

## Assessment of atmospheric parameters influence on dilution degree: a case study focused on formation of explosive atmospheres in bioethanol storage

Roberto Lauri<sup>1</sup>

<sup>1</sup>*Department of Technological Innovations and Safety of Plants, Products and Human Settlements, Inail, Via del Torraccio di Torrenova 7, Rome 00133, Italy*

**Abstract:** In Europe, there are bioethanol storage depots, which are often subjected to Seveso Directive. Accidental bioethanol releases can become hazardous, because its evaporation from pool could generate potentially explosive atmospheres. In bioethanol storage depots, there are some components (flanges, valves, pumps, etc.), which can become potential emission sources in case of failure. In accordance with European Directive Atex 99/92/EC, the employer is obliged to identify and classify the workplaces, where potentially explosive mixtures may occur. The International Standard IEC EN 60079-10-1 is generally used to classify the hazardous areas due to the possible formation of explosive atmospheres. The Standard reports the parameters, which have to be determined in order to classify the zones (hazardous or non-hazardous). One of these parameters is the dilution degree, which is a measure of the ability of natural or artificial ventilation to dilute a release to a safe level (flammable compound concentration is below its lower flammability limit). In case of high-boiling flammable liquids release, such as bioethanol, this parameter is strongly dependent on evaporation rate, which is influenced by air velocity. The paper reports the results of bioethanol evaporation study from pool by a specific software, which is able to predict the trend of evaporation rate and pool size as function of time. With reference to evaporation from pool, the air velocity influence on evaporation rate has been investigated.

**Keywords:** bioethanol, dilution degree, evaporation rate, potentially explosive atmospheres, wind velocity.

### I. INTRODUCTION

With reference to climate and energy framework, the European Union policy has established specific targets for the period from 2021 to 2030. In particular, at least 32% share for renewable energy must be achieved. The bioethanol produced from biomass, such as wheat, maize, sugar beet, etc., is a promising resource for achieving this goal. Indeed, it can be considered as a transport fuel to replace gasoline and as an important fuel for power generation by thermal combustion. This scenario generates attention to the potential hazards, which are associated with flammable biofuels storage and production. Indeed, one of the main hazards, referred to bioethanol, is the possible formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases. This phenomenon is more hazardous in indoor zones in case of failure of artificial ventilation system or inadequate air flow. In bioethanol production plants or storage depots, there are several components (flanges, valves, tanks, transfer pumps, etc.), which can release the mentioned biofuel in case of failure [1]. The International Standard IEC EN 60079-10-1 allows to verify the emission source potentiality to generate hazardous areas due to the presence of explosive mixtures. In order to estimate the evaporation rate of flammable liquids, the Standard suggests an equation, which does not take into account the different behaviour of low and high-boiling liquids. This approach could cause a rough estimate of dilution degree and therefore possible mistakes in the classification of hazardous areas due to the formation of potentially explosive mixtures.

A wrong classification undermines the safety level of bioethanol storage depots and production plants. In particular, the evaporation rate of low-boiling flammable liquids is mainly influenced by the thermal exchange between the liquid and the surface (soil, containment basin, etc.), whereas the evaporation of high-boiling flammable liquids is strongly dependent on mass transfer. Therefore, the paper is aimed at decreasing the uncertainty due to evaporation rate estimate. In order to achieve this goal, the bioethanol evaporation from pool has been studied by a specific software (Effects), which is generally used to assess the accidents outcomes in industrial plants subjected to Seveso Directive. In particular, the atmospheric parameters (air velocity) influence on evaporation rate has been investigated, because the wind velocity is a crucial parameter [2] for studying the evaporation of high-boiling flammable liquids, such as bioethanol. An accurate study of flammable liquids evaporation is a fundamental tool for ensuring a rigorous classification of zones (hazardous or non-hazardous) characterized by the formation of potentially explosive mixtures and for improving the industrial plants safety. Indeed, this classification influences the choice of equipment and machineries, which can be used in Atex zones

without generating potential ignition sources. An explosion can occur if a flammable substance (its concentration must be included within its flammability limits), oxygen and the required activation energy (it is provided by an ignition source) are simultaneously present. The evaporation rate allows to determine the dilution degree, which is a required parameter for identifying the areas, where explosive atmosphere could occur.

## II. FLAMMABLE LIQUIDS CLASSIFICATION

The flammable liquids classification depends on boiling temperature [3]. With reference to this parameter, the flammable liquids can belong to two specific categories:

- 1) High-boiling liquids (the boiling temperature is higher than ambient temperature);
- 2) Low-boiling liquids (the boiling temperature is lower than ambient temperature).

The bioethanol is characterized by the same chemical properties (Table 1) of ethanol, which is produced by the processes of the traditional chemistry.

Table 1. Chemical bioethanol properties

Parameter	Value
Lower flammability limit (% v/v)	3.5
Upper flammability limit (% v/v)	15
Boiling temperature (°C)	78
Vapour pressure at 20°C (Pa)	6,000
Flash-point (°C)	13

With regard to its boiling temperature and vapour pressure, the bioethanol is classified as a high-boiling liquid.

## III. EVAPORATION OF HIGH-BOILING LIQUIDS

The knowledge of liquids evaporation rates from pools is crucial in order to estimate the possible outcomes associated with the generated vapour cloud, which may include the ignition of flammable vapours (flash fires or vapour cloud explosion could occur) or the dispersion of a toxic cloud. The flammable liquids evaporation from pool depends on solar radiation (Fig.1), convective heat flux from air, heat flux from land and mass transfer due to wind velocity.

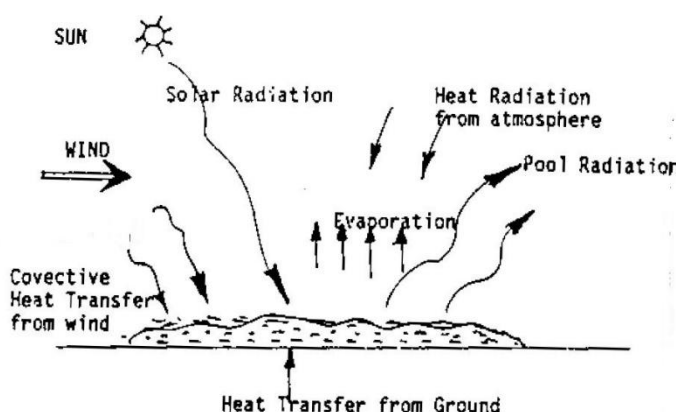


Fig. 1. Flammable liquids evaporation (Van den Bosch and Weterings, 2005)

In particular, when high-boiling flammable liquids are released, the evaporation mainly occurs by vapour diffusion [4] and the driving force is the difference between the liquid vapour pressure and partial pressure of liquid in the atmosphere [5]. The high-boiling pools evaporation strongly depends on the rate, at which the vapour is removed by the wind [6], which flows above the pool.

An accurate calculation of evaporation rate is extremely important, because such parameter has strong outcomes on classification of zones, where potentially explosive atmospheres could occur, and on safety of bioethanol production plants and storage depots. Indeed, the evaporation rate influences the dilution degree,

which is a fundamental parameter (Fig. 2) reported in International Standard IEC EN 60079-10-1 for identifying the hazardous areas [7] due to the flammable gases or vapours presence.

Grade of release	Effectiveness of Ventilation						
	High Dilution			Medium Dilution			Low Dilution
	Availability of ventilation						
	Good	Fair	Poor	Good	Fair	Poor	Good, fair or poor
Continuous	Non-hazardous (Zone 0 NE)	Zone 2 (Zone 0 NE)	Zone 1 (Zone 0 NE)	Zone 0	Zone 0 + Zone 2	Zone 0 + Zone 1	Zone 0
Primary	Non-hazardous (Zone 1 NE)	Zone 2 (Zone 1 NE)	Zone 2 (Zone 1 NE)	Zone 1	Zone 1 + Zone 2	Zone 1 + Zone 2	Zone 1 or zone 0
Secondary	Non-hazardous (Zone 2 NE)	Non-hazardous (Zone 2 NE)	Zone 2	Zone 2	Zone 2	Zone 2	Zone 1 and even Zone 0

Fig. 2. Classification of hazardous zones due to the explosive atmospheres presence (IEC, 2016)

#### IV. MATERIALS AND METHODS

The paper is based on two phases:

- 1) estimate of bioethanol evaporation rate ( $W_g$ ) from pool by software Effects, which is able to describe the  $W_g$  and pool radius trends as time function;
- 2) dilution degree determination by the diagram (Fig. 3) reported in International Standard IEC EN 60079-10-1.

The methodological approach, described in the paper, is reported in Fig. 4. The first approach phase is based on the meteorological data analysis of industrial sites, where the bioethanol storage depots or production plants are built. This step is a very useful tool, because it delimitates the more probable range of ventilation velocity variation and therefore it allows to hypothesize extremely real values, which are fundamental for improving the accuracy of evaporation rate estimate. The software calculates  $W_g$  due to all factors of thermal exchange (solar radiation, convective heat flux from air, heat flux from land and mass transfer due to ventilation velocity). In order to estimate the dilution degree, the worst scenario has to be considered. It is characterized by the maximum value ( $W_{gmax}$ ) of evaporation rate. The paper examines a case study focused on a bioethanol storage depot, which is located in Italy. In order to study the wind velocity ( $u_w$ ) influence on evaporation rate, the data, reported in Italy wind Atlas, have been examined. The site, where the depot has been built, is characterized by an annual average ventilation velocity, which is lower than 4-5 m/s [8] and therefore 4 m/s, 6 m/s, 8 m/s and 10 m/s have been considered for calculating  $W_g$ . 10 m/s is the fixed threshold, because it corresponds to the maximum value of air velocity, which is reported in International Standard IEC EN 60079-10-1 (Fig. 3). The Atlas shows velocity values, which are referred to the height of twenty-five metres [8], whereas the software requires a wind velocity ( $v_{10}$ ), referred to 10 metres above the ground [9]. The conversion has been carried out by the following equation [10]:

$$v(z) = v_{10} \cdot (z/10)^p \quad (1)$$

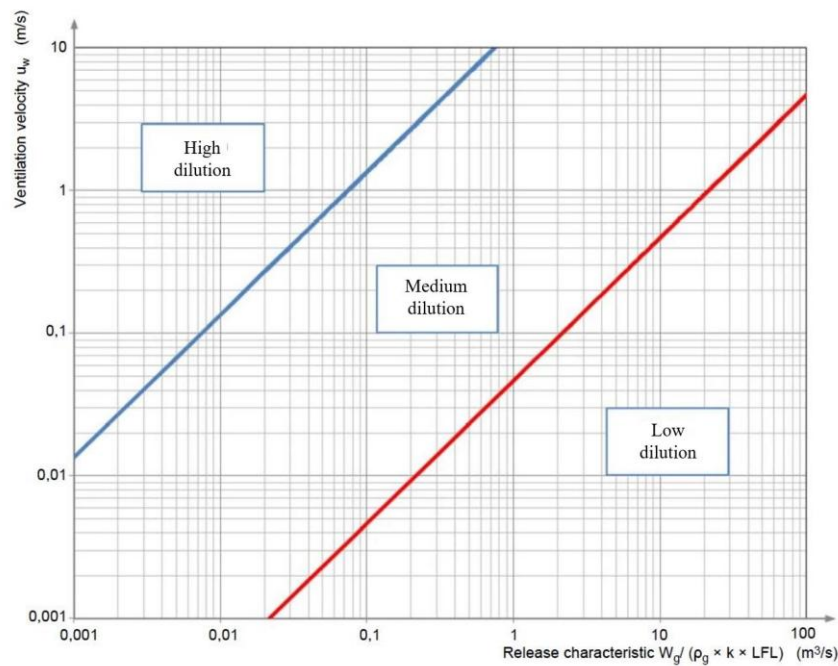


Fig. 3. Dilution degree assessment (IEC, 2016)

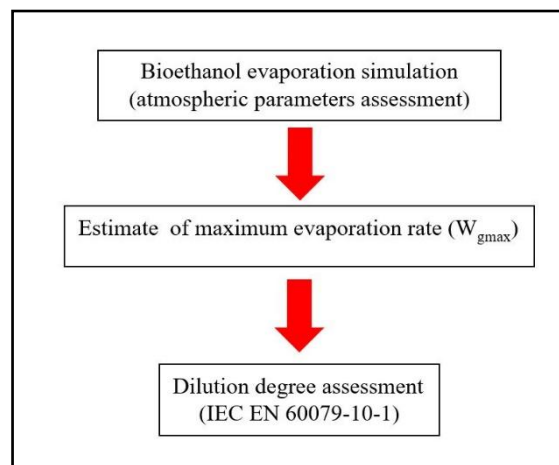


Fig. 4. The methodological approach

$Z$  is a specific height above the ground and  $p$  is a dimensionless parameter [10], which depends on the ambient (urban or rural) and atmospheric stability class. The depot is located in a rural zone and atmospheric stability class D (neutral conditions) has been assumed. The Table 2 [10] shows the  $p$  dependence on atmospheric stability class and ambient. It follows that  $p$  is equal to 0.15. In Table 3 the converted velocities are shown.

Table 2. Values of parameter  $p$ 

Atmospheric stability class	$p$ (urban district)	$p$ (rural district)
A	0.15	0.07
B	0.15	0.07
C	0.2	0.1
D	0.25	0.15
E	0.4	0.35

Table 3. Wind velocities referred to 10 metres above the ground

	Height (z=25 m)	Height (z=10 m)
Wind velocity (m/s)	4	3.5
	6	5.2
	8	7
	10	8.7

The parameters reported in Fig. 3 are:

- $W_g$  (kg/s) is the evaporation rate;
- $\rho_g$  (kg/m<sup>3</sup>) is the vapour/gas density;
- $k$  is a safety coefficient (dimensionless parameter), which is lower than 1. In the present paper,  $k$  has been assumed equal to 0.5 ;
- LFL indicates the lower flammability limit expressed in volumetric percentage (v/v %).

The dilution degree can be:

- 1) High. The explosive mixture concentration (near the emission source) quickly decreases and the explosive atmosphere will not be present after the release is stopped;
- 2) Medium. The concentration is controlled and could generate a stable zone boundary, whilst the release is in progress and the explosive mixture does not persist after the release is stopped;
- 3) Low. There is a significant concentration, whilst the release is in progress, and/or there is a significant persistence of potentially explosive atmosphere after the release is stopped.

In accordance with International Standard IEC EN 60079-10-1, the vapour density ( $\rho_v$ ) is referred to environment conditions in terms of pressure and temperature [7] and it is calculated by the ideal gases equation (Eq. 2):

$$\rho_v = p_a \cdot PM_b / RT_a \quad (2)$$

Where:

- $p_a$  indicates the atmospheric pressure (101325 Pa);
- $PM_b$  is the molecular weight of bioethanol (46.07 kg/kmol);
- $R$  indicates the gas constant (8,314 J/ kmol K);
- $T_a$  is the ambient temperature (298.15 K).

## V. THE CASE STUDY: BIOETHANOL STORAGE DEPOT

The depot is located in Italy and has two bioethanol storage tanks ( $V_{\text{tank}}=3,300 \text{ m}^3$ ). The biofuel is stored in outdoor fixed roof tanks, having an internal floating roof. The potential release source, which has been examined, is the control valve used to adjust the biofuel flow to the transfer pump. The emissions from valves can be due to the stem leakage. The bioethanol transfer pipe diameter ( $D_p$ ) is equal to 12.5 cm and the valve is installed at six meters from the storage tank. The emission hole diameter ( $D_h$ ) has been assumed equal to 0.1  $D_p$ . In order to assess the solar radiation contribution to bioethanol evaporation, the clouds cover has been assumed equal to 50 % .

## VI. RESULTS AND DISCUSSION

The simulation of bioethanol evaporation from pool has been based on the following hypotheses:

- 1) constant ventilation velocity (in the examined period);
- 2) constant ventilation direction (in the examined period).

In Table 4 the parameters, which have been used to study the biofuel evaporation, are reported. The results of bioethanol evaporation simulation are reported in Table 5, whereas the trends of evaporation rate ( $W_g$ ) and pool radius ( $r_p$ ) as function of time are reported in Figures 5 and 6. In Table 5,  $W_{g\text{max}}$  is the maximum evaporation rate in the examined period (900 s),  $M_{\text{ev}}$  is the total evaporated mass and  $m_r$  indicates the mass flow from the control valve. From Fig. 5 it is possible to note that the bioethanol evaporation rate increases from 0 s to 600 s and it decreases from 600 s to 900 s. Indeed, during the first 600 seconds, the flow control valve releases biofuel and pool area increases, because  $W_g$  is lower ( $m_r$  ranges between  $4W_{g\text{max}}$  and  $5W_{g\text{max}}$ ) than the mass flow rate ( $m_r$ ). Therefore, the evaporation rate increases, because a higher bioethanol amount can be removed by ventilation velocity. After the release is stopped (from 600 s to 900 s), the pool starts to shrink

because of evaporation, thus decreasing the available surface, which can evaporate. The direct outcome is the  $W_g$  decrease. There is also another reason, which causes the  $W_g$  decrease from 600 s to 900 s. In particular, there is not bioethanol renewal in the pool and so the pool temperature gradually decreases.

Table 4. Bioethanol evaporation study: parameters

Parameters	Value
Storage tank volume	3,300 m <sup>3</sup>
Pipeline diameter ( $D_p$ )	125 mm
Hole diameter ( $D_h$ )	12.5 mm
Pipeline length	6,000 mm
Tank filling degree	85%
Discharge coefficient	0.7
Release duration from control valve	600 s
Bioethanol temperature	28°C
Soil temperature	27°C
Clouds cover	50%
Air humidity	60%
Heat flux from solar radiation	1.41 kW/m <sup>2</sup>
Evaporation duration	900 s

Table 5. Results

$v_{10}$ (m/s)	$W_{gmax}$ (kg/s)	$r_p$ (m) at 900 s	$m_r$ (kg/s)	$M_{ev}$ (kg)
3.5	0.16	5.5	0.79	97.7
5.2	0.18	5.44	0.79	108
7	0.19	5.35	0.79	116.3
8.7	0.21	5.3	0.79	123

Therefore, the biofuel evaporation due to heat transfer with the soil (the contribution is not so relevant, because the ethanol forms high-boiling pools) also decreases. The wind velocity passage from 3.5 m/s to 8.7 m/s causes a  $W_g$  and total evaporated mass growth. In particular, the  $W_{gmax}$  and  $M_{ev}$  increases are respectively equal to 25 % and 25.9 %. On the contrary, the ventilation velocity increase causes a pool radius decrease (3.6 %), which is exiguous, because evaporation rate is much lower than mass flow released from the control valve. The pool radius trend strongly influences the biofuel evaporation rate. From Fig. 6 it is possible to note that when the flow control valve releases biofuel (from 0 s to 600 s), the pool radius starts to increase until the maximum radius is reached. The maximum value is reached at 600 s. From 0 s to 600 s the pool is increasing in size, while the discharge occurs. Indeed, though evaporation is occurring, it is not seen in the first 600 s, because the evaporation rate ( $W_g$ ) is lower than  $m_r$ . Once the maximum pool area is achieved, the radius starts to decrease, because from 600 s to 900 s the pool is only evaporating. In fact, there is not mass flow (the release is stopped), which increases the bioethanol amount in the pool. Finally, the Table 6 shows the dilution degree assessment as function of atmospheric parameters (wind velocity) variation. In the same table,  $\rho_v$  is the bioethanol vapour density. In this case study, the ventilation velocity increase causes an evaporation rate growth, which is not particularly high and therefore it is not able to modify the dilution degree (its value is medium).





Fig. 5. Evaporation rate trend

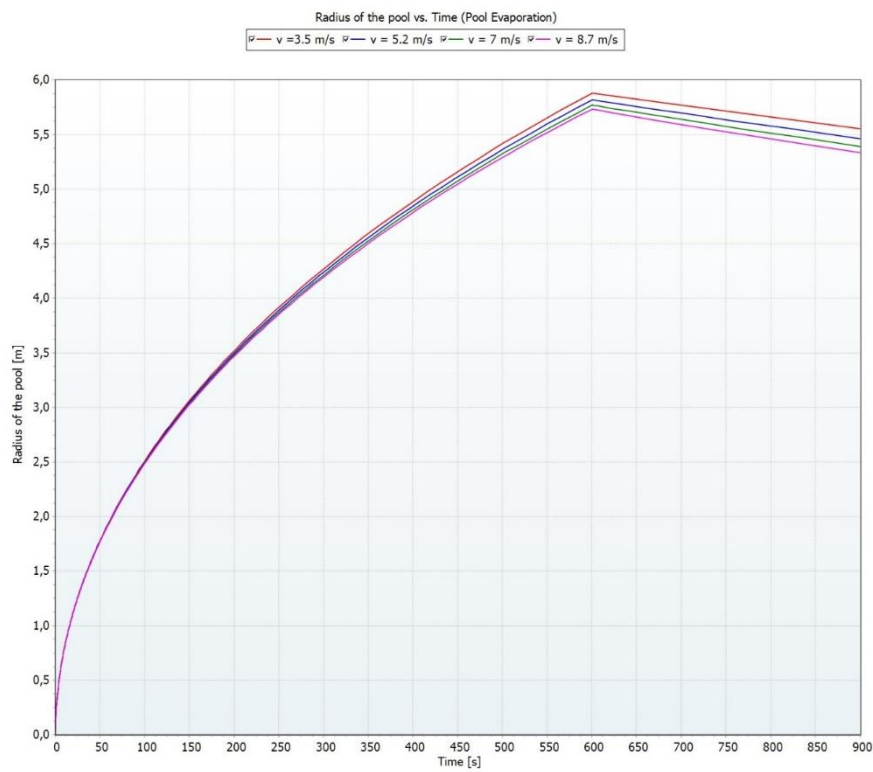


Fig. 6. Pool radius trend

Table 6. Dilution degree assessment

$v_{10}$ (m/s)	$\rho_v$ (kg/m <sup>3</sup> )	$W_{gmax}/\rho_v kLFL$ (m <sup>3</sup> /s)	Dilution degree
3.5	1.88	4.9	Medium
5.2	1.88	5.5	Medium
7	1.88	5.8	Medium
8.7	1.88	6.1	Medium

## VII. CONCLUSIONS

The evaporation rate of high-boiling flammable liquids is mainly due to the mass transfer, which is strongly dependent on atmospheric parameters, such as the air velocity. It follows that the meteorological data analysis of industrial sites, where the bioethanol storage depots or production plants are located, is a very useful tool in order to delimitate the more probable range of ventilation velocity variation and hypothesize extremely real values. However, an unavoidable simulation uncertainty is due to the possible variation of wind direction and velocity in the established period. This preliminary analysis is crucial for achieving realistic simulations of flammable liquids evaporation from pool. With regard to the equation reported in IEC EN 60079-10-1, it is important to highlight that the software Effects is able to give more reliable and accurate predictions of evaporation rate, because the Standard does not take into account the different behaviour of low and high-boiling liquids. This approach could cause a rough estimate of dilution degree and therefore possible mistakes in the classification of hazardous areas due to the formation of potentially explosive mixtures. A wrong classification undermines the safety level of bioethanol storage depots and production plants. Because of this reason, the use of specific software is recommended for improving the accuracy of evaporation rate estimate. An interesting coming study, aimed at assessing the influence of air velocity variation on  $W_g$ , could be represented by the comparison of results achieved by software and CFD (Computational Fluid Dynamics) models, which are able to solve the fluid dynamics equations (Navier-Stokes, Euler, etc.).

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