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Quantitative risk assessment for ethylene oxide storage tank in Shree Vallabh Chemical in Ahmedabad

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Abstract-*Ethylene oxide (EO) is produced in large volumes and is mainly utilized as an intermediate raw material in the manufacture Emulsifiers & De – Emulsifiers. EO is stored in horizontal storage tank in liquid state under pressure with adequate cooling and only in well-ventilated area .Unfortunately, EO is highly flammable and in vapor form, is subject to explosive decomposition, therefore it can pose risk s to personnel, equipment facilities and environment. With risks becoming more complex and diverse, risk evaluation approaches are required to quickly identify hazards, effectively assess safety performances. Risk Assessment is one of the majortechniques used byvarious industries throughout the world. In this paper quantitative risk assessment of an ethylene oxide storage tank situated in Ahmedabad. The hazards identification are carried out systematically,furthermore, identification of the worst possible accident scenarios which arising from the tank due to the valve or pipe failure. The over pressure from Vapor Cloud Explosion and heat radiation intensity from fire as considered as criteria for assessing the effects towards humans and structures. The effect of thermal radiation on people is mainly a function of intensity of radiation and exposure time. The effect is expressed in terms of the probability of death and different degrees of burn.For mentioned purpose, these scenarios are further modeled in ALOHA software and the analyses are carried out primarily for weather classes such as 5 D, 1 F. The prediction process show that , the most serious threat zone in case of stable weather will extend to a distance greater than in neutral weather if the BLEVE or VCE takes place .On other hand , the red threat zone resulting from jet fire will be less extended in stable weather as compared with neutral weather. Risk-Matrix has been established to determine the risk rank of the EO storage tank.Based on the risk assessment study and the outputs from the model , Set of measures and procedures which should be taken in order to reduce possibility and limit consequences of accident.*

Keywords*-QRA , jet fire, AlOHA , thermal radiation , vapor cloud explosion , Hazard identification, Risk matrix.*

I. INTRODUCTION

Storage tanks are usually used as containers for large volumes of flammable explosive, corrosive and toxic chemicals in petrochemical and chemical plants. When a tank fire occurs, the accident usually leads to million dollar property losses andposes risks to personnel, equipment facilities and environment[1–2].The global production of ethylene oxide in 1985 was estimated to have been greater than 5.5 million tones[3]. Ethylene oxide (EO) is produced in large volumes and basically used as an intermediate raw material in the manufacture of several industrial chemicals[4] , For instance, in the studied facility where EO is utilized to produce various ethoxylate products.EO is stored as liquid under pressure in horizontal storage tank .Unfortunately, EO possesses several physical and health hazards due to its hazardous properties.Firstly ,Ethylene oxide is an extremely flammable liquid [5] , which results in fire and explosion in case if it leaks during the unloading or loading process as well as from the storage tank if any failure occurs. The various fire scenarios associated with EO storage are jet fire, pool fire, flash fire. Secondly,liquid ethylene oxide itself is quite stable to detonating agents, but the vapor will explode when exposed to an electric spark, static electricity etc.[5] . Furthermore, Ethylene oxide vaporizes rapidly at atmospheric temperatures and pressures,Its vapor is moderately toxic to exposed human by inhalation. The threshold limit value (TLV)* of ethylene oxide in air is 1 pp m (90 mg/m3) for 7 to 8 hour s work-day an d 40 hour s work-week. Ethylene oxide is suspected human carcinogen. In EO storage system fire and explosion accidents are usually happened due to leakage from tank valve or pipelines. QRA (Quantitative Risk Analysis) is basic tool applied to identify the potential risks of major disasters having damage potential to life and property and provide a scientific basis for decision makers to be satisfied about the safety levels of the facilities to be set up. QRA is used for different purposes it is one of the most important risk management program[6].Risk assessment study is to guide engineering solutions, design safety, emergency preparedness and planning etc. [7].Risk analysis is a methodology developed in middle of 1970 to take care of process industry by the loss prevention in process industries. [8].

II. PROCESS DESCRIPTION

Ethylene oxide is used to manufacture Emulsifiers & De - Emulsifiers .Ethylene oxide is added to the reactors to achieve ethoxylation process of the phenol materials and produce phenol ethoxylate products as example below:

$$\text{Nonyl Phenol} + \text{ethylene oxide} + \xrightarrow{\text{catalyst}} \text{Nonyl Phenol ethoxylate}$$

$$C_{15}H_{24}\,O \quad + C_2H_4\,O \qquad\qquad C_{15}H_{25}\,O\,(C_2H_4\,O)_{10}$$

The ethylene oxide is received to the premise through road tankers and unloaded in horizontal cylindrical Tank with dimensions (Dia 1.5 × 5.6, m, 9 MT) figure-1. It is stored in liquid state under pressure with adequate cooling and only in well-ventilated area . Storage pressure and temperature ranges are (240-410) kPa and (10-15°C) respectively. When long storage periods and wherever possible refrigerated storage, held preferably at temperatures below the boiling point of ethylene oxide (10.7ºC), is recommended to minimize polymerization. Storage tanks should be equipped with stainless steel cooling coils and should be well insulated.

Fig-1-ethylene oxide storage tank

III. QUANTITATIVE RISK ASSESSMENT METHODOLOGY

Risk assessment: it is the quantitative evaluation of the likelihood of the undesired events and their consequences being caused together and a value judgment concerning the significance of the results after comparing with set, legal or accepted value of standards [10]. The main goal of risk assessment is to identify potential accidents, analyses the causation and evaluate the effects of the risk reduction measures. Risk assessment is broadlyclassified as qualitative such as (hazop and safety audit) and quantitative such as (QRA and event tree analysis) methods. Quantitative Risk Assessment is carried out to find the risk in numerically , identifying the risk from the potential hazards , evaluate the risk score using modeling and establish risk matrix , figure below illustrate the basic steps in QRA method.

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Fig.2. Typical QRA flow diagram

3.1.Hazard identification

Hazard identification: it is the initial key step in risk assessment studyand defined as an identification of sources of hazards and their causes; it is qualitative study , it is known as hazop [10]. HAZOP study is used to identify the hazards in the EO storage tank, it is by reviewing the numerous parameters, for instance , quantity used and its composition, operating temperature and weather data, storage condition , maintenance periods , site inspection , existing PPE and fire protection equipment , previous accident in the premises or another one etc.

3.1.1 **Identification of possible causes of tank accident**:

The most common failure causes are:

1. Operational errors: These comprise of: a- tank over filling, owing to a failure of level metering systems or human error in the loading procedure,b-the discharge valve failure cause fuel release Causes lead to leakage of fuel in the retention bund and creation of an air vapor mixture that can be easily ignited on the occasion of an ignition source, leading to a pool fire even in the whole bund area.
2. Lightning is a major accident initiator, due to poor grounding of the tank to prevent the full absorbing of a direct strike.
3. Static electricity caused by fluid transfer during tank filling can lead to the creation of a spark, especially when the loading rate is high.
4. Maintenance errors may lead to the occurrence of accidents, namelywelding/cutting operations, producing uncovered sparks and circuit shortcuts.
5. Piping rupture:valve or pump leaking which result in smaller or bigger liquid out flow, possible ignition and creation of a pool fire.
6. Supporting safety systems failures refer to the: a- electric power system, b- insufficient tank cooling, which could lead to total tank demolition, c- water supply system for fire extinguishing.

3.2. Data collection

- **description of ethylene oxide:**

Ethylene Oxide (C_2H_4 O) Tank Scenario (Dia 1.5 × 5.6,m Horizontal Tank: 9 MT) from the site visit , Molecular Weight: 44,05 , Boiling point : 10.5 °C (51.26 °F) , Flash point : -20 °C (-4 °F) from MSDS for EO [17].

- **Weather condition:**

The wind speeds, wind direction, relative humidity, outside temperature are the significant parameters effect on the dispersion of leakage gases. The site metrological data are collected from the metrological station situated at the location. The analyses are carried out primarily for weather classes D, F with wind speed (5, 1) m/s respectively. The annual average maximum temperature recorded was 34.4℃. The average relative humidity was around 51%. The prevailing wind direction is the southwest.

3.3.Risk estimation:

Risk is defined as the product of the frequency and consequences of an accident [10] :

Risk = Frequency · Consequences

3.3.1Frequency estimation:

Risk estimation involves the quantitative assessment of probability of an unwanted events and the consequence severity i.e. the damage caused to life, property, environment etc. The sudden and accident leakage of tank or pipeline or catastrophic failure can happen due to failure of any component in the system. The failure probability of the system is depends up on the individual components.

3.3.2. Analysis of consequences:

The jet fire ,flash fire, pool fire (delayed ignition), vapor cloud explosion (delayed ignition-explosion), toxic cloud (no-ignition), safe dispersion are the outcome cases of any leak of hazardous material leakage [12].List of accident scenarios result fromthe storage of ethylene oxide are usually because of valve damage.In order to plan a safe response and ensure public safety, the potential severity of these threats must be evaluated. Therefore,i will use ALOHAmodel to predict the threat zones for each of these potential scenarios according to stability class (F,D).All of theoutcomesare displayed in the Text Summary in Table1.

- **Possible accident scenarios modeling using program ALOHA :**

1. BLEVE tank explodes and chemical burns in a fireball:

The fireball is usually associated to the sudden loss of containment of a pressurized liquefied fuel or gas, The two-phase cloud can burn only on its outer surface as inside there is no oxygen. The best known cause of a fireball is a boiling liquid expanding vapor explosion (BLEVE). Fireball duration is typically (5 – 20)seconds [9] .ALOHA model was applied for this scenario for each stability class and(Fig 3, Fig4) are plotted.

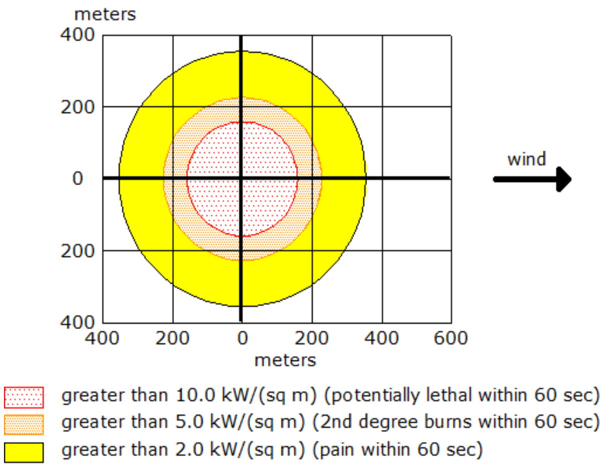


Fig.3.Thermal radiation threat zone, class F

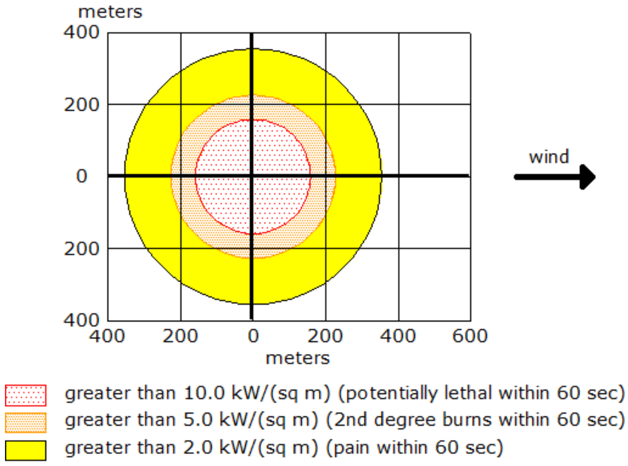


Fig.4.Thermal radiation threat zone, class D

ALOHA's estimation shows three thermal radiation threat zones, the red threat zone is the worst hazard level and will extend up to 158 meter in all directions for both stability classes(F ,D), the thermal radiation intensity is greater than 10 KW/(sq m) and has potential to be fatal within 60 sec . The orange and yellow threat zones represent areas of decreasing intensity and that is accompanied with decline in health effects.

2. Leaking tank, chemical is burning as jet fire:

Jet fires occur when there is a release and ignition of a flammable gas or two-phase flow through from limited openings (e.g. due to small leak in broken drain valve), at a relatively high speed, thermal effects can be locally very intense, especially if there is flame impingement.ALOHApredict a threat zones for this release as shown in (Fig.5 and Fig.6).

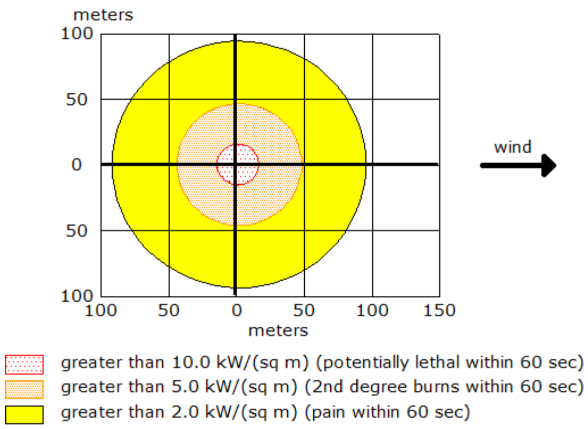


Fig.5.Thermal radiation threat zone , class F

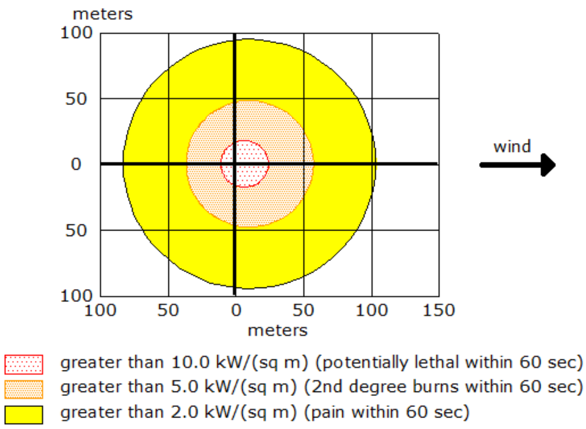
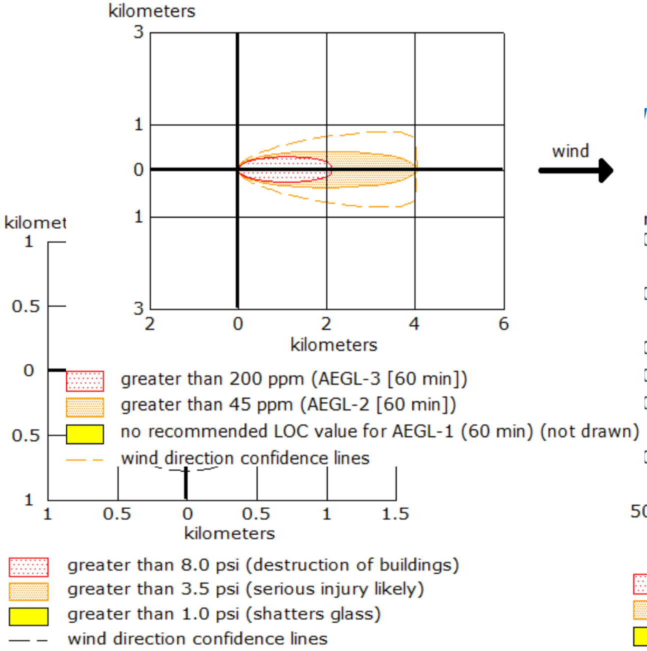


Fig.6.Thermal radiation threat zone , class D

It is clear from graph above that, the jet fire red zone is only predicted to extend about 17 meter in all directions for class F and also is potentially lethal within 60 sec,whereas in case of class D was little more 25 meter. In the orange and yellow threat zones thermal radiation intensity has decreased drastically and their impacts lowered as well.However, the BLEVE will last about 7 seconds, while the jet fire is predicted to last over an hour.

3. Overpressure (blast force) from vapor cloud explosion

Now that you've considered the flammable area and the overpressure hazard from a vapor cloud explosion.When a large quantity of flammable vapor or gas is released, mixes with air to produce sufficient mass in the flammable range and is ignited, the result is a vapor cloud explosion (VCE) [9]. ALOHA model was applied for this scenario and (Fig.7 and Fig.8) produced below according to stability class.



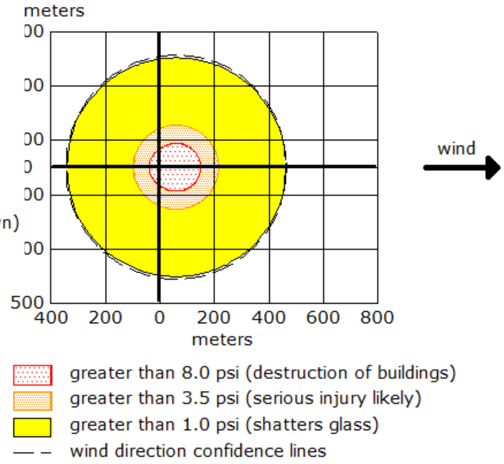


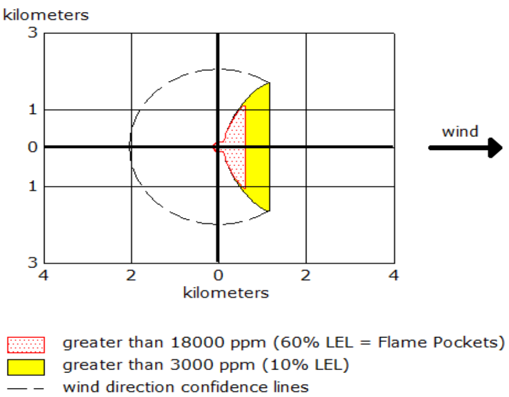
Fig.7. Blast area of VCE, Class F

Fig.8.Blast area of VCE , class D

It is noticeably that, the red zone of blast area will extend to 511 yards in class F and 150 meter in class D. The vapor pressure in red area is greater than 8 psi which capable to destroy buildings. In the orange and yellow area, it is likely to cause serious injury. ALOHA ran explosion scenarios for a range of ignition times encompassing all of the possible ignition times for your scenario .From the analysis approximately 791 m and 465 m distance contour for class F and D and respectively , the glass and repairable damage may occurred to people due to this scenario.

4. Flammable vapor cloud

Ethylene oxide is an extremely flammable liquid and, introduces a potential fire hazard when it is stored, handled or used Volatile flammable liquid with heavier than air vapors that may travel considerable distance to a source of ignition[16], ALOHA was utilized to predict the flammable threat zone based on existing input data.



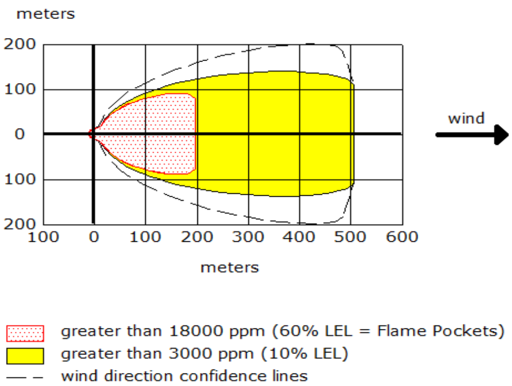


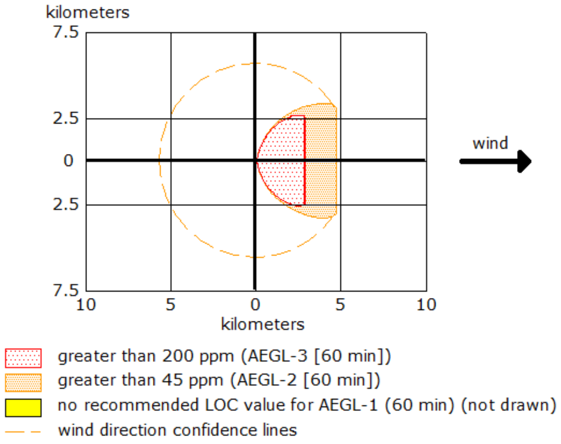
Fig.9. Flammable threat zone, class F

Fig.10.Flammable threat zone , class D

The display the threat zone estimate for the flammable area of the vapor cloud. The flammable area is the predicted area where the ground-level vapor (fuel) concentration in air is within the flammable range and can be ignited. Then , The red threat zone represents the estimated flammable area where a flash fire or a vapor cloud explosion could occur at some time after the release begins. ALOHA estimates that the red threat zone will extend 594 and 198meter in class F and D respectively in the downwind direction , the concentration of EO will be around 60% LEL. The yellow threat zone represents the estimated area where EO concentrations could exceed 10% LEL.

5. Toxic threat zone:

Ethylene oxide vaporizes rapidly at atmospheric temperature s an d pressures, Its vapor is moderately toxic by inhalation, so ALOHA was used to estimate threat zone toxic level concern. Distance to the ERPG-2 level if the puddle evaporates and forms a toxic vapor cloud.



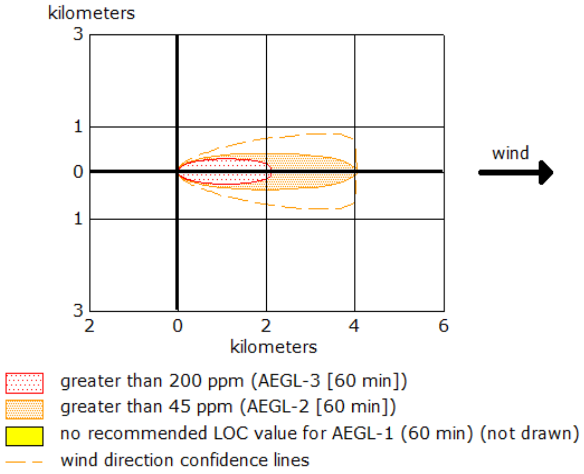


Fig.11.Toxic threat zone, class F Fig.12. Toxic threat zone , class D

You want to know the downwind distance to the AEGL-2 level specified by the Local Emergency Planning Committee. ALOHA estimates that the orange threat zone will extend 5280 in class F and 4100 in class Dmeter downwind exceed the AEGL-2 and concentration greater than 45ppm.At concentrations above the AEGL-2 level, people could experience serious health effects or find their ability to escape to be impaired (if they are exposed for about an hour).Table1describes the model output for different wind stability classes .

Table .Summary of affected threat zone for possible scenarios for class (F, D).

Scenario	***Threat Modeled***	***Maximum distance (meter)***					
		Class 1F			**Class 5D**		
		Red threat zone	Orange treat zone	Yallow threat zone	Red threat zone	Oraneg threat zone	Yallow threat zone
BLEVE	Thermal radiation	158	228	355	158	228	355
FLAMMABLE AREA	FLAMMABILITY	594	NO LOC SELECTED	1200	198	NO LOC SELECTED	507
BLAST AREA OF VCE	OVER PRESSURE	511	552	791	150	216	465
JET FIRE	THERMAL RADIATION	17	49	96	25	58	104
TOXIC AREA	TOXICITY	2900	4800	no LOC selected	2100	4100	no LOC selected

- **Assessment of possible consequences** :

The consequences of a major accident are the measure of its effects on people, the environment or material property. For people, the consequences are estimated as the number of per-sons that are killed or injured due to the accident; for the environment, they are the quantity of a natural vector that is affected; for material property, they are the level of damage caused by the accident.Possible consequences for ethylene oxide storage tank accidentswere expected based on the available indicators , they have been summarized in table 2.

Table.2. Possible consequences for storage tank accident

Indicators	*Possible consequences*					
	Negligible	Significant	Moderate	Serious	High	Disastrous
Fatalities			1-3	4-10	11-15	>20
Number of injured		1-10	11-50	51-100	101-200	>200
Extent of injury	minor	Lost time	major	Long time hospitaliz ation	Permanent disabilities	Large number of disabilities
Type of exposure	Very rare	rare	unusual	occasional	frequent	continuous
Contaminated area	<1	1-10 ha	10-50 ha	>50-100 ha	1-5km2	>5km2
Extent of damages(Rupee s)	<1000	>1000	>10000	>100000	>1000000	>100, 00, 000

3.4.3. Risk matrix:
From combining the consequence analysis and frequency analysis the risk matrix is established .These risk levels are depends up on many factor such as input data, methodology followed, process condition, meteorological data, generic frequency data and modeling software, assumptions made etc [14] .

Table.3.Risk matrix.

Probability	***Possible consequences***					
	Negligible	Significant	Moderate	Serious	High	Disastrous
Certain	Medium	High	Extreme	Extreme	Extreme	Extreme
Imminent	Moderate	Medium	High	Extreme	Extreme	Extreme
Very likely	Low	Moderate	Medium	High	Extreme	Extreme
Likely	Low	Moderate	Medium	Medium	High	Extreme
Unlikely	Low	Low	Moderate	Medium	Medium	High
Rare	Low	Low	Low	Low	Moderate	Medium

3.4.5 Risk acceptability
Risk is acceptable if it could be managed under certain conditions regulated by regulations (implementation of appropriate safety, technical, organizational measures..).

IV. RISK CONTROL MEASURES

Based on the risk assessment study and the results the following are to be adopted further to the design requirements to mitigate the risk. Set of measures and procedures which should be taken in order to reduce possibility and limit consequences of accident.

1. Ethylene oxide is very volatile an d should be stored under pressure with adequate cooling [5].
2. Temperature Requirement s : Ethylene oxide in storage tank s should be maintained at a temperature not exceeding 30ºC , Wherever possible refrigerated storage, held preferably at temperature s below th e boiling point of ethylene oxide (10.7ºC), is recommended.
3. All storage tanks must be equipped with level indicator, flame arrestors and breather valves.
4. In order to reduce the risk of fire and explosion, ethylene oxide is mixed with inert gas such as carbon dioxide [9] .
5. Pumping stations should be provided with drainage systems capable of quickly and safely draining away the flammable should a spill occur.
6. Extra precautions against over filling/spillage. Spillage is also the main cause of vapor cloud explosions which either start pool fires or follow them[15].

7. Adequate diking and drainage should be provided in the tank area to confine and dispose of the liquid in case of tank rupture.
8. Compatibility with Other Material s : Storage tank s i n ethylene oxide service should be used only for ethylene oxide unless thoroughly cleaned and purged .
9. Explosion Venting Requirement s : An adequate system for normal and emergency venting should be installed. All vent lines should extend to a safe area .
10. Grounding : Storage tank s for ethylene oxide should be protected from electrical storm s and induced static electricity by the grounding of all equipment .
11. Employee education an d training: Workers who handle ethylene oxide, or ma y be exposed to it in any form, should be instructed carefully in accepted methods of handling and be familiar with the protective equipment required for safe handling.
12. Personal Protective equipment: Eye (Protection Chemical Safety Goggles) ,Head Protection : Safety or hard hats will provide protection against accidental liquid leaks. Foot Protection: PVC or rubber safety shoes with built-in steel toe caps are recommended. Body, Skin and Hand Protection : Suits mad e of a suitable protective material .
13. Water Cooling Systems : Cooling of an adjacent atmospheric storage tank wall and roof is an effective means of maintaining temperatures within acceptable limits that will not cause the steel to collapse, the flammable vapors to be discharged to the atmosphere or the hot surfaces to form a source of ignition. Water can be useful for extinguishing EO fires and cooling equipment subject to fire impingement[16].
14. Foam Systems: Foam methods are the most widely used in firefighting system; they provide an acceptable level of protection. Foam firefighting systems, in which foam is directed on to the fire.
15. Good layout should be provided for adequate firefighting access, means of escape in case of fire.

V. CONCLUSION

In the present This papers review the overall QRA (Quantitative Risk Assessment) methodologies applied for EO storage tank and software's used to do this QRA studies. From the consequence analysis it was found that jet fire, VCE, BLEVE are the potential scenarios. The frequency analysis for a leak and probability of ignition is used to find the overall outcome failure frequency. The over pressure from VCE and heat radiation intensity from fire as considered as criteria for assessing the effects towards humans and structures. For mentioned purpose, modeling of the possible scenarios using ALOHA has been applied and outcomes obtained that, the most serious threat zone in case of clear weather will extend to a distance greater than in neutral weather if the BLEVE or VCE takes place .on other hand, the red threat zonearising from jet fire will be less in clear weather as compared with neutral weather.The effect of thermal radiation on people is mainly a function of intensity of radiation and exposure time. The effect is expressed in terms of the probability of death and different degrees of burn.The thermal radiation of the in the red threat zone will be greater than (10 KW/sq m) which in turn adversely impact on people and cause death in worst cases.When considering thermal radiation hazards it is important to consider both the thermal radiation level and the length of time over which someone might be exposed to that level.Risk-Matrix was established to determine the risk rank of the EO storage tank..Based on the risk assessment study and the results , Set of measures and procedures which should be taken in order to reduce possibility and limit consequences of accident.Provided safety and fire protection system in the plant are adequate and well maintained to take care in case of any emergency. . The emergency preparedness plan especially the off site plan need to be studied and conducted regularly. Computer modeling usedto assess the safety distances are varies however available data are to be further verified by field work to increase the reliability.

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