



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

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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.

Table 1
Incidents of fires or explosions caused by organic peroxides [1,10,11].

Date	Location	Material	Injuries	Fatalities	Hazard	Cause
1964.07.14	Japan	MEKPO	114	19	Explosion (storage)	External fire
1979.07.13	Taiwan	MEKPO	49	33	Explosion (storage)	Thermal decomposition
1981.04.21	Taiwan	CHP	3	1	Explosion (distillator)	Thermal decomposition
1982.02.18	Taiwan	MEKPO	55	5	Explosion (reactor)	Thermal decomposition
1986.05.02	Taiwan	CHP	0	0	Explosion (reactor)	Thermal decomposition
1987.09.05	Taiwan	Hydrogen peroxide	20	0	Explosion (tank)	Incompatible contamination
1988.07.25	Taiwan	TBHP	19	0	Explosion and fire (tank)	Cooling failure
1989.03.14	Taiwan	Organic peroxides	0	0	Fire (tank)	Cooling failure
1989.08.04	Taiwan	Organic peroxides	0	0	Explosion (tank)	Cooling failure
1989.09.01	Taiwan	MEKPO	5	7	Explosion (tank)	Thermal decomposition
1996.10.07	Taiwan	MEKPO	47	10	Explosion (tank)	Fire
2003.01.02	USA	BPO	1	0	Explosion (dryer)	Thermal decomposition
2000.08.24	Korea	MEKPO	11	3	Explosion (storage)	Unknown
2008.01.30	Taiwan	DCPO	0	0	Explosion (reactor)	Thermal decomposition
2009.06.22	Taiwan	TBHP	0	0	Explosion (reactor)	Thermal decomposition
2010.01.08	Taiwan	CHP	0	0	Explosion (reactor)	Catch fire

Table 2
Classification of organic peroxides used in the process units [13].

Organic peroxide	Purity	Dilution	Process or unit	Class of NFPA 432
CHP	80%	Cumene	Storage	III
CHP	30%	Cumene	Reactor	Undefined
CHP	24%	Cumene	Reactor	Undefined
CHP	<80%	Cumene	Condensation reactor	Undefined
DCPO	99% solid	–	Storage	IV
DCPO	Slurry	Cumene	Condensation reactor	Undefined
TBHP	70%	Water	Storage	IV
TBHP	<70%	Water	Reactor	Undefined

Note: Hazard classification of organic peroxide in NFPA 432.

Class I formulations: present a deflagration hazard through easily initiated, rapid explosive decomposition.

Class II formulations: present a severe fire hazard similar to class I flammable liquids. The decomposition is not as rapid, violent, or complete as that produced by class I.

Class III formulations: present a fire hazard similar to class II combustible liquids. They are characterized by rapid burning and high heat liberation, due to decomposition.

Class IV formulations: present a fire hazard that is easily controlled. Reactivity has little effect on fire intensity.

Class V formulations: do not themselves burn and do not present a decomposition hazard.

2.2. Accelerating rate calorimeter (ARC)

For the reason of safety, the runaway reactions of organic peroxides were conducted in an accelerating rate calorimeter (ARC) with excellent shielding, manufactured by Columbia Scientific Industries of Austin, TX [23]. The detailed performance and theory of the ARC instrument can be found elsewhere [24]. Spherical bombs were made of titanium, SS304 or Hastolloy C with a volume of 10 ml for containing solid, liquid, or slurry samples.

2.3. Vent Sizing Package 2 (VSP2)

For better performances of probing reactive hazards or thermal kinetics, exothermic behaviors in the test cell can therefore be extrapolated directly to the industrial scale due to the low thermal inertia at about 1.05–1.2. The Vent Sizing Package 2 (VSP2) manufactured by FAI [25] is another alternative tool for this purpose of assessing nearly adiabatic runaway or credible worst scenarios suggested by process engineers.

3. Descriptions of the incidents

Four incidents of thermal runaway reactions caused by deviations of process conditions or by external fire were analyzed as shown in Tables 3–6 and discussed latter. Fig. 1 depicts the simplified lay out of the plant and represents the reaction zone related to individual incident.

Table 3
Incident 1.

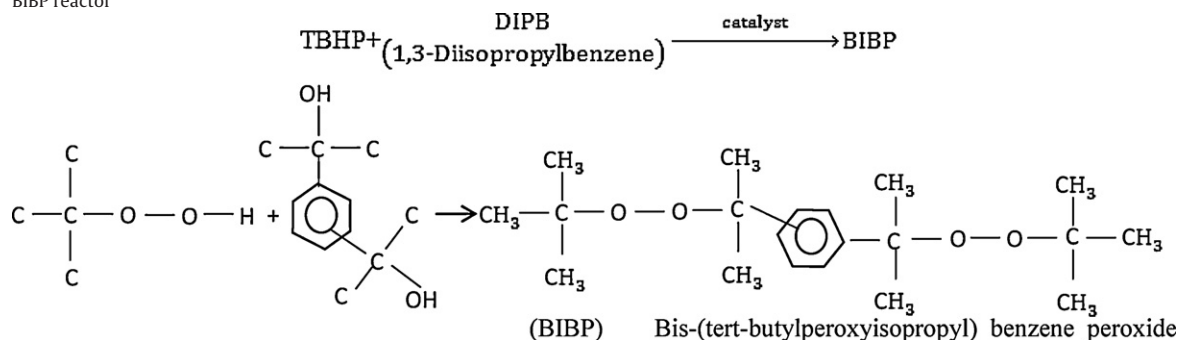
Year	2003
Date	April
Fatalities	0
Injuries	0
Process unit	DCPO reactor
Reaction	CHP + Cumyl alcohol $\xrightarrow{45\% \text{NaOH}}$ DCPO + H ₂ O
Description and cause of incident	Thermal decomposition of CHP or DCPO resulted in runaway reaction
Consequence	Rupture of the top cover of reactor with a volume of 15 m ³ . Steel frame was destroyed in the reaction region
Loss	Property

Table 4
Incident 2.

Year	2008
Date	January 30
Fatalities	0
Injuries	0
Process unit	DCPO reactor
Reaction	CHP + Cumyl alcohol $\xrightarrow[45\% \text{NaOH}]{\text{cumene}}$ DCPO + H ₂ O
Description and cause of incident	Erroneous dosing of catalyst resulted in the increase of a viscosity of reactant and the poor capacity of heat transferred to the jacket of reactor.
Consequence	This situation activated the thermal runaway and explosion of reactor
Loss	Rupture of the top plate of the reactor was caused by lack of emergency relief system
Loss	Property

Table 5
Incident 3.

Year	2009
Date	June 22
Death	0
Injured	0
Process unit	BIBP reactor



Reaction	
Description and cause of incident	Erroneous dosing of catalyst caused the faster reaction rate and heat-releasing then commenced the thermal runaway of the reaction. Two-phase effluents were released from man hole in the reaction area. A big fire and explosion was ignited just after the flammable vapor mixture liberated from the reactor
Consequence	Fire and explosion in the process plant
Loss	Property

Table 6
Incident 4 (this calamity caused the plant has been shut down until now).

Year	2010
Date	January 08
Fatalities	0
Injuries	0
Process unit	CHP reactor
Reaction	Cumene + O ₂ → CHP
Description of incident	Leaking in the pipe line connected to the bottom of the cumene oxidation reactor then caught fire onto the surface of the first reactor. Thermal runaway and explosion in the first reactor inducted into the consecutive thermal runaway and explosions in-side the second and third reactors
Consequence	Serious damages were happened in the cumene oxidation zone. Fire spread into the storage area resulted in another destruction in the storage
Loss	Property and plant shut down

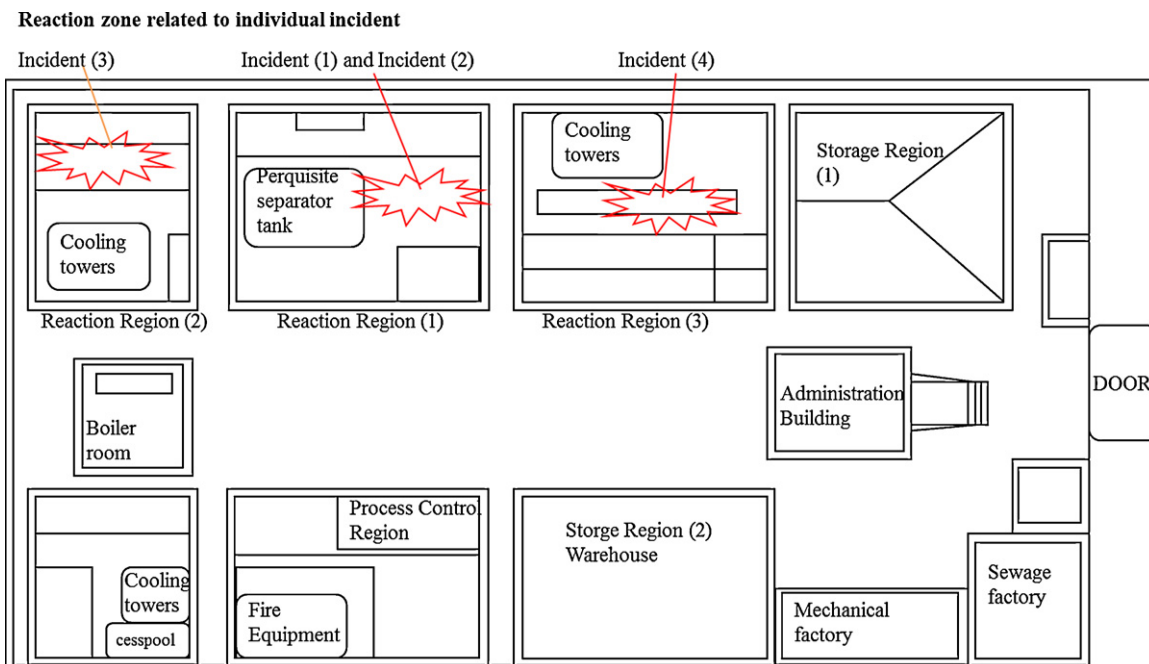
**Fig. 1.** Reaction zone related to individual incident.

Table 7a

Standard tests developed by ASTM for thermal analysis on unstable compounds [26–29].

Test	Instrument	Temperature range (°C)	Pressure range	Weight sample	Summary of test
E476-87 (reapproved 1993)	Bomb assembly	0–500	0–5000 psi	0.3 g (recommended)	Thermal stability (confinement) test
E487-79	DSC or DTA	$T > 25$	Not defined	≤ 50 mg	Constant-temperature stability
E537-86	DSC or DTA	–150 to 1000	100 Pa–7 MPa	5 mg	Thermal stability (differential thermal analysis)
E689-79	DSC or DTA	Not defined	Not defined	≤ 5 mg	Arrhenius kinetic constants for thermally unstable materials

Table 7b

Practice or standard for emergency relief system design.

Practice or standard	Engineering or industrial purposes	Vapor, gas, or two-phase flow	Applicable system
API RP 520	Sizing, selection, and installation of pressure-relieving devices in refineries	Vapor or gas	Reactor, storage tank, distiller or high pressure vessel in refinery and petrochemical industry
API RP 521	Guide for pressure-relieving and de-pressuring systems	Vapor or gas	Practice on the design of piping, knock-out drum, catch tank and disposal system in case of blow-down
DIERS	Design methodology or technology for emergency relief system under runaway reaction	Two-phase flow which was not stressed or included in API RP 520 and API RP 521	Reactor or pressure vessel associated with runaway reaction and two-phase flow
NFPA 68	Venting of deflagration	Vapor or gas	Vent sizing of rupture window or rupture disc of an oxidation reactor

Table 7c

Hazard evaluation by various calorimeters.

Calorimeter	Measured data	Applications or engineering purposes
DSC	Onset temperature; heat of reaction; thermogram (thermal curve)	Exothermic onset point; heat released; reaction kinetics (only for a simple thermal curve, by the methodology proposed of Borchartd and Daniel)
ARC or VSP2	Temperature of reactant related to time; pressure curve under self-heat condition	Exothermic onset point; adiabatic temperature rise (ΔT_{ac}); final temperature (T_f); self-heat rate (dT/dt) for calculating vent area; maximum self-heat rate (dT/dt) _{max} for evaluating vent area and cooling capacity under worst case; reaction kinetics by ARC theory proposed by Townsend; temperature of no return (T_{NR}) and time-to-maximum rate TMR _{ad} for emergency response; maximum pressure (P_{max}) with respect to MAWP or worst credible case

4. Results and discussions

4.1. Thermal stability of organic peroxide

The committee of ASTM (American Society for Testing and Materials) has established the completely standard practices or tests for assessing the hazards of unstable compounds and acquiring the thermokinetics on decompositions. Related safety parameters include exothermic onset temperature, enthalpy change, thermal stability, Arrhenius parameters and confinement effect can be verified by the corresponding methods [26–29]. Table 7a lists the standard tests or practices issued by the ASTM committee for thermal analysis on unstable compounds; Table 7b registers the practices or standards for emergency relief system design; Table 7c presents the applicable evaluations on hazards by various calorimeters. The ASTM: E537-86 [28] was employed as the standard method for assessing the thermal stability of organic peroxide. DSC was chosen as the screening instrument for thermal

analysis. Table 8 summarizes the data from DSC for primary hazard evaluation. Lower onset temperature and higher heat of decomposition possessed higher probability and severe consequence in case of thermal runaway caused by self-reactive or reactive decomposition. Exothermic onset temperature of CHP (80 wt% in cumene), TBHP (70 wt% in H₂O) and DCPO (99 wt%, solid) were determined to be 100, 65 and 110 °C, respectively. Heat of self-reactive reaction (or thermal decomposition) of CHP (80 wt% in cumene), TBHP (70 wt% in H₂O) and DCPO (99 wt%, solid) were integrated and calculated by software in DSC to be 1786 ± 40 , 2096 ± 200 and 968 ± 25 J g⁻¹ organic peroxide, respectively. These data investigated from thermal analysis technique agreed with each other and were wholly close to the comparable results reported in the literature [30,31,9]. Key parameters that determine safe operation of chemical plant include the physical/chemical properties of chemicals, reaction kinetics, process design and operation and risk assessment/control system. Thermal analysis methodology in DSC only reveals the physical/chemical properties of materials. Due to the drawbacks

Table 8

Screening data for thermal analyses of organic peroxides acquired from DSC.

Organic peroxide	Weight (mg)	Scanning rate (°C min ⁻¹)	Onest temperature (°C)	Heat of decomposition (J g ⁻¹ , 100 wt% organic peroxide)
CHP 20 wt%/cumene	4.15	10	130	1571
CHP 30 wt%/cumene	4.40	10	110	1743
CHP 35 wt%/cumene	4.50	10	100	1790
CHP 80 wt%/cumene	4.9	2	100	1825
TBHP 70 wt%/H ₂ O	1.83	4	65	1892
TBHP 70 wt%/H ₂ O	1.71	4	65	2300
DCPO > 90 wt%, solid	2.1	4	110	993
DCPO > 99 wt%, solid	2.82	4	110	942

of DSC such as small quantity (less than 20 mg), no agitation, batch addition and lack of pressure detection and process condition, the potential hazards or worse scenarios should be further corroborated by adiabatic calorimetry.

4.2. Adiabatic runaway of organic peroxide

Credible worst cases that might be encountered in process deviation were verified by using adiabatic calorimeters. Heat-wait-search mode is quite the effective operation procedure to force or increase the temperature of reactant to the onset point of exothermic reaction. Exothermic behaviors can be one kind of self-reactive, reactive, incompatible or autocatalytic reaction. Once, the onset point was detected by the data acquisition system, adiabatic calorimeter shut down radiation (or main) heater and opened tracking heater to keep the environment to be adiabatic around the test cell. Then, the exothermic reactant proceeded to a self-heat situation until runaway reaction completed thoroughly. Table 9 listed the runaway of organic peroxides under adiabatic conditions to simulate the credible worse or worst scenarios the might be confronted in case of process deviation. Maximum or final temperature (T_f), maximum pressure (P_{max}), exothermic onset temperature (T_{onset}), maximum self-heat rate ($(dT/dt)_{max}$), maximum pressure-rising rate ($(dP/dt)_{max}$) and adiabatic time-to-maximum-rate (TMR_{ad}) are frequently utilized to assess the potential hazards of organic peroxides in case of adiabatic decomposition. We inferred that the higher concentrations within the organic peroxides possessed higher risks if it went overboard. Maximum pressure can reveal that the tolerance limit or MAWP (maximum allowable working pressure) of vessel will be exceeded or not. If P_{max} greatly exceeded 4 times of MAWP, the thermal runaway accompanied high pressure will rupture the reactor. Maximum temperature or ΔT_{ad} (adiabatic temperature rise) disclose the released mixture with flammable behavior which might be ignited automatically in case of final temperature exceeding the AIT (auto-ignition temperature) or by external sources after the rupture of reactor.

4.3. Credible worst cases

Although the pressure hazards can be authenticated by the confinement test of the practice in ASTM 476-87, the insufficient adiabatic isolation of the confinement cell, the pressure test is usually replaced by an adiabatic calorimeter. The adiabatic calorimeter can simulate the credible worst scenarios that may be encountered in process deviations. In general, cooling failure or heat-flux from external fire occurred in a vessel can be demonstrated directly by adiabatic calorimeter. Due to the low thermal inertia near 1.05 in VSP2, the measured data can be practically extrapolated to the industrial scale condition. The worst cases were deduced from the adiabatic runaway of unexpected/unwanted side reactions. Table 9 lists the essential data of runaway reactions caused by the exothermic decomposition which were implemented by adiabatic calorimeter in CHP (15, 20, 30, 35 and 80 wt% in cumene), TBHP (15, 20, and 70 wt% in H₂O) and DCPO (99 wt%, solid), respectively. Maximum pressure of these upset scenarios can all explode the vessels or storage tanks operated at one atmosphere. Due to the safety concern of experimental operation, CHP 80 wt% and TBHP 70 wt% were conducted at high ϕ value of 9.29 and 3.68, respectively. Thermal hazards are extremely descended the test specimen in high ϕ values, the intrinsic behaviors then can be simulated in analytical equations in the following paragraph. From the self-heat rate and pressure-rising rate, the risk of CHP in 15 wt% and 20 wt% synthesized from the oxidation of cumene can be controlled by the installation of emergency relief systems. The worst cases met in these various organic peroxides in Table 9 were deduced

Table 9
Runaway reaction of organic peroxide from adiabatic calorimeters.

Organic peroxide	Adiabatic calorimeter	Test cell	M_0 (g)	M_b (g)	ϕ (thermal inertia)	T_{onset} (°C)	T_f (°C)	P_{max} (psig)	$(dT/dt)_{max}$ (°C min ⁻¹)	$(dP/dt)_{max}$ (psi min ⁻¹)	ΔT_{ad} (°C)
CHP 15 wt%	VSP2	s.s.316	56.47	43.00	1.19	100.0	206.9	208.0	2.8	3.5	106.2
CHP 20 wt%	VSP2	s.s.316	56.03	43.20	1.18	100.0	214.7	216.5	8.5	6.3	114.7
CHP 20 wt%	ARC	Ti	6.95	8.75	1.31	111.0	192.4	210.1	3.8	5.1	106.7
CHP 30 wt%	ARC	Ti	7.16	8.82	1.30	106.1	229.4	226.9	46.8	33.2	160.7
CHP 35 wt%	ARC	Ti	7.40	8.85	1.28	101.2	250.5	506.6	336.8	746.8	190.9
CHP 80 wt%	ARC	Hast. C	0.84	18.44	9.29	111.3	172.3	179.0	13.3	12.5	61.0
TBHP 15 wt%	VSP2	s.s.316	49.50	43.20	1.11	105.7	336.1	487.0	524.7	235.9	230.4
TBHP 20 wt%	VSP2	s.s.316	49.35	43.40	1.11	105.0	326.2	509.6	616.5	371.7	221.2
TBHP 70 wt%	ARC	s.s.316	2.04	18.45	3.68	75.5	184.9	418.8	45.5	172.3	109.3
DCPO 99 wt%	VSP2	s.s.316 open cell (112 ml)	56.47	43.00	1.19	75.0	254.5	76.8	4021.0	Not determined	179.5

ASME stamped vessels fabricated of low carbon steel and low alloy stainless steel, rupture pressure at ultimate strength is equal to 4 times of MAWP, and permanent deformation pressure at yield strength is equal to 2 times of MAWP.

Four times of MAWP of reactor operated at 1 atmosphere is 14.7 (psi) \times 4 = 58.8 (psi).

Maximum pressure of these organic peroxides under runaway reactions shall burst the containers.

Table 10
Normal reaction and unwanted decomposition or side reaction in reactor [17,30,31,9,34].

Reactor	Normal reaction	Unwanted decomposition or side reaction result in runaway
CHP	cumene $\xrightarrow{O_2}$ CHP/cumene 30–35 wt%	1. CHP \xrightarrow{KT} α -cumyl alcohol \rightarrow α -Metyl styrene 2. CHP \xrightarrow{KT} Acetophenone + Methanol 3. Deflagration of vapor phase
DCPO	CHP + C ₆ H ₅ C(CH ₃) ₂ OH \rightarrow DCPO + H ₂ O	DCPO \xrightarrow{KT} Acetophenone
BIBP	TBHP + DIPB $\xrightarrow{catalyst}$ BIBP + 2H ₂ O	1. TBHP \xrightarrow{KT} CH ₃ COCH ₃ + CH ₃ OH 2. TBHP \xrightarrow{KT} C ₃ H ₈ + CO + H ₂ O

to be thermal explosion in case of insufficient pressure relief in case of runaway reactions. Data of the maximum pressure will greatly exceed four times MAWP of reactor. If the final decomposition temperature (T_f) exceeds the auto-ignition temperature (AIT), then severe fire will accompany the explosion or follow the footsteps of explosion. As a rule of thumb, adiabatic self-heat rate at about 10 °C min⁻¹ is an upper limit for design an appropriate emergency relief system to avoid worst case scenario. Furthermore, adiabatic self-heat rate exceeds 100 °C min⁻¹ which always accompanies large incondensable gas will certainly explode the reactor or storage tank. Besides, under such conditions and characters of wicked reactor, self-heat rate (dT/dt) proportionally related to the vent sizing was too large to be good for safe designing an emergency relief system. Table 10 depicts the normal reactions and unwanted reactions that even happened in these incidents [17,30,31,9,34]. In general, unacceptable risk of fire or thermal explosion should be avoided or exclude by inherently safer design or process control.

The spontaneity or origin of autocatalytic reaction ascribed to the compound is possessed of an unstable functional group or product catalyzes the reactant. Autocatalytic reaction is considered to be a troublesome or hazardous case due to the hardly detected initiation and suddenly heat evolution which may cause a thermal or pressure runaway. Calorimeters operated in isothermal mode or isothermal aging test is effectively to differentiate whether a reaction is autocatalytic or n th order. An autocatalytic effect can be characterized by a maximum rate of heat release at about 40–60% conversion of the reactant in the isothermal thermogram; however, the maximum rate of an n th order reaction must occur at 0% conversion or at initial state demonstrated by rate law. Moreover, an induction period associated with unobserved enthalpy change prior to the initiation or acceleration of the exothermic reaction.

Heat loss or leak from sample to cell is considered natural and inevitable in testing system of an adiabatic calorimeter. Townsend developed a mathematical methodology, “ ϕ -correction”, to countervail the high ϕ deviation into true adiabatic state of ϕ is equal to unity [24]. Suggested equations have been compensated by the ϕ value are as follows,

$$T_A = T_{A_0} + \phi(T_M - T_{M_0}) \quad (1)$$

$$\frac{1}{T_{A_0}} = \frac{1}{T_{M_0}} + \frac{R}{E_a} \ln \phi \quad (2)$$

$$\left(\frac{dT}{dt}\right)_{M(\phi=1)} = \phi \left(\frac{E_a}{R} \left(\frac{1}{T_M} - \frac{1}{T_A}\right)\right) \left(\frac{dT}{dt}\right)_{M(\phi>1)} \quad (3)$$

$$TMR_{ad}(\phi=1) = \frac{TMR_{exp}(\phi>1)}{\phi} \quad (4)$$

An ARC or similar equipment with a high ϕ value from 2 to 10 has been used in the earlier development of adiabatic calorimeter. However, the ϕ value of industrial reactor is about from 1.1 to 1.3. Therefore, the self-heat rate or related rate data detected at high ϕ condition should be corrected to a phi factor as low as 1.3 for simulating industrial vessel. From the mid 1980s, types of

various test cans with a volume of 110 ml were modified to sustain a phi factor from 1.3 to 1.1. Thus, the runaway reaction in an industrial reactor associated to the credible worst case can be observed in a bench calorimeter such as VSP2. Adiabatic temperature rise ΔT_{ad} and onset temperature can be corrected to adiabatic condition due to their feature of thermodynamics in Eqs. (1) and (2), respectively. For a highly exothermic reaction, less quantity of reactant results in high ϕ value. Correction of self-heat rate and adiabatic time-to-maximum rate for the effect of ϕ spend more efforts, and Eqs. (3) and (4) may lead to deviation from ideally adiabatic date with ϕ equalizes unity. Nitro-compounds and organic peroxides of high concentrations have been operated with a small quantity in adiabatic calorimeter under the ϕ value quite larger than unity. Hence, high ϕ value can weaken or distort the hazards of runaway reactions, the relevant vent sizing or mass flow rate might be underestimated as well.

For both n th order on auto-catalytic reactions these corrective methods may be unable to obtain the actual self-heat rate and time-to-maximum rate, because they do not take reaction order, auto-catalytic behaviors, gas evolution and heat transfer effect into account due to their dynamic characteristics. For avoiding an incorrectly sized relief area, self-heat rate has better to be measured from an excellent adiabatic calorimeter or calculate from chemically kinetic parameters. Both n th order reaction and auto-catalytic reaction were selected for verification. For a n th order reaction,

$$\frac{dT}{dt} = - \left(\frac{\Delta H_{tot}}{C_p}\right) \frac{d\alpha}{dt} = - \left(\frac{\Delta H_{tot}}{C_p}\right) k(1-\alpha)^n \quad (5)$$

For an auto-catalytic decomposition which possessed the simplified mechanism as following



The rate law can be expressed as

$$r = -k_1[A] - k_2[A]^m[B]^n \quad (8)$$

or

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^1 + k_2\alpha^m(1-\alpha)^n \quad (9)$$

The self-heat rate can be deduced to be

$$\frac{dT}{dt} = - \left(\frac{\Delta H_{tot}}{C_p}\right) [k_1(1-\alpha)^1 + k_2\alpha^m(1-\alpha)^n] \quad (10)$$

In these equations, α is evaluated from the thermal curve detected by DSC,

$$\alpha = \frac{\int_{T_0}^T \dot{Q} dt}{\int_{T_0}^{T_f} \dot{Q} dt} \quad (11)$$

Typical corrections or actions for preventing or controlling runaway reaction in a reactor

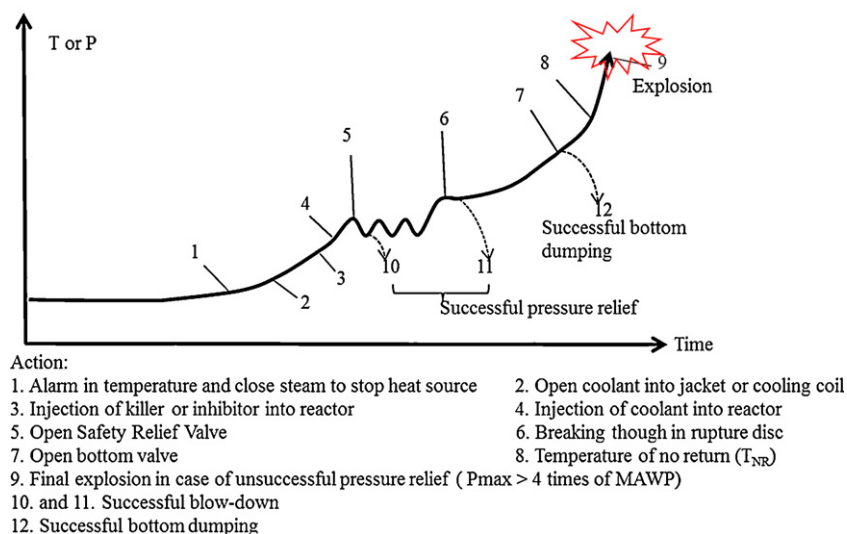


Fig. 2. Typical corrections or actions for preventing or controlling runaway reaction in a reactor.

4.4. Lessons learnt from these incidents

By taking into account the above incidents, most of the direct or indirect causes were the poor or lack of knowledge of applying the emergency relief system to reduce the risk of thermal runaway triggered by the decomposition of organic peroxide. Traditionally, a reactor operated under atmosphere does not equip with emergency relief system for relieving the overpressure of vessel. Engineers believe that the runaway is moderate and can be controlled by either jacket cooling, reflux solvent in condenser, inhibitor, emergency coolant or bottom dump in which reactor system is open to air via a condenser. In the basic viewpoint of operating an organic peroxide reactor in safe margin, the operators on duty should pay all attention to standard operation processes, reaction schemes, safety equipments, safety rules and suitable procedures in case of emergency response to enforce safety management and supervision. In short, the lessons learnt in the disastrous damages were unclear in the thermal runaway of organic peroxide even without installing suitable emergency relief system.

4.4.1. Incident 1 and 2 (DCPO reactor) (listed in Tables 3 and 4, respectively)

These two incidents were caused by without or poor design of emergency relief systems during runaway decomposition in reactors. Dosing of catalyst by engineer should obey standard operation process. Enforced and intense training is needed to avoid near-miss accident or incident caused by human factor. Design of an ERS is necessary for a reactor in synthesizing DCPO.

4.4.2. Incident 3 (BIBP reactor) (listed in Table 5)

Effluent control was excluded in the process design. Advance concept in emergency relief system design will be adopted as much as possible. Dosing of catalyst by engineer should obey standard operation process. Enforced and intense training is needed to avoid near-miss accident or incident caused by human factor. Design of an ERS is necessary for a reactor in synthesizing BIBP.

4.4.3. Incident 4 (CHP reactor) (listed in Table 6)

Leaked solvent caught fire then caused thermal runaway and explosion in CHP reactor. Mechanical integrity is the most important issue in this incident. The adiabatic self-heat rate of CHP 30 wt% was determined to be $46.8^{\circ}\text{C min}^{-1}$ in Table 9. It means that the

runaway reaction in a CHP 30 wt% reactor is serious and emergency relief system cannot be enough to relieve the overpressure of reactor or handle the effluent of two-phase flow not to say under fire. A design of large vessel or reservoir is needed for receiving the ejected effluent from the opening in the bottom valve of reactor in case of the temperature of reactor is approaching temperature of no return.

4.5. Risk assessment and loss prevention

Effective and appropriate design and installation of emergency relief system (ERS) is the cardinal concept in risk assessment and loss prevention in a reactor containing or producing organic peroxide. ERS developed by DIERS plays a successful role in prevention and control the runaway reaction of a reactor associated highly exothermic, high liquid level, high pressure, high viscosity or flashing liquid systems. Delicate ERS can be achieved by the simulation by software package. Simplified ERS is the most popular method used by the engineers or researchers. Fauske had proposed the empirical formula or chart method associated with calorimetric data for vent sizing [32]. Besides, Leung created the analytical equation and omega-method for sizing the vent area for flashing or non-flashing two-phase flow [33]. The adopted viewpoint of safe handling a reactor accommodating organic peroxide is reappraised and depicted in Fig. 2. We summarized the simplified flow scheme for establishing the ERS for controlling the risk when the reactor is going to runaway. ERS for the reactor containing organic peroxide might be successfully designed in an inherently safer stage after following the steps of Fig. 3. Under such discipline, the achieved set of ERS was exaggerated to sizing of vent nozzle, evaluation of piping system, knock-out drum for separation of vapor from two-phase flow and disposal system handling vapors or gases in whole.

The pressure behaviors of organic peroxides during relieving might be tempered vapor, hybrid or gassy system occurred at the low, middle and high concentrations of organic peroxides. The very characteristics of pressure features and effluent behaviors in two-phase flow during venting or blow-down should be verified by bench-scale calorimeters. As usual, more conservative vent sizing and mass flow rate are considered for the reason of safety. For example, vent sizing calculation of a CHP 35 wt% reactor with volume 6 m^3 was implemented by Duh et al. [17]. The vent area was actualized by vapor and gassy limit systems to be 0.00055 m^2

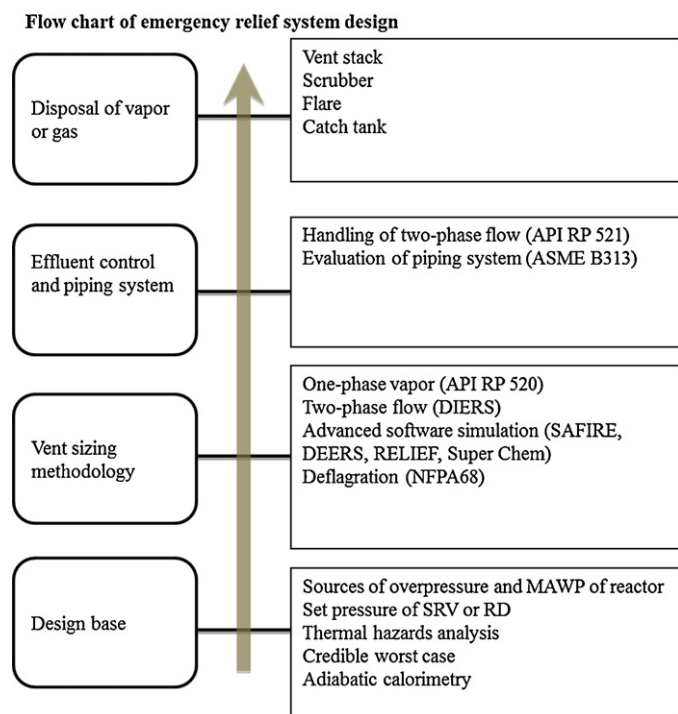


Fig. 3. Flow chart of emergency relief system design.

(equivalent to 2.65 cm in diameter (about 1–2 in.)) and 0.02 m² (equivalent to 16 cm in diameter (about 6–7 in.)) with a set point of 1.8 bar and 114 °C, respectively [17]. Moreover, Leung et al. conducted the vent area to be 0.0014 m² per 1000 kg TBHP (10 wt%) at relief set point of 6895 kPa and 172 °C under tempered system [34]. Through effective but not accepted worldwide, emergency handling procedures are urgently suggested in preventing runaway reaction and risk control in highly threatening organic peroxides reactors. Corrections or actions in process deviation before critical (or no return) point are based on the adiabatic runaway curve accompanied best preparation in advance.

Detailed calculation on vent area in the decomposition of CHP 35 mass% in cumene is given as follows. Table 11 displays the emergency relief conditions of a CHP 35 mass% tank [17]. CHP is widely used in Taiwan as an initiator in polymerization, especially for the copolymerization of acrylonitrile–butadiene–styrene (ABS). CHP is also used for producing phenol and acetone by acidic cleavage. It was produced by the oxidation reaction of cumene and oxygen in air. CHP was controlled at first stage from 20 to 35 mass% then for continuing concentration process. It may be further concentrated

to 80 mass% or reacted with inorganic acid to make phenol or dehydrated to be a dicumyl peroxide (DCPO). Decomposition of organic peroxide can release non-condensable gases and major component of CHP 35 mass% is cumene, the pressure behavior of CHP is a hybrid system. Decomposition of CHP 35 mass% is treated as a vapor system. Here, the Leung's ω -method was applied [33,34]. At the set point of pressure relief,

$$\omega = \alpha_0 + \rho_0 C_p T_0 P_0 \left(\frac{v_{fg}}{h_{fg}} \right)^2$$

$$\alpha_0 = 1 - \frac{m_0 v_f}{V_0} = 1 - \frac{(4162.05)(0.00108)}{6} = 0.25$$

$$\rho_0 = \frac{m_0}{V} = \frac{4162.05}{6} = 693.7 \text{ kg m}^{-3}$$

$$\omega = 0.25 + (693.7)(1790)(387)(1.8 \times 10^5) \left(\frac{0.14992}{348400} \right)^2 = 16.27$$

Mass flux was corrected by using empirical curve-fitted equation.

$$\frac{G}{\sqrt{P_0 \rho_0}} = \frac{[0.6055 + 0.1356 \ln \omega - 0.0131(\ln \omega)^2]}{\omega^{0.5}} = 0.219$$

That is

$$G = 0.219 \sqrt{P_0 \rho_0} = 0.219(1.8 \times 10^5 \times 693.7)^{0.5} = 2447.2 \text{ kg m}^{-2} \text{ s}^{-1}$$

Over-temperature

$$\Delta T = T_m - T_s = 150 - 114 = 36 \text{ K}$$

Average self-heat rate:

$$q = \frac{1}{2} C_p \left[\left(\frac{dT}{dt} \right)_s + \left(\frac{dT}{dt} \right)_m \right] = \frac{1790}{2} [0.002 + 0.033] = 31.325 \text{ J kg}^{-1} \text{ s}^{-1}$$

Mass flow rate:

$$W = \frac{m_0 q}{[(V/m_0)(h_{fg}/v_{fg})^{1/2} + (C_p \Delta T)^{1/2}]^2} = \frac{(4162.05)(31.325)}{[(6/4162.05) \times (348,400/0.14992)^{1/2} + (1790 \times 36)^{1/2}]^2} = 1.342 \text{ kg}^{-1} \text{ s}^{-1}$$

Table 11
Runaway and emergency relief conditions of a CHP 35 mass% tank [17].

	1.8 bar set	5.5 bar peak
v_f^a (m ³ kg ⁻¹)	0.00108	0.00108
v_g (m ³ kg ⁻¹)	0.151	0.151
C_p (kJ kg ⁻¹ K ⁻¹)	1.79	1.79
h_{fg}^a (kJ kg ⁻¹)	348.4	348.4
V	6 m ³	
m_0	4500 (L) \times $d = 4500$ (L) \times (0.35 \times 1.038 + 0.864)/(0.35 + 0.65) (kg L ⁻¹) = 4162.05 kg	
P_s	1.8 bar abs. = 1.8 \times 14.7 psia = 26.46 psia	
T_s	114 °C (387 K)	
$(dT dt^{-1})_s$	0.1 °C min ⁻¹ = 0.002 K s ⁻¹	
P_m	1.1 \times 5 bar (10% above MAWP) = 5.5 \times 14.7 psia = 80.85 psia	
T_m	150 °C (423 K)	
$(dT dt^{-1})_m$	2 °C min ⁻¹ = 0.033 K s ⁻¹	

^a Ideal gas assumed.

Vent area for emergency relief is then calculated to be $A = W/G = 1.342/2447.2 = 0.00055 \text{ m}^2$.

If a credible worst case with $(dT/dt) = 100^\circ\text{C min}^{-1}$, from the former vent area equation related to mass flow rate, vent area is directly proportional to vent area in CHP 35 wt% with a self-heat-rate of 10 times larger. Whenever the self-heat rate reaches $100^\circ\text{C min}^{-1}$ at credible worst case, vent area will be too large to be unacceptable for installation in the limited space on cover flange of reactor and disposal systems. Besides, the effectiveness of cooling capacity can be assessed by comparing the heat-generating power and heat removal by cooling system. Parameters of reactor and process conditions are adopted from the previous study [35].

$$\begin{aligned} Q &= \text{Heat generation rate} = m_0 C_p \left(\frac{dT}{dt} \right) \\ &= 4162.05 \text{ kg} \times 1.79 \text{ (kJ/kg K)} (\text{K}/60 \text{ s}) \\ &= 1.24 \times 10^7 \text{ W (CHP 35 wt\% in a } 6 \text{ m}^3 \text{ reactor),} \end{aligned}$$

$$\begin{aligned} \text{Cooling capacity} &= UA(T_m - T_c) = 581 \text{ W/m}^2\text{K} \times 40 \text{ m}^2 \\ &\times (150 - 20)^\circ\text{C} = 3.02 \times 10^6 \text{ W (Assume } U = 581 \text{ W/m}^2\text{K)} \end{aligned}$$

$A = 40 \text{ m}^2$ wet area of a 6 m^3 reactor,

$$T_m \text{ is reactant temperature at } \left(\frac{dT}{dt} \right) = 100^\circ\text{C min}^{-1}.$$

From the above evaluation, heat-generating rate is much larger than cooling capacity, the reactor is uncontrollable beyond the temperature of no return (T_{NR}) or is running away.

In addition to the vent sizing related to the runaway reaction, consideration of deflagration effect on pressure relief should be included in a reactor containing oxygen or organic peroxide. Oxygen as a reactant or came from the decomposition of peroxy group ($-\text{O}-\text{O}-$) is capable of deflagrating under some specified environments. NFPA (National Fire Protection Association) has regulated and issued the calculation of vent area to release the overpressure under deflagration phenomena. Relief of vapor deflagration or pressure propagation is treated in NFPA 68 [36]. Installation of a rupture disc is inevitable and necessary in an oxidation reactor to reduce the risk and consequence in the petrochemical industry. Fig. 2 depicts the suitable corrections or emergency actions in a runaway trace for risk management and loss control with respect to production process.

5. Conclusions

By the verifications and applications of the calorimetric data, these four incidents were attributed to either unexpected decomposition of organic peroxides, poor emergency relief system design or unqualified training of operation engineers. Consideration of safety distance, isolation of highly hazardous region, effluent control and emergency relief system were not conducted successfully in this plant which then suffered from these calamitous impacts and losses. More than one case can be avoided or prevented by better process safety management by adopting the API RP 520, API RP 521, DIERS technology, OSHA 1910.119 and AIChE's CCPS recommended PSM elements in advance. Especially, emergency relief system design is an excellent engineering practice for reducing risk in a chemical plant producing dangerously organic peroxide.

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