Evaluating relief events in binary mixtures with dynamic simulations

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ABSTRACT

Relieving rates in ethanol/water and ethylene glycol/water mixtures were investigated using dynamic models of an emergency relief scenario due to an external heat source. A commonly used shortcut method was compared to two rigorous calculation methods—one using ideal conditions and another using non-ideal conditions. In several cases, the shortcut method provides a reasonable estimate compared to the rate predicted by the more rigorous methods. However, in many cases the shortcut method over or under-predicts the required relieving rate—sometimes by a significant amount. Several discrepancies are also noted between non-ideal and ideal conditions. This study demonstrates that each multi-component mixture must be carefully considered before sizing emergency relief systems and devices.

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1. Introduction

Properly sizing emergency relief systems and devices is critical to ensure safe operation of a chemical production unit. A safety relief valve (SRV), rupture disc, and the inlet and outlet piping from the device must be properly sized to pass the maximum possible flow in the event of an emergency situation such as an external fire. Several investigators have studied many different relieving scenarios including two phase relief (Leung and Fischer, 1989; D'Alessandro, 2004a,b; Westman, 2008; Huff, 1985; Leung, 1996), runaway batch reactions (Leung, 1986; Brown-Brulant et al., 1995; Dellavedova et al., 2010), and pressure vessel blowdown simulations (Pokki et al., 2001; Mahgerefteh and Wong, 1999; Mahgerefteh et al., 2000, 2002). Multicomponent relief calculations are routinely performed in the chemical process industry and there are references to emergency relief systems in multi-component systems in the literature (Liptak, 2003). Other multi-component studies include cumene hydroperoxide/water (Sun et al., 2014), two-phase mixtures (Lenzing et al., 1998), methanol/acetic anhydride (Jiping et al., 2014) and various hydrocarbon mixtures (Raimondi, 2007). Leung and Fischer (1989) compared a shortcut method to a rigorous simulation in ethylene glycol/water and tertiary and quaternary mixtures with ethanol and methanol. This paper evaluates the same shortcut method, and a comparison to the Leung and Fischer study is included in the results discussion.

This study focuses on the dynamic behavior of a vessel containing a mixture while subjected to an external heat source (fire, failed steam or heat control valve, etc.). External fire scenarios are advantageous to study because they rarely produce two-phase relieving situations (Crowl and Louvar, 2011). Since heat is input via the vessel wall surface, vapor formation is limited to the vessel surface, which makes it difficult to entrain liquid. However, two-phase relief is possible in an external fire scenario, and liquid level is an important consideration to determine if two-phase relieving must be considered. The vapor flow rate generated by the heat source is required to determine the size of the relief device and inlet/outlet piping. As a result, the prediction of the vapor flow rate is the focus of this study.

Predicting emergency relief rates for single component systems is determined via Equation (1) if latent heat data for the pure species are available. The heat input (Q) can be determined by methods such as API 520 (2014). The same equation can be applied to multi-component systems; however, latent heat data may not be known. Additionally, the composition can change as one component is preferentially distilled from the system over time. Depending on the properties of the mixture, the vapor flow rate will increase or decrease as the composition changes. Therefore, a dynamic model should be used to determine whether the initial vapor flow rate is indeed the highest flow rate.

$$m_V = \frac{Q}{\lambda_{mix}} \qquad (1)$$

Dynamic models require a considerable amount of physical property and mixture data since the temperature and composition

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change over time. These models are computationally expensive due to iterative sub-routines; however, commercial options exist to perform dynamic relief models. Superchems (Melhem and Fisher, 1997) is a powerful software specifically designed to perform relief calculations and dynamic models. Other options include dynamic simulation engines like AspenBatch or AspenDynamics or model development with in-house software or code. In all cases, good data and ample set up time are required. Consequently, engineers employ shortcut methods to estimate the relieving rate of a mixture. While shortcut methods are convenient and easier to use than dynamic models, there are some pitfalls and shortcomings to their use. These methods also provide a single relieving flow rate at the initial condition. Since the composition of a mixture changes as heat is input to a system, the flow rate could increase if the heavier component has a lower heat of vaporization. For this reason, a combination of a shortcut method with a dynamic model should be considered.

A common method to calculate vaporization rates is applying Equation (1) assuming that the mixture heat of vaporization is a linear function of the component heats of vaporization, weighted by the vapor mass fraction. This estimation is shown in Equation (2). The vapor mass flow rate can then be calculated by Equation (1), which is similar to the method used to calculate the vapor flow rate in a pure liquid. This method makes several critical assumptions that may not be valid for every system: the solution is ideal (excess enthalpy or heat of mixing is negligible), the maximum vapor flow rate occurs at the onset of vaporization (i.e. time = 0), and all heat input leads to vapor generation.

$$\lambda_{mix} = \sum_i y_i^w \cdot \lambda_i \tag{2}$$

In this study, Ethanol/water and ethylene glycol/water mixtures were chosen because data are widely available (Curme, 1952; Fosbøl, 2008; Wang et al., 2013; Yaws, 2003), including specific heat: Ethylene glycol/water (Yaws, 2003; Nan et al., 2002; Stephens and Tamplin, 1979; Yeh et al., 1994), ethanol/water (Yaws, 2003), thermodynamic properties-including vapor liquid equilibrium (VLE) and Excess Functions: ethylene glycol/water (Gonzalez and Van Ness, 1983; Villamanan et al., 1984; Hortstmann et al., 2004; Nath and Bender, 1983; Lancia et al., 1996; Chiavone-Filho et al., 1993; Suleiman and Eckert, 1994; Kracht et al., 1999), and ethanol/ water (Larkin, 1975; Pemberton and Mash, 1978; Chaudhry et al., 1980; Kolbe and Gmehling, 1985a,b), and phase change data [ethylene glycol/water (Hortstmann et al., 2004)], [ethanol/water (Ambrose and Sprake, 1970)]. They are also industrially relevant mixtures (Curme, 1952; Chenier, 2002), and are miscible with water over the entire composition range. Ethanol and ethylene glycol differ by a hydroxyl functional group; however, ethanol has a normal boiling points below water's boiling point, while ethylene glycol's boiling point is above water's. Furthermore, both species have heat of vaporizations that are significantly less than water. These differences in physical properties yield markedly different vaporization behavior.

2. Model description

2.1. Test system description

The system shown in Fig. 1 is based on an actual 2000 gallon, closed-loop, ethylene glycol/water system that is used in a refrigeration application. The same system is used for the ethanol/water cases. The design basis for the relief rates is an external fire scenario where the heat flux into the vessel was determined using API 520 methods (2014).
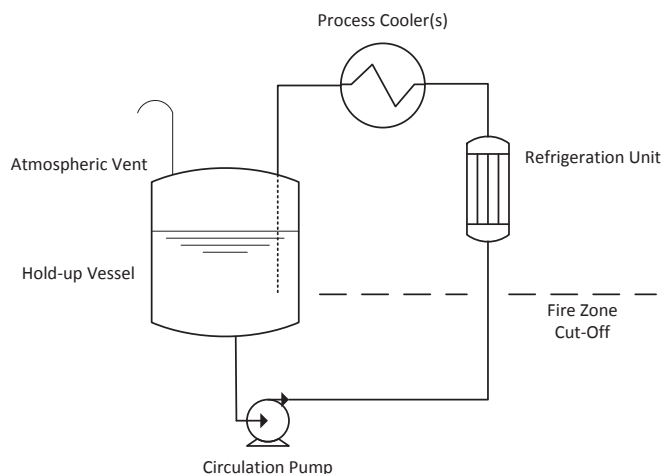

Fig. 1. Schematic of the equipment layout used in this study.

The heat input was assumed constant throughout the course of the model. This is a reasonable assumption if the wetted surface area is constant which occurs if a portion of the liquid level is outside of the fire zone. Most cases considered in this study used a heat input of 1 MW. In all but one case, the pressure was assumed constant at 1 atm (absolute). A case with 80 wt% ethylene glycol used 300 kW of heat input and a lower pressure to ensure temperatures were less than the available data range. The low pressure condition assumes the vessel relieves directly to the atmosphere with negligible pressure drop through the exit nozzle. In practical applications, the vessel may vent through an emergency header to an emissions control device or to the atmosphere at a safe location some distance from the vessel. The piping configuration determines the built up back-pressure on the vessel. In a multi-component mixture, the back pressure changes as the relieving rate changes over time since the discharge flow rate varies. The impact of the choice of relieving model on safety and economics will be discussed in a subsequent section.

2.2. Mass and energy balances

A vessel exposed to an external fire with a vent pipe is analogous to a single-stage batch distillation unit where the reboiler is replaced by the heat input from fire (or other excess heat source). The overall mass and energy balances for this system are described by Equations (3) and (4), and depicted in Fig. 2. A component mass balance is given by Equation (5). The volume balance provided in Equation (6) accounts for the effects of vapor and liquid volume changes (Lubbe and Kornelius, 1998). In a rigid vessel, the total volume is conserved, and liquid volume lost due to vaporization is
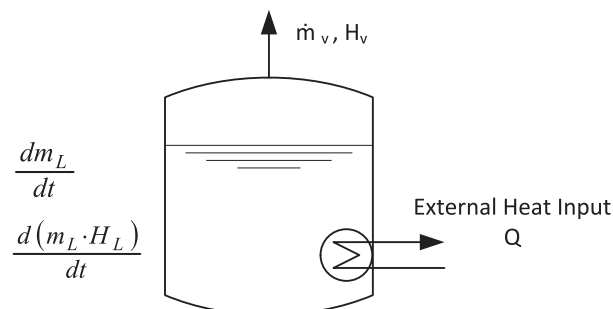

Fig. 2. Depiction of overall mass and energy balances.