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Runaway reaction and thermal hazards simulation of cumene hydroperoxide by DSC

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Abstract

A simplified self-heating rate equation was developed to simulate the adiabatic thermal hazards of 88 mass% cumene hydroperoxide (CHP) in cumene. CHP has been predominantly used in producing phenol and acetone by catalytic cleavage and as initiator in the acrylonitrile–butadiene–styrene (ABS) copolymer polymerization process. In this study, we acquired experimental data, such as the heat of decomposition (ΔH_d) and exothermic onset temperature (T_0) by differential scanning calorimetry (DSC). The data were, in turn, used to simulate a runaway reaction and thermal analysis on 88 mass% CHP under various scenarios. The thermal safety software (TSS) series was employed to evaluate reaction kinetics, to simulate the runaway excursion of interest and to allow determination of critical conditions or thermal explosion of the tank. The liquid thermal explosion (LTE) model to simulate thermal explosion of CHP is aimed at ensuring safe storage or transportation. The reliability of both model simulations was assessed by experimentally comparing the thermal hazards with DSC. This simplified methodology is a sound, efficient tool for thermal hazards assessment of energetic chemicals.

Keywords: Simplified self-heating rate equation; Cumene hydroperoxide (CHP); Differential scanning calorimetry (DSC); Runaway reaction; Thermal explosion

1. Introduction

Organic peroxides which decompose exothermically demand intrinsically safer design during manufacturing preparation, transportation and storage, because they can release large amounts of thermal energy and result in high pressure during runaway excursion, leading to fire or explosion. Thermal explosions or runaway reaction accidents, as displayed in Table 1, caused by organic peroxides such as cumene hydroperoxide (CHP) have been important issues in the past four decades in Taiwan. Calorimetric and related methodologies for preventing thermal hazards of organic peroxides have been proposed (Duh, Kao, Hwang, & Lee, 1998; Wang, Shu, Duh, & Kao, 2001).

CHP has been broadly employed in the chemical industry and is easily recognized as a typical thermally unstable and hazardous substance. Numbers of thermal explosions have been induced by CHP on oxidation reactors or storage tanks in Taiwan. Exothermic runaway reactions may occur when impurities or alien materials are present in the reactors, storage tanks, or pipelines. During any stage, thermal energy could accumulate via self-acceleration decomposition or thermal polymerization, and is subject to various upsets or abnormal conditions, such as cooling failure, mischarging, over-dosing, or external fire exposure. Prevention of a runaway reaction is more important than any other protective insulation. This study simulated the thermal hazard characteristics of 88 mass% CHP via dynamic differential scanning calorimetry (DSC) thermal scanning experiments to predict the heat of decomposition (ΔH_d), exothermic onset temperature (T_0) and to simulate the adiabatic runaway behaviors.

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Nomenclature

A	frequency factor ($\text{sec}^{-1}\,\text{M}^{1-n}$)
A	vessel wetted surface area (m^2)
C_p	liquid specific heat at constant pressure ($\text{kJ}\,\text{kg}^{-1}\,{}^{\circ}\text{C}^{-1}$)
E_a	activation energy ($\text{kJ}\,\text{mol}^{-1}$)
K	pre-exponential factor (s^{-1})
k_i	reaction rate at stage i (s^{-1})
M	mass of reactant (g)
n	order of reaction
P_{max}	maximum pressure during overall reaction (psig)
$\dot{Q}$	heat flow ($\text{W}\,\text{g}^{-1}$)
Q	calorific capacity ($\text{J}\,\text{g}^{-1}$)
R	ideal gas constant ($8.314\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$)
$SADT$	self-accelerating decomposition temperature (°C)
T_A	final adjusted temperature (K)
T_{A_0}	initial adjusted temperature (K)
T_M	final measured temperature (K)
T_0	exothermic onset temperature (°C)
T_{M_0}	initial measured temperature (K)
T_{NR}	temperature of no return (°C)
T_{max}	maximum temperature during overall reaction (°C)
T_{wall}	temperature on the wall (°C)
TMR_{ad}	time to maximum rate under adiabatic system (min, h)
U	heat transfer coefficient ($\text{kJ}\,\text{min}^{-1}\,\text{m}^{-2}\,\text{K}^{-1}$)
ϕ	thermal inertia
$(\text{d}T/\text{d}t)$	self-heating rate ($^{\circ}\text{C}\,\text{min}^{-1}$)
$(\text{d}T/\text{d}t)_A$	actual self-heating rate ($^{\circ}\text{C}\,\text{min}^{-1}$)
α	degree of conversion
ΔH_d	heat of reaction ($\text{J}\,\text{kg}^{-1}$)
ΔH_{tot}	heat of decomposition via DSC trial ($\text{J}\,\text{kg}^{-1}$)
λ	heat conductivity ($\text{J}\,\text{ms}\,\text{K}^{-1}$)

In such a runaway situation, the underlying physicochemical properties lead to a self-heating rate equation profile. To calculate the adiabatic behavior, we used kinetic and thermodynamic data from a DSC experiment with the thermal safety software (TSS) series. A thermal hazards evaluation can be performed by a number of approaches. The approaches we applied are grouped into three categories: nomographs, detailed TSS model simulations and simplified analytical methodology. A computer model can trace the thermodynamic behavior of the system during the runaway stages that may occur in the vessel and the like. Nevertheless, by adopting a computer model, a large number of chemical and physical properties are necessary to describe the system during a runaway excursion. However, the simplified approaches provided an easier equation and demonstrated excellent results, which differ from the required results from the computer model.

For exothermic decomposition under runaway trajectories, the potential thermal hazards make it essential to comprehend the data of kinetic parameters, which are known or determined experimentally by the DSC. This study, as planned, combining DSC with the TSS software and a simplified analytical methodology, is both useful and available as well as cheaper and quicker. However, to date, the field of thermal hazards evaluation has been limited only to simulating the behavior of a runaway reaction. Our previous studies (Hou, Shu, & Duh, 2001; Wang, Duh, & Shu, 2006; Wang et al., 2001) attempted to evaluate thermal hazards of energetic chemicals, such as CHP by DSC and vent sizing package 2 (VSP2) experiments. Up to now, we have developed one simulated model, which fits the data from DSC thermal curves to a kinetic equation and to the TSS software, to demonstrate the severity of the hazards of CHP thermal decomposition.

Table 1
Selected thermal explosion accidents caused by CHP in Taiwan

Year	Chemical	Deaths/injuries	Hazard
1981	CHP	1/3	Explosion during storage
1986	CHP	0/0	Explosion in reactor
1999	CHP	0/0	Explosion in reactor
2003	CHP	0/2	Explosion in reactor
2005	CHP/DCP*	0/0	Release from reactor

*DCP, dicumyl hydroperoxide.

2. Experimental design and methods

2.1. Sample

A sample of experimental material, purchased from the Fluka Co., was analyzed directly: 88 mass% CHP with 12 mass% cumene. It was stored in a refrigerator at 4 °C. Density information was received directly from the Fluka Co. of about $1.038\,\text{g}\,\text{cm}^{-3}$. Table 2 displays the sample stability tests of 88 mass% CHP under β at $4\,^{\circ}\text{C}\,\text{min}^{-1}$ by the DSC. From Table 2, we used the DSC to test three 88 mass% CHP (β at $4\,^{\circ}\text{C}\,\text{min}^{-1}$). However, ΔH_d and T_0 from the DSC tests were determined to be about 105 °C and $1500\,\text{J}\,\text{g}^{-1}$, respectively.

Table 2
Sample stability of 88 mass% CHP under β at $4\,^{\circ}\text{C}\,\text{min}^{-1}$ by DSC

β ($^{\circ}\text{C}\,\text{min}^{-1}$)	Mass (mg)	T_0 (°C)	ΔH_d ($\text{J}\,\text{g}^{-1}$)	T_{max} (°C)	E_a ($\text{kJ}\,\text{mol}^{-1}$)
4	4.3	105	1490	186	187
4	4.4	104	1500	189	190
4	4.5	105	1513	190	193