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Emission rates, ALOHA simulation and Box-Behnken design of accidental releases in butyl acrylate tank - case study

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Abstract
The leakage of hazardous compounds in chemical industries has always been one of the factors threatening workers, plants, and the environment. Among them, butyl acrylate is one of the most harmful materials that are widely used in chemical plants. In the present study, a butyl acrylate tank located in a real tank farm in Kocaeli-Turkey was analyzed for the examination of emissions and trinitrotoluene (TNT) equivalent explosion model of the vapor cloud. Areal Locations of Hazardous Atmospheres (ALOHA) program was used to define threat zones of butyl acrylate leakage based on different scenarios, such as a leakage from the tank without fire, burning as a jet fire, and also burning as a fireball during Boiling Liquid Expanding Vapor Explosion (BLEVE). In addition, since the most important parameters that enhance the effects of explosion and the spread of volatile organic compounds (VOCs) are wind speed, filling ratio of the tanks, and temperature, the interaction of these parameters on the threat zones and the highest threat zones of explosions were investigated using the Box-Behnken experimental design and one-way Analysis of Variance (ANOVA), respectively. As butyl acrylate, one of the most dangerous chemicals for industrial facilities, and its explosion effects have not been studied so far, it can be safely mentioned that this paper representing the first study in the literature is highly original and novel.

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1. Introduction

Volatile organic compounds (VOCs) are used as solvents in many industrial processes, especially in printing, dyeing, and surface finishing in the world as well as in Turkey (Xie et al., 2021). Air pollution, explosions, injuries, and deaths can be observed during the storage and processing of volatile chemicals. VOCs are the most common chemical pollutants in the air. They are aliphatic or aromatic hydrocarbons with a boiling point of up to 260 ºC. Among them, butyl acrylate (butyl ester of acrylic acid) belongs to the group of acrylic esters. Butyl acrylate is an inflammable, light-sensitive, and colorless liquid and used in paints, dyes, coatings, adhesives, fuels, resins, textiles, and plastics. It is listed in the

Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation and produced or imported between 100,000 and 1,000,000 tons in the European Economic Area. For the storage of butyl acrylate in a chemical plant, a petrochemical storage facility is essential. Storage tanks should be in a good condition, i.e. located in a cool, dry, and well-ventilated area. While dispensing butyl acrylate into bulk tanks or tank trucks, the potential emissions and the explosion of the storage tanks can lead to serious problems. In

Turkey, in order to control emissions, the storage tanks is operated under some strict regulations.

The annual average emissions of VOCs are determined using the regulatory emission model of United States Environmental Protection Agency (US EPA) (Dertli and Saloglu, 2021). With the TANKS Emissions Estimation Software, Version 4.09d[1] (TANKS 4.09d), breathing and filling/discharge losses, and total emissions can be investigated for organic liquids. Overall, the TANKS results show that the model statistically performed well with a 95% confidence interval (Kocak, 2022).

In addition to atmospheric emissions of VOCs, explosions may occur in the storage tanks and the threat zones arising from these explosions are also crucial. The programs such as EXplosion SIMulator (EXSIM), FLame ACceleration Simulator (FLACS), Computational Fluid Dynamics (CFD), and Areal Locations of Hazardous Atmospheres (ALOHA) can detect safety zones using an explosion simulation. Among them, the ALOHA can model the spread of chemicals, and threat zones from chemical release, thermal radiation, and vapor cloud explosions. It is also used to estimate the maximum distance of threat zones in case of the release of toxic materials. In addition, the ALOHA calculates the extent of hazard at the time of the release of toxic and flammable substances and the areas of impact of flammable substances at the time of combustion/explosion. The program creates real-time models using the characteristics of the chemical substances released (Terzioglu and Iskender, 2021).

Inorganic and/or organic compounds, such as solvent vapors, corrosive acids and bases, can cause both air pollution and explosions under certain conditions. As acrylates are one of the most dangerous chemical compounds for both emissions and explosions, butyl acrylate was selected as a model compound in this research and evaluated for the emissions and different explosion scenarios. Therefore, the main subject of the following paper is following the impact of an accidental release of butyl acrylate in a real tank farm in Kocaeli-Turkey. Firstly, breathing and filling/discharge losses, and total emissions were examined. Secondly, the trinitrotoluene (TNT) equivalent explosion model was applied for the vapor cloud explosion (VCE). In addition, the ALOHA program was used for the modelling of the explosion according to different scenarios, such as leakage from the tank without fire, burning as a jet fire, and also burning as a fireball during BLEVE. Then, the Box-Behnken experimental design was used to evaluate the interactions of parameters such as wind speed, filling ratio of the tank, and temperature. One-way Analysis of Variance (ANOVA) was used for defining the highest threat zones of butyl acrylate.

It appears that the following study has new approaches and methods that will be a guide for both literature and industrial plants based on the research of atmospheric emissions, threat zones, and risk determination.

[1]Developed by the US EPA

2. Materials and methods

2.1. Location and properties of butyl acrylate tank

In order to investigate the effect of accidental release of butyl acrylate, the study was conducted on a tank located in a real tank farm and transport facility in Kocaeli Industrial Zone (company name not indicated). Kocaeli is in the Central European Time zone (GMT +3) and the average annual temperature reaches 19.7°C.

2.2. Emissions of butyl acrylate and application of TANKS 4.09d

TANKS is a Windows-based software to calculate VOCs and hazardous air pollutant (HAP) emissions from fixed and floating-roof storage tanks. TANKS is designed for use by consultants, experts, and scientists who need to calculate air pollutant emissions from organic liquid storage tanks. The program uses chemical, meteorological, and roof fitting data to generate emissions calculations for several types of storage tanks. The program employs a chemical database of over 100 organic liquids and different meteorological factors (US EPA). As with all simulation programs, TANKS 4.09d is based on some assumptions and limitations, such as a series of input data, mass balances, thermodynamic equilibria hypothesis, and semi-empirical correlations. Like any mathematical model based on physical considerations, the program can be affected by the uncertainty of the required input in addition to the inherent uncertainty of some assumptions and correlations. For this reason, the correct and meaningful data input significantly alters the results to be obtained.

In this study, the breathing and filling/discharge losses and total emissions of butyl acrylate were calculated using TANKS 4.09d (Table 1). This program can be downloaded free of charge at the website of https://www3.epa.gov/ttnchie1/software/tanks/.

Table 1. Properties of butyl acrylate storage tank

Identification	
City	Kocaeli
State	Turkey
Company	Case Study 1
Material of Storage Tank	Steel
Type of Storage Tank	Vertical Fixed Roof Tank
Dimensions	
Height (ft)	39.30
Diameter (ft)	24.93
Average Liquid Height (ft)	19.65
Volume (gallons)	71,349.71
Turnovers	12.00
Net Throughput (gal/yr)	856,196.48
Is Tank Heated (y/n)	No
Paint Characteristics	
Shell Color/Shade	White/White
Shell Condition	Good

Roof Color/Shade	White/White
Roof Condition	Good
Roof Characteristics	
Type	Cone
Height (ft)	0.00
Slope (ft/ft) (Cone Roof)	0.06
Breather Vent Settings	
Vacuum Settings (psig)	-0.03
Pressure Settings (psig)	0.03
Temperature (ºC) (avg.)	15.72

2.3. TNT equivalent explosion model for VCE of butyl acrylate

There are several simplified models such as the TNT equivalent method, multi-energy and the Baker- Strehlow-Tang (BST) models to simulate the effect of VCEs. In this study, TNT equivalent explosion model was chosen because it is simple and tends to be better for estimating far-field damage (Ding et al. 2022).

The TNT equivalent of a vapor cloud is defined using the W_{TNT} equation below:

$$W_{TNT} = \frac{aWQ}{Q_{TNT}} \quad (1)$$

where *a* is the efficiency factor of the VCE (equal to 0.04); W is the mass of butyl acrylate in vapor (kg); Q is the heat of the combustible of butyl acrylate vapor (kJ/g;) and Q_{TNT} is the explosion heat of the TNT (kJ/g; equal to 4,000 kJ/g).

2.3.1. Explosion damage radius for VCE of butyl acrylate

The explosion damage radius can be determined using Eq. (2).

$$R_1=0.396W_{TNT}^{1/3}\exp(3.503-0.724\ln\Delta P+0.039(\ln\Delta P)^2) \quad (2)$$

where R_1 is the explosion damage radius (m) and ΔP is the overpressure (kPa) (Zhang et al. 2019). The effects of overpressure are presented in Table 3.

2.3.2. Death and minor injury radius for VCE of butyl acrylate

The death radius (R_2) in case of an explosion can be calculated using Eq. (3).

$$R_2 = 13.6(W_{TNT} /1,000)^{0.37} \quad (3)$$

Also, the minor injury radius (R_3) can be calculated using Eq. (4) and (5).

$$\Delta P = 0.137[R_3/(E/p_0)^\wedge(1/3)]^{-3} + 0.119\ [R_3/(E/p_0)^\wedge(1/3)]^{-2} + 0.269\ [R_3/(E/p_0)^\wedge(1/3)]^{-1}\ 0.019 \quad (4)$$

$$E = W_{TNT}\, Q_{TNT} \quad (5)$$

where p_0 is atmospheric pressure (101 kPa) (Zhang et al. 2019).

2.4. Modeling butyl acrylate explosion scenarios using ALOHA

ALOHA is a hazard modeling program for the CAMEO® software suite that is used widely to plan for and respond to chemical emergencies. ALOHA allows entering data about a real or potential chemical release in order to generate threat zones for various types of hazards. There are some assumptions in ALOHA program. The program assumes that the hazardous chemicals are released into the atmosphere, release occurs in a mixture, and concentration of the chemicals shows a bell-shaped curve throughout the vapor cloud. The concentration estimates can be less accurate at very low wind speeds and very stable atmospheric conditions. Another assumption of ALOHA is that wind speed and direction are constant throughout the area downwind of a chemical release. In addition, as ALOHA uses averages for concentration, the concentration patchiness can occur in dispersing cloud near the source. "Gaussian model" provides reasonable concentration estimates in most cases in ALOHA. The program also assumes that the ground is flat, resulting in different implications depending on the release scenario. ALOHA is designed to model the release and dispersion of pure chemicals and a few selected solutions. Byproducts of combustion or chemical reactions as well as particulates cannot be simulated using ALOHA. The program assumes that a dispersing cloud does not react with the gases, such as oxygen and water vapor.

In this research, ALOHA 5.4.7 was used. It can be downloaded free of charge at the website of https://www.epa.gov/cameo/aloha-software (US EPA). Based on the parameters such as type of chemical, tank type, filling ratio of the tank, wind speed and direction, temperature, and humidity etc., the program shows effects of an explosion with different colors. These graphs and colors define the threat zones of an explosion (Iskender, 2021). There are no significant differences between the threat zones obtained with different software programs. ALOHA detects threat zones up to 10 km away with a 95% confidence interval. Therefore, it is recommended to use the ALOHA software primarily and use other software in higher impact distance applications.

In the present study, butyl acrylate explosion and gas leakage in a cylindrical storage tank were examined using the ALOHA. To investigate the explosion effects, possible scenarios were considered for a butyl acrylate tank (540 m^3 in the form of a cylinder; D: 7.6 m and H: 11.91 m) on a day at 15 ºC and 50% humidity. In the first scenario, butyl acrylate escaped directly into the atmosphere and formed VCE, flammable area, and overpressure. In the second scenario, it was considered that butyl acrylate leaked from a hole in the tank without burning. In the third scenario, it was simulated that butyl acrylate storage tank exploded, and gas burned as a jet fire, BLEVE occurred, and butyl acrylate burned in a fireball.

2.5. Modeling butyl acrylate explosion using Box-Behnken experimental design (BBD)

BBD is defined as a collection of statistical tools for determination of a relationship between an objective function and a set of independent variables. BBD mainly aims to optimize the objective function that is influenced by various independent variables. An important assumption is that the independent variables are controllable by experiment and trials with negligible errors.

In the present study, BBD was used to investigate the effect of variables on the threat zones of the explosion and the relationship between these variables using Design Expert version 11.0.5.0 software (Jawad et al., 2020). The trial version of the program can be downloaded from free at the website of https://www.statease.com/software/design-expert/. Licensed MINITAB program can also be accessed from Istanbul Technical University.

Temperature and filling ratio of the storage tanks, which are effective parameters for breathing and filling/discharge losses and total emissions, can cause an explosion or fire, or accelerate and/or increase the effects of an explosion or fire. Wind speed is also one of the parameters enhancing the effect of an explosion. For this reason, BBD has been examined over these three effective independent variables. A confidence interval of 95% was employed to determine the independent variables considered significant. The interactions of these independent variables with each other are also predicted to be effective on an explosion. As literature shows that the effects of these independent variables on an explosion have not been studied so far, they were examined with BBD and one-way ANOVA in our research.

The experimental design matrix for the independent variables and responses is listed in Table 5. The experimental design included three independent variables with three levels and five central points for a total of 17 runs. The independent variables consisted of the temperature (A) (0-30°C), wind speed (B) (1-7 m/s), and filling ratio of the tank (C) (20-80%). The central point conditions of the process variables were selected to be 15 °C for temperature (A), 4 m/s for wind speed (B), and 50% for filling ratio of the tank (C) (Ozcan et al. 2022).

Adjusted-R^2, predicted-R^2, probability value at 95% confidence interval, coefficient of variation, and one-way ANOVA were used to examine the results (Aliemeke and Oladeine, 2020, Ozcan et al. 2022).

3. Results and discussion

3.1. Emissions of butyl acrylate

According to General Directorate of Meteorology data, average monthly temperatures were 9.6 °C, 10.5 °C, 13.2 °C, 18.5 °C, 23.2 °C, 27.4 °C, 29.4 °C, 26 °C, 20.9 °C, 16.4 °C, 14.5 ºC, and 11.7 °C in Kocaeli. The average annual temperature was 19.7 °C, which was used in TANKS 4.09d.

Table 2 shows the breathing and filling/discharge losses, and total emissions from butyl acrylate tank. The emissions of butyl acrylate were 30.21 kg/year and 27.79 kg/year during filling/discharge and breathing, respectively. The total emission was also calculated as 58 kg/year using TANKS 4.09d.

Table 2. Emission rates of butyl acrylate in Kocaeli

Emissions	kg/year
Breathing loss	27.79
Filling/discharge loss	30.21
Total emissions	58.00

These emission values change with some factors, such as amount of chemical in the tank, filling ratio of the tank, volatility of the chemical, weather conditions, wind speed and direction, and ambient temperature. It should be noted that temperature is one of the important factors increasing emissions as shown in our previous study (Dertli and Saloglu, 2021). These emission values were obtained under the conditions showed in Table 1. Higher butyl acrylate content (>filling ratio of the tank: 50%), larger tank volume (>71,349.71 gallons), and higher turnover values (>12) can increase emissions.

3.2. TNT equivalent explosion model for VCE of butyl acrylate

For an explosion of butyl acrylate tank, the consequences of the accident and the calculations for the explosion damage were as follows:

3.2.1 Explosion damage radius for VCE of butyl acrylate

Half of the tank was filled with butyl acrylate, and the amount of butyl acrylate vapor in the tank was calculated accordingly. Eq. (1) yielded the W_{TNT} of 77 kg.

Overpressure refers to the sudden onset of a pressure wave after an explosion. This pressure wave results from the energy released in the initial explosion, while the next pressure waves are instantaneous. Although a pressure wave may sound less dangerous than a fire or a toxic cloud, it can be damaging as much as them. The pressure wave radiates outward and generates hazardous fragments. These waves can damage buildings and injure people. The sudden change in pressure can also affect pressure-sensitive organs, e.g. ears and lungs (Zhang et al. 2019).

The radius values of the explosion damage of butyl acrylate calculated using Eq. (2) are listed in Table 3. It can be seen that the fatal and serious injury radius values were 13.44 and 23.86 m, respectively. The minor explosion damage radius resulting in the rupture of the eardrum of a person was 102.55 m.

Table 3. Explosion damage radius values of butyl acrylate

Overpressure (kPa)	Explosion effect	R_1 (m)
1.04	Glass window damage	5,067.17
2.07	10% of the glass is broken	1,674.74
3.45	Windows are damaged and the building structure is less damaged	783.57
6.90	Parts of the structure are damaged	301.78
13.80	Parts of walls and roofs collapsed	126.92
16.56	Eardrum ruptures	102.55
17.25	Critical illnesses	97.86
20.70	Fracture of steel structure buildings	79.66
34.50	Fracture of wood structure buildings	46.24
69.00	Almost all buildings collapsed, and the lungs of personnel bleed	23.86
138.00	Direct shockwaves are 100% fatal	13.44

3.2.2 Death and minor injury radius for VCE of butyl acrylate

In this study, the death radius (R_2) was calculated as 5.26 m using Eq. (3).

For any given radius, corresponding overpressure value is obtained from Eq. (4). While the minor injury radius was higher at lower pressures, it decreases sharply at higher pressures, which can be explained by the destructive effect of pressure on the environment (Table 4).

Table 4. Minor injury radius values for VCE of butyl acrylate

Overpressure (kPa)	R_3 (m)
1.04	10.07
2.07	7.34
3.45	5.91
4.83	5.16
6.90	4.48
13.80	3.44
16.56	3.22
17.25	3.17
20.70	2.96
34.50	2.46
69.00	1.93
138.00	1.51

3.3. Modeling butyl acrylate explosion scenarios using ALOHA

3.3.1 The first scenario: Butyl acrylate escaped directly into the atmosphere from the tank

VCEs can result in great impact on the surroundings due to pressure waves. The area of toxic threat zone, flammable area of the vapor cloud, and overpressure (blast force) from VCE can be simulated using ALOHA (Zhang et al. 2019).

The results of modelling of threat zones around the butyl acrylate storage tank showed the toxic threat zones with a maximum distance of 9.6 km (Fig. 1(a)). When toxic vapor of butyl acrylate was simulated, the red, orange, and yellow threat zones occurred at 838 m, 1.9 km, and 9 km, respectively. Based on the definitions of Acute Exposure Guideline Levels (AEGL) (Kim et al. 2021), the risk in the red, orange and yellow threat zones are described as exposure of 480 ppm, 130 ppm, and 8.3 ppm for 1 hour, respectively. These threat zones can cause serious health effects and also death, long-lasting health effects, and irritation effects.

Fig. 1(b) shows the flammable area of butyl acrylate vapor cloud. The red and yellow zones were determined as 178 and 491 m, respectively. The red zone stands for fire risk and everything closer than 178 m from the tank may burn (Hoscan and Cetinyokus, 2021). At a distance of 491 m from the tank, the concentration equals 10% of the lower explosive limit of butyl acrylate, while the concentration of butyl acrylate was 1,200 ppm.

Fig. 1(c) presents the results of the blast area of a VCE. The red zone in the figure indicates an 8.0 psi (55.15 kPa) overpressure which was never exceeded; the orange zone was as large as 141 m where the overpressure was 3.5 psi (24.13 kPa) (Abbaslou and Karimi, 2019). The yellow zone was as large as 210 m where the overpressure was 1.0 psi (6.89 kPa). The risk of orange zone comes from triggering any fire or explosion. In addition, the effects of 3.5 psi (24.13 kPa) overpressure results in buildings' collapse due to self-framing steel buildings and snapping failure of the wooden utility tanks. The yellow zone presents less dangerous effects to buildings at 1.0 psi (6.89 kPa) overpressure, with shattering glass windows and occasional damage to window frames (Terzioglu and Iskender, 2021).

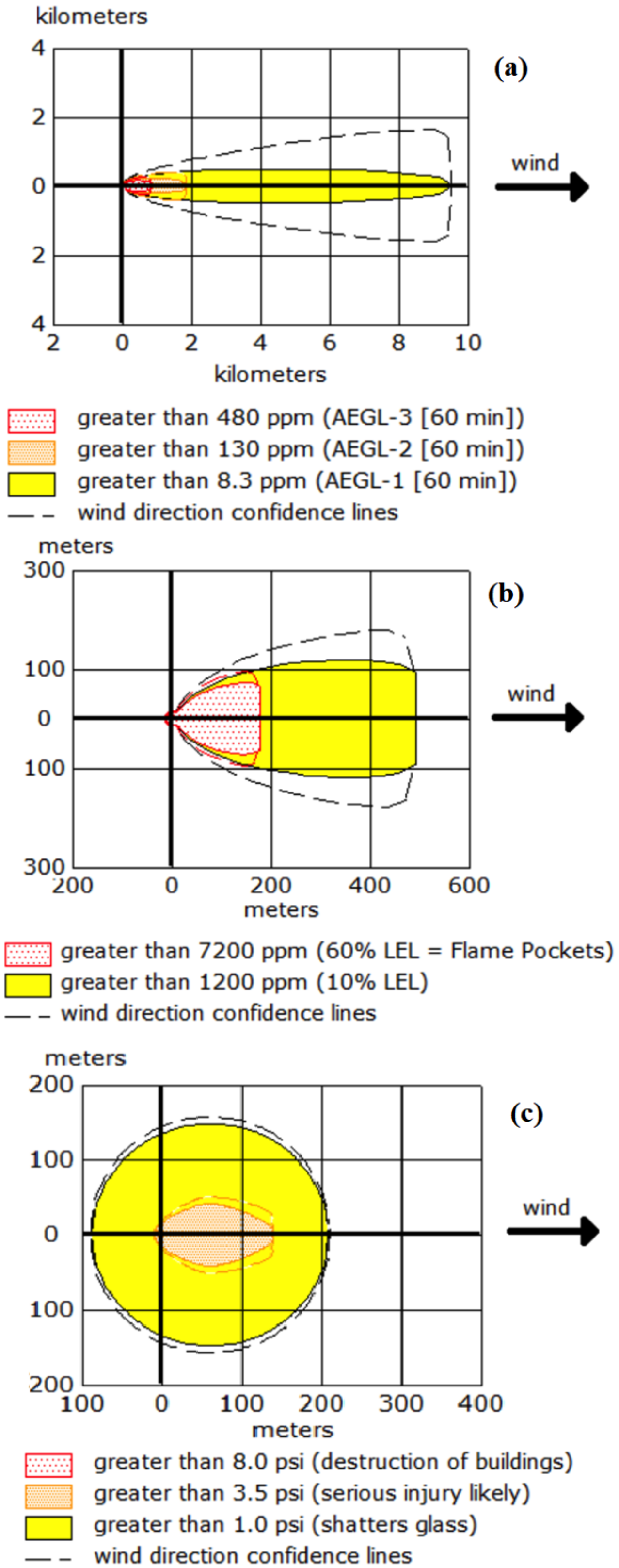

Fig. 1. Graphs for modeling of butyl acrylate escaped directly - (a) VCE, (b) flammable area, and (c) overpressure of vapor cloud

3.3.2 2nd scenario: Butyl acrylate escaped from a leak in the tank (not burning)

For the second scenario, butyl acrylate escaped from a leak in the tank, without burning. The characteristics of the source of butyl acrylate were as follows: it was in a 540 m^3 tank with a 5.08 m (2 inch) diameter (0.1 m from the tank bottom). The simulation results were obtained according to the total amount of butyl acrylate of 270 m^3 in the tank and the released amount of 289 kg. Butyl acrylate threshold values of 480 ppm for the red threat zone, 130 ppm for the orange threat zone, and 8.3 ppm for the yellow threat zone were defined. Additionally, red, orange, and yellow zones were calculated as 20, 26, and 211 m (Fig. 2). Because the effects of near-field roughness make scatter prediction for short distances less reliable, the orange and red threat zones were not plotted.

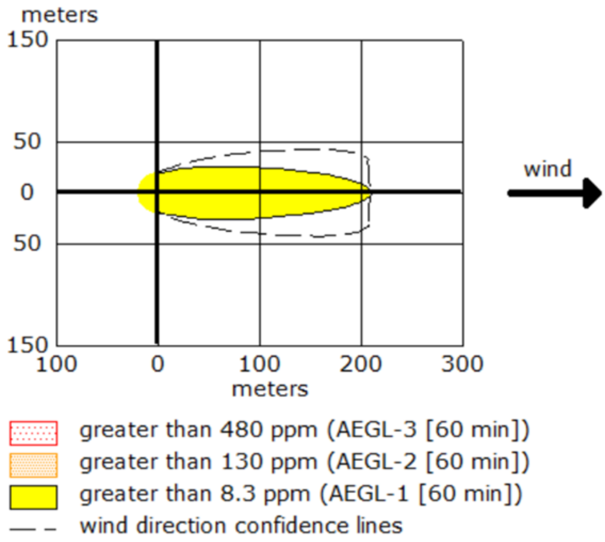

Fig. 2. Graph for modelling of butyl acrylate escaped from a leak in the tank (not burning)

The flammable area of vapor cloud of butyl acrylate was also investigated during the escape of butyl acrylate from a leak of the tank, without burning. Both red and yellow zones were calculated as 20 m. At a distance of 20 m from the tank, the concentration equals 10% of the lower explosive limit (10% LEL) and the concentration was 1,200 ppm (Beheshti et al. 2018). In addition, the overpressure area of a vapor cloud explosion was examined. However, no part of the cloud is above the LEL at any time. Therefore, an explosion did not occur.

3.3.3 3rd Scenario: Butyl acrylate storage tank exploded, and gas burned as a jet fire and BLEVE occurred

Fig. 3(a) shows the simulation results for the burning of butyl acrylate as a jet fire. The red zone was modelled to be 14 m wherein thermal radiation is 10.0 kW/m^2 and potentially lethal in 60 s. The orange zone was calculated as 18 m, with a thermal radiation of 5.0 kW/m^2 which will lead to seconddegree burns. The amount of radiation was 2 kW/m^2 at a distance of 25 m from the tank and the radiation can cause pain (Lowesmith and Hankinson, 2012).

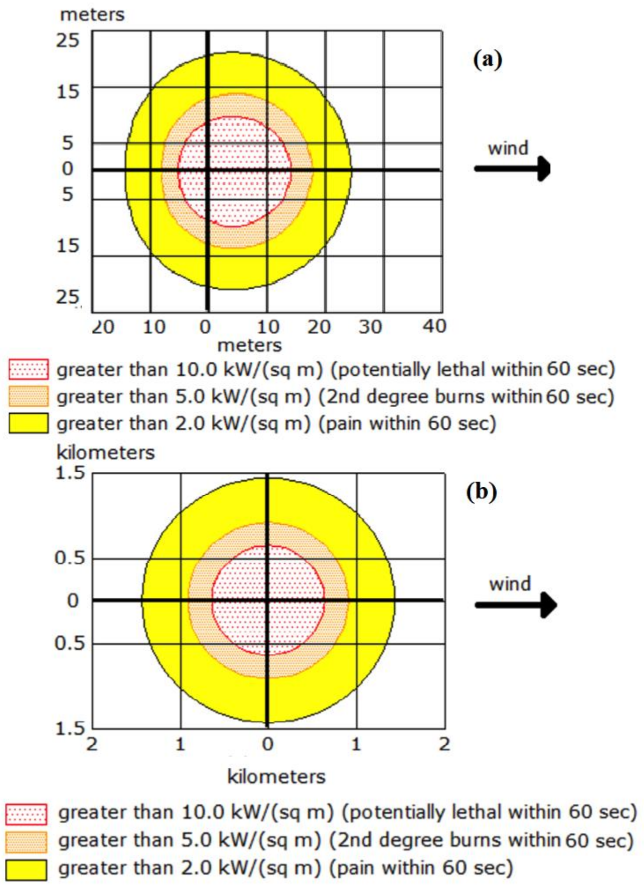

Fig. 3. Graphs for modelling of butyl acrylate storage tank exploded - (a) jet fire and (b) BLEVE

When BLEVE occurred, the red and orange threat zones showed 10.0 kW/m^2 and 5 kW/m^2 thermal radiation extending to 642 m and 915 m, respectively.

The yellow threat zone showed 2 kW/m^2 thermal radiation extending to 1.4 km (Fig. 3(b)).

3.4. Modeling butyl acrylate explosion using BBD

In this section, temperature, wind speed, and filling ratio of the tank were examined as independent variables in the BBD analysis to achieve threat zones of the VCE, jet fire, and BLEVE explosions.

Table 5 shows the experimental design matrix for these independent variables (temperature, wind speed, and filling ratio of the tank) and responses (red, orange, and yellow threat zones).

The results in Table 5 shows that although there were no significant changes in the red threat zones for VCE and jet fire of butyl acrylate, the red threat zone ranged from nearly 456 to 787 m for BLEVE.

Based on the results for BLEVE, the highest red threat zone of 787 m occurred at 0ºC, 4 m/s of wind speed, and 80% of filling ratio of the tank, while the lowest red threat zone of 456 m occurred at 30 ºC, 4 m/s of wind speed, and 20% of filling ratio of the tank. The red threat zone decreased sharply when temperature increased from 0 ºC to 30 ºC. It can be safely mentioned that the filling ratio of the tank was the most effective parameter on the BLEVE of butyl acrylate.

The orange threat zone ranged from nearly 20 to 119 m for VCE, and 650 to 1,100 m for BLEVE. The yellow threat zone ranged from nearly 82 to 682 m for VCE; 1,000 to 1,800 m for BLEVE.

Table 5. Independent variables and experimental design matrix for threat zones for VCE, jet fire, and BLEVE of butyl acrylate

Run	A	B	C	Vapor Cloud Explosion			Jet Fire			BLEVE		
				Red Threat Zone (m)	Orange Threat Zone (m)	Yellow Threat Zone (m)	Red Threat Zone (m)	Orange Threat Zone (m)	Yellow Threat Zone (m)	Red Threat Zone (m)	Orange Threat Zone (m)	Yellow Threat Zone (m)
1	0	4	20	20	20	82	14	18	25	506	721	1,100
2	15	1	80	20	24	194	<10	14	23	745	1,100	1,700
3	15	7	80	20	62	209	14	17	23	745	1,100	1,700
4	30	7	50	28	119	682	14	17	22	608	868	1,400
5	15	4	50	20	26	211	14	18	25	642	915	1,400
6	15	4	50	20	26	211	14	18	25	642	915	1,400
7	0	4	80	20	26	92	14	18	25	787	1,100	1,800
8	30	4	20	20	41	374	14	18	24	456	650	1,000
9	30	1	50	19	37	340	<10	13	22	608	868	1,400
10	15	7	20	20	24	194	14	18	23	480	684	1,100
11	0	7	50	20	20	75	14	17	23	677	965	1,500
12	15	4	50	20	49	382	14	17	25	642	915	1,400
13	15	1	20	20	26	211	<10	18	23	480	684	1,100
14	30	4	80	20	41	374	14	14	24	706	1,000	1,600
15	15	4	50	20	26	211	14	18	25	642	915	1,400
16	0	1	50	20	20	201	<10	18	24	677	965	1,500
17	15	4	50	20	26	211	14	15	25	642	915	1,400

Two different statistical tests were applied to the modelling results to assess the adequacy of the linear, two-factor interactions (2FI), quadratic and cubic models for describing the threat zones for VCE, jet fire, and BLEVE of butyl acrylate (Abdollahi et al. 2012). The results are presented in Table 6.

Table 6. Regression analysis for threat zones for VCE, jet fire, and BLEVE of butyl acrylate

VCE	Orange Threat Zone		Yellow Threat Zone				
Source	Adjusted R^2	Predicted R^2	Adjusted R^2	Predicted R^2			
Linear	0.5683	0.3377	0.7623	0.6448			
2FI	0.5519	0.5311	0.6922	0.6160			
Quadratic	0.9565	0.9458	0.9541	0.9589	Suggested		
Cubic	1.0000		1.0000				
Jet Fire	**Orange Threat Zone**		**Yellow Threat Zone**				
Source	Adjusted R^2	Predicted R^2	Adjusted R^2	Predicted R^2			
Linear	0.2592	0.1163	0.0284	0.4443			
2FI	0.0714	0.3849	0.3167	1.9612			
Quadratic	0.9754	0.8278	0.9711	0.7976			
Cubic	1.0000		1.0000				
BLEVE	**Red Threat Zone**		**Orange Threat Zone**		**Yellow Threat Zone**		
Source	Adjusted R^2	Predicted R^2	Adjusted R^2	Predicted R^2	Adjusted R^2	Predicted R^2	
Linear	0.9693	0.9534	0.9693	0.9517	0.9749	0.9575	
2FI	0.9625	0.9034	0.9612	0.8912	0.9722	0.9116	
Quadratic	0.9999	0.9993	0.9903	0.9824	0.9931	0.9818	Suggested
Cubic	1.0000		1.0000		1.0000		

The quadratic model was very effective compared to the others with higher R^2 values. It can be said that the quadratic model can describe the relationship between responses (red, orange, and yellow threat zones) and the interactive variables (temperature, wind speed, and filling ratio of the tank). The R^2 values of 0.95 indicated that the models were statistically significant and 95% of the total variance in the threat zones was explained by the model. Also, the difference between the R^2adj and R^2pre values less than 0.1 was acceptable (Table 6) (Ozcan et al., 2022). It is obvious that the case in which these two values were close to each other is applicable for quadratic model only.

An experimental relationship between the response and the three independent variables was demonstrated in quadratic model equations with coded factor [temperature (A), wind speed (B), and filling ratio of the tank (C)] values in Eq. (6) and Eq. (10). The theoretical values for responses can be estimated by using these equations for VCE. In addition, quadratic model was not suitable for red threat zones of VCE results as seen from Table 5.

Orange threat zone of VCE $=+26 + 16.13A - 23.37B - 13.25AB + 8.87A^2 + 21.38B^2 - 4.37C^2$ (6)

Yellow threat zone of VCE $=+211 + 143.63A - 134.87B - 8.75AB + 42.62A^2 + 116.12B^2 - 25.62C^2$ (7)

Table 6 shows that, in case of a jet fire, the quadratic model was not supported because the difference between the regression coefficients was very high, and, therefore, quadratic model equations for the jet fire of butyl acrylate are not presented. This was also supported by the design matrix in Table 5.

Red threat zone of BLEVE $=+642 - 33.62A + 132.63C - 7.75AC + 0.8750A^2 - 0.3750B^2 - 29.12C^2$ (8)

Orange threat zone of BLEVE $=+915 - 45.62 + 195.13 - 7.25AC - 11.38A^2 + 12.87B^2 - 35.87C^2$ (9)

Yellow threat zone of BLEVE $=+1400 - 62.5A + 312.5C - 25AC + 12.5^2 + 37.5B^2 - 37.5C^2$ (10)

where, 'A, B, and C' are the temperature, wind speed, and filling ratio of the tank, respectively. 'AB, AC, and BC' represent the interaction of two independent variables, e.g., AB is the interaction between the temperature and wind speed, AC is the interaction between the temperature and filling ratio of the tank, and BC is the interaction between the wind speed and filling ratio of the tank on the red, orange, and yellow threat zones. 'A^2, B^2, and C^2' indicate the squared effect of independent variables. The '-' and '+' in the equations represent that the response is affected negatively and positively, respectively.

In order to examine the optimum independent variables for the highest threat zones, one-way ANOVA was performed.

The ALOHA modelling results were analyzed with ANOVA to understand the suitability of the regression model with a confidence interval of 95% and also an analysis of ANOVA was used to determine whether there were significant differences in the mean of the experimental results. To define the simulation results more confidently, the models for threat zones were improved based on the F-value, p-value, R^2, and lack of fit test examined by one way-ANOVA analysis. A p-value less than 0.05 indicated that the independent and dependent terms in the model are statistically significant. Furthermore, the F-value and R^2 values should be relatively high for an acceptable model (Bertinetto et al. 2020).

The p-values of the quadratic model for orange and yellow threat zones for VCE were <0.0005 and <0.0001, respectively, demonstrating the significance of the model. The F-values of the model for orange and yellow threat zones were calculated as 18.25 and 48.74, respectively. The very low p-values and relatively high F-values in the models for the threat zones indicated that the quadratic model was significant and there was a good relationship between responses (threat zones) and independent variables (temperature, wind speed, and filling ratio of the tank). In addition, the p-values for the temperature and filling ratio of the tank were 0.0005 and <0.0001, respectively (Table 7). The F-values for temperature and filling ratio of the tank was greater than that of the others. It can be safely mentioned that the temperature and filling ratio of the tank were much more effective parameters on VCE of butyl acrylate, while wind speed has a major effect on the dispersed cloud area.

Table 7. ANOVA for threat zones of VCE of butyl acrylate

VCE						
Orange Threat Zone						
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9,530.22	9	1,058.91	18.25	0.0005	Significant
Temperature (A)	2,080.13	1	2,080.13	35.84	0.0005	
Wind speed (B)	0.0000	1	0.0000	0.0000	1.0000	
Filling ratio of the tank (C)	4,371.12	1	4,371.12	75.32	<0.0001	
Yellow Threat Zone						
Model	3.789E+05	9	42,096.18	48.78	<0.0001	Significant
Temperature (A)	1.650E+05	1	1.650E+05	191.25	<0.0001	
Wind speed (B)	0.0000	1	0.0000	0.0000	1.0000	
Filling ratio of the tank (C)	1.455E+05	1	1.455E+05	168.65	<0.0001	

The p-values of the quadratic model for all threat zones for BLEVE were <0.0001 (Table 8). The F-values of the model for red, orange, and yellow threat zones were calculated as 19,113.42, 183.27, and 257.26, respectively. The very low p-values and high F-values in the models for all threat zones showed that the quadratic model was significant for BLEVE.

The F-values for temperature and filling ratio of the tank were 10,130.54 and 15,760 for the red threat zone; 83.73 and 1,531.43 for the orange threat zone; and 87.5 and 2,187.5 for the yellow threat zone (Table 8). It is obvious that the filling ratio of the tank was the most effective parameter on the BLEVE of butyl acrylate.

Table 8. ANOVA for threat zones of BLEVE of butyl acrylate

BLEVE						
Red Threat Zone						
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1.536E+05	9	17,065.55	19,113.42	<0.0001	Significant
Temperature (A)	9,045.12	1	9,045.12	10,130.54	<0.0001	
Wind speed (B)	0.0000	1	0.0000	0.0000	1.0000	
Filling ratio of the tank (C)	1.407E+05	1	1.407E+05	1.576E+05	<0.0001	
Orange Threat Zone						
Model	3.281E+05	9	36,451.14	183.27	<0.0001	Significant
Temperature (A)	16,653.13	1	16,653.13	83.73	<0.0001	
Wind speed (B)	0.0000	1	0.0000	0.0000	1.0000	
Filling ratio of the tank (C)	3.046E+05	1	3.046E+05	1,531.43	<0.0001	
Yellow Threat Zone						
Model	8.269E+05	9	91,879.08	257.26	<0.0001	Significant
Temperature (A)	31,250.00	1	31,250.00	87.50	<0.0001	
Wind speed (B)	0.0000	1	0.0000	0.0000	1.0000	
Filling ratio of the tank (C)	7.813E+05	1	7.813E+05	2,187.50	<0.0001	

3.5. Response surface analysis (RSM)

In this study, the effects of independent variables (temperature, wind speed, and filling ratio of the tank) on the responses (red, orange, and yellow threat zones) were determined by three-dimension (3D) surface graphs generated from Design Expert software using RSM (Kim et al. 2020). The 3D surface graphs obtained based on the quadratic model are illustrated in Fig. 4 and 5. Fig. 4(a-c) and Fig. 5(a-c) show the combined effects of temperature and wind speed; filling ratio of the tank and temperature; and filling ratio of the tank and wind speed on threat zones of VCE and BLEVE, respectively. There were no significant changes on the threat zones for jet fire and the 3D graphs were not generated.

The orange and yellow threat zones of VCE increased significantly from 20 m to 41 m and 82 m to 374 m, respectively when the temperature was raised from 0ºC to 30ºC at a constant wind speed (4 m/s) and filling ratio (20%). At a constant temperature, the values of the orange and yellow threat zones decreased significantly when the wind speed and filling ratio of the tank were decreased. In addition, when the temperature and wind speed were elevated together, the orange and yellow threat zones increased too. The orange and yellow threat zones of VCE expanded from 26 m to 49 m and 211 m to 382 m, respectively, when the wind speed rose from 1 m/s to 4 m/s and filling ratio of the tank from 20% to 50%. It can be safely mentioned that temperature, wind speed, and filling ratio were very effective parameters for VCE. Wind speed is also very effective on the dispersion of the vapor cloud.

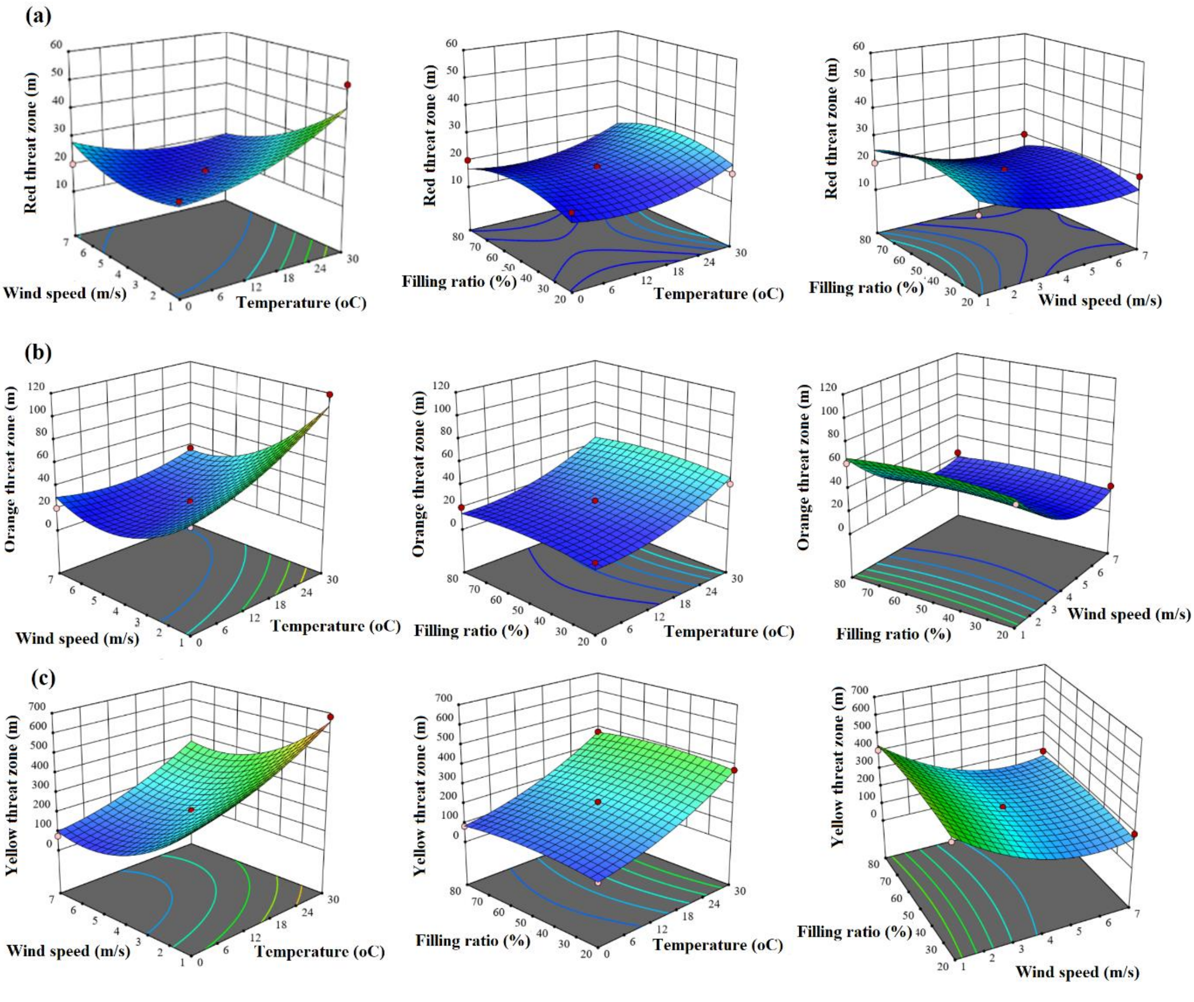

Fig. 4. Effects of variables on VCE of butyl acrylate

Given the effects of temperature and filling ratio of the tank as the two important independent variables for VCE, it can be stated that, by increasing the temperature, the vapor pressure of the liquid and the amount of vapor formed on the liquid increase. As a result, the intensity of the explosion enhances and the distances to the danger zones expand. In addition, the higher filling ratio of the tank will result in the increased amount of vapor formed due to temperature, and the intensity of the explosion and the distance to the threat areas will increase significantly with the larger amount of vapor.

The red, orange and yellow threat zones of BLEVE decreased from 677 m to 608 m; 965 m to 868 m; and 1,500 to

1,400 m, respectively, when the temperature increased from 0 ºC to 30 ºC at constant wind speed (7 m/s) and filling ratio (50%). All threat zones decreased sharply when temperature increased effectively. The red, orange, and yellow threat zones of BLEVE expanded from 506 m to 787 m; 721 m to 1,100 m; and 1,100 to 1,800 m, respectively when the filling ratio of the tank increased from 20% to 80%. It was seen that the wind speed did not affect all threat zones of BLEVE, despite the filling ratio of the tank significantly did so. Therefore, the increase in the amount of butyl acrylate in the tank greatly expanded the boundaries of the threat zones. It can be safely stated that the filling ratio of the tank was the most effective parameter for BLEVE. Also, the combined effect of temperature and wind speed decreased all threat zones. As explained when interpreting the model equations, the temperature reduced all threat zones, while the wind speed remained ineffective.

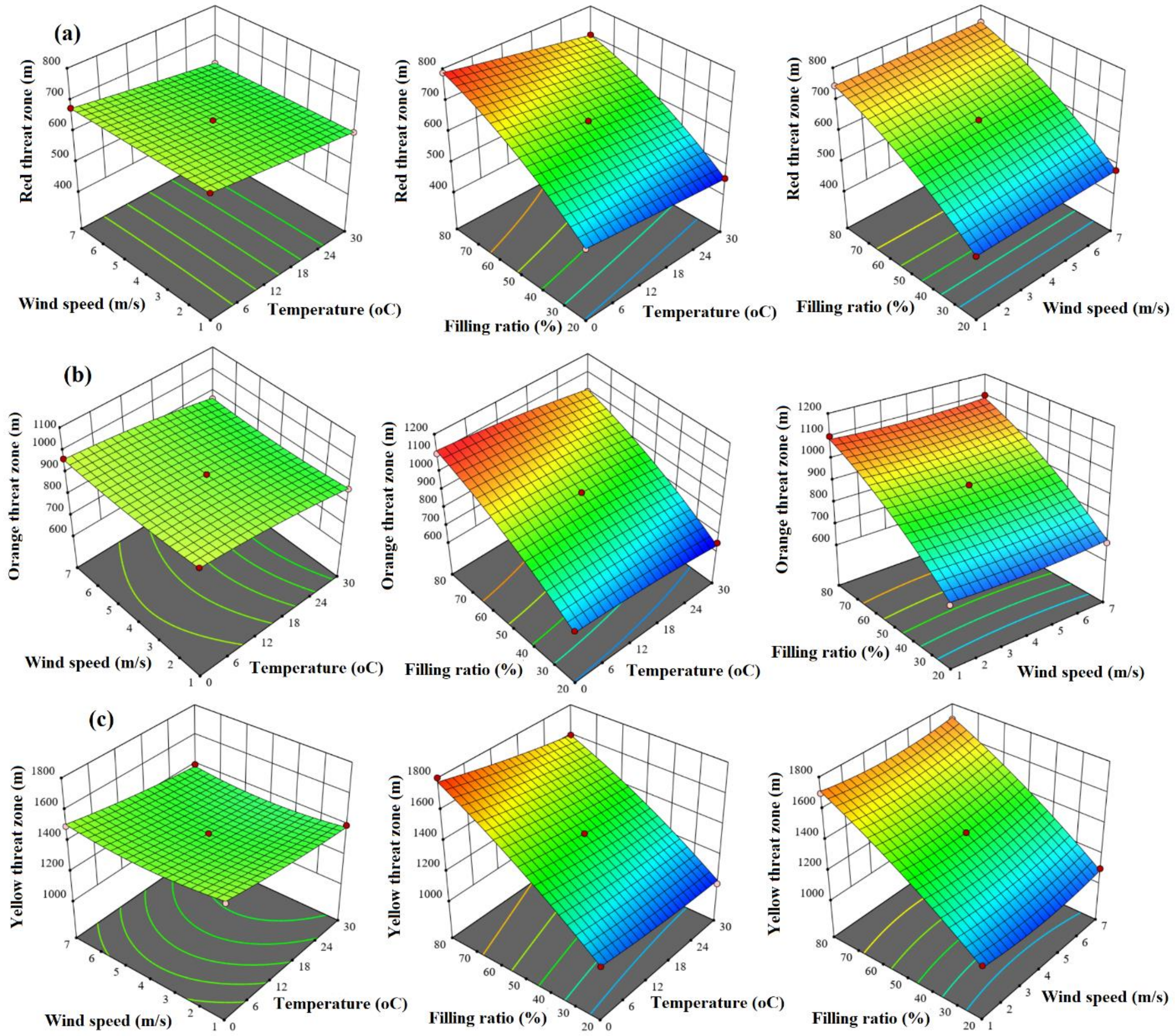

Fig. 5. Effects of variables on BLEVE of butyl acrylate

In the case of BLEVE, it was observed that the diameter of all threat zones decreased with increasing temperature. This situation can be explained by the combined heat transfer by conduction, convection, and radiation.

Combined heat transfer can be expressed using Eq. (11):

$$Q_T/A = Q_{cond.}/A + Q_{Conv.}/A + Q_{Radiat.}/A = k(Tw - Ts) + h(Tw - Ts) + \varepsilon(Tw^4 - Ts^4) \quad (11)$$

The heat flux of conduction, convection or radiation is lower when the difference between the tank temperature and ambient temperature (*Tw -Ts)* is smaller. The lower heat flux cause lower heat transfer area (Ranjan et al. 2019).

In other words, as the ambient temperature rises, the difference between the temperature of the burning tank and the ambient temperature decrease, and thus the heat transfer area decreases so that the amount of heat transferred per unit surface remains constant. Therefore, with increasing temperature, the radius of the threat zones reduces. Since the BLEVE is a very violent explosion occuring in seconds, it is expected that the wind speed is ineffective.

4. Summary and conclusion

In this study, a butyl acrylate tank located in a real tank farm in Kocaeli-Turkey was analyzed for examination of breathing and filling/discharge losses, and total emissions using TANK 4.09d. The breathing and filling/discharge losses, and total annual emission of butyl acrylate were determined to be 27.79, 30.21, and 58 kg/year. TNT equivalent explosion model was applied to vapor cloud of butyl acrylate and explosion damage radius plus death and minor injury zones were calculated. The death radius calculated by the TNT equivalent explosion model was 13.57 m and the equivalent radius of serious injury was 24.08 m. ALOHA program was used to define threat zones of butyl acrylate leakage based on different scenarios such as a leakage from the tank without fire, burning as a jet fire, and also burning as a fireball during Boiling Liquid Expanding Vapor Explosion (BLEVE). According to ALOHA results, in VCE, both orange and yellow threat zones were 838 m, and the red one was 1.9 km. The red and yellow threat zones were 178 m and 491 m, respectively, for modeling of flammable area. In addition, temperature, wind speed, and filling ratio of the tank were selected significant independent variables for red, orange, and yellow threat zones of VCE, jet fire, and BLEVE according to the results from ALOHA. The interaction of these independent variables on the threat zones were investigated using the Box-Behnken experimental design and also one-way ANOVA. ANOVA results showed that temperature and filling ratio of the tank were much more effective on VCE, despite filling ratio was the most effective parameter on the BLEVE of butyl acrylate.

Some suggestions can be made based on the results of this research. As known, the ALOHA does not show the threat zone in an area further than 10 km. Different programs (PHAST, MODLOW etc.) can be used to compensate for this. Modeling studies can be repeated by using different parameters (pressure, humidity, place, etc.). Evaluation of the outputs of the obtained model can provide more effective results. In the present study, especially for BLEVE, it has been observed that the effect distance of an explosion increases with the increased filling ratio of the tank. For this reason, the safe storage conditions of the tanks should be known and the tanks should not be filled with more than their capacities. Tanks should be located in an open area; otherwise, the environment should be continuously ventilated. In this case, storage conditions are very important. Increasing inspections on storage tanks, creating emergency cards, posting warnings and monitoring processes on storage tanks can be recommended for industries using tank farms.

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Conflict of interest

The authors declare no conflicts of interest.

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丙烯酸丁酯罐中意外释放的排放率、ALOHA 模拟和 Box-Behnken 设计 - 案例研究

關鍵詞
蒸气云爆炸
喷射火
布尔维
箱-本肯
方差分析

摘要

化工行业的有害化合物泄漏一直是威胁工人、工厂和环境的因素之一。其中，丙烯酸丁酯是化学工厂中广泛使用的有害物质之一。在本研究中，分析了位于土耳其科贾埃利（Kocaeli）一个真实罐区的丙烯酸丁酯罐，用于检查蒸汽云的排放和三硝基甲苯（TNT）当量爆炸模型。危险大气区域位置 (ALOHA) 程序用于根据不同情况定义丙烯酸丁酯泄漏的威胁区域，例如从罐中泄漏而没有火，燃烧为喷射火，以及在沸腾液体膨胀蒸汽过程中燃烧为火球爆炸（BLEVE。此外，由于增强爆炸效果和挥发性有机化合物 (VOC) 扩散的最重要参数是风速、储罐填充率和温度，因此这些参数对威胁区域和最高威胁的相互作用分别使用 Box-Behnken 实验设计和单向方差分析 (ANOVA) 研究爆炸区域。由于丙烯酸丁酯是工业设施中最危险的化学品之，其爆炸效应迄今尚未研究过，可以肯定地说，这篇代表文献中第一项研究的论文具有很高的原创性和新颖性。