Journal of Innovative Technology, Vol. 1, No. 1, pp. 21-27, March 2019
http://doi.org/10.29424/JIT.201903_1(1).0003

VENT SIZING DESIGN FOR PERACETIC ACID USING VSP2 ADIABATIC CALORIMETRY AND THERMAL ANALYTIC METHODS

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ABSTRACT

Thermal analysis for the explosive potential of peracetic acid is evaluated using the calorimetric testing. The time-temperature-pressure and flow regime data of peracetic acid are measured under adiabatic conditions by a vent sizing package 2 calorimeter, which is capable of simulating real-time venting condition. The thermo-physical parameters of 40 wt% peracetic acid through calorimetric testing were calculated the reaction kinetics and evaluated by thermal analytical programming model for pressure relief consideration during a runaway scenario. The emergency relief system regarding to a gassy venting is calculated by simplified vent sizing equations in a peracetic acid reactor during overpressure. The adiabatic calorimetry methodology combining with fundamentals on homogenous flow model developed useful vent sizing criteria for proactive loss prevention of peracetic acid process.

Keywords: Peracetic acid, Calorimetric testing, Gassy venting, Vent sizing.

1. INTRODUCTION

In view of the industrial applications, organic peracid (OPA), which is one of the organic peroxides (OPs), is a reagent widely used in the oxidizing reactions that are commonly known as the crosslinking agents for the production of alkenes to epoxides and the ketones into esters (Wang *et al*. 2015). Furthermore, OPA has been used vastly as the promoters and catalysts because of their exceptional reactivity and oxidative capacity. However, OPs have caused some incidents due to theirs' reactivity and thermal instability in chemical process, including heat accumulation during the catalytic reaction, failure of temperature control, inadequate vent sizing relief system, contamination, etc., which might initiate the self-heating decomposition, thermal runaway, and possible fire or explosion incidents (Prana *et al*. 2014; Wang, 2018). It is evident that OPs are highly sensitive to induce the thermal decomposition or runaway reaction (Donald, 2000). OPAs contain the peroxy-carboxyl bond (R_1−C=O−O−O−R_2), which is an energetically functional group to provide free radicals to execute polymerization and also contain the weak peroxide bond (−O−O−) linkage which is readily broken to release heat at particular temperatures even at an ambient temperature. If the adequate safe prevention (such as temperature control and pressure relief system) is not performed during the runaway excursion of OPAs' processing, fire or explosion inevitably might be followed.

In essence, organic peracetic acid (PAA) is used as the catalyst or strong oxidant in bleaching, disinfection, and epoxidation (Zhao *et al*. 2007). The industrial application of PAA is widely used as an epoxidation agent in the olefins plants. The reaction is performed by use of PAA with the catalysts of strong acids or combining transition metal~~s~~ catalysts to enhance a rapid conversion. Lower concentration of PAA (16-20%) in the sanitation, pulp and paper industry worldwide is also applied because of its effective bleaching ability and chlorine-free property (Appels *et al*. 2011; Wood *et al*. 2013). It is also commonly used in wastewater treatment as a disinfection agent due to its excellent virucidal, sporicidal and fungicidal activities; PAA reagent is also used as a disinfectant—in medical fields, food-processing, and beverage industries. In addition, application of PAA in industry were effectively reduced the water pollution as a result of chlorine cleaners and shorten the residual PAA in the water body due to its short half-life (Kitis 2004; Milchert and Smagowicz 2009). There are two methods for the production of PAA, one reaction is mixing with the acetic acid (AA) (or acetic anhydride, AAh) and hydrogen peroxide (HP), which uses sulfuric acid as a catalyst (Zhao *et al*. 2007). During the AA-HP reaction, distillation is employed to remove H_2SO_4 to produce higher concentration of PAA solutions. The other method for producing PAA is via~~-~~the oxidation of acetaldehyde (Vineyard *et al*. 2006). However, AAh–HP reaction is difficult to master due to the possible formation of explosive diacetyl peroxide (Zhang *et al*. 2007).

The heat accumulation potential for OPAs during preparation, use, storage and transport have been concerned because of their considerable runaway potential that could be initiated in shipping or storing for extending the periods of time or in case of heat sources. Therefore, the thermal runaway behaviors should be identified by accurate calorimetry technique for recognizing these kinds of explosive chemicals. However, the past research was focused principally and mostly on the synthesis, hydrolysis, and applications of PAA in industry; fewer study has evaluated the exothermic reactions and safety suggestions for PAA regardless of their popular applications to commercial production (Kitis 2004; Milchert and Smagowicz 2009). The reactive properties of the concentrated PAA solutions are easy to corrosive, flammable, and explosive (Wang *et al*. 2015). Industrially, PAA is used mostly as an epoxidation agent, and general concentration is higher than 40 wt% according to UN Recommendations on the

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Manuscript received April 29, 2018; revised July 20, 2018; accepted September 14, 2018.

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Transport of Dangerous Goods and NFPA (National Fire Protection Association) 432 code for the storage of organic peroxide formulation (Wang 2018; Vineyard *et al.* 2006). Therefore, it is necessary to study the thermos-physical characteristics for PAA solutions. Consequently, a chemical process of PAA should be greatly crucial to pay attention to thermal runaway. In our previous study, the calorimetric instruments, including differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2), have been applied to test the thermal decomposition and runaway reactions for PAA and other OPs (Wang *et al.* 2015; Wang 2018; Wang and Shu 2010; Wang 2018). DSC is used to obtain the essential kinetics for thermal decomposition of PAA solutions, and the adiabatic calorimetry testing as well as thermo-physical data are determined by VSP2. This study is accessed the calorimetric data to evaluate the vent sizing calculation and mass flow rate from the thermal analytical approaches. To recognize the thermal runaway hazards of PAA solutions by calorimetry methods and to estimate the emergency relief system (ERS) of the reactors or tanks for vent sizing design were illustrated in this work. Through the fundamental equations, the vent sizing criteria could be applied as proactive loss prevention in PAA chemical processes.

2. EXPERIMENTAL

2.1 Samples

PAA solutions were prepared by a reaction of AA and HP which used H_2SO_4 as a catalyst (Eq. 1), and the distillation was used to remove H_2SO_4. In addition, H_2O was a thinner to obtain concentration of 40% PAA solution (Zhao *et al.* 2007; Zhao *et al.* 2008).

$$CH_3CO_2H + H_2O_2 \xleftrightarrow{H_2SO_4} CH_3CO_3H + H_2O \qquad (1)$$

The testing samples were prepared by a local chemical manufacturer and applied potassium iodine (KI) titration method to make sure of the concentration of PAA solutions. Furthermore, the calorimetric tests for all samples were measured in a short time to prevent the degradation of active PAA solutions.

2.2 VSP2 Adiabatic Calorimetry Testing

To meet with the vent sizing design for the pressure relief valves or rupture disks of a reaction vessel is applied to an emergency relief technique. Consequently, an adiabatic calorimetric instrument, VSP2, was used to evaluate thermal runaway reaction of PAA solution under an adiabatic condition that provide temperature–pressure–time (T–P–t) trajectories, such as the initially self-heating temperature (T_0), maximum temperature ($T_{\max}$), maximum pressure ($P_{\max}$), self-heating rate (dT/dt) and pressure elevation rate (dP/dt), and to thoroughly ascertain the exothermic characteristics. Therefore, the thermo-physical and kinetic parameters of a runaway reaction for an energetic substance are important for the safe design during the industrial operations. In addition, the emergency relief system applying adiabatic calorimetry data for PAA solutions could be designed precisely for a process reactor or a tank in case of the thermal runaway reaction or inadequate heat removing capability and to prevent the industrial accidents. It should be equipped the applicable control devices for the process vessels of PAA in the chemical plants to avoid the failure of operation (Wang 2018).

In the VSP2 experimental setup, the ranges of screening temperatures were from a room temperature to 300°C. Usually a series of several heat-wait-search cycles will need to be programmed, typically in intervals of 5°C. This function can trace onset of exotherm until designated the exothermic temperature under adiabatic circumstance. The high pressure custom-made test bomb was used to determine the runaway reaction of 40% PAA in VSP2 experiments. The T_0 is traced at a detectable sensitivity threshold of 0.15°C min^{-1}. The related thermos-physical parameters of thermal runaway reaction include SADT (Self-accelerating decomposition temperature) which is corrected at adiabatic condition; $T_{\max}$ and $P_{\max}$, dT/dt, and dP/dt are also determined for 40 wt% PAA solution by VSP2 calorimetry testing. In practice, the ϕ-values of a chemical reactor itself was approximate to 1.0 because of the considerable quantities of reactant mass with lower heat loss during the process reactions. For a vent sizing design, the ϕ-value is used for correction of the calorimetry measurement and should be modified to agree with the industrial chemical process. On account of the quantitative testing by VSP2, the runaway behaviors of PAA solutions were approached the pilot test to modify the chemical process reaction. Above data can particularly well be designed by the calculation of vent sizing with emergency relief methods.

3. RESULTS AND DISCUSSION

3.1 Adiabatic Calorimetry Test of PAA

From the VSP2 adiabatic experiments, the calorimetry data of 40 wt% PAA solutions were analyzed to evaluate the thermal runaway characteristics. Various concentration of PAA solutions were tested to determine T_0, $P_{\max}$, $(dT/dt)_{\max}$, and $(dP/dt)_{\max}$, which were shown in Figs. 1 and 2. It was obviously that the gases evolution of 40 wt% PAA solutions was exceedingly enormous by the VSP2 test, in which $P_{\max}$ and $(dP/dt)_{\max}$ are 126.0 bar and 83,598 bar/min, respectively. The result showed that the runaway reaction for higher concentration of PAA solutions have explosive potential. During the VSP2 experiments of 40% PAA solutions that each was fed 10.0 g sample into the test bomb because the test bomb could hold the sudden and violent gases evolution for 40 wt% PAA solutions to fit safer experimental operation. It can be recognized that the runaway level with greater than 40 wt% PAA solutions is exceedingly hazardous from calorimetry method, which could provide the relation of thermal runaway at various T–P–t profiles under an adiabatic circumstance and apply in response of the emergency relief or draw off at unusual operation case for PAA solutions.

In addition, PAA solutions may be consumed by the reversible hydrolysis reaction in Eq. (1); the thermal decomposition starts the O–O hemolysis to yield radicals according to Eqs. (2) and (3) (Wang 2018; Zhao *et al.* 2008).

$$\begin{aligned}&CH_3COOOH \xrightarrow{\Delta} CH_3COO\cdot + \cdot OH \longrightarrow \\ &\qquad CH_3\cdot + CO_2 + \cdot OH \xrightarrow{O_2} 2H_2CO + \frac{1}{2}O_2 \qquad (2)\end{aligned}$$

$$CH_3COOOH \longleftrightarrow CH_3COOH + \frac{1}{2}O_2 \qquad (3)$$

The thermal decomposition mechanisms of PAA solutions were complicated because of whose gases consist of PAA, AA, H_2O_2, CO_2 and O_2, which are consumed by the reaction with methyl radicals to yield formaldehyde (H_2CO). The gigantic gases evolution of the concentration greater than 40 mass% PAA solutions should enhance the safety concerns for process and storage in case of the self-heating reaction induced at elevated temperatures that may cause a thermal explosion. Whereas an explosion would undergo an increasing rate of pressure elevation and a P-t curve has steeply ascent after runaway beginning. If overpressure in the reactor or tank should not be successfully or adequately vent during the runaway reaction, the serious accident including explosion or fire would be occurred that would devastate the plants and surrounding areas. Therefore, the experimental T–P–t profiles and physical-chemical parameters are applied in the sizing relief devices and emergency relief system to avoid process runaway. Thermal runaway of PAA solutions is not on its own sufficient to make an exothermic hazard. It is necessary to evaluate the pressure elevation rate of PAA solutions that classified from equations (2) and (3) which the non-condensed gases (CO_2 and O_2) and steam (H_2O) were generated by thermal or metal-ion induced decompositions, and the final pressure did not return to atmospheric pressure at ambient temperatures after the runaway reaction by VSP2 adiabatic test.

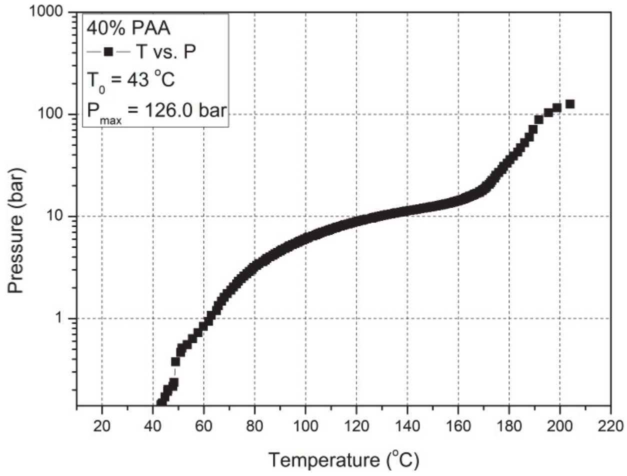

Fig. 1 Temperature versus pressure curves for 40 wt% PAA in VSP2 trials. In which the maximum pressure of 40 wt% PAA was reaching 126.0 bar.

3.2 Vent Sizing Design for PAA Solutions

A system of runaway behavior is characterized by the pressure generated from the substances including the reactants, intermediates, and products in case of the exothermic reaction of PAA solutions. Most of the non-condensable gases came from the decomposition of PAA contributed to the pressure built-up of a homogenous venting system. A large quantity of gases evolution which released during a self-heating reaction causes the potential danger associated with a thermal explosion in the container, such as the T-P curves of PAA solution. Figure 3 illustrated a nomograph approach of the self-heating rate and P-T data for 40 % PAA solution for vent sizing design. An exothermic runaway reaction as example of PAA solutions at higher concentration in which the temperature dependence of the gas evolution is much larger than the temperature dependence of vapor pressure, then the type of vapor-pressure cause the thermal explosion in case of an insufficient relief system.

By plotting the natural logarithm of the self-heating rate versus the inverse of temperature form the VSP2 experimental data, the activation energy (E_a) can be calculated from the slope, and the frequency factor (k_0) of the simplified Arrhenius equation is determined from the intercept of the fitted line. Figure 4 is a plot of ln (dT/dt) vs 1000 (1/T); the product ($k_0 \cdot \Delta T_{ad}$) is the intercept and E_a is calculated from the slope ($-E_a/R$). Therefore, the thermos-physical and kinetic parameters of a runaway reaction for an energetic substance are important for the safe design of industrial operations. Because of the runaway behaviours of PAA solutions, calorimetry testing through VSP2 is an alternative approach to the pilot test for optimizing the safety levels of chemical processes. In addition, an ERS established through adiabatic calorimetry data for PAA solutions could be designed precisely for the process reactor or tank in case of a thermal runaway

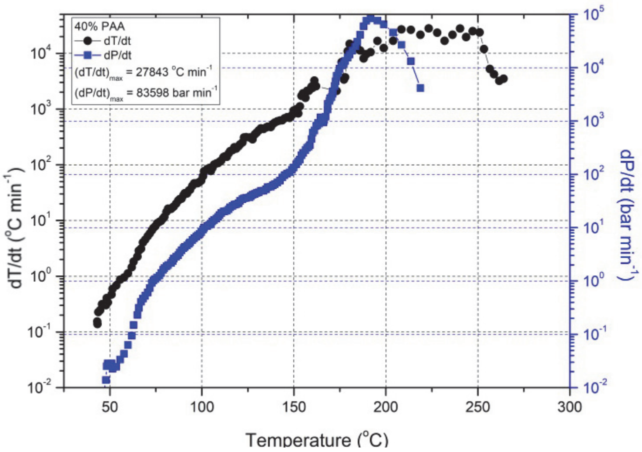

Fig. 2 Self-heating rate and pressure elevation rate for 40 wt% PAA in VSP2 trials

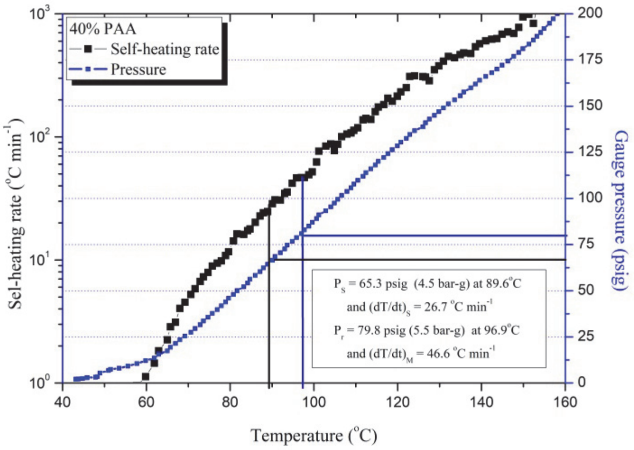

Fig. 3 Nomograph approach of the self-heating rate and P-T data for 40 % PAA solution for vent sizing design

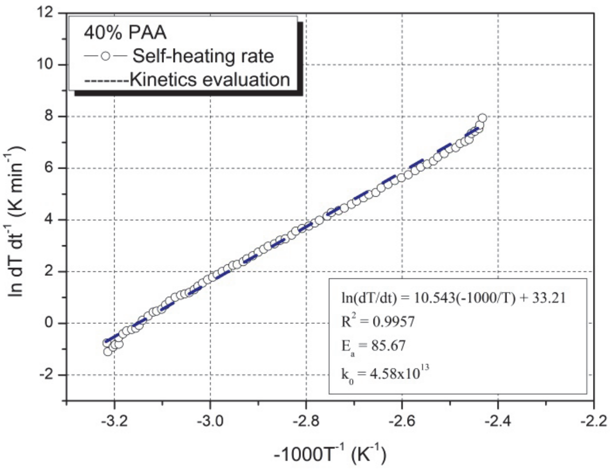

Fig. 4 Kinetic evaluation for 40 mass% PAA by linear fitting simulation

reaction initiating or inadequate heat removing capability. It should be equipped with applicable safety devices for the process vessels of PAA to avoid the failure of operations in chemical plants. Under an adiabatic condition, a runaway reaction leads to a temperature increase, which causes an exponential increase with the rate constant and therefore accelerates the reaction. Calorimetry tests must be performed to determine the thermos-physical parameters and modify the self-heating rate of PAA. To illustrate the thermal runaway effect, the reaction rate was calculated according to the Arrhenius equation for n-th order reactions. A more accurate simulation can be performed by fitting runaway trajectories and comparing the exothermic activity from VSP2 tests to calculate the related kinetic data. Relief systems are a protective measure for chemical reactors and tanks. Vent sizing can be calculated from the calorimetry data using thermal analytical equations and ERS methodology (Wang 2018; Hans and Fauske 2013; Wang *et al*. 2006).

In a closed reactor, the pressure generated by the gases evolution could destroy the vessel. The pressure elevation rate from the decomposition of a condensed PAA solution is larger by several orders of magnitude than the pressures generated by the ordinary vapor clouds and dust explosions. The relief systems are a protective measure of safety devices for the chemical reactors and tanks. Table 1 was listed runaway scheme of 40 wt% PAA in a normal pressure storage tank. Vent sizing can be calculated from the calorimetry data using the thermal analytical equations and DIERS methodology (Fauske 2006; Molkov 2001; Véchot *et al*. 2008).

The thermal kinetic data from the VSP2 calorimetry experiments could present an exothermic reaction trend. The self-heating rate dependence of high energy of exothermic reaction, and higher pressure elevation rate associated with the large gas evolution of the gasification or volatilization of the reactants is a critical loss for PAA runaway reaction. The self-heating rate of PAA could calculate the exothermic kinetics and modify the adiabatic self-heating rate for correction as follows (Wang *et al*. 2006).

$$\frac{dT}{dt} = \Delta T_{ad} \cdot k_0 \cdot \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

Table 1 Runaway scheme of 40 wt% PAA in a normal pressure storage tank

Conditions	40 mass% PAA
C_p	2.61 kJ kg^{-1} K^{-1}
A	4.25*10^{13} min^{-1}
ϕ^a	1.55
E_a	85.67 kJ mol^{-1}
V (storage tank)	20 m^3
m_0 (storage mass)	7000 kg
MAWP	5 bar
P_s (venting setup pressure)^b	4.5 bar
P_r (1.1 MAWP)	5.5 bar
T_s	89.6°C (362.6 K)
$(T_s)_c$	84.1°C (357.1 K)
$(dT/dt)_s$	26.7 K/min^b = 0.45 K s^{-1}
$(dT/dt)_{s'}$ (ϕ-value correction)	1.08 K s^{-1}
T_r	96.9°C (369.9 K)
$(T_r)_c$	91.1°C (364.1 K)
$(dT/dt)_r$	46.6 K/min^b = 0.78 K s^{-1}
$(dT/dt)_{r'}$ (ϕ-value correction)	1.88 K s^{-1}

$$\frac{1}{(T_s)_c} = \frac{1}{362.6} + \frac{1}{10250} \ln 1.55 \rightarrow (T_s)_c = 357.1\ \mathrm{K}$$

$$\frac{1}{(T_f)_c} = \frac{1}{369.9} + \frac{1}{10250} \ln 1.55 \rightarrow (T_f)_c = 364.1\ \mathrm{K}$$

$$\left(\frac{dT}{dt}\right)_{c'(\varphi=1)} = 1.55 \times \exp\left[10250\left(\frac{1}{357.1} - \frac{1}{362.6}\right)\right](0.45) = 1.08\ \mathrm{K\ s^{-1}}$$

$$\left(\frac{dT}{dt}\right)_{r'(\varphi=1)} = 1.55 \times \exp\left[10250\left(\frac{1}{364.1} - \frac{1}{369.9}\right)\right](0.78) = 1.08\ \mathrm{K\ s^{-1}}$$

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[a] The volume and mass of a test bomb are ca. 24.0 mL and 32.1 g, respectively. The ϕ-values were 1.55 for 10.0 g of PAA which were calculated as follow: $\phi = (M_a \cdot C_p + M_b \cdot C_{pb}) / (M_a \cdot C_p) = (10.0 \times 2.61 + 32.1 \times 0.45) / (10.0 \times 2.61) = 1.55$

[b] The values are obtained from Fig. 3.

$$\frac{1}{T_c} = \frac{1}{T_E} + \left(\frac{R}{E_a}\right) \cdot \ln \varphi \tag{5}$$

$$\left(\frac{dT}{dt}\right) c(\varphi = 1) = \varphi \cdot \exp\left[\frac{E_a}{R}\left(\frac{1}{T_E} - \frac{1}{T_c}\right)\right] \cdot \left(\frac{dT}{dt}\right) E(\varphi > 1) \tag{6}$$

Once the self-heating rate and kinetics are solved, these analytical equations render the evaluation of characteristics for PAA solutions. A vent sizing calculation performs the adequate safe design for the emergency relief system. Overpressure and venting behaviors during emergency relief of the flow regimes were discussed by DIERS. From these studies, the largest relief vent rate was generally the homogeneous-vessel venting that turnaround in T and P occurred at the same time during overpressure relief (Wang *et al*. 2006; Fauske 2006; Molkov 2001; Véchot 2008). Thermal decomposition of PAA accompanies considerable quantity of releasing of non-condensable gases. In addition, at the same overpressure situation the largest relief area needed due to the homogeneous venting flow. For a more conservative and straight-forward viewpoint for engineering purpose for PAA, the flow regime of homogeneous flow in a gassy system that pressure due to gas accumulation within reactor was proposed. For the gassy and non-tempered system, it is important to size the relief area and evaluate the mass flow rate. Based on the steady-state assumption, the design method is based on the volumetric rate balance. This simplified volumetric rate balance was assessed at the maximum allowable pressure, so that the evaluation is conservative one. Consequently, the calorimetry tests for the homogeneous venting system and various simplified sizing equations relating to ERS method are discussed in this study. Vent area of a homogeneous venting system is calculated by the following equations that we applied for PAA solutions. By making certain simplifications and assumptions, an analytical equations for the mass flow rate (*W*), mass flux (*G*), average self-heating rate ($\bar{q}$), and vent area (*A*) were therefore reached.

$$W = GA = \frac{\bar{q} m_0}{\left[\sqrt{C_P \Delta T_{ad}} + \sqrt{V h_{fg} / m_0 v_{fg}}\right]^2} \tag{7}$$

$$G = \frac{dP}{dt}\sqrt{\frac{T_s}{C_p}} = \frac{P_r - P_s}{T_r - T_s}\sqrt{\frac{T_s}{C_p}} \tag{8}$$

$$\bar{q} = \frac{1}{2} C_P \left[\left(\frac{dT}{dt}\right)s' + \left(\frac{dT}{dt}\right)r'\right] \tag{9}$$

$$D = \sqrt{\frac{4A}{\pi}} \tag{10}$$

The entropy of gasification at a temperature *T* is equal to h_{fg}/T; approximation h_{fg}/v_{fg} by Clapeyron equation for closed system data evaluation.

$$\frac{h_{fg}}{v_{fg}} = T\frac{dP}{dT} \tag{11}$$

UN recommendations on the transport of dangerous goods indicated that SADT of 41.5 mass% PAA in 20 m_3 insulated tank was 40°C by an adiabatic storage test, and the control temperature and emergency temperature should be limited at 30°C and 35°C, respectively (United Nations 2000). This study applied the UN's recommendable parameters in industrial process design to modify the vent sizing for PAA solutions. We selected 40 wt% PAA solutions as an example to evaluate the ERS under runaway conditions in Table 1. By making certain simplifications and assumptions, the analytical equations of $\bar{q}$, *G*, *W* and *A* were arrived.

$$\bar{q} = \frac{1}{2} C_P \left[\left(\frac{dT}{dt}\right)s' + \left(\frac{dT}{dT}\right)r'\right] = 0.5 \times 2.61 \times (1.08 + 1.88) = 3.86\ \mathrm{J\ kg^{-1}\ s^{-1}}$$

$$G = \left(\frac{dP}{dT}\right)_s \sqrt{\frac{(T_s)_c}{C_P}} = \frac{\Delta P}{\Delta T}\sqrt{\frac{(T_s)_c}{C_P}} = \frac{P_r - P_s}{T_r - T_s}\sqrt{\frac{(T_s)_c}{C_P}} = \frac{5.5 - 4.5\ \mathrm{bar}}{364.1 - 357.1\ \mathrm{K}} \times \sqrt{\frac{357.1\ \mathrm{K}}{2610\ \mathrm{J\ kg^{-1}\ s^{-1}}}}$$

$$= \frac{1 \times 10^5\ \mathrm{N\ m^{-2}}}{7.0\ \mathrm{K}} \times \sqrt{\frac{357.1\ \mathrm{K}}{2610\ \frac{\mathrm{kg\ m^2\ s^{-2}}}{\mathrm{kg\ K}}}} = 5284.2\ \mathrm{kg\ m^{-2}\ s^{-1}}$$

$$A = \frac{\bar{q} m_0}{G\,[\sqrt{\left(\frac{V}{m_0}(T_s)_c \frac{dP}{dT}\right)} + \sqrt{+(C_P \Delta T]}^2}$$

$$= \frac{7000\ \mathrm{kg} \times 3860\ \mathrm{J\ kg^{-1}\ s^{-1}}}{5284.2\ \mathrm{kg\ m^{-2}\ s^{-1}}\,[\sqrt{\left(\frac{20\ \mathrm{m^3}}{7000\ \mathrm{kg}} \times 357.1\ \mathrm{K} \times \frac{10^5}{7.0}\ \mathrm{N\ m^{-2}\ K^{-1}}\right)} + \sqrt{2610\ \mathrm{J\ kg^{-1}\ K^{-1}} \times 7.0\ \mathrm{K}]}^2} \cong 0.078\ \mathrm{m^2}$$

$$D = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4 \times 0.078}{\pi}} = 0.32\ \mathrm{m}$$

It is clearly to use calorimetry methodology reflected by the vent sizing equations is an effective calculation of vent area for PAA solutions. We could recognize that the diameter of relief valve is 0.32 m (ca. 12 in) in a 20 m^3 insulated tank to reduce the consequences of PAA runaway reaction. However, this case was taking account of approximate 1:3 sample volume ratio in a container, the relief valve size will increase with lager sampling volume ratio.

4. CONCLUSIONS

The consequence of thermal runaway for 40 wt% PAA solution is the generation of a large quantity of gases producing by the reactants at accessible temperatures and an ERS design should be prudently designed on the plant safety. Thermal hazard characteristics of PAA solutions at various concentration were determined by VSP2 calorimetry testing. From this study, PAA solutions decomposed at near-ambient temperature (ca. 43°C) should take the temperature control in process industries. The self-heating rate increased exponentially to reach 27,843°C min^{-1} and the gas evolution of the 40 mass% PAA solution was extremely large and P_{max} and $(dP/dt)_{max}$ were 126.0 barg and 83,590 bar min^{-1}, respectively. The exothermic hazards should be gingerly concerned in the manufacturing process, storage, and transportation. In addition, the adiabatic calorimetry method and vent sizing calculation for PAA solutions were effective to design the ERS in a chemical plant. To take into account the PAA solutions in a 20 m^3 tank/reactor that sample volumes ratio in a container was only 1/3, it is conducted that an applicable pressure relieve valve sizing is 0.32 m (12 inch) diameter should to equip with the emergency relief devices and the size of a relief valve will increase with larger volumes of sample in the reactor. To emphasize that an essential in vent sizing is laboratory thermal runaway testing, the reaction rate dampening by thermal inertia of test cell and time of event greatly extended. Both limitations should be corrected that support their extrapolation to a real plant scale. Consequently, the safer design for PAA solutions should take temperature control in the reactor, distillation column and tank, and pressure relief devices as the essential equipment in proactive loss prevention program.

NOMENCLATURE

A	vent area (m^2)
C_{pb}	heat capacity of the stainless-steel test bomb (0.45 kJ kg^{-1} K^{-1})
C_p	heat capacity of the sample (2.61 kJ kg^{-1} K^{-1})
D	diameter of a pressure relief valve (m)
E_a	activation energy (kJ $mole^{-1}$)
G	mass flux in vent leaving vessel (kg m^{-2} min^{-1})
h_{fg}	latent heat of vaporization (J g^{-1})
k_0	rate constant (sec^{-1})
M_a	mass of the sample (g)
$MAWP$	maximum allowable working pressure
M_b	mass of the test bomb (g)
M_f	mass of sample after a VSP2 test (g)
m_0	mass of reactant (kg)
P_f	pressure after a VSP2 test (bar-g or psig)
P_{max}	maximum pressure (bar-g or psig)
P_r	venting relief pressure (bar-g or psig)
P_s	venting setup pressure (bar-g or psig)
dP/dt	pressure elevation rate measured by VSP2 (bar min^{-1})
$(dP/dt)_{max}$	maximum pressure elevation rate (bar min^{-1})
$\overline{q}$	the average heat-releasing rate (J kg^{-1} sec^{-1})
R	ideal gas constant (8.314 J mol^{-1} K^{-1})
T	temperature (K)
t	time
$(T_s)_c$	temperature after correction (K)
T_E	experimental temperature measured by VSP2 (°C)
T_{max}	maximum temperature measured by VSP2 (K)
T_r	venting relief temperature (K)
$(T_r)_c$	venting relief temperature after correction (K)
T_s	venting setup temperature (K)
dT/dt	self-heating rate (°C min^{-1})
$(dT/dt)_r$	venting self-heating rate (K min^{-1})
$(dT/dt)_{r'}$	venting self-heating rate after ϕ correction (K min^{-1})
$(dT/dt)_s$	setup self-heating rate (K min^{-1})
$(dT/dt)_{s'}$	setup self-heating rate after ϕ correction (K min^{-1})
ΔT_{ad}	adiabatic temperature rise (°C)
V	volume of vessel (m^3)
v_{fg}	net volume change in vaporization (m^3)
W	relief mass flow rate (kg min^{-1})
ϕ	thermal inertia

Subscripts

$_c$	ϕ correction
$_f$	final log data of VSP2 experiment
$_g$	gas phase
$_r$	relief point
$_s$	set point

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