out prior to the blowdown tests. They allowed the characterization of the thermodynamic and the kinetics of the runaway reaction of concern.

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Nomenclature

A/V	vent area to reactor (or test cell) volume ratio (m^{-1})
CHP	Cumene Hydro peroxide
m	mass of reactor (or test cell) contents (kg)
P	absolute pressure in reactor (or test cell) (bar)
T	temperature in reactor (or test cell) (°C)
T_{bp}	boiling temperature at ambient pressure (°C)
τ	filling ratio (%)
Δt	time between safety vent opening and turnaround (s)

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ini or 0	at the beginning of test, before reaction begins
max	when pressure is maximum (i.e. at turnaround)
end	at the end of blowdown, after cooling down
s	at vent opening (i.e. at set pressure)

2. Experimental set up

2.1. DIERS adiabatic calorimetry

Closed and open cell tests according to the DIERS approach were carried out using a Vent Sizing Package 2 (VSP2) adiabatic calorimeter (Fauske & Associates, LLC). Closed cell experiments consist in performing the runaway reaction under adiabatic conditions in a 110 ml closed cell. The gases/vapour generated by the runaway reaction pressurise the test cell. Open cell experiments consist in performing the runaway reaction in a 110 ml test cell open to a 4 l containment vessel. In this case, the generated gases/vapour pressurise a larger volume, thus avoiding the bursting of the test cell. For both configurations the liquid temperature and the generated pressure (either in the test cell or in the containment vessel) are recorded. All the open and closed tests were performed with stainless steel test cells.

2.2. Setup for blowdown experiments at laboratory scale

A recently developed 0.1 l scale tool ([6,16], Fig. 1) was used to run blowdown experiments at laboratory scale. This tool is an extension of the VPS2 adiabatic calorimeter in its blowdown configuration which consists in the addition of a main safety relief line, a feed bleed line and a real time vented mass measurement system. The main safety relief line (1/8" diameter, 0.6 m long) includes an actuated ball valve, which simulates the opening of the safety relief system, followed by a metering valve where most of the pressure drop occurs. An equivalent A/V ratio can be defined for different settings of the metering valve. Stainless steel test cells were used for all the tests. This experimental setup allows the measurement of the liquid temperature, the cell pressure and the vented mass during the blowdown. The small scale of the experimental setup allows the study of the sensitivity of the blowdown to the A/V ratio. The measurement of the vented mass is subsequently used to assess the vented mass at turnaround (second pressure peak).

3. Chemical system and experimental conditions

Cumene hydroperoxide (CHP; T_{bp} = 116 °C at 20 mbar abs pressure) and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (T_{bp} = 280 °C at atmospheric pressure) were chosen respectively as the substance subject to thermal decomposition and the solvent. CHP is widely used as an initiator for polymerization reactions. It decomposes to mainly produce methane (0.3–0.5 mol/mol), dimethylbenzyl alcohol (0.6–0.9 mol/mol), acetophenone (0.2–0.4 mol/mol), and phenol and acetone when cumene is present (≈0.06 mol/mol each) [17].

Table 1
Closed cell test conditions and main results.

CHP concentration (%, w/w)	15
Filling ratio (%)	52.4
Initial mass (g)	52.6
P_{end} after cooling (bar)	10.4
$(dT/dt)_{max}$ (°C s^{-1})	5.36
$(dP/dt)_{max}$ (bar s^{-1})	1.95
T_{max} (°C)	250

The decomposition of 30% (w/w) CHP under external heat input conditions of $dT/dt = 0.5$ °C min^{-1} (0.0083 °C s^{-1}, fire simulation) was studied. CHP was obtained as a 80% (w/w) solution in cumene. The composition of the investigated chemical mixture is therefore 30% (w/w) CHP, 7.5% cumene and 62.5% solvent. It has to be noted that cumene (T_{bp} = 153 °C) is the most volatile chemical in this mixture. Assuming no decomposition, this mixture would lead to a vapour pressure of around 0.8 bar at 250 °C.

4. Results of the experimental investigation

4.1. Characterisation of the chemical system using the DIERS approach

4.1.1. Procedure

For both open and closed cell experiments, the chemical mixture is first quickly heated up (~3 °C min^{-1}) to 85 °C (at this temperature the decomposition reaction is very slow and can not be detected by the VSP2 in adiabatic mode). External fire exposure is then simulated through constant power input (0.5 °C min^{-1}) until the end of the decomposition.

4.1.2. Results of the closed cell experiments [6,16]

We had to lower CHP concentration to 15% (w/w) for the closed cell DIERS calorimetric tests in order to avoid the bursting of the cell. The closed cell experiment however provided some qualitative information about vapour and non-condensable gas production during the runaway reaction. Table 1 and Fig. 2a give the test conditions and main results. As expected, the pressure at the end of the closed cell experiment, after cooling P_{end} = 9.4 bar after correction for the pad gas clearly indicated that the decomposition of CHP leads to the formation of non-condensable gases.

Two rough assumptions were made in order to estimate possible presence of vapour during the post decomposition period (cooling down to ambient temperature):

- The vapour contents are completely condensed at T_{end}.
- The non-condensable gases are not soluble in the liquid phase, independently of the temperature.

After correcting for the pad gas, it is possible to assess the respective contributions of the non condensable gases and the vapour to the total pressure during the cooling period. Fig. 2b shows that a linear Antoine type plot can be obtained for the assessed vapour pressure between 83 °C and T_{max} (242 °C). Vapour would thus contribute to P_{max} as high as 10.4 bar, which would be significant compared to 16 bar for non condensable gases.

The vapour pressure would be around 4 bar at 150 °C after decomposition whereas the pressure (non condensable + vapour) is almost zero at the same temperature before decomposition starts (Fig. 2a). This means that the vapour pressure is mainly due to the decomposition products. When dealing with an unknown reaction, it is therefore necessary to investigate the presence of vapour not only before decomposition occurs, but also after its completion.