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Modelling Transient Leaks of Multi-Component Fluids Including Time-Varying Phase Composition

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A fast time-varying discharge model with safety system capabilities has been extended to handle the accidental release of multi-component mixtures. Previously the model could only handle pure components or “pseudo-component” mixtures, but the new multi-component model carries out vapour-liquid equilibrium (VLE) calculations. This allows accurate predictions of the phase envelope between a mixture’s bubble point and dew point. In this region liquid and vapour compositions inside the vessel vary over time, as will the composition of material leaking into the atmosphere. The theory of the model is presented, and a case study illustrates the importance of rigorous multi-component modelling to get an accurate source-term description of releases of hazardous mixtures.

1. Introduction

Operations in the petro-chemical industry may involve accidental releases of hazardous materials from pressure vessels, and there is a need for mathematical models to characterize such events. Quantitative risk assessments (QRAs) often include variations in hole sizes, detection times and safety system behaviour, resulting in a very large number of release cases where the use of computational fluid dynamics models or process simulators may be prohibitively expensive. Consequently, simple steady-state or instantaneous source term models has traditionally been applied to characterize these accidental outflows in QRA studies. However, in reality source terms will often be highly dynamic, with reducing release rates as pressure drops and inventories reduce following the initial loss of containment. Furthermore the consequences of such a release may be mitigated by the operation of safety systems, including blowdown and isolation, and to evaluate their effectiveness it is crucial to include time-varying effects. To address these specific QRA needs, a new version of the time-varying discharge model, referred to as TVDI, has been developed for inclusion in the Phast (consequence) and Safeti (risk) software packages. A detailed description of this new model including verification and validation was presented by Stene et al. (2014).

While the TVDI model as presented by Stene et al. (2014) is appropriate for the release of single component materials, it relies on a “pseudo-component” (PC) approach for handling the outflow of multi-component (MC) mixtures. The PC approach is a commonly applied simplistic thermodynamic method for calculating vapour-liquid equilibrium (VLE). It is presumed that the multi-component mixture is thermodynamically equivalent to an imaginary single-component fluid whose saturation curve corresponds to the mixture ideal bubble point. Furthermore composition of all phases is constant and equal to the bulk composition of the mixture. However, the behaviour of the pseudo-component fluid may be significantly different from the actual mixture, especially for mixtures that include a wide range of volatilities. As such mixtures are common, the TVDI model has been extended to handle multi-component mixtures in a rigorous manner. A description and application of the extended multi-component (MC) TVDI model is the topic of the present paper.

Several methods for studying the rapid depressurization of pressure vessels containing MC mixtures have been presented in the literature, including the oft-cited BLOWDOWN model by Haque et al. (1992a,b). Recently D’Allesandro et al. (2015) presented VBsim, a model similar to BLOWDOWN. Common to both methods are that they aim to aid in the design of pressure vessels by carrying out very detailed analysis of wall and fluid temperatures during blowdown processes. In particular the focus is whether the wall temperature will fall below the ductile-brittle transition temperature of the vessel material. To enable such

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studies, non-equilibrium conditions between three distinct phases of vapour, liquid and water is considered with detailed heat transfer between fluid phases, vessel walls and the exterior also taken into account. In consequence assessment and QRAs, however, a large number of release cases are typically studied to characterize source terms for dispersion and fire calculations, where quantities like the mass flow rate is of key importance. Models like BLOWDOWN and VBsim may be more detailed than required in a QRA setting, thus possibly requiring excessive execution times. Consequently the MC TVDI model presented here includes simplifying assumptions tailored to have run times and robustness suited for inclusion in the Phast and Safeti software packages while still providing sufficiently accurate outflow predictions.

Modelling assumptions and governing equations of the new MC model are presented in Section 2, while applications and results are included in Section 3.

2. Model description

This section discusses key aspects of the MC TVDI model for the case of an accidental leak through a circular orifice of a pressure vessel. The model determines the transient storage (containment) and exit conditions. The contained fluid may be single phase or two-phase multi-component mixture, and homogeneous equilibrium is assumed within the containment throughout the release. The model is capable of simulating the simultaneous effects of production inflow and outflows (e.g. from connected pipework), blowdown, and isolation on the overall discharge process. The fluid phase approaching the orifice may be either vapour or liquid; the phase is determined by the transient liquid height in relation to the outflow height. The accidental leak calculations are split into two distinct stages: Firstly an expansion of the fluid from stagnation conditions within the vessel to the orifice (DISC model, Harper et al., 2014a), and secondly a final expansion from the orifice to atmospheric pressure (ATEX model, Witlox et al., 2014). Together with vapour-liquid equilibrium (VLE) and cubic equations of state, a complete description of the dynamic evolution of the vessel can be obtained, including time-varying compositions of vapour and liquid phases.

2.1 Governing equations - mass and energy balance

The control volume considered consists only of the fluid contained in the vessel and excludes vessel walls. Conservation equations for mass and internal energy are applied to this control volume, and a schematic overview of the inflows and outflows taken into account by the model is given in Figure 1. With regards to the mass balance, the adopted assumptions are as follows:

- Production flows: The model can account for fluid entering the vessel as a single production inflow with a user-specified, constant flow rate. In addition there is fluid leaving the vessel as a liquid production outflow and/or a vapour production outflow. These outflows are modelled dynamically with the flows stopping when the vessel pressure drops to a user-specified downstream pressure.
- Accidental outflow: The accident is modelled as fluid leaving the system through one single orifice, either as vapour or liquid, depending on whether the hole is located above the liquid level or below it. The multiple simultaneous leak locations shown in Figure 1 are only for illustration purposes.
- Safety systems: As a safety system measure, production inflow and outflows may be shut off at a user-specified isolation time. Furthermore, to reduce the pressure driving the accidental release, fluid may be evacuated from the vapour space through a blowdown valve with a user-specified diameter. This evacuation commences at a user-specified blowdown time.

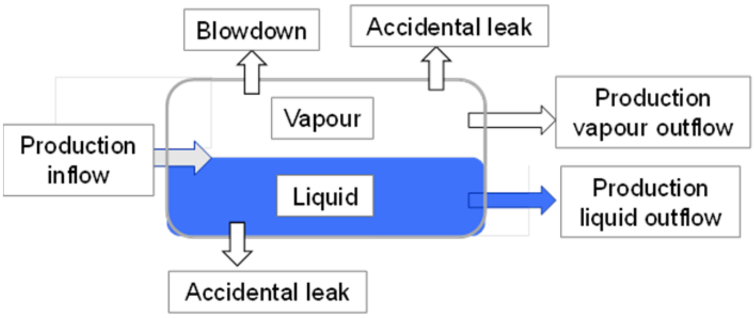

Figure 1: Control volume with the inflows and outflows taken into account in the multi-component TVDI model.

The mass of each component of the mixture in the system is tracked explicitly, resulting in *N* ordinary differential equations (ODE) for the mass balance of a multi-component mixture with *N* components. If we define X_i^{tot} , X_i^{liq} and X_i^{vap} as the mass fraction of component *i* in the total system of fluid, liquid phase and vapour phase, respectively, then the mass balance for the *i*-th component may be expressed as

$$\frac{dM_i(t)}{dt} = X_{t=0,i}^{tot}\ \dot{m}_{in} - X_i^{ph}\ \dot{m}_{acc} - X_i^{vap}\ \dot{m}_{BD} - X_i^{vap}\ \dot{m}_{out}^{vap} - X_i^{liq}\ \dot{m}_{out}^{liq}\ . \tag{1}$$

Here $M_i(t)$ is the total mass of component *i* of the mixture in the system at time *t*. The production inflow rate is denoted $\dot{m}_{in}$, while $\dot{m}_{out}{}^{vap}$ and $\dot{m}_{out}{}^{liq}$ is the production vapour and liquid outflow, respectively. Both the accidental flow rate $\dot{m}_{acc}$ and blowdown flow rate $\dot{m}_{BD}$ are calculated by utilizing the steady-state DISC sub-model at each time step. Note that the superscript *ph* is liquid, vapour or total phase depending on the leak location and fluid state.

With regards to the energy balance, the following assumptions are applied:

- Homogeneous equilibrium between phases as a single control volume
- Heat loss due to loss of fluid from production vapour and liquid outflows, accidental outflow, and blowdown outflow
- Heat gain due to production inflow
- No heat transfer between fluid and vessel wall
- Negligible potential energy and no external work is added to the system by e.g. pumps

The energy balance of the system may then be expressed in terms of an ODE for the total internal energy U, namely

$$\begin{aligned}\frac{dU}{dt} = {} & \dot{m}_{in}\ h\left(P(t=0), T(t=0); \eta_{in}^{liq}\right) - \dot{m}_{acc}\ h\left(P_{acc}, T_{acc}; \eta_{acc}\right) - \dot{m}_{BD}\ h\left(P_{BD}, T_{BD}; \eta_{BD}\right) \\ & - \dot{m}_{out}^{vap}\ h\left(P, T; \eta_{out}^{vap}\right) - \dot{m}_{out}^{liq}\ h\left(P_{st}, T; \eta_{out}^{liq} = 1\right)\end{aligned} \tag{2}$$

Here *P* is the vapour space pressure, *T* the uniform fluid temperature, *h* the specific enthalpy) and *η* the liquid mass fraction; all quantities relate to fluid entering/leaving the vessel. The superscripts (*vap*) and (*liq*) refer to production vapour and liquid outflow, respectively.

The internal energy of the system *U* is related to the system enthalpy *H* through pressure-volume work, and assuming constant pressure *P* throughout the vessel, we get the relation

$$H(P,T) = U(P,T) + PV\ , \tag{3}$$

where *V* is the vessel volume. Together with the vapour-liquid equilibrium assumption and an appropriate cubic equation of state, Eq(1), Eq(2) and Eq(3) are sufficient to solve for the *N*+3 main unknowns: the mass of each of the *N* components, M_i, the total fluid enthalpy *H*, the total fluid internal energy *U* and the system pressure *P*. From these all other quantities of interest (e.g. accidental flow rates, temperature, liquid volume, compositions etc.) can be determined.

Note that experimental evidence, e.g. Haque (1992b), indicates that the homogeneous equilibrium assumption strictly speaking is not valid. However, Cumber (2001) investigated the significance of this assumption and concluded that non–equilibrium effects only have minor impact on the mass flow rate predictions.

2.2 Vapour-liquid phase equilibrium

The thermophysical properties utilized by the MC TVDI model are obtained from the multi-component property system package described by Witlox et al. (2006) and more extensively by Harper et al. (2014b) . Key features of this MC property system are vapour-liquid equilibrium and cubic equations of state like Peng-Robinson and Soave-Redlich-Kwong. VLE calculations in the property system can accurately reproduce the behaviour of real hydrocarbon mixtures, including the phase envelope between a mixture's bubble point and dew point. In this region liquid and vapour compositions inside the vessel vary, as will the composition of any leak. This MC approach contrasts the simpler pseudo-component (PC) approach where the mixture is assumed to have a constant composition throughout the model and to behave like a single component. Not only does the MC approach give better characterization of the release than using a PC approach, but it also prevents users of the model from having to arbitrarily adjust storage conditions or compositions to get the 'correct' phase. The advantage of MC calculations is further demonstrated in the case study presented in Section 3.

3. Case study

In this section we will look at the accidental release of a hydrocarbon mixture from a pressure vessel. Three different modelling approaches for assessing this scenario are considered, and the section concludes with a comparison of the results from each approach, illustrating the importance of rigorous multi-component modelling. The MC TVDI results presented here are based on using ideal fugacities in combination with the Soave-Redlich-Kwong equation of state for a majority of the physical properties involved.

3.1 Accident scenario

Consider the accidental release of a hydrocarbon mixture through the orifice a 6.0 m high vertical cylinder that is 2.0 m in diameter. The mixture is stored at an absolute pressure of 68 bar and 80 °C and consists of methane, ethane, propane, butane and pentane in equal mass proportions, i.e. each component has a mass fraction of 0.2. This gives a total fluid mass of about 2302.5 kg, and Table 1 shows the vapour and liquid compositions and masses as calculated based on vapour-liquid equilibrium. Further assume that the fluid is stratified with vapour above the liquid, which yields a liquid level of 0.90 m. The accident scenario of interest is a leak from the vapour space through a circular orifice of 50 mm in diameter.

3.2 Three different modelling approaches

The first approach relies on pseudo-component logic where the mixture is assumed to have a constant composition throughout the model and to behave like a single component. In particular a saturation curve is applied, and at 68 bar and 80 °C this PC approach gives that all the fluid is stored as vapour. With the original vessel volume, this gives an initial vapour mass of 2444.3 kg, all of which in principle would be available to be expelled during the accidental release. Here the released vapour has a constant composition equal to the bulk composition of the mixture, and we refer to this approach as “PC bulk”.

The second approach is similar to the approach described above and is also based on PC modelling. However, an important modification is applied. The system is effectively redefined with the liquid removed and the vessel volume reduced accordingly, leaving an initial inventory of 1119.4 kg. The initial composition of the vapour corresponds to the phase split of Table 1, and remains constant thereafter. The released vapour has the same constant composition, and we refer to the approach as “PC vapour”.

The third and final approach we consider is to use rigorous multi-component modelling in form of the model previously presented in this paper. The model carries out a phase split with vapour above the liquid at the bottom of the vessel. Prior to the onset of the accidental leak the compositions of the phases are given in Table 1. As expected we see that the lighter components of methane and ethane dominate the vapour space, the heavier components butane and pentane dominate the liquid space, while the propane mass is fairly evenly split between the two phase. Since equilibrium is maintained between vapour and liquid in the vessel, as the release evolves the composition of the vapour space (and therefore the accidental outflow) changes.

3.3 Results comparison

This section compares some key results using the three different approaches for modelling the accident scenario set out in Section 3.1. Following the onset of the accidental leak at time t = 0 s, the pressure and temperature evolve as can be seen in Figure 2. The quickest depressurization is predicted by the PC vapour approach, while the slowest depressurization occurs for the PC bulk approach. The MC modelling predicts a pressure evolution in between the two PC approaches.

Table 1: Initial vessel mass and compositions given as mass fractions.

Mixture components	Vapour composition	Liquid composition	Vapour mass [kg]	Liquid mass [kg]
Methane	0.377	0.032	422.0	37.9
Ethane	0.305	0.101	341.4	119.5
Propane	0.190	0.209	212.7	247.2
Butane	0.090	0.304	100.8	359.6
Pentane	0.038	0.354	42.5	418.7

These trends can be explained by considering the initial vapour inventory. The PC vapour and MC approach both initially have 1119.4 kg of vapour in the vessel. However, since the MC approach considers liquid flashing off into the vapour space during the release, the pressure in the MC case will reduce more slowly than in the PC vapour case. The PC bulk approach starts out with 2444.3 kg of vapour, which is more than the entire vapour and liquid mass in the MC case, resulting in the slowest depressurization. By the time the vessels have depressurized and the release is over, the MC approach predicts temperatures more than 100 °C higher than the PC cases.

Figure 3 compares of flow rates and expelled masses of the different approaches. The flow through the orifice is largely pressure driven, and hence the trends for the flow rates mirror the trends observed for the pressure decay. Note though that the PC bulk approach gives a higher initial flow rate despite the initial pressure being equal in all cases. This is because the PC bulk approach initially releases a heavier mixture based on the bulk composition in contrast to the actual vapour composition released by the two other approaches. The total expelled mass for the two PC approaches is close to the respective initial vapour masses at the beginning of the release. The MC approach, however, predicts a total expelled mass just above 1500 kg while the initial vapour mass was 1119.4 kg. This means that about 400 kg of liquid has flashed off into the vapour space during the release, and the dynamics of this will be discussed further in Section 3.4.

We may conclude that the PC bulk approach seems to be too conservative. It releases all the mass as vapour despite that some of this mass in reality would be liquid and remain in the vessel, and the mass release rate is too high because of density effects and slower depressurization. The PC vapour approach which releases just the initial vapour mass ignores the effect of liquid flashing off into the vapour space during depressurization, and the resulting hazards are probably underpredicted. The most realistic predictions are likely provided by the MC model that is able to dynamically update the vapour and liquid phases throughout the release.

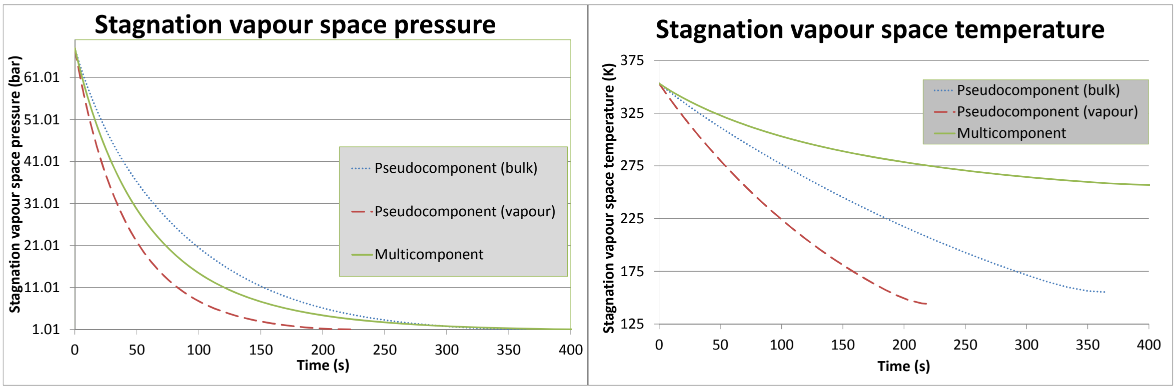

Figure 2: Pressure and temperature evolution of the fluid in the vessel during accidental release for the three different modelling approaches.

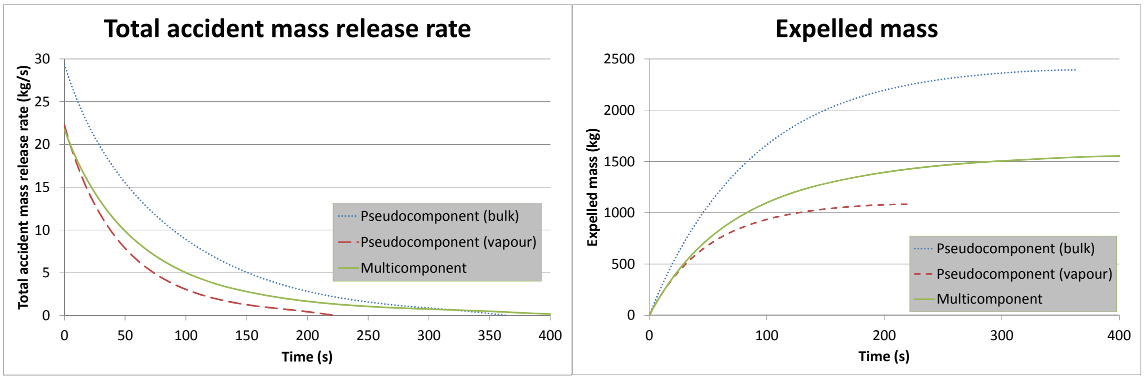

Figure 3: Mass release rate and total expelled mass during accidental release for the three different modelling approaches.

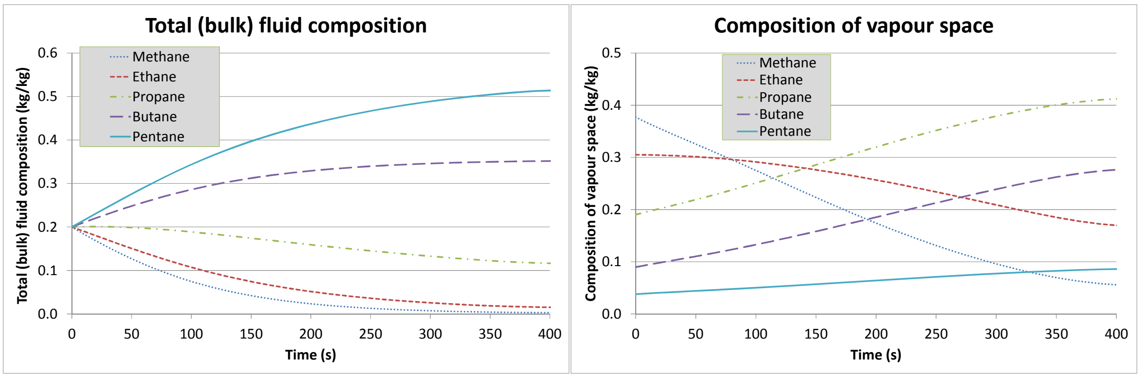

Figure 4: Composition of the bulk fluid and vapour space during the accidental release as predicted by the MC TVDI model.

3.4 Time-varying compositions

In Section 3.3 we saw how important it is to take into account liquid flashing into the vapour space to avoid underpredicting the hazards. Together with the accidental loss of vapour, this flashing liquid leads to the compositions changing over time as seen in Figure 4. Initially the released material is dominated by the light components methane and ethane, but the composition changes significantly over time and the molecular weight of the released vapour becomes much larger as the release proceeds. Capturing these variations in composition may be crucial from a hazards perspective as their effects on key physical properties (e.g. density, heat of combustion, LFL) can influence the outcomes of downstream flammable and toxic consequences of the release.

4. Conclusions

A multi-component time-varying discharge model, MC TVDI, for leaks from pressure vessels has been developed for use in consequence and quantitative risk assessments. The model is ideally suited to modelling accidental releases of hydrocarbon mixtures as the cubic equation of state methods used for the calculations are considered accurate for such mixtures. A case study with three different modelling approaches was presented and illustrates the benefits of MC modelling. Tracking transient phase compositions shows how potential hazards may change during release due to change in composition of the material being discharged.

It is hoped that further work will include comparison against other multi-component discharge models and against experimental data for mixture releases.

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