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Article

Accidental Continuous Releases from Coal Processing in Semi-Confined Environment

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Abstract: Notwithstanding the enforcement of ATEX EU Directives (94/9/EC of 23 March 1994) and safety management system application, explosions in the coal sector still claim lives and cause huge economic losses. Even a consolidated activity like coke dry distillation allows the opportunity of preventing explosion risk connected to fugitive emissions of coke oven gas. Considering accidental releases under semi-confined conditions, a simplified mathematical approach to the maximum allowed gaseous build-up is developed on the basis of the intrinsic hazards of the released compound. The results will help identifying and assessing low rate release consequences therefore to set-up appropriate prevention and control measures. The developed methodology was tested at the real-scale and validated by numerical computational fluid dynamics (CFD) simulations showing the effectiveness of the methodology to evaluate and mitigate the risk connected to confined hazardous releases.

Keywords: CFD analysis; gas release; hydrogen; mathematical modeling

Nomenclature:

A_r	radiating surface (m^2)
$\tilde{c}_{pe}$	mean molar heat of the explosive mixture, in the temperature interval T_0–T_e (kJ $kmol^{-1}$ K^{-1})
$\tilde{c}_{pf}$	mean molar heat of smokes in the temperature range T_0–T_f (kJ $kmol^{-1}$ K^{-1})
d	distance between source of radiation and target (m)

f_w	view factor (-)
h	height of the enclosure (m)
k	coefficient defined by Equation (5) (-)
n_0	air quantity inside the building before the release (mol)
n_a	flammable compound quantity (mol)
n_a^*	maximum allowed build-up of flammable gas (mol)
$n_{a,P}^*$	maximum allowed gas accumulation considering overpressure (mol)
$n_{a,Q}^*$	maximum allowed gas accumulation considering radiation (mol)
n_e	gas quantity inside enclosure after the explosion (mol)
n_f	smoke moles in the cloud at the end of complete combustion (mol)
n_{ia}	quantity of the compound *i* entrained by the release (mol)
n_{ig}	quantity of the compound *i* consumed or produced by combustion (mol)
$n_{i,smoke}$	quantity of the compound *i* in the combustion smokes (mol)
p_e	pressure inside the enclosure after the explosion (Pa)
p_0	internal pressure before the release (Pa)
Q_r	total energy radiated (kW)
$\dot{Q}_r''$	radiated thermal flux density (kW·m^{-2})
R	radius of radiating surface (m)
t	exposure duration (s)
T_0	ambient temperature before the release (K)
T_e	temperature after the combustion (K)
T_f	flame temperature in the cloud (K)
x_i	volume fraction of *i* in the mixture (-)
y_a	molar fraction of flammable gas (-)
y_{as}	molar ratio of flammable gas to the total gas in the cloud (-)
y_L	lower flammable limit (-)
α	coefficient defined in Equation (4) (-)
β	coefficient defined by Equation (16) (kW$^{4/3}$ m$^{-8/3}$)
γ	fraction of the total combustion energy converted to radiation for hydrocarbons (HC) (-)
ΔH_c	standard molar hydrocarbon enthalpy of combustion at 298 K (J mol^{-1})
ε	flame emissivity (-)
v_i	stoichiometric coefficient (-)
ρ_a	air density (kg·m^{-3})
ρ_m	gaseous mixture density (kg·m^{-3})
σ	5.67×10^{-11} kW·m^{-2}·K^{-4}
ω_i	mass fraction of *i* in the mixture (-)
*	limiting value

1. Introduction

Coal still represents an abundant energy resource in USA, China and Europe and with the development of the coal chemical industry, coke oven gas (COG) is widely used in the process industry and power production. As widely reported, coal can be defined as a complex sedimentary rock, a heterogeneous mixture of higher-plant-derived organic materials which have undergone chemical changes in connection with the depositional environment and the diagenetic history. Since coal is not a homogenous substance, it is characterized by wide variations in its properties and compositions. The most common coal classification is by rank, *i.e.*, the degree of coalification that organic plant sediment has reached in its metamorphosis from peat to near-graphite-like material [1]. As well known, coke oven gas is a by-product of coal carbonization to coke which is co-generated during the dry distillation process [2] and it clearly reflects the characteristics of parent coal. Typically, 1.25–1.65 t of coal produces 1 t of coke, in connection with approximately 300–360 m^3 of COG (6–8 GJ/t coke), while currently 20%–40% of produced COG is normally utilized as fuel in the actual coke oven [3]. As an indication, Table 1 shows the energy balance for a typical coke-making plant along with different raw materials and product distribution [4].

Table 1. Mass and energy flow of a typical coke-making plant.

Input		Output	
Energy	42.7 GJ/t coke	Energy loss	8.65%
Coal	91.44%	Coke	69.63%
Electric power	0.37%	Coke oven gas (COG)	17.92%
Fuel gas (firing gas)	7.61%	Tar	2.77%
Steam	0.58%	Benzene, toluene, xylenes (BTX)	0.98%
-	-	Sulphur	0.05%

The key principle of an inherently safer design approach is to reduce hazards associated with materials used and operations, instead of controlling them with add-on protective barriers. This approach is recently applied also in emerging fuel/energy technologies (e.g., [5,6]). Notwithstanding improvement in the design and process management, the steel industry is the largest energy consuming industrial sector worldwide, with an expected steel production raise during the next few decades [7], so that COG will continue to be produced in large quantities in the future, as coke cannot be substituted in the blast furnace. Therefore, despite the continuous move towards inherently safe materials, accidental releases of dangerous toxic/flammable gases still represent a serious concern in the coal processing industries. Even if the potential development of explosive atmospheres is generally typical of industries classified at major hazard, it is also possible in other industries where flammable materials are handling and requires quantitative methodologies based on a probabilistic risk assessment starting from a detailed knowledge of the analyzed system [8].

The composition of COG after leaving the coke oven is rather complex: after the cooling stage to separate tar and the scrubbing processes eliminating NH_3, H_2S and benzene, toluene, xylenes (BTX), the gas contains H_2 (55%–60%), CH_4 (23%–27%), CO (5%–8%), CO_2 (<2%) with other hydrocarbons (HC) in small proportions [9].

The importance of hazardous gaseous releases containing methane was recently highlighted by Chen *et al.* [10] who studied the relationship between different equivalent ratios and gas explosion dynamic behavior with the aim of providing guidance for preventing and controlling gas explosion disasters.

A statistical survey on accidents occurring in the coal sector based on FACTS data bank (managed by the Unified Industrial & Harbour Fire Department in Rotterdam-Rozenburg-NL) evidenced that from the beginning of this century to 2011, 72 accidents connected to coal were recorded: 19 with fatalities and 28 with injuries [11]. Making reference to the main accident scenario classification, as expected from coal inherent hazards, the highest percentage of entries corresponds to Explosion (47.8%), followed by Fire (35.8%) and Release (16.4%). Recalling the classification into three main headlines of accident causes and the subsequent analysis of concurring causes [12], plant/process accounted for 35.3% of total entries, organization collected 49.9% of entries, while the remaining 14.8% are connected to environment. Long term accident analysis on occupational accidents revealed as well the determining contribution of so-called human factors to the accident severity, especially in the process sector [13]. In many instances, moderate releases of flammable gases in confined or semi-confined geometry are known to present a serious risk, since explosive mixtures may form. Therefore, there is a need in the assessment of the maximum admissible gas build-up, in connection with adverse effects, so as to foresee the effectiveness of techniques in reducing the possible consequences of the unwanted events.

In this paper, theoretical investigation on low rate continuous release under semi-confined conditions is presented, in the context of preventing related accident evolving scenarios, by designing proper technical and managerial measures. The main purpose of this work is to develop a simplified mathematical approach for the evaluation of the maximum allowed hazardous substance build-up is developed, considering the intrinsic hazards of the released compound. The remainder of this paper includes a description of the short-cut method and an example of its application to a coke dry distillation process, in semi-confined volumes, after a proper experimental characterization of the gas potentially involved. The results will help to understand and assess small hazardous releases consequences in closed area and therefore to set-up appropriate control measures. A comparative simulation using computational fluid dynamics (CFD) techniques is presented to validate the obtained figures with detailed data such as the mole fraction of flammable gas, the flammable region, the spatial dispersion. In fact, as commented by Mazzoldi *et al.* [14], CFD can be applied for the most rigorous treatment of the physics of fluid flows and atmospheric dispersion within the framework of pipeline risk assessment. The here-developed methodology can be applied to more complex situations, allowing, as well, the attainment of a more generalized approach for the design, once given the release parameters, the building and plant layout.

2. Theoretical Model

2.1. Allowed Gas Build-up Considering Overpressure

Following the preliminary approach presented in [15] the allowed build-up is here defined as the maximum amount of the flammable compound in the environment following the continuous release, evaluated on the basis of tolerable effects on human vulnerable structures in case of ignition. On this basis, the allowed build-up can be identified making reference to the corresponding hazards for man inside the building, namely overpressure and radiating heat exposure. Clearly, in case of compounds characterized by different intrinsic hazards, the safety evaluation must also consider the corresponding hazardous scenarios, e.g., toxicity (CO) or thermal instability (C_2H_2). The analysis of accidental events related to the rupture of pipes and the related frequencies need as well extended approaches based on the introduction of probability models as recently discussed from a theoretical point of view and from a practical risk analyst perspective [16]. In order to approach the allowed build-up evaluation, reference is made to following scenario: instantaneous combustion of the whole mass of flammable substance and complete mixing of combustion products with air inside the building. Explosion injury is basically caused by the blast effect causing eardrum rupture and lung damage or by whole body displacement, or bodily translation and thermal effect. We assume that the maximum admissible overpressure corresponds to the threshold obtained from average conservative values by different sources [8,17,18]. The adoption of threshold values is envisaged by legislation (e.g., already mentioned DM 151/2001), as well as in the criteria adopted by technical standards [19]. The considered threshold value represents a consistent assumption also for possible failure of connection in small equipment caused by static overpressure [20] and a conservative value, when considering tube deformation and possible resulting domino effect, for which the threshold value is 0.2 Pa [21]. The safety criterion can easily be expressed by Equation (1):

$$p_e - p_0 = \Delta p \leq \Delta p^* = 0.07\ \text{Pa} \tag{1}$$

Final pressure can be roughly calculated by Equation (2):

$$p_e = p_0 \frac{n_e}{n_0} \frac{T_e}{T_0} \tag{2}$$

The values of n_e and T_e are calculated taking into account the most conservative situation, *i.e.*, those corresponding to the maximum overpressure value. Assuming by definition that n_a be the flammable release build-up inside the building up to the ignition time, the maximum temperature value, corresponding to the whole absorption of the reaction heat by the air-smoke mixture, can be easily calculated by:

$$T_e = T_0 + \frac{n_a(-\Delta H_c)}{n_e \tilde{c}_{pe}} \tag{3}$$

The value of n_e depends upon the degree of confinement of the building where the release takes place and the combustion stoichiometry, as follows:

$$n_e = n_0 + \alpha n_a + n_a \sum \nu_i \tag{4}$$

The term αn_a accounts for the gas quantity connected to the combined effects of the release and the exchange with the external environment due to aeration. Generally speaking, it results: $0 \leq \alpha \leq 1$, with following limiting cases:

- completely sealed enclosure: $n_a = n_r$; $\alpha = 1$;
- well ventilated building, small quantity released: $\alpha \approx 0$;
- condensed phase release: $\alpha \approx 0$.

In connection with the most critical situation, *i.e.*, totally confined environment, Equation (4) can be rearranged as:

$$n_e = n_0 + kn_a \tag{5}$$

where:

$$k = 1 + \sum \nu_i \tag{6}$$

By combining Equations (2)–(5), one can write:

$$\Delta p = \frac{p_0}{n_0}\left(k + \frac{(-\Delta H_c)}{\tilde{c}_{pe} T_0}\right) n_a \cong \frac{p_0}{n_0 T_0} \frac{-\Delta H_c}{\tilde{c}_{pe}} n_a = \frac{R}{V} \frac{-\Delta H_c}{\tilde{c}_{pe}} n_a \tag{7}$$

The approximation in Equation (7) is justified, being:

$$k \equiv 10^{-2} \frac{-\Delta H_c}{\tilde{c}_{pe} T_0} \tag{8}$$

The allowed build-up can be calculated from Equation (7), by imposing $\Delta p = \Delta p^*$:

$$n_a^* = \frac{\Delta p^* \tilde{c}_{pe}}{-\Delta H_c} V \tag{9}$$

and assuming $\tilde{c}_{pe}$ = 29.1 kJ kmol^{-1} K^{-1}:

$$n_a^* = \frac{25}{-\Delta H_c} V \tag{10}$$

or else, being:

$$y_a = \frac{n_a}{n_0} \tag{11}$$

$$y_a^* = \frac{\Delta p^*}{p_0} \frac{\tilde{c}_{pe} T_0}{-\Delta H_c} \tag{12}$$

that under standard environmental conditions (SATP) yields:

$$y_a^* = \frac{600}{-\Delta H_c} \tag{13}$$

From Table 2, one can notice that y_a* <<< 1, so that it results that the maximum allowed accumulation form the practical viewpoint corresponds to the mean molar fraction of flammable gas accumulated within the enclosure before the ignition:

$$y_a^* = \frac{n_a^*}{n_0} \cong \frac{n_a^*}{n_0 + n_a^*} \tag{14}$$

This value can be compared with the low flammable limit (LFL) of the released compound in air showing a value lower by at least an order of magnitude, as clearly demonstrated in Table 2. From this observation, it results that the condition $y_a < y_a$* guarantees the impossibility of fire propagation inside the building, even in presence of an effective ignition source.

Table 2. Maximum allowed build-up and mean molar concentration calculated for different positively/neutral buoyant gases and dense gases under the overpressure constraint and corresponding average molar concentration in the volume.

Compound	y_a^*	y_L	y_a^*/y_L	n^*_a/V
H_2	0.00248	0.040	0.062	0.1034
CH_4	0.00075	0.051	0.015	0.0311
C_2H_2	0.00048	0.025	0.019	0.0199
C_2H_4	0.00045	0.031	0.015	0.0189
CO	0.00212	0.155	0.014	0.0883
C_2H_6	0.00042	0.030	0.014	0.01750
C_3H_6	0.00031	0.024	0.013	0.01298
C_3H_8	0.00029	0.022	0.013	0.01224
C_4H_8	0.00024	0.016	0.015	0.00984
C_4H_{10}	0.00023	0.019	0.012	0.00941
C_5H_{10}	0.00019	0.015	0.013	0.00799
C_5H_{12}	0.00018	0.015	0.012	0.00770
C_6H_6	0.00019	0.014	0.014	0.00797
C_6H_{12}	0.00016	0.013	0.012	0.00669
C_6H_{14}	0.00016	0.012	0.013	0.00648

However, it is noteworthy noting that the presence of limited internal regions where $y_a > y_L$ cannot be excluded "*a priori*", for example referring to the neighborhoods of the release point. The volumes connected to a possible fire would result intrinsically limited, especially under well mixing conditions (released gas density comparable with air density and adequate ventilation). Under these circumstances, even in presence of an ignition source, the consequences would be negligible, due to the low mass fraction of fuel involved. On the contrary, a different approach must be considered in case of formation of gas pockets with density significantly different from the air one, in connection with low aeration condition and/or particular geometrical configuration of the room where the release occurs. In this case, even if the safety constrain expressed by the Equation (1) and the derived limitation according to Equations (9) and (12) be respected, a fire development in the flammable regions would give rise to possible relevant thermal radiation damage for a man operating in the proximity of the flame. The theoretical analysis of the above-mentioned situation is performed in the following section, so as to define further safety conditions that in some instances can represent the limiting and most conservative constraints. These considerations well apply to the peculiar case of coke oven gas, owing to its chemical composition. As already remarked, when considering a CO release, the reference for the threshold value is connected to toxic exposure and therefore to the immediately dangerous to life and health (IDLH) limit set by the National Institute for Occupational Safety and Health (NIOSH).

2.2. Allowed Gas Build-up Considering Thermal Radiating Exposure

In order to quantify the maximum allowed accumulation in a confined volume, reference is made to the following scenario:

- build-up of a flammable gas/air cloud resulting from a finite duration subsonic leak and stratification due to density difference between gas and air;
- dimensions and shape of the cloud constrained by the geometric characteristics of the room;
- flammable cloud ignition → flame development → thermal radiation from a plane radiating surface of area A_r.

We assume that the maximum allowed duration of exposure corresponds to the threshold values of damage to humans, properly derived as shown in the following. Starting from reference [22], the duration t^* decreases in connection with the increase of the thermal flux reaching the target, according to the empirical equation here proposed:

$$t^* = \beta \dot{Q}_i''^{-4/3} \tag{15}$$

where:

$$\beta = 631 \text{ kW}^{4/3}\,\text{m}^{-8/3} \tag{16}$$

The safety criterion, in terms of exposure duration, can be expressed by:

$$t \le t^* \tag{17}$$

so that the threshold build-up corresponds to the condition $t = t^*$.

On one side, the total energy radiated by the flame can be calculated by:

$$Q_r = \gamma n_a (-\Delta \tilde{H}_c) \tag{18}$$

where γ is quoted in the range 0.15–0.35 [23].

Equation (18) is a conservative estimate being based on the assumption that the whole flammable mass is contained within the confined cloud. On the other side, one can write:

$$Q_r = \dot{Q}_r'' A_r t \tag{19}$$

Again, it can be noticed that Equation (19) is a conservative evaluation, in that due to thermal exchanges the temperature T and, consequently, the heat radiated flux decrease as times goes on. By combining Equations (18) and (19), one can write:

$$t = \frac{\gamma n_a \left(-\Delta \tilde{H}_c\right)}{\dot{Q}_r'' A_r} \tag{20}$$

The received thermal flux can be calculated by:

$$\dot{Q}_i'' = \dot{Q}_r'' f_w \tag{21}$$

By virtue of Equation (21), Equation (16) can be rearranged as:

$$t^* = \beta \dot{Q}_r''^{-4/3} f_w^{-4/3} \tag{22}$$

The allowed build-up, $n_a = n_a^*$, can be obtained under the condition $t = t^*$:

$$n_a^* = \frac{\beta}{\gamma\left(-\Delta \tilde{H}_c\right)} \dot{Q}_r''^{-1/3} A_r f_w^{-4/3} \tag{23}$$

Considering that n_a^* decreases as $\dot{Q}''$ increases, in Equation (23) it is advisable to consider with a conservative approach the maximum theoretical value of $\dot{Q}''$, according to the following procedure, and starting from the simple Equation (24), already applied in evaluating heat radiating from the unit surface of a flame from a pool fire [24]:

$$\dot{Q}_r'' = \varepsilon\sigma T_f^4 \tag{24}$$

Assuming that T_f corresponds to the adiabatic combustion temperature, one can write:

$$T_f = T_0 + \frac{n_a\left(-\Delta\tilde{H}_c\right)}{n_f \tilde{c}_{pf}} \tag{25}$$

By defining y_{as} as the molar ratio of flammable gas, n_a, to the total gas in the cloud, n_{as}, before the combustion, one can write:

$$y_{as} = \frac{n_a}{n_{as}} \tag{26}$$

The maximum adiabatic temperature corresponds to the stoichiometric conditions ($y_a = y_{a,st}$), so that Equation (25) can be modified as:

$$T_f = T_0 + y_{a,st}\frac{-\Delta\tilde{H}_c}{\tilde{c}_{pf}} \tag{27}$$

Considering Equations (24) and (27), Equation (23) can be modified as follows:

$$n_a^* = \frac{\beta}{\gamma\left(-\Delta\tilde{H}_c\right)}(\varepsilon\sigma)^{-1/3}\left(T_0 + y_{a,st}\frac{-\Delta\tilde{H}_c}{\tilde{c}_{pf}}\right)^{-4/3} A_r f_w^{-4/3} \tag{28}$$

Assuming $T_0 = 298$ K and $c_{pf} = 32$ kJ kmol^{-1} (average value in the range 298–200 K) and $\varepsilon = 0.20$ [23], following expression is obtained:

$$n_a^* = \frac{7055}{\left(-\Delta\tilde{H}_c\right)}\left(1 + 1.05\cdot 10^{-4} y_{a,st}\frac{-\Delta\tilde{H}_c}{\tilde{c}_{pf}}\right)^{-4/3} A_r f_w^{-4/3} \tag{29}$$

3. Results and Discussion

The maximum allowed build-up of flammable gas, n_a^*, is obviously attained, by comparing the two potential evolving scenarios, under the condition:

$$n_a^* = min\left(n_{a,P}^*, n_{a,Q}^*\right) \tag{30}$$

In the following, as an applicative case-study we discuss from a practical viewpoint the limiting conditions expressed in analytical form by Equations (12) and (29), considering the rather common situation $T = 298$ K (see Table 3).

The condition $n_{a,P}^* \gtreqless n_{a,Q}^*$ can be expressed in explicit form by Equation (31):

$$\frac{V}{A_r} f_w^{4/3} \quad \eta = \left[1 + 1.05\cdot 10^{-4} y_{a,st}\left(-\Delta\tilde{H}_c\right)\right]^{4/3} \tag{31}$$

The calculated values of η corresponding to some common positively buoyant gases and dense buoyant gases are reported in Table 4.

Table 3. Maximum allowed build-up per unit surface calculated for different positively/neutral buoyant gases and dense gases, considering radiating heat constraint.

Compound	$-\Delta H_c$ **(J mol^{-1})**	$f_w = (1 + d^2/A_r)^{-1}$						
		1	**0.9**	**0.8**	**0.7**	**0.6**	**0.5**	**0.4**
		n^*_a/A_r **(mol m^{-2})**						
H_2	241,800	1.68204	1.93574	2.26491	2.70628	3.32380	4.23848	5.70721
CH_4	802,600	0.46972	0.54057	0.63249	0.75574	0.92819	1.18362	1.59377
C_2H_2	1,257,000	0.22360	0.25732	0.30108	0.35975	0.44184	0.56342	0.75866
C_2H_4	1,323,000	0.24503	0.28198	0.32993	0.39423	0.48419	0.61743	0.83138
CO	283,000	1.19235	1.37219	1.60553	1.91840	2.35615	3.00454	4.04567
C_2H_6	1,428,600	0.24615	0.28327	0.33144	0.39603	0.48640	0.62025	0.83518
C_3H_6	1,925,700	0.16997	0.19561	0.22887	0.27347	0.33587	0.42830	0.57671
C_3H_8	2,043,100	0.16841	0.19381	0.22677	0.27096	0.33278	0.42436	0.57141
C_4H_8	2,540,800	0.12871	0.14812	0.17331	0.20709	0.25434	0.32433	0.43672
C_4H_{10}	2,657,300	0.12797	0.14727	0.17232	0.20590	0.25288	0.32247	0.43421
C_5H_{10}	3,129,600	0.10549	0.12141	0.14205	0.16973	0.20846	0.26583	0.35794
C_5H_{12}	3,244,900	0.10505	0.12089	0.14145	0.16901	0.20758	0.26470	0.35642
C_6H_6	3,136,000	0.10502	0.12086	0.14141	0.16897	0.20753	0.26464	0.35634
C_6H_{12}	3,739,400	0.08826	0.10158	0.11885	0.14201	0.17442	0.22241	0.29948
C_6H_{14}	3,855,100	0.08794	0.10121	0.11842	0.14149	0.17378	0.22160	0.29839

Table 4. Values of the parameter η (m) calculated for different positively/neutral buoyant gases and dense gases.

Compound	M_i **(g mol^{-1})**	V/A_r
H_2	2	16.3
CH_4	16	15.1
C_2H_2	26	11.2
C_2H_4	28	13.0
CO	28	13.5
C_2H_6	30	14.1
C_3H_6	42	13.1
C_3H_8	44	13.8
C_4H_8	56	13.1
C_4H_{10}	58	13.6
C_5H_{10}	70	13.2
C_5H_{12}	72	13.6
C_6H_6	78	13.2
C_6H_{12}	84	13.2
C_6H_{14}	86	13.6

In the absence of structural complexity of the enclosure/building, A_r corresponds simply to the surface of the ceiling or of the pavement and assuming that $f_w = 1$, one can write:

$$\frac{V}{A_r} = h \gtreqless \eta \qquad (32)$$

From the already quoted Table 4, for all the considered gaseous substances it results $\eta > 11$ m, so that in the common situations of building with "standard" height it results $h < \eta$ or in other words, the constraint based on overpressure is the limiting one, being more restrictive than the one based on radiating heat. When dealing with a gas whose density is greater than the density of the ambient air through which it is being released, due to its slumping towards the ground and its stratification the hypothesis $f_w = 1$ is adequate, as the operator in the proximity would be in contact with the flame. On this basis, a simplified evaluation on the main parameters determining radiating heat exposure and the consequent risk severity should include at least following items:

- exposure time to the flame;
- height of the flammable layer;
- thermal flux density;
- protective clothes worn by workers.

Considering neutrally and positively buoyant gases, in case of building with complex geometry (beams, tunnel, confined volumes in the ceiling, *etc.*), it is foreseeable the formation of build-up volumes of gas characterized by $A_r << A$. Under these circumstances, from one side the limiting safety constraint is connected to the evaluation of the tolerable radiating heat, from the other side the hypothesis $f_w = 1$ results too conservative (as, generally speaking, f_w shows a decreasing trend as A_r decreases). It is therefore mandatory evaluating the effect of f_w, for example according to the simplified approach here outlined. By assimilating the radiating surface to a circle a cautious estimate of f_w is provided by the following expression:

$$f_w = \frac{R^2}{R^2 + d^2} = \frac{1}{1 + \pi d^2 / A_r} \qquad (33)$$

Table 5 are reported the values of the ratio V/A_r corresponding to the condition $n^*_{a,P} = n^*_{a,Q}$, in connection with different values of f_w ranging from 0.4 to 1.

Table 5. Values of the parameter η (m) calculated for different positively/neutral buoyant gases and satisfying the condition $n^*_{a,P} = n^*_{a,Q}$.

Compound	f_w					
	0.9	**0.8**	**0.7**	**0.6**	**0.5**	**0.4**
H_2	18.7	21.9	26.2	32.1	41.0	55.2
CH_4	17.4	20.3	24.3	29.8	38.0	51.2
C_2H_2	12.9	15.1	18.1	22.2	28.3	38.1
C_2H_4	14.9	17.5	20.9	25.6	32.7	44.0
CO	15.5	18.2	21.7	26.7	34.0	45.8

Results summarized in Table 5 evidence as the limiting condition to quantify the maximum allowed build-up is usually determined by the maximum overpressure (*i.e.*, $n^*_a = n^*_{a,P}$), apart from some rather peculiar and well-defined situations.

4. Case-Study Application

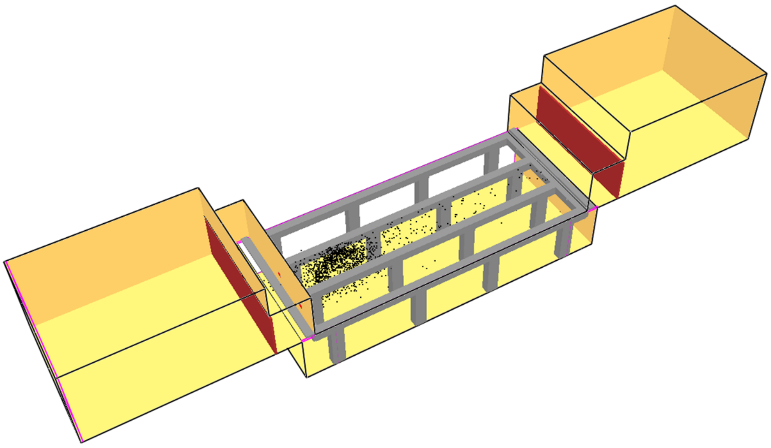
As a numerical application, we consider the peculiar case of a mixture of gases taken from an industrial plant performing coal dry distillation of coal and reproduced in Figure 1.

Figure 1. Picture of the industrial process plant.

The plant is addressed to the production of low grade (metallurgical) coke and foundry coke. The process is carried out by four parallel coke oven batteries, fed with fossil coal and heated by process coke gas conveniently desulphurized. The average daily production is 900 t of foundry coke and 400 t of low-grade coke. The average COG production is in the range 450,000–500,000 Nm^3 d^{-1} and is utilized as fuel in the coke oven in a proportion of 50%, while the surplus is utilized in a cogeneration power plant for internal use.

The gas feeding section of each oven is localized in separated local beneath each battery (see Figure 2) with following conditions: maximum pressure 152 bar; feeding pressure 76 bar. COG resulting from the process is characterized by a variability connected to the characteristics of the coal utilized in the dry distillation plant.

Figure 2. Schematization of the local beneath each coke oven battery.



The average results of the chemical composition of coke oven gas, obtained on yearly basis, by standard analytical methods is shown in Table 6. The average flammability range [LFL-upper flammability limit (UFL)] was experimentally obtained by laboratory tests as 8%–36% *v*/*v*.

Table 6. Average chemical composition of coke oven gas (COG) expressed as weight and volume percentage.

Compound	ω_i (% *w*/*w*)	x_i (% *v*/*v*)
O_2	0.79	0.29
N_2	26.22	11.17
CH_4	30.95	23.07
CO	10.76	4.58
CO_2	8.32	2.07
C_2H_4	4.85	2.07
C_2H_6	2.38	0.94
H_2	9.00	53.65
H_2O	2.31	1.53
C_nH_m	4.44	0.63

According to the developed approach, immediately after the release it follows a dilution of each compound forming COG, followed by a stratification towards the ceiling of the enclosure of the gaseous mixture characterized by a density ρ_m, lower than the air density ρ_a. Among the possible gaseous mixtures, we explored those of primary interest, as detailed in the following. The stochiometric mixture is connected to the maximum burning velocity and flame temperature and is calculated in Table 7.

Table 7. Characterization of stoichiometric mixture (molar fraction: x_r = 0.19; average molar mass: M_m = 25.7 g mol^{-1}).

Compound	n_{ir} (mol)	n_{ig} (mol)	n_{ia} (mol)	n_{im} (mol)	n_{ismoke} (mol)	m_{im} (g)	m_{ir} (g)
O_2	2.9	−921.1	918.2	921.1	0.0	29,476	93
N_2	111.7	0.0	3,454.3	3,566.0	3,566.0	99,847	3,128
CO_2	20.7	376.5	-	20.7	397.2	911	911
H_2O	15.3	1,089.1	-	15.3	1,104.4	275	275
CO	45.8	−45.8	-	45.8	0.0	1,282	1,282
H_2	536.5	−536.5	-	536.5	0.0	1,073	1,073
CH_4	230.7	−230.7	-	230.7	0.0	3,691	3,691
C_2H_4	20.7	−20.7	-	20.7	0.0	580	580
C_2H_6	9.4	−9.4	-	9.4	0.0	282	282
C_6H_6	4.41	−4.41	-	4.41	0.0	344	344
C_7H_8	1.30	−1.30	-	1.30	0.0	120	120
$C_8H_{1}0$	0.39	−0.39	-	0.39	0.0	42	42
C_5H_{12}	0.04	−0.04	-	0.04	0.0	3	3
C_6H_{14}	0.06	−0.06	-	0.06	0.0	5	5
C_7H_{16}	0.03	−0.03	-	0.03	0.0	3	3
C_5H_{10}	0.03	−0.03	-	0.03	0.0	2	2
C_6H_{12}	0.04	−0.04	-	0.04	0.0	3	3
Mixture	1,000	−304.8	4,372.5	5,372.5	5,067.7	137,939	11,836

The mixture corresponding to the LFL experimentally obtained and calculated in Table 8, is characterized by the lowest difference with air and, correspondingly, to the minimum exit velocity from the enclosure due to ventilation (either natural or forced).

Table 8. Characterization of lower flammable limit (LFL) mixture (molar fraction: $x_r = 0.08$; average molar mass: $M_m = 27.6$ g mol^{-1}).

Compound	n_{ir} (mol)	n_{ig} (mol)	n_{ia} (mol)	n_{im} (mol)	n_{ismoke} (mol)	m_{im} (g)	m_{ir} (g)
O_2	2.9	2,625	2,628	−921.1	1,707	84,093	93
N_2	111.7	9,875	9,987	0.00	9,987	279,628	3,128
CO_2	20.7	-	20.7	376.5	397.2	911	911
H_2O	15.3	-	15.3	1,089	1,104	275	275
CO	45.8	-	45.8	−45.80	0	1,282	1,282
H_2	536.5	-	536.5	−536.5	0	1,073	1,073
CH_4	230.7	-	230.7	−230.70	0	3,691	3,691
C_2H_4	20.7	-	20.7	−20.70	0	580	580
C_2H_6	9.4	-	9.4	−9.40	0	282	282
C_6H_6	4.41	-	4.41	−4.41	0	344	344
C_7H_8	1.30	-	1.30	−1.30	0	120	120
C_8H_{10}	0.39	-	0.39	−0.39	0	42	42
C_5H_{12}	0.04	-	0.04	−0.04	0	3	3
C_6H_{14}	0.06	-	0.06	−0.06	0	5	5
C_7H_{16}	0.03	-	0.03	−0.03	0	3	3
C_5H_{10}	0.03	-	0.03	−0.03	0	2	2
C_6H_{12}	0.04	-	0.04	−0.04	0	3	3
Mixture	1,000	12,500	13,500	−305	13,195	372,336	11,836

Taking into account the different geometrical characteristics of each coke battery of the industrial plant, Table 9 shows the results of the maximum allowable build-up, under the radiating heat constraint.

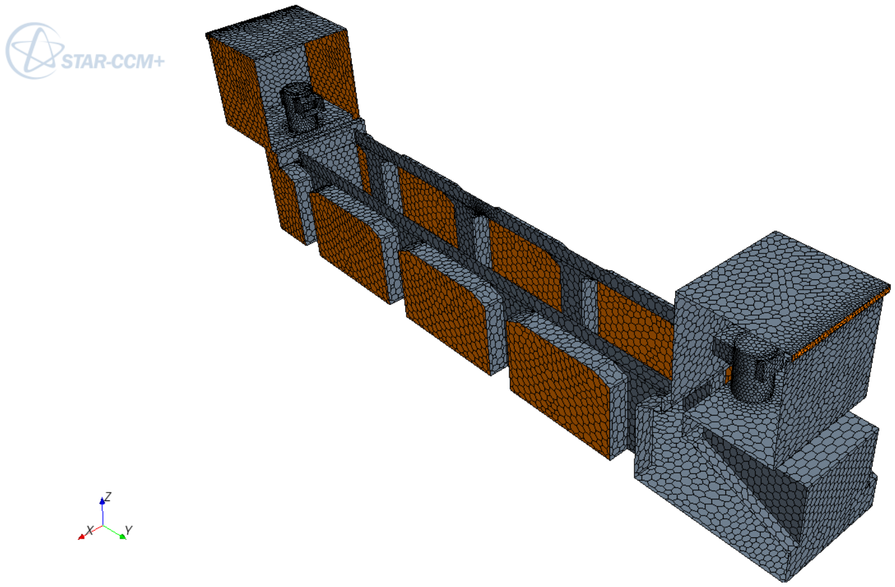
Table 9. Maximum allowed build-up, under the radiating heat constraint.

Battery	Gas mixture	A_r (m^2)	Q (kJ)	$n_{r\text{-}amm}$ (mol)	x_r	$n_{m.amm}$ (mol)	V_{amm} (m^3)	h_{amm} (m)
A	Stoichiometric	22	9,797	22.4	0.19	120	3.0	0.14
	LFL	22	21,564	49.3	0.08	616	15.6	0.72
B, C, D	Stoichiometric	23	10,334	23.6	0.19	127	3.2	0.14
	LFL	23	22,747	52.0	0.08	650	16.4	0.72

Dealing with explosion risk, it must be underlined that a minimum mass is required to allow transition from flash fire to explosion: under semi-confined geometry MacDiarmid and North [25] report a minimum value of 30 kg. The results obtained considering the fugitive emissions in the under oven enclosures are connected to total hydrogen volumes at least three orders of magnitude lower than the previously quoted, even under the worst considered release scenario.

A schematic representation of the under coke oven enclosure A where the scenario of fugitive COG emissions was considered is depicted in Figure 3. All the simulation works presented in this paper were performed using the commercial STAR-CCM + CFD code. The simulation using CFD techniques provides detailed data about the flammable region and the spatial dispersion of coke gas, allowing verifying the goodness of the design of the required ventilation, performed on the basis of the developed simplified approach and optimizing the interval between two human inspections. The considered plant sections is modeled into three volumes, including the under coke oven local and the utility rooms where the air/smoke valves are installed. Polyhedral meshes were selected with characteristic dimensions ranging from 0.002 m to 0.2 m; a total of 38,099 volume meshes and 27,486 surface meshes are utilized in simulating coke batteries B, C and D, while 34,695 volume meshes and 26,622 surface meshes are designed for coke battery A. It should be noticed that in analogy with the approach suggested in [26], we used a nested domain with a mesh finer grid in proximity of the source term (minimum cell size 0.002 m) and ventilation openings (minimum cell size 0.02 m), where simulations need to be more precise and where large concentration gradients are expected. Given the characteristics of the enclosure where human presence and interaction is very limited, the operative conditions and the control/emergency instrumentation of the plant, the purpose of the simulation is limited to low-rate fugitive emissions of coke oven gas, excluding full-bore ruptures.

Figure 3. Computational fluid dynamics (CFD) model: polyhedral meshing of the geometry (battery A).



In order to minimize error due to discretization errors, a grid independence analysis was performed. In addition, a sensitivity study allowed to validate the meshes presented on the Figure 3, and to choose the model of turbulence for all the calculations. The convergence criterion is chosen to be 10^{-6} for the RMS (Root Mean Square) Max residuals.

The flows are simulated by solving the non-stationary Navier-Stokes equations with turbulence using a standard k-ε model.

The equations solved in the calculations performed are based on some assumptions: the fluid considered is a mixture of gases, as explained in Table 6, taken to be mixed at the molecular level (multi-species formulation). The flow is turbulent, isothermal and weakly compressible. The gaseous mixture is considered to be an ideal gas.

Standard wall functions were used for velocity (no slip), turbulent kinetic energy and its dissipation rate on solid surfaces. A hydrodynamic roughness of 1 mm was assigned to all solid surfaces including the ground. Initial air temperature is 306 K.

The location of the leak is pinpointed at coordinates 5 m × 1.8m × 2.1 m, whilst its emerging direction is horizontal. The release flow rate is 0.00164 $m^3 \cdot s^{-1}$.

Figure 3 shows the detailed geometry of a single coke oven battery A proposed for the comparative case-study utilizing CFD simulation. Figures 4 and 5 evidence the release stratification of coke oven gas respectively in absence of ventilation and with the designed ventilation, in the same coke oven battery A.

Figure 4. CFD model: mole fraction of coke gas at 600 s from the beginning of the release in the coke battery A.

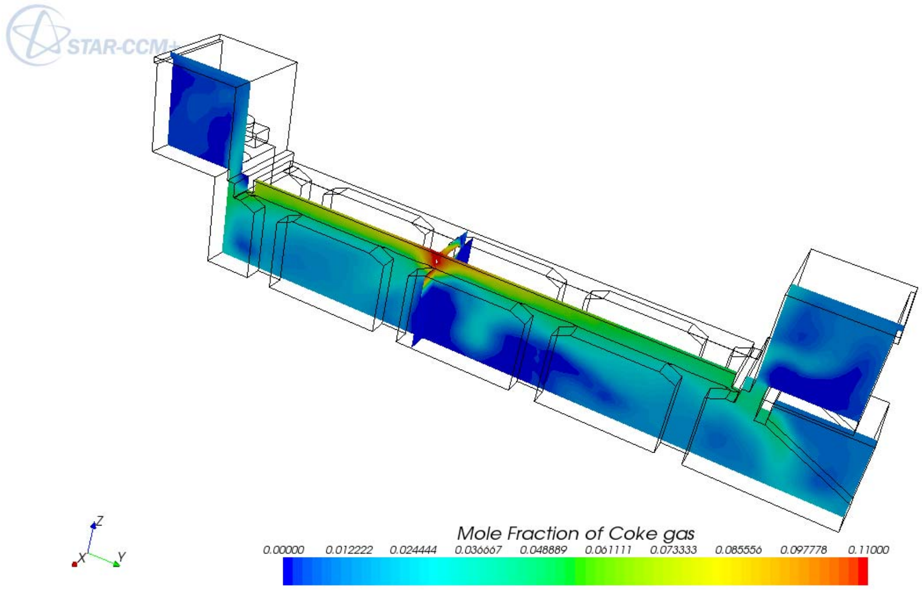
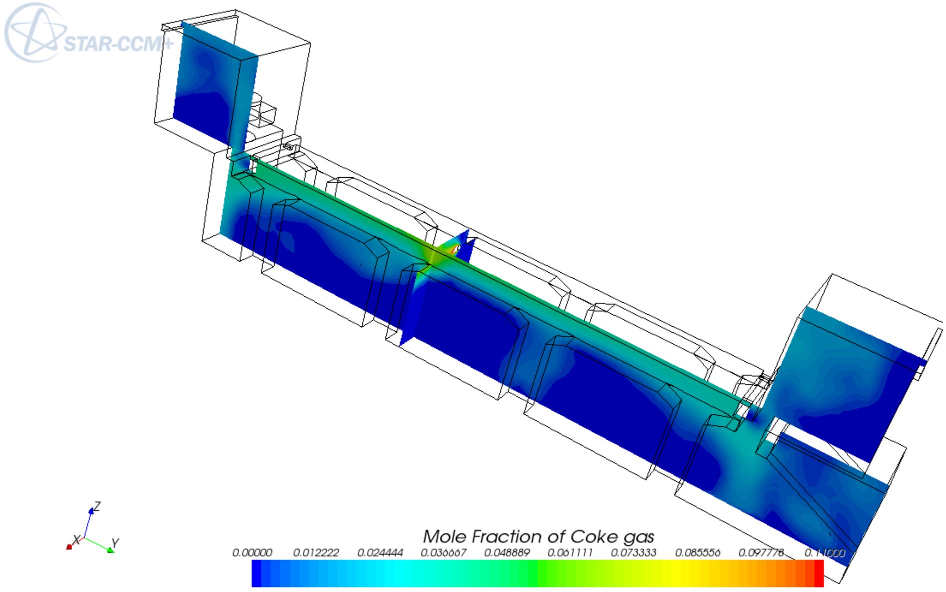
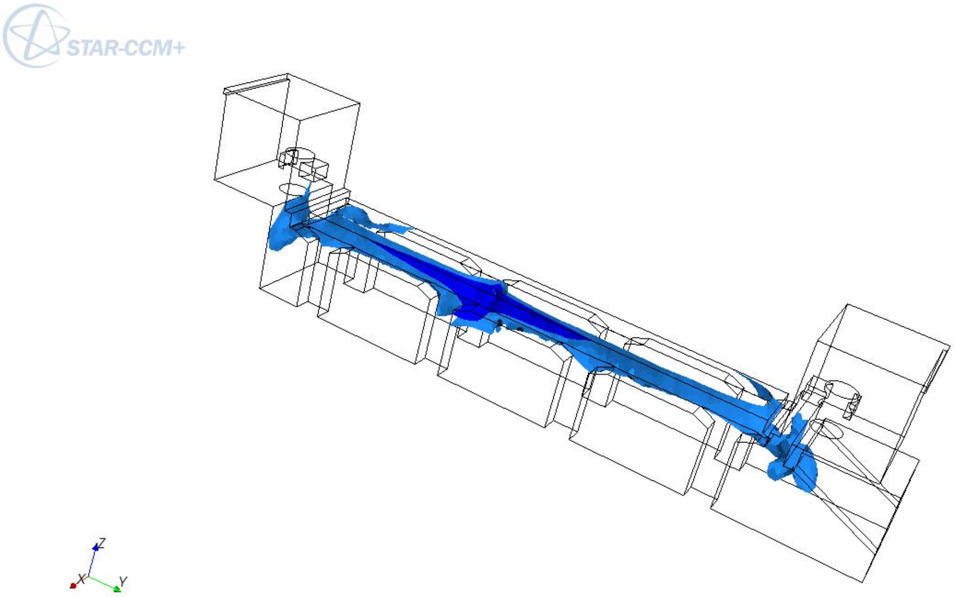


Figure 5. CFD model: mole fraction of coke gas at 600 s from the beginning of the release in coke battery A under the designed ventilation conditions.



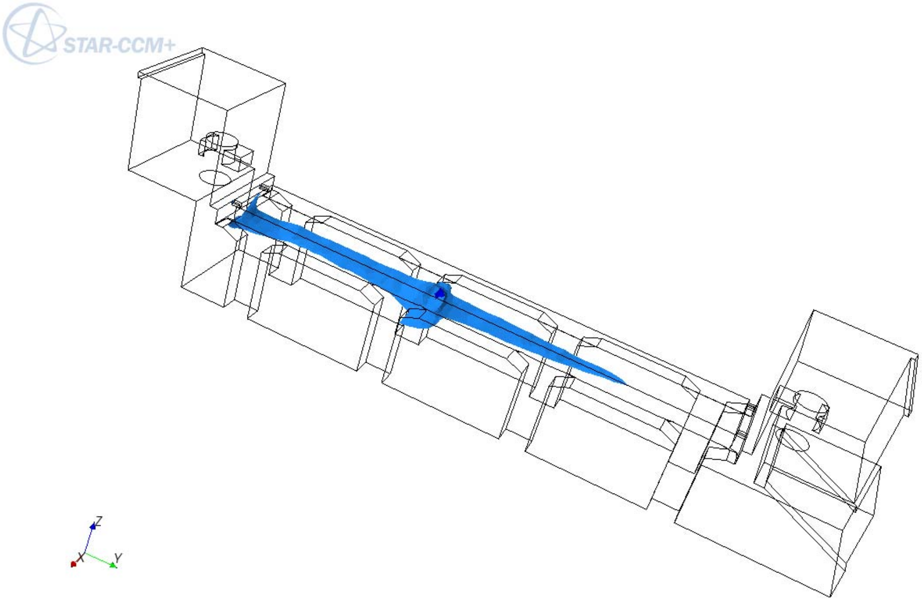
CFD simulations allowed verifying the role of natural ventilation in connection with the possible formation of flammable gas pockets resulting from fugitive emissions in the under coke oven locals. In fact, Figure 6 shows a three-dimensional (3D) view of CFD predicted concentration iso-surfaces corresponding to LFL and 0.5 LFL for the investigated scenario under the original layout.

Figure 6. CFD model: LFL and 0.5 LFL concentration iso-surfaces at 600 s from the beginning of the release in coke battery A.



Similarly, Figure 7 depicts the CFD predicted concentration iso-surfaces corresponding to LFL and 0.5 LFL, considering the influence and the impact of the natural ventilation openings. Numerical simulations performed considering ventilation conditions indicate that both CFD and analytical model are consistently similar for the investigated low-rate release scenarios.

Figure 7. CFD model: LFL and 0.5 LFL concentration iso-surfaces at 600 s from the beginning of the release in coke battery A under the designed ventilation conditions.



Consequently, the under coke oven locals of the industrial plant were provided with natural ventilation openings, sized according to the maximum allowed gas build-up. As detailed elsewhere [27], analysis showed the need to install as well gas sensors (CO/H_2) and ensure a reliable periodic inspection program, according to a frequency preventing the attainment of critical build-up, calculated according to the mathematical model previously outlined [28]. The gas detector network positioned in proximity of the ceilings of each enclosure provides a direct empirical check of the validity of CFD simplified modeling. Furthermore, in order to reduce possible piping failure in the considered setting and referring to a more managerial issue, a useful approach can be based on the definition of the links between the causes of failure and the measures adopted by the company to prevent them considering in detail the effects of management and organizational variables [29].

5. Conclusions

The problem of concentration build-up in closed environment is of practical interest in many industrial processes, as well as in natural or forced ventilation design for health and safety purposes.

Applying the developed approach to the under coke oven enclosures, where low flow rate releases of gas mixture (mainly hydrogen, methane and light HC) can occur, it is possible to size venting areas and needed ventilation rates. The proposed analytical tool, even under the limitations of the simplifying hypotheses adopted, can help understanding and assessing the hazards from small releases during coal processing under semi-confined geometry and take appropriate preventive and control measures. The inherent limitations of the study, both in the analytical and CFD modeling provide the opportunity of further experimental and theoretical refinement. The methodology can be applied to more complex situations involving fugitive emissions, allowing, as well, the attainment of a more generalized approach for the preliminary design, once given the release parameters, the building and plant layout.

Conflicts of Interest

The authors declare no conflict of interest.

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