

Assessment of the maximum gas generation rate of a gas generating system under runaway conditions

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Runaway reactions are characterized by the exponential increase of the temperature of an exothermic chemical reaction as well as the pressure of the reactor or storage vessel in which the runaway occurs. The consequences of a runaway reaction can be catastrophic as it can lead to the overpressurization of a vessel and its potential explosion. Emergency relief systems (ERS) can act as the last line of defense against vessel overpressure and prevent the vessel explosion, providing they are adequately sized. In the case of the runaway of gas producing chemical systems (gassy or hybrid reactive systems), the assessment of the maximum gas generation rate under runaway conditions is a critical parameter for sizing an ERS.

In the 1980's the Design Institute of Emergency Relief System (DIERS) developed experimental methods to assess the maximum for gas generation rate for runaway reaction based on adiabatic calorimetry data (mainly temperature and pressure measurement under adiabatic runaway conditions). There is still need to improve such methods in the particular case of gas generating systems. Indeed, there's currently no consensus in the industry as per the best configuration (close or open cell) of the adiabatic test for the study of gas generating systems nor the interpretation of the experimental data for the assessment of the maximum gas generation rate.

This paper performs a critical analysis of the current method to assess the maximum gas generation rate of a gas generating system under runaway condition. It presents the results of the modeling of the decomposition of a solution of 20% Di-tert-butyl Peroxide (DTBP) in Toluene in a closed vessel using a rigorous thermodynamic evaluation of component and mixtures properties coupled with the kinetic model of the decomposition reaction. The model is able to accurately evaluate the composition of the liquid and gas phases in the calorimetric cell at each time step of the runaway. The simulation results are used to evaluate the ability of the current method proposed by the DIERS (based on the evaluation of the gas generation from temperature and pressure data and the ideal gas law) to assess the actual maximum specific gas generation rate inside the calorimetric cell during the runaway. The simulation results highlighted that the general approach assuming that the sole use of the temperature and pressure readings of a calorimetric test cell to calculate the maximum gas generation rate is limited and needs significant improvements.

Keywords: Runaway reactions, Maximum gas generation rate, DIERS method, Rigorous thermodynamic model

Introduction

An exothermic chemical reaction over which control of the temperature has been lost is known as runaway reaction (Crowl & Louvar, 2001). A runaway reaction is characterized by an exponential increase of the temperature and pressure on the reactor vessel or storage tank in which the reaction takes place, which can lead to the explosion of the vessel. The consequences of a runaway reaction can therefore be very severe in terms of life, economic and environmental losses.

Emergency Relief Systems (ERS, e.g. bursting disc and relief valves) are the most commonly used risk reduction measures used to protect the reactor or vessel from the consequences of a runaway reaction. The main advantages associated with their applications are that they are independent of the main control system, and they may still provide adequate protection if all other systems fail (J Etchells, Wilday, & Britain, 1998). The proper sizing of the ERS to protect a vessel in the case of a runaway reaction requires the understanding of the reaction kinetics and thermodynamics, and fluid dynamics of the reactive system. Such phenomena are quite complex and yet to be fully understood.

In the 1980's the Design Institute for Emergency Relief Systems (DIERS) developed ERS sizing methodologies for runaway reaction cases based on adiabatic calorimetry techniques. While significant efforts were devoted to ERS sizing for vapor systems (for which the pressure increase in the vessel results from the vapor pressure of the vessel contents), very few research was done for non-condensable gas generating systems such as the decomposition of peroxide mixture. There is still very significant work to be done to improve the methods for the measurements of the maximum gas production rate corresponding to the decomposition of a gas generating system under runaway conditions to subsequently improve the design of ERS.

This paper first presents a review of the current methods used to estimate the maximum gas generation rate of a gas generating system under runaway conditions using small scale adiabatic calorimeter tests (in closed and open cell configuration). Such methods use the pressure and temperature data measured in the adiabatic calorimeter to calculate the maximum gas generation rate under runaway conditions using the ideal gas law. The limitations associated with these methods are summarized.

The paper then evaluates the ability of closed cell tests to evaluate the maximum gas generation rate using a model that simulates the adiabatic runaway of the decomposition of DTBP in toluene in a closed vessel. The model is able to accurately evaluate the composition of the liquid and gas phases as well as the temperature and pressure in the closed vessel at each time step of the runaway. The maximum gas generation rate from the simulated results are compared with the maximum gas generation rate calculated from the pressure and temperature data.

Current experimental methods for the evaluation of the maximum gas generation rate

In the 1980's, the DIERS made an outstanding effort to develop methods to design of ERS based on adiabatic calorimetry measurements to characterize the runaway reaction experimentally and two-phase flow models describing the hydrodynamics of the flow in the vessel.

According to DIERS classification, when the pressure generation in a chemical system by the runaway reaction is entirely due to the production of permanent gas (e.g. CO₂, CH₄, O₂), the system is classified as a gassy system. In this case, the pressure relief following the opening of the ERS does not control the temperature of the reactive mixture as shown in *Figure 1*. As a result, after the first pressure peak corresponding to the opening of the ERS at P_{set} , the reaction keeps running away until it reaches the maximum rate of gas production which can result in a second pressure peak ($dP/dt = 0$) at a given P_{max} . This P_{max} , or second pressure peak, is also referred to as the turnaround. The condition $dP/dt = 0$ at turnaround is achieved when the volumetric vented flow through the ERS equals the volumetric gas production rate in the vessel ($Q_{g\ max}$) (Janet Etchells & Wilday, 1998), (Leung & Fauske, 1987).

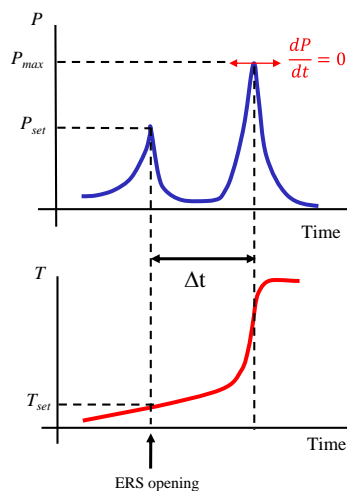


Figure 1: DIERS vent sizing criteria for gas generating systems

The relief vent area (A) necessary to protect the reactor of volume (V_R) is therefore given by:

$$A = \frac{1}{G} Q_{g\ max} \frac{m_R}{V_R} \quad (1)$$

Where G is the two-phase flux, m_R the reactant mass and $Q_{g\ max}$ the maximum volumetric gas generation rate in the vessel at the second pressure peak. $Q_{g\ max}$ in the vessel is proportional to the maximum specific gas generation rate (dn_g/dt) in moles/s that is evaluated experimentally by using adiabatic calorimetry.

Adiabatic calorimeters are laboratory bench scale equipment that allows the experimental investigations of runaway reactions in adiabatic conditions, i.e. approaching the adiabatic behavior of large scale vessels. In such calorimeters, adiabaticity (elimination of the heat losses) is achieved by placing a sample of the reactive mixture (usually 5 – 100 ml depending on the type of calorimeter used) into a test cell surrounded by electrical heater that follows the temperature of the sample during the runaway (see *Figure 2*). The temperature difference between the sample and the surrounding being close to zero, the heat losses to the surroundings are eliminated, and the test can be conducted under adiabatic conditions.

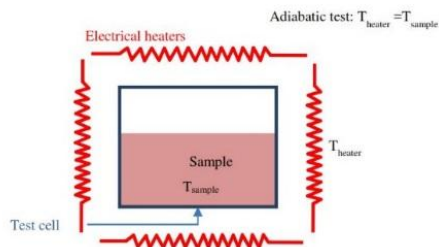


Figure 2: Schematic of an adiabatic calorimeter

Two test cell configurations can be used with adiabatic calorimeters for the characterization of runaway reactions (see *Figure 3*). The main difference lies in the assessment of the gas production through the measurement of the pressure and the temperature of the gas generated by the runaway.

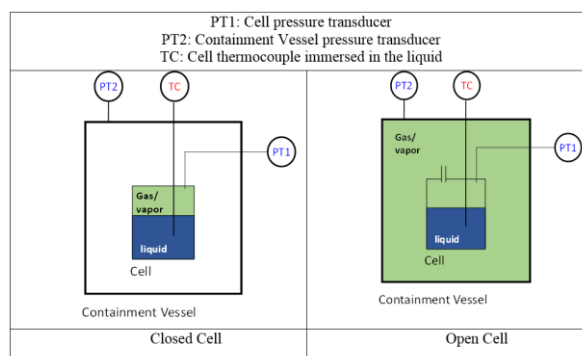


Figure 3: Schematic diagram of the closed cell and open cell configurations

Closed Cell Configuration: For the closed cell configuration (*Figure 3* - left), the gas produced by the runaway pressurizes the cell itself (J Etchells et al., 1998). In this configuration, the temperature of the liquid sample and the gas phase are well defined. The volume available for the gas in the cell depends on the test cell fill level and is relatively small.

Open Cell Configuration: In the open cell configuration (*Figure 3* - right), the test cell is opened to the containment vessel (e.g. with a hole in the upper side/lid of the test cell). The gas produced by the runaway reaction pressurizes the containment vessel which offers a much larger volume for the gas compared to the closed cell configuration.

Figure 4 shows typical runaway curves which are obtained from adiabatic calorimeters. The following characteristics of the runaway reactions can be extracted from that data:

- The onset temperature (T_{on}), i.e. the temperature at which self-heating is detected by the calorimeter in adiabatic conditions;
- The temperature and pressure evolution;
- The temperature and pressure rise rate and their maximum values, and;
- The time to reach a maximum rate of reaction.

The equation of maximum specific gas generation rate $(dn_g/dt)_{max}$ in the test cell can be derived from the temperature of the gas (T_g) and pressure (P) at the maximum pressure rise rate $(dP/dt)_{max}$ data and the ideal gas law as follows:

$$\left(\frac{dn_g}{dt}\right)_{max} = \frac{V_g}{m_{sam} RT_g @ \left(\frac{dP}{dt}\right)_{max}} \left[\left(\frac{dP}{dt}\right)_{max} - \left[\frac{P}{T_g} \left(\frac{dT_g}{dt}\right) \right] @ \left(\frac{dP}{dt}\right)_{max} \right] \quad (2)$$

Where V_g is the volume available for the gas in the cell and m_{sam} the sample mass.

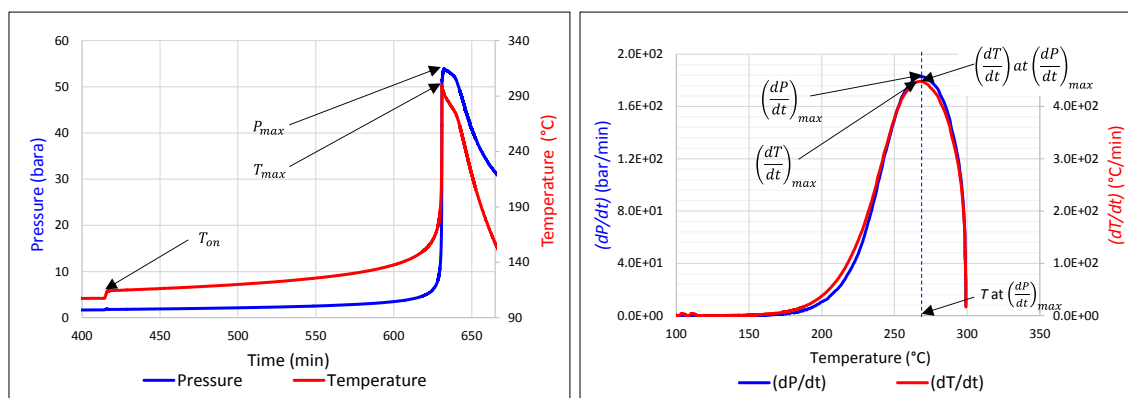


Figure 4: Temperature and pressure profiles (left), temperature and pressure rise rates (right)

This equation can be used for both closed and open cell experiment. For closed cell experiments, T_g is assumed to be equal to the liquid temperature. For open cell experiments, (dT_g/dt) is often neglected.

While this method to assess $(dn_g/dt)_{\max}$ is simple and practical, it still presents issues and limitations. Indeed differences in the test conditions and interpretation of the experimental data directly influence the value of the calculated maximum gas generation rate (Véchet, Kay, & Wilday, 2011). Moreover, there's no consensus in the industry as per the best choice of the experimental conditions to be used with the adiabatic calorimeter for the experimental determination of the gas production rate (closed and open cell).

When experiments are performed with the closed cell configuration, the temperature of the gas and the thermal inertia (ϕ factor) are pretty well defined which represents an advantage in the calculation of the gas production rate. On the other hand, closed cell tests are associated with potential issues of explosion of the test cells with low- ϕ calorimeters. The high pressure rise rate may lead to the explosion of the test cell during the exponential pressure increase of the runaway and the failure of the test. Besides, the high pressure of the cell encourages gas dissolution phenomena, which may lead to the underestimation of the gas specific production rate.

For open cell tests, lower pressures are reached as the gas is released in a much larger volume. This may reduce the gas dissolution effects and potential explosion of the test cell is much less likely. However, significant uncertainties remain associated with the temperature of the gas phase (when the gas temperature is not measured) to be used for the calculation of the gas production rate. In addition, during an experiment a significant amount of the reactant can be lost to the containment vessel. Indeed, it is only possible to measure the mass of the liquid sample at the beginning and the end of the experiment. It is not possible to the exact mass of reactant still in the test cell when the gas production rate is maximum. This adds a significant uncertainty on the calculated value of the maximum specific gas production rate.

Véchet, Kay, & Wilday, 2011 Vechot et al (2011) highlighted that the gas generation rate measured is very sensitive to the choice of cell configuration (open/closed).

The following focuses on the evaluation of the capability of closed cell tests to evaluate the maximum gas generation rate. The idea is to simulate the adiabatic runaway of the decomposition of a gas generating system in a closed vessel using a model that is able to accurately evaluate the composition of the liquid and gas phases as well as the temperature and pressure in the closed vessel at each time step of the runaway. The maximum gas generation rate from the simulated results will be compared with the maximum gas generation rate calculated from the pressure and temperature data.

Simulation of the adiabatic decomposition of DTBP in toluene in a closed vessel

Description of the model

A sophisticated model developed by Kanés et al (2016) using a rigorous thermodynamic evaluation of component and mixtures properties coupled with a reaction kinetic model is used to simulate the decomposition of a gas generating system under runaway conditions (Kanés, Basha, Véchet, & Castier, 2016). It rigorously calculates the change of liquid and gas phase composition at each time step of the runaway in a rigid vessel of known volume. The model is developed by using a set of differential and algebraic equations for the mass and energy balances, the cumulative amount of each component during the simulated time, and a trivial differential equation for time. Algebraic equations allow the calculation of fluid condition inside the vessel. The heat capacity of the vessel's construction material is neglected and the fluid in the vessel is assumed to be in phase equilibrium at all times. A detailed description of the model is available in the original reference (Kanés et al., 2016).

Description of the simulation

The chosen chemical system for the simulation is the decomposition of Di-tert-butyl Peroxide (DTBP) in Toluene that produces acetone and ethane (making it a gas generating system) gas according to the following equation:



The simulation is performed for a vertical cylinder closed vessel with height and diameter equal to 0.28320 m and 0.21204 m respectively. Fill level of the vessel is considered as 60% of the vessel. In this case, the thickness of the vessel's wall is considered as zero which correspond the thermal inertia, $\phi = 1$. At the beginning of the simulation, the vessel comprises 0.3245 mole of nitrogen, 6.42514 mole of DTBP, and 40.7878 mole of toluene. A very little amount (10^{-8} mole) of acetone and ethane is also considered at the beginning of the simulation to avoid the numerical problems in thermodynamic properties. The initial temperature and pressure is 388.3 K and 2.97 bara respectively.

Simulation results

The temperature and pressure profiles predicted by the simulation are shown in *Figure 5*. As mentioned above, the model is able to rigorously evaluate the composition of the liquid and gas phase at each time step of the runaway. *Figure 6* and *Figure 7* show the mass fraction of the liquid and gas phase respectively. The number of moles of all components in the liquid phase increase as the runaway proceeds except DTBP, which is consumed by the decomposition reaction to produce acetone and ethane. The

number of moles of acetone, ethane and toluene in the gas phase increase as the runaway occurs. However, at the maximum reaction rate (maximum of dT/dt and dP/dt), the moles number of acetone, ethane, and toluene in gas phase start to decrease. This is because at high pressure, toluene and acetone tend to condensate. At the same time, some amount of ethane dissolved into the liquid.

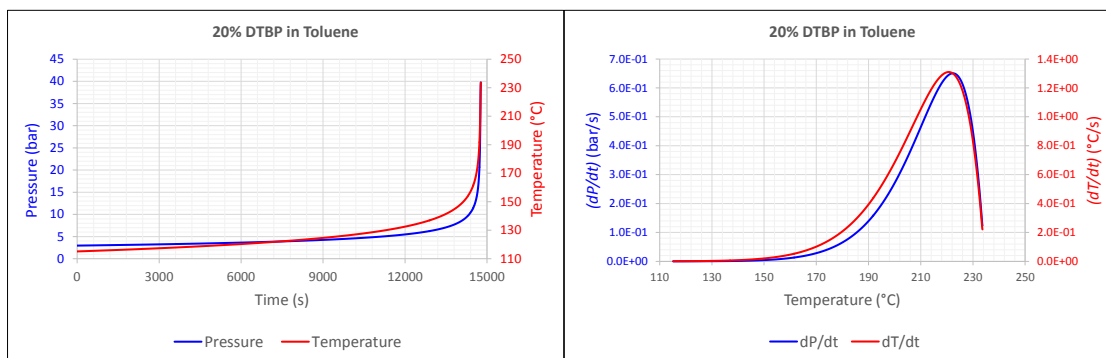


Figure 5: Simulation of the decomposition of DTBP in toluene; left: temperature and pressure profiles, right: temperature and pressure rise rates

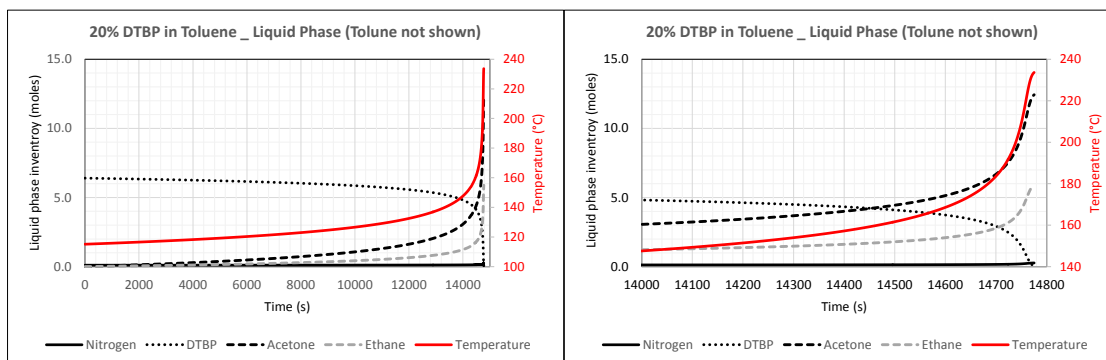


Figure 6: Simulation of the decomposition of DTBP in toluene; number of moles in liquid phase; left: overall profile; right: zoom around the maximum temperature rise rate

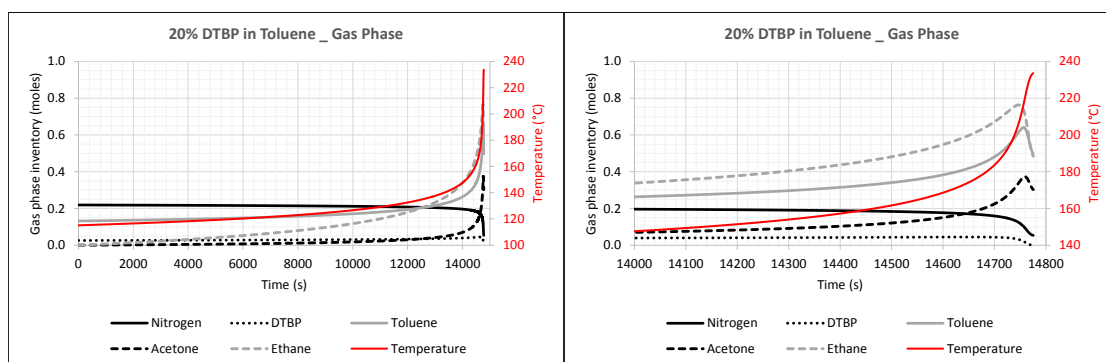


Figure 7: Simulation of the decomposition of DTBP in toluene; number of moles in gas phase left: overall profile; right: zoom around the maximum temperature rise rate

Assessment of the maximum gas generation rate

Figure 8 represents the simulated total gas generation rate in the gas phase (**TOTAL**). This total gas generation rate is the derivative of the total number of moles in the gas phase *as calculated rigorously by the model*. It can be seen that the specific gas generation rate in the closed vessel is *negative* when the temperature rise rate reaches its maximum value. This was an unexpected observation, as the general approach when analyzing calorimetric data assumes that the maximum gas generation rate occurs at the maximum temperature or pressure rise rate. This is in disagreement with the prediction of the rigorous model.

We used the simulated temperature and pressure data (*Figure 5*) as if they were experimental data to calculate the gas generation rate using the ideal gas law. This is using an approach identical to the way that DIERS proposed to calculate the gas generation rate as describes in Equation (2). The resulting maximum specific gas generation rate is referred to as TOTAL Calculated from P and T on *Figure 8*. It can be seen that the maximum gas generation rate calculated using this approach is 5.35×10^{-3} moles of gas/kg of liquid/s and it occurs at $t = 14757$ s. The simulated total gas generation rate (TOTAL) in the gas phase by the rigorous model shows that the maximum generation rate is 1.63×10^{-3} moles of gas/kg of liquid/s and it occurs earlier at $t = 14737$ s. Therefore, the simple use of the temperature and pressure data along with the ideal gas law to calculate the gas generation rate cannot reflect the actual gas generation rate in a closed vessel.

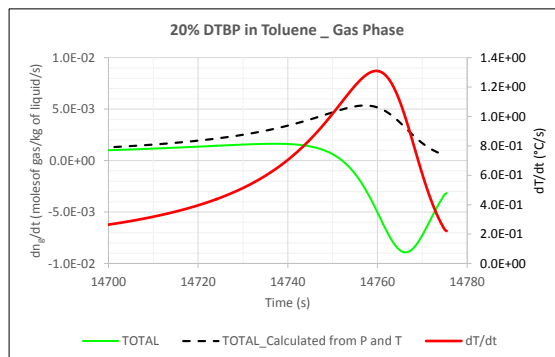


Figure 8: Simulated and calculated specific gas production rate

The general approach used for the interpretation of calorimetric data described by Equation (2) assumes that the pressure and the temperature of the gas in the closed test cell is a good indicator of the evolution of the number of moles of the gas phase. This may be a wrong assumption. The pressure reading is a consequence of different phenomenon that includes: gas dissolution, the amount of production of gas, the amount of production of vapor, condensation of vapor and expansion of gasses. However, none of the simple existing methods considered the above phenomenon to evaluate the maximum specific gas generation rate. Moreover, the simulation shows that the maximum gas generation rate may not occur when the runaway reaction reached its maximum temperature rate (maximum reaction rate).

Conclusion

This paper presented a review of the current experimental methods used to estimate the maximum gas generation rate of a gas generating system under runaway conditions using small scale adiabatic calorimeter tests. Such methods use the pressure and temperature data measured in the adiabatic calorimeter to calculate the maximum specific gas generation rate under runaway conditions using the ideal gas law. The pros and the cons of performing the tests in closed and open cell configurations were discussed.

The paper then evaluated the ability of closed cell tests to evaluate the maximum gas generation rate using a model that simulates the adiabatic runaway of the decomposition of a 20% solution of DTBP in toluene in a closed vessel. The model was able to accurately evaluate the composition of the liquid and gas phases as well as the temperature and pressure in the closed vessel at each time step of the runaway. The maximum specific gas generation rate *as calculated rigorously by the model* were compared to the calculated maximum specific gas generation rate calculated from the simulated pressure and temperature data and the ideal gas law. The analysis of the simulation results showed that the general approach that use the temperature and pressure reading of a closed cell test along with the ideal gas law to calculate the specific gas generation rate may not reflect the actual gas generation rate in the closed cell. Indeed, the pressure reading is a consequence of different phenomenon (including gas dissolution, the amount of production of gas, the amount of production of vapor, condensation of vapor and expansion of gasses) that are not taken into account by the current methods. This puts into question the current usage of closed cell calorimetric data and their interpretation for the estimation of the specific gas generation rate.

Major efforts are still needed to improve the gas generation rate calculation from adiabatic calorimetry data. Future work will look at the limitation of open cell tests for the evaluation of the specific gas generation rate and the methodology for the correction of the adiabatic data to take into account the thermal inertia (ϕ) for gas generating systems using the simulation tool presented in the paper.

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Nomenclature

A	ERS venting area	m^2
$(dn_g/dt)_{max}$	Maximum specific gas generation rate	moles of gas /kg of liquid/s
dP/dt	Pressure rise rate in the calorimeter	Pa/s
$(dP/dt)_{max}$	Maximum pressure rise rate in the calorimeter	Pa/s
dT/dt	Temperature rise rate in the calorimeter	K/s
dT_g/dt	Maximum Temperature rise rate of the gas in the calorimeter	K/s
G	Mass flux through the ERS	$kg/m^2/s$
m_R	Liquid mass in the reactor vessel	kg
m_{sam}	Mass of the sample in the test cell	kg
P	Pressure	Pa
P_{max}	Maximum pressure	Pa
R	Ideal gas constant	$kJ/mole.K$
T_g	Temperature of the gas in the calorimeter	
T_{on}	Reaction onset temperature	K
T_{max}	Maximum liquid temperature in the calorimeter	K
V	Volume	m^3
V_R	Volume of the reactor	m^3
$Q_{g max}$	Maximum volumetric gas production rate in the reactor vessel	m^3/s
n_g	Specific number of moles of gas	Moles of gas /kg of liquid
φ	Thermal inertia	-
<i>Subscript</i>		
max	Maximum	
on	Onset	