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Simulation of vented pressure vessel tests for organic peroxides

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Abstract

It is current practice to classify the transportation hazards category of organic peroxides using a variety of test methods including a vented pressure vessel test (PVT). This test procedure can be simulated analytically provided certain thermal calorimetry data are available for the peroxide of interest. It is the purpose of this paper to illustrate important insights into the pressure vessel test procedure which can be gained through simulation. Through simulation of the test procedure one finds sensitivities to sample size and concentration which are not readily apparent from many typical pressure vessel test results.

Keywords: Organic peroxides; Hazards classification; Calorimetry; Safety tests; Simulation

1. Introduction

Organic peroxides are an important class of reagents widely used in the manufacture of polymer products. The concern for safe handling of these materials arises from their inherent self-reactive thermal instability.

It is current practice to classify the transportation hazards category of organic peroxides using a variety of test methods, including a vented pressure vessel test [1]. In most versions of the test procedure, a 5 g sample of peroxide and diluent (if any) is placed in a 233×10^{-6} m³ pressure vessel which is heated on a standard 700 W laboratory hot plate until a decomposition reaction occurs. The sample heat up rate is approximately 25 °C/min. The pressure vessel has a frangible disk set to burst in the range of pressure 720 kPa (absolute) to 860 kPa (absolute), (90–110 psig), but is otherwise vented by an orifice whose diameter may be varied in increments between 1 mm and 24 mm. The classification number is the smallest orifice diameter (in

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millimeters) which does not lead to failure of the frangible disk at 720 kPa (absolute), (90 psig). Several repetitions are required by the procedure for confirmation. Some specifics of the above procedure are varied in different countries and it is also the case that certain modifications to the pressure vessel test procedure are under consideration with a view to minimizing country specific variations. These modifications, if adopted, may affect sample size, heating rate, and the number of distinct orifice sizes, but the general characteristics of the test protocol discussed in this paper remain valid.

The above described test procedure can be simulated analytically, provided certain thermal calorimetry data are available for the peroxide of interest. Use of bench scale calorimetry data is becoming prevalent in safety evaluations of emergency pressure relief vent requirements for run away reactions using the DIERS¹ methodology [2], or for SADT² determinations [3, 4]. In the latter case, the use of calorimetry data provides greater insight into the reaction kinetics than obtained with traditional 'prototypical' tests and often at reduced cost. In much the same spirit, it is the purpose of this paper to illustrate how calorimetry data can be used in analysis which simulates the pressure vessel classification procedure. The insights obtained from this initial attempt provide some important conclusions about the significance of many standard pressure vessel classification test results which would not otherwise be apparent.

The use of analytical methods based on calorimetry data, as will be illustrated, may in certain instances offer significant advantages when used in conjunction with standard PVT procedures. These might include the following: (a) prescreening, (b) independent estimate of PVT classification results, (c) elimination or reduction in numbers of tests, (d) provide more generally applicable information and (e) offer alternative classification means when empirical test facilities are not readily available.

It is to be emphasized, that the material presented in this paper is preliminary and conceptual. Approximations and assumptions will be clearly noted. Nonetheless, certain general characteristics emerge which should be useful to any technical evaluation and deeper understanding of peroxide classification methods.

2. Thermal calorimetry data and peroxide decomposition reactions

Organic peroxide decomposition reactions are usually first order reactions which can be characterized by an Arrhenius rate constant expression of the form

(1)

$$k = A \exp\left(-\frac{E_{\rm a}}{RT}\right),$$

where E_a is the activation energy, A is the preexponential or frequency factor, R is the gas constant and T is the absolute temperature. The activation energy and frequency

¹ DIERS is an acronym for Design Institute for Emergency Relief Systems.

²SADT is an acronym for Self Accelerating Decomposition Temperature.

factor can be readily obtained from the tabulations of half-life temperatures which are widely available in supplier's product literature. In the absence of such tabulations, many bench scale calorimeters in current use by industry such as the Accelerating Rate Calorimeter [5], Vent Sizing Package [6], Reactive System Screening Tool [7] as well as others [8] are capable of yielding this information. Further, since the reaction rate is an exponential function of temperature, the heat release on decomposition leads to a rapidly accelerating rate.

The heat of reaction for the decomposition of organic peroxides is less frequently tabulated than half-life data. Since the decomposition of organic peroxides typically yields non-condensable gaseous products, an important, but not widely recognized and/or tabulated index of the hazards potential is the moles of non-condensable gas produced per mole of peroxide. Both heat of reaction and decomposition gas yields can be obtained from calorimetry data once the significance of this information is recognized.

It is not the purpose of this paper to discuss the various calorimetry test techniques, but it is sufficient to note that, the following peroxide characteristics can be obtained: E_a : activation energy, A: frequency factor, ΔH_{rx} : heat of decomposition, N_{neg} : moles non-condensable gas/mole peroxide.

It is the purpose of this paper to indicate the utility of this thermal calorimetry data in simulation and interpretation of PVT classification results.

In addition to the above cited primary data, it is important at the outset to indicate the sensitivity of decomposition reaction rates to peroxide concentration. Fig. 1 shows a calculation of the rate of temperature rise in a simulated adiabatic run-away reaction of 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane (2,5-DMTBPH). Parameters for this case will be discussed later. The reaction starting temperature is taken as the 10 h half-life temperature of 120 °C. One can see from Fig. 1 that as the 2,5-DMTBPH concentration is varied from 20 wt% to 100 wt% the magnitude of the peak reaction rate as indicated by the adiabatic self heat rate, (dT/dt) increases over eight orders of magnitude. Peak reaction rates for a given concentration can be further increased by external heating.

It would normally be expected that a given vent orifice in the standard pressure vessel test would pass or fail depending on the capacity for venting the decomposition gas products at the maximum reaction rate, at a pressure less than or equal to the frangible burst pressure. With this assumption, it would also be expected that the peak reaction rate sensitivity to peroxide concentration would also be seen in tabulations of US PVT results. Surprisingly, this does not seem to be the case. Some known PVT results for 2,5-DMTBPH [13] are indicated in Table 1.

The indicated orifice diameters in Table 1 vented the decomposition gaseous products without bursting the PVT rupture disk. These are small diameters indicating a benign result (1 mm diameter is the smallest standard size). The difference between 45 wt% concentration and technically pure (tp), 95 wt% concentration does not correspond to the difference in maximum reaction rates suggested by Fig. 1. These results are not untypical for many highly concentrated peroxides tested in the PVT apparatus. The following sections attempt to shed some light on these observations.



Fig. 1. Adiabatic runaway decomposition simulation for various initial concentrations of 2,5-DMTBPH.

Table 1 PVT Results for 2,5-DMTBPH			
2,5-DMTBPH Concentration (wt%) (5 gm test sample)	PVT Orifice diameter (mm)		
45	1		
77	1		
90	2.5		
95 wt% (tp)	2.5		

3. Simulation of PVT results

The essential characteristics of the PVT test and peroxide decomposition can be simulated in a quite straightforward manner. The following set of equations will be sufficient in most instances. Let X represent the peroxide weight concentration in the test sample. The rate of peroxide consumption is assumed to be first order in

concentration and represented by

$$X^{*} = Xk, \tag{2}$$

where k is given by Eq. (1). The rate of sample temperature increase is given by

$$T^{\,\prime} = -\frac{\Delta H_{\rm rx}}{C\phi} X^{\,\prime} + T^{\,\prime}_{\rm ext}.$$
(3)

The rate of non-condensable gas production is given by (molar basis)

$$n_{\rm ncg}^{\cdot} = -\frac{n_{\rm ncgt}}{X_0} X^{\cdot} \tag{4}$$

and the molar gas vent rate is given by

$$n_{\rm v}^* = C_{\rm d} A_{\rm v} G/M w_{\rm g}. \tag{5}$$

The PVT transient pressure is given by

$$P^{\star} = \frac{RT}{V} (n_{\text{neg}} - n_{\text{v}}) + \frac{P}{T} T^{\star}.$$
(6)

The terms in Eqs. (2)–(6) not previously defined are: C the sample heat capacity; ϕ the vessel thermal inertia factor, T_{ext}^{*} the external heating rate, n_{negt} the total number of moles of non-condensable gas contained in the peroxide sample, X_0 the initial peroxide concentration, C_d the PVT orifice discharge coefficient assumed to be 0.62, A_v the PVT orifice vent area, V the PVT volume, G the orifice vent mass flux assumed to be all vapor, sonic flow defined by the conventional relation (See [1 or 9], for example) and Mw_g is the molecular weight of decomposition gases. The superscript dot indicates a time derivative, i.e. X^{*} means time derivative of X and so on.

The total moles of non-condensable gas contained in the peroxide sample is related to the sample size m_0 , the initial peroxide concentration X_0 , the molecular weight of the peroxide Mw_p , and the gas production index N_{neg} :

$$n_{\rm ncgt} = N_{\rm ncg} X_0 m_0 / M w_{\rm p}. \tag{7}$$

The above set of Eqs. (1)-(6) can be integrated numerically to simulate a vented pressure vessel test. It should be pointed out that the equation set treats only non-condensable gas generation and does not include diluent volatility effects which may be significant in specific cases. Examples will be shown in the next section for 2,5-DMTBPH and di-cumyl peroxide, both of which are available at high concentrations and are often diluted with high boiling point organic solvents. For these illustrations, latent heat effects are of minimal significance.

In addition one must make assumptions regarding the sample heat capacity (here assumed to be known and temperature independent), the vessel thermal inertia effects and the molecular weight of the decomposition gases. In the PVT, the thermal mass of the apparatus is quite large relative to the sample. However, under high external heating and subsequent rapid reaction rates it can be argued that the effective role of the vessel thermal inertia is minimal, and hence a value of $\phi = 1.1$ will be used.

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Typical gaseous decomposition products of organic peroxides are methane, ethane, acetone and carbon dioxide having a molecular weight in the range of 20-50. An approximation of $Mw_g = 40 \text{ kg/kgmole}$ is sufficient since this parameter appears only in a term of $\frac{1}{4}$ power dependency.

The following parametric evaluations will illustrate that in addition to the fundamental calorimetry data, E_a , A, ΔH_{rx} and N_{ncg} , the most important additional factors affecting the outcome of analytic PVT simulations are the sample size and peroxide concentrations.

4. Example illustration: 2,5-DMTBPH

Calorimetry data have been obtained for 2,5-DMTBPH which yield the necessary parameters. Table 2 summarizes a 2,5-DMTBPH parameter set sufficient for a numerical simulation. Fig. 2 illustrates a simulated pressure time trace for a 5 gm 2,5-DMTBPH sample at 50 wt% concentration with a 1 mm PVT orifice diameter. The indicated peak transient pressure is only 29 psig (200 kPa, g), which is insufficient to burst the 90 psig (620 kPa, g) rupture disk. This result is consistent with PVT test observations. Fig. 3 shows the same 5 gm sample simulated at 95 wt% concentration with a 2 mm vent orifice and a 4 mm vent orifice. Again these results are consistent with actual PVT test observations.

Table 3 summarizes results with comparable test results.

In addition to the relatively good agreement with actual test results suggested by Table 3, the significant observation is the calculation of the maximum corresponding closed vessel pressure. This value is estimated from the relation,

$$P_{\max, \text{ closed vessel}} = P_0 \frac{T_{\max}}{T_0} + n_{\text{ncgt}} \frac{RT_{\max}}{V}.$$
(8)

The maximum temperature T_{max} is based on the heat of decomposition and the external heating effect and can be evaluated by detailed integration of Eqs. (1)-(6) or by approximate methods discussed in [9, 10]. In Eq. (8), sample size, concentration and the gas production index N_{neg} which define the parameter n_{negt} , are the significant terms.

Table 2 2,5-DMTBPH Parameter values for PVT simulation

Peroxide	2,5-DMTBPH
Peroxide molecular weight	290.4 kg/kgmole
Activation energy	39.6 kcal/gmole
Frequency factor	$1.0 \times 10^{19} \text{ min}^{-1}$
Heat of decomposition	77 kcal/gmole
Moles of non-condensable gas/mole peroxide	1.2 mole/mole
Sample heat capacity	0.47 cal/(gm K)
PVT volume	$233 \times 10^{-6} \text{ m}^{3}$
PVT frangible disk burst pressure	722 kPa, abs (90 psig)
External heat up rate	25°C/min
Thermal inertia factor	1.1
Gaseous product molecular weight	40 kg/kgmole



Fig. 2. Pressure vs. time for PVT simulation with 2,5-DMTBPH at 50 wt% concentration.

It is therefore easy to explain lowest PVT test results (1 mm diameter) even for relatively high concentration peroxides if the combination of sample size, concentration and N_{neg} index cannot yield sufficient gas to exceed the PVT burst pressure with zero orifice diameter. This is frequently the case. Two significant conclusions follow. First, if the four key calorimetry data parameters are known in advance, and calculations indicate insufficient gas generation potential to burst the PVT diaphragm for n unvented 5 gm sample, one need hardly proceed with the test. Second, if one considers samples and concentrations whose gas generation potential exceeds the minimum closed vessel bursting requirements, one might expect drastically different results. Exploratory simulations, indeed show this to be the case.

5. Example illustration: Di-cumyl peroxide

Table 4 shows a parameter data set for di-cumyl peroxide. Fig. 4 shows a PVT test simulation pressure time history for a 5g sample at 40 and 94 wt% concentrations. Table 5 compares simulation results with PVT test data.



Fig. 3. PVT simulation with 95 wt% 2,5-DMTBPH (5 gm sample) for 2 and 4 mm orifice vent.

Table 3 Comparison of simulation results with comparable PVT test results for 2,5-DMTBPH

Concentration (wt%)	Maximum required PVT orifice diameter (mm)		Maximum closed vessel pressure (psig)	Peak transient pressure
	Simulation result	PVT test result	Eq. (8) Si	Simulation
50	1	1	68	29 psig
77	1	1	92	60 psig
95	3	2.5	107	2 mm/98 psig 4 mm/84 psig

In the case of di-cumyl peroxide all simulation results lead to the lowest standard orifice (1 mm) diameter since the maximum closed vessel pressure is always estimated to be less than the PVT diaphragm burst pressure.

Peroxide	Di-cumyl peroxide
Peroxide molecular weight	270.4 kg/kgmole
Activation energy	37.5 kcal/gmole
Frequency factor	$1.8 \times 10^{18} \text{ min}^{-1}$
Heat of decomposition	52.5 kcal/gmole
Moles of non-condensable gas/mole of peroxide	0.66

 Table 4

 Di-cumyl peroxide calorimetry data parameters for use in PVT simulation



Fig. 4. PVT simulation with di-cumyl peroxide (5 gm sample) at 94 and 40 wt% concentration.

The indicated test result at 99 wt% concentration could be the result of detonation-like characteristics (not included in this simulation) or could be due to uncertainty in the calorimeter based parameter N_{ncg} . Although one can find some independent confirmation of the value of N_{ncg} from [11] (reported value of $N_{ncg} \approx 0.53$ mole non-condensable gas/mole of peroxide), one should recognize that the limited data base demands allowance for different values to evolve as test

Concentration (wt%)	Maximum required orifice diameter (mr	PVT n)	Maximum closed vessel pressure (psig) — Eq. (8)
	Simulation result	PVT test result	
40	1	1	35
94	1	1	58
99 wt% (tp)	1	2	60

Table 5 Comparison of simulation results with comparable PVT test results for di-cumyl peroxide

techniques become better focused on this parameter index. Overall, the difference between 1 and 2 mm orifice diameter is trivial except for the indication that with the 2 mm orifice the gas generation potential may have been in excess of the closed vessel pressure limit.

Again as noted for 2,5-DMTBPH, one would expect different results as sample size is increased to allow for gas generation substantially in excess of that required to exceed the closed vessel pressure limits. While results of numerous simulation cases could be presented, it is more instructive to illustrate the underlying sensitivities by means of an approximate integral analysis.

6. Effects of peroxide concentration at large sample size

One of the observations thus far is to question the relevance of minimal PVT orifice diameter results if (particularly at high peroxide concentrations) there is insufficient gas generated to exceed the diaphragm burst pressure in a closed vessel. These results may only serve to mask the true energetic hazards of large quantities of the material. This point is especially valid in cases where direct pressure time simulation with larger samples leads to extremely rapid variation in the estimated critical orifice diameter with small changes in concentration.

The observed simulation results are best illustrated with the following criteria. Eq. (6) defines the rate of pressure change in a vented vessel with a decomposition reaction generating a gaseous source. If one sets dP/dt = 0 at conditions corresponding to maximum reaction rate one can find a relation for the minimum vent diameter, D, required not to exceed a given diaphragm burst pressure P. This relation is presented as

$$D = FT \left\{ \frac{3.36n_{g,mr}^{*} \sqrt{Mw_{g}RT_{mr}}}{P} \right\}^{1/2}.$$
 (9)

In Eq. (9), FT is a dimensionless factor having values between 1.0 and 2.0, and 3.36 is a dimensionless numerical factor made up of $4/\pi$, C_d and a function of the gas specific heat ratio. The subscript 'mr' refers to conditions at the temperature corresponding to the maximum rate, $T_{\rm mr}$. The maximum non-condensable gas generation



Fig. 5. Orifice diameter vs. concentration for hypothetical 50 gm sample 2,5-DMTBPH and di-cumyl peroxide (90 psig burst pressure).

rate is

$$n_{\rm g,\,mr} = N_{\rm ncgt} X_{\rm mr} k_{\rm mr}.\tag{10}$$

Expressions for evaluation of maximum rate parameters may be found in [9]. However $n_{g,mr}^*$ should show the concentration sensitivity presented graphically for the maximum temperature rate in Fig. 1. Eq. (9) applies to a vented vessel so long as the test sample can generate gas in excess of that required for exceeding the closed vessel burst pressure *P*. Exceeding this value by a factor of 2 will suffice for general validity. Fig. 5 shows the results of Eq. (9) applied to 2,5-DMTBPH and di-cumyl peroxide for a 50 gm sample in a standard PVT vessel ($V = 233 \times 10^{-6} \text{ m}^3$).

The difference between the two peroxides is related to the calorimetry parameter differences in fairly obvious ways. Fig. 5 graphically illustrates that at low concentrations and hence low reaction rates, small or negligible orifice openings (D) will suffice. However, because of the exponential increase in maximum reaction rate with increasing concentration, the required orifice diameter passes quickly through the range of

interest (1–24 mm) over a narrow range of concentration. This simulated behavior conforms more closely to results anticipated from the reaction characteristics underlying Fig. 1 for a peroxide decomposition reaction. The important point is that sample mass, peroxide concentration and test apparatus configuration interact in ways which must be well understood in order to give proper significance to any given PVT result.

Now it should also be pointed out that energetic decomposition reactions may not always be homogeneous over the entire concentration and extent of reaction range. A given instance could be more or less severe. It is well known that many peroxide decomposition reactions at high concentrations have the potential to change from homogeneous to propagating reactions and many are subject to detonating characteristics.

The clear danger to be avoided is to infer benign characteristics from low classification values (orifice diameter) obtained from the standard PVT test (5 gm sample) when the underlying contributing factor to the low numbers is insufficient gas generation potential constrained by a small sample size. This initial attempt at simulation of PVT results suggests that with a significant increase in sample size one might expect a substantial change in the order of ranking of organic peroxides from PVT test results and their interpretation.

A word of caution is in order. One should not consider 50 gm samples tests with highly concentrated peroxides, in a sample volume typical of the standard PVT without prior screening with much smaller samples. Using simulation techniques indicated here, vent size requirements can be so large that the standard PVT will appear as unvented and pressures exceeding 100 atm could be attained. Detonation potential may also be an added hazard. Further development of the use of calorimetry data and simulation of PVT can have obvious benefits in anticipation of such results.

7. Closed vessel tests

The concern for insufficient sample size in the PVT yielding too little gas and any substantial increase in sample size yielding too much gas for safe handling renews interest in the thermal explosion vessel (TEVT) test [12]. In this closed vessel test, a measure of decomposition severity can be given by the index S where

$$S = \Delta P_{\max} (dP/dt)_{\max}.$$
 (11)

In Eq. (11) ΔP_{max} is the measured maximum overpressure and $(dP/dt)_{\text{max}}$ is the observed maximum rate of pressure increase. Both empirical observations are amenable to simulation from standard calorimetry data as noted for the vented PVT. The severity index S should vary exponentially with concentration as reflected in the $(dP/dt)_{\text{max}}$ term while the ΔP_{max} term should be nearly linear dependent on sample size and concentration. This procedure is attractive because of the potential for confirmation of the non-condensable gas production index N_{neg} by measuring pre-and posttest pressures at constant temperature.

In fact, the attractiveness of the closed vessel test is enhanced because it is fundamentally comparable to a bench scale calorimetry test. This said, the same information can in fact be obtained from well conceived calorimetry tests, although it would be incorrect to give the impression that at present all bench scale adiabatic calorimeters are well suited or easily adapted to such service.

8. Concluding remarks

This paper has shown that in principle, the classification of organic peroxides in a standard vented pressure vessel test can be simulated analytically with thermal data which can be obtained from bench scale calorimetry tests.

This analysis suggests that some reported standard PVT results indicating benign results (low classification numbers) might well be questioned in terms of the adequacy of the sample size. One wishes to avoid underestimating the hazard potential of highly concentrated organic peroxides on such basis without confirmation from other types of tests or considerations of the possible significance of PVT results with larger samples.

The PVT procedure was undoubtedly configured to provide a simple figure of merit index for classification (ranking) of hazards potential. This attempt to analytically simulate the standard test procedure has, while achieving a certain degree of success, indicated an underlying strong sensitivity in the concept of the PVT to sample size and peroxide concentration. Owing to the present small (5 gm) sample size, many current test results may be of questionable value. If sample size is increased one can anticipate large sensitivities in observed results to peroxide concentration, heating rate and other control parameters including uncertainties associated with the test vessel thermal inertia. The closed vessel TEVT overcomes the most significant of the PVT concerns. However, when considering the TEVT, one should also consider the potential for even superior results using bench scale adiabatic calorimetry methods. In this way classification could easily be based on fundamental thermal calorimetry data.

There is reason to believe that much additional progress can be made using simulation methods and generic calorimetry data to classify and relate the relative hazards of various peroxides and diluents. Finally, when subjecting peroxides to thermal decomposition in bench scale calorimetry tests, it is hoped that more attention can be given to obtaining measures of the gas production potential once its significance is better appreciated.

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