CHEMICAL ENGINEERING TRANSACTIONS

VOL. 79, 2020

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Enrico Bardone, Antonio Marzocchella, Marco Bravi

ISBN 978-88-95608-77-8; **ISSN** 2283-9216

DOI: 10.3303/CET2079029

Bioethanol Storage Depots: Study of Evaporation from Pool for the Classification of Hazardous Zones due to the Possible Formation of Potentially Explosive Atmospheres

Roberto Lauri

INAIL, Department of Technological Innovations and Safety of Plants, Products and Human Settlements, Via del Torraccio di Torrenova 7, 00133 Rome, Italy.
r.lauri@inail.it

In many European Countries, there are bioethanol storage depots, which are often subjected to Seveso Directive. Indeed, accidental bioethanol releases can be hazardous, because its evaporation from pool can generate potentially explosive atmospheres. In bioethanol production plants or storage depots, there are several components (flanges, valves, pumps, etc.), which can become potential emission sources in case of failure. In accordance with Atex Directive 99/92/EC, the employer is obliged to carry out the classification of workplaces, where explosive mixtures could be generated. International Standard IEC EN 60079-10-1 is generally used to classify the hazardous zones due to the possible presence of potentially explosive atmospheres. The Standard reports the parameters, which have to be determined in order to classify the areas. In particular, the dilution degree is a required parameter for classifying the zone (hazardous or non-hazardous) generated by the potential source. In case of flammable liquids releases, such as bioethanol, this parameter is strongly dependent on evaporation rate. 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, pool size and temperature as function of time. The chosen software is diffusely used to assess the accidents outcomes in plants subjected to Seveso Directive. With reference to evaporation from pool, the wind velocity influence on evaporation rate has been investigated. Indeed, the wind velocity is a very important parameter for studying the evaporation of high-boiling flammable liquids, such as bioethanol.

1. Introduction

The growing bioethanol use is strongly dependent on processes efficiency and safety level of production plants and depots. Indeed, one of the main hazards, associated with bioethanol production or storage, is the possible formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases. Therefore, 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. The use of an advanced software, which is able to model the behaviour of flammable gases and liquids, allows to improve the accuracy of evaporation rate calculation, though an unavoidable uncertainty is due to hypotheses, which are used to overcome specific obstacles. In case of releases of high-boiling flammable liquids, such as bioethanol, the most important obstacle is the wind variation in terms of velocity and direction.

2. Evaporation of high-boiling liquids

The knowledge of the liquids evaporation rates from pools is very important in order to assess the outcomes associated with the generated vapour cloud (Bubbico and Mazzarotta, 2016). Indeed, they may include the ignition of flammable vapours and/or the dispersion of a toxic cloud. Bioethanol is characterized by the same chemical properties (Table 1) of ethanol, which is produced by the processes of the traditional chemistry (Lauri et al., 2017).

Paper Received: 4 July 2019; Revised: 20 December 2019; Accepted: 13 March 2020
Please cite this article as: Lauri R., 2020, Bioethanol Storage Depots: Study of Evaporation from Pool for the Classification of Hazardous Zones Due to the Possible Formation of Potentially Explosive Atmospheres, Chemical Engineering Transactions, 79, 169-174 DOI:10.3303/CET2079029

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 reference to its boiling temperature and vapour pressure trend (Figure 1), bioethanol is classified as a high-boiling liquid. When flammable liquids with a boiling temperature above the ambient temperature are released and spread, the evaporation mainly occurs by vapour diffusion (Brighton, 1990) and the driving force is the difference between the liquid vapour pressure and partial pressure of liquid in the atmosphere. The high-boiling pools evaporation strongly depends on the rate, at which the vapour is removed by the wind (Mackay and Matsugu, 1973), which flows above the pool. Therefore, in case of release of high-boiling flammable liquids, the mass transfer due to the diffusion is the limiting factor especially after the initial stages of spill.

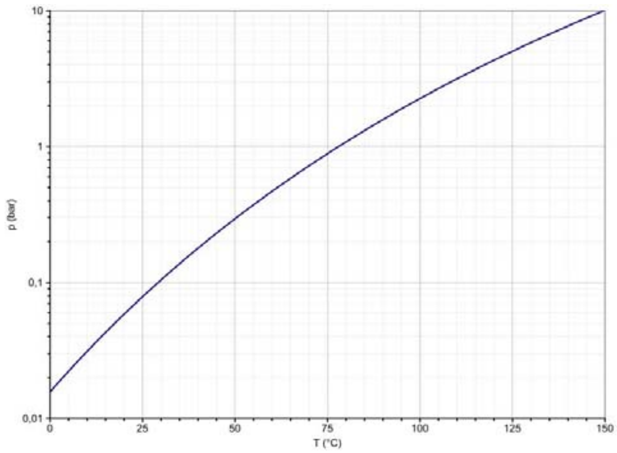

Figure 1: Bioethanol vapour pressure

3. Relationship between evaporation rate and classification of hazardous zones due to the possible formation of potentially explosive atmospheres

One of the main hazards, associated with bioethanol production and storage, is the possible formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases (Lauri and Pietrangeli, 2019). In the industrial plants, several components (valves, flanges, pumps, compressors, etc.) can become potential sources of hazardous compounds release in case of failure. In order to classify the hazardous zones due to the possible formation of explosive mixtures, International Standard IEC EN 60079-10-1 can be used. It indicates three parameters, which have to be determined to classify the areas (IEC, 2016):

1) source release grade;
2) ventilation availability;
3) dilution degree (Figure 2).

The dilution degree is a measure of the ability of forced ventilation or atmospheric conditions to dilute a release to a safe level (the flammable compound concentration is lower than lower flammability limit). In case of flammable liquids releases, the last parameter depends on evaporation rate and can be determined by the diagram reported in International Standard IEC EN 60079-10-1 (Figure 2), where:

- u_w is the wind velocity (m/s);
- W_g is the mass flow (evaporation rate in case of flammable liquids) of flammable compound (kg/s);
- LFL is the lower flammability limit of flammable substance (% v/v);
- ρ_g indicates the gas or vapour density (kg/m^3);
- k represents a safety factor (dimensionless parameter).

It follows that the calculation of evaporation rate is an extremely important phase for determining the dilution degree and classifying the zone (hazardous or non-hazardous) generated by the potential release source. In the case study, the bioethanol evaporation rate (W_g) from pool has been calculated by a specific software (Effects), which is often used to assess the accidents outcomes in plants subjected to Seveso Directive.

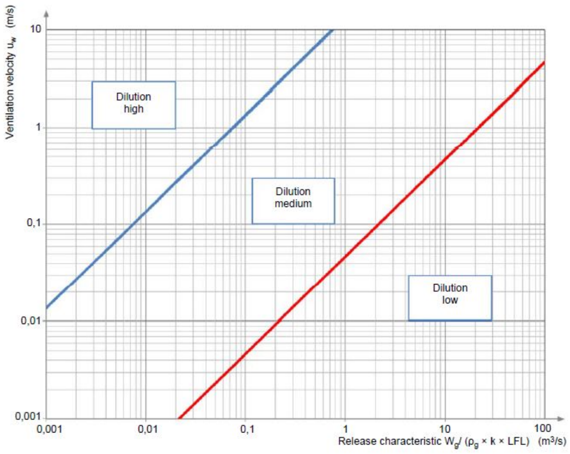

Figure 2: Dilution degree assessment (IEC EN 60079-10-1)

4. The case study: the bioethanol storage depot

The depot is located in the Northern Italy and has two bioethanol storage tanks (V_{tank}=1,044 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 flange used to connect the bioethanol transfer pipe with the tank. The leakages from flanges are usually due to the gaskets wear. The transfer pipe diameter is equal to 20.3 cm. In order to study the wind velocity 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 wind velocity, which is lower than 3 m/s (RSE, 2019) 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 wind velocity, which is reported in International Standard IEC EN 60079-10-1 (Figure 2). The Atlas shows velocity values, which are referred to the height of twenty-five metres, whereas the software requires a wind velocity (v_{10}), referred to 10 metres above the ground (Van den Bosch and Weterings, 2005). The conversion has been carried out by the following equation (Mazzarotta, 2006):

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

Z is a specific height above the ground and p is a dimensionless parameter, 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 (Mazzarotta, 2006) shows the parameter 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

5. Results and discussion

In order to estimate the emission hole surface, the Purple Book has been examined. In particular, the book considers the flanges failures included in pipeline failures and suggests a hole (CPR, 2005) diameter (D_h), which is equal to 0.1 D_p (D_p = pipeline diameter). In order to assess the contribution of heat flux from solar radiation to bioethanol evaporation, the clouds cover has been assumed equal to 50 % (Mazzarotta, 2006). The heat flux, which has been calculated by the software, is reported in Table 4. The simulation of biofuel evaporation from pool has been based on the following hypotheses:

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

In Table 4 the parameters, which have been used to study the bioethanol evaporation, are reported. The results of bioethanol evaporation simulation are reported in Table 5, whereas the trends of pool radius (r_p), evaporation rate (W_g) and pool temperature (T_p) as function of time are reported in Figures 3, 4 and 5. In Table 5 W_g is the average evaporation rate in the examined period (900 s), W_{gmax} is the maximum evaporation rate, M_{ev} is the total evaporated mass, M_b is the released bioethanol mass, m_L indicates the mass flow rate from the flange, whereas r_p and T_p are referred to 900 s. In particular, the increase of evaporated mass due to ventilation velocity is included between 18.2 % and 22.3 %. From Figure 3 it is possible to note that when the flange releases bioethanol (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 t=0 s to t=600 s the pool is spreading (and increasing in size), while the discharge occurs.

Table 4: Bioethanol evaporation study (parameters)

Parameters	Value
Storage tank volume	1,044 m^3
Pipeline diameter (D_p)	20.3 cm
Hole diameter (D_h)	2.03 cm
Discharge coefficient	0.7
Tank filling degree	85 %
Bioethanol temperature	30 °C
Release duration from flange	600 s
Soil temperature	23 °C
Clouds cover	50 %
Air humidity	50 %
Heat flux from solar radiation	1.2 kW/m^2
Evaporation duration	900 s

Table 5: Results

v_{10} (m/s)	W_g (kg/s)	W_{gmax} (kg/s)	r_p (m)	T_p (°C)	M_b (kg)	m_L (kg/s)	M_{ev} (kg)
3.5	0.19	0.39	9.2	25.4	1,284	2.1	234
5.2	0.21	0.43	9.1	20.9	1,284	2.1	255
7	0.22	0.45	8.9	17.7	1,284	2.1	273
8.7	0.24	0.48	8.8	15.6	1,284	2.1	287

Though evaporation is occurring, it is not seen in the first 600 s, because the evaporation rate (W_g) is much lower ($m_L \cong 10\ W_g$) than the mass flow rate (m_L). Once the maximum pool area is reached, the pool radius starts to decrease, because from t=600 s to t=900 s the pool is only evaporating. In fact, there is not mass flow rate (the release is stopped), which increases the bioethanol amount in the pool. The wind velocity passage from 3.5 m/s to 8.7 m/s causes W_g and total evaporated mass increases, which are respectively equal to 26.3 % and 22.6 %. On the contrary, the ventilation velocity increase causes a pool radius (4.3 %) and temperature (38.6 %) decrease. The radius decrease is exiguous, because evaporation rate is much lower than mass flow (m_L) released from the flange. The pool radius trend strongly influences the biofuel evaporation rate. Indeed, the evaporation rate increases from 0 s to 600 s and it decreases from 600 s to 900 s (Figure 4). In Figure 5 the pool temperature trend is reported. During the first 600 seconds the bioethanol is added and pool area increases. Therefore, the evaporation rate increases because a higher biofuel quantity can be removed by wind velocity. After the release is stopped (from 600 s to 900 s), the pool starts to shrink because of evaporation, thus reducing the available surface, which can evaporate. The direct outcome is the evaporation rate decrease. There is also another reason, which causes the evaporation rate decrease from 600 s to 900 s. Indeed, there is not biofuel renewal in the pool and so the pool temperature gradually decreases. Therefore, the bioethanol evaporation due to heat transfer with the soil (the contribution is not so relevant, because ethanol forms a high-boiling pool) also decreases. As soon as the biofuel is released, it starts to cool down due to heat transfer while evaporating. The temperature decreases until an equilibrium is reached at approximately 600 s. When the release is stopped, the pool temperature again decreases until a new equilibrium is reached.

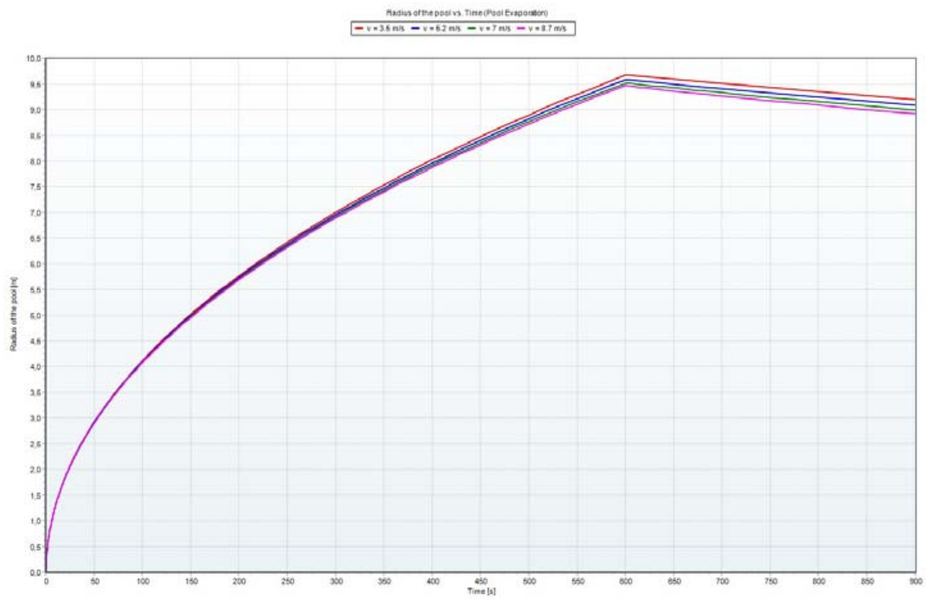

Figure 3: Trend of bioethanol pool radius

Figure 4: Trend of bioethanol evaporation rate

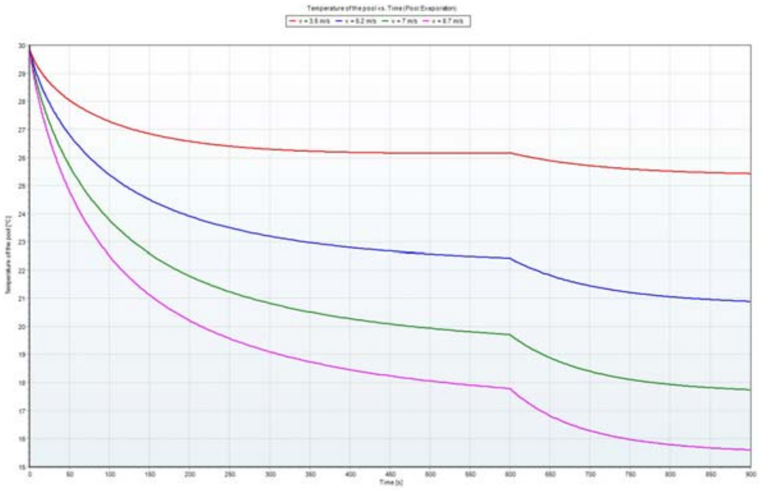

Figure 5: Pool temperature trend

6. Conclusions

The evaporation of high-boiling flammable liquids is mainly due to the mass transfer, which is strongly influenced by wind velocity. The meteorological data analysis of industrial sites, where the bioethanol depots or production plants are located, is a very useful tool in order to delimitate the wind velocity range and hypothesize extremely real values. With reference to the equation reported in International Standard IEC EN 60079-10-1, the software is able to give more reliable 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 zones due to the formation of potentially explosive atmospheres. Because of this reason, the use of specific softwares is recommended for improving the accuracy of bioethanol evaporation study. An interesting step, aimed at assessing the influence of wind velocity variation on evaporation rate, 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.). However, the CFD models use is particularly expensive in terms of time and computational calculation, but it would be able to provide useful information in order to achieve more reliable predictions of evaporation rate.

References

Brighton P. W. M., 1990, Further Verification of a Theory for Mass and Heat Transfer from Evaporating Pools, Journal of Hazardous Materials, 23, 215-234.

Bubbico R., Mazzarotta B., 2016, Predicting Evaporation Rates from Pools, Chemical Engineering Transactions, 48, 49-54.

CPR, 2005, Guidelines for Quantitative Risk Assessment –Purple Book, The Hague, The Netherlands.

IEC, 2016, IEC EN 60079-10-1: Classification of areas – explosive gas atmospheres, 163-164.

Lauri R., Grospietro B., Cova A., Accardi D.S., Pietrangeli B., 2017, Pool Fires: a Model for Assessing Meteorological Parameters Influence on Thermal Radiation, Chemical Engineering Transactions, 57, 229-234.

Lauri R., Pietrangeli B., 2019, Biorefineries Safety: a Case Study Focused on Bioethanol Production (in press DOI: 10.5772/intechopen.87990), Chapter In: V Beschov (Ed.), Biorefinery Concepts, ISBN 978-1-78985-676-7, Intech Open, London, UK.

Mackay D., Matsugu R. S., 1973, Evaporation Rates of Hydrocarbon Spills on Land and Water, Canadian Journal of Chemical Engineering, 51, 434-439.

Mazzarotta B., 2006, Rischio Incendi ed Emissioni, Dispensa del Corso di Laurea in Ingegneria della Sicurezza e Protezione, 62-63.

RSE, 2019, atlanteeolico.rse-web.it/ accessed 8.10. 2019.

Van den Bosch C. J. H., Weterings R. A. P. M., 2005, Methods for the Calculation of Physical Effects – Yellow Book, 3rd Ed., The Hague, The Netherlands.