

## A Theoretical Approach to Risk Evaluation in Connection with Oxygen Releases

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Oxygen-enriched combustion offers several advantages, including higher combustion efficiency (Hu et al., 2001) and higher CO<sub>2</sub> concentration in the flue gas, allowing an easier and cheaper CO<sub>2</sub> separation from the gas itself (Hu et al., 2000). In addition, oxygen combustion is considered in the IPCC list as a category of CCS options for large point source emitters. Oxygen enriched process can be adopted to enhance sulphur recovery in the effluent stream adopting modified Claus processes in refineries. According to international historical data, accidents involving gas pipelines still happen and often result in severe consequences. This implies that measures need to be adopted in order to adequately quantify and thereby to mitigate the risks. In relative terms, the problem of HazMat pipeline risk assessment does not come with hazard analysis, or the estimation of failure frequency, but with the calculation of the consequences. In this paper, we consider the peculiar case of oxygen instantaneous or continuous releases from a pipeline and consequent evolving scenarios. A novel modelling approach to risk evaluation is elaborated starting from the rather common situation of a pipe-way where several gas/liquid lines are localized, in a rather congested industrial area. As an applicative case-study, it is considered a downstream oil industry where the possibility of replacing the air feeding to Claus plant with oxygen enriched line is investigated, with the aim of enhancing sulphur recovery yield. This technical option from one side can be seen as an approach to process intensification, from the other side poses obvious safety issues.

### 1. Oxygen accident statistics

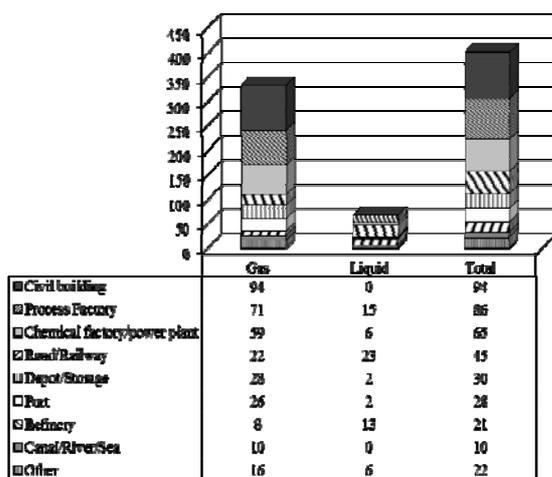


Figure 1: Number of accidents involving gas and liquid oxygen, sorted by accident location.

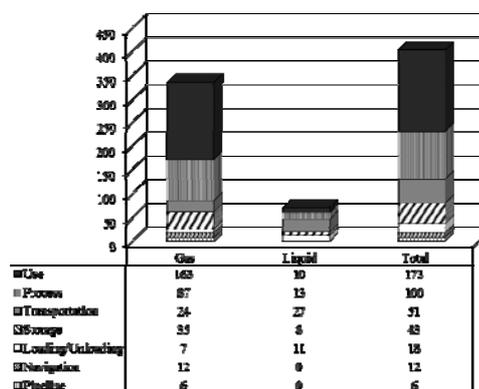


Figure 2: Number of accidents involving gas and liquid oxygen, sorted by activity.

Table 1: Reference composition and consequent target dilution for different releases.

Release	Reference composition	Target dilution (v/v)
O <sub>2</sub>	75% O <sub>2</sub>	y <sub>d,in</sub> = 0.68
	50% O <sub>2</sub>	y <sub>d50</sub> = 0.37
	25% O <sub>2</sub>	y <sub>d25</sub> = 0.051
O <sub>2</sub> + CH <sub>4</sub>	HFL	y <sub>dH</sub> = 0.15(1+k)/(1-1.18k)
	Stoichiometric condition	y <sub>dS</sub> = 0.095(1+k)/(1-0.36k)
	LFL	y <sub>dL</sub> = 0.051(1+k)
CH <sub>4</sub>	HFL	y <sub>dHc</sub> = 0.15
	Stoichiometric condition	y <sub>dSc</sub> = 0.095
	LFL	y <sub>dLc</sub> = 0.051

The majority of companies in the process sector recognize the importance of learning from accidents by reporting all incidents with the potential to cause injury or loss and by using analytical techniques to establish the root cause of incidents so as to identify technical, organizational and human factors which may have contributed to the incident (Fabiano and Currò, 2012). The accident cases, which were used to carry out the statistical survey, were taken from the database FACTS (Failure and Accidents Technical information System) managed by managed by the Unified Industrial & Harbour Fire Department in Rotterdam-Rozenburg (NL). A total of 401 accidents were selected and validated: 83.3 % are referred to gas and 16.7 % to liquid. Statistical results in form of immediate readability are summarized in Figures 1 and 2, respectively accounting for accident location and activity. Over a total of 168 accidents recording injuries (41.9 % of the total), 141 involved gas and 27 liquid. In 122 events (30.4 % of the total) it was recorded at least one fatality: 107 involved gas and 15 liquid oxygen. It is noteworthy noting that on the contrary to process plant statistics, gas phase is by far the most frequent condition connected to accidents.

## 2. Theoretical

The risk levels connected to an oxygen release, possibly in presence of other hazardous releases (inhalation, deflagration, detonation), depend upon the interaction with the environment and the consequent dispersion or build-up in semi-confined regions. Oxygen clearly plays a role determining maximum flame temperature and thermal power in given scenarios, e.g. pool fire (Palazzi et al., 2012). As a short-cut approach, with a hazard analysis orientation, three kinds of scenarios/release time modes can be considered, following a loss of containment in a pipeway where an oxygen line is present: pure O<sub>2</sub> near-instantaneous or continuous release and over-oxygenation of the atmosphere; concurrent release of O<sub>2</sub> and HC, of near instantaneous or continuous duration and consequent formation of explosive mixtures; build-up of O<sub>2</sub> and HC in semi-confined spaces and formation of explosive pockets. The methodological approach here outlined is based on the following steps: identification of the “critical reference concentrations” for the different scenarios (health effect for pure O<sub>2</sub> release on the basis of vulnerability to human beings and explosive limits for O<sub>2</sub>/HC releases); analytical calculation of the dilution required to attain the reference concentrations; short-cut dispersion modelling for continuous and instantaneous releases to develop contour map describing the gas concentration; interaction of O<sub>2</sub> and HC releases (as an example we refer to methane). The results of air dilution needed to attain reference compositions starting from pure oxygen and HC releases, calculated on the basis of mass balance and stoichiometry are summarized for the sake of brevity in Table 1. The following analytical approach considers a neutrally buoyant dispersion, considering the slight gas density difference between oxygen and ambient air, as well as the absence of considerable auto-refrigeration during release, under the given conditions.

### 2.1 Continuous release

In order to evaluate ground concentration (v/v) of a continuous release of given release rate, we started from the well-known Gaussian model and dispersion coefficients available from BNL (Brookhaven National Laboratory) (Pasquill and Smith, 1983):

$$y_d(X, Y, 0) = \frac{Q_r}{\varepsilon X^{2\beta}} e^{-\frac{\eta Y^2}{X^{2\beta}}} \quad (1)$$

The isopleth equation corresponding to the ground level concentration boundaries in connection with the given dilution factor is attained from Eq. (1) as follows:

$$Y = \eta^{-1/2} X^\beta \left( \ln \frac{Q_r}{\varepsilon y_d X^{2\beta}} \right)^{1/2} \quad (2)$$

The maximum downwind distance, at ground level, where the given target dilution is attained, can be calculated as:

$$X = \left( \frac{Q_r}{\varepsilon y_d} \right)^{1/2\beta} \quad (3)$$

Making reference to the worst conditions (atmospheric stability D, according to BNL) and to the corresponding set of parameters:  $u = 1 \text{ m s}^{-1}$ ;  $\alpha = 0.31$ ;  $\beta = 0.71$ ;  $\gamma = 0.06$ ;  $\varepsilon \cong 0.058$ ;  $\eta \cong 5.2$ , (Pasquill and Smith, 1983) previous equations can be modified respectively as:

$$Y = 0.44 X^{0.71} \left( \ln \frac{17 Q_r}{y_d X^{1.42}} \right)^{1/2} \quad (4) \quad X = 7.3 \left( \frac{Q_r}{y_d} \right)^{1/2\beta} \quad (5)$$

Considering a given release, we define as a hazard indicator the extension of the flammable region at the ground level. In this respect, the quantitative effect of an oxygen release can be evaluated making reference to the relative increase of the hazardous area, compared to the absence of the oxygen release, according to Eq. (6).

$$\Delta A_{ir} = \frac{A_i - A_{ic}}{A_{ic}} \quad (6)$$

It must be noticed that in the most common situation when regions characterized by gas concentration exceeds HFL, the areas  $A_{ic}$  and  $A_i$  can be calculated by subtracting the area with boundary corresponding to isopleth LFL to the area with boundary HFL. Starting from Eq. (2), the maximum is easily found as:

$$Y_{max} = \alpha \left( \frac{2Q_r}{\varepsilon y_d} \right)^{1/2} \cong 1.1 \left( \frac{Q_r}{y_d} \right)^{1/2} \quad (7)$$

At last, we can calculate the hazard index corresponding to the relative increase of the ground level flammable region:

$$\Delta A_{ir} = 0.38 \left[ 1 - (1 - 1.18k)^{1.20} \right] \quad (8)$$

## 2.2 Instantaneous release

Again, we evaluate ground concentration ( $v/v$ ) of a near-instantaneous release of given volume, by the Gaussian model and corresponding dispersion coefficients by BNL (Pasquill and Smith, 1983):

$$y_d(X, Y, 0) = \frac{V_r}{\varepsilon_i X^{3\beta}} e^{-\eta[(X-x)^2 + Y^2]} \quad (9)$$

The isopleth corresponding to the ground level concentration boundaries in connection with the given dilution factor are circle with centre  $C(x,0)$  and radius  $r$ , both varying with time. From Eq. (9), one can write:

$$r = \eta^{-1/2} X^\beta \left( \ln \frac{Q_r}{\varepsilon y_d X^{3\beta}} \right)^{1/2} \quad (10)$$

The maximum downwind distance, at ground level, where the given target dilution is attained, can be calculated from Eq. (9) for  $X = x$  e  $Y = 0$ :

$$X = \left( \frac{V_r}{\varepsilon_i y_d} \right)^{1/3\beta} \quad (11)$$

Table 2: Analytical formulae of the characteristic distance for different release duration.

Release	Reference composition	Characteristic distance [m]	
		Continuous release	Instantaneous release
O <sub>2</sub>	75% O <sub>2</sub>	$X_{75} = X_{in} = 9.6Q_1^{0.70}$	$X_{75} = X_{in} = 5.2V_1^{0.47}$
	50% O <sub>2</sub>	$X_{50} = 15Q_1^{0.70}$	$X_{50} = 6.9V_1^{0.47}$
	25% O <sub>2</sub>	$X_{25} = 59Q_1^{0.70}$	$X_{25} = 17V_1^{0.47}$
O <sub>2</sub> + CH <sub>4</sub>	HFL	$X_H = 28[(1-1.18k)Q_3]^{0.70}$	$X_H = 10[(1-1.18k)V_3]^{0.47}$
	Stoichiometric condition	$X_S = 38[(1-0.36k)Q_3]^{0.70}$	$X_S = 13[(1-0.36k)V_3]^{0.47}$
	LFL	$X_L = 59Q_3^{0.70}$	$X_L = 17V_3^{0.47}$
CH <sub>4</sub>	HFL	$X_{Hc} = 28Q_3^{0.70}$	$X_{Hc} = 10V_3^{0.47}$
	Stoichiometric condition	$X_{Sc} = 38Q_3^{0.70}$	$X_{Sc} = 13V_3^{0.47}$
	LFL	$X_{Lc} = 59Q_3^{0.70}$	$X_L = 17V_3^{0.47}$

As a conservative estimate, Eqs. (9) and (10) are utilized referring to the worst meteorological conditions (atmospheric stability D, according to BNL) and to the corresponding set of parameters:  $u = 1 \text{ m s}^{-1}$ ;  $\alpha = 0.31$ ;  $\beta = 0.71$ ;  $\gamma = 0.06$ ;  $\varepsilon \cong 0.058$ ;  $\eta \cong 5.2$ , so that one can write:

$$r = 0.44x^{0.71} \left( \ln \frac{22V_r}{y_d x^{2.13}} \right)^{1/2} \quad (12) \quad X = 4.3 \left( \ln \frac{Q_r}{y_d} \right)^{0.47} \quad (13)$$

Also dealing with the instantaneous release we can define the hazard index as the relative increase of the flammable region at the ground level; from eq. (6) the index is evaluated by:

$$\Delta A_{ir} = \ln(1 - 1.18k)^{0.93} \quad (14)$$

A summary of the analytical formulae obtained with straightforward calculations for the characteristic distances in connection with the different release modes, is shown in Table 2.

### 3. Case-study

#### 3.1 Plant layout

As an applicative case-study, we consider a pipeline suitable to feed a Claus plant located in a middle size oil refinery. Due to stringent environmental regulations, an upgrade to oxygen-enriched process is considered, in order to increase the overall sulphur recovery. The technical data of the designed oxygen pipeline at an operative pressure  $p_m$  are summarized in Table 3.

According to the framework outlined in part 2, following scenarios are considered:

- Continuous point source release: oxygen release rate corresponding to the maximum designed value of the pipe:  $Q_1 = 0.788 \text{ m}^3\text{s}^{-1}$  at 298 K and 1 atm.
- Instantaneous point source release: oxygen discharged volume corresponding to 100 m of the pipe:  $V_1 = 20 \text{ m}^3$  at 298 K and 1 atm.

Table 3: Designed technical data of oxygen pipeline and corresponding operative conditions.

Pipeline length and diameter	$L = 2.5 \text{ km}$ ; $d = 0.203 \text{ m}$
Mean pressure	$p_m = 6.26 \cdot 10^5 \text{ Pa}$
Temperature	$T = 298 \text{ K}$
Maximum flow rate	$Q = 2600 \text{ Nm}^3\text{h}^{-1} \cong 0.788 \text{ m}^3\text{s}^{-1}$ at 298 K and 1 atm
Oxygen molar fraction	$y_1 = 0.995$
Oxygen volume in the pipeline	$V_{1c} = AL = 81 \text{ m}^3$
Oxygen volume at 298 K and 1 atm	$V_1 = V_{1c} p_{atm} / p_m \cong 500 \text{ m}^3$
Oxygen flow rate at 298 K and 1 atm	$Q_1 = 0.788 \text{ m}^3\text{s}^{-1}$
Oxygen density at $p_M$	$\rho_M = p_M M_1 / RT \cong 8.41 \text{ kg m}^{-3}$

Table 4: Characteristic distances corresponding to oxygen releases.

Characteristic distance [m]	Continuous release	Instantaneous release
$X_{75} = X_{in}$	8.1	21
$X_{50}$	12	28
$X_{30}$	50	71

Table 5: Characteristic distances for oxygen/methane release, compared to methane release.

Release composition	Characteristic distance [m]	Continuous release $Q_3$ ( $m^3s^{-1}$ )			Instantaneous release $V_3$ ( $m^3$ )		
		1.23	1.58	7.88	31.25	40	200
$O_2 + CH_4$		$k=0.64$	$k=0.5$	$k=0.1$	$k=0.64$	$k=0.5$	$k=0.1$
	$X_H$	12	21	109	27	39	119
	$X_S$	32	38	119	53	59	127
$CH_4$	$X_L$	67	80	246	86	96	205
		$k=0$	$k=0$	$k=0$	$k=0$	$k=0$	$k=0$
	$X_{Hc}$	37	45	157	58	67	154
	$X_{Sc}$	44	52	161	66	74	157
	$X_{Lc}$	67	80	246	86	96	205

Table 6: Hazard index increase for oxygen/methane release, compared to methane release.

Release composition	Flammable region increase [%]	Continuous release $Q_3$ ( $m^3s^{-1}$ )			Instantaneous release $V_3$ ( $m^3$ )		
		1.23	1.58	7.88	31.25	40	200
$O_2 + CH_4$		$k=0.64$	$k=0.5$	$k=0.1$	$k=0.64$	$k=0.5$	$k=0.1$
	$\Delta A_i$	31	25	5	131	83	12

Table 4 summarizes the results of the “characteristic distances” obtained utilizing the dilution factors in Table 1, by means of Eqs. (5) and (13), respectively for the continuous and instantaneous discharge mode. Table 5 shows the results of the “characteristic distances” calculated for oxygen and methane releases and pure methane releases, by means of Eqs. (5) and (13), utilizing the corresponding values of the dilution factors.

### 3.2 Flammable region extension

Table 5 summarizes the results of the hazard index calculation performed starting from Eqs. (8) and (14), for different proportions of the concurrent hazardous releases into ambient air.

## 4. Discussion and conclusions

Coeteris paribus, the probability of fire propagation increases as the flammable region increases. As clearly depicted making reference to the applicative example in Figures 3 and 4, an oxygen release modifies the hazardous area by exerting its effect on the isopleth corresponding to HFL, so as to reduce the zones occupied by mixture with higher HC concentration. Also taking into account Table 6, following consideration can be drawn, with respect to the hazard index:

- considering methane releases comparable or lower than oxygen ones ( $k > 0.64$ ), the oxygen effect is negligible as the source concentration is lower than HFL;
- when a massive methane release ( $k < 0.1$ ) is concerned, again the oxygen contribution to the hazard increase can be considered negligible.

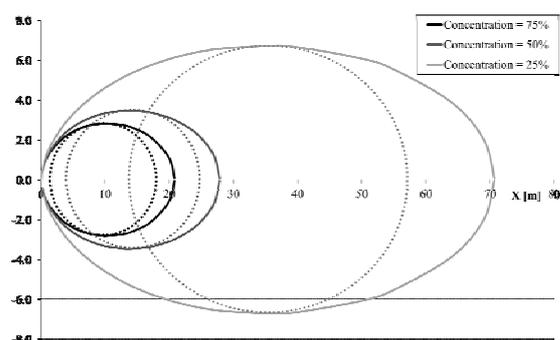


Figure 3: Maximum isopleths for three target concentrations (dotted lines) and curves enveloping all maximum concentrations (solid lines) for instantaneous  $O_2$  release ( $V_1=20 m^3$ ).

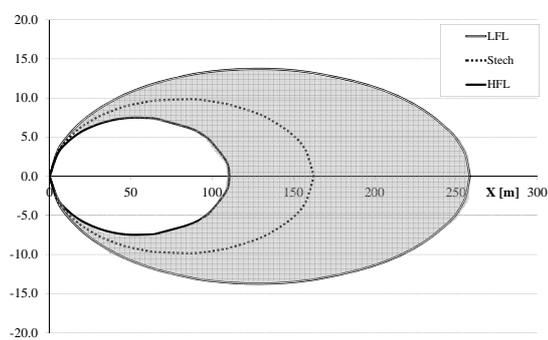


Figure 4: Isopleth curves (lower flammable limit, upper flammable limit and stoichiometric conditions) referred for a continuous release of oxygen and methane ( $Q_1=0.788 m^3 \cdot s^{-1}$ ,  $k=0.5$ ).

The area of the flammable region and, therefore, the hazard index here defined, can be significantly enhanced by an oxygen release only when the HC release (total volume or discharge rate is two three times the oxygen one, with an incremental value reaching 100 % in case of near instantaneous release, for example due to third party interaction. In any case, it can be noticed that the incremented hazardous area is limited to approximately 200 m from the release point. Dealing with the severity of a large fire and therefore the intensity of the effects and the vulnerability of people and property, it is known that an oxygen release can enhance the fire thermal power and the flame temperature. This item can be critical in presence of vulnerable components in a congested pipeway: e.g. high intensity fire exposure of steel flanges may easily result in further escalation, as bolt on flanges are pre stressed (nearly 50 % of ultimate strength) (Opstad and Berge, 2010). Moreover, proper risk prevention measures, including the safety management system, can be considered in order to reduce the frequency of the pipeline failures (Milazzo et al., 2010). On the basis of the theoretical approach, it follows that the incremental effect is negligible both in connection with HC releases of small volume and in case of catastrophic HC releases. In fact, in the former event, atmospheric environment supplies the required oxidant for combustion in the neighbourhood of the release point, so allowing a fully developed fire. In the latter, released oxygen represents only a small fraction of the oxidant needed to ensure a complete combustion of a massive quantity of HC. The most significant effects in term of relative flame temperature increase and the consequent additional hazards are relevant to HC release of medium severity and are limited to 10-20 m from the source point, as clearly indicated by the isopleths curves depicted in Figures 3 and 4. Results obtained by the analytical model were compared with available integral models, showing output differences not exceeding 20 %. The mathematical approach here outlined allows obtaining, by means of explicit formulae, the safety distances of sensible targets from the release location for both pure oxygen and concurrent oxygen/HC release, so as to identify incremental hazards and set-up technical/managerial measures to avoid ignitions, explosions and serious toxic effects.

### Nomenclature

$A_i$ = flammable area for a release of oxygen and hydrocarbons, i.e. $Q_r = (1+k)Q_3$ , $m^2$	$x$ = downwind distance from the mass centre of a release at time $t$ , m
$A_{ic}$ = flammable area for a release of hydrocarbons, i.e. $Q_r = Q_3$ , $m^2$	$X$ = downwind distance from the emission point, m
$k$ = ratio of oxygen to hydrocarbons rate in the release, -	$Y$ = transversal coordinate, m
$Q_1$ = oxygen volumetric rate at 298 K and 1 atm, $m^3 \cdot s^{-1}$	$y_d$ = release dilution, $v/v$
$Q_3$ = hydrocarbon volumetric rate at 298 K and 1 atm, $m^3 \cdot s^{-1}$	$\alpha$ = parameter defined according to BNL, -
$Q_r$ = release volumetric rate at 298 K and 1 atm, $m^3 \cdot s^{-1}$	$\beta$ = parameter defined according to BNL, -
$r$ = radius of the isopleth for instantaneous release, m	$\gamma$ = parameter defined according to BNL, -
$u$ = wind velocity at 10 m above ground level, $m \cdot s^{-1}$	$\varepsilon$ = parameter defined as $\varepsilon = \pi \alpha \gamma \mu$ , -
$V_1$ = oxygen volume at 298 K and 1 atm, $m^3$	$\varepsilon_i$ = parameter defined as $\varepsilon_i = (2\pi^3)^{1/2} \alpha^2 \gamma$ , -
$V_3$ = hydrocarbon volume at 298 K and 1 atm, $m^3$	$\eta$ = parameter defined as $\eta = 1/(2\alpha^2)$ , -
$V_r$ = release volume at 298K and 1 atm, $m^3$	

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