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Original article

Simulation and analysis of the failure of the methanol storage base in bio-refineries

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INFORMATIONS

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ABSTRACT

The work includes examination of emergency events in the methanol storage base. The article presents physical effects and hazards that may arise as a result of uncontrolled emission of methanol to the environment.

KEYWORDS

hazardous materials, risk analysis, critical infrastructure

Introduction

The development of civilization and technological progress caused a sharp increase in the consumption of classic energy sources. Crude oil, natural gas and coal are currently fuels whose resources are gradually shrinking. In connection with this, new process solutions are being sought that allow obtaining alternative fuel sources [1]. One of such solutions is biodiesel, which is currently an addition to car fuels or direct fuel for self-ignition vehicles [2]. The annual research conducted by BP Company shows that in recent years there has been a steady increase in the use of biofuels. In 2014, compared to 2013, this increase was of 7.4% on a global scale [3]. The biofuel production technology may bring with it hazards resulting from the inappropriate manner of storing substrates or products. It should be noted that even small deviations from the set parameters could result in serious consequences for the environment and human life and health. According to the Environmental Protection Law Act of 27 April 2001, a failure is: "an event, in particular an emission, a fire or an explosion, occurring during an industrial process, storage or transport in which one or more hazardous substances is present, leading to an immediate threat to human life or health or to the environment, or the occurrence of such a threat with some delay" [4].

The aim of the article is to estimate the hazard zones created due to the failure of methanol storage tanks.

1. Characteristics of the storage base

Methanol is one of the components needed to produce biodiesel. It is a flammable substance and, consequently, creates a potential fire hazard. It also has toxic properties, which causes its uncontrolled release into the environment may cause undesirable consequences for human life and health [5, 6]. Biodiesel is diesel fuel constituting or containing a biological component in the form of fatty acid methyl esters. The Act of 25 August 2006 on the fuel quality monitoring and control system defines this fuel as “diesel oil containing up to 5.0% by volume of fatty acid methyl esters, referred to in the Act of 25 August 2006 on biocomponents and biofuels liquid, used in vehicles, agricultural tractors, as well as non-road machinery, equipped with self-ignition engines” [7].

In turn, Article 2 of the Act of 25 August 2006 on biocomponents and liquid biofuels gives the following definition: “diesel oil containing more than 5.0% by volume of biocomponents” [8].

Based on the reaction of formation of methyl esters, the theoretical demand for raw material for the production capacity of 150,000 tons of biodiesel per year. The stoichiometry of the reaction (after assuming that the molecular weight of 1 mole of the obtained esters is about 900 g/mol [9]) it was calculated that 16,000 tons of methanol are needed annually to obtain the assumed efficiency of the biodiesel plant. In terms of continuous production (considering the maintenance breaks, cleaning of equipment, periodic inspections and unplanned stops – approximately 60 days) this gives the demand for 53,333 kg of methanol per day. Given the methanol density of 792 kg/m^3 [6] and the condition that the stock of substrate is to be enough for 3 days of continuous production, the storage base should have tanks with a total capacity of about 300 m^3.

The size of a single storage tank was adopted as follows:

- the medium mass: 53,333 kg,
- the density: 792 kg/m^3,
- the fill factor – α: 0.7,
- the assumption: the height equal to twice the diameter (D=2H).

$$Vworking = \frac{daily\ consumption\ of\ raw\ material}{d} = \frac{53333\ kg}{792\ \frac{kg}{m^3}} = 67.3\ m^3 \quad (1)$$

where:

Vworking – the working volume of the tank (m^3),

d – the density (kg/m^3);

$$Vtotal = \frac{V\ rob}{\alpha} = \frac{67.3\ m^3}{0.7} = 96.14\ m^3 \quad (2)$$

where:

$Vtotal$ – the total volume of the tank (m^3),

α – the tank filling factor.

Vtotal = 100 m^3 was assumed.

$$Vtotal = \frac{\pi D^2}{4} * H = \frac{\pi D^2}{4} * 2D = \frac{2\pi D^3}{4} \quad (3)$$

$$D = \sqrt[3]{\frac{Vtotal*4}{2\pi}} = 3.99\ m \quad (4)$$

where:

D – the tank diameter (m).

D = 4 m was assumed.

$$H = \frac{Vtotal*4}{\pi D^2} = 7.96\ m \quad (5)$$

where:

H – the tank height (m).

H = 7.96 m was assumed.

The calculations carried out indicate that three tanks with the capacity of 100 m^3 are needed for storage of methanol to guarantee production for three days. However, it should be noted that it is necessary to provide the fourth tank (also with the volume of 100 m^3) as an object with additional capacity in case of emergency events.

An exemplary storage base is depicted in Figure 1.

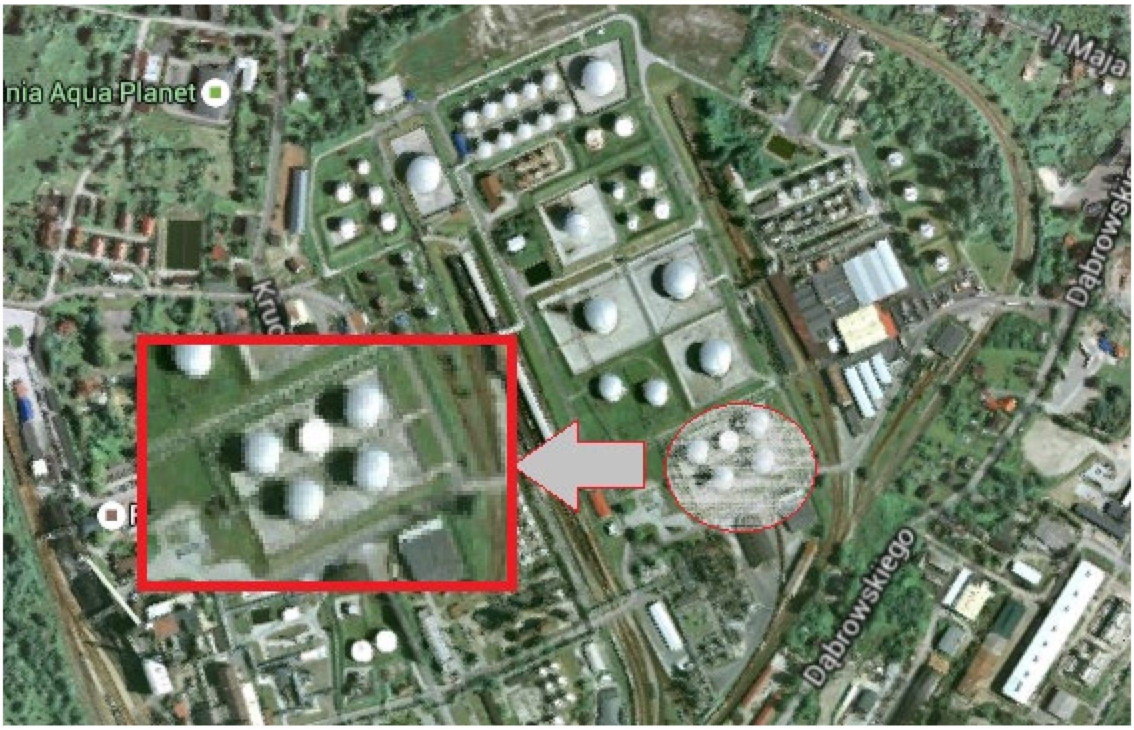

Fig. 1. Location of the storage base

Source: Own elaboration.

2. The risk analysis

The methodology of conducting risk analysis is based on *determining all factors that create the possibility of dangerous situations for the object* [10]. Qualitative and quantitative methods used to identify threats to an object can be distinguished.

In the case of process safety, the authors [See more: 10] propose the selection of the so-called Representative Emergency Events (RZA) according to the following classification:

a) the criterion of the probability of an undesired event occurrence,

b) the type and amount of losses incurred,

c) the size of the risk obtained in previous analyzes.

A risk matrix was used as part of the development of events that were deemed to be of high risk. The risk matrix is based on a comparison of the probability of occurrence of an event with the effects that this event may cause. It can be described with the formula:

$$R = P * S \tag{5}$$

where:

R – the level of risk,

P – the probability indicator of occurrence of the event under examination,

S – the indicator of the effects of the occurrence of the investigated event.

The values from Table 1 were adopted to determine the frequency of adverse events, while the category of effects is assessed based on the information contained in Table 2. The frequency category presents the scale of probability of an undesired event occurrence. The category of effects refers to the magnitude of the effects of adverse events.

Table 1. Category of frequency

Category	Description
1 – unlikely	Once per century
2 – likely	Once in a dozen or so years
3 – quite likely	Several times a year

Source: Own elaboration.

Table 2. Category of effects

Category	Description
1 – negligible effects	Medical consultation
2 – significant losses	Sick leave, minor injuries
3 – catastrophe	Severe injuries, death of an employee

Source: Own elaboration.

On the basis of the information contained in the above tables, the risk matrix presented in Figure 2 was developed. A detailed description of the matrix is presented below in Table 3.

		Effects		
Frequency		1	2	3
	1	1	2	3
	2	2	4	6
	3	3	6	9

where:
A – green, acceptable risk, values 1-3;
TNA – yellow, tolerable unacceptable risk, values 4-6;
N – red, unacceptable risk, values 9

Fig. 2. Risk matrix
Source: Own elaboration.

Table 3. Risk analysis for methanol storage tanks

Activity	P	S	R
slight crack of the tank's jacket (3 cm hole)	2	2	4
failure of the valve on the storage tank – leak of dangerous substance	3	2	6
catastrophic cracking due to corrosion (40 cm hole)	1	3	3
catastrophic unsealing due to external fire	2	3	6
rupture of the valve on the storage tank – leak of dangerous substance	1	3	3

Source: Own elaboration.

Based on the analysis of the risk matrix, three RZAs were defined:

a) a slight crack of the tank's jacket (3 cm hole) – leak of a dangerous substance,
b) a failure of the valve on the storage tank – leak of a dangerous substance,
c) catastrophic unsealing due to external fire.

These events carry the level of tolerable unacceptable risk (TNA).

3. Parameters of threshold values for determining threat zones

The area, which is defined as a threat zone, depends on the ERPG (Emergency Response Planning Guidelines), i.e. markers determining the exposure of people within 1 hour to a specified concentration of a dangerous substance. There are three degrees of ERPGs [11]:

a) ERPG 3 – the maximum concentration of a dangerous substance in the air, below which people exposed to it within one hour will experience effects that threaten their life and health,
b) ERPG 2 – the maximum concentration of a dangerous substance in the air, below which people exposed to it within one hour will feel slight health effects and undertake an evacuation action,
c) ERPG 1 – the maximum concentration of a dangerous substance in the air, below which people exposed to it within one hour, will not experience any effects on health and life.

For methanol:

a) ERPG 3 is 5000 ppm,
b) ERPG 2 is 1000 ppm,
c) ERPG 1 is 200 ppm.

Additionally, the methodology proposed by the ALOHA program interface, i.e. the ranges of thermal radiation, was used to determine the fire zones:

a) 10 kW/m^2 – potentially fatal in 60 seconds,
b) 5 kW/m^2 – second degree burns in 60 seconds,
c) 2 kW/m^2 – pain within 60 seconds.

4. Using computer simulations

In order to obtain threat zones, computer simulations require determining the boundary conditions needed to carry out calculations. It was assumed that due to the high vapor pressure of methanol in the event of outflow it would be a two-phase stream outflow. Meteorological parameters are another decisive condition for the propagation of dangerous substances. The weather conditions occurring in the studied area in December 2015 were used for the purpose of the article (these conditions were assumed to be the most probable in the winter period) [12]:

a) wind direction – south-east wind (60°),
b) wind speed – 5.4 m/s,
c) air temperature – 12°C,
d) humidity – 15-20%,
e) weather stability class[2] – *D*.

Performing spatial analyses of the propagation of toxic substances is possible due to the use of dedicated software. Simulations were carried out using computer programs such as ALOHA and Marplot.

Three RZAs were determined in the effect of the risk matrix analysis. A variant with predefined meteorological conditions was considered for each of them.

4.1. Variant I

A slight crack in the tank's jacket. In the effect of a failure, which may be due to the increase in pressure, corrosion of the camera, a mechanical damage or industrial sabotage, the storage vessel may become unsealed. The hole with the diameter of 3 cm was adopted for the tests. The substance parameters and the extents of the contamination zones are given in Table 4.

4.2. Variant II

The failure on the valve on a storage tank (DN 100). In the effect of a failure, which may be due to damage to the jumper of the valve, a mechanical damage or industrial sabotage, the storage vessel may become unsealed. The hole with the diameter of 10 cm was adopted for the tests. Table 5 shows the substance parameters as well as the extent of contamination zones for this scenario.

Table 4. Basic information about the substance used for simulation I

Sub-stance	Weather conditions	Time of outflow [min]	Amount of released substance [kg/min]	Extent of ERPG 3 con-tamination zone [m]	Extent of ERPG 2 con-tamination zone [m]	Extent of ERPG 1 con-tamination zone [m]
metha-nol	the most frequent	60	14.5	10	21	85

Source: Own elaboration.

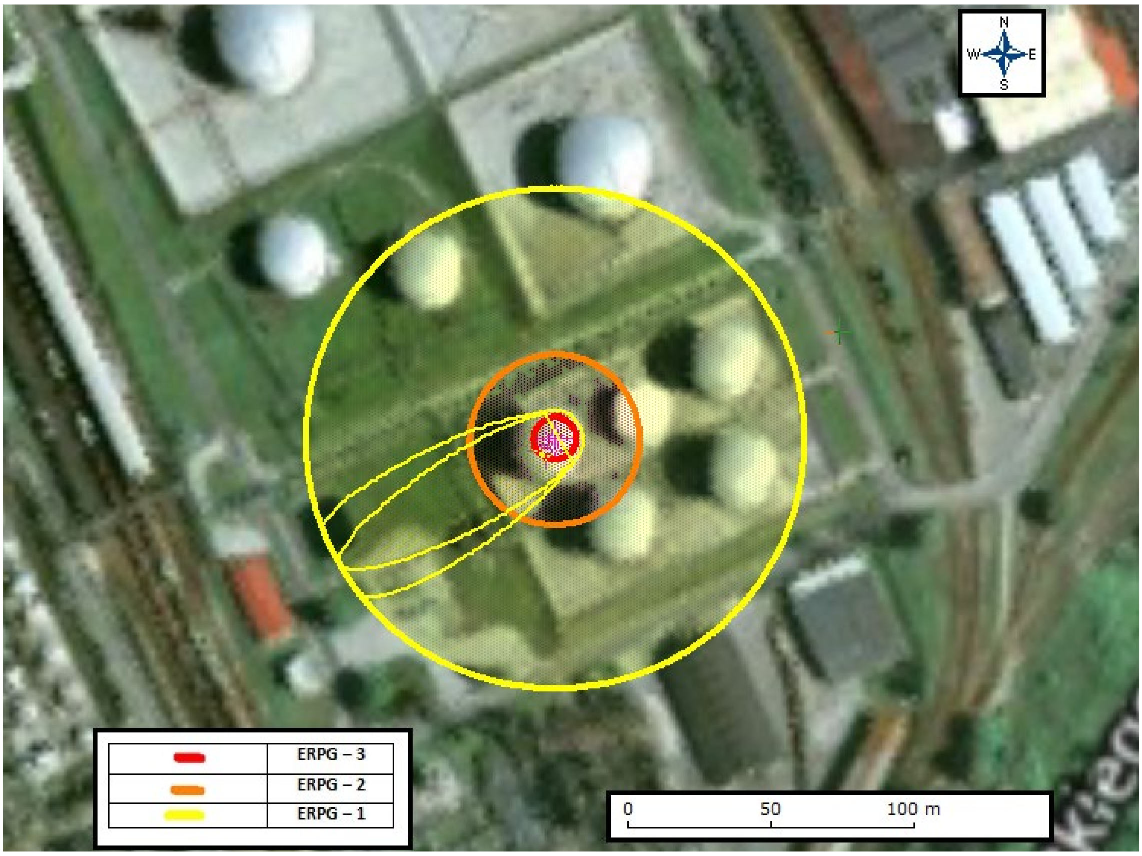

Fig. 3. Simulation I, the map of threat zones
Source: Own elaboration.

Table 5. Basic information about the substance used for simulation II

Sub-stance	Weather conditions	Time of outflow [min]	Amount of released substance [kg/min]	Extent of ERPG 3 con-tamination zone [m]	Extent of ERPG 2 con-tamination zone [m]	Extent of ERPG 1 con-tamination zone [m]
metha-nol	the most frequent	60	153	34	70	302

Source: Own elaboration.

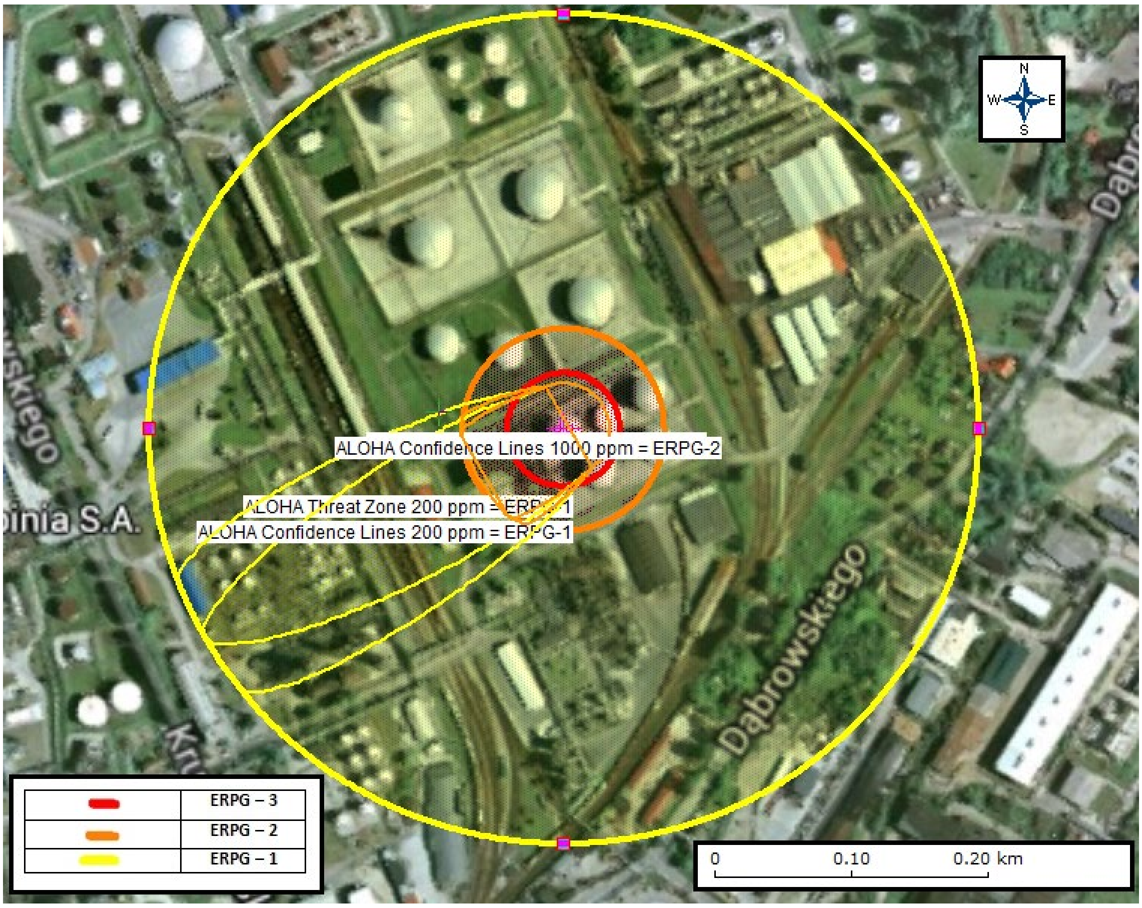

Fig. 4. Simulation II, the map of threat zones
Source: Own elaboration.

4.3. Variant III

Catastrophic unsealing of the tank due to external fire. In the effect of a failure, which may be due to industrial sabotage or accidental fire, catastrophic unsealing of the storage vessel may occur. The hole with the diameter of 1 m was adopted for the tests. Information on the substance and the extents of individual zones can be found in Table 6.

Table 6. Basic information about the substance used for simulation III

Substance	Weather conditions	Combustion time [min]	Amount of combusted substance [kg]	Extent of the zone 10 kW/m^2 [m]	Extent of the zone 5 kW/m^2 [m]	Extent of the zone 2 kW/m^2 [m]
methanol	the most frequent	6	34	87	104	139

Source: Own elaboration.

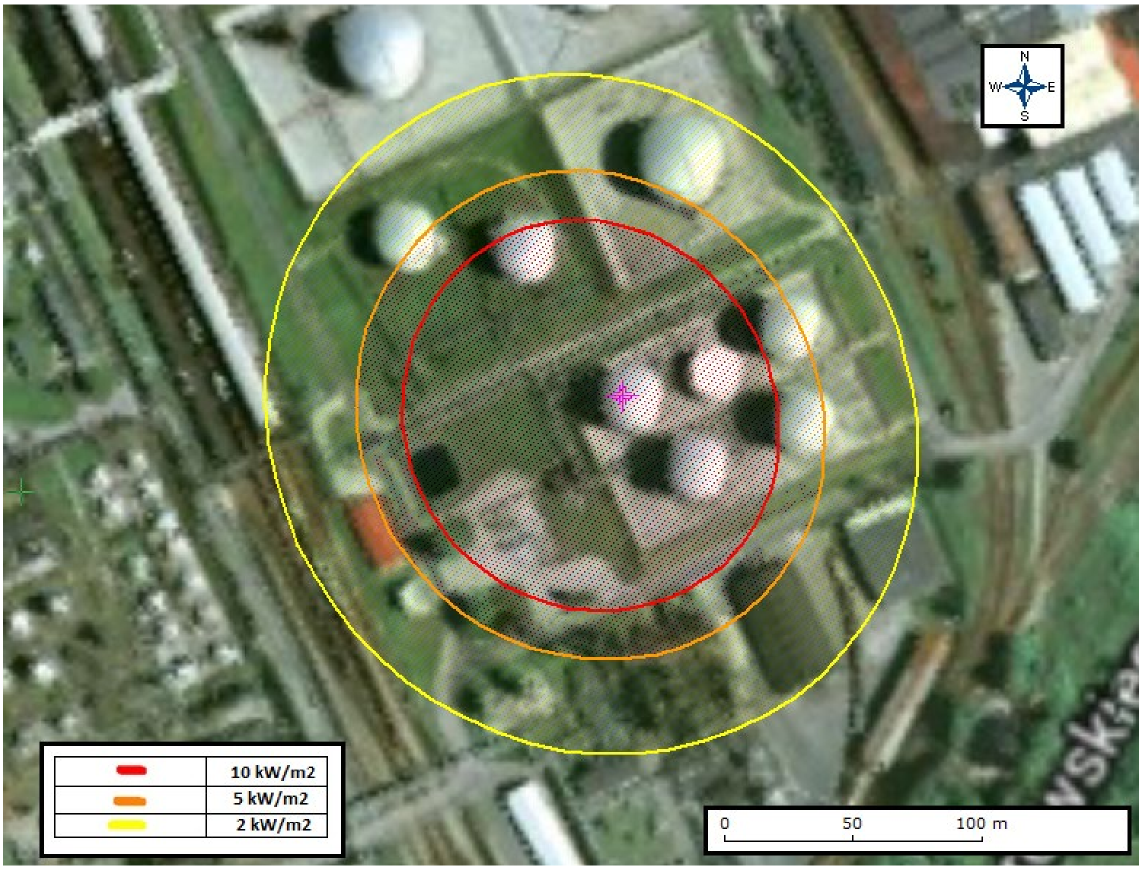

Fig. 5. Simulation III, the map of threat zones
Source: Own elaboration.

6. Analysis of results and conclusions of the tests

The aim of the estimation and presentation of the extents of dangerous zones was to visualize the physical effects and potential consequences of a failure for previously calculated RZAs. The application of the ALOHA and Marplot programs allowed for performing a series of simulations, resulting in the extents of toxic and fire zones for the considered cases.

The results obtained show that in each of the considered cases there is a significant risk arising from the emergence of the methanol outflow into the environment. The extents of toxic zones for the simulations I and II for the ERPG 3 concentrations indicate that employees being close to the failure will be exposed to permanent health impairment. It should be noted that the scenarios I and II are largely dependent on weather conditions, because the toxic cloud will move in the direction of the wind. In the case of the scenario III, the zone with the greatest threat is definitely higher (84 m). What is more, in the event of a fire, the zone takes the shape of a circle, so that a larger area is exposed to potential damage and risks to human life and health.

Due to the limitations of the software used, it is not possible to perform tests for the domino effect, which is why it is omitted in the scenario III. In the event of fire in one of the tanks, self-ignition or spreading of flames to tanks located nearby (the domino effect) may occur. For this reason, the leftmost tank was assumed as an unsealed tank.

The analyses and calculations made for the purposes of the article are only a kind of approximation and estimation of the possibility of the emergence of a threat within the bio-refineries.

The purpose of the article was to estimate the extent of threat zones created as a result of the emission of a dangerous substance (methanol) to the environment.

The conducted research may be a contribution to further detailed analyses in the case of obtaining more detailed data. It should also be noted that any such type of study might support emergency services on existing installations.

In everyday life, it cannot be predicted what consequences an industrial failure can bring. The methods of risk analysis, computer simulations, prediction of the consequences of occurrence of dangerous events are additional support for increasing the sense and security of an industrial plant. When performing this type of work, one should bear in mind how many variables have a direct impact on the results obtained and treat them only as a certain approximation of reality.

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Conflict of interests

All authors declared no conflict of interests.

Author contributions

All authors contributed to the interpretation of results and writing of the paper. All authors read and approved the final manuscript.

Ethical statement

The research complies with all national and international ethical requirements.

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Biographical note

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Symulacja i analiza awarii bazy magazynowej metanolu w biorafinerii

STRESZCZENIE Praca zawiera badania zdarzeń awaryjnych w bazie magazynowej metanolu. Opracowanie prezentuje efekty fizyczne oraz zagrożenia mogące powstać w wyniku niekontrolowanej emisji metanolu do otoczenia.

SŁOWA KLUCZOWE materiały niebezpieczne, analiza ryzyka, infrastruktura krytyczna

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