

HSL – INERIS VENT SIZING ROUND ROBIN EXERCIZE ON 40% DI-CUMYL PEROXIDE IN DI-ISOBUTYRATE SOLUTION

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A round robin exercize was proposed by the HSL (U.K.) and INERIS (France) consisting of the experimental study of the decomposition of a 40% w/w di-cumyl peroxide in 2, 2, 4-trimethyl-1,3 pentanediol di-isobutyrate solution, followed by a vent sizing exercise based on this runaway reaction occurring in the HSL pilot facility reactor installed in the HSL site in Buxton, Derbyshire, UK.

The decomposition of the di-cumyl peroxide in di-isobutyrate solution was studied in the Process Safety Lab of Rhodia in CRTL Saint-Fons (France) using DSC tests and VSP tests. The results obtained are presented in this paper.

A literature review on the decomposition of di-cumyl peroxide was also completed to allow a comparison of the results obtained with literature data and to collect information on the venting behaviour of di-cumyl peroxide solutions in various solvents.

The decomposition of the 40% di-cumyl peroxide in di-isobutyrate solution is an un-tempered gassy reaction. In this case, vent sizing is based on the maximum rate of gas production. The maximum rate of gas production was measured in VSP closed test cell with various filling ratios and corrected to adiabatic conditions. Vent sizing was then achieved considering a gas only release and following the DIERS methodology. The details of the vent sizing calculations are given. The results obtained are compared to the other participant results and to the field tests carried out by INERIS in their 10 litre vessel.

KEYWORDS: Dicumylperoxide, vent sizing round robin exercize, DIERS.

1. INTRODUCTION

Vent sizing for runaway reactions following the DIERS methodology is based on small-scale experiments carried out in pseudo adiabatic calorimeters like the VSP. VSP is for Vent Sizing Package, the DIERS bench scale apparatus. This experimental set-up allows the study of runaway reactions in conditions close to the adiabatic conditions, requiring only limited corrections to represent industrial size conditions. The relevant methods of correction to adiabatic conditions are described and exemplified in the DIERS project Manual and in other publications. The DIERS methodology does not imply necessarily the assumption of a two-phase release in the vent line, in particular when it is known that a gas only release will occur. A gas only release is frequent for gassy reactions where no or limited vapor pressure may build up. In the case considered in this paper a literature review led to the conclusion that a gas only release was expected. This was also confirmed by the huge data presented in the thesis dissertation of W. S. Minko. The decision was made to carry-out closed cell VSP experiments since the rate of pressure rise obtained could be controlled by the pressure equilibration system. Further to this decision we checked that the test cell filling ratio considered did not influence the rate of gas production. The experimental maximum rate of gas production was corrected to adiabatic conditions because the strong correlation between the rate of pressure rise and the heat-rate in our VSP experiments suggested that this method of correction should be also applied to the maximum rate of gas production. Vent

sizing was then achieved using the Boyle equation for this pure gassy reaction.

2. EXPERIMENTAL STUDY OF THE DECOMPOSITION OF 40 % W/W DI-CUMYL PEROXIDE IN 2, 2, 4-TRIMETHYL-1, 3 PENTANEDIOL DI-ISOBUTYRATE SOLUTION

2.1 RESULTS OBTAINED IN DSC AND THE C80 ISOTHERMAL CALORIMETER

Two DSC experiments were carried out on samples of 39.5% by weight di-cumyl peroxide in the so-called di-isobutyrate solvent. In the first experiment, a 22.99 mg sample of 39.49% w/w di-cumyl peroxide was studied in the Setaram DSC Sensys, in closed Incoloy Alloy A286 test cell under 2°C/min temperature scan conditions. The sample exhibited a 358.86 J/g exotherm between 115°C and 190°C.

In the second experiment, a 19.47 mg sample of 39.52% w/w di-cumyl peroxide was studied in the Setaram DSC 111, in closed 316 L stainless steel test cell under 2°C/min temperature scan conditions. The sample exhibited a 388.6 J/g exotherm between 105°C and 190°C.

The integration base-line is subject to discussion. There may be also some influence of the test cell wall material on the exotherm pattern. The resulting decomposition exotherm for pure di-cumyl peroxide would be of $\Delta H_D = -908.7 \text{ J} \cdot \text{g}^{-1}$ in the first experiment and $\Delta H_D = -983.3 \text{ J} \cdot \text{g}^{-1}$ in the second experiment.

A review of the literature concerning the heat of decomposition of di-cumyl peroxide provided the following information. Wu, Hou, & Shu (2006) [1] obtained a heat of decomposition of $\Delta H_D = -750.752 \text{ J} \cdot \text{g}^{-1}$ for 99% di-cumyl peroxide using DSC technique.

In a subsequent paper by Chi-Min Shu et al, (2009) [2], the heat of decomposition of 99.3% di-cumyl peroxide was measured in DSC closed cell of unspecified wall material, using different rates of temperature scan. The following results were obtained after a Fork simulation:

Rate of temperature scan ($^{\circ}\text{C} \cdot \text{min}^{-1}$)	ΔH_D ($\text{J} \cdot \text{g}^{-1}$)
1	-679
2	-698
4	-735
10	-800

Grolmes, M. (1998) [3] gave the heat of decomposition of neat di-cumyl peroxide $\Delta H_D = -774 \text{ J} \cdot \text{g}^{-1}$. The heat of decomposition of di-cumyl peroxide deduced from our DSC tests is greater than the data found in the literature for the decomposition of neat di-cumyl peroxide. This may result of some degree of oxidation of the solvent by the reacting di-cumyl peroxide as shown by Wu, Hou & Shu (2006) [1].

Heat capacity or specific heat of the 40% w/w di-cumyl peroxide in di-isobutyrate solution

No data concerning the solvent heat capacity and very limited data concerning di-cumyl peroxide heat capacity could be found in the literature. Therefore the 40% w/w di-cumyl peroxide in di-isobutyrate solution heat capacity was measured between 30°C and 70°C using the Setaram C80 isothermal calorimeter. A heat capacity of $C_P = 1.845 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ was measured between 30°C and 70°C . This data allowed obtain data for the heat of reaction of di-cumyl peroxide which proved to be quite consistent with the data found in the literature [1, 2].

2.2 VSP TESTS ON THE 40% WT. DI-CUMYL PEROXIDE IN DI-ISOBUTYRATE SOLUTION

The runaway decomposition of the 40% wt. di-cumyl peroxide in di-isobutyrate solution was studied using VSP tests carried out in closed test cell conditions. This test method provides the benefit of a good calorimetric method where the sample and gas phase temperatures are well defined and known. The draw-back of this method or approach is that the gas production estimate does not include the gas dissolved in the liquid phase under pressure. However the influence of the total pressure on the gas dissolved in the liquid phase may be observed by varying the test cell filling ratio. The other testing option, consisting of open cell tests, presents the drawbacks of a poor precision on

the gas temperature and on the rate of gas production. The VSP apparatus used in this study is the number 25 of the original device. It was obtained from Fike Europe in 1985 and was further updated to improve the pressure compensation dynamics. It is now operated under Lab view software.

Four VSP tests were carried out in 115 cm^3 stainless steel closed test cells under stirring conditions. The sample charges were varied to determine the influence of the test cell filling ratio on the reaction rate. The decomposition reaction was initiated by a $0.3^{\circ}\text{C} \cdot \text{min}^{-1}$ temperature scan in three tests with different filling ratios. In one experiment the reaction was initiated by a $0.5^{\circ}\text{C} \cdot \text{min}^{-1}$ temperature scan, to meet the fire case conditions and to allow a comparison of experiments carried out with the same filling ratio and different initiation conditions i.e. $0.3^{\circ}\text{C} \cdot \text{min}^{-1}$ and $0.5^{\circ}\text{C} \cdot \text{min}^{-1}$ temperature scan. The design base case filling ratio could be used without cell rupture, thus proving that this test method could be applied to the design base case filling ratio. The test results are also summarized in Table 1 to allow a comprehensive comparison of the results obtained for different operating conditions.

First of all, the heat of reaction measured per gram of neat di-cumyl peroxide ΔH_R was fairly constant and compared well with the results published in the literature. This supports the conclusion that the experimental data obtained and its interpretation is quite consistent. The different test cell filling ratios had no influence on the heat of reaction estimate. The solvent used did not influence the heat of reaction, compared to the heat of reaction obtained for the decomposition of pure di-cumyl peroxide.

The decomposition reaction activation energy E_a was obtained from the heat-rate versus temperature curve slope in a temperature range where the reaction is zero order. The activation energy obtained is also fairly compatible with the data published in the literature for the decomposition of neat di-cumyl peroxide and for di-cumyl peroxide solutions [1, 2]. The reaction activation energy is necessary to correct the maximum heat-rate and the maximum rate of gas production to adiabatic conditions, if necessary. The maximum rate of gas production $(\frac{dn_g}{dt})_{\text{MAX}}$ per kg sample was derived from the maximum heat-rate $(\frac{dT}{dt})_{\text{MAX}}$ and the maximum rate of pressure rise $(\frac{dP}{dt})_{\text{MAX}}$, using a formula presented in [4–6]. In our experiments both maximum rates were obtained at the same temperature. See Figure 1. A conservative method was applied to estimate $(\frac{dn_g}{dt})_{\text{MAX}}$, where the decomposition gas production rate estimate was based on the total pressure measured and not on the decomposition gas partial pressure only. The results were obtained by hand calculations for traceability reasons. The maximum rate of gas production appeared to be influenced by the initial rate of temperature scan. The maximum rate of gas production increased when the rate of temperature scan was increased from $0.3^{\circ}\text{C}/\text{min}$ to $0.5^{\circ}\text{C}/\text{min}$. See Table 1.

The maximum rate of gas production decreased when the test cell filling ratio was increased from

Table 1. Summary of VSP test results

VSP #	m_0 (g)	$\left(\frac{dT}{dt}\right)_0$ ($^{\circ}\text{C} \cdot \text{min}^{-1}$)	T_0 ($^{\circ}\text{C}$)	T_F ($^{\circ}\text{C}$)	ΔT_{EXP} ($^{\circ}\text{C}$)	$\left(\frac{dT}{dt}\right)_{MAX}$ ($^{\circ}\text{C} \cdot \text{min}^{-1}$)	$\left(\frac{dP}{dt}\right)_{MAX}$ (bar $\cdot \text{min}^{-1}$)	P at $\left(\frac{dP}{dt}\right)_{MAX}$ (bar abs)	$\left(\frac{dn_G}{dt}\right)_{MAX}$ ($\text{mol min}^{-1} \cdot \text{kg}^{-1}$)	φ	ΔH_R ($\text{J} \cdot \text{g}^{-1} \cdot \text{dicup}$)	E_a ($\text{kJ} \cdot \text{mol}^{-1}$)
191009A	44.36	0.3	125.81	244.06	118.25	456.57	149.00	27.730	4.3806	1.28038	-698.3	142.46
201009A	44.19	0.5	130.68	251.20	120.52	573.98	187.16	24.985	5.5799	1.26146	-701.2	135.66
021109A	59.61	0.3	123.39	249.99	126.60	585.94	284.29	43.321	4.4037	1.19378	-697.1	138.69
041109A	70.71	0.3	123.18	254.02	130.84	604.45	350.90	53.652	3.2909	1.16290	-701.8	129.29

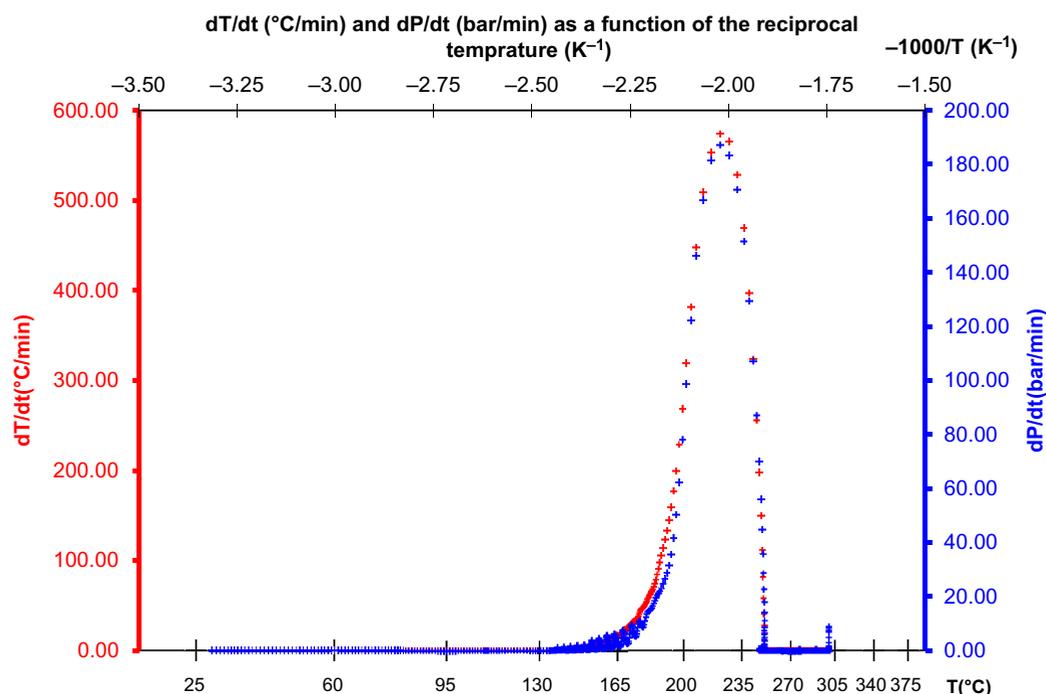


Figure 1. Round robin exercise – VSP # 201009A: Heat-rate and rate of pressure rise as a function of the reciprocal temperature

44.36 g sample to 70.71 g sample in 115 cm³ volume test cells. This may be explained by the increased solubility of the decomposition gases in the liquid reaction mixture under an increased pressure, and the increased volume of the liquid phase. Also there was an adverse effect of the reduced thermal inertia which would increase the experimental maximum rate of gas production if a lower φ factor was achieved. This phenomenon is frequently mentioned to support the choice of open cell testing for gassy reactions. However this effect was not observed until a filling ratio of 59.6 g sample in a 115 cm³ test cell. The data concerning the above discussion is presented in Table 2.

On the basis of the above results the more conservative maximum rate of gas production for 1 kg sample obtained in the VSP test # 201009A was considered for vent sizing. See Figure 2.

We now consider the correction of this maximum rate of gas production for 1 kg sample to adiabatic conditions.

The method of correction was described in the literature to correct the heat rate to adiabatic conditions [4–6]. The strong correlation between the rate of pressure rise and the heat-rate in our VSP experiments suggests that this method of correction should be also applied to the maximum rate of gas production. The correction method is a “one order” correction method taking into account the reactant consumption. In this method the corrected exotherm onset temperature is $\frac{1}{T_{0AD}} = \frac{1}{T_0} + \frac{R}{E_a} \ln \varphi$ where T_0 (°K) is the first measured temperature or the experimental onset temperature, T_{0AD} (°K) is the corrected adiabatic onset temperature, E_a (J · mol⁻¹) is the reaction activation energy, φ is the experiment thermal inertia and R (J · mol⁻¹ · °K⁻¹) is the perfect gas constant.

The corrected temperature at which the maximum rate of gas production was reached is: $T_{MAD} = T_{0AD} + \varphi^* (T_M - T_0)$ In this formula, T_M is the temperature measured at the experimental maximum rate of gas production. Then

Table 2. Influence of the test cell filling ratio on the maximum rate of gas production measured in VSP tests.

VSP #	m_0 (g)	Volume fill ratio τ	$\left(\frac{dT}{dt}\right)_0$ (°C · min ⁻¹)	P at $\left(\frac{dP}{dt}\right)_{MAX}$ (bar abs)	$\left(\frac{dn_G}{dt}\right)_{MAX}$ (mol · min ⁻¹ · kg ⁻¹)	φ
191009 A	44.36	0.4434	0.3	27.730	4.3806	1.28038
201009 A	44.19	0.4416	0.5	24.985	5.5799	1.26146
021109 A	59.61	0.5958	0.3	43.321	4.4082	1.19378
041109 A	70.71	0.7067	0.3	53.652	3.2909	1.16290

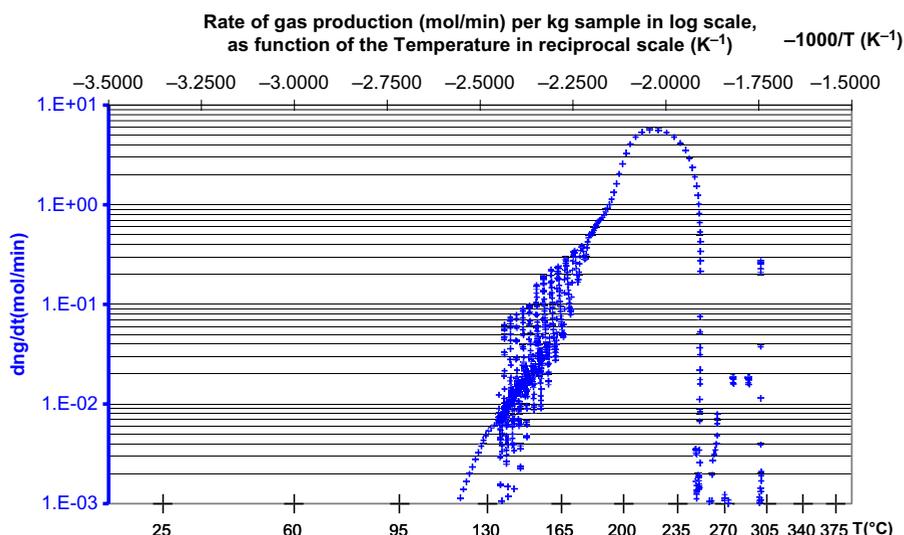


Figure 2. Round robin exercise – VSP # 201009A on 40% w/w dicumyl peroxide in di-isobutyrate solvent

the corrected adiabatic maximum rate of gas production is

$$\left(\frac{dn_G}{dt}\right)_{\text{MAX},\varphi=1} = \varphi * \text{Exp}\left[\frac{E_a}{R}\left(\frac{1}{T_M} - \frac{1}{T_{MAD}}\right)\right] * \left(\frac{dn_G}{dt}\right)_{\text{MAX},\varphi>1}$$

This correction method applied to the VSP # 201009A test results gives the corrected rate of gas production: $\left(\frac{dn_G}{dt}\right)_{\text{MAX},\varphi=1} = 27.8236 \text{ mol} \cdot \text{min}^{-1} \cdot \text{kg}^{-1}$ di-cumyl peroxide 40% in di-isobutyrate solution. This maximum rate of gas production was reached at the corrected temperature $T_{MAD} = 516.57^\circ \text{ K} = 243.42^\circ \text{ C}$. This temperature was lower than the solvent atmospheric boiling temperature $T_{Eb} = 280^\circ \text{ C}$. Therefore the reaction mixture may be considered as a gassy reaction system unless condensable or soluble volatile products are formed by the reaction. However, the results presented above show that the total pressure obtained in VSP tests does not influence the rate of gas production until a filling ratio of 0.5958.

3. VENT SIZING

3.1 DESCRIPTION OF THE ROUND ROBIN EXERCISE

The round robin exercise scenario was the decomposition of the 40% w/w di-cumyl peroxide solution in 2, 2, 4-trimethyl-1,3-pentenediol di-isobutyrate solvent occurring in a 340 litre glass lined Pfaudler reactor under external fire conditions represented by a $0.5^\circ \text{ C}/\text{min}$. heat-rate. This fire scenario was chosen to allow a check of the results using the UN 10 litre test vessel. The input data available for vent sizing are summarized in Table 3.

The purpose of the Round Robin exercise was to determine the vent area necessary to protect the 340 litre reactor vessel which has a maximum allowable pressure of 7 bar abs. The exercise was limited to the calculation of the size of a bursting disc to be installed on a short vent line open to the atmosphere, present on the reactor vessel. The rupture disc is assumed to have a low frictional resistance after bursting. A discharge coefficient $C_d = 0.816$ is specified to describe the vent line overall dissipation effect on the flow capacity.

3.2 ANSWER PRESENTED TO THE ROUND ROBIN EXERCISE

The VSP tests carried out to provide an experimental basis for the vent sizing calculations were implemented in VSP closed test cells. In these conditions, there was no second pressure peak observed and the whole di-cumyl peroxide

Table 3. Input data for vent sizing

Reactor volume V	0.340 m ³
Volume filling ratio τ	70%
Reactor inventory m_0	207.06 kg
Volume of reaction mixture V_L	0.238 m ³
Reaction mixture specific mass ρ_0	870 kg · m ⁻³
Vent set pressure P_S	4.5 bar abs
Maximum allowable Pressure P_{MAX}	7 bar abs
Fire case heat-rate	0.5 °C · min ⁻¹
Cd of the emergency vent line	0.816
Ideal orifice diameter of the permanent vent line	5.8 10 ⁻³ m

decomposition occurred in one peak only, for the pressure rate and for the heat rate. In addition, the pressure rate and the heat rate peaks obtained are well correlated one with the other. The heat of reaction deduced from the VSP test results, was consistent with the data found in the literature for the decomposition of neat di-cumyl peroxide, proving that this unique decomposition reaction peak involves the full decomposition of the di-cumyl peroxide and does not involve a side reaction of the solvent.

Type of reacting system in the DIERS methodology

The data obtained from the VSP tests shows that the solvent vapour pressure is small compared to the pressure resulting from the decomposition gas production. However a fraction of the decomposition products dissolves in the liquid phase or condensates on test cell cooling. The number of gas or vapour mole present in the gas phase after reaction completion, decreased on cooling.

H. K. Fauske, J. C. Leung et al. (1995) showed that a 40% by weight di-cumyl peroxide in ethyl benzene solution was a gassy un-tempered system under atmospheric pressure [7]. H. K. Fauske [8] showed that 100% di-cumyl peroxide was an un-tempered gassy system and that under 1°C/min imposed heating rate all gas venting was observed in the RSST and in 550 gallon IBC vessel up to a A/V ratio of $0.5 \cdot 10^{-3} \text{ m}^{-1}$.

The decomposition of di-cumyl peroxide 40% w/w and 75% w/w solutions in ethyl benzene as well as the decomposition of neat di-cumyl peroxide were proposed in a round robin exercise by the US DIERS User's Group. The results obtained were presented in reference [9]. It was observed that the decomposition of di-cumyl peroxide followed a first order kinetic until 250°C. Di-cumyl peroxide venting tests were carried out on 75% di-cumyl peroxide in ethyl benzene and 98% di-cumyl peroxide in usual VSP test cells. The vent had an inner diameter of 5.3 mm and 100 mm length. The best estimate effective vent area was $A = 182 \text{ mm}^2$ for a 90 g charge. The results presented focus on the venting peak pressure, 100 to 145 psig for 75% wt di-cumyl peroxide and on the final mass left behind 2.1 to 2.9 g, but not on the release type, two-phase or gas only release.

Venting tests for the decomposition of neat di-cumyl peroxide were reported by the HSE in the UMIST Hazard XVI conference (2001). [10]. Some tests with low external heating rates (0.8°C/min to 2°C/min) and large vessels seemed to fit the DIERS gas-only vent sizing and UN methods. If a gas only release is assumed, then it is important to know the gas release molecular weight. If a two-phase flow occurs, it is necessary to specify the actual density and the mass flux of the vented mixture. For the decomposition of di-cumyl peroxide, the production of methane is generally considered.

Venting tests and determinations of the release type were presented by W. S. Minko (2008) in his thesis dissertation [11]. The open test release was found to be all-gas, also in the case of an initial rate of temperature scan of 0.5°C/min. In addition, a significant vent oversize was

obtained if the homogeneous hypothesis and gas + liquid homogeneous two phase release were assumed.

Choice of the in-vessel dynamics

This section aims at determining if the vessel release in case of venting for the specified fire case is a gaseous only release or if liquid carry-over must be considered. In this vent sizing design exercise, the solvent atmospheric boiling point i.e. 280°C is likely to be reached as shown by the decomposition reaction adiabatic final temperature estimate. However, solvent boiling should not occur under the vent set pressure of 4.5 bar abs or under vessel maximum allowable pressure of 7 bar abs. As a matter of fact, all gas venting was reported [10, 11]. The decomposition gas produced by the decomposition of di-cumyl peroxide is methane and the experimental results obtained show that the reaction exotherm is that of the decomposition of di-cumyl peroxide only. No soluble volatile decomposition product should be obtained. This reaction system may be compared to the decomposition of 40% hydrogen peroxide where a gas only release, even in the case of atmospheric venting, was reported [12]. Based on the above considerations, a gas only release will be considered for vent sizing and the decomposition gas considered is methane, $M_w = 16$.

Vent sizing equation

The vent sizing equation applied is the Boyle equation

$$A_0 = \frac{\dot{Q}_{\text{Gas,Max}}}{G^* v_0}$$

In this equation A_0 is the ideal vent area (m^2), $\dot{Q}_{\text{Gas,Max}}$ is the maximum volumetric gas generation rate in the vessel ($\text{m}^3 \cdot \text{s}^{-1}$), G is the vent mass flux ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), v_0 is the vented fluid specific volume under the stagnation conditions ($\text{m}^3 \cdot \text{kg}^{-1}$) $\cdot v_0 = \frac{1}{\rho_0}$. Where ρ_0 is the vented fluid density ($\text{kg} \cdot \text{m}^{-3}$). In the case of all gas venting, i.e. a gas only release, v_0 is the volume of 1 kg methane under the vessel stagnation conditions. In the Boyle equation $\dot{Q}_{\text{Gas,Max}} = m_0 \cdot v_G \cdot \left(\frac{dm_G}{dt}\right)_{\text{MAX}}$ where m_0 is the vessel inventory (kg), v_G is the vented gas molar volume, under the vessel stagnation conditions ($\text{m}^3 \cdot \text{mol}^{-1}$), $\left(\frac{dm_G}{dt}\right)_{\text{MAX}}$ is the maximum rate of gas production per kg inventory ($\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$).

The stagnation conditions may be specified at the vessel maximum allowable pressure P_{MAP} and at the temperature where the maximum rate of gas production was obtained or at the temperature where the maximum rate of gas production would be obtained under adiabatic conditions. In this exercise, VSP test n°201009A is considered to provide the most representative conditions i.e. the fire case and the lowest filling ratio.

In this VSP experiment, the maximum rate of gas production was obtained at a temperature of $T = 221.88^\circ\text{C} = 495.03^\circ\text{K}$. The experimental maximum rate of gas production was (see Figure 2): $\left(\frac{dm_G}{dt}\right)_{\text{MAX}} = 5.5799 \text{ mol} \cdot \text{min}^{-1} \cdot \text{kg}^{-1}$

The corresponding adiabatic temperature was $T_{MAD} = 243.42^{\circ}\text{C} = 516.57^{\circ}\text{K}$.

The adiabatic maximum rate of gas production was $(\frac{dn_G}{dt})_{MAX, \varphi=1} = 27.8236 \text{ mol} \cdot \text{min}^{-1} \cdot \text{kg}^{-1} = 0.46373 \text{ mol} \cdot \text{s}^{-1} \cdot \text{kg}^{-1}$

Consequently the vessel stagnation conditions are defined as follows

$$P_0 = P_{MAP} = 7 \text{ bar abs} = 7.10^5 \text{ Pa}$$

$$T_0 = T_{MAD} = 243.42^{\circ}\text{C} = 516.57^{\circ}\text{K}$$

$$v_G = \frac{R * T_0}{P_0} = \frac{8.314 * 516.57}{7.10^5}$$

$$= 6.1354 * 10^{-3} \text{ m}^3 \cdot \text{mol}^{-1}$$

The vessel inventory was $m_0 = 207.06 \text{ kg}$. The maximum volumetric gas generation rate in the vessel was $\dot{Q}_{Gas, Max} = 207.06 * 6.1354 * 10^{-3} * 0.46373 = 0.5891 \text{ m}^3 \cdot \text{s}^{-1}$

The vented gas specific volume in the stagnation conditions was

$$v_0 = \frac{1}{Mw} * v_G = \frac{1}{Mw} * \frac{R * T_0}{P_0} v_0 = \frac{1}{16 * 10^{-3}} * 6.1354 * 10^{-3}$$

$$= 0.38346 \text{ m}^3 \cdot \text{kg}^{-1}$$

$$\rho_0 = \frac{1}{v_0} = 2.6078 \text{ kg} \cdot \text{m}^{-3}$$

The release mass flux for a gas only release is in the present case the critical mass flux for the release of gaseous methane. At 500°K for methane under 7 bar abs $\gamma = \frac{C_p}{C_v} = 1.222$. The non-dimensional critical mass flux for a gas only release with $\gamma = 1.222$ was $G_C^* = \frac{G_C}{\sqrt{P_0 * \rho_0}} = 0.641$.

The dimensional critical mass flux for a gas only release was

$$G_C = 0.641 * \sqrt{P_0 * \rho_0} \quad G_C = 0.641 * \sqrt{7.10^5 * 2.6078}$$

$$= 866.05 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$$

The ideal vent area was

$$A_0 = \frac{\dot{Q}_{Gas, Max}}{G_C * v_0} = \frac{0.5891}{866.05 * 0.38346} = 1.77395 * 10^{-3} \text{ m}^2$$

The ideal vent diameter was $D_0 = \sqrt{\frac{4A_0}{\pi}} = 0.04754 \text{ m}$

A discharge coefficient was suggested for the vent line inlet: $CD = 0.816$.

The final vent area taking into account this discharge coefficient was $A_0 = A^* C_D$

$$A = \frac{A_0}{C_D} = \frac{1.77395 * 10^{-3}}{0.816} = 2.17396 * 10^{-3} \text{ m}^2$$

The requested vent diameter, taking into account the vent inlet coefficient was:

$$D = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4 * 2.17169 * 10^{-3}}{3.14}} = 0.05262 \text{ m}$$

Maximum vessel temperature

Assuming an adiabatic behaviour for the reactor, the adiabatic final temperature of the reaction should be a good estimate of the reactor final temperature.

Considering the VSP test n° 201009A representing the so called fire case, the experimental final temperature was 251.20°C .

The adiabatic final temperature would be $T_{FAD} = T_{0AD} + \varphi * (T_F - T_0)$.

$$T_{FAD} = 401.52 + 1.26146 * 120.52 = 553.55^{\circ}\text{K}$$

$$= 280.40^{\circ}\text{C}$$

The adiabatic final temperature may reach the solvent atmospheric boiling point.

Maximum release flow rate

According to our conclusion based on a literature review and on the experimental results presented, the vent release should be a gas only release. The release maximum mass flow rate would be $W = A_0 * G_C = 1.5363 \text{ kg} \cdot \text{s}^{-1}$. The gas released was assumed to be methane, on the basis of the literature review.

Reactor inventory when the second pressure surge appears

The reactor pressure may increase first due to the pressure build-up caused by accumulation of the decomposition gases in the reactor gas phase. When the rupture disc burst pressure is reached ($P_s = 4.5 \text{ bar abs}$), no liquid release of the reactor inventory is expected. So the reactor inventory when the second pressure surge occurs is the same as the initial vessel inventory.

Influence of an open process vent of 5.8 mm diameter and $C_d = 0.61$ on the reactor gas phase

In the case of an emergency relief vent sized for a pure gassy reaction as above, the vent size is determined on the basis of the maximum rate of gas production obtained under adiabatic conditions. Therefore the presence of a permanent process vent line does not modify the reactor venting requirement i. e. the required ideal vent area.

$$A_0 = \frac{\dot{Q}_{Gas, Max}}{G_C * v_0} = 1.77395 * 10^{-3} \text{ m}^2$$

In most instances, the existing process vent lines are not taken into account in the vessel venting capacity, because they have limited and unreliable flow capacity. In the present example of an unhindered short vent line, the merit

of the small process vent line could be taken into account in the vessel venting capacity. This may be done as follows:

$$A_0 = A * C_D + A_{PV} * C_{DPV}$$

Where A_{PV} and C_{DPV} are the area and discharge coefficient of small vent line. Consequently, the new emergency vent requirement would be reduced to:

$$A = \frac{A_0 - A_{PV} * C_{DPV}}{C_D}$$

However, the status of this small process vent line is not clear for us. We don't understand if the diameter of 5.8 mm corresponds to an ideal vent area or if a discharge coefficient ($C_d = 0.61$) must be applied to this vent area.

4. CONCLUSION

This round robin exercise was a blind exercise. The results presented by the different participants were analysed and compared in the paper presented by the round robin organizers and referees to the I. Chem. E. Hazards XXII conference held on April 11–14, 2011 in Liverpool U.K. [13]. The vent area estimates of the participants were also compared to the results of the UN 10 litre vessel tests carried out by INERIS (France) after the round robin exercise was completed. The comparison was based on vent area to vessel volume A/V ratio, for the same fill ratio observed in the round robin exercise and in the UN 10 litre vessel tests. The conclusion was that the suitable A/V ratio for $P_{MAP} = 7$ bar abs would be approximately $A/V = 0.006 \text{ m}^{-1}$. In our contribution to the round robin exercise, the A/V ratio obtained was $A/V = 0.00639 \text{ m}^{-1}$. In this paper, we share the details of the approach followed in this round robin exercise. We are looking forward to reading of the tests to be carried out in the HSL Buxton facility to allow a further validation of the vent sizing calculations. So far, the DIERS methodology applied here did not lead to oversize the emergency relief vent compared to the UN 10 litre test since the same A/V ratio was obtained using both approaches.

We understand that the other participants, who assumed a two phase release in case of the emergency vent actuation, obtained a much more conservative vent size. The participants who preferred open cell tests may have obtained a different estimate of the gas production. The choice of closed cell tests carried out in the VSP led to make the decision to correct the rate of gas production to adiabatic conditions. This method of calculation allowed us to determine the good vent area estimate so far.

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