



SCIENTIFIC BASIS OF INNOVATION

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MODELING AND RISK ASSESSMENT OF MAN-MADE DISASTERS AT PETROCHEMICAL ENTERPRISES

Introduction. *Emergency modeling technologies have been increasingly used to prevent man-made disasters. At the same time, in order to expand (clarify) the obtained results, additional risks need to be assessed.*

Problem Statement. *The issue of safety in the production and storage of petroleum products is very important, because there is a high risk of toxic emissions, fires, and explosions, which may lead to catastrophic situations with casualties.*

Purpose. *The purpose of this research is to model possible scenarios and to assess the risks of emergencies at oil production and storage facilities.*

Material and Methods. *Based on the analysis of literature sources on this and related topics, we have used the empirical method consisting of mathematical calculations and computer simulations with the use of software.*

Results. *Three computer simulations of emergencies at a refinery, which may occur under different circumstances, have been made. With the help of these simulations, possible consequences of the emergency have been obtained. The probable risks of human exposure to heat radiation have also been assessed. With the use of probit functions, the dependencies of the conditional probability of exceeding the pain threshold, as well as 1st, 2nd, and 3rd degree burns have been determined. This has allowed improving and balancing the management decision-making system regarding the implementation of emergency response measures. Recommendations have been given for controlling zones and reducing the potential risk of emergency situations on petrochemical enterprises (factories).*

Conclusions. *The obtained results can be used to modernize the existing system of continuous observations, laboratory and other control, to assess the status of protection of the population, territories, and objects under increased risk of danger, as well as to rationalize the system of medical and evacuation support. The obtained cartographic materials can be used for training officers and employees of the State Emergency Service of Ukraine.*

Keywords: emergency situation, mathematical modeling, conditional probability of human lesion, and probit function.

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Modeling emergency situations is an extremely important stage of scaling the explosion of hazardous chemicals and locating the enterprises that have dangerous objects, given weather conditions, with the subsequent superimposition of the results of calculations on a map of the area, which allows evaluating management decisions on the localization and elimination of emergency situation and making an operational assessment of the readiness of the relevant infrastructure to overcome the potential consequences of such a situation.

Ensuring safety of the production and storage of oil products is very important problem, because there is a great risk of toxic emissions, fires, and explosions, which may lead to catastrophic situations with casualties [1–5]. In the city of Kremenchuk [1], there are many high-risk industrial facilities in various industries, such as mechanical engineering, petrochemicals, energy, construction industry, light and food industry. Among them, there is PJSC *Ukratnafta* [2] that produces and provides storage for a huge amount of energy-rich substances (gasoline, diesel Fuel, and petroleum gas), so emergency situations pose the greatest threat to the life and health of the population and the surrounding environment and may pollute a large area of the city of Kremenchuk and suburbs (the villages of Litvynenky, Rokytne, Omelnyk, and others). According to the regulatory document [3], the employer shall determine the level of danger based on the risk of an explosive environment, given the probability of an explosive environment and the duration of its existence, and take all measures so that, should an explosion does occur, it is controlled, localized at one workplace and equipment, and its spread is minimized. At workplaces, it is necessary to take measures to minimize the physical impact of explosion on workers.

Since there are many tanks containing energy-rich substances at this enterprise, it is necessary to urgently study possible scenarios of emergency situations that may be caused by a spill and explosion of vapors from a benzene storage tank.

The modern solutions for prompt response to emergency situations shall be based on modern principles of spatial modeling and comprehensive approaches to the use of modern software applications [4], which allow developing and implementing at the enterprise an action plan and a procedure for response to emergency situations, as well as raising the efficiency of designing and operating the existing security systems at high-risk enterprises. These applications should calculate how quickly toxic substances are released from a damaged tank, determine the direction of their explosion, and predict how these parameters change over time, given the scale of potential consequences of emergency situations.

In *ALOHA* [5], there are three mathematical models that calculate different types of fires:

- ◆ fireball that occurs when a tank that contains a flammable liquid explodes because of excess pressure and immediately ignites, usually referred to as a BLEVE (boiling liquid expanding vapor explosion, with fire on the fireball surface);
- ◆ jet fire that occurs when a flammable liquid leaks from a vessel or pipeline to form a fluid reservoir, which then ignites (fire at the exit and at the edges of the active zone);
- ◆ pool fire that occurs when flammable liquids ignite and burn directly above the pool.

To solve the problem, we have compared the results of the calculations for these models. To start the calculation, it is necessary to specify the location of the emergency situation, that is, the place where there is a risk of an explosion. To this

Table 1. Geographical Data

Altitude	Latitude	Longitude	Location
190 m	49° 04' 47" northern latitude 49° 09' 40" northern latitude	33° 25' 57" eastern longitude 33° 27' 45" eastern longitude	City of Kremenchuk Reservoir at the Kremenchuk refinery

end, the geographical data (the coordinates of the source of danger), as shown in Table 1, are input into the ALOHA program from *Google Maps*.

The meteorological conditions are known to affect the spread of the pollutant (that is, affect its gaseous and liquid states). The data are taken from the Internet resource as of 06.10.2021, time 1243, and shown in Table 2.

Further, it is necessary to choose a chemical substance. In accordance with the purpose of this research, we have chosen benzene [6] (C_6H_6), CAS number 71-43-2.

The results of benzene explosion impact can be characterized by AEGL (acute exposure guideline levels) [7] that is an exposure level designed to help emergency responders identify areas of exposure associated with an explosion or other catastrophic event where the population is exposed to a hazardous airborne chemical (critical exposure is a single, unique exposure that does not exceed established levels within 8 hours).

The three levels of AEGL are defined as follows:

- ◆ AEGL-3 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death;
- ◆ AEGL-2 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, inclu-

ding susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

- ◆ AEGL-1 is the airborne concentration (expressed as parts per million or milligrams per cubic meter [ppm or mg/m^3]) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects.

Acute Exposure Guideline Levels (AEGL) (quantity/concentration of substance measured in ppm — parts per million)

For benzene, we have chosen the following exposure levels AEGL-1 (60 min): 52 ppm; AEGL-2 (60 min): 800 ppm; and AEGL-3 (60 min): 4000 ppm.

We have set the limits of immediate danger to life and health (IDLHs) that is the concentration that is instantly dangerous to the life or health of workers when they are exposed to toxic chemicals while working. Accordingly, we have set IDLH500 ppm, for a potential occupational carcinogen. The next step is to set the lower explosive limit LEL 12,000 ppm and the upper explosive limit UEL 80,000 ppm.

From the literature data we know the following properties of benzene: the boiling point is 79 °C; the evaporation pressure is 0.066 atm., and the saturation concentration in the air is 66.901 ppm or 6.69%.

The data on the storage tank are given in Table 3, the parameters are given for the three above mentioned scenarios.

The three different emergency scenarios have been simulated.

Scenario 1: Spillage of benzene without ignition followed by the formation of a toxic cloud:

- ◆ the data on the location, the meteorological conditions, the properties of the chemical and the storage tank are listed in Table 1;
- ◆ the leak occurred as a result of the formation of a 10 × 4 cm rectangular hole at a height of 50 cm from the bottom of the tank;
- ◆ the type of flooring under the tank is concrete;
- ◆ the surface temperature is equal to the air temperature;

Table 2. Meteorological Data

Description	Unit of measurement	Value
Wind speed	m/s	7
Wind direction, eastern	degree	90
Atmospheric stability class	—	D
Air temperature	degree Celsius	12
Cloudiness	—	Clear
Relative humidity	%	32
Roughness of the Earth's surface	—	Built-up area or forest

- ◆ the maximum diameter of the spill is unknown;
- ◆ the duration of simulation time is limited to 1 hour;
- ◆ the rate of leakage of the substance is 137 kg/min, the total amount of the spilled chemical is 5541 kg;
- ◆ the spill has a diameter of 42 m.

Let us determine the consequences of exposure of workers to the concentration of benzene with the use of the ERPG parameter that characterizes the effect of a dangerous chemical substance in the air during 1 hour. The dangerous zones are calculated by the program in accordance with the Emergency Response Planning Guidelines (ERPG) [8]. Chemicals can have up to three ERPG values, each having an adverse effect and corresponding to a specific health effect level. The three levels of ERPG are defined as follows:

ERPG-3 is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening effects or death.

ERPG-2 is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or

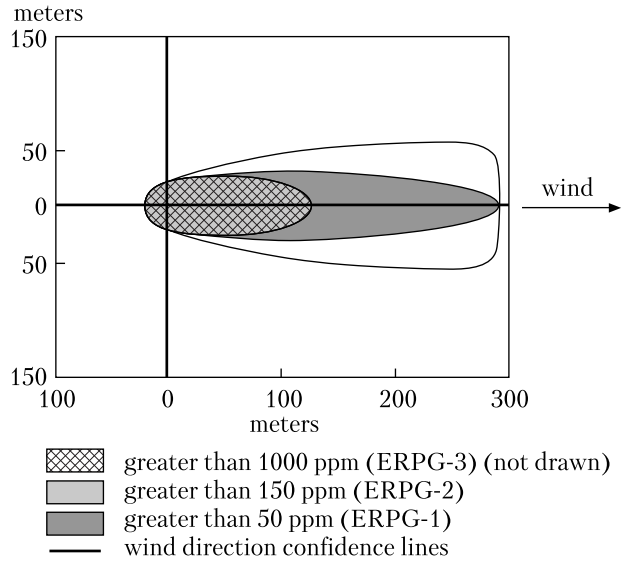


Fig. 1. Dangerzones in ALOHA software

developing serious effects or symptoms of poisoning by a chemical substance.

ERPG-1 is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing more than mild, transient adverse health effects.

The danger zones are described in Table 4.

Table 3. Benzene Storage Tank Parameters

Scenario	Type of reservoir	Diameter, m	Height, m	Volume, m ³	Type of chemical substance	Volume of liquid, l	Level of liquid, %
1	Vertical cylinder	12.34	8.84	1057	Liquid	1057238	100
2	Vertical cylinder	12.34	8.84	1057	Liquid	1057238	100
3	Vertical cylinder	12.34	8.84	1057	Liquid	845789	80

Table 4. Danger Zones for Scenario 1

Zone	Color	Title	Concentration of chemical substance	Length, m	Notes
1	Red	ERPG-3	1000 ppm ≥	31	Not plotted by the program, because of short-range scattering effects that make scattering predictions less reliable for short distances
2	Orange	ERPG-2	150 ppm ≥	127	-
3	Yellow	ERPG-1	50 ppm ≥	291	-

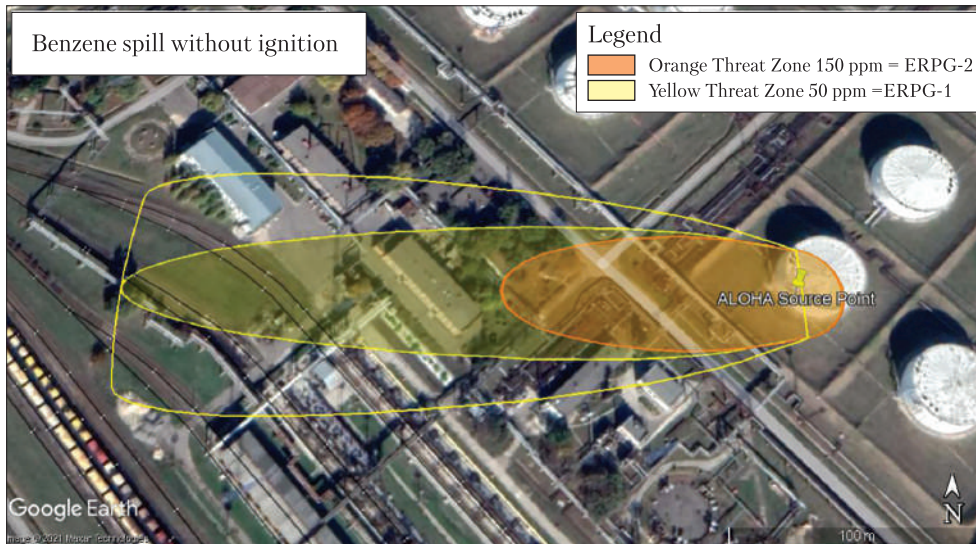


Fig. 2. Danger zones imported to Google Earth

The results of the calculation of danger zones by the program are shown in Figs. 1 and 2.

Scenario 2: benzene spill with ignition and subsequent formation of a burning spill:

- ◆ the data on the location, the meteorological conditions, the properties of the chemical and the storage tank are described above;
- ◆ the leak occurred as a result of the formation of a 10×4 cm rectangular hole at a height of 50 cm from the bottom of the tank;
- ◆ the type of flooring under the tank is concrete;
- ◆ the surface temperature is equal to the air temperature;
- ◆ the maximum diameter of the spill is unknown;
- ◆ the duration of simulation time is limited to 1 hour;
- ◆ the maximum height of the flame is 13 meters;
- ◆ the maximum combustion rate of the chemical substance is 196 kg/min.;
- ◆ the total amount of burned substance is 11,618 kg.

Note: the chemical is released as a liquid and formed a burning spill with a diameter of 7.3 meters.

The program calculates the danger zones for this scenario according to the following principle.

Heat flux density (level of concern, LOC) [9] is the limit level of thermal radiation; usually the level above which danger may exist.

When the fire scenario is triggered, *ALOHA* suggests typical LOC values (kW/m^2):

- 1) red: $10 \text{ kW}/\text{m}^2$ (potentially fatal after 60 s exposure);
- 2) orange: $5 \text{ kW}/\text{m}^2$ (second degree burns after 60 s exposure);
- 3) yellow: $2 \text{ kW}/\text{m}^2$ (pain after 60 s exposure).

The effects of thermal radiation experienced by people depend on the duration of exposure to a certain thermal radiation. Longer exposure, even at a low thermal radiation, can lead to serious physiological consequences. The danger zones displayed by *ALOHA* are the levels of thermal radiation; the accompanying text indicates the consequences for people who are exposed to these levels of thermal radiation but able to seek shelter within one minute. The red, orange, and yellow danger zones indicate the areas where thermal radiation is predicted to exceed the corresponding LOC in a certain time after the release begins.

The danger zones for this scenario are listed in Table 5.

The results of the danger zone calculations are shown in Figs. 3 and 4.

Scenario 3: Boiling liquid vapor explosion:

- ◆ the data on the location, the meteorological conditions, the properties of the chemical and the storage tank are described above;

- ◆ the tank is 80% full;
- ◆ the share of the chemical mass that burns in the fireball is 50%;
- ◆ the fireball diameter is 418 m;
- ◆ the burning time is 22 s;
- ◆ the diameter of the fiery pool is 200 m;
- ◆ the burning time is 2 min;
- ◆ the flame height is 164 m.

The danger zones are calculated in the same way as for Scenario 2.

The danger zones are listed in Table 6.

The results of danger zone calculations are shown in Figs. 5 and 6.

Modeling is considered one of the most important stages of risk management [10]. With the help of specialized software *ALOHA*, the consequences of possible accidents and adverse events

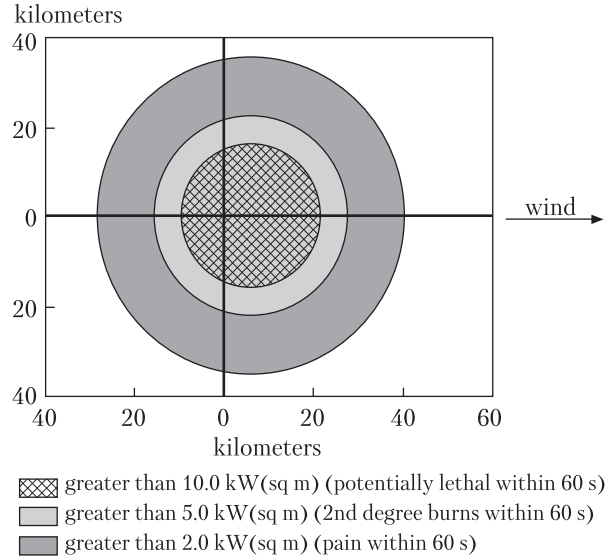


Fig. 3. Danger Zones for Scenario 2 in ALOHA software

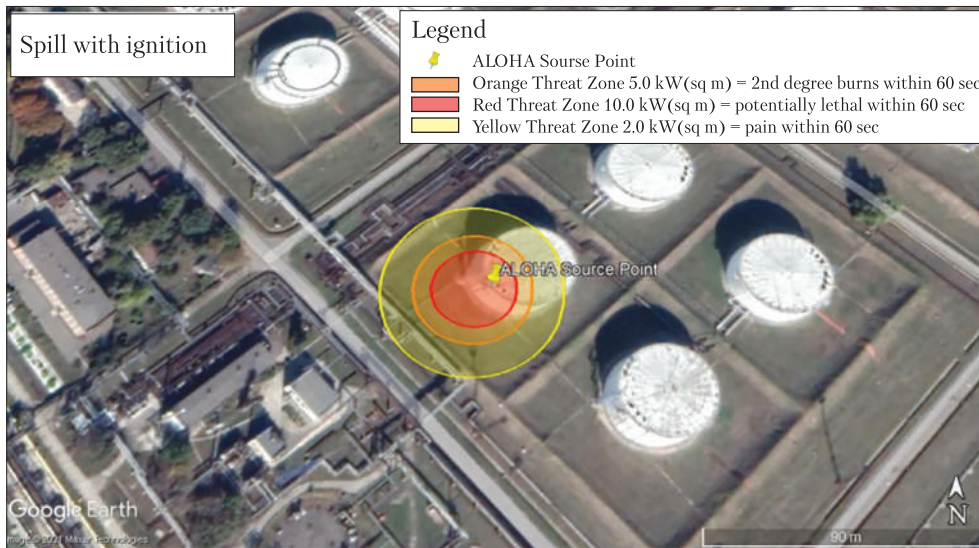


Fig. 4. Danger zones for Scenario 2 imported to Google Earth

Table 5. Danger Zones for Scenario 2

Number	Color	Title	Thermal radiation power	Length, m	Notes
1	Red	LOC-3	$10.0 \text{ kW/m}^2 \geq$	22	Potentially causes death after 60 s exposure
2	Orange	LOC-2	$5.0 \text{ kW/m}^2 \geq$	28	2 nd degree burns after 60 s exposure
3	Yellow	LOC-1	$2.0 \text{ kW/m}^2 \geq$	41	Pain after 60 s exposure

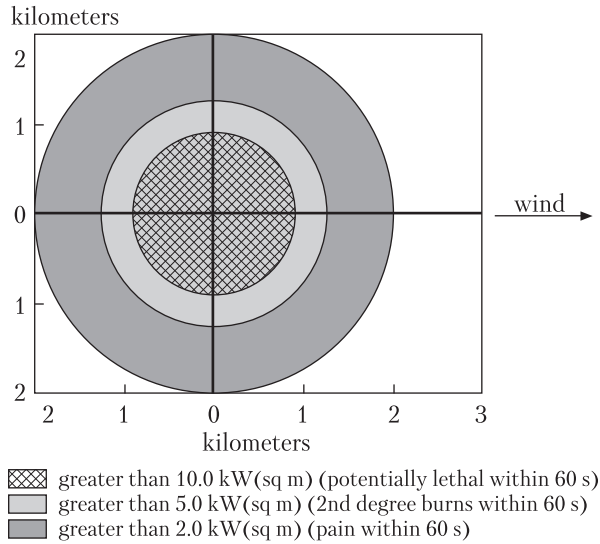


Fig. 5. Danger zones for Scenario 3 in ALOHA software

for the case of only one benzene storage tank have been simulated. Given that the oil storage is located in the suburbs, in close proximity to the residential areas of the amalgamated territorial communities, for detailed emergency response planning it is necessary to estimate the conditional probability of human injury at different intensities of thermal radiation for the scenario with the most catastrophic consequences, namely the explosion of benzene vapors.

The literary sources give various calculation formulas for determining the conditional probability of human injury by the thermal radiation of a fireball [11]. In practice, for analyzing the damage effect (death and/or harm to health) for a human being, probabilities are usually described by the normal distribution law, the argument of which is the probit function Pr.

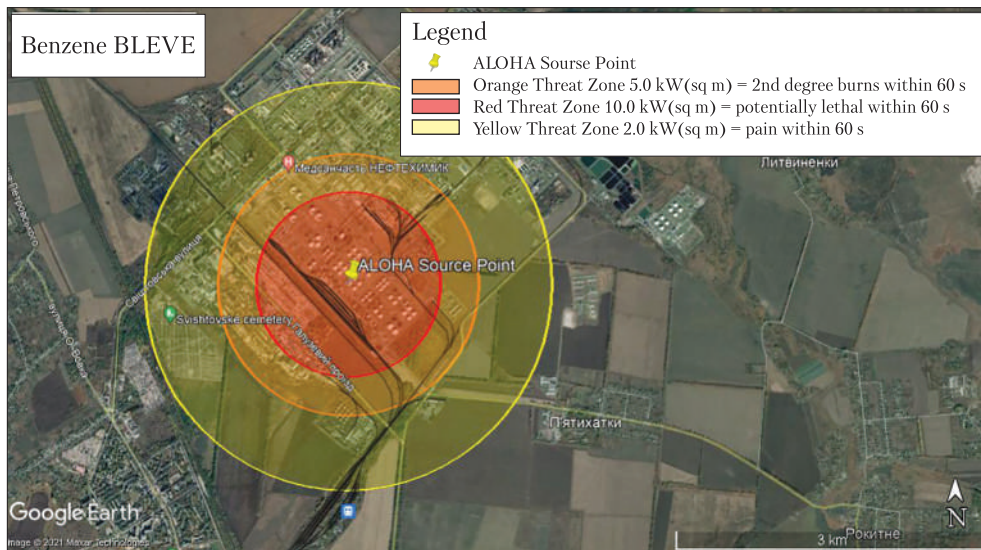


Fig. 6. Danger zones for Scenario 3 imported to Google Earth

Table 6. Danger Zones for Scenario 3

Number	Color	Title	Thermal radiation intensity	Length	Notes
1	Red	LOC-3	$10,0 \text{ kW/m}^2 \geq$	890 m	Potentially causes death after 60 s exposure
2	Orange	LOC-2	$5,0 \text{ kW/m}^2 \geq$	1,3 km	2 nd degree burns after 60 s exposure
3	Yellow	LOC-1	$2,0 \text{ kW/m}^2 \geq$	2,0 km	Pain after 60 s exposure

$$P_{\text{yпax}} = f\left(P_r = -\frac{1}{\sqrt{2\pi}}\right) \int_{-\infty}^{P_r - 5} \exp\left(-\frac{t^2}{2}\right) dt.$$

To assess the risks, let us consider the conditional probabilities of exceeding the pain threshold, 1st, 2nd, and 3rd degree burns for the benzene vapor explosion scenario (Figs. 5, 6).

The analysis of the calculation of probit functions has proven the need to use the formulas with the maximum possible damage [11]:

1. $P_r = -8.93 + 2.99 \cdot \ln(t \cdot q^{4/3})$ – pain threshold;
2. $P_r = -9.34 + 2.99 \cdot \ln(t \cdot q^{4/3})$ – 1st degree burn;
3. $P_r = -11.58 + 2.99 \cdot \ln(t \cdot q^{4/3})$ – 2nd degree burn;
4. $P_r = -12.6 + 2.99 \cdot \ln(t \cdot q^{4/3})$ – 3rd degree burn;

where t is the time of existence of the fireball, s, and q is the intensity of heat radiation of the fireball, kW/m².

The conditional probabilities have been calculated for each danger zone with minimum thermal radiation: 10 kW/m² for the red zone; 5 kW/m² for the orange zone; and 2 kW/m² for the yellow zone. The calculations have been made for different time from the explosion to the extinction of the fireball (1, 5, 10, 15, 20, and 22 s). The probit function has been calculated with a theoretical fireball burn time of 30 s.

The obtained calculation results are given in Tables 7–10 and shown with the help of diagrams in Figs. 7–10.

The analysis of Fig. 7 has proven that exceeding the pain threshold in the red zone is quite sharp: as quick as in 15 s after the explosion, with a 100% probability, the injured person feels an acute pain. In the orange zone, the probability grows less sharply, but in 20 s of exposure, the injured person feels an acute pain. In the yellow zone, the probability of exceeding the pain threshold is 10% at 30 s. Therefore, we may assume that the middle and the outer border of the yellow zone is safe for humans, where the intensity of thermal radiation is less than 4 kW/m² [12].

The analysis of Fig. 8 has shown that the probability of 1st degree burns grows sharply for the red and orange zones. There is a 100% burn probability for the red zone, at 15 s. For the orange

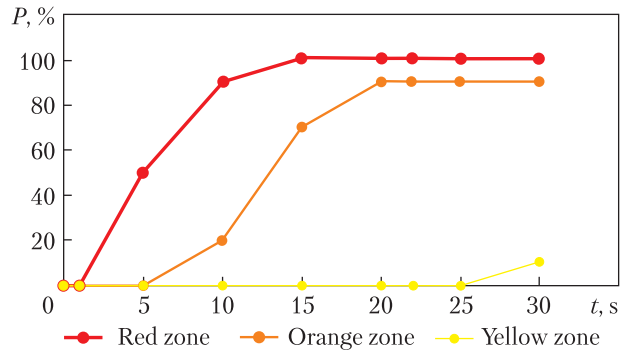


Fig. 7. Conditional probability of exceeding the pain threshold

Table 7. Conditional Probability of Exceeding the Pain Threshold

Time (t), s	Probability (P, %) red zone	Probability (P, %) orange zone	Probability (P, %) yellow zone
1	0	0	0
5	50	0	0
10	90	20	0
15	100	70	0
20	100	90	0
22	100	90	0
25	100	90	0
30	100	90	10

Table 8. Conditional Probability of 1st Degree Burn

Time (t), s	Probability (P, %) red zone	Probability (P, %) orange zone	Probability (P, %) yellow zone
1	0	0	0
5	30	0	0
10	90	10	0
15	99	50	0
20	100	80	0
22	100	90	0
25	100	90	0
30	100	90	0

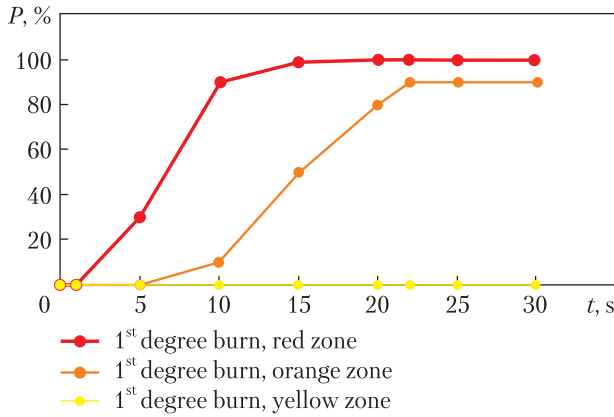


Fig. 8. Conditional probability of 1st degree burn

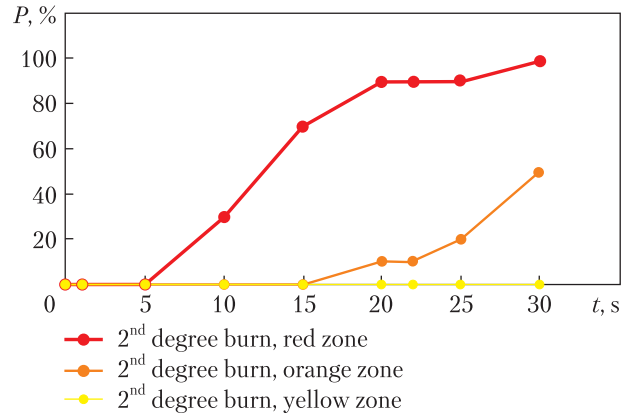


Fig. 9. Conditional probability of 2nd degree burn

Table 9. Conditional Probability of 2nd Degree Burn

Time (t), s	Probability (P, %) red zone	Probability (P, %) orange zone	Probability (P, %) yellow zone
1	0	0	0
5	0	0	0
10	30	0	0
15	70	0	0
20	90	10	0
22	90	10	0
25	90	20	0
30	99	50	0

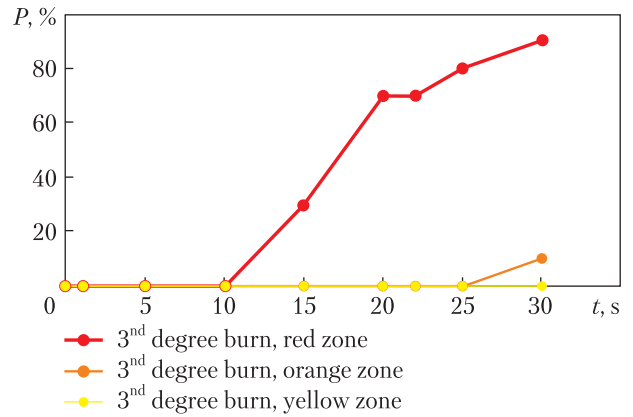


Fig. 10. Conditional probability of 3rd degree burn

Table 10. Conditional Probability of 3rd Degree Burn

Time (t), s	Probability (P, %) red zone	Probability (P, %) orange zone	Probability (P, %) yellow zone
1	2	3	4
0	0	0	0
1	0	0	0
5	0	0	0
10	0	0	0
15	30	0	0
20	70	0	0
22	70	0	0
25	80	0	0
30	90	10	0

zone, the maximum probability reaches 90%, at 22 s. The probability for the yellow zone is 0%.

The increase in the probability of 2nd degree burn (Fig. 9) has a sharp jump-like character: at 10 s, the probability is 30 %, and as quick as at 20 s, it reaches 90%, after which the growth gets stabilized, and from 25 s of burning to 30 s, the probability is 99%.

In the orange zone, the probability moderately grows. Until the end of the burning (22 s), the probability of burn is 10%, but from 22 s to 30 s, it quickly increases to 50%.

The analysis of Fig. 10 has shown that the probability of 3rd degree burn for a person in the red zone increases sharply, from 10 to 20 s. In this period, it is equal to 70% and lasts until the

end of the burning. Also, there is observed a rapid growth in the probability up to 90% during the burning up to 30 s.

For the orange zone, the probability of getting burned is 0%, but in the case of longer burning, the probability increases to 10%, at 30 s. For the yellow zone, the probability of burn is 0%.

CONCLUSION

1. The software product *ALOHA* is a universal means of simulation for planning and responding to emergency situations (ES) and assessing their consequences, which make it possible to graphically present data on the actual or potential release of chemical substances. *ALOHA* in combination with GIS (*MARPLOT*, *Arc Map*, *Google Earth*, and *Google Maps*) makes it possible to visually demonstrate on the map the possible consequences of disasters and to identify danger zones.

2. In order to rationalize the system of medical and evacuation support, the results of calculations in the form of cartographic materials have been recommended to be used for training and education of students on civil security, as well as employees of the State Emergency Service and others.

3. The obtained results of modeling the potential risk zones with the use of *ALOHA* software have been recommended to be used for moder-

nizing the existing system of continuous observations, laboratory and other control to assess the status of protection of the population and territories, as well as high-risk objects.

4. On the basis of the obtained cartographic materials, given the maximum possible damage to a person by the thermal radiation of a fireball for the scenario of an explosion of benzene vapors, with the use of probit functions, the dependencies of the conditional probabilities of exceeding the pain threshold and 1st, 2nd, and 3rd degree burns have been determined and constructed, which allows improving and balancing the system of management decisions regarding the response to emergency situations.

5. The following recommendations have been given to the enterprise for controlling the zones, reducing potential risk, and preventing the spread of a toxic spill, fire or explosion:

- ◆ to use danger signs in the places of increased risk;
- ◆ to use video surveillance of critical equipment nodes, especially when carrying out repair works;
- ◆ to install heat, smoke, and fire sensors, as well as air quality sensors at tanks, unload stations, etc.; and
- ◆ to conduct regular inspections of the above-mentioned systems and nodes.

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МОДЕЛЮВАННЯ ТА ОЦІНКА РИЗИКІВ ТЕХНОГЕННИХ КАТАСТРОФ НА ПІДПРИЄМСТВАХ НАФТОХІМІЧНИХ КОМПЛЕКСІВ

Вступ. Для техногенної безпеки останнім часом все частіше використовують технології моделювання надзвичайних ситуацій (НС). Разом з цим для розширення (уточнення) отриманих результатів додатково розраховують ризики.

Проблематика. Питання безпеки у процесі виробництва та зберігання нафтопродуктів є дуже важливим, оскільки існує значний ризик токсичних викидів, пожеж, вибухів, які можуть призвести до катастрофічних ситуацій, зокрема й з травмуванням і загибеллю людей.

Мета. Моделювання можливих сценаріїв та оцінка ризиків розвитку надзвичайних ситуацій на об'єктах виготовлення і зберігання нафтопродуктів.

Матеріали й методи. На основі аналізу літературних джерел зазначеної тематики застосовано емпіричний науковий метод, що полягає у математичних розрахунках, комп'ютерних симуляціях за допомогою програмного забезпечення.

Результати. Проведено три комп'ютерні симуляції надзвичайних ситуацій на нафтопереробному заводі, які можуть виникнути за різних обставин. Отримано можливі наслідки НС та розраховано ймовірні ризики ураження людей тепловим випромінюванням та з використанням пробіт-функцій визначено залежності умовної ймовірності перетину больового порогу опіків першого, другого та третього ступенів, що дозволяє удосконалити та збалансувати систему прийняття управлінських рішень щодо здійснення заходів реагування на надзвичайні ситуації. Наведено рекомендації для контролю зон і зниження потенційного ризику надзвичайних ситуацій на нафтохімічних підприємствах (заводах).

Висновки. Отримані результати можна використовувати при модернізації існуючої системи безперервних спостережень, лабораторного та іншого контролю для оцінки стану захисту населення і територій та об'єктів підвищеної небезпеки, для раціоналізації системи лікувально-евакуаційного забезпечення, а отримані картографічні матеріали — для навчання працівників ДСНС.

Ключові слова: надзвичайна ситуація, математичне моделювання, умовна ймовірність ураження людини, пробіт-функція.