ACCIDENT CONDITION INFLUENCE ON ITS CONSEQUENCES FOR TWO CASE STUDIES: BLEVE FIRE FROM A MALEIC ANHYDRIDE PRODUCTION PLANT, AND PUFF RELEASE FROM AN ANILINE SYNTHESIS REACTOR

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(Petro)chemical complexes include high-risk plants processing large quantities of hazardous substances in complex chemical reactors, vessels, or separation units operating at intense temperature and pressures. When highly exothermic, hazadous reactions are conducted, evaluation of possible accident consquence scenarios according to engineering models is necessary. The case study includes two risky plants for the synthesis of aniline and maleic anhydride respectively. The study applies BLEVE fire and toxic PUFF release models to evaluate the influence of various accident conditions on the effects (radiative heat flux, and toxic aniline concentration), consequences (P% of fatalities), and possible Domino effect occurrence at various distances from source. The results highlight the importance of considering all accident conditions related to the plant capacity and operating severity, location, and stock level of hazardous substances in intermediate vessels.

Keywords: accident consequences and effects; BLEVE fire; puff toxic release; aniline; butane

Notations

b	-	puff radius
C	-	Concentration
C_r	-	regulation threshold for the toxic gas concentration in the atmosphere
D_i	-	puff characteristic dimension
$D_{initial}$	-	initial ground level fireball hemisphere diameter
D_{max}	-	maximum diameter of the fireball
E	-	the emitted flux at the surface of the fireball
E_r	-	thermal radiation flux received by the receptor
F_{21}	-	geometrical view factor between fireball and the receptor
g	-	gravitational acceleration
g_o	-	initial buoyancy factor

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G	-	total initial mass of the released toxic vapours
H_{BLEVE}	-	center height of fireball
H_c	-	heat of combustion
L	-	distance from fireball center to the receptor at ground level
M	-	molar H_2/NB feed ratio, or initial mass of the fuel in the fireball
n, k_1, k_2	-	constants of the probit equation for dose lethality evaluation
p_w	-	water partial pressure in air
P, P%	-	percentage of fatalities
R	-	radiative factor of H_c
R_H	-	relative humidity of air
t_{arriv}	-	puff center arrival time to the receptor
t_{BLEVE}	-	fireball combustion duration
t_{pass}	-	vapour cloud passage time
T_a	-	ambient air temperature , or cooling agent temperature
u	-	wind speed
V	-	cloud volume
x	-	axial distance
X_{c}	-	path length from fireball center to the receptor
X_{s}	-	path length from fireball surface to the receptor
y_o	-	toxic gas volumetric fraction at source
Y	-	probit variable
Greeks		
β	-	parameter in the B-McQ model (Table 2)
δ_{puff}	-	axial puff thickness
ρ	-	Density
σ_x , σ_y , σ_z		the Pasquill-Gifford dispersion coefficients for puff dispersion in the (x, y, and z) directions respectively
τ_{air}	-	atmospheric transmissivity
Index		
a	-	ambient air, or cooling agent
hor	-	Horizontal
max	-	Maxim
o	-	Initial
ref	-	reference value
ver	-	Vertical
w	-	Water
Abbreviations		
AN	-	Aniline
BLEVE	-	boiling liquid expanding vapour explosion
Bu	-	Butane
CPQRA	-	chemical process quantitative risk analysis
DTL	-	toxic dose
MA	-	maleic anhydride
ME	-	Biodiesel (vegetal oil methyl ether)
NB	-	Nitrobenzene
PUFF	-	Toxic cloud release

1. Introduction

Petrochemical platforms are particularly subjected to complex risk analyses because they include a large number of hazardous installations processing important quantities of dangerous compounds. Large amount of toxic / flammable substances, intense temperature and pressure conditions, complex physico-chemical processes make these chemical plants potential sources of severe accidents. Besides, due to intervention congestions and a high level of interactions among subsystems, the accidents in the petrochemical plants are quite frequent, making the consequences worse, or even can generate accidents in-chain to the neighboured plans (the so-called Domino effects [1,7]).

Safe operation of such chemical plants including highly sensitive (catalytic) chemical reactors remains a challenge, especially when exothermic/hazardous reactions are conducted in the presence of a significant parametric uncertainty. Recently, Maria & Dan [2-3] introduced a new failure probability index that characterizes the operation of chemical reactors of high thermal sensitivity, and determines the working conditions leading to a high probability of runaway. However, frequent perturbations in the operating parameters, raw-material recycling conditions, catalyst replacement or reactivity modifications, all require periodical updates of the safety limits for the operating variables, and evaluation of the runaway risk when the reactor operates in a close vicinity of such boundaries [4-6]**.** Runaway of such thermally sensitive reactors may lead to fire of the auxiliary raw-material / product tanks, or to the release of toxic puffs. The effects and consequences of such chemical accidents strongly depend on the accident meteorological conditions, plant location, severity of plant operating conditions, and human population and equipment density, being evaluated through a quantitative risk analysis (CPQRA) using various accident scenarios [7-9].

The aim of this paper is to use the classical BLEVE fire and toxic Puff release models to evaluate the influence of various accident conditions on the effects, consequences and possible Domino effect occurrence involving two chemical plants with highly sensitive reactors: one plant including the hazardous tubular reactor for the catalytic oxidation of butane (Bu) to maleic anhydride (MA), and a second plant including the reactor for nitrobenzene (NB) catalytic hydrogenation to aniline (AN) in vapour phase. The two highly sensitive reactors present a similar construction, consisting in thousands of tubes (filed with granular catalyst) immersed in a bath where a cooling agent vigorously stirred takes over the heat of reaction generated inside tubes by the very exothermic reactions.

In the MA-plant case (with a reactor operated at low pressures 1.3-2 atm., 350-450^{o}C temperature, and inlet butane molar fraction lower than 3% [2]), the considered hazard source is the butane storage tank which, from safety reasons, do not contains butane stocks larger than the necessary for one week of reactor time-on-stream. The butane is a very flammable fuel, easily creating accident conditions for a BLEVE fire with possible subsequent Domino effects. The considered Bu-accident parameters refers to:

- The influence of the *butan fuel mass;*
- The influence of the *used model relationships* to evaluate the radiative flux at various distance from source;
- The influence of the *atmospheric humidity;*
- The influence of the *fuel heat of combustion* (butane in this case) by comparison with other fuels.

In the AN-plant case, the considered hazard source is the AN-reactor, operated at low pressures (1.3-3 atm), 300-400^{o}C temperature and high inlet molar H_2/NB ratios (15/1-200/1). In practice, to increase the reactor productivity, very often the operating conditions (nominal point) are set in a vicinity of the critical conditions of ca. 10/1 H_2/NB feeding ratio [4-6]. This is why, under runaway conditions, the toxic AN puff released by the relief valve contains maximum 10%vol. aniline. Such an AN toxic puff was released during several reported accidents, such as those from Eastman Chemical Company (Kingsport, TN, 1960)[16], DuPont Co. (Beaumont, TX, 2011)[15], First Chemical Corporation Co. (Pascagoula, MS, 1986)[11]. The toxic puff was released over tenths of seconds, the AN vapours and aerosols being transported over hundreds of meters distance, eventually leading to nano-/micro-metric spots at the ground level. The considered AN-accident parameters in the present study refers to:

- The influence of the used *Gaussian vs. Britter-McQuaid* adopted model;
- The influence of the released *aniline mass* on the accident consequences;
- The influence of the *Pasquill meteorological conditions;*
- The influence of the *wind speed.*

2. BLEVE model relationships and application rule

A boiling liquid expanding vapour explosion (BLEVE) happens when there is a sudden loss of containment of a pressure vessel containing a superheated liquid or liquefied gas, leading to the rapid expansion of the liquid (flashing) to the atmosphere. The blast wave produced by a sudden release of a fluid, followed by the flammable vapour ignition, depends on several factors [7,8]. This includes the type of fluid released, the expansion energy which is produced, shape of the vessel, rate of energy release, the presence of reflecting surfaces in the surroundings and type of rupture. The materials below their normal boiling point do not produce BLEVE fires.

The effects and consequences of BLEVE depends on the flammable liquid combustion heat, its boiling point / vapour pressure, the released mass, and the distance to the receptor. Most of the fireball parameters (i.e. fireball diameter, combustion duration, center height of fireball, and thermal emissive power, Table 1, Fig. 1) have been correlated empirically with the released fuel mass. By summarizing, the relationships necessary for evaluation of the BLEVE fire consequences and effects are given in the Table 1. The thermal radiation is also correlated by means of several empirical relationships, such as the horizontal, or vertical receptor surface model, the Roberts' formula, or the Hasegawa-Sato formula. More conservative predictions are given by taking the maximum of radiative flux predicted by all these models.

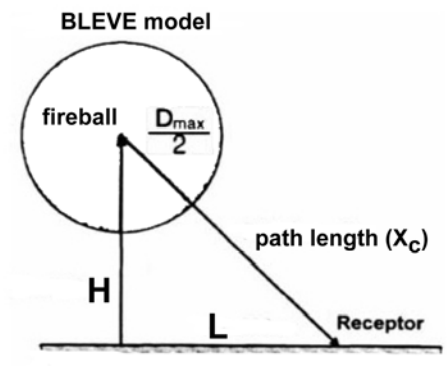

Fig. 1. Geometry of a BLEVE fireball (adapted after [7])

The fireball consequences expressed by the fatality level $P(Y_{Bu}(x))$ (that is P% human fatalities resulting from the exposure of a population to the radiative dose DTL) at various distances (x) from the fire source can be evaluated by means of the Probit variable $Y_{Bu}(x)$, with the general relationship [7]:

$$P\% = 50\left[1 + \frac{Y-5}{|Y-5|} erf\left(\frac{Y-5}{\sqrt{2}}\right)\right], \text{ with } Y_{Bu} = k_1 + k_2 \ln(\text{DTL}), \tag{1}$$

where k_1 and k_2 are given in Table 1, while the thermal radiative dose DTL = $t_{\text{BLEVE}} E_r^{4/3} / 10^4$ is evaluated by using the butane fireball (BLEVE) model.

Table 1

BLEVE fire and probit models for evaluating the radiation heat flux and fatality levels respectively (after AIChE [7]; Maria et al. [1]).

Variable	*Evaluation formula*
Maximum diameter of the fireball (D_{max})	$D_{max} = 5.8M^{1/3}$, (m)
Fireball combustion duration (t_{BLEVE})	$t_{\mathrm{BLEVE}} = 0.45M^{1/3}$ (for $M <$ 30 t) , (s) $t_{\mathrm{BLEVE}} = 2.6M^{1/6}$ (for $M >$ 30 t) , (s)
Center height of fireball (H_{BLEVE})	$H_{\mathrm{BLEVE}} = 0.75\ D_{max}$, (m)
Initial ground level hemisphere diameter	$D_{initial} = 1.3\ D_{max}$, (m)
The emitted flux at the surface of the fireball (E)	$E = RMH_c /(\pi D_{max}^2 t_{\mathrm{BLEVE}})$, (kW m^{-2})
The horizontal geometrical view factor between fireball and the receptor	$F_{21,\mathrm{hor}} = H_{\mathrm{BLEVE}}\ (0.5D_{max})^2/(L^2 + H_{\mathrm{BLEVE}}^2)^{1.5}$
The vertical geometrical view factor between fireball and the receptor	$F_{21,\mathrm{ver}} = L\ (0.5D_{max})^2/(L^2 + H_{\mathrm{BLEVE}}^2)^{1.5}$
Path length from fireball center to the receptor (X_c)	$X_c = \sqrt{H_{\mathrm{BLEVE}}^2 + L^2}$, (m)
Path length from fireball surface to the receptor (X_s)	$X_s = \sqrt{H_{\mathrm{BLEVE}}^2 + L^2} - 0.5D_{max}$, (m)
Water partial pressure in air (p_w)[10]	$p_w = 101325\ R_H \exp(14.4114\text{-}5328/T_a)$, (Pa)
Atmospheric transmissivity (τ_{air})	$\tau_{\mathrm{air}} = 2.02(p_w X_s)^{-0.09}$
Received radiation flux at the receptor (horizontally)($E_{r,\mathrm{hor}}$)	$E_{r,\mathrm{hor}} = \tau_{\mathrm{air}}\ E\ F_{21,\mathrm{hor}}$, (kW m^{-2})
Received radiation flux at the receptor (vertically)($E_{r,\mathrm{ver}}$)	$E_{r,\mathrm{ver}} = \tau_{\mathrm{air}}\ E\ F_{21,\mathrm{ver}}$, (kW m^{-2})
Received radiation flux at the receptor (formula of Roberts)($E_{r,\mathrm{R}}$)	$E_{r,\mathrm{R}} = 2.2\cdot10^{-3} RH_c M^{2/3}/(4\pi X_c^2)$, (kW m^{-2})
Received radiation flux at the receptor (formula of Hasegawa-Sato)($E_{r,\mathrm{RHS}}$)	$E_{r,\mathrm{RHS}} = 828 * M^{0.771}/ X_c^2$, (kW m^{-2})
Considered radiation flux for effects evaluation	max ($E_{r,\mathrm{hor}}$, $E_{r,\mathrm{ver}}$, $E_{r,\mathrm{R}}$, $E_{r,\mathrm{RHS}}$), (kW m^{-2})
Probit variable (Y)	$Y = -14.9 + 2.56\ \ln\left(t_{\mathrm{BLEVE}} E_r^{4/3} / 10^4\right)$, ($E_r$ in W m^{-2})
Thermal radiation intensity threshold	4.7 kW m^{-2}

Notations: M = initial mass of the fuel in the fireball (kg); L = distance from fireball center to the receptor at ground level (m); H_c = heat of combustion (kJ kg^{-1}); R = radiative factor of H_c (adopted R = 0.4, for fireballs from vessels bursting at or above the relief set pressure); T_a = ambient air temperature (K); R_H = relative humidity of air (%)

3. Puff toxic gas release dispersion model

To predict the fate of an accidentally released toxic cloud / plume, several categories of dispersion models are available depending on the available information, and modelling detailing degree. One can classify them according to the way the pollutant is produced (instantaneous, continuous source), or the spatial type of the source (point, line, area, volume source), the ground morphology and the atmospheric conditions, the composition of the pollutants (chemical, radioactive, etc.), their state (solid, liquid, gas) or the scale of their consequences (local, middle or large scale)[7,8,11].

Empirical models are not based on a full mathematical analysis, but only correlate the accident parameters and consequence indices by means of simple algebraic relationships with no physical meaning of model constants [7]**.** Because of that, more evaluated deterministic or probabilistic models have been elaborated based on fluid mechanics, and chemical engineering principles.

For the puff relaese case, the deterministic Gaussian models defining the pollutant transport in the atmosphere are based on the generalized dispersion equation, that is the Navier-Stockes differential mass balance written for a continuous point source and one direction of transport (x – downwind) (see the Fig. 2 scenarios for a discontinuous toxic gas release). The Gaussian model should be applied for neutrally or positively buoyant gas/vapour cloud (of molecular mass lower or equal to those of the air). For dense (or negativelly) buoyant gas / vapours, other models, such as the Britter and McQuaid model [1,7,11] should be applied. Equations of these models are presented in Table 2. Examples of Puff accidents are reviewed for instance by Assael & Kakosimos [11].

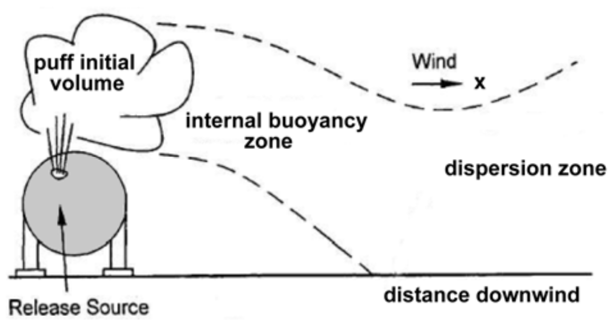

Fig. 2. Toxic puff release from a vessel, initial acceleration and buoyancy, and cloud dispersion for a neutrally or a dense buoyant gas (adapted after [7]).

One essential parameter of the Gaussian model is the meteorological stability classes evaluated given the environmental conditions (wind speed, daytime insolation, nightime conditions, degree of cloudiness, solar elevation angle):

A = very unstable	*C = slightly unstable*	*E = slightly stable*
B = unstable conditions	*D = neutral conditions*	*F = stable conditions*

Table 2

Puff and probit models for evaluating the toxic vapour cloud dispersion and fatality levels respectively (after AIChE [7]; Assael & Kakosimos [11]; Maria et al. [1]).

Variable	*Evaluation formula*
a) Gaussian model (Gauss; gas molecular weight ≤ 30 g mol^{-1})	
Puff center concentration $C(x)$ at distance (x) downwind	$C(x,0,0,t) = G/(\pi^{1.5}\sqrt{2}\sigma_y^2\sigma_z)\cdot$ $exp\{-[(x-ut)/\sigma_y]^2/2\}\cdot 10^6$, (mg m^{-3}) (a)
Axial puff thickness (δ_{puff}) at a certain distance (x) from source (C_r isopleth)	$\delta_{\text{puff}} = 2\sigma_y\sqrt{-2\ln(C_r\pi^{1.5}\sqrt{2}\sigma_y^2\sigma_z/G)}$, (m) ($C_r$ in kg m^{-3})
Vapour cloud passage time (t_{pass})	$t_{\text{pass}} = \delta_{\text{puff}}/u$, (s)
Toxic dose (DTL) of the puff at distance (x_{ref}) downwind	DTL = $\int_{x=0}^{x\to\infty}[C(x,0,0,x_{ref}/u)]^n\, d(x/u)$, (ppm^n min) ($C$ in ppm, exposure time $t_e = x/u$ in min)
a) Britter-McQuaid model (B-McQ; gas molecular weight > 30 g mol^{-1})	
Initial buoyancy factor (g_o)	$g_o = g(\rho_o - \rho_a)/\rho_a$, (m s^{-2})
Initial cloud volume (V_o), initial radius (b_o), and characteristic dimension (D_i)	$V_o = (G/\rho_o)/y_o$, (m^3); b_o, $= 0.5\sqrt[3]{6V_o/\pi}$, (m); $D_i = \sqrt[3]{V_o}$, (m)
Instantaneous release condition	$\sqrt{g_oV_o}/(uD_i) \geq 0.2$
Puff center concentration $C(x)$ at distance (x) downwind	$C(x)/C_o$ correlations of Maria et al. (2014), as function where: $\beta = \log(x/V_o^{1/3})$
Elapsed time (t_{arriv}, s) of the puff center to arrive at distance (x, m), and the puff radius (b, m) at distance x	Iteratively solve the nonlinear set: $\begin{cases} b = \sqrt{b_o^2 + 1.2\,t_{arriv}\sqrt{g_oV_i}} \\ t_{arriv} = (x-b)/(0.4u) \end{cases}$
Vapour cloud passage time (t_{pass})	$t_{\text{pass}} = \delta_{\text{puff}}/u$, (s) ; $\delta_{\text{puff}} = 2b$, (m)
Toxic dose (DTL) of the puff at distance (x_{ref}) downwind	DTL = $C^n(x_{\text{ref}})t_{\text{pass}}$, (ppm^n min)
Probit variable (Y)	$Y = k_1 + k_2\ln(DTL)$; $n = 1$, $k_1 = -18.97$, $k_2 = 2.23$ for aniline [1,12]
Romanian regulation threshold (C_r)	20 mg m^{-3} (for aniline)

Notations: G = total initial mass of the released toxic vapours (kg); u = wind speed (m s^{-1}); n, k_1, k_2 = constants of the Probit equation (1) for lethal toxicity; DTL = toxic dose, C^nt_e (ppm^n min); ρ_o = initial cloud density (kg m^{-3}); V_o = initial cloud volume (m^3); y_o = toxic gas volumetric fraction at source; ρ_a = ambient air density (kg m^{-3}); g = gravitational acceleration (10 m s^{-2}); C_o = puff center concentration at source (kg m^{-3}).

(a) The Pasquill-Gifford dispersion coefficients for puff dispersion are the following ($\sigma_x = \sigma_y$) [7]: $\sigma_y = 0.18x^{0.92}$; $\sigma_z = 0.60x^{0.75}$ (stability class A); $\sigma_y = 0.14x^{0.92}$; $\sigma_z = 0.53x^{0.73}$ (stability class B); $\sigma_y = 0.10x^{0.92}$; $\sigma_z = 0.34x^{0.71}$ (stability class C); $\sigma_y = 0.06x^{0.92}$; $\sigma_z = 0.15x^{0.70}$ (stability class D); $\sigma_y = 0.04x^{0.92}$; $\sigma_z = 0.10x^{0.65}$ (stability class E); $\sigma_y = 0.02x^{0.89}$; $\sigma_z = 0.05x^{0.61}$ (stability class F).

The Britter and McQuaid model is not appropriate for jets or two-phase plume releases due to the entrainment effect noted earlier. The model is based only on data taken in flat, rural terrain, and can only be applied to these types of releases. The model is only based on the conditions of the test data and is unable to account for the effects of parameters such as release height, ground roughness, wind speed profiles, etc.

Application of the Gaussian dispersion model for the heavier-than-air toxic clouds over-estimates the consequences, i.e. the dispersion length, puff center concentration, toxic dose and resulted P% of fatalities. For such cases, the Britter-McQuaid model (B-McQ) should be applied of which relationships do not depend on the meteorological stability class, but only on the wind speed (u). In this case, the AN toxic dose (DTL) of the puff at distance (x_{ref}) downwind, is dependent on the distance (x), and vapour cloud passage time (t_{pass}): DTL = $C_{AN}^{n}(x_{\text{ref}})t_{\text{pass}}$, (ppm^n min), where the aniline concentration $C_{AN}(x)$ in ppm units is determined with either Gauss-model or B-McQ model (Table 2).

4. Analysis of two case studies

The analysis of the influence of butane BLEVE fire accident conditions on the accident consequences is based on scenario simulations using the nominal, minimum, and maximum values of the model parameters specified in Table 3.

Table 3

The fire conditions and BLEVE model parameter range considered in the butane accident sensitivity analysis. The receptor is situated at maximum L = 300 m from fire source. The ambiental temperature is 298 K. The Pasquill class of stability is D (neutral) (MA plant characteristics given by Maria & Dan [2-3]).

Model parameter	*Nominal value (model)*	*Other tested values (models)*
Type of model for the received flux at the receptor (Er, kW/m^2)	Maximum (Er)	Vertically Roberts formula Hasegawa & Sato formula The maximum Er value
Heat of Combustion of fuel (kJ/kg)	49700 (butane)	42800 (Diesel) 36500 (Biodiesel vegetable oil methyl ester, ME)[17]
Butane mass in the stock tank at the ignition moment (1 day stock = 7.5 t)	3 days stock (22.5 t)	1 days stock 7 days stock
Relative humidity of air (fraction from saturation level)	0.8	0.2 0.5

The BLEVE fireball model output are the followings:

- Maximum fireball diameter

- Fireball combustion duration
- Fireball height
- Radiative heat flux (E_r) at various distances from source
- Heat radiative dose (DTL), and P% of fatalities at various radius around source

The analysis of the influence of butane BLEVE fire accident conditions on the accident consequences is based on scenario simulations using the nominal, minimum, and maximum values of the model parameters specified in Table 4.

Table 4

The toxic puff release conditions and PUFF model parameter range considered in the aniline cloud accident sensitivity analysis. The receptor is situated at maximum L = 300 m from puff source. The percent of aniline in the released vapours of 10% (runaway conditions (Stefan & Maria [4]; Maria & Stefan [5,6])

Model parameter	*Nominal value (model)*	*Other tested values*
Released toxic vapours mass (Aniline) (kg)	100	50 150
Pasquill meteorological class	D D	A, F (Gauss model) A, F (B-Q model)
Wind speed (m/s)	0.5	0.1 2.0
Ambiental temperature (K)	298	298
Relative humidity of air (%)	80	80
Wind speed (m/s)	0.5	0.1 1.0
Used puff dispersion model	Gaussian	Britter & McQuaid

The PUFF model outputs are the followings:

- Puff center concentration at various distances (x) downwind
- Axial puff thickness at a certain distance from source (C_r isopleth)
- Vapour cloud passage time
- Toxic dose (DTL) of the puff at distance (x_{ref}) downwind
- Initial buoyancy factor (B-McQ model only)
- Initial cloud volume, initial radius, and characteristic dimension (B-McQ model only)
- P% of fatalities at various distances (x) from source downwind

5. Results discussion

The theoretical study of the accident parameter influence on the accident consequences related to BLEVE-fires and PUFF-toxic cloud release is exemplified by simulation of various accident scenarios for the two case studies (fireball to the butane tank from the MA-plant, and AN toxic cloud release from the AN-reactor runaway).

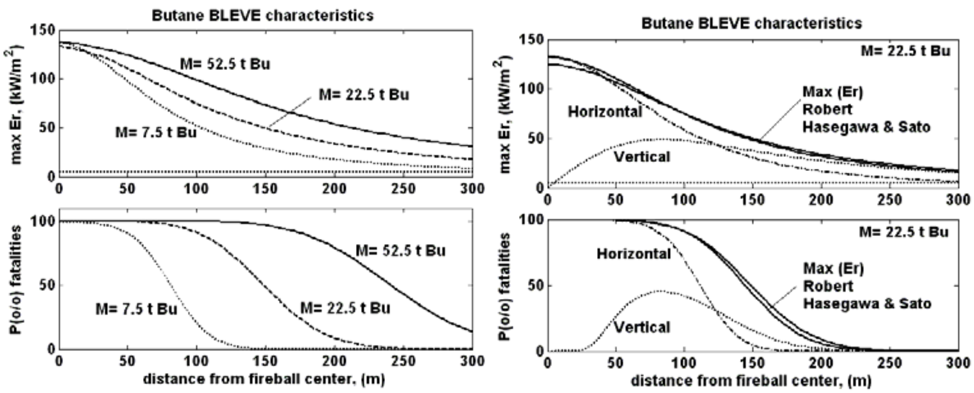

Fig. 3. The influence of the fireball butane fuel mass (left), and of the used relationship to evaluate the radiative heat flux (*Er*, kW/m^2) (right) on the accident effects (radiative flux *Er*, and P% of fatalities) at various distances from the fireball center (nominal conditions of Table 3).

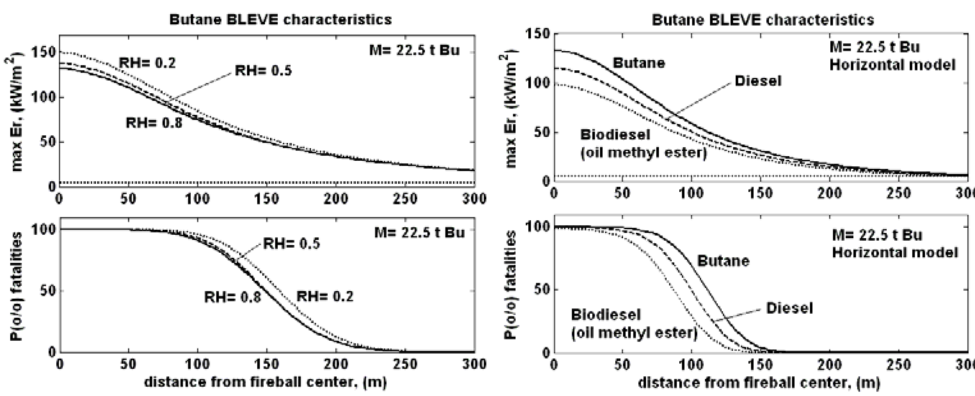

Fig. 4. The influence of the athmosphere relative humidity (left), and the heat of combustion of the fuel (right) on the accident effects (radiative flux Er, and P% of fatalities) at various distances from the fireball center (nominal conditions of Table 3).

The model-based simulation of the influence of accident conditions on the BLEVE fire consequences, involving a butane tank from the MA-production industrial plant, leads to the following conclusions:

- The effect of *butane fuel mass* on the fireball is very high (left of Fig. 3), the percentage of fatalities P(%) and emitted radiative flux (*Er*) sharply increasing with the involved mass of butane in the fire. The worst scenario corresponds to the stock-tank explosion including a 3 to 7 days-butane-stock, the value of *Er* being higher than the threshold of 37.5 kW m^{-2} [7] causing damages to the process equipment over more than 200 m radius (P% > 30%). It is to observe that the fireball life-time is relatively short (i.e. 10-30 seconds) compared to reported minutes required to cause serious plant damages [13], but the flux intensity is very high (usually ca. 150-400 kW m^{-2} at source) [14] possible generating Domino effects in a close vicinity.

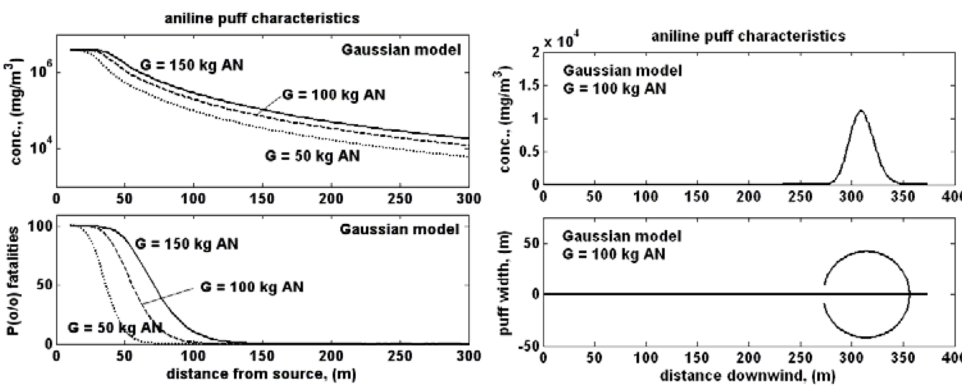

Fig. 5. The influence of the released mass of aniline (G) in the toxic Puff (left), on the AN concentration in the puff center, the P% of fatalities (left), and on the width of the cloud (of 20 mg/m^3 on the border) for various distances downwind from source (100 kg released AN, Gaussian model; nominal conditions of Table 4).

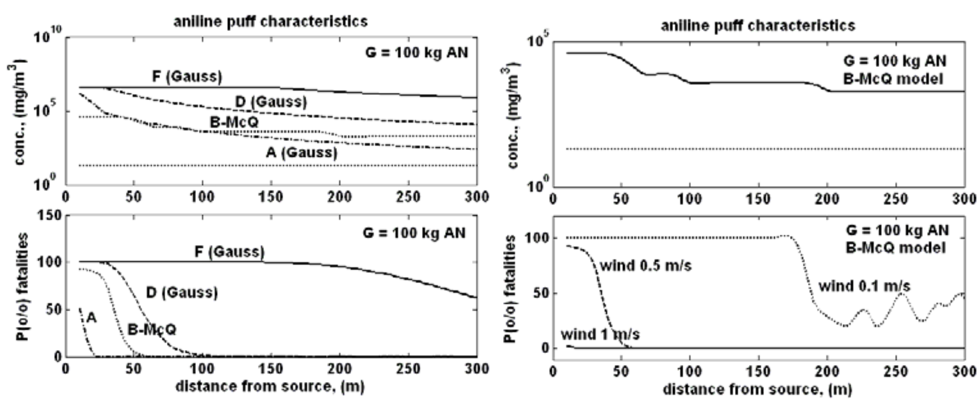

Fig. 6. The influence of the Pasquill-Gifford meteorological class of stability and type of puff model used (left), and of the wind speed (right; B-McQ model) on the accident effects (puff center concentration, and P% of fatalities) at various distances from the puff source downwind (nominal conditions of Table 4).

- The *used model* to calculate the radiative heat flux is also very important (right of Fig. 3). Evaluation of *Er* at various distances from fire source reports significant differences between the correlation models (denoted by Er-horizontal, Er-vertical, Er-Robert, Er-Hasegawa-Sato). Because of that, the Max (Er) is recommended to be adopted in further risk assessment calculations as being the worst possible case. The lowest effect of the fireball is given by (Er vertical) model as long as such a receptor surface exposes a low receptor area to the fireball sphere, especially when it is located below the fireball. The dangerous radius around fireball where the radiative flux E_r > 37.5 kW m^{-2} is about 200 m.

- A low influence of the *relative humidity* on for P (%) fatalities and radiative heat flux (E_r) is reported, irrespectively to the distance from the fireball center (left Fig.4)
- The influence of the *heat of combustion* of the fuel on P (%) fatalities and radiative heat flux (E_r) is very high. Usually, a high heat of combustion (butane in this case) leads to a high value for the radiative flux and, consequently, to high values of the P% of fatalities over a larger radis around the fire source (Fig. 4-right). The biodiesel fuel exhibits the lowest fire consequences under similar accident conditions.

The model-based simulation of the influence of accident conditions on the toxic PUFF release consequences, involving the industrial aniline synthesis reactor, leads to the following conclusions:

- The influence of the *released AN mass* in the toxic-PUFF on the accident consequences is very high, the radius of significant P% fatalities doubling when the aniline mass is doubling (Fig. 5). Of course, such a parameter is in directly relationship with the AN-reactor operating severity, a high plant productivity inherently increasing the magnitude of a possible accident.
- The influence of the *Pasquill-Gifford meteorological* conditions on the PUFF-accident consequences is extremely high when the Gaussian Puff model is employed (Fig. 6-left). It is to note that the B-McQ model is not influenced by the meteorological class, being one of the model limitations. By comparing the Gauss and B-McQ model predictions when assuming meteorological classes A, D, and F on the accident moment, it is to observe that the worst situation is reported for the *F (stable conditions)* class, when the aniline aerosols/vapors are spread over a large distance, increasing the radius of high P% fatalities.
- The *Gaussian model* offers over-estimated predictions of the accident consequences (puff center concentrations, DTL, and P% fatalities as function of distance) as biased as the toxic cloud density is higher than those of the air and the meteorological conditions are more stable (F-class; Fig. 6-left). By contrast, the *B-McQ model* for heavy vapors indicates a too low radius of high P% lethality and toxic substance concentration, as long as heavy vapors have the tendency to fall down in a vicinity of the source, and then to not be

dispersed by the wind so easily. Such under-estimated predictions are unrealistic for this case study involving toxic clouds of molecular weight (35 g mol^{-1}) close to those of the air; the experimental evidence in the DuPont Co. accident (Beaumont, TX, 2011; [15]) reveals much larger dispersion distances (up to 500 m) for the spread AN aerosols.

- The Gaussian model, even if offering over-estimated results, can be used in further risk analysis as the ‘worst possible scenario”. For this case study, probably an average between Gauss and B-McQ model predictions might be a more realistic representation of the accident consequences.
- The influence of *the wind* on the rapid dispersion of the toxic cloud and, consequently, on the radius of high P% fatalities is extremely high (Fig. 6 - right). While negligible P% fatalities are reported for u = 1 m/s wind speed, high P% fatalities are reported over more than 150 m distance downwind for very stable accident conditions of 0.1 m/s wind speed.

6. Conclusions

Both BLEVE-fire and PUFF-toxic-release models are suitable for simulating the accident effects and consequences involving industrial plants. Such models are quite flexible, by accounting not only for the accident source characteristics (toxic substance / fuel mass, physico-chemical properties, toxicological characteristics), but also for the environmental conditions (meteorological class of stability, wind speed, air humidity, temperature).

The study highlights the tremendous importance of considering all parameters influencing the accident magnitude and occurrence risk (not included in this paper), directly related to the severity of industrial plant operating conditions, plant location, stock level of hazardous substances in the intermediate vessels, etc.

The use of adequate simulation models of potential accident effects and consequences associated with risky plants from a petrochemical complex is of significant importance not only in the process design phase, but also during the process operation and risk management, by adjusting the severity of plant operation conditions vs. the associated risk. Such a complex analysis of the consequences of various accident scenarios, completed with an evaluation of the accident occurrence probability, may lead to valuable conclusions related to the dangerous operating conditions of the chemical plants.

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