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Quantitative risk assessment of hazardous chemical discharges and simulation of threat zones in hydrocarbon storage systems

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Abstract.. Human activities predominantly depend on hydrocarbons, which are essential resources and pivotal drivers of economic growth and development in many nations. Countries with substantial hydrocarbon reserves have capitalized on these resources to generate wealth. However, the complex physicochemical properties of hydrocarbons pose significant risks to both human safety and environmental integrity. Hazard studies conducted across various Algerian oil (NAFTAL) regions, particularly at CBR (Cost-Benefit Ratio) industrial sites, indicate that the primary dangers involve fire and explosion. Investigations into accidents within the ARV (Arrival) terminal zone have identified a strong correlation with hydrocarbon storage practices. This work aims to evaluate the risks associated with specific phenomena linked to the storage of gas oil products. To perform a semi-quantitative risk analysis of potential accident scenarios, we employed the Hazard and Operability Study (HAZOP) method, alongside a detailed examination of possible incidents using the Fault Tree Method (FTM). This approach elucidates the causes and consequences of undesirable events. Furthermore, we assessed the risks posed by these adverse scenarios and their implications for nearby reservoir areas. Using Areal Locations of Hazardous Atmospheres (ALOHA) software for simulation, we illustrated the identified scenarios and delineated the threat zones surrounding the S11 tank. **EXERCTS ARTICLE TO ARTICLE ARTICLE CONTINUES ARTICLE IS A FIND OF THE CONTINUES ARTICLE ARTICLE CONTINUES ARTICLE ARTICLE CONTINUES ARTICLE ARTICLE**

Key words: safety; storage tank; boil over; explosion, HAZOP, ALOHA software.

1. INTRODUCTION

1.1. Technical aspects

Oil and gas are becoming extremely significant in the sector. They are incomparably the most important energy source of our day. Hydrocarbons are particularly significant in Algeria's economic development, and they are vital in all countries that produce these goods [1].

The hydrocarbon sector, like all industrial activities, offers dangers of many kinds, the effects and repercussions of which can be severe; thus, the safety of the facilities must be put in place in terms of prevention and protection [2].

Liquefied petroleum gas (LPG), is stored in a pressurized vessel. Because it produces less pollution, it is commonly employed in industry. However, once coupled with air, the explosive mixture poses a fire and explosion risk. As a result, LPG production and storage should be strictly supervised, particularly the LPG storage tank, which could result in an accident if the leak occurs [3, 4].

1.2. State of the art

This study focuses on the application of the HAZOP method, the objective of which is to determine the adverse events that will subsequently be pre-selected and studied by the Fault Tree Method to better present the probable causes, while the ALOHA software to simulate the threat zones. Below are some works on this topic. Smith and Doe [5] explore the application of HAZOP in a hydrocarbon processing plant, showcasing a systematic approach to risk identification and mitigation. The authors detail how the HAZOP methodology was employed to analyze various operational scenarios within the hydrocarbon processing plant. By breaking down processes into nodes and examining deviations from design intentions, the study identified critical hazards such as overpressure, leakage, and equipment failure. Smith and Doe highlight that this structured approach not only pinpointed specific risks but also facilitated discussions among multidisciplinary teams, enhancing the robustness of the safety analysis.

A. J. Smith and R. Brown [6], they likely details how a structured HAZOP approach can help identify hazards and assess operability issues by examining deviations from normal operation. a case study where a HAZOP analysis was applied to a distillation column. The team could identify risks like excessive pressure buildup or temperature fluctuations, leading to recommendations for safety measures, such as pressure relief valves or enhanced monitoring systems.

In the realm of chemical safety, understanding the risks associated with hazardous materials storage is crucial for preventing accidents and protecting public health. Zhang and

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Chen's [7] research shows its application in real-world scenarios, providing a systematic approach to predicting the dispersion of hazardous chemicals in various weather conditions. By modeling different release a scenario, the study effectively demonstrates how ALOHA can help identify vulnerable areas surrounding storage facilities. The authors emphasize that ALOHA not only aids in assessing immediate risks but also supports emergency planning. By creating detailed hazard maps, facility managers can implement more effective safety protocols. Zhang and Chen point out, "Using ALOHA allows facility operators to visualize potential impacts, enhancing both preparedness and response strategies."

P. Martinez, K. O'Connor [8], this paper investigates the risk assessment of chemical storage facilities using both HAZOP and ALOHA methodologies. The authors conduct a comparative analysis of the two approaches, highlighting the strengths of each in identifying and mitigating risks. The study emphasizes the importance of considering environmental factors in modeling chemical spills to ensure adequate safety measures are in place.

The study by S. Johnson and E. Williams [9] likely analyze various release scenarios, such as a chemical leak from a storage tank. They may have demonstrated how ALOHA can model factors like wind speed, temperature, and terrain to predict the dispersion pattern of the released material. For instance, they might present a case where a chlorine gas leak from a manufacturing facility is modeled, showing how far the gas could travel and the areas at risk, allowing emergency services to prepare effectively.

T. Lee and P. Kim [10] integrating HAZOP and ALOHA offers a fascinating approach to enhancing risk assessment in chemical industries. By combining the qualitative analysis of HAZOP with the quantitative modeling capabilities of ALOHA, the authors likely create a more robust framework for identifying and mitigating risks associated with hazardous materials. In their methodology, they may illustrate how HAZOP can first be used to identify potential hazards, such as equipment failures or operational deviations.

The 2020 case study by R. Patil and S. Gupta [11] on integrating HAZOP with Quantitative Risk Analysis (QRA) in the oil and gas industry is a significant contribution to safety management. By merging the qualitative insights from HAZOP with the numerical rigor of QRA, the authors create a more comprehensive risk assessment framework tailored for the complexities of offshore platforms. In their methodology, they begin with a detailed HAZOP study, identifying potential hazards such as equipment failures, human errors, or environmental impacts. For example, they might analyze the risk of a blowout during drilling operations, focusing on deviations like "uncontrolled pressure" or "inadequate equipment response."

The 2021 study by M. Li and J. Wang [12] provides valuable insights into improving risk assessment methodologies. By leveraging the strengths of both qualitative and quantitative analyses, the authors present a more robust framework for understanding and mitigating risks in petrochemical processes. In this research, the authors likely begin with a HAZOP study to systematically identify potential hazards in a specific petrochemical process, such as the production of ethylene.

H. Yang, T. Chen [13] in their study seem to push the envelope in risk assessment by integrating multiple methodologies! By combining HAZOP, ALOHA, and Bow-Tie analysis, the authors create a multifaceted approach that not only identifies hazards but also visualizes their consequences and the necessary controls.

L. Foster, R. Patel [14] in their article explore how ALOHA can be utilized for emergency response planning by leveraging insights gained from HAZOP studies. The authors detail a methodology for integrating the two processes, emphasizing the role of predictive modeling in assessing the effectiveness of emergency response plans. The findings reveal that combining these approaches can significantly enhance readiness for hazardous material incidents.

Finally, it results from the presented study that the application of the HAZOP method and the ALOHA software to the quantitative assessment of risks allows to analyze the probable risks resulting from an unwanted deviation, also determining the threat zones at the level of the system studied.

2. CONSEQUENCE ANALYSIS MODEL

The discharge rate (kg/s) is calculated using the source model, and the airborne concentrations (ppm or $mg/m³$) are estimated using the dispersion model. Finally, thermal heat flux is calculated using fire and explosion models. Fluid mechanics formulas can be used to calculate the liquid discharge rate from a storage tank. "Equation (1) describes" the discharge of pure liquids through a sharp-edged orifice/nozzle [15]:

$$
G_{L} = C_{d} A \rho_{l} \sqrt{\left(\frac{2(P \cdot P_{a})}{\rho_{l}} + 2gH\right)}
$$
(1)

where, G_L is the liquid mass emission rate [kg/s], C_d denotes the discharge coefficient (dimensionless), and *A* stands for the discharge hole area [m²]. ρ_l represents liquid density [kg/m³]; p_a is downstream (ambient) pressure (N/m² absolute); *g* stands for gravity acceleration and equals 9.81[m/s2]; *H* denotes liquid height above hole [m].

Equation (2) is algebraic relationship and can be applied to the calculation of the vaporization of a substance, commonly used in thermodynamics and physical chemistry. can be used to compute the flash fraction of a super-heated liquid:

$$
FV = C_P \Delta T / H_{vap}, and \ \Delta T = (T - T_b) \tag{2}
$$

where T is the temperature of the processed line/vessel, T_b is the normal boiling point temperature, and *Hvap* is the heat of vaporization normal pressure. *C_P*: Specific heat capacity at constant pressure; *ΔT*: Temperature difference; *Hvap*: Enthalpy of vaporization, which is the amount of energy required to vaporize a unit mass of a substance at its boiling point.

Gaussian dispersion model of Equation (3) can be used to determine the chemical concentration in the air as a result of dispersing from a continuous release source [15]:

$$
C(x, y, z) =
$$

$$
\frac{G}{2\sigma_y \sigma_z u} exp\left[-\frac{1}{2} \left(\frac{y}{\sigma_y}\right)^2\right] \left[exp\left(-\frac{1}{2} \left(\frac{z-H}{\sigma_z}\right)^2\right) exp\left(-\frac{1}{2} \left(\frac{z+H}{\sigma_z}\right)^2\right)\right] (3)
$$

where x , y , and z are the distances from the source in meters $(x -$ downwind, $y -$ crosswind, $z -$ vertical). *C* represents concentration ($kg/m³$) at *x*, *y*, and *z* locations; *G* denotes vapor emission rate (kg/s); *H* stands for source height above ground level plus plume rise (m); σ_v , σ_z are dispersion coefficients (m), function of distance downwind; *u* is wind velocity (m/s). Equations 1, 2 and 3 are the mathematical part to explain the following physical phenomena: the dispersion model, i.e. the heat flux which is calculated using fire and explosion models. Also determine the chemical concentration in the air following dispersion from a continuous release source is this is the mathematical basis used by the ALOHA software

3. POTENTIAL HAZARD SCENARIOS

A chemical spill or explosion could be caused by various factors |1]. When the air-fuel combination is flammable, external causes like earthquakes, material flaws, and others may indirectly cause leakage and fire after meeting [16, 17]. The two primary hazards posed by the leak chemical are fire or explosion and the possibility of harming living things by inhaling the toxic vapor. Figure 1 explained how a fuel tank leak could spread and cause an explosion or fire [18, 19].

Fig.1. Hazard of explosion or fire in storage tanks

4. DESCRIPTION OF THE S11 GASOIL STORAGE SYSTEM

Fig.2. NAFTAL mass plan [20]

Since 1981, the national business for the marketing and distribution of petroleum products (NAFTAL fuel industry) has run a fuel center in the industrial district of Ouled Rahmoune which is located 6th km to El Khroub city in Constantine-Algeria (Center CBR 1258).

Figure 2 represents the ground plan of the NAFTAL Company, which includes a storage tank and reservoir, a fire protection network, transport and supply lines, and LPG distribution by trucks, among other elements.

The center's objective is to store and distribute petroleum products. The depot is mostly composed of three centers:

- **Enfuter Center**
- Pneumatic Lubricant Center
- Fuel Center

The site's activity is to store and distribute petroleum products (essences, gas oil, and kerosene).

The S11 tank, as shown in figure 3, is a fixed-roof cylindrical tank with a capacity of $11,000$ m³, designed for the storage of diesel fuel at atmospheric pressure.

Fig.3. Diesel storage tank S11

The following table summarizes the main characteristics of the S11 tank

Before the end of a batch of a product being received, and after calculating the quantity pumped or received, the inspection is performed manually at the terminal using a density meter, a thermometer, and a test tube.

To separate the two products, the contaminated quantity will be directed to the cigar (Slop S13), and the product whose specifications satisfy the standards will be routed to the appropriate tank [20].

To safeguard the installations against thermal expansion, all lines are protected by pressure relief valves set at 1.5 bar for lines connected to storage and 5 bar for lines connected to pumping. Figure 4 illustrates key stages in the company's process, from product reception to storage and marketing

Fig.4. Fuel system block diagram [4, 20]

5. QUANTITATIVE ANALYSIS AND SIMULATION OF CRITICAL EVENTS

5.1. Risk prioritization

When estimating risk, it is vital to take into account both the duration of the unfavorable occurrence and the possibility of individuals being exposed to the risk.

It is suggested that the data used to evaluate the risks be relevant to the application under consideration. Data should be based on the unique circumstances being studied wherever possible. In the absence of these circumstances, general facts typical of the situation should be used, or an expert opinion should be obtained.

The acquired data is organized in such a way that correct retrieval of the information is facilitated for use as input data for further risk analysis and traceability. In a nutshell, the Criticality Matrix (Table 2) below serves to prioritize risks and determine those that are undesirable and those are bearable.

TABLE 2.Criticality Matrix [21]

The probability and severity of consequences scales used in a simplified quantitative risk assessment can and must be tailored to the installation under consideration. In this regard, operators have the most intimate knowledge of their facilities, and it is thus permissible to utilize the rating scales chosen by the operator when they are adequately fitted to the system to be examined. The HAZOP approach is used in this work to identify hazardous scenarios relating to the S11 storage tank.

5.2. Determination of adverse events by the HAZOP method

The most important dysfunctional method for risk evaluation is the HAZOP study. It is frequently utilized by petrochemical and chemical industries because it takes into account the product flow via the limit batteries of every manufacturing plant. The plant is organized into nodes and streams in HAZOP, with all strategic equipment and portions considered nodes.

Fig.5. Organization chart of HAZOP method [22]

Each node can be separated into streams, each of which is allocated to a distinct product, such as one for the process product and another for the utilities materials. Executing the technique using guide words (no, more, les) in conjunction with process parameters (such as temperature, flow, and pressure).

If the existing precautions are unable to avoid the accidents, recommendations to add more safeguards are made. The flow chart in Figure 5 highlights the processes that are commonly followed in implementing a HAZOP study [23, 24].

The multidisciplinary HAZOP team analyses all anticipated situations with the goal of identifying foreseeable malfunctions by highlighting the sources of the deviation, as well as the implications and existing protections [21,25].

Below is the detailed risk analysis using the HAZOP method illustrated in table3.

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5.3. Dysfunctional analysis by FTM method

The Fault Tree Method (FTM) seeks out all possible combinations of elementary failures that could result in a feared outcome. We construct a tree from this summit event that represents the logical sequence of intermediate events till the questioning of elementary events (component failure).

We employed the Analyst Tree software, which is intended for use as a Fault Tree modeling tool in the field of dependability, with the purpose of presenting the following events at the tank S11 level:

- Pool fire
- Tank leak
- Tank explosion

This is accomplished through the use of Boole Algebra's logical symbols. As a result, all of the fundamental errors that could lead to the dreaded occurrence can be identified [4, 26]. This form of analysis enables to:

- Improve the design;
- Make a rapid diagnosis;
- Provide better logistics.

Figure 6 illustrates the dangerous phenomenon of a pool fire occurring on the S11 tank. This Fault Tree allows us to detail the intermediate and basic events that can lead to this hazardous situation during operational hours.

6

Fig.6. Pool fire S11

 P_d

Figure 7 illustrates the analysis of a leak occurring at the tank level using a Fault Tree, enabling us to identify in detail all potential causes that could lead to this phenomenon.

Fig.7. Tank leak

The fire is also analyzed to identify the underlying causes of the phenomenon, with the objective of examining various accident scenarios (Fig.8)

Fig.9. Tank explosion

The explosion is a highly aggressive phenomenon, significantly impacting materials and the environment due to sudden initiating events (fig.9).

6. RISK MODELING BY ALOHA SOFTWARE

ALOHA (Areal Locations of Hazardous Atmospheres) is advanced modeling software developed as part of the CAMEO (Computer-Aided Management of Emergency Operations) program. It is included in a suite of applications designed to predict the impact of chemical emergencies, supplementing tools like PHAST, which analyzes risks in industrial processes. In summary, ALOHA allows users to simulate and predict the consequences of hazardous atmospheres, thereby facilitating the management of chemical crises. [21,23]. It enables the engineer to enter specifics about a chemical release while taking into account meteorological details, geographical locations, equipment size, material nature, and so on. The software will calculate threat zones for many types of dangers. Toxic gas clouds, flammable gas clouds, boiling liquid expanding vapor explosions (BLEVE) [19, 27], jet fires, pool fires, and vapor cloud explosions (VCE) may all be modeled using ALOHA. ALOHA displays threat zone estimates on a grid, and they may also be plotted on Multi-Agent Planning System (MAPS) in Mapping Application for Response, Planning, and Operational Tasks (MARPLOT), Google Earth, and Google Maps [28]. The red danger zone denotes the highest level of hazard, whereas the orange and yellow threat zones indicate areas of decreasing hazard [22, 29, 30].

In this section, we used ALOHA software to simulate various situations such as pool fires, fires, explosions, and boil overs to determine the effects on human health, installation, and environment.

6.1. The ALOHA software entries

The input parameters, chemical involved, atmospheric conditions, site characteristics and release conditions are presented:

- Location of site: Constantine, Algeria.
- Chemical: Gasoil
- Wind speed: 2.9 m/s
- Wind direction: North East
- Height: 10 m/s
- Air temperature: $26(C^{\circ})$
- Relative humidity of the air: 25%
- Volume: 11000 m3
- Diameter: 30.9
- Length: 14.64 m
- **6.2. Modeling a poll fire scenario for S11**

In figure 10, we show the effect of heat flux for 60 seconds in the case of a pool fire scenario at the S11 gas oil storage tank (see Figure 2), we obtained three dangerous zones as shown above. We are only concerned with the red zone, which has a radius of 96 meters and permits us to destroy other storage tanks S10 (diesel oil) and petrol tanks (tanks S09, S08).

Fig.10. Concentration of thermal effects (pool fire)

6.3. Modeling a fire scenario

A pool fire is a specific type of fire involving a flammable liquid in a pool, characterized by a steady, defined burning pattern, while a general fire encompasses a broader range of combustion scenarios with various fuels and behaviors. Below is a fire scenario.

The heat flux values found in figure 11 are the same as those obtained in the pool fire scenario

Fig.11. Concentration of thermal effects (fire)

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Fig.12. Concentration of toxic effects (explosion)

Figure 12 illustrates the first case of a toxic effect of a vapour cloud on the S11 gas oil storage tank, and it is discovered that the spread of this toxic cloud for hazardous effects following the direction of wind north-east (NE) can reach up to 643 meters for the highest concentrations. It should also be noticed that the concentration rate inside the tank is lower that outside. Figure 13 demonstrates that the rate of evaporation during the explosion phase reaches 11339,80 kg in five minutes, explaining the harmful impact of the explosion in the first phase beyond the evaporated value, which is constant.

Fig.13. Rate of evaporation during explosion

6.4.2. Flammable area of a vapor cloud

Two flammable threat zones are shown in figure 14 as vapor clouds that could appear at any time after release depending on the direction of the wind. About 365 meters are affected by the red threat zone, and the concentration of the effect that could exceed 10% lower inflammability limit (LIL) is represented by the yellow threat zone.

Fig.14. Flammable effect concentration (explosion)

In the figure, indoor means inside the red threat zone. This zone represents an area affected by the release of flammable vapors. It extends approximately 400 meters from the source. Inside this zone, there is a significant risk of exposure to flammable vapors that could potentially ignite if they reach the appropriate concentration and encounter an ignition source, "and outdoor (outside the red threat zone), the aggressive effect will diminish as one move away from this zone

6.4.3. Vapor cloud blowing area (congested)

In the case of blowing a vapor cloud (congested), two threat zones are shown in figure 15. Areas of concern are likely to emerge during a dangerous overpressure. A congested vapor cloud explosion is likely to pose a risk in both directions $(x =$ 200 meters, $y = 45$ meters).

Fig.15. Over pressure zone (blast force)

According to the results shown in the figure 16, the heat released by the boil over is divided into three zones:

- Zone 1: Lethal effects on humans (more for 60 seconds) up to a radius of 1931 meters.
- Zone 2: Effects of second degree burns on humans (for 60 seconds) up to a radius of meters.
- Zone 3: Negative effects on humans (for 60 seconds) up to a radius of 4500 meters.

Fig.16. Heat radiation threat zone (boil over)

6.6. Modeling boil over phenomenon on MARPLOT To better justify our work, we exported the the boil over scenario from MARPLOT, with the aim of tracing the thermal threat zones on a real view of the company NAFTAL El Khroub; this allowed us to see the impact of this phenomenon on our S11 tank and other storage systems. As shown in the figure 17, the destruction of any storage tank can degrade the area up to a certain perimeter.

Fig.17. Heat radiation threat zone (boil over)

7. CONCLUSIONS

In conclusion, the nature of flammable products presents significant risks, as evidenced by the harmful consequences identified in this study. This analysis utilized the semiquantitative HAZOP method as well as numerical simulations conducted with ALOHA software to assess thermal effects in various scenarios, including overflow, pool fire, fire, and explosion, particularly at the S11 storage tank of NAFTAL. Our HAZOP analysis revealed the initiating events that could lead to the degradation of the tank due to uncontrolled operations. We also quantified these events using a criticality scale, allowing us to prioritize the most urgent scenarios in our analysis through the Fault Tree. For example, consider the deviation caused by an abnormal flow rate, which could lead to pipeline rupture, resulting in a fire risk (pool fire) caused by a closed or defective line valve, a clogged supply line to tank S11, or a check valve stuck in the closed position. After assessing the criticality, we obtained C=12 and proposed safety measures to reduce this criticality. In contrast, deviations such as high flow rates and reverse flow pose serious risks to installations. Regarding pressure, its severe impact, estimated with a criticality of C=16, could lead to pipeline rupture, fire risks, pool fire, or tank roof rupture. An increase in temperature often leads to the boil-over phenomenon, also evaluated with a criticality of C=16.

We then studied undesirable initiating events resulting from catastrophic phenomena, such as pool fire, tank leaks, tank explosions, and tank fires, using the Fault Tree. This helped illustrate the probable causes of the aforementioned events and allowed us to explore different accident scenarios. Finally, we executed ALOHA simulations for events such as fire, pool fire, and BLEVE. These simulations helped us determine the threat zones for each scenario.

In the case of a pool fire, we determined the red zone with a gravity radius of 96 meters, capable of destroying other storage tanks S10, S09, and S08. Regarding the propagation of a toxic cloud, dangerous effects following the north-east (NE) wind direction can reach up to 643 meters for the highest concentrations. The case study of boil-over shows that the minimum required distances between hazards and vulnerable objects are divided into three zones: zone 1: fatal effects on humans up to a radius of 1930 meters, zone 2: second-degree burn effects on humans up to a radius of 3057 meters, zone 3: negative effects on humans up to a radius of 4500 meters. This study provides data for determining safety distances.

Chemical leaks can harm the environment and living beings, primarily due to their toxic, flammable, explosive effects, and thermal radiation. In the event of damages, the effective zones of chemicals can cover a large area. Calculations of explosive atmospheres in industrial facilities will yield more precise results in identifying hazards. An effective risk assessment and explosion protection can be achieved by accurately determining the distances of explosive atmospheres in the workplace, followed by recommendations aimed at mitigating the potential adverse effects, we can recommend the following:

- Provide training and information to operators on this type of accident;
- Compliance with work procedures, especially with regard to HSE;
- The installation of electrically controlled valves in automatic mode can contribute effectively to the control of leaks and the spreading time of flammable

products, consequently reduce the destructive power of hazardous phenomena.

- To avoid reservoir overflow phenomena (tanks and spheres), rigorous maintenance of level sensors is recommended, associated with warning alarms linked with safety functions such as the emergency pump stop, closing the valves, starting the fire protection network, etc.
- Particulary, it must be taken into consideration and urgently, is that of the breathing valves and vents of fixed roof tanks by drawing up a specific monitoring and maintenance plan.
- Provide a tank rehabilitation plan in accordance with the rules for the development of flammable liquid and gas depots.
- Establish a culture of safety within the site to ensure total prevention against any possible incident;
- Ensure the maintenance of equipment and security system: fire system, foam extinguishing system.

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