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Pressure relief sizing of reactive system using DIERS simplified methods and dynamic simulation method

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ABSTRACT

Incidents involving uncontrolled chemical reactions continue to result in fatality, injury and economic loss. These incidents are often the result of inadequate pressure relief system designs due to a limited knowledge of the chemical reactivity hazard. A safe process design requires knowledge of the chemical reactivity of desired as well as undesired chemical reactions due to upset conditions. Simplified, cost effective methods to relief system sizing are presented by The Design Institute of Emergency Relief Systems (DIERS). They require multiple experiments, and sizing is only valid for the system composition and thermal inertia represented by the small scale experiments. Results are often conservative, especially for gassy systems. Detailed, dynamic computer simulation is highly accurate and can be used for iterative design and multiple scenario evaluation.

In this study, an accelerating rate calorimeter (ARC®) and a low thermal inertia calorimeter (automatic pressure tracking adiabatic calorimeter – APTAC™) were used to collect chemical reactivity data for the dicumyl peroxide and toluene system. Results of the pressure relief system sizing using the dynamic simulation method are presented and compared with DIERS simplified methods.

1. Introduction

The detailed computer simulation methods described in the DIERS Project Manual Fisher (1992) and by Melhem et al. (1995), Melhem (1995), advocate a fundamental approach to pressure relief design, especially for a reactive system. In this approach, the reaction chemistry is qualified using small-scale experiments. A kinetic model of the system is developed, including an estimation of the vapor-liquid equilibrium of the reactants and products. Simulations of the full scale system coupling fluid dynamics are completed to design the pressure relief system. The method is highly accurate, can handle complex systems (Melhem et al., 1995; Melhem, 1995), and is valuable for sensitivity analysis (Melhem and Fisher, 1997) (i.e., iterative design and what-if analysis). The direct evaluation of the impact of temperature, pressure, composition, fill level, solvent boiling point, reduced charge, etc. can be simply and quickly completed. This detailed method also provides the necessary flow data for relief containment design (if required), structural support, etc. The dynamic simulation method does have limitations in that it requires thermophysical properties of many chemicals and chemical mixtures and an understanding of the vent flow regime. It is important to know the vent flow regime, which can be determined experimentally, in order to estimate the correct relief size. Reaction chemistry is difficult to characterize for many chemicals and mixtures because the individual components interact in complex ways. Thermophysical properties are either estimated using computational methods or measured experimentally. Estimating properties is not only time consuming but also requires expert skill. Townsend and Tou (1980) presented in detail how to estimate the kinetic parameters from the accelerating rate calorimeter experimental data. ICTAC (Vyazovkin et al., 2011) kinetic committee also provided recommendations for performing kinetic computations on thermal analysis. There are many reactive emergency relief system design computer programs including DIERS SAFIRE and the SuperChems™ component of ioMosaic Corporation's Process Safety Office™ software. Melhem and Fisher (1997) and Melhem et al. (1995) provided an overview of dynamic simulation method for emergency relief system and effluent handling designs using SuperChems.

The simplified analytical and direct scale-up methods explained in the DIERS manual (Fisher, 1992), while mostly applicable to non-reactive systems, are often applied to reactive systems (Fauske,

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1998a; Kurko, 2015; Leung and Fauske, 1987) because of their simplicity. The analytical methods described in Appendix VI-A of the DIERS Project Manual include FAI's (Fauske & Associates, LLC.) nomograph/analytical method and Leung's analytical methods (Leung and Fauske, 1987). The DIERS Project Manual also presents a direct scale-up method based on relief area to vessel charge scaling. This method is similar to the United Nations' method to determine the minimum required emergency vent area for tanks and intermediate bulk containers (IBC) for transporting organic peroxides (Hare and Adams, 2001; Poteet et al., 2002). The scale-up data, developed from analytical and direct-scale-up methods, is only valid for the system composition and thermal inertia represented by the small-scale experiments; the results are often conservative (especially for gassy systems), and the presence of long inlet lines and the impact of downstream equipment are not considered. Sensitivity analysis requires additional experiments.

Use of adiabatic runaway reaction test information in combination with computer simulation is a powerful method to design a pressure relief system when consideration of alternatives is required. It allows for quantification of rates of heat release and pressure and temperature changes in a variety of operating and upset conditions.

Once a chemical reaction model is developed, various design possibilities can be examined, for example operating temperature, feed rate, cooling capacity under upset conditions, heat loss, fire exposure heat flux, and fire exposure duration. A pressure relief system could be evaluated for relief device set pressure, vessel fill ratio, volatile solvents, relief valve vs rupture disc, vent piping, etc.

The detailed computer simulation method is a three step approach:

- Conduct a closed small-scale adiabatic test using accelerating rate calorimeter (ARC®) and/or automatic pressure tracking adiabatic calorimeter (APTAC™).
- Define reaction stoichiometry using measured vapor-liquid equilibrium and develop a reaction model that simulates the adiabatic test
- Simulate the actual full-scale vessel

1.1. Adiabatic calorimetry test

The accelerating rate calorimeter (ARC®) and automatic pressure tracking adiabatic calorimeter (APTAC™) generate data on the temperature and pressure response of the system to heating. This data forms the basis for development of the kinetic model and estimation of the vapor-liquid equilibrium.

The data sets from ARC/APTAC experiments provide a good understanding of the nature of the reactions involved. Key parameters obtained from the experiments include temperature and pressure profiles, reaction onset temperatures, heats of reaction, reaction kinetic parameters, and temperature and pressure rise rates of the exothermic reactions. The onset temperature and temperature rise rates measured are thermal inertia dependent and therefore are adjusted for thermal inertia correction before using them for relief size evaluation using simplified analytical methods. The onset temperature is also sensitive to self-heat rate of the system; therefore, it is always reported at a threshold heating rate as described by Townsend and Tou (1980) and in ASTM E1981 standard (Anon, 2004). The adiabatic temperature rise and heat of reaction estimates were made as per ASTM E1981 standard (Anon, 2004).

1.2. Reaction kinetics model development

A kinetic model is developed from the closed ARC/APTAC test data to find a good fit based on the measured data. The slope of temperature rise rate vs 1/T (ARC data set) is the activation energy, and its intercept is the pre-exponential factor as described by Townsend and Tou (1980), Vyazovkin et al. (2011), and Melhem et al. (1995). The heat of reaction is calculated from adiabatic temperature rise and heat capacity of the mixture. By selecting order of reaction, the thermodynamic properties of reactants and products in stoichiometric concentration, and applying kinetic parameters, a kinetic model is developed. The kinetic model fits the ARC experimental temperature and pressure history. SuperChems database has thermodynamic properties of >4500 chemicals. For a chemical not in the database, thermophysical properties are estimated using SuperChems property estimator.

1.3. Pressure relief system design

To complete the pressure relief system evaluation, simulations of the full-scale system are completed, using the kinetic model developed to fit calorimetry data. This model is applied to a full-scale system to simulate the system response under thermal runaway scenarios. Various pressure relief system designs can be evaluated until an adequate system is found.

1.4. Application to a 400 gallon reactor system

The reactor is 400-gallons with a rated MAWP (maximum allowable working pressure) of 58 psig at 400 °C. It is equipped with one top mounted rupture disc which is vented directly to atmosphere. As part of the operating procedure, 400 kg of 50% dicumyl peroxide in toluene solution is stored in the vessel at room temperature. The kinetic model developed from the ARC experimental data set is used for simulating this system. A significant amount of work on vent sizing has been done on neat dicumyl peroxide (Hare and Adams, 2001; Fauske, 2000), organic peroxide (Fauske, 1998b) and 40% dicumyl peroxide in diisobutyrate (Kurko, 2015).

Murphy (2012) conducted an adiabatic calorimetry study of dicumyl peroxide in a toluene system. Melhem et al. (1995) developed a reaction kinetic model and relief size predictions of this system. Singh and Murphy (2015) used calorimeter data generated by low thermal inertia calorimeter called automatic pressure tracking adiabatic calorimeter (APTAC) to estimate required relief area using DIERS analytical and direct scale-up methods. In all of these methods, sizing was estimated for both vapor and two phase flow regimes.

In this study, the required relief areas are estimated using a dynamic computer simulation program and the reaction kinetic model developed from an accelerating rate calorimeter (ARC®) test. The relief area was estimated for vapor and two phase (homogeneous and bubbly) flow regimes. These results are compared with the required relief area estimates using DIERS analytical and direct scale-up methods, earlier reported by Singh and Murphy (2015). Vent sizing results from the two methodologies are presented and compared.

2. Material and methods

2.1. Material

The adiabatic calorimeter test was conducted using dicumyl peroxide and toluene. Dicumyl peroxide 98% (CAS No. 80-43-3 and Sigma-Aldrich SKU 329541) and toluene >99.5% (CAS No. 108-88-3, Sigma-Aldrich SKU 244511) were procured from Sigma-Aldrich Corporation. Dicumyl peroxide was stored at refrigerated temperature (2–8 °C) and toluene at room temperature before use.

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