



Calorimetric studies and lessons on fires and explosions of a chemical plant producing CHP and DCPO

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ARTICLE INFO

Article history:

Received 8 August 2011

Received in revised form

21 November 2011

Accepted 21 December 2011

Available online 8 March 2012

Keywords:

Organic peroxide

Chemical incident

Thermal runaway

Risk assessment

Emergency relief system

ABSTRACT

Cumene hydroperoxide (CHP) has been used in producing phenol, dicumyl peroxide (DCPO) and as an initiator for synthesizing acrylonitrile–butadiene–styrene (ABS) resin by copolymerization in Taiwan. Four incidents of fire and explosion induced by thermal runaway reactions were occurred in a same plant producing CHP, DCPO and bis-(tert-butylperoxy isopropyl) benzene peroxide (BIBP). The fourth fire and explosion occurred in the CHP reactor that resulted in a catastrophic damage in reaction region and even spread throughout storage area. Descriptions on the occurrences of these incidents were assessed by the features of processes, reaction schemes and unexpected side reactions. Calorimetric data on thermokinetics and pressure were used for explaining the practical consequences or which the worst cases encountered in this kind of plant. Acceptable risk associated with emergency relief system design is vital for a plant producing organic peroxide. These basic data for designing an inherently safer plant can be conducted from adiabatic calorimetry. An encouraging deduction has been drawn here, these incidents may be avoided by the implementation of API RP 520, API RP 521, DIERS technology, OSHA 1910.119 and AIChE's CCPS recommended PSM elements.

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1. Introduction

Fires or explosions caused by thermal decompositions of organic peroxides have been studied in the past two decades [1]. Thermal or reactive hazards ratings for organic peroxides have been thoroughly discussed in the previous studies [2,3]. Calorimetry associated with methodologies of DIERS (Design Institute for

Emergency Relief System) has been widely studied for preventing thermal runaway or reactive hazards of organic peroxides [4–9]. Special attentions were paid to two thermal explosions caused by methyl ethyl ketone peroxide (MEKPO) which led to disastrous losses [10]. The first one was caused by thermal accumulation in storing a huge quantity of MEKPO in 1978, then the fire developed and led to the huge explosion in the storage region; this incident killed 33 people and many were injured. The other thermal explosion killed 10 and injured 47 people in 1996, unfortunately, the propagating fireball in this explosion killed six firefighters during firefighting around the storage tank [1,2].

Organic or inorganic peroxide is characterized by the presence of a weak oxygen–oxygen bond in the molecule. All typical features of reactivities or incompatibilities are ascribed to the breaking of O–O bond which can undergo radical or ionic decomposition of several kinds. Organic peroxides are regarded as the derivatives of hydrogen peroxide (HOOH), which are generalized in the form of ROOR' in which R and R' can symbolize various kinds of substitution groups. Examples of the most popular types of organic peroxides are dialkyl peroxides, alkyl hydroperoxide, diacyl peroxide, peroxy ester and ketone peroxide.

Most organic peroxides are either used as a curing agent or used to initiate free radical polymerization in the petrochemical industry. Fires and explosions were the readily types of incidents which were caused by ill-conditioned handling of organic

Abbreviations: ABS, acrylonitrile–butadiene–styrene; AIChE, American Institute of Chemical Engineers; API, American Petroleum Institute; ARC, accelerating rate calorimeter; ASME, American Society of Mechanical Engineers; ASTM, American Society of Testing and Materials; BIBP, bis-(tert-butylperoxy isopropyl) benzene peroxide; CCPS, Center for Chemical Process Safety; CHP, cumene hydroperoxide; DCPO, dicumyl peroxide; DIBP, 1,3-diisopropylbenzene; DIERS, Design Institute for Emergency Relief Systems; DSC, differential scanning calorimeter; DTA, differential thermal analyzer; ERS, emergency relief system; FAI, Fauske and Associates Incorporations; OSHA, Occupational Safety and Health Administration; MAWP, maximum allowable working pressure; MEKPO, methyl ethyl ketone peroxide; NFPA, National Fire Protection Association; PSM, process safety management; RD, rupture disk device; RP, recommended practice; SADT, self-accelerating decomposition temperature; SAFIRE, systems analysis for integrated relief evaluation; SRV, safety relief valve; TBHP, tert-butyl hydroperoxide; TMR_{ad}, adiabatic time-to-maximum-rate; TMR_{exp}, experimental time-to-maximum-rate; TNO, Netherlands Organization for Applied Scientific Research; UN-TDG, United Nation Committee of Experts on the Transports of Dangerous Goods; VSP2, Vent Sizing Package 2.

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Nomenclature

A	vent area or wet area of reactor (m^2)
C_p	specific heat at constant pressure ($\text{kJ kg}^{-1} \text{K}^{-1}$)
E_a	activation energy (kJ mol^{-1})
G	mass flux in vent leaving vessel ($\text{kg m}^{-2} \text{min}^{-1}$)
ΔH_{rea}	heat of reaction or decomposition (J kg^{-1})
ΔH_{tot}	heat of reaction or decomposition (J kg^{-1})
h_{fv}	latent heat of vaporization (J kg^{-1})
k_i	rate constant ($\text{s}^{-1} \text{M}^{1-n}$)
m, n	order of reaction
m_0	mass of reactant (kg)
P_0	pressure at set point (psi)
P_{max}	maximum pressure of organic peroxide after adiabatic runaway (psi)
\dot{Q}	energy flux (W g^{-1})
\bar{q}	heat-releasing rate ($\text{J kg}^{-1} \text{s}^{-1}$)
R	gas constant ($8.314 \text{ J g}^{-1} \text{K}^{-1}$)
t	time (s)
T	absolute temperature ($^{\circ}\text{C}$ or K)
T_{onset}	exothermic onset temperature ($^{\circ}\text{C}$ or K)
T_f	final temperature of organic peroxide after adiabatic runaway ($^{\circ}\text{C}$ or K)
T_A	final adjusted temperature ($^{\circ}\text{C}$ or K)
T_{A0}	initial adjusted temperature ($^{\circ}\text{C}$ or K)
T_M	final measured temperature ($^{\circ}\text{C}$ or K)
T_{M0}	initial measured temperature ($^{\circ}\text{C}$ or K)
$(dT/dt)_m$	maximum self-heat rate ($^{\circ}\text{C min}^{-1}$ or K min^{-1})
$(dT/dt)_{\text{max}}$	maximum self-heat rate of an adiabatic runaway reaction ($^{\circ}\text{C min}^{-1}$ or K min^{-1})
$(dT/dt)_s$	self-heat rate ($^{\circ}\text{C min}^{-1}$ or K min^{-1})
(dT/dt)	temperature derivative with respect to time ($^{\circ}\text{C min}^{-1}$ or K min^{-1})
(dP/dt)	pressure-rising rate of an adiabatic runaway reaction (psi min^{-1})
$(dP/dt)_{\text{max}}$	maximum pressure-rising of an adiabatic runaway reaction (psi min^{-1})
ΔT_{ad}	adiabatic temperature rise ($^{\circ}\text{C}$)
U	heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
V	volume of vessel (m^3)
V_0	volume of sample (m^3)
v_{fv}	net volume change in vaporization (m^3)
W	relief mass flow rate (kg min^{-1})
ϕ	thermal inertia
α	degree of conversion
ρ_0	density (kg m^{-3})

Subscripts

f	liquid phase
fg	difference between gas (vapor) phase and liquid phase
g	gas phase
l	liquid phase
max	maximum
r	rate of reaction (M s^{-1})
s	set point
t	VSP 2 test cell
v	specific volume ($\text{m}^3 \text{kg}^{-1}$)

peroxides in Taiwan. Table 1 lists many serious disasters caused by organic peroxides in several countries [1,10,11], particular attentions were paid to several disastrous explosions caused by the thermal runaway of MEKPO induced by external fires. Besides, cumene hydroperoxide (CHP) and tert-butyl hydroperoxide (TBHP)

are the other two kinds of alkyl hydroperoxides in possession of intrinsically unstable-O—O—H groups. CHP and TBHP are extremely labile or unstable in contact with acids, bases, metal ions, rust and other contaminants.

Formulations of commercial organic peroxides are classified as type A, B, C, D, E, F and G as regulated by the UN-TDG (United Nation Committee of Experts on the Transports of Dangerous Goods) [12]. NFPA (National Fire Protection Association) specifies the quantity, conditions for storage, solvents for dilution, materials for packing, and types of hazards of organic peroxides [13]. In the UN manual of tests and criteria, the thermal stability is identified by the self-accelerating decomposition temperature (SADT) [14]. A substance with a SADT below 50°C should be subject to temperature control in transportation. Netherlands Organization for Applied Scientific Research (TNO) has devoted considerable efforts to the testing, package materials and classification for organic peroxides. DIERS (Design Institute for Emergency Relief Systems) which is a branch society of AIChE (American Institute of Chemical Engineers) emphasizes researches on the safe designs of emergency relief systems for organic peroxides under thermal runaway [15–17]. Besides, the classification of organic peroxides from traditional viewpoints or calorimetric approaches was reviewed in the literature [18–20].

Commercialized organic peroxides of DCPO, CHP and TBHP in different formulations are classified by NFPA and listed in Table 2 [13]. However, even low concentration of unclassified CHP or TBHP frequently operated in process units is also possessed of highly reactive or incompatible hazards. Thermal runaway in a CHP/cumene oxidation or TBHP/ H_2O reactor was reported in previous studies [8,21]. The self-reactive and incompatible properties of these unstable or labile organic peroxides have not been clearly defined in NFPA or UN regulations, more efforts on extended studies are necessary. In this study, we focus on the phenomena that initiate or induce the resulted incidents associated to the process unit or operation which is upset or uncontrolled. Calorimetric data are utilized to verify the credible worst cases which were occurred in this plant. Effectiveness of DIERS technologies for vent sizing, relief devices or installations and are also assessed or discussed in these incidents for loss prevention or controlling the risk of an organic peroxide plant. From the inspection of causes in incidents, process design, deviations of operation, calorimetric data, reactive hazards, emergency relief system, and safety management, we can draw the lessons learnt from these cases to prevent or minimize the consequences in similar plants.

2. Experimental

TBHP formulation of 70 wt% in water and DCPO with purity higher than 99% were purchased from Sigma Aldrich Co. 80 wt% CHP in cumene was supplied from the Grand Pacific Petrochemical Company. These chemicals were stored in a refrigerator at 4°C environment for sustaining stability and purity.

2.1. Differential scanning calorimeter (DSC)

Thermal instabilities of organic peroxides were screened in a Mettler TA-4000 system coupled with a DSC25 measuring cell [22]. A disposable crucible (ME-26732) which can stand to about 100 bar was used for detecting a thermal curve. Data were acquired and stored by a PC system for further evaluation. Onset temperature (T_{onset}) was chosen at the point with an exothermic power of 0.2 W g^{-1} (equivalent to a signal-to-noise (S/N) around 5). Scanning rate was selected to be 4 K min^{-1} in temperature-programmed ramp for the reason of sustaining better thermal equilibrium in the heating oven.

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