

A Novel Index Based Framework for Assessing Hazards of Toxic and Flammable Gaseous Releases in Process Plants

Emilio Palazzi, Fabio Currò, Erika Lunghi, Bruno Fabiano*

DICCA – Civil, Chemical and Environmental Engineering Department – Polytechnic School University of Genoa, Via Opera Pia, 15 – 16145 Genoa, Italy
brown@unige.it

Generally speaking, chemicals are the main source of fire, explosion and toxicity hazards. Notwithstanding technological development, enforcement of ATEX Directives and safety management system application, hazardous releases and following toxic dispersion or explosions in the process sector still claim lives and severe economic losses. Additionally, rather moderate releases of hazardous gases under semi-confined geometry are known to present a serious risk so that there is a need in the assessment of the maximum admissible gas build-up, in connection with adverse effects. For purpose of providing comprehensive warning of the hazardous nature of the considered gas and obtaining a simplified tool, we present a simple unified approach which, starting from the chemical-physical and hazardous properties of the released gas allows estimating both asphyxiation, fire/explosion and toxic exposure hazards.

1. Introduction

The inherent safety approach, which can be applied also to consolidated processes aims at eliminating or reducing hazards, or exposure to them, or the chance of occurrence, by applying well known principles, e.g., “substitution” or “intensification”. Indeed, inherently safer design and technical topics related to hazardous phenomena/properties of substances are recognized as prioritized research issues for the 21st century (De Rademaeker et al., 2014). However, raw materials in petrochemical plants (e.g. flammable and toxic hydrocarbons) are often impossible to be replaced by inherently safer materials, while the application of “intensification” in the downstream oil industry, by inventory reduction connected to changes in equipment and process design, is still limited as evidenced by accident statistics (Fabiano and Currò, 2012). Additionally, as new plants capacities are increasing and often by simple linear extrapolations of existing designs, the hazard size is increased, either in proportion to the necessary inventory increases, or over this threshold (e.g. piping inventory increases with capacity more than linearly and extended risk assessment approaches seem advisable (Milazzo and Aven, 2012). This implies that measures need to be adopted in order to adequately quantify release hazard and thereby to mitigate the risks. For example (Windhorst and Koen, 2001), considering ethylene plant, the higher value of individual risk increases to the power 1.33 of capacity and the risk is proportional to the square of fixed capital. Reasons are mainly connected to larger equipment and nozzle sizes resulting in larger release rates and mass released. Chemical releases are the main source of fire, explosion and toxicity related events. As reported in Mannan & Lees (2005), about two thirds of impacts were mainly initiated by explosion compared to fire, while toxicity exerts a determining role on the number of affected people, compared to fire and explosion. Many accidents have occurred in the past as a result of inadequate understanding of the post-release evolution or not-correct design of technical protection measures. Referring to these last issues, the year 2014 and 2016 mark respectively the 30th and 40th anniversary of Bhopal and Seveso disasters: two notable chemical accidents connected with toxic release into the atmosphere, which caused severe and unparalleled damage to both the country and its neighbouring (Palazzi et al., 2015). For purpose of providing comprehensive warning of the hazardous nature of a broad range of gas and obtaining a simplified tool useful for risk assessment specific for chemical industry installations, we present a short-cut unified approach. Starting from the triangle approach, the paper further discusses simple hazard indices that can be obtained in analytical form under simplifying but conservative hypotheses.

2. Unified approach to release hazards

In the event of a release, the knowledge of safety properties of the material is essential for estimating hazardous areas and set-up proper emergency and evasive actions. All humans exposed within the “consequence zone”, defined as areas where the gas concentration exceeds threshold values, are at risk of experiencing the adverse effects associated with the exposure to the material originally released in the environment. The purpose of this work is to consider release events and connected risk, possibly simultaneous, related to the different incident outcomes after containment has failed, namely asphyxiation, self-ignition, exposure to toxic substance, radiating heat exposure etc. A rapid approximated method of estimating asphyxiation, or toxicity, or flammability characteristics of ternary mixtures is developed starting from the hypothesis of homogeneous gas mixtures. The method can consider both nearly instantaneous and continuous release mode from a single component or binary mixture point source. Based on the hazardous concentration level, it is possible to attain a cautious and accurate knowledge of a particular compound’s hazardous region, by means of a ternary diagram depicting in a coordinate fashion of immediate readability:

- the concentration region, R_p , where the release is inherently hazardous;
- the concentration region, R_d , where the release, originally at non-hazardous conditions, may fall within the region R_p as a consequence of dilution and air entrainment;
- the concentration range, $R = R_p \cup R_d$, where the release is always potentially at risk;
- the critical dilution, y_d^* , needed to attain the critical compositions, $M^*(y_1^*, y_2^*, y_3^*)$, at the boundaries of the inherently hazardous region, R_p . Any further dilution of the release P determines a reduction of the hazard, down to a reasonably acceptable level.

2.1 Release characterization

Scenarios connected to hazardous release clearly consider the logical chain: initiating event-loss of containment-hazmat release-effects-damage on targets. The short-cut method here discussed allows considering following release type/duration at the point source conditions and connected hazards:

<i>Single gas:</i>	O ₂	over oxygenated atmosphere formation
	N ₂ , CO ₂ , etc.	under oxygenated atmosphere formation
	Cl ₂ , NH ₃ , CO ₂	toxic cloud formation
	NH ₃ , CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈ , etc.	flammable cloud formation
<i>Binary gas mixture</i>	O ₂ , with different gas e.g. NH ₃ , CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈	flammable cloud formation
<i>Duration</i>	Nearly instantaneous point source of a total given mass/volume;	
	Continuous point source at a continuous mass flow rate.	

The graphical representation considers that in a three dimensional perspective form, we can depict the hazardous limits of a ternary system representing the actual characteristics of the release into the atmosphere at constant pressure and temperature, as shown in Figure 1. Under these conditions and the working hypothesis of homogeneous mixture and release in air, since the sum of the three molar fraction terms (oxygen O, nitrogen N and gas G) equals 1, one can draw the different conditions by the projection of the three-dimensional plane, as described in the following chapters, so as to attain the composition evolution from the starting conditions taking into account the intrinsic chemical property of the material and the relevant hazards.

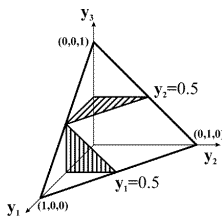


Figure 1: Three dimensional composition of a ternary system.

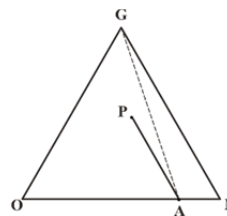


Figure 2: Composition of a ternary release P and evolving ideal dilution with air.

2.2 Air dilution of the release

As amply known, hazard is not solely an inherent property of the chemical involved but it depends also on the conditions under which the release P evolves.

The analytical formulae presented in the following are obtained considering the most general application of a ternary mixture release-air. Eqs (1)-(3) summarize the composition of a ternary mixture M as a function of air dilution, from the starting point source release composition, under the ideal assumption.

$$y_1 = y_{1p} y_d + 0.21 (1-y_d) \quad (1)$$

$$y_2 = y_{2p} y_d + 0.79 (1-y_d) \quad (2)$$

$$y_3 = y_{3p} y_d \quad (3)$$

Being:

y_d = release dilution (v/v) $0 < y_d \leq 1$; y_{ip} = molar fraction of i -th component in the release P;

y_{ia} = molar fraction of i -th component in air A (e.g. $y_{1a} = 0.21$; $y_{2a} = 0.79$).

We can depict the release dilution in a ternary graph, obtained by simple projection of the three dimensional plane previously presented, as shown in Figure 2, identifying all three constituents of interest simultaneously, where $P(y_{1p}; y_{2p}; y_{3p})$, $A(y_{1a}; y_{2a}; 0)$, $M(y_1; y_2; y_3)$. It follows that the upon dilution the resulting gas mixture M \in to the line PA (see Figure 2), or, in other words, the composition modifies from the point $P(y_{1p}; y_{2p}; y_{3p})$ to the point A (0.21; 0.79; 0).

3. Hazardous releases and critical dilution estimation

The risk levels connected to a generic gaseous release, possibly characterized by different hazards (asphyxiation, inhalation, deflagration, etc.), clearly depends upon the interaction with the environment and the consequent dispersion, or build-up in semi-confined regions. As previously remarked the approach here outlined is based on the ideal assumption of perfect mixing and is based on following steps: identification of the "critical reference concentrations" for the different scenarios (health effect, fire/explosion); analytical calculation of the dilution required to attain the reference concentrations; graphical representation of contour map describing the concentration region, R_p , where the release is inherently hazardous; the concentration region, R_d , where the release, originally at non-hazardous conditions, may fall within the region at risk R_p as a consequence of dilution and air entrainment; the concentration range, $R = R_p \cup R_d$, where the release is always potentially at risk.

3.1 Single gas release

First of all we discuss the rather simple event of a single gas release characterized by different potential health effect, different from combustion hazard. For the sake of simplicity, Table 1 summarizes the results obtained according to this scenario, by applying Eqs (1)-(3). From Table 1, it can be argued that the hazard connected to over-oxygenation extends until by dilution (the critical dilution is easily obtained by Eq(1)), it is attained the critical concentration $y_1^* = 0.25$ corresponding to health effect for man (K), so that in the ternary diagram the risk region is simply $R = R_K$ as shown in Figure 3. The boundaries of his region can be expressed as:

$$R_p \equiv R_K \begin{cases} y_1 \geq y_1^* = 0.25 \\ 0 \leq y_2 \leq 0.75 \\ 0 \leq y_3 \leq 0.75 \end{cases} \quad (4)$$

Additionally, it must be pointed out that oxygen clearly plays a role determining maximum flame temperature and thermal power in given scenarios (e.g. pool fire), especially in enclosures (Vianello et al., 2012). The risk levels connected to an oxygen release, possibly in presence of other hazardous releases depends upon the interaction with the environment, including increased flammability by oxygen enrichment, and the consequent dispersion, or build-up in semi-confined regions (Palazzi et al., 2010), as it will be discussed in the following. Analogously, considering a potential suffocating release, hazard region is attained assuming as critical concentration $y_1^* = 0.17$, corresponding to under-oxygenation risk (S) that can lead to asphyxiation. In this way we obtain the ternary diagram depicted in Figure 4, where it is noteworthy noting that the critical dilution value obtained by means of Eq(1), $y_d^* = 0.19$ holds its validity for any release composition consisting of different non-toxic compounds, in the absence of any oxygen content. In this case, the boundaries of the hazard region are obtained according to the conditions summarized in Eq. (5).

Table 1: Single gas release P: hazardous scenario, calculated critical parameters to attain the corresponding boundaries of the hazard region R in a triangular diagram (G= gas; O= oxygen; N = nitrogen).

Scenario	Release P characterization	Critical concentration y^*	Critical dilution y_d^*
Overoxygenated atmosphere	Pure oxygen: P \equiv O (1; 0; 0)	$y_1^* = y_{1K} = 0.25$	$y_d^* = y_{dK} = 0.051$
Asphyxiating atmosphere	Pure nitrogen: P \equiv G (0; 1; 0)	$y_1^* = y_{1S} = 0.17$	$y_d^* = y_{dS} = 0.19$
	Pure carbon dioxide: P \equiv G (0; 0; 1)	$y_1^* = y_{1S} = 0.17$	$y_d^* = y_{dS} = 0.19$
Toxic release	Pure carbon dioxide: P \equiv G (0; 0; 1)	$y_3^* = y_{3T} = 4 \cdot 10^{-2}$	$y_d^* = y_{dT} = 4 \cdot 10^{-2}$
	Pure ammonia: P \equiv G (0; 0; 1)	$y_3^* = y_{3T} = 3 \cdot 10^{-4}$	$y_d^* = y_{dT} = 3 \cdot 10^{-4}$
	Pure chlorine: P \equiv G (0; 0; 1)	$y_3^* = y_{3T} = 10^{-5}$	10^{-5}

$$R_p \equiv R_S \begin{cases} 0 \leq y_1 \leq y_1^* = 0.17 \\ 0 \leq y_2 \leq 1 \\ 0 \leq y_3 \leq 1 \end{cases} \quad (5)$$

The case of toxic compound release the critical concentration is defined by a threshold value for the physical effect (T) corresponding for example to IDLH (Mannan and Lees, 2005) expressed as y_T . In this case, the critical dilution value may be derived from Eq (3) by imposing $y_3^* = y_{3T}$. The corresponding ternary diagram is depicted in Figure 5, and the resulting boundaries of the hazard region are:

$$R_p \equiv R_T \begin{cases} 0 \leq y_1 \leq 1 - y_3^* \\ 0 \leq y_2 \leq 1 - y_3^* \\ y_3 \geq y_3^* \end{cases} \quad (6)$$

3.2 Flammable gas

Flammable gases and liquids are prevalent in today's process and petrochemical sectors and their flammability characteristics are usually represented by index based on flammability limits data.

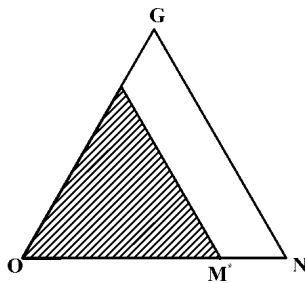


Figure 3: Risk region belonging to overoxygenated atmosphere scenario (K).

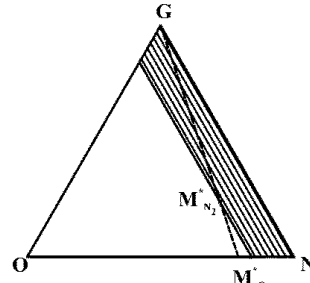


Figure 4: Risk region belonging to asphyxiating atmosphere scenario (S).

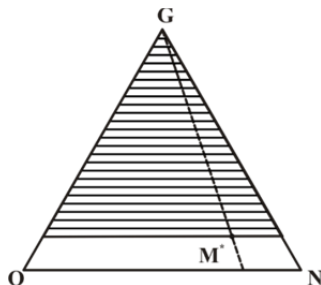


Figure 5: Risk region belonging to toxic atmosphere scenario (T).

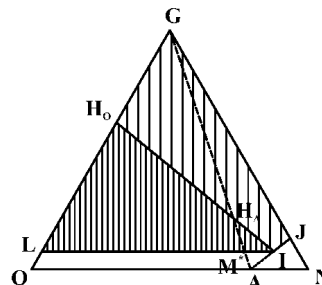


Figure 6: Risk region belonging to flammable gas scenario (F).

Theoretical and experimental research on flammability limits is still an up-to-date research topic, and a new method for estimating the flammability range of fuel-oxidizer mixtures, with or without inert gas was recently presented (Giurcan et al., 2015). Referring to the triangular diagram reproduced in Figure 6, the two different hazardous regions connected to flammability can be described by simple geometry:

- Inherent hazardous release $R_p \equiv$ triangle HoLI;
- Hazardous release upon air dilution $R_d \equiv$ quadrangular GH₀IJ;
- Resulting flammable mixture hazardous region in the ternary system: $R \equiv R_p \cup R_d$.

In order to obtain the formal definition of the release hazard, the knowledge of the compound flammability region as a function of fuel, oxygen and nitrogen concentrations is the starting point.

We consider as a relevant example, the flammable limits summarized in Table 2 (Lewis and von Elbe, 1987), where, to the purpose of this simplified but conservative approach, we assume for each flammable compound:

- a constant value of the lower flammable limit LFL corresponding to the minimum value: $y_{3La} \equiv y_{3Lo} = y_{3L}$;
- a variable upper flammable limit UFL by linear dependence on the composition.

Making reference to the already mentioned Figure 6, the analytical approach to a release characterized by fire/deflagration hazard requires calculating:

- the equation of the line H₀H_a;
- the intersection point, I, between the line H₀H_a and the line described by the equation $y_3 = y_L$;
- the equation of the line AI.

An account of these calculation follows.

The line where the original release is diluted down to HFL, described by the equation H₀H_a, is given by:

$$(y_3 - y_{3Ho}) / (y_{3Ha} - y_{3Ho}) = y_2 / [0.79(1 - y_{3Ha})] = (y_1 - y_{1Ho}) / 0.21(1 - y_{3Ha}) - y_{1Ho} \quad (7)$$

so that the hazardous region describing the inherent flammability conditions of the release can be expressed:

$$R_p \equiv R_F \begin{cases} y_1 \geq y_L \\ y_2 \geq 0 \\ y_3 \leq y_{3Ho} - y_2 (y_{3Ho} - y_{3Ha}) / [0.79(1 - y_{3Ha})] \end{cases} \quad (8)$$

Analogously to the previous approach, we can assume the “critical reference concentration” starting from the conservative values of LFL and UFL available in literature by a stepwise calculation. The dilution requirement can be determined in terms of “critical dilutions” y_{dL}^* and y_{dU}^* , as follows. Starting from Eq (3) one can write:

$$y_d = y_3 / y_{3p} \quad (9)$$

so that y_{dL}^* is easily calculated, by utilizing the values of y_{3p} and of $y_3 = y_{3L}$ shown as an example in Table 3.

y_{dU}^* can be obtained by substitution into Eq (7) of the corresponding values of y_2 and y_3 respectively given by Eq (2) and Eq (3). From the resulting Eq (10), it follows that if $y_{3p} = 1 \rightarrow y_{dH} = y_{3Ha}$; and if $y_{3p} = y_{3Ho} \rightarrow y_{dH} = 1$

$$y_d = y_{3Ha} (1 - y_{3Ho}) / [y_{3p} (1 - y_{3Ha}) + y_{3Ha} - y_{3Ho}] \quad (10)$$

At last, by substitution into Eq (9) of the values of y_{dH} obtained by Eq (10), the resulting y_{3H} is easily calculated.

4. Discussion

By applying the proposed method, in Table 3 we consider some selected flammable gases and some pertinent examples of different release composition P, namely (see Figure 6 for symbol explanation):

$P \equiv G$ pure flammable gas; $P \equiv P_1$ corresponding to the midpoint of the line GH₀;

$P \equiv H_0$ flammable gas at UFL; $P \equiv P_2$ corresponding to the midpoint of the line H₀L.

Starting from the discussed theoretical approach and the triangle representation, rather simple hazard indices can be obtained in analytical form under simplifying but conservative hypotheses.

The quantitative indices of immediate applicability can include: critical distance; critical area; flammable mixture volume; man exposure and hazardous dose (Palazzi et al., 2014). In particular, the model output parameter considered of primary importance is the distance from the release point to the predicted critical concentration in the given hazardous scenarios (dilution concentration), defined as “effect distance”. An approximated approach can assume a neutrally buoyant dispersion, considering a neutral gas and the absence of considerable auto-refrigeration during release. The isopleths ground concentration (v/v) of a nearly-instantaneous release of given volume, of a continuous release of given rate can be obtained by as a first approach by the Gaussian model and corresponding dispersion coefficients by BNL (Pasquill and Smith, 1983).

Table 2: Lower and upper flammable limits of selected hydrocarbons in air and oxygen.

Pure compound	Air mixture		Oxygen mixture	
	HFLY _{3Ha}	LFLY _{3La}	HFLY _{3Ho}	LFLY _{3Lo}
NH ₃	0.28	0.15	0.79	0.15
CH ₄	0.15	0.053	0.61	0.051
C ₂ H ₄	0.32	0.031	0.80	0.03

Table 3: Calculation of critical concentration and critical dilution for selected flammable releases.

Release P characterization		Critical concentration		Critical dilution	
		Y _{3c} = Y _{3L}	Y _{3c} = Y _{3H}	Y _{dc} = Y _{dL}	Y _{dc} = Y _{dH}
G (0; 0; 1)	(pure NH ₃)	0.15	0.150	0.150	0.150
P ₁ (0.40; 0; 0.60)	(NH ₃ and O ₂)	0.15	0.210	0.168	0.261
H ₀ (0.79; 0; 0.21)	(NH ₃ and O ₂)	0.15	0.610	0.190	1.000
P ₂ (0.47; 0; 0.53)	(NH ₃ and O ₂)	0.15		0.319	
G (0; 0; 1)	(pure CH ₄)	0.051	0.280	0.051	0.280
P ₁ (0.31; 0; 0.69)	(CH ₄ and O ₂)	0.051	0.392	0.063	0.438
H ₀ (0.61; 0; 0.39)	(CH ₄ and O ₂)	0.051	0.790	0.084	1.000
P ₂ (0.33; 0; 0.67)	(CH ₄ and O ₂)	0.051		0.154	
G (0; 0; 1)	(pure C ₂ H ₄)	0.031	0.320	0.030	0.320
P ₁ (0.40; 0; 0.60)	(C ₂ H ₄ and O ₂)	0.031	0.436	0.033	0.485
H ₀ (0.80; 0; 0.20)	(C ₂ H ₄ and O ₂)	0.031	0.800	0.038	1.000
P ₂ (0.42; 0; 0.58)	(C ₂ H ₄ and O ₂)	0.031		0.072	

5. Conclusions

For purpose of identifying release hazards and assessing over/under-oxygenation, toxic and fire/deflagration risk we present a simple approach and a graphical representation useful as a tool relative risk ranking and an indication of whether further study is warranted in a given context. Starting from the relevant information on the chemical physical properties of the gas, the method provides comprehensive warnings of the hazardous nature of a release. A short-cut dispersion modelling for continuous and instantaneous releases allows developing contour map describing the hazardous area following different gas releases. The framework here outlined may be used as a simple analytical tool to perform an approximate conservative evaluation and a preliminary screening for selecting cases where an in-depth safety analysis may be needed.

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