Intentional Or Accidental Spills Of Hazardous Materials In Harbours Areas: Evaluation Of Critical Distances From Sensible Targets

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1. Introduction

The ever increasing volume of globalized port trade poses a particular security threat, in the post 11th September 2001, connected to possible major spill caused by intentional act. The consequence severity from hydrocarbon releases in open sea, or in port areas are very different. In the former case, the expected effects are normally connected to the environmental impact and the most effective protective actions, as release containment and recovery are mainly based on the knowledge of the long time evolution of the oil spot. In the latter case, besides the environmental effects, the most severe consequences can derive from the development of flammable and/or toxic clouds, due to hydrocarbon vaporization. Specific safety measures are to be adopted, based on the knowledge of the extension of the risk area, so as determined from the relatively short time evolution of the cloud. Toxic effects are mainly due to the duration and mean concentration of human exposure to the volatile pollutants, whilst the flame development is related to the instantaneous concentration of the cloud coming in contact with an ignition source. Both in case of toxic and flammable releases, the knowledge of the space and time distribution of the concentration of the hydrocarbon vapours in the cloud is needed, in order to plan proper safety actions. Among these, one can distinguish: prevention measures, aimed at reducing the accident frequency, e.g. the study of ship courses, suitable procedures for maintenance and control, and so on; protection measures addressed to mitigate the consequences of the dangerous events, e.g. division of tank in watertight compartments, hole repair, suction and partial recovery of oil from the tank and/or the spot, mechanical containment and/or sorption of spot, reduction of evaporation rate of the hydrocarbons by foaming and possibly freezing the liquid surface, warnings and evacuating the risk areas. Moreover, a detailed response plan, that address a “worst case discharge” is an essential requirement, especially foreseeing the possibility of deliberate attack in port area. This paper is focused on cloud evolution and on the safety, or critical distances of sensible targets from the release location, so to avoid ignitions, explosions and serious toxic effects. Since the evaporation rate plays a fundamental role in determining the level of risk, an in-depth discussion is devoted to the main parameters related with it, i.e., spot extension and heat exchange with the environment, wind speed, molecular and atmospheric turbulent diffusion.

2. Theory

In the most general case, an accidental release in a port area originates an oil spot, a relatively dense cloud and a passive plume. The hydrocarbons can be released partly instantaneously and partly according to a continuous flow-rate; moreover, they can directly split into the different sub-systems (liquid spot, cloud and plume) since both liquid and vapour phases could be involved in the release. Considering the rate of hydrocarbon mixing, evaporation and transport into the passive plume, due to the atmospheric turbulence, starting from the set of boundary conditions, the material balances can be solved to map the risk areas. Usually, only numerical solutions can be obtained, since the flow rates generally vary with the time, in connection with release and weather conditions and with the geometrical parameters characterizing each particular situation. The accomplishment of the safety actions further complicates the problem, by putting additional terms and/or modifying some of the flow-rates in the material balances. As an example, repairing the tank damage stops the release before the tank emptying, suction of the hydrocarbons from the tank reduces the mass and duration of the release, spot containment hinders the oil spreading and then the rate of evaporation, and so on. Different scenarios are to be considered, after the occurrence of the spill.

2.1 Instantaneous releases of liquid hydrocarbons at normal boiling point T_b, windy conditions.

As well known, the accidents involving pressurized and refrigerated liquid hydrocarbons generally involve the maximum risk levels. Indeed, a considerable part of the release almost instantaneously vaporizes, giving rise to a dense cloud, where the hydrocarbon concentration normally exceeds the dangerous levels and a liquid spot, both at normal boiling point. In such instances, the only effective safety action near the release is limited to avoiding the contact of the cloud with the target and must be realized in very short times. As regards toxic effects, it is required at least the immediate availability of breathing masks and/or air-tight shelters, whereas the risk of fires and explosion can be avoided only in absence of ignition sources. Far from the release, the extent of the risk areas is mainly determined from the meteorological conditions. Usually, under the wind action, the quasi-instantaneously developed cloud is transported and diluted more and more, down to non-dangerous concentrations. Various mathematical models (e.g., Elliott, A.J. and Hurford, N., 1989) are available in literature to calculate the behaviour of vapour concentration and to map the risk areas. Even at some distance from the release, relatively short time are available in windy conditions to put in action typical safety measures, e.g. sheltering or evacuation in the case of a toxic cloud. In this case, the most effective protective action consists in planning and designing ship courses and docking points conveniently far from sensible targets, so to avoid possible domino effects.

2.2 Continuous releases of hydrocarbons at T_b and instantaneous or continuous releases of hydrocarbons far from T_b, windy conditions.

In the situations here considered, the behaviour of the release is initially dominated by the spreading of the liquid spot on the sea. Increasing the spot area, the evaporation rate also increases. Then, the volume of a spot deriving from an instantaneous release decreases with time, down to vanish. On the other hand, a continuous release of liquid hydrocarbons gives rise to a liquid volume increasing as long as the evaporation rate does not exceed the source flow-rate, later it again reduces down to zero. Owing to windy conditions and to the absence of an initial cloud, it is reasonable to assume that the hydrocarbon vapours deriving from evaporation and those directly released be immediately transported in the plume, without formation of a significant dense cloud. In the model developed in section 3, specifically tailored on these situations, the phases of liquid spreading, evaporation rate and cloud dispersion will be considered.

2.3 Still air conditions.

Whatever the kind of release may be, in the case of absence of wind and atmospheric stability, typical nightly meteorological conditions, owing to spot evaporation, the cloud continuously grows and spreads on the sea, even attaining the entire port area if no corrective action is performed. Changing meteorological conditions, for example following sun rise, a great mass of hydrocarbons can be transported in short time by the wind, originating a cloud even more dangerous than the instantaneous one. The description of these situations requires to take into account also the spreading of the dense cloud. However, in opposition to the previous case, relatively long times are available and different safety measures can be established to reduce the risk into acceptable levels, just because the growth of the cloud in still air is usually very slow, so that the probability of the aforesaid extreme situations can reasonably be excluded.

3. Modelling

The here considered scenario considers accidental/intentional continuous or instantaneous release of a liquid hydrocarbon at a temperature below its T_b, in standard environmental conditions (wind velocity at 10 m, $u_{10} \geq 2$ ms^{-1}). The purpose is to allow developing a quantitative risk analysis and in particular to evaluate safety distances of sensible targets from the release location, so to avoid ignitions, explosions and serious toxic effects. These distances depend on factors determining the spill rate (release time, release volume or volumetric rate), on physical properties of the release (normal boiling point, density, thermal conductivity, heat of vaporization, vapour pressure, molar mass, LFL etc.), on physical conditions of the atmosphere (stability class, ambient temperature, wind speed, solar radiation etc) and on conditions of the water body (water temperature, density, tide/current etc). In the following, reference will be made to the most common situations in terms of weather combinations (atmospheric stability and wind speed, current absence and calm/smooth sea).

The behaviour of the liquid phase had been studied in a previous work, by means of a conservative approach (Palazzi et al, 2004). The most interesting results, summarized in the following, are the attainment of the values of the maximum hazardous area A_{LM} and of the liquid volume, in connection with the different release scenarios: instantaneous or continuous release. In case of instantaneous release, of a volumeV_{L0} = Vr, it results:

$$t_{ALM,i} \cong 1.5 V_{L0}^{1/4} \left(\alpha_{sL}\alpha_{vap}\right)^{-1/2} \tag{1}$$

$$A_{LM,i} = \left(\frac{4}{3}\frac{\alpha_{sL}}{\alpha_{vap}}\right)^{1/2} V_r^{3/4} \tag{2}$$

When dealing with a continuous release lasting a finite time t_c, it is convenient to calculate the liquid spill rate (defined as “critical spill rate”) in correspondence of which the release ends exactly at the time t_{ALM} when the slick area reaches its maximum value:

$$\frac{V_r}{\dot{V}_L^*} = t_r^* = t_{ALM,c}^* = 2.8 \dot{V}_L^{*1/3} \left(\alpha_{sL}\alpha_{vap}\right)^{-2/3} \tag{3}$$

The slick parameters can be obtained as a function of V_r:

$$\dot{V}_L^* \cong 0.46(\alpha_{sL}\alpha_{vap})^{1/2} V_r^{3/4} \tag{4}$$

$$t^*_{ALM,c} = t_r^* \cong 2.2(\alpha_{sL}\alpha_{vap})^{-1/2} V_r^{1/4} \tag{5}$$

$$A^*_{LM,c} = 2\frac{\dot{V}_L^*}{\alpha_{vap}} \cong 0.92\alpha_{sL}^{1/2}\alpha_{vap}^{-1/2} V_r^{3/4} \tag{6}$$

By comparing eq. (2) with eq. (5) and eq. (1) with eq. (6), respectively, one can observe that $A^*_{LM,c} \approx 0.80\ A_{LM,i}$ and $t^*_{ALM,c} \approx 1.44\ t_{ALM,i}$. According to this approach, the vaporization rate was calculated as a function of wind velocity only.

3.1 Model development

In this work, we consider the heat balance too, being the previous approach strictly valid only for substances of low saturation pressure and low latent evaporation heat (Flothman et al., 1980). In order to evaluate the specific vaporization rate, we assume steady-state conditions, so that the specific evaporation velocity due to heat exchanges is equal to the specific vaporization velocity due to atmospheric diffusion and transport: $\dot{m}''_{vap,q} = \dot{m}''_{vap,u}$, being

$$\dot{m}''_{vap,q} = M\frac{\dot{q}''_r + h_w(T_w - T) + h_a(T_a - T)}{\Delta\tilde{H}_{vap}} \tag{7}$$

$$\dot{m}''_{vap,u} = h_u y^0 c M \tag{8}$$

Considering that, according to the Watson relation the depedency of the enthalpy of vaporization can be expressed by: $\Delta\tilde{H}_{vap} = \Delta\tilde{H}_{vap,b}\left(\frac{T_c - T}{T_c - T_b}\right)^{0.38}$ (Watson, 1943), assuming, $h_u = h(u) = 2.35u^{0.85}$ (Pinho, 2002) utilizing the classic simple Antoine equation for correlation of vapour pressure as a function of temperature: $p^0 = \exp\left\{A - \frac{B}{C+T}\right\}$, it follows: $\frac{\dot{q}''_r + h_w(T_w - T) + h_a(T_a - T)}{\Delta\tilde{H}_{vap}} = h_u y^0 c$ (9)

A numerical solution of eq. (9) allows obtaining T and then the corresponding specific vaporization rate $\dot{m}''_{vap}$. We must observe that, as u increases, the temperature of the evaporating liquid decreases, so that the enhanced heat exchange can increase the vaporization rate (heat exchange controlling conditions). At low wind velocity, especially when $T_w <<< T_b$ (and in connection with high solar heat flux), liquid temperature and evaporation rate may increase above the initial values (Flothman et al., 1980), so that a more concentrated vapour can be transported by the wind. In this case, atmospheric dispersion is the rate limiting step. In the situations considered in this work, temperature T corresponding to the equlibrium described by eq. (9) is rather proximate to T_w, so that, by means of its linear interpolation, aT + b, in the range of temperature $T_w - 10 < T < T_w$, it is possible to approximate the expression: $y^0(T)c(T)\Delta\tilde{H}_{vap}(T)$. The linearization assumption allows the attainment of conservative results, connected to an over-estimation of the vapour fraction, in the range of temperature considered.

Under the above-mentioned hypothesis, it results:

$$T = \frac{\dot{q}_r'' + h_w T_w + h_a T_a - b h_u}{h_w + h_a + a h_u} \qquad (10)$$

$$\dot{m}_{vap}'' = \frac{M h_u}{\Delta \widetilde{H}_{vap}} \frac{a(\dot{q}_r'' + h_w T_w + h_a T)_a - b(h_w + h_a)}{h_w + h_a + a h_u} \qquad (11)$$

$\Delta \widetilde{H}_{vap} = \Delta \widetilde{H}_{vap}(T)$ is the latent heat of vaporization at the resulting temperature.

In order to evaluate the mass flow rate of the emission, under the hypothesis of neglecting possible saturation effect, one can write: $\dot{m}_{val,\max} = \dot{m}_{vap}'' A_{\max}$. The above-mentioned hypotheses allow the attainment of conservative results.

4. Results and discussion

When dealing with an instantaneous release, which is the most common scenario when dealing with intentional risk, $A_{\max} = A_{LM,I}$, so that it results:

$$\dot{m}_{val,\max} = \frac{M h_u}{\Delta \widetilde{H}_{vap}} \frac{a(\dot{q}_r'' + h_w T_w + h_a T)_a - b(h_w + h_a)}{h_w + h_a + a h_u} \left(\frac{4}{3} \frac{\alpha_{sL}}{\alpha_{vap}} \right)^{1/2} V_r^{3/4} \qquad (12)$$

In order to evaluate the cloud evolution due to atmospheric dispersion, taking into account the real source of emission with given area $A_{\max}$, reference is made to a virtual point source. The virtual source is located upwind from the hydrocarbon spot (along x-axis), such that if a plume were originated at the virtual source it would disperse and match the concentration of vapour at the downwind boundary of the spot. Assuming a Gaussian model and Pasquill-Gifford dispersion coefficients $\sigma_y = \alpha\, x^{\beta}$; $\sigma_z = \gamma\, x^{\beta}$, it follows:

$$\rho(x) = \rho^0 = \frac{\dot{m}_{vap,\max}}{\pi \alpha \gamma u x^{2\beta}} \qquad (13)$$

In the following simulations, three common weather combinations are used: B2 at u = 1 ms^{-1} typical for unstable situations; C at u = 3 ms^{-1} typical for neutral conditions; D at u = 2 ms^{-1} typical of stable conditions, according to Brookhaven National Laboratory. By means of the developed approach, different instantaneous releases of n-pentane, n-hexane and toluene were considered, to identify the extent of the flammable zone and the safety distance corresponding to the lower flammability limit (LFL) isopleth.

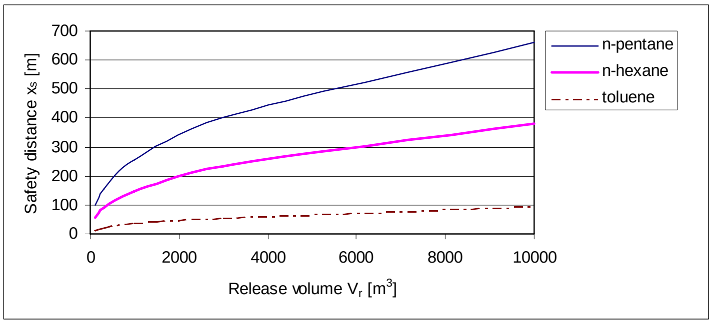

Fig.1 Safety distance as a function of instantaneous released volume for very unstable weather conditions (stability class B2 ; u = 1 m s^{-1})

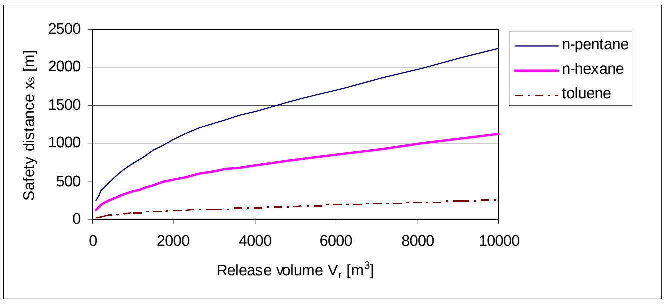

Fig.2 Safety distance as a function of instantaneous released volume for neutral weather conditions (stability class C; u = 3 ms^{-1}).

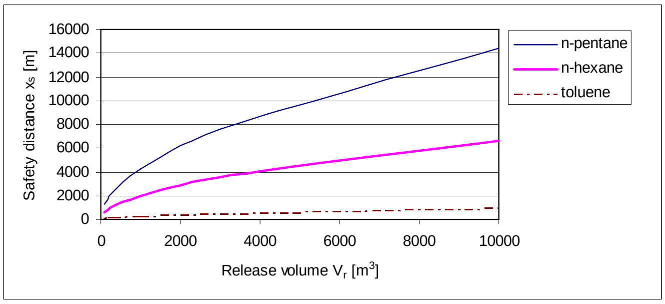

Fig.3 Safety distance as a function of instantaneous released volume for stable weather conditions (stability class D ; u = 2 m s^{-1}).

As shown in Figs. 1-3, the mathematical model developed in this study gives the safety distances of sensible targets from the release location, so to avoid ignitions, explosions and serious toxic effects, as a function of the characteristics of the release, either by means of explicit formulae or in graphycal form.

Nomenclature

$\alpha_{sL}=2[\pi g(1-\rho_L/\rho_v)]^{0.5}$ spreading liquid coefficient, m$^{1/2}$ s^{-1}	T temperature, K (subscript: a air, b boiling point, c critical, w water)
α_{vap} specific vaporization rate, m^3 m^{-2} s^{-1}	M molar mass, kg kmol^{-1}
t time from release start, s	A,B,C regression constants of Antoine
t_{ALM} characteristic spreading time, s	u wind velocity, m s^{-1}
$\dot{q}_r''$ solar radiation, kW m^{-2}	$\Delta\tilde{H}_{vap}$ enthalpy of vaporization, kJ kmol^{-1}
h_w conv. heat transf. coeff. (water), kW m^{-2} °C^{-1}	h_u specific liquid evaporation rate, m^3 m^{-2} s^{-1}
h_a conv. heat transf .coeff. (air), kW m^{-2} °C^{-1}	ρ release mass concentration, kg m^{-3}
A spot area, m^2	V_r release volume, m^3

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