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# Safety distances for the sour biogas in digestion plants

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## Abstract

The presence of sulfur-based substances in the biogas (sour) produced from digestion plant imposes several treatments to match the market and regulation requirements. Besides, it lays the production plants open to safety and environmental risks related to the accidental release of toxic species. This work is devoted to the investigation of the consequences of the accidental release of biogas containing hydrogen sulfide up to 10 %vol. To this aim, a schematic 3-D representation of a biogas productive plant was developed and implemented in a Computational Fluid Dynamics (CFD) model. The effects of the initial composition and the wind velocity on the cloud dispersion were evaluated. The calculated stand-off distances for lethality resulted from the numerical simulation were compared with the results of standard integral models commonly adopted in the process industry.

Results indicated the dramatic effects of the toxicity of hydrogen sulfide on the downwind safety distance in the case of accidental release of sour biogas, and the negligible effects for the flammability concerns.

**Keywords:** Biogas; Hydrogen Sulfide; Computational Fluid Dynamic; Anaerobic Digester Plant

## Highlights:

- Representation of a simplified process flow diagram of an anaerobic digestion plant
- Determination of unit operations involved in the accidental release of biogas
- Evaluation of the downwind safety distance of sour biogas using CFD and integral models
- Estimation of downwind safety distance for different wind velocity and acid gas content
- Quantification of the effects of the toxicity of H<sub>2</sub>S on the downwind safety distances

## 1. Introduction

Renewable energy has become a driving force in the effort to reduce the impact and consumption of global natural resources [1]. Among the available production routes for alternative sources of energy, anaerobic digestion plants (AD) represent a valid option because of the reduced impact on the environment and combustor systems, combined with elevated flexibility in terms of raw materials [2]. For instance, an AD process may reduce complex biological wastes to simpler constitutive components producing biogas [3]. Indeed, 2 billion tons per year of municipal solid waste are generated globally, of which a large part (about 34–53 %<sub>v</sub>) is represented by organic biodegradable waste [4].

For these reasons, the number of projects aiming for the realization of AD plants has been continuously and vigorously increased in the last years, especially in Europe, where stringent regulations limiting the emissions are applied [5]. Besides, the resulting gaseous streams need to be purified to match the market requirements. Indeed, the chemical composition may change according to the raw material and operative conditions adopted throughout the digestion process. However, the gaseous streams outcoming from the digester are usually composed of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and hydrogen sulfide (H<sub>2</sub>S), with limited concentrations of nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), and hydrogen (H<sub>2</sub>) [6]. The CO<sub>2</sub> sequestration is conveniently performed to reduce the inert volume and to increase the heating value, and the reduction of H<sub>2</sub>S content is required to comply with several international regulations [7][8].

Regardless of its content, the presence of H<sub>2</sub>S represents a serious threat in terms of safety [9]. Although the level of congestion plays a crucial role in the case of gaseous release [10], most of the studies on sour gas are focused on offshore applications [11]. Considering the nature of the unit operations composing an AD plant, several potential accidental scenarios can be identified in the case of the release of biogas, including explosion, dispersion of toxicity substances, and fire. Recently, a study performed by Casson Moreno et al. (2016) [12] has listed the accidents related to the biogas production that occurred in the previous two decades, indicating the leak from the separation unit as the main initiating event. The causes of biogas releases are generally attributed to equipment failure, component failure, and operational error, whereas fire and explosion scenarios are mainly related to maintenance or design errors [12]. Once released, the presence of a toxic compound in gaseous mixtures requires proper comparisons between H<sub>2</sub>S concentration and toxicological endpoints, especially in the areas where personnel may be present [13]. Besides, the flammability of the H<sub>2</sub>S/air mixture requires proper investigations on accidental scenarios generated by the presence of an ignition source. In the case of combustion, a toxic mixture, mainly containing SO and SO<sub>2</sub>, can be produced [14]. However, it should be mentioned that combustion products are less toxic than H<sub>2</sub>S, according to a report published by the World Health Organization (WHO) [15]. In addition, the occurrence of exothermic reactions (i.e., partial and complete oxidation) will lead to higher gaseous temperature, compensating the increase in molecular weight, thus resulting in less dense clouds [16]. The combination of these aspects, namely lower toxicity and density, makes the accurate modeling of H<sub>2</sub>S-containing mixtures dispersion of paramount importance for the decision-making process since larger areas may be involved. The atmospheric dispersion contributes to drive away the substance emitted from the source and to dissolve it due to the mixing with air. Firstly, considerations related to the density of the released gas should be done. Indeed, heavy and light gas models can be distinguished [17]. Regardless of methane and hydrogen sulfide ratio, the investigated mixture behaves like a light gas, thus it can be modeled by using gaussian dispersion. At this scope, different approaches can be applied. In particular, the Computational Fluid Dynamics (CFD) software calculates the gas diffusion starting from the primitive Navier-Stokes equations, whereas alternative tools are based on less expensive models [18]. Employing the first approach, it is possible to consider the presence of obstacles increasing the computational effort required. Typical examples of a consequence modeling tool and CFD are PHAST (Process Hazard Analysis Software Tool) code by DNV-GL [19] and ANSYS Fluent [20], respectively. Both have been largely validated [21][22]. For the PHAST software, particular attention was posed on the calculation of the uncertainty [23], demonstrating the robustness of the code. According to the procedure proposed in the current literature [24][25], the implementation of CFD implies the presence of additional source terms of uncertainties, e.g., material properties and turbulence models. Nevertheless, encouraging results have been obtained when a CFD code was compared with experimental measurements for gas dispersion [26].

In this work, the accidental release of several biogas mixtures leading to flash fire and toxic cloud dispersion were modeled. Results were obtained by using the consequence modeling tool the PHAST (Process Hazard Analysis Software Tool) code by DNV-GL [19], and the CFD software ANSYS Fluent [20]. In the latter case, a simplified representation of the main unit operation potentially involved in biogas release was implemented to evaluate the effect of the layout on the consequence analysis.

## 2. Methodology

### 2.1 Generalized approach

A continuous release of biogas from an anaerobic digester due to a crack/hole located on the surface of the tank shell in an unconfined environment was first considered. The main constituents of the biogas were considered CH<sub>4</sub> and H<sub>2</sub>S. The presence of inert species, like CO<sub>2</sub>, and other very-low content species as H<sub>2</sub> were neglected for the sake of simplicity. This hypothesis represents a conservative assumption on the safe side regardless of the investigated scenario. Three different compositions were then investigated (Table 1). The maximum content of hydrogen sulfide was posed to 10 %<sub>v</sub> (Mixture 1), according to the literature [27]. Thus, an intermediate composition (Mixture 2), representing the typical mixture resulting from digestors [28], was studied to assess the effects of substrate on the toxic effects. Finally, pure methane (Mixture 3) was considered for the sake of comparison.

The accurate estimation of the safety parameters for the two sour mixtures, in particular, the lower and upper flammability limits (LFL, UFL) [29], has represented a challenging task [30]. In this work, the experimental data of LFL and UFL were used when available [31][32]. Alternatively, estimations reported in the literature and obtained by the implementation of the detailed kinetic mechanism were considered [30].

To evaluate the biogas toxicity, two concentration levels were considered as reference values. The second level of the Emergency Response Planning Guideline (ERPG-2), defined by the AIHA (American Industrial Hygiene Association) was employed. This value is defined as the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action [33]. Furthermore, the IDLH (immediately dangerous to life and health) defined by the NIOSH (National Institute for Occupational Safety and Health) was utilized. This value is defined as the maximum concentration of a toxic substance to which a good health person can be exposed for thirty minutes without suffering irreversible effects on his health or without suffering effects of exposure that preventing the possibility to escape [33].

Besides, for what concerns the toxicity of the three mixtures, the method developed by the compressed gas association (Equation 1 and Equation 2) was considered [34]. This approach mimics the well-established Le Chatelier's correlation [35], commonly adopted for the estimation of the reactivity of gaseous mixtures [36].

$$ERPG - 2 = \frac{1}{\sum_i \frac{ppm \text{ of toxic component } i}{ERPG-2 \text{ of the component } i}} \quad (1)$$

$$IDLH = \frac{1}{\sum_i \frac{ppm \text{ of toxic component } i}{IDLH \text{ of the component } i}} \quad (2)$$

Peterson et al. [37] have reported IDLH and ERPG-2 values for H<sub>2</sub>S equal to 100 and 30 ppm, respectively. Being the other species included in biogas mixtures non-directly affecting the human and animal health, the concentration giving asphyxiation, i.e., when the oxygen concentration falls below 18 %<sub>v</sub> [38], was considered as the threshold value for non-toxic compounds. As concerning the CH<sub>4</sub>, IDLH and ERPG-2 values can be estimated starting from the permissible exposure limit [39], as reported in the literature [40].

Table 1. The composition and the main safety parameters for the three different biogas mixtures investigated in this work.

Mixture	CH <sub>4</sub> [vol/vol]	H <sub>2</sub> S [vol/vol]	LFL [vol/vol]	IDLH [vol/vol]	ERPG-2 [vol/vol]
Mixture 1	0.90	0.10	$4.36 \times 10^{-2}$	$1.00 \times 10^{-3}$	$3.00 \times 10^{-4}$
Mixture 2	0.95	0.05	$4.38 \times 10^{-2}$	$2.00 \times 10^{-3}$	$6.00 \times 10^{-4}$
Mixture 3	1.00	0.00	$4.40 \times 10^{-2}$	$6.02 \times 10^{-1}$	-

Regardless of the investigated scenarios, data on the storage and transportation conditions (namely composition, temperature, and pressure), the characteristics of the containing vessel and the rupture generating the release are essential to individuate the source term model [17]. Considering that elevated hazards have been identified for biogas release from the separation unit following the digestors, operative conditions reported in Table 2 can be considered. Starting from these data, chemical and physical properties can be estimated, and thus the main top events individuated (i.e., dispersion and jet fire) [41][42]. Furthermore, the plant layout (e.g., congestion) affects the dispersion and explosion scenarios, as well. The releasing flow rates from the biogas tanks were estimated by using the specific source model for the case of gaseous release from an operating vessel [17] and the boundary conditions indicated as representative for accidental release of gaseous mixture from the investigated plant [43] (Table 2)

Table 2. Summary of the input data and boundary conditions adopted for the evaluation of the releasing flow rate [43].

Input	Value
Type of tank	Vertical, atmospheric steel cylindrical tank
Tank height [m]	20
Tank diameter [m]	6
Operating pressure [kPa]	101.8
Operating temperature [°C]	25
Inventory [kg]	1640
Hole diameter [m]	0.05
Hole position from the ground [m]	2
Flow direction	Horizontal

Under these hypotheses, the releasing rate of the gaseous mixture resulted in a constant value of 0.35 kg/s.

For the analysis of the effects of atmospheric conditions, the Pasquill atmospheric stability classes 5D and 2F were considered, according to the standard approach used in the risk assessment [44].

The following equations were implemented to perform CFD analyses, as reported in the generic form:

$$\frac{\partial(\rho\varphi)}{\partial t} + \nabla \times (\varphi\rho\vec{v}) = \nabla \times (D^{(\varphi)} \nabla\varphi) + S_{\varphi} \quad (3)$$

where  $\rho$  is the density of the fluid and  $\vec{v}$  the velocity vector. The general coefficient  $D^{(\varphi)}$  is determined through local sources  $S_{\varphi}$  and the temporal change of variable property  $\varphi$ . This equation represents the continuity conservation when  $\varphi$  is equal to the unity, the momentum conservation when  $\varphi$  is equal to the velocity vector  $\vec{v}$ , or energy conservation when  $\varphi$  is equal to the total energy  $E$  (Equation 4) [45][46].

$$E = h + \frac{v^2}{2} + gz \quad (4)$$

where  $h$ ,  $v$ ,  $g$ , and  $z$  stand for enthalpy, velocity, gravitational acceleration, and height, respectively. The effect of turbulence was accounted for the  $k - \omega$  method [20].

## 2.2 Case oriented approach

The geometry of the AD plant, as described by Sebola et al. [43] (Figure 2), was implemented in a reduced form in ANSYS Fluent. In particular, only the biogas separation unit (S), the two anaerobic digesters (D1 and D2), and the primary mixer treatment tank (M) were taken into consideration. The gas leakage was considered generated by the pipelines connecting the separator unit and digesters.

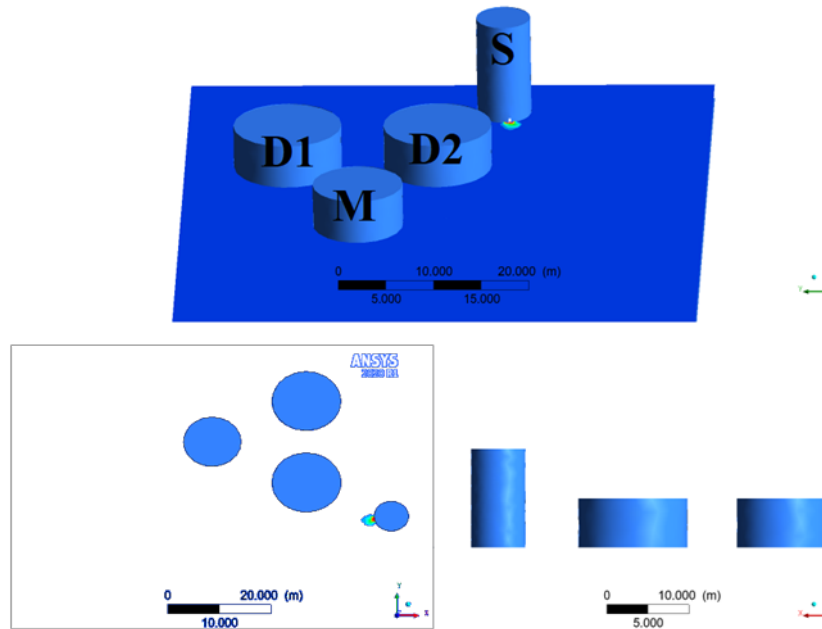


Figure 1. Scheme of the AD plant configuration considered in this work.

The numerical domain was consequently defined to reduce the effects of boundary conditions on the obtained data. A grid sensitivity analysis was performed to individuate the optimal grid settings in terms of results robustness and computational time required. The meshes indicated by this analysis consist of different volumes and average skewness factors (Table 3). The PHAST results were also used as per preliminary analysis for the determination of the computational domain to be implemented in ANSYS Fluent.

Table 3. Main parameters characterizing the numerical domains resulting from the grid sensitivity analysis. The sizes of 3D domain (X, Y, Z) are expressed in meters.

		X [m]	Y [m]	Z [m]	Average skewness factor
<b>Mixture 1</b>	5D	370	55	50	0.50
	2F	800	100	50	0.75
<b>Mixture 2</b>	5D	370	55	50	0.50
	2F	800	100	50	0.75
<b>Mixture 3</b>	5D	80	55	50	0.25
	2F	80	55	50	0.25

The value of  $0.5 \cdot \text{LFL}$  and  $0.1 \cdot \text{IDLH}$  were considered respectively for the fire scenarios and the toxic dispersion as the lower concentration for the beginning of lethality, whereas LFL and ERPG-2 were considered as a high lethal level.

The obtained numerical results were examined and compared in terms of influential factors. The effects of the adopted models, the initial composition, and the atmospheric ambient conditions were analyzed in terms of variation of the downwind distance result (DDR). To this aim, three indicators ( $\Delta S$ ,  $\Delta M$ , and  $\Delta A$ ) were defined as reported in Equations 5-7, representing the effect of methodology (integral model vs. CFD), composition, and wind speed, respectively.

$$\Delta S [\%] = \left( \frac{DDR_{Mix i}^P - DDR_{Mix i}^{AF}}{DDR_{Mix i}^{AF}} \right) \cdot 100\% \quad (5)$$

$$\Delta M [\%] = \left( \frac{DDR_{Mix i} - DDR_{Mix 1}}{DDR_{Mix 1}} \right) \cdot 100\% \quad (6)$$

$$\Delta A [\%] = \left( \frac{DDR_{Mix i}^{2F} - DDR_{Mix i}^{5D}}{DDR_{Mix i}^{5D}} \right) \cdot 100\% \quad (7)$$

where the superscripts P, AF, 2F, and 5D stand for PHAST, ANSYS Fluent, and the atmospheric conditions indicated as 2F and 5D, respectively; the subscripts  $Mix i$ , and  $Mix 1$  represent the generic composition of the  $i$ -th mixture and the composition previously indicated as Mix 1.

### 3. Results

The dispersion of the sour gas was evaluated by the procedure described above. Figure 2 shows the numerical output obtained employing ANSYS Fluent for the 5D atmospheric class by considering the toxicity parameters of the sour gases (Mixtures 1 and 2), as reported in Table 1. Similar results for the 2F atmospheric class were obtained and omitted in this work for the sake of brevity.

These results are confirmed by the integral model PHAST, as reported in tables 4 and 5, which shows the safety distances for the two representative atmospheric classes, respectively, for the three mixtures analyzed in this work.

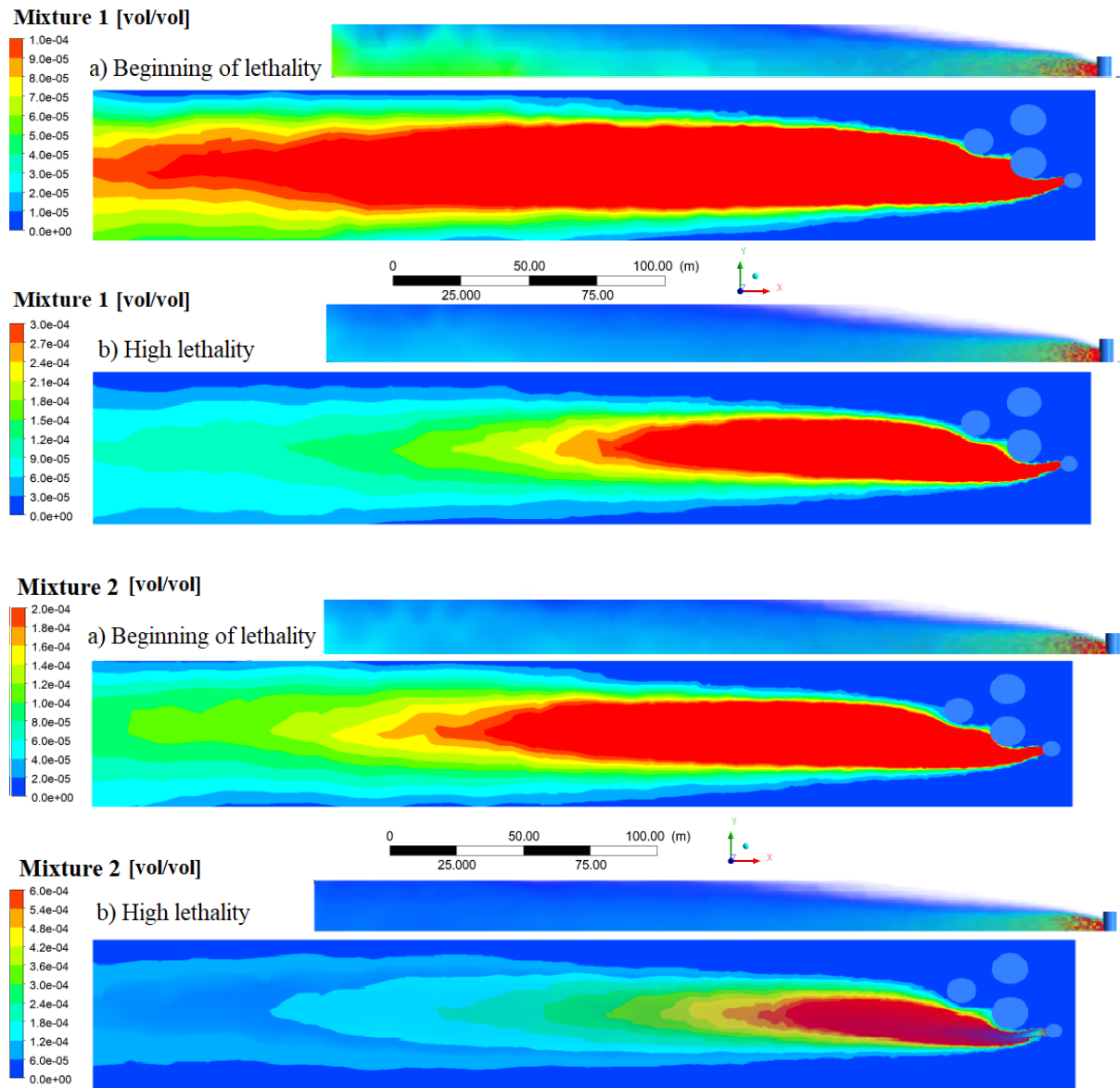


Figure 2. Cloud footprint distance at steady state as calculated by the CFD ANSYS Fluent for the accidental release of the two mixtures 1 and 2 for the atmospheric class 5D. The red color describes the corresponding lethality zone boundary, as reported in Table 1.



Table 4 Safety distances calculated by ANSYS Fluent and by PHAST for the three mixtures evaluated in this work, for the stability class 5D.

		DDR Flammability (m)		DDR Toxicity (m)	
		0.5 LFL	LFL	0.1 IDLH	ERPG-2
<b>Mixture 1</b>	ANSYS	6.5	4.5	330.0	165.0
	PHAST	8.6	5.8	350.0	195.0
<b>Mixture 2</b>	ANSYS	7.0	4.6	209.0	96.0
	PHAST	9.0	6.0	246.0	140.0
<b>Mixture 3</b>	ANSYS	7.0	4.6	0.4	-
	PHAST	9.0	6.0	0.2	-

Table 5 Safety distances calculated by ANSYS Fluent and by PHAST for the three mixtures evaluated in this work, for the class stability 2F.

		DDR Flammability (m)		DDR Toxicity (m)	
		0.5 LFL	LFL	0.1 IDLH	ERPG-2
<b>Mixture 1</b>	ANSYS	8.7	4.8	456.0	195.0
	PHAST	11.3	6.2	580.0	205.0
<b>Mixture 2</b>	ANSYS	9.0	5.0	320.0	144.0
	PHAST	11.5	6.5	310.0	146.0
<b>Mixture 3</b>	ANSYS	9.0	5.2	0.5	-
	PHAST	12.0	6.5	0.2	-

Quite clearly, the effect of the presence of hydrogen sulfide is dramatic in terms of toxicity, whereas it is almost negligible for flammability, which shows only a near field effect. For this reason, DDRs indicating the beginning of the lethality area for this scenario were reported in Figure 3 with respect to the initial composition for the approaches adopted in this work.

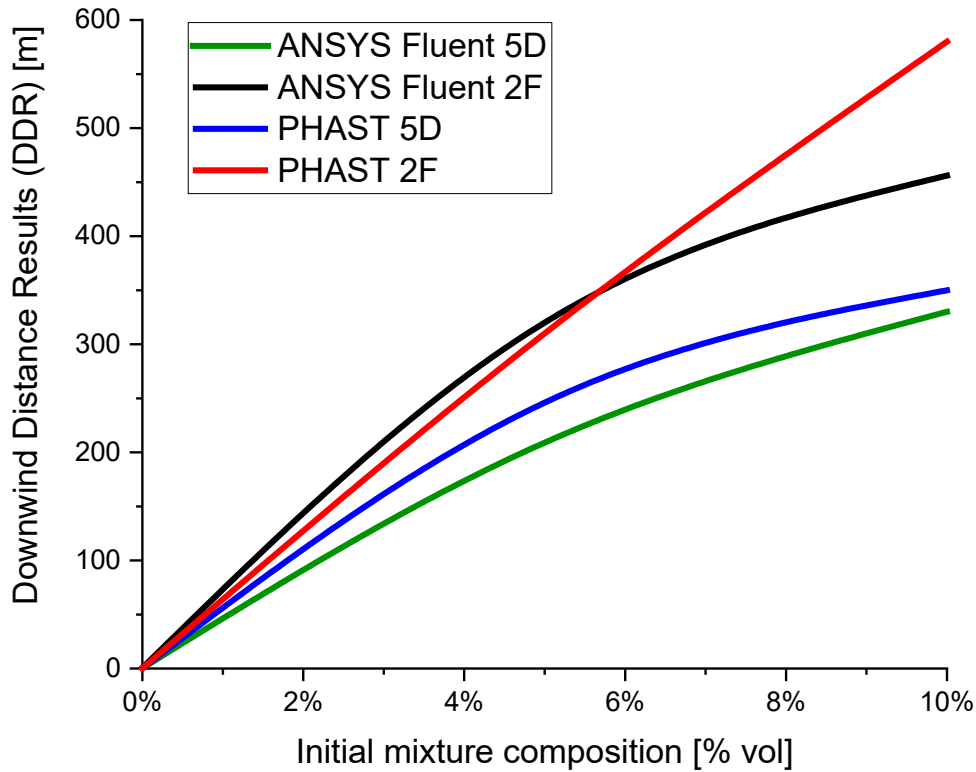


Figure 3 Comparison of the downwind distance results beginning of toxicity safety distances.

Similar absolute values and trends with respect to the composition can be observed when 5D results are compared, indicating that the presence of obstacles has a negligible effect on this scenario. On the other hand, it is worth mentioning that PHAST tends to provide more conservative results with the exception of accidental release of mixtures having low H<sub>2</sub>S content under 2F conditions. Indeed, under these conditions, almost equal DDRs were reported by both approaches, indicating differences in the evaluation of the effect of wind speed on the DDRs. These results will be discussed in the next section.

#### 4. Discussion

Starting from the given results, the following table shows the sensitivity analysis in terms of  $\Delta S$ ,  $\Delta M$ , and  $\Delta A$  for the mixtures analyzed in this work. Table 6 reports the difference in the safety parameters for flammability and lethality expressed in terms of  $\Delta S$  (Eq. 5), i.e., the relative difference between PHAST and ANSYS Fluent, in the case of stability class 5D and 2F.

Table 6 Comparison of the effect of the adopted approach on downwind distance results (DDR) obtained for Mixture 1 (CH<sub>4</sub>: 90 %; H<sub>2</sub>S: 10 %) expressed as the normalized variation of the safety distances calculated by PHAST and ANSYS (i.e.,  $\Delta S$ , as defined in Eq. 5). Atmospheric stability classes are 5D and 2F.

		$\Delta S$ Flammability (%)		$\Delta S$ Toxicity (%)	
		0.5 LFL	LFL	0.1 IDLH	ERPG-2
<b>Mixture 1</b>	5D	+32	+29	+6	+18
	2F	+30	+29	+27	+5
<b>Mixture 2</b>	5D	+29	+30	+18	+46
	2F	+28	+30	-3	+1
<b>Mixture 3</b>	5D	+29	+30	-50	-
	2F	+33	+25	-60	-

From this table, the significant discrepancies between the two investigated methods can be observed for the flammability areas, however in the very near field. As expected, the integral method tends to provide considerably more conservative results for what concerns the flash fire scenarios. A similar analysis was performed in terms of  $\Delta M$ , which shows the differences between the DDR obtained for the different initial mixture (i.e., Mixture 2 and Mixture 3) and the Mixture 1, which is considered as the reference (worst) case. Results are reported in Tables 7, and 8, for the two investigated stability classes 5D and 2F.

Table 7. Comparison of the effect of composition on downwind distance results as obtained by ANSYS Fluent and PHAST in the atmospheric stability class 5D expressed as the normalized variation of the safety distances calculated for a generic composition and Mixture 1 (i.e.,  $\Delta M$ , as defined in Eq. 6).

		$\Delta M$ Flammability (%)		$\Delta M$ Toxicity (%)	
		0.5 LFL	LFL	0.1 IDLH	ERPG-2
<b>Mixture 2</b>	ANSYS	+8	+2	-37	-42
	PHAST	+5	+3	-30	-28
<b>Mixture 3</b>	ANSYS	+8	+2	-100	-
	PHAST	+5	+3	-100	-

Table 8 Comparison of the effect of composition on downwind distance results as obtained by ANSYS Fluent and PHAST in the atmospheric stability class 2F, expressed as the normalized variation of the safety distances calculated for a generic composition and Mixture 1 (i.e.,  $\Delta M$ , as defined in Eq. 6).

		$\Delta M$ Flammability (%)		$\Delta M$ Toxicity (%)	
		0.5 LFL	LFL	0.1 IDLH	ERPG-2
<b>Mixture 2</b>	ANSYS	+3	+4	-30	-26
	PHAST	+2	+5	-47	-29
<b>Mixture 3</b>	ANSYS	+3	+8	-100	-
	PHAST	+6	+5	-100	-

Although  $H_2S$  is more reactive than  $CH_4$ , its addition causes a decrease in the DDR related to the scenario involving ignition. Besides, in contrast with the trend reported in the literature for LFL [30], DDR is weakly affected by the investigated composition. This phenomenon can be attributed to the differences in the molecular weight of the examined species. More specifically, the addition of heavier compounds makes less effective the dispersion phenomena, reducing the area involved by flammable mixtures. This indication can be of interest in the case of ignition, as well. Indeed, recalling that the combustion of  $CH_4$  is more exothermic than the combustion of  $H_2S$ , lower flame temperatures can be expected for mixtures 1 and 2, thus resulting in denser gaseous mixtures containing toxic species (e.g.,  $SO_x$  and unburned  $H_2S$ ). However, the presence of toxic species in the burned mixture should be carefully examined, coupling chemical aspects and dispersion models.

Under these considerations, it is possible to conclude that neglecting the presence of  $H_2S$  in bio-syngas mixtures represents a conservative assumption on the safe side for combustion-related scenarios. In addition to that, it is interesting to underline the differences between the two models in predicting the gas concentration in the proximity of the release point. As a matter of fact, ANSYS Fluent considers the geometry of the plant and, consequently, the possibility of stagnation areas that can limit the dispersion of the gas. This discrepancy can be the cause of the larger DDR reported for Mixture 3 by ANSYS Fluent than the one predicted by PHAST at the same conditions.

In contrast with the observation reported for combustion-related scenarios, the addition of  $H_2S$  leads to significant variations in terms of DDR for the case of toxic dispersion. Indeed, data obtained by PHAST reports that the beginning of the lethality area reaches a DDR of 246 m and a corresponding cloud height of 5 m, while the maximum height reached from the gas cloud is 12. m. Moreover, the high lethality zone reaches a downwind distance of 140 m. These toxicity distances are 30 % lower than the ones obtained for Mixture 1, characterized by a higher presence of  $H_2S$ . The ANSYS Fluent DDR obtain a similar trend. The beginning of lethality and the high lethality areas are characterized by DDR of 209

and 96 m, respectively, resulting in  $\Delta M$  of 40 %. In addition to that, the toxicity distances obtained for Mixture 3 (100 %<sub>v</sub> CH<sub>4</sub>) are negligible, due to the non-toxicity properties of methane, except for extremely high concentration. The obtained results were also compared in terms of flammability distances. The DDR is for all the investigated mixtures lower than the toxicity, and they are characterized by an increasing trend in the distances at which the LFL and the 0.5LFL values are obtained. More specifically, the  $\Delta M$  of the flammability zones varies from 2 and 8. From these considerations, it is possible to affirm that the flammability DDR is weakly affected by the initial mixture composition. On the other hand, the toxicity DDR is hardly influenced, and the higher is the initial presence of the H<sub>2</sub>S, the more significant are the DDR.

In Table 9, the values of the  $\Delta A$  parameter, which represents the difference between the 5D and the 2F atmospheric class, for a fixed initial mixture composition, are reported.

*Table 9 Comparison of the effect of atmospheric conditions on downwind distance results as obtained by ANSYS Fluent and PHAST, expressed as the normalized variation of the safety distances calculated at 2F and 5D conditions (i.e.,  $\Delta A$ , as defined in Eq. 7).*

		$\Delta A$ Flammability (%)		$\Delta A$ Toxicity (%)	
		0.5 LFL	LFL	0.1 IDLH	ERPG-2
<b>Mixture 1</b>	ANSYS	+34	7	+38	+45
	PHAST	+31	7	+66	+5
<b>Mixture 2</b>	ANSYS	+29	9	+53	+50
	PHAST	+28	8	+26	+4
<b>Mixture 3</b>	ANSYS	+29	13	+25	-
	PHAST	+33	8	+0	-

As it is possible to note, the atmospheric conditions have a strong impact on the DDR determining the toxicity area, where relative increase up to 66 % and 50 % can be observed. Besides, the effect of atmospheric conditions seems to be accounted for in considerably different ways by the approaches. Indeed, an almost constant relative increase can be observed for estimations obtained by ANSYS Fluent, whereas the area that PHAST characterizes as high lethality is considerably less affected by variation in atmospheric conditions. On the other hand, the DDR determining the flammable areas are weakly influenced by this factor, being the  $\Delta A$  values included in the range between 7 % and 34 % regardless of the approach utilized.

## 5. Conclusions

This work tackled the safety aspects related to the accidental release of sulfur-containing biogas from bio-digester plants. The two different numerical models based on integral and finite volume approach, namely PHAST and ANSYS Fluent, were adopted and compared. In the latter case, a simplified layout representing a typical biodigester plant was implemented.

The implementation of the finite volume method provides lightly larger safety distances for the case of toxic cloud dispersion when low H<sub>2</sub>S content and 2F atmospheric condition are applied. Similar values of the downwind distance (DDR) with respect to PHAST can be observed, and, for this reason, the CFD approach can be considered reliable. Nevertheless, different trends were observed when different initial conditions were imposed, possibly due to the implementation of additional input parameters such as plant geometry. Quite clearly, the implementation of the 3D geometry requires a higher computational cost than PHAST, up to three orders of magnitude. Regardless of the adopted approach and atmospheric conditions studied, neglecting the presence of sulfur-containing species in unburned mixtures leads to conservative results on the safe side for the flash fire scenario because of the increase in density.

The presence of H<sub>2</sub>S in the releasing stream containing hydrocarbons poses concerns on the production of toxic species during the combustion process, e.g., COS. In this light, the combination of toxic cloud dispersion and combustion kinetic models is suggested for the sake of a comprehensive evaluation of the consequence analysis of digester plants or any other industrial installation when dealing with sour

gases. In general, additional data on the toxicity of mixtures containing several sulfur species are essential for an accurate evaluation of the accidental release of biogas.

## Bibliography

- [1] H. M. Wee, W. H. Yang, C. W. Chou, and M. V. Padilan, "Renewable energy supply chains, performance, application barriers, and strategies for further development," *Renewable and Sustainable Energy Reviews*, 16, 5451–5465, 2012.
- [2] R. Lora Grando, A. M. de Souza Antune, F. V. da Fonseca, A. Sánchez, R. Barrena, and X. Font, "Technology overview of biogas production in anaerobic digestion plants: A European evaluation of research and development," *Renew. Sustain. Energy Rev.*, 80, 44–53, 2017.
- [3] C. A. Salman, S. Schwede, E. Thorin, and J. Yan, "Enhancing biomethane production by integrating pyrolysis and anaerobic digestion processes," *Appl. Energy*, 204, 1074–1083, 2017.
- [4] V. Abad, R. Avila, T. Vicent, and X. Font, "Promoting circular economy in the surroundings of an organic fraction of municipal solid waste anaerobic digestion treatment plant: Biogas production impact and economic factors," *Bioresour. Technol.*, 283, 10–17, 2019.
- [5] V. Casson Moreno, S. Papisidero, G. E. Scarponi, D. Guglielmi, and V. Cozzani, "Analysis of accidents in biogas production and upgrading," *Renew. Energy*, 96, 1127–1134, 2016.
- [6] A. Molino, F. Nanna, Y. Ding, B. Bikson, and G. Braccio, "Biomethane production by anaerobic digestion of organic waste," *Fuel*, 103, 1003–1009, 2013.
- [7] O. A. Habeeb, R. Kanthasamy, G. A. M. Ali, S. Sethupathi, and R. B. M. Yunus, "Hydrogen sulfide emission sources, regulations, and removal techniques: A review," *Rev. Chem. Eng.*, 6, 837–854, 2018.
- [8] L. Meier, D. Stará, J. Bartacek, and D. Jeison, "Removal of H<sub>2</sub>S by a continuous microalgae-based photosynthetic biogas upgrading process," *Process Saf. Environ. Prot.*, 119, 65–68, 2018.
- [9] D. Panza and V. Belgiorno, "Hydrogen sulphide removal from landfill gas," *Process Saf. Environ. Prot.*, 88, 420–424, 2010.
- [10] R. Raman and P. Grillo, "Minimizing uncertainty in vapour cloud explosion modelling," *Process Saf. Environ. Prot.*, 83, 298–306, 2005.
- [11] S. Wu, L. Zhang, J. Fan, and Y. Zhou, "Dynamic risk analysis of hydrogen sulfide leakage for offshore natural gas wells in MPD phases," *Process Saf. Environ. Prot.*, 122, 339–351, 2019.
- [12] V. Casson Moreno, S. Papisidero, G. E. Scarponi, D. Guglielmi, and V. Cozzani, "Analysis of accidents in biogas production and upgrading," *Renew. Energy*, 96, 1127–1134, 2016.
- [13] A. Bertelsmann, G. Knight, A. Tiwary, and A. Calico, "PHA guidance for correlating H<sub>2</sub>S concentrations in process streams to severity of adverse health outcomes in the event of a leak," *J. Loss Prev. Process Ind.*, 60, 282–287, 2019.
- [14] A. K. Gupta, S. Ibrahim, and A. Al Shoaibi, "Advances in sulfur chemistry for treatment of acid gases," *Prog. Energy Combust. Sci.*, 54, 65–92, 2016.
- [15] World Health Organization, "Concise International Chemical Assessment. Hydrogen sulfide : human health aspects," 2003.
- [16] I. A. Gargurevich, "Hydrogen sulfide combustion: Relevant issues under claus furnace conditions," *Ind. Eng. Chem. Res.*, 44, 7706–7729, 2005.
- [17] C. van den Bosch and R. Weterings, "Yellow Book - Methods for the calculation of physical effects due to releases of hazardous materials (liquids and gases)," *CPR 14E, 3rd edn, TNO*, 1997.
- [18] R. Ohba, A. Kouchi, T. Hara, V. Vieillard, and D. Nedelka, "Validation of heavy and light gas dispersion models for the safety analysis of LNG tank," *J. Loss Prev. Process Ind.*, 17, 325–337, 2004.
- [19] DNV-GL, "PHAST Process Hazard Analysis Software Tool." .
- [20] "Ansys® Academic Research Mechanical, Release 18.1." 2018.
- [21] B. Zhang and G. M. Chen, "Hydrogen sulfide dispersion consequences analysis in different wind speeds: A CFD based approach," *2009 Int. Conf. Energy Environ. Technol. ICEET 2009*, 3, 365–368, 2009.
- [22] H. W. M. Witlox, M. Harper, and R. Pitblado, "Validation of phast dispersion model as

- required for USA LNG siting applications,” *12th Top. Conf. Gas Util. 2012 - Top. Conf. 2012 AIChE Spring Meet. 8th Glob. Congr. Process Saf.*, 31, 263–275, 2012.
- [23] N. Pandya, N. Gabas, and E. Marsden, “Uncertainty analysis of phast’s atmospheric dispersion model for two industrial use cases,” *Chem. Eng. Trans.*, 31, 97–102, 2013.
- [24] A. S. Markowski, M. S. Mannan, A. Kotynia (Bigoszezewska), and D. Siuta, “Uncertainty aspects in process safety analysis,” *J. Loss Prev. Process Ind.*, 23, 446–454, 2010.
- [25] D. Siuta, A. S. Markowski, and M. S. Mannan, “Uncertainty techniques in liquefied natural gas (LNG) dispersion calculations,” *J. Loss Prev. Process Ind.*, 26, 418–426, 2013.
- [26] I. Ahmed, T. Bengherbia, R. Zhvansky, G. Ferrara, J. X. Wen, and N. G. Stocks, “Validation of geometry modelling approaches for offshore gas dispersion simulations,” *J. Loss Prev. Process Ind.*, 44, 594–600, 2016.
- [27] L. M. Frare, M. G. A. Vieira, M. G. C. Silva, N. C. Pereira, and M. L. Gimenes, “Hydrogen sulfide removal from biogas using Fe/EDTA solution: gas/liquid contacting and sulfur formation,” *Environ. Prog. Sustain. Energy*, 29, 34–41, 2010.
- [28] J. J. Milledge, B. V. Nielsen, S. Maneein, and P. J. Harvey, “A brief review of anaerobic digestion of algae for BioEnergy,” *Energies*, 12, 1166, 2019.
- [29] EN 1839:2017, *Determination of the explosion limits and the limiting oxygen concentration (LOC) for flammable gases and vapours*. 2017.
- [30] G. Pio, D. Barba, V. Palma, and E. Salzano, “A Numerical Study on the Effect of Temperature and Composition on the Flammability of Methane–Hydrogen Sulfide Mixtures,” *Combust. Sci. Technol.*, 191, 1–17, 2019.
- [31] H. F. Coward and G. W. Jones, “Limits of flammability of gases and vapors,” *Industrial & Engineering Chemistry Research*, 52, 6057–6067, 1952.
- [32] B. E. Poling, G. H. Thomson, D. G. Friend, R. L. Rowley, and W. V. Wilding, *Perry’s Chemical Engineers’ Handbook Section 2: Physical and Chemical Data*, 8th ed. McGraw-Hill, 2007.
- [33] Center for Chemical Process Safety (CCPS), *Guidelines for Evaluating Process Plant Buildings for External Explosions, Fires, and Toxic Releases*, Wiley, 2nd Edition, 2012.
- [34] Compressed Gas Association, “CGA P-20: Standard for classification of toxic gas mixtures,” 2003.
- [35] V. Schroeder, “Calculation of Flammability and Lower Flammability Limits of Gas Mixtures for Classification Purposes,” 1–17, 2016.
- [36] G. Pio and E. Salzano, “Laminar Burning Velocity of Methane, Hydrogen and Their Mixtures at Extremely Low Temperature Conditions,” *Energy & Fuels*, 32, 8830–8836, 2018.
- [37] S. L. Malone Rubright, L. L. Pearce, and J. Peterson, “Environmental toxicology of hydrogen sulfide,” *Nitric Oxide - Biol. Chem.*, 71, 1–13, 2017.
- [38] T. Watanabe and M. Morita, “Asphyxia due to oxygen deficiency by gaseous substances,” *Forensic Sci. Int.*, 1, 47–59, 1998.
- [39] P. Saurabh, Z. Linlu, and E. James, Go, “Methane and Natural Gas Exposure Limits,” *Epidemiology*, 22, 29–124, 2011.
- [40] N. P. Cheremisinoff, “Handbook of Industrial Toxicology and Hazardous Materials.” .
- [41] G. Pio and E. Salzano, “Flammability parameters of liquified natural gas,” *J. Loss Prev. Process Ind.*, 56, 424–429, 2018.
- [42] G. Pio and E. Salzano, “Evaluation of safety parameters of light alkenes by means of detailed kinetic models,” *Process Saf. Environ. Prot.*, 119, 131–137, 2018.
- [43] M. Sebola and H. Tesfasgiorgis, “Economic evaluation of anaerobic digestion technology.,” *South African J. Chem. Eng.*, 20, 80–90, 2015.
- [44] I. Iervolino, D. Accardo, A. E. Tirri, G. Pio, and E. Salzano, “Quantitative risk analysis for the Amerigo Vespucci (Florence, Italy) airport including domino effects,” *Saf. Sci.*, 113, 472–489, 2019.
- [45] J. D. J. Anderson, *Computational Fluid Dynamics: The Basics with Applications*, 2nd ed. McGraw-Hill, 1995.
- [46] G. H. Yeoh and K. K. Yuen, *Computational Fluid Dynamics in fire engineering: Theory, modelling and practice*, 1st ed. Butterworth-Heinemann, 2009.