An Approach to Carbon Dioxide Particle Distribution in Accidental Releases

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The main problem in calculating the consequences of a carbon dioxide dispersion following an accidental release is the formation of solid CO_2 during the expansion to ambient pressure. The dispersion models more frequently used in the framework of quantitative risk analysis, cannot describe the carbon dioxide behaviour, in particular with respect to the calculation of the rainout fraction. Moreover, only scarce data is available for two phase CO_2 releases.

In the present study, a specific approach was developed to calculate the particle size distribution following the release of pressurized liquid (or supercritical) CO_2. The approach combines several sub-models accounting for the different mechanisms of jet break-up and specifically addresses the possible formation of solid particles. The model was validated using experimental data available for CO_2 and for the release of other pressurised, superheated liquids. The model developed can find further applications in rain-out calculations for two-phase releases of conventional substances.

1. Introduction

After the release of a liquefied, pressurised gas there is an expansion region where the out-flowing fluid is subjected to a very quick pressure drop to ambient pressure, causing a flash of the fluid. The result is a two-phase, turbulent jet of vapour and droplets. These droplets can eventually rainout to the ground and form a liquid pool. The amount of rainout and of airborne droplets is highly dependent on the droplet size distribution, as well as on other specific release features like release height, wind, temperature. Thus, droplet size distribution after flashing of the jet is an important parameter to take into account when modelling accidental releases. However, at atmospheric pressure CO_2 is only stable as solid and gas, instead of liquid and gas, so, once released, solid CO_2 directly transforms into gaseous CO_2 without forming a liquid. This changes the outflow process, i.e. solid CO_2 is formed instead of droplets during the flashing and the rain-out (when it is present) results in a solid CO_2 ice bank instead of a liquid pool. In the present study a model based on Monte Carlo simulations is presented for the assessment of the particle size distribution for pressurized liquefied gases, i.e. CO_2.

2. Physical background

When a liquid jet emerges from a nozzle as a continuous cylindrical shape, the cohesive and disruptive forces acting on the surface of the liquid create oscillations and perturbations. If the relative velocity or the density difference between the jet and the surrounding air are big enough, the oscillations are amplified and the liquid disintegrates into droplets. This phenomenon is known as primary atomization

and depends on the fluid properties, release pressure and orifice geometry and it is strongly enhanced by the effect of cavitations due to friction between the orifice wall and the liquid. If the diameters of the droplets exceed some critical dimension imposed by aero-dynamical stability, they will then disintegrate even further into smaller droplets. This process, called secondary atomization (Polanco et al., 2010), affects every single droplet in the jet and produces an aerosol of droplets with a wide distribution of different diameters. The mechanisms by which disturbances disintegrates droplets in a jet flow are two: aerodynamic break-up and thermodynamic break-up.

Aerodynamic break-up describes the break-up as a consequence of the susceptibility of the droplet to disturbances by the surrounding vapour flow. A detailed description of this phenomenon is reported by Kolev (1993). The ratio between disruptive drag forces and the cohesive surface forces is described by the Webber number (We):

$$We = \frac{\rho_{air} u^2 D}{\sigma} \tag{1}$$

Where σ is the surface tension, ρ_{air} is the air density, u is the relative velocity between the droplet and the gas in its surrounding and D is the droplet diameter.

Thermodynamic break-up is a process that occurs for substances that become superheated upon release to the atmosphere. The break-up of liquid droplets is due to a violent phase-change from liquid to vapour of a portion of the released substance. The amount of superheat determines the effectiveness of this mechanism. Many authors relate the thermodynamic break-up to the internal boiling of liquid droplets (Razzaghi, 1989; Shusser and Weihs, 1999; Zeng and Lee, 2007), but for consequence analysis only empirical correlations are available (van den Bosch and Weterings, 2005; Witlox et al., 2010). In the study by Witlox (Witlox et al., 2010; Kay et al., 2010) experimental results are analysed for different degrees of superheat showing three different regions: i) a region, called "mechanical break-up region", close to the normal boiling temperature of the substance where the droplet diameters are constant at high values and the influence of thermodynamic break-up is null; ii) a region at higher degree of superheat, called "transition to flashing region", where the droplet diameters decrease linearly with the temperature and the effect of thermodynamic break-up grows in strength with temperature; and iii) a region at very high degree of superheat called "fully flashing region" where droplet diameters do not reduce with temperature (Figure 1).
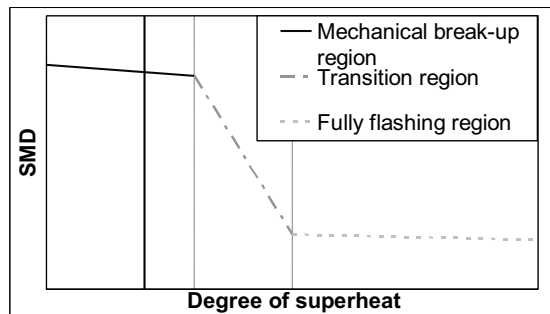

Figure 1: A qualitative view of the three regimes of break-up with the superheat degree (T-Tboil). SMD: Sauter Mean Diameter

Formation of solid particles is a phenomenon which is specific to the release of liquid CO_2. Most substances have a liquid-vapour equilibrium at ambient conditions and jet break-up results in the formation of liquid droplets. In contrast, CO_2 has a solid-vapour equilibrium at ambient conditions. This results in the formation of solid particles upon release to the atmosphere (Liu et al., 2010). The freezing of droplet implies a substantial diameter reduction. Thus, the prediction of particle size distribution in the break-up of a CO_2 jet resulting in the formation of solid particles needs to address three phenomena: break-up of the jet into many droplets, thermodynamic break-up of the droplets and formation of solids. In order to calculate the diameter distribution modification due to all the three

mechanisms a sample of initial droplet diameters is taken from a distribution of starting diameters by Monte Carlo method (Razzaghi, 1989).

3. Modelling

Following the approach of Razzaghi (1989), the thermodynamic break-up of the jet is considered as the product of the break-up of every single primary droplet in the jet. As this is a statistical process and no analytical relations can be found to describe these phenomena, a Monte Carlo method is used to model this step. It is assumed that the initial droplet distribution is due to aerodynamic break-up. This sub-model is deterministic and it is calculated with the method of Pilich (Pilich et al. 1987) for the maximum stable droplet diameter (D_{max}), but adapted for the calculation of the average diameter (D_{av}):

$$D_{av} = \frac{D_{max}}{v^3} = \sqrt{\frac{We_{crit}}{(1 - u_d/u)^2} \frac{\sigma}{\rho_{air} u^2}}$$
(2)

The initial diameter distribution is considered log-normal like with deviation v:

$$v = \left(\frac{We_{crit}}{(1 - u_d/u)^2} \right)^{1/6}$$
(3)

The result is a "primary" probability distribution function $f(D)$ for the droplet diameters.

$$f(D) = \frac{1}{D \log(v) \sqrt{2\pi}} \exp \left\{ -\frac{1}{2} \left[\frac{\log(D) - \log(D_{av})}{\log(v)} \right]^2 \right\}$$
(4)

When the primary distribution is defined, the Monte Carlo method starts calculating the break-up of a large number of randomly generated droplets that follows the "primary distribution". For each droplet selected, the method tests whether the droplet can boil or not. A minimum boiling temperature can be calculated as a function of diameter by the following expression (Razzaghi, 1989):

$$T_{min} = T_{boil} \left(1 + \frac{T_{boil} \Re}{L_v M} \frac{4\sigma}{D \rho_{liq} \Re T_{boil}} \frac{\rho_{liq}}{\rho_{vap}} \right) = T_{boil} \left(1 + \frac{1}{L_v M \rho_{vap}} \frac{4\sigma}{D} \right)$$
(8)

where T_{boil} is the bulk boiling temperature, M the molar weight, $\Re$ the gas constant, L_v the heat of vaporisation and ρ_{vap} the density of the substance in the gas phase. The process of boiling starts with the formation of a nucleus (bubble) inside the droplet. For this process a nucleation rate can be defined as follows (Zeng and Lee, 2007):

$$J = K \exp \left(-\frac{\Delta A_{max}^{*}}{k_B T} \right)$$
(9)

where J represents the number of nuclei generated per unit volume per unit time, k_B is the Boltzmann's constant and ΔA^{*}_{max} is the free energy of formation of the critical nucleus (or free energy barrier). Details for the calculation of K are reported in Zeng and Lee (2007). Due to the very small volume of a droplet and the very short time to reach the thermodynamic equilibrium, the model considers a nucleation probability, instead of a nucleation rate. The probability of nucleation ($\Gamma_{nucleation}$) in a given time t can be estimated as (Maris, 2006):

$$\Gamma_{nucleation} = 1 - \exp(-JVt)$$
(10)

where V is the droplet volume. Before the nucleation evaporation occurs at the outside surface, thereby causing the droplet temperature to decrease. The equations for mass and energy conservation can be summarised, assuming negligible heat exchange by thermal conduction with the surroundings, as:

$$\frac{dm}{dt} = \dot{Q}A \tag{11}$$

$$\frac{dH}{dt} = \dot{Q}AL_v \tag{12}$$

Where m is the droplet mass H is the droplet enthalpy, A is the total surface of the droplet and $\dot{Q}$ is the maximum evaporation flux given by the Hertz & Knudsen formula (Shusser and Weihs, 1999):

$$\dot{Q} = P^*_{sat} \sqrt{\frac{M}{2\pi\Re T_{sat}}} \tag{13}$$

Where P^*_{sat} is the vapour pressure, and T_{sat} is the equilibrium temperature with the outside pressure. The total droplet surface of outside droplet radius R_2 and bubble radius R_1 is:

$$A = 4\pi(R_1^2 + R_2^2) \tag{14}$$

Before nucleation R_1=0. The droplet temperature T_d is calculated by:

$$\frac{dT_d}{dt} = -\frac{\dot{Q}AL_v}{mCp_L} \tag{15}$$

where C_{pL} is the specific heat of the liquid and L_v is the latent heat of evaporation. When nucleation has occurred, the bubble inside the droplet grows at a constant radial velocity estimated by (Shusser and Weihs, 1999):

$$\frac{dR_1}{dt} = \frac{2}{3}\frac{\dot{Q}}{\rho_{liq}}\frac{\Re}{M}T_{sat} \tag{16}$$

The external radius of the droplet is calculated by mass conservation:

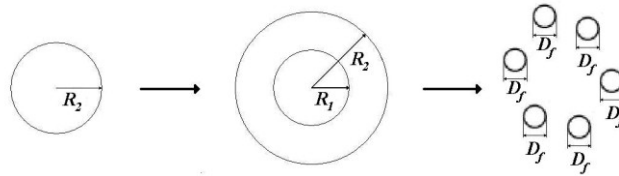$$R_2(t) = \left[\frac{m(t)}{4/3\,\pi\rho_{liq}} + R_1(t)^3\right]^{1/3} \tag{17}$$

Figure 2: the initial droplet, bubble growth and droplet blasting

The bubble continues to grow until the outside radius of the complete droplet has reached a critical value, i.e. the double of initial diameter. When this value is reached, the droplet blasts into several parts (secondary droplets). A random number between 1 and 10 is used to determine the number of resulting droplets (Figure 2). These droplets all have the same volume and their diameter is calculated by mass conservation. All these droplets are checked against whether their temperature is high enough to be able to boil again (Razzaghi, 1989) and eventually the algorithm for boiling will start over. When the temperature of the droplets is below the minimum boiling temperature, T_{min}, the nucleation of bubbles is no longer possible and no more boiling can occur. To reach the thermodynamic equilibrium temperature at ambient pressure, the droplets cool down by vaporization at the external surface. This process reduces the droplet diameter and the final diameter is expressed by the following equation:

$$D_f = \left[D_{in}{}^3 \, \frac{\rho_l(T_{in})}{\rho_l(T_{boil})} \, \frac{\left(L_v(T_{boil}) - Cp_L(T_{in} - T_{boil}) \right)}{L_v(T_{boil})} \right]^{\frac{1}{3}} \qquad (18)$$

In case of transition to solid phase the droplets cool down by the effects of vaporization, solidification and sublimation; the result is a stronger diameter reduction:

$$D_f = \left[D_{in}{}^3 \, \frac{\rho_l(T_{in})}{\rho_s(T_{boil})} \, \frac{\left[C_{p,L}(T_{in} - T_{tp}) - L_v(T_{tp}) - C_{p,v}(T_{boil} - T_{tp}) \right]}{\left[(C_{p,s} - C_{p,v})(T_{boil} - T_{tp}) - L_s(T_{tp}) - L_v(T_{tp}) \right]} \right]^{\frac{1}{3}} \qquad (19)$$

Finally the droplet diameters obtained are arrayed to form a diameter distribution.

4. Results

The model has been tested for a water jet with 8.2 bar and 140 °C as initial conditions. The resulting particle size distribution is represented in Figure 3a; the dark line represents the primary droplet distribution and the light line represents the final droplet distribution after all droplet have boiled and evaporated. The Sauter Mean Diameter (SMD) for the initial distribution is 1048 µm and for the final distribution it is 66 µm. Figure 3b shows the obtained of the Sauter mean diameters for water at different initial temperatures (reported as superheat degree) at the same release pressure (8.2 bar). In Figure 3b the three regimes of break-up are well visible.
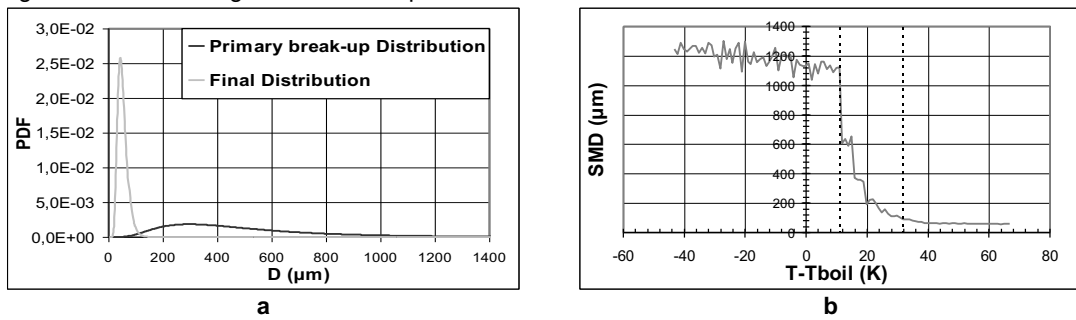

Figure 3:a-water droplet diameter primary and final distributions produced in a 8.2 bar and 140 °C release; b-water SMDs produced at 8.2 bar and different superheat degree

The result of this algorithm for a typical liquid CO_2 release at 100 bar and 290 K is the particle size distribution shown in Figure 4. The initial (primary) diameter distribution is represented by the dark line and the final diameter distribution by the light line. For this specific release, boiling does not occur, because the initial droplets are so small that they cool down due to evaporation before the nucleation takes place. The difference between primary and final droplet sizes is simply due to evaporation and solidification. The final SMD is 3 µm; this value indicates that CO_2 particles are too small to rain-out.
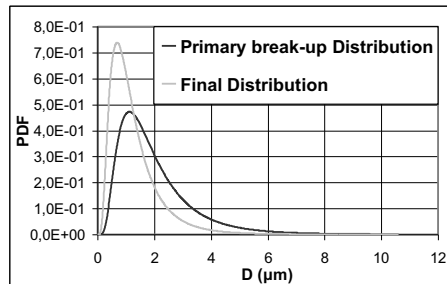

Figure 4: CO_2 droplet diameter primary and final distributions produced in a 100 bar and 290 K release

Since no specific experiments are available in the literature for carbon dioxide particle size determination the model has been validated for common pressurized liquefied gases and pressurized superheated liquids. Most of the simulations show SMDs within a 30 % difference from the corresponding experimental measurements.

5. Conclusions

A model for the formation of droplets and solid particles is presented. The model can be applied to any liquid or two-phase outflow and is also able to describe solid particle formation. All three break-up regimes: aerodynamic break-up, flashing break-up and the transition regime are taken into account and may be reproduced. The model provides the droplet size distribution. The final solid particle size from a dense phase CO_2 release in common transport conditions is of the order of a few microns. This result corresponds to experimental results and validates the assumption concerning the absence of solid CO_2 rain-out to the ground, frequently introduced in previous studies.

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