Chapter

Biorefinery Safety: A Case Study Focused on Bioethanol Production

Roberto Lauri and Biancamaria Pietrangeli

Abstract

With reference to the framework for energy and climate, the European Union (EU) has stated that at least a 32% share of renewable energy consumption has to be achieved within 2030. This context generates attention to the potential hazards, which are associated with flammable biofuels, such as the bioethanol. One of the main hazards, referred to such biofuel, is the formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases. In fact, in a bioethanol production plant (biorefinery), there are several components (flanges, valves, pumps, etc.), which can become potential emission sources in case of failure. Bioethanol is a high-boiling liquid, because its boiling temperature ($T_{\text{boiling}} = 78^\circ\text{C}$) is higher than ambient temperature. Therefore, in case of release and spreading on a certain medium, evaporation occurs because of vapor diffusion. The chapter is focused on a case study. In particular, the chapter illustrates a comparison between two predictive models aimed at estimating the bioethanol evaporation rate, which is a fundamental parameter for determining the dilution degree and classifying the workplaces, where potentially explosive atmospheres could occur. The study investigates the influence of bioethanol release temperature and therefore of its vapor pressure on evaporation rate.

Keywords: bioethanol, evaporation rate, safety, potentially explosive atmospheres, high-boiling liquids

1. Introduction

One of the most demanded challenges for human being in the near future is the development of new energy strategies, which are alternative to fossil energy and characterized by low environmental impacts. In the European Union (EU), the original renewable energy directive 2009/28/EC (RED I) establishes an overall policy for the production and promotion of energy from renewable sources. It requires to fulfill at least 20% of total energy needs with renewables by 2020 [1]. All EU countries must also ensure that at least 10% of their transport fuels come from renewable sources by 2020. In December 2018, the revised renewable energy directive 2018/2001/EU (RED II) came into force as part of the clean energy for all European package. Such directive is aimed at keeping the EU as a global leader in renewables and, more broadly, helping the EU to meet its emission reduction commitments [2] under the Paris Agreement. A common biofuel is the bioethanol, which is a leading candidate to substitute the gasoline as a transport fuel. In the chapter, “bioethanol” is used to indicate ethanol produced by fermentative processes, which convert the sugars into energy. The fermentation mainly uses
biomass. Bioethanol is a renewable fuel, which can be made from grains, such as corn or wheat, or from cellulose sources, such as prairie grass or agricultural, forestry, or municipal wastes. It can be used in vehicles or small engines, which are fed by conventional fuels, and it is utilized as a fuel extender and octane improver with blends that usually are 10% ethanol and 90% unleaded gasoline. Indeed, several researches showed that ethanol/gasoline blends had the potentiality to reduce petroleum fuel use and greenhouse gas emissions. In the last years, the bioethanol use has undergone a fast growth, because it can make easier the replacement of fossil fuels with renewable fuels. In particular, in Europe, the framework for climate and energy, established by the European Council in 2014, caused this growth. Indeed, a specific target for 2030, included in this framework, has stated that at least a 32% share of renewable energy consumption has to be achieved. This context generates attention to the potential hazards, which are associated with flammable biofuels, such as the bioethanol, and has given birth to this chapter, which is focused on the study of bioethanol evaporation rate from liquid pools. In fact, one of the main hazards, referred to such biofuel, is the formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases. Indeed, in a bioethanol production plant (biorefinery), there are several components (flanges, valves, pumps, etc.), which can become potential emission sources in case of failure. Bioethanol can be considered as a high-boiling liquid, because its boiling temperature \( T_{\text{boiling}} = 78^\circ\text{C} \) is higher than ambient temperature. Therefore, in case of release and spreading on a certain medium, evaporation occurs because of vapor diffusion. This is the result of the difference in terms of vapor pressure between the liquid surface and surrounding area. The chapter carries out a comparison between two predictive models (the model referred to low mass transport and the generally applicable formula) aimed at estimating the bioethanol evaporation rate, which is a fundamental parameter for determining the dilution degree and classifying the workplaces, where potentially explosive atmospheres could occur. It is important to highlight that Atex Directive 99/92/EC obliges the employers to carry out such classification [3]. The dilution degree is a parameter, which measures the ventilation (natural or artificial) ability to dilute a release to a safe level (flammable substance concentration is lower than its lower flammability limit) and is reported in International Standard IEC EN 60079-10-1. In particular, the study investigates the influence of bioethanol release temperature and therefore of its vapor pressure on evaporation rate. Finally, the difference between the bioethanol evaporation rates is calculated to determine the reliability range of the model, referred to low mass transport. Therefore, the work is aimed at giving some guidelines about the vapor pressure (such parameter is strictly dependent on temperature) range, where the simplified model is able to provide reliable predictions.

2. Occupational health and safety (OHS) in the biofuel industry

In accordance with the Renewable Fuels Association [4], at 2018 year end, the ethanol industry approximately comprised 210 plants in 27 states with nameplate capacity equal to 16.5 billion gallons. According to the Biotechnology Innovation Organization (BIO), the direct job creation from advanced biofuel production could reach 190,000 units by 2022 [5]. This context generates attention to occupational safety, which has to take into account all actions aimed at protecting the safety, health, and welfare of people engaged in such industrial sector. This can include safety assessments, accident investigations, training programs, and other
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activities, which can reduce or eliminate workplace injuries and illnesses. In the face of growing development of the biofuel industry and the consequent increase in employed workforce, there are still limited data, which are referred to the occupational health and safety of these production processes. Petrochemical processing industry is very advanced in terms of risk assessment and management, while the biofuel production industry has not yet gained enough experience in these topics [6]. Indeed, occupational health and risks during all phases of the processes are not always considered. The former available data suggest that renewable energy will also offer benefits to workers in terms of reduced occupational injury, illness, and death [7], but considering that the biofuels industry is a developing and growing sector and many of the involved companies are small entrepreneurial activities, studies of worker safety and health should be implemented. In Europe, there are a high number of small-scale industrial units, such as the biogas production plants, which are generally characterized by lower quantities than the thresholds for the application of legislation (the Seveso Directive) aimed at the control of major accidents [8]. Such industrial activities have neither the ability for thinking about the risks and the hazards nor the resources or the expertise for managing those. This aspect is generally underestimated for occupational health and safety management. In Italy, INAIL experience showed that providing the biogas industry with a practical tool, such as the checklist approach, could be useful to carry out the analysis of the main hazards (biohazard, fires, and potentially explosive atmospheres) and a valuable support for the plant operators in order to evaluate periodically the actual effectiveness of the overall safety measures [9]. Furthermore, a tailored database, which collects information about accidents of the biofuel industry, should be implemented. The Institut National de l’Environnement Industriel et des Risques (INERIS) database was aimed at collecting all accidents (explosions, fires, spills, derailments, road accidents, etc.), which occurred during the life cycle of biofuel production plants [10]. The accidents study is a very useful tool, which can surely improve the plant safety level.

3. Bioethanol: classification according to CLP Regulation (CLP) No. 1272/2008 EC

Bioethanol is characterized by the same chemical properties (Table 1) of ethanol, which is produced by the processes of the traditional chemistry [11].

With reference to its boiling temperature, bioethanol is classified as a high-boiling liquid. In accordance with Regulation No. 1272/2008 EC, such biofuel belongs to Category 2 (Table 2), and therefore it is classified as highly flammable liquid and vapor [12] (Figure 1).

| Parameter                     | Value |
|-------------------------------|-------|
| Lower flammability limit (%) v/v | 3.5   |
| Upper flammability limit (%) v/v | 15    |
| Boiling temperature (°C)      | 78    |
| Vapor pressure at 20°C (Pa)   | 6000  |
| Flash point (°C)              | 13    |

Table 1. Chemical bioethanol properties.
4. Investigation of evaporation of high-boiling liquids

In order to calculate the evaporation rate of high-boiling liquids, no exact calculation procedure can be found in literature. In most cases, equations, based on experimental results coming from tests, are used. The main relations are referred to:

1. Low mass transport (simplified equation)

2. High and low mass transport (general equation)

In the chapter, the bioethanol evaporation rate is calculated by the two mentioned models in order to quantify the result difference and determine the validity range of simplified model as function of variation of biofuel vapor pressure ($p_v$). The following diagram [13] has been used to determine the vapor pressure variation as function of bioethanol release temperature (Figure 2). An accurate calculation of evaporation rate is extremely important, because such parameter has strong outcomes on classification of zones, where explosive mixtures could occur, and on

| Category | Criteria |
|----------|----------|
| 1        | Flash point <23°C and initial boiling point ≤35°C |
| 2        | Flash point <23°C and initial boiling point >35°C |
| 3        | 23°C ≤ flash point ≤60°C |

Table 2. Criteria for flammable liquids.

Figure 1.
Bioethanol classification (Regulation No. 1272/2008 EC).

Figure 2.
Bioethanol vapor pressure.
plant safety. Indeed, one of the main hazards, referred to bioethanol, is the formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases. In fact, in a bioethanol production plant, there are several components (flanges, valves, pumps, etc.), which can become potential emission sources in case of failure.

5. Hazards associated with bioethanol production: possible formation of potentially explosive atmospheres

One of the main hazards, associated with bioethanol production, is the formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases. Such biofuel can be considered a high-boiling liquid, because its boiling temperature \(T_{\text{boiling}} = 78^\circ\text{C}\) is higher than ambient temperature. Therefore, in case of release and spreading on a certain medium, evaporation mainly occurs by vapor diffusion. This is the result of the difference in terms of vapor pressure between the liquid surface and surrounding area. 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 [14]:

1. Release grade
2. Ventilation availability
3. Dilution degree

In particular, in case of flammable liquid releases, the last parameter depends on evaporation rate and can be determined by the diagram [14] reported in International Standard IEC EN 60079-10-1 (Figure 3), where:

- \(u_w\) is the ventilation velocity (m/s).
- \(W_g\) is the mass flow of flammable compound (kg/s).
- \(\rho_g\) indicates the gas or vapor density (kg/m\(^3\)).
- \(K\) represents a safety factor (dimensionless parameter).
- \(LFL\) is the lower flammability limit of flammable substance.

In case of flammable liquid releases, the calculation of \(W_g\) becomes particularly complex, because several phenomena (solar heat flux, heat transfer from subsoil, convective heat flux from air, and mass transfer due to diffusion) have to be examined. For liquids (such as the bioethanol), which have boiling temperature above ambient temperature, mass transfer by diffusion is the predominant factor. Indeed, the wind removes vapor from the pool surface and because of resultant concentration gradient, mass transfer is induced. Liquid evaporates for restoring the partial pressure, which is in thermodynamic equilibrium with the liquid in the pool at its temperature. Therefore, the high-boiling liquid evaporation strongly depends on the rate, at which vapor can be removed by the airflow above the pool. With reference to this topic, the chapter carries out a comparison between two predictive models aimed at estimating the bioethanol evaporation rate from pool. The evaporation rate
calculation is an extremely important phase for determining successively the dilution degree. Indeed, an accurate estimate of such parameter is fundamental for classifying the zone (hazardous or non-hazardous) generated by the potential release source.

5.1 Bioethanol evaporation: predictive models

Bioethanol is a high-boiling liquid, and the evaporation of high-boiling liquid pools mainly depends on the rate, at which the vapor can be removed by the wind, which blows above the pool. Thus, for high-boiling liquids, the mass transfer by diffusion is the predominant factor, especially after the initial stages of the spill [15]. The mass transfer is induced by the resultant concentration gradient [16]. The driving force is the difference between the liquid vapor pressure and the partial pressure of liquid in the atmosphere. In literature, a simplified model, referred to low mass transport, uses the following expression for calculating the evaporation rate [17]:

\[
m = \frac{k \cdot MW_b \cdot (p_v - p_{amb})}{RT}
\]

(1)

where:

- \( m \) is the bioethanol evaporation rate (kg/s m^2).
- \( k \) indicates the mass transfer coefficient (m/s).
- \( MW_b \) is the molecular weight of bioethanol (46.07 kg/kmol).
- \( p_v \) represents the bioethanol vapor pressure at its temperature (Pa).
- \( p_{amb} \) is the partial pressure of biofuel in the atmosphere (Pa).
- \( R \) indicates the gas constant (8314 J/kmol K).
• T represents the biofuel release temperature (K).

The properties of air, flowing over the liquid pool, are included in the material transfer coefficient (k). Equation (1) is often used for the calculation of high-boiling liquid evaporation rate. However, it has been found that this model is not applicable in case of high mass transport. This is due to the fact that the material transfer coefficient is not independent of the mass flow. Therefore, the chapter goal is aimed at investigating the applicability range of simplified model. Based on the film theory, a correction ($k_1$) of mass transfer coefficient is given [17] in the following expression, which can be applied to all cases:

$$k_1 \left( \frac{m}{s} \right) = \frac{k \cdot (p_{atm} - p_v)}{p_v - p_{amb}} \cdot \ln \left( 1 + \frac{p_v - p_{amb}}{p_{atm} - p_v} \right)$$  \hspace{1cm} (2)

where:

• $p_{atm}$ is the atmospheric pressure (101,325 Pa).

The abovementioned film theory is based on the following principles: it is considered that wind velocity, temperature, and partial vapor pressure of the evaporating liquid are only dependent on the direction, which is perpendicular to the liquid surface, while in the other directions, the values of all the abovementioned parameters are assumed constant. The introduction of the corrected material transfer coefficient ($k_1$) gives the following expression (generally applicable equation), which is applicable to high and low mass transport [17]:

$$m = \frac{k \cdot MW_b \cdot p_{atm}}{RT} \cdot \ln \left( 1 + \frac{p_v - p_{amb}}{p_{atm} - p_v} \right)$$  \hspace{1cm} (3)

In literature, different relations for the coefficient k have been derived. In this study, the model given by MacKay and Matsugu has been used. Such model has been validated by experimental tests and takes into account both the pool geometry (radius) and wind velocity [18]:

$$k(\frac{m}{s}) = 0.005 \cdot v_{10}^{0.78} \cdot (2r_p)^{-0.11} \cdot Sc^{-0.67}$$  \hspace{1cm} (4)

where:

• $r_p$ is the radius of the bioethanol pool (m).

• $v_{10}$ represents the wind speed at 10 meters of height (m/s).

• Sc is the Schmidt number (dimensionless parameter).

In the analysis, it has been assumed that the Schmidt number is equal to 0.8 as reported in the Yellow Book in case of gases and vapors [18].

6. Results and discussion

In order to estimate the wind velocity, a bioethanol production plant, sited in the Northern Italy (Piedmont), has been considered. In particular, the Italy wind Atlas reports an annual average wind velocity, which is lower than 3 m/s for the place
where the plant has been built. Therefore, the wind velocity has been assumed equal to 3 m/s. In order to calculate \( m \), the pool radius has been assumed equal to 1 m. The following temperatures of bioethanol release have been examined to calculate the evaporation rate: 20, 30, 40, 50, and 60°C. Such temperatures are usually found in bioethanol production plants. In Table 3 the vapor pressures, referred to such temperatures, are reported. As the examined temperatures are lower than biofuel boiling temperature, the liquid pool is high-boiling, and therefore the partial pressure of the biofuel in the atmosphere (\( p_{\text{amb}} \)) is negligible. The study results are shown in Table 4, where \( m_1 \) indicates the evaporation rate calculated by the equation, referred to low mass transport, whereas \( m_3 \) indicates the evaporation rate, determined by the generally applicable model.

The variation (\( \Delta \)) between the generally applicable equation and the simplified expression is calculated by the following formula:

\[
\Delta(\%) = 100 \cdot \left( \frac{m_3 - m_1}{m_1} \right) \quad (5)
\]

The values of such difference are reported in Table 5, whereas its trend as function of vapor pressure is shown in Figure 4.

The increase of bioethanol release temperature and therefore of vapor pressure causes a difference growth, which is moderate and acceptable (the difference does not exceed 10%) till the pressure is lower than 18,000 Pa, whereas \( \Delta \) is equal to 32.2% at 45,000 Pa. Therefore, Eq. (1) (simplified model) can be used in the case of bioethanol vapor pressure, which is lower than 18,000 Pa, because it shows an adequate reliability. Such pressure represents a threshold, which determines the range of reliability of the model, referred to low mass transport. Over 18,000 Pa the expression (3) (generally applicable model) has to be used to achieve a more accurate estimate of the evaporation rate, which is a fundamental parameter in order to determine the dilution degree and classify the workplaces, where there is the possibility of formation of potentially explosive atmospheres due to bioethanol releases. It follows that the evaporation rate estimate has a strong influence on the safety of an industrial plant, which uses or produces bioethanol, because it allows to assess if the biofuel release source is able to generate an hazardous or a non-hazardous zone. Indeed, a less accurate calculation of bioethanol evaporation rate could generate a mistake during the area classification procedure, and therefore the hazard of explosive atmosphere formation could be underestimated. Such scenario could decrease the plant safety level, because the choice of equipment and protective systems, which must be used in hazardous zones, depends on area classification as reported in Atex Directive 99/92/EC. This choice is aimed at avoiding that equipment and protective systems become active ignition sources. Therefore, there is a strong connection between the evaporation rate calculation and the choice of protective systems.
and safety of plants, which use or produce bioethanol. Finally, it has to be mentioned that the two models are based on the assumption that the partial vapor pressure can be considered constant [20]. This is correct as long as the temperature of the evaporating pool does not change.

Such condition occurs, as long as there is equilibrium among the convective heat flow produced by the air flowing over the pool, the solar heat flow, the heat flow from the subsoil, and the heat flow required for the evaporation. In reality, the evaporating pool temperature gradually decreases. It follows that the evaporation rate, calculated by Eqs. (1) and (3), represents a maximum quantity, referred to isothermal conditions, and therefore it can be considered valid only at the evaporation beginning.
7. Conclusions

One of the main hazards, referred to bioethanol, is the formation of potentially explosive atmospheres due to its evaporation from pools in case of accidental releases. In order to classify the workplaces, characterized by possible formation of potentially explosive mixtures, as the bioethanol is a high-boiling flammable liquid, a particular attention has to be addressed to the thermodynamic release parameters, such as the temperature, because it influences the vapor pressure. In particular, the study has shown that:

- Analysis of thermodynamic parameters is very important, because it allows to choose the best predictive model for calculating the evaporation rate, which is successively used to determine the dilution degree.

- In case of bioethanol releases, the simplified model, referred to low mass transport, cannot be always used, because its reliability is strongly dependent on the vapor pressure.

- The simplified model is only applicable when the partial vapor pressure is lower than 18,000 Pa.

- For all other cases, Eq. (3), based on the film theory, has to be used to achieve a more accurate estimate of the evaporation rate.

The calculated evaporation rates are referred to isothermal conditions and represent maximum values, because the majority of the evaporating liquids cool down after the evaporation beginning; therefore, the evaporation rate decreases. In order to improve the calculation accuracy, computational fluid dynamics that is able to solve simultaneously the equations, which govern the liquids spreading and evaporation, has to be used. However, the illustrated predictive models are abundantly used in technical international standards, concerned with the classification of areas where flammable gases or vapors can generate potentially explosive atmospheres.

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