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Runaway decomposition of dicumyl peroxide by open cell adiabatic testing at different initial conditions

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ABSTRACT

Low-thermal inertia experiments in the open cell configuration were carried out to perform a comprehensive sensitivity analysis of the parameters affecting the runaway self-decomposition of dicumyl peroxide (DCP). This study facilitates a better understanding on how concentration, initial back pressure, and fill level influence DCP runaway severity. The outcome of this experimental study was compared to previous adiabatic closed cell experiments, with the aim of clarifying the discrepancies reported in the literature and contributing to essential knowledge about self-decomposing peroxide systems.

Results showed that the detected onset temperature, maximum temperature, maximum pressure, and time to maximum rate are affected by the configuration of the equipment and initial back pressure of the experiments, while the adiabatic temperature rise did not seem to be affected. The roles that the kinetics, fluid dynamics, and thermodynamics play on these observations is addressed and discussed through the manuscript.

1. Introduction

Since the Bhopal disaster, runaway reactions have been extensively studied and many advances in terms of fundamental scientific understanding and changes to regulations have occurred (Saada et al., 2015).

Dicumyl peroxide (DCP) is extensively used in polymer manufacturing and petrochemical industries as a crosslinking agent, initiator, hardener and drying accelerator (Wu et al., 2006). However, its use entails an intrinsic hazard due to the presence of the highly unstable peroxy group (O—O bond); when enough energy is available, DCP will readily decompose. Its decomposition is highly exothermic and can lead to a runaway reaction, usually accompanied by a large and fast pressure rise (Hsu et al., 2012; Reyes Valdes et al., 2015a).

Process units in which this type of hazardous chemical are processed or simply stored, should be equipped with emergency pressure relief systems (EPRS), i.e., pressure safety valves—PSVs or bursting disks) (Center for Chemical Process Safety (CCPS), 1998) in order to minimise the possibility of equipment rupture and unplanned loss of containment. The design of the protective device(s) will depend on the nature of the system under runaway as well as their reliability (Stoessel, 2009). There are some cases, where EPRS, might not be suitable (*e.g.* fast reactions that generate gas at a very fast rate upon decomposition as in some batch polymerization

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Nomenclature

A	frequency factor [s^{-1}]
$C_{P\,cell}$	heat capacity of the cell and magnetic stirrer [$kJ\,kg^{-1}\,K^{-1}$]
$C_{P\,sample}$	heat capacity of DCP solutions in DIB and CUM [$kJ\,kg^{-1}\,K^{-1}$]
$\left(\frac{dn_G}{dt}\right)_{max,\varphi>1}$	experimental maximum gas generation rate [$mol\,min^{-1}\,kg^{-1}$]
$\left(\frac{dn_G}{dt}\right)_{max,\varphi=1}$	maximum gas generation rate (corrected by the phi factor) [$mol\,min^{-1}\,kg^{-1}$]
dP/dt_{max}	maximum self-pressurization rate [$bar\,min^{-1}$]
dT/dt_{max}	maximum self-heating rate [$K\,min^{-1}$]
$\left(\frac{dT}{dt}\right)_{\varphi>1}$	experimental self-heating [$K\,min^{-1}$]
$\left(\frac{dT}{dt}\right)_{\varphi=1}$	adiabatic self-heating (corrected by the phi factor) [$K\,min^{-1}$]
dX/dt	rate of reaction [$mol\,s^{-1}$]
E_a	activation energy [J/mol]
ΔH	enthalpy change [kJ/mol]
k	first order kinetic constant [s^{-1}]
m	mass [kg]
m_{cell}	mass of cell (including magnetic stirrer) [kg]
m_s	mass of solution [kg]
Δm	difference between initial mass of solution and final mass of solution [kg]
n	order of the reaction
Δn	moles of non-condensable gases formed [mol]
n_{final}	final moles of gases after cooling down [mol]
n_g	moles of gases at maximum dP/dt [mol]
$n_{initial}$	initial moles of gases inside the cell (air gas) [mol]
P	pressure [bar]
P_c	methane critical pressure 4.6 [MPa], 46.04 [bar]
$P_{initial}$	initial pressure before starting the experiment [bar]
P_{final}	pressure inside the test cell after cooling down [bar]
P_{max}	maximum pressure [bar]
ΔP_{max}	pressure build-up [bar]
R	universal gas constant [$J\,K^{-1}\,mol^{-1}$]
ΔS	entropy change [kJ/mol]
T	temperature [°C]
T_c	methane critical temperature [190.564 K]
T_o	onset temperature [°C]
$(T_o)_{\varphi=1}$	adiabatic onset temperature after phi factor correction [°C]
T_{MAD}	temperature of solution at maximum pressure rise [°C]
T_{max}	maximum temperature [°C]
ΔT_{ad}	adiabatic temperature rise [K]
T_r	ratio between temperature after cooling to critical temperature [dimensionless]
$(T)_{\varphi=1}$	adiabatic temperature after phi factor correction [°C]
TMR	experimental time to maximum rate [min]
X	conversion [dimensionless]
V_m	molar volume of the gas [$m^3\,mol^{-1}$]
φ	phi factor or thermal inertia factor [dimensionless]
ρ	density [$g\,ml^{-1}$]
ω	acentric factor methane 0.011 [dimensionless]

reactions) because the size of the relief device could be too large to be economically feasible. For such cases, other strategies such as prevention, quenching, inhibition, and dumping are used. Layer of protection analysis (LOPA) is also used in these cases to determine if the runaway likelihood may be reduced by adding additional layers of protection so that the runaway scenario is no longer is considered to be possible (Center for Chemical Process Safety (CCPS), 2011). LOPA can also be used to determine if adding other, or extra, layers of protection would be cost effective (Pasman and Rogers, 2013).

Based on the fact that, on an industrial scale, reactors and large storage tanks have a low-thermal inertia and they behave as an essentially adiabatic system when undergoing a runaway reaction (i.e., heat losses are negligible) (HarsNet, 2002; Varma et al., 2005), the existing methodologies for vent sizing calculation need experimental data obtained at laboratory scale by using adiabatic calorimeters (Etchells and Wilday, 1998; HarsNet, 2002). As these data are sensitive to the equipment and experimental configuration (Casson Moreno et al., 2015; Reyes Valdes et al., 2015a,b), the accuracy of the parameters characterizing a runaway system from laboratory scale experiments is a critical step in the vent sizing process (Fisher et al., 1992).

From a pressure relief point of view, when dissolved in a high boiling point solvent DCP has been classified as gassy system (mainly non-condensable gases are formed during the runaway) (Fauske et al., 1987); its main decomposition products are methyl radicals, acetophenone, and dimethylphenylcarbinol (Somma et al., 2011). This kind of system typically shows an untempered behavior during venting, i.e., the temperature continues to increase even after the relief operation (Véchot et al., 2008). Currently, there are very few experimental data available on the behavior of DCP during an uncontrolled runaway reaction (Reyes Valdes et al., 2015a; Wu et al., 2008, 2009; Hou et al., 2006) most of which were collected at low concentrations and by screening techniques, *e.g.*, small-scale isothermal micro-calorimeters or high-thermal inertia adiabatic calorimeters (Hou et al., 2006; Hsu et al., 2012; Wu et al., 2006, 2008, 2009).

The importance of experimental data obtained in low-thermal inertia equipment has been recently discussed by the authors (Reyes Valdes et al., 2015b) as well as the problem of collecting reliable experimental data for concentrated solutions of peroxide being tested in a closed cell configuration. As the gases formed during DCP decomposition can exert pressure on the test cell at very rapidly increasing rates, it may not be possible to obtain meaningful adiabatic experimental data at a significant concentration in closed cell configuration with a thin-walled, low-thermal inertia sample holder (unless the pressure compensation system capabilities are modified). Therefore, the use of the open cell configuration may be more appropriate as it helps to avoid bursting the test cell. In addition, the use of the open cell configuration reduces the solubility and non-ideal behavior of the generated gases (Singh, 1993).

In order to obtain data capable of simulating a real worst case industrial scenario, the runaway behavior of DCP was studied by performing low-thermal inertia experiments in an open cell configuration. DCP was dissolved in 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (DIB) at concentrations of 20%, 30% and 40% by weight. DIB was chosen as a solvent due to (1) its high stability within DCP runaway range of temperatures and (2) to have a comparable set of experiments with data reported in a previous study (Reyes Valdes et al.,