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Modeling of the venting of an untempered system under runaway conditions

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A B S T R A C T

The prediction of the consequences of a runaway reaction in terms of temperature and pressure evolution in a reactor requires the knowledge of the reaction kinetics, thermodynamics and fluid dynamics inside the vessel during venting. Such phenomena and their interaction are complex and yet to be fully understood, especially reactions where the pressure generation is totally or partially due to the production of permanent gases (gassy or hybrid systems). Moreover, these phenomena cannot be easily determined by laboratory scale experiments. In this paper, a dynamic model developed to simulate the behavior of an untempered reacting mixture during venting is presented. The model provides the temperature, pressure and mass inventory profiles before and during venting. A sensitivity study of the model was performed. This modeling work provides some insight regarding the interpretation of the data obtained from untempered system venting experiments. The outcome of this work contribute to improving the design of emergency relief systems for hybrid and gassy systems, where significant progress is still to be made in the experimental and modeling areas.

1. Introduction

The hazards associated with chemical reactivity are one of the main concerns in the chemical and petrochemical industries, where many manufacturing processes involve the transport, handling and storage of reactive substances. In 2001, in their report on "Improving Reactive Hazard Management", the US Chemical Safety Board (CSB) reported that 167 incidents involving reactive chemicals occurred in the US between 1980 and 2001, resulting in 108 fatalities. More recently, the ARIA French database (French Ministry of Ecology Energy Sustainable Development, 2001) operated by the French Ministry of Ecology, Sustainable Development and Energy indicated that between 2005 – 2010 in France alone, 352 incidents involved sites of polymer production and manufacturing of plastic materials and resins. In 24 of the incidents considered, one or more people were injured and in 2 cases there were 2 fatalities. 8 incidents resulted in significant economic losses and 6 led to the evacuation of the surrounding population because of toxic exposure.

One of the main hazards associated with the use of reactive chemicals is the loss of the thermal control of a chemical system, leading to a runaway reaction or thermal explosion. A runaway reaction is characterized by the exponential increase of the temperature and pressure in the vessel containing the reactive substance (Barton and Rogers, 1997; Crowl and Louvar, 2001). The consequences of runaway reactions include the initiation of undesired side reactions, the production and release of toxic and/or flammable substances and the potential explosion of the vessel. In 1995, Vilchez et al. reported that, out of 5325 incidents involving hazardous materials, thermal explosions are likely to occur mostly during transportation (39%), process (24%), storage (19%), and other operations (19%) (Vilchez et al., 1995). A relatively recent incident caused by a runaway reaction is the one that occurred at the T2 Laboratories, Florida, in 2007 resulting in 4 fatalities and 32 people injured (U.S. Chemical Safety And Hazard Investigation Board, 2009).

To manage the hazards associated with runaway reactions, a risk assessment of the process needs to be carried out and appropriate safety measures have to be selected, implemented and maintained. These measures include: (i) reduction of the hazards by inherently safer design; (ii) prevention of the runaway,

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and; (iii) mitigation of the consequences of a runaway. Emergency relief systems (ERS), such as bursting disks or relief valves, belong to the third category, and act as a last barrier of protection to prevent the explosion of the vessel. ERS are designed to open at a given pressure, P_{set}, and vent the gas/vapor evolved during the runaway reaction thereby protecting the equipment from overpressure. The methodologies for the design of ERS for reactive systems are quite complex and have mainly been developed by the Design Institute for Emergency Relief Systems (DIERS) (Fisher et al., 1992). According to the DIERS classification, a reactive system may be a classified as a *vapor system* when the pressure increase in the vessel results from the vaporization of its components. Vapor systems are "tempered" because the operation of the ERS will result in the removal latent heat of vaporization of the liquid mixture. This behavior allows the control of the reactive mixture temperature and the reaction rate. On the other hand, the reactive mixture may be a classified as a *gassy systems* when the pressure increase is due to the production of permanent gas only. Gassy systems are "untempered" because the operation of an ERS does not control the rate of temperature rise and thus the reaction rate. The ERS simply acts to relieve the pressure and remove material from the reactor. As the reactive mixture cannot be tempered after the ERS opening, the runaway reaction can reach its maximum rate with the associated maximum gas production rate. When both gas and vapor are generated simultaneously from the reactive mixture, the chemical system may be classified as *hybrid* and can exhibit an either tempered or untempered behavior.

While vapor systems have been extensively studied since the early 1980's by DIERS, there are currently very few experimental data and studies available on the behavior under runaway conditions of untempered systems (hybrid and gassy) during venting (Chi et al., 2009; Hou et al., 2012; Véchot et al., 2008; Véchot et al., 2011a; Wu et al., 2012b; Wu et al., 2012a). Most of the recent studies focus on peroxide decomposition kinetics (Di Somma et al., 2011; Iizuka and Surianarayanan, 2003; Levin et al., 2006; Marco et al., 2000; Tseng et al., 2011), the identification and experimental characterization of the thermal hazards and the prevention of the runaway (Casson et al., 2012; Casson and Maschio, 2011; Graham et al., 2011; Maschio et al., 2010; Tsai et al., 2012a; Tsai et al., 2012b; Tsai et al., 2012c; Wu et al., 2012b; Wu et al., 2012a).

Significant effort is still needed in the modeling of the behavior of untempered systems under runaway conditions during venting. This involve the understanding of the links between thermodynamics, kinetic and fluid dynamics inside the vessel from the onset of the runaway until the end of the venting. Such model would allow the prediction of the temperature and pressure profiles in a vessel before and during the operation of the ERS and could to be used for ERS sizing purposes and consequence analysis (Raimondi, 2007).

The work presented in this paper represents a step forward in this direction, as it proposes a dynamic model that simulates the behavior of a purely gassy untempered system in a reactor under fire load conditions during venting. Since many peroxide compounds exhibit an untempered behavior when undergoing decomposition (Leung and Fauske, 1987), the chemical reaction chosen for the simulation is decomposition of cumene hydroperoxide. The model predicts the liquid temperature in the vessel (T), the vessel pressure (P) and the vented mass to initial mass ratio ($\Delta m/m_0$) profiles before and during venting. A sensitivity study of the model variables to the following parameters is performed: initial fill level (fl), external heat input ($(dT/dt)_{fire}$), ERS area (A_{ERS}), secondary venting system area (represented by a permanent orifice, A_{or}) and vessel aspect ratio (D/H) and vessel volume (V).

2. Relevant parameters for a vessel before and after the opening of the ERS

In a closed vessel undergoing a runaway reaction, the pressure increase depends on the gas production rate and the available gas space in the vessel. In addition to a main ERS, vessels may also be equipped with secondary venting systems, such as pressure-vacuum relief valves, to reduce problems resulting from thermal effects, and filling/emptying processes. In this case, the pressure starts to increase only when the gas production rate exceeds the gas-venting rate through the secondary venting device. Thus, the presence of a secondary venting system affects the ERS opening time. Fig. 1 shows the relevant parameters that can influence the temperature and pressure rise in the vessel before the opening of the ERS.

Following the opening of the ERS, if two-phase venting occurs, the decrease of the liquid mass in the vessel, m, results in an increase of the thermal inertia, thereby influencing the temperature and ultimately the reaction kinetics. The pressure profile is more complex, and depends on various factors. The first of these, is the gas production rate, which is proportional to m, which in turn decreases when two-phase flow occurs. The second factor is the gas free space, which increases when two-phase flow occurs. The last factor is the venting rate, which depends on A_{ERS}, and the void fraction at the ERS inlet (α_{IN}). Whether the venting is one-phase or two-phase is determined by the level swell, which depends on gas density, the gas production rate, the liquid properties, and vessel geometry. These phenomena are linked in a complex manner. The maximum pressure (P_{max}) reached in the vessel is due to the coexistence of all these phenomena. When a gassy runaway reaction occurs, the vessel pressure is controlled by the volumetric gas generation rate that induces a pressure increase in the vessel and the volumetric vessel discharge rate through an ERS that causes a pressure decrease. The liquid temperature is controlled by the reaction energy release rate, the external heat exchanges and the thermal inertia.

The temperature and pressure profiles will depend on a set of parameters relative to the vessel configuration (V, D/H, A_{ERS}, A_{or}, insulation, cooling system, agitation), system conditions (fl, $(dT/dt)_{fire}$, P_{set}) and the chemical mixture (concentration, type of solvent or presence of catalyst). Fig. 2 shows the relevant parameters that can influence the temperature and pressure rise in the vessel after the ERS opening.

3. Model description

The model proposed in this paper solves the mass and energy balance for a cylindrical vertical vessel equipped with an ERS (bursting disk) and a secondary venting system represented by a permanent orifice (Fig. 3). The system under study is the decomposition of a solution of 80% cumene hydroperoxide (CHP) solution in aryl hydrocarbon (Li and Koseki, 2005). The model is limited to the description of purely gassy systems (untempered) for which the pressure increase is only due to the production of permanent gases. The effect of the latent heat of vaporization of the reacting liquid and product is therefore not considered to stay in the particular case of a purely gassy system. The addition of such effect in the model would indeed extend it to the study of hybrid systems.

The results of the simulations are the liquid temperature in the vessel (T), the vessel pressure (P) and the vented mass to initial mass ratio ($\Delta m/m_0$) profiles before and after the opening of the ERS. The detailed equations are reported below.

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